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Review Article

Change in SO_4^{2-}, NO_3^- and NH_4^+ levels in $PM_{2.5}$ in Beijing from 1999 to 2016

Xiaoyi Zhang, Yijing Chen, Yuhong Qin and Weili Lin*

College of Life and Environmental Sciences, Minzu University of China, Beijing, China

Abstract

Extant literature was reviewed to analyze the trend of three water-soluble ions-sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+) in $PM_{2.5}$ in Beijing in recent years, and the reasons affecting changes were investigated. From 1999 to 2016, the concentrations of SNA (the total SO_4^{2-}, NO_3^-, and NH_4^+ in $PM_{2.5}$) in Beijing showed a zigzag fluctuation. Pollution control measures have been successfully used in controlling the primary fine particles and SO_4^{2-} in atmospheric fine particles, but not in controlling NO_3^- and NH_4^+. From 2013 to 2016, the changes in $PM_{2.5}$ and SNA showed the same trends in summer and autumn, indicating that SNA made a dominant contribution to $PM_{2.5}$ in summer and autumn and that PM2.5 was mainly produced through secondary formation. However, the changes in $PM_{2.5}$ and SNA were inconsistent in winter and spring, indicating that primary $PM_{2.5}$ had a considerable contribution in winter and spring. The values of $[NO_3^-]/[SO_4^{2-}]$ in $PM_{2.5}$ increased year by year, and the proportion of NH_4^+ in $PM_{2.5}$ also increased, demonstrating that the contributions of nitrogen-containing compounds to the secondary $PM_{2.5}$ became increasingly critical in Beijing. Therefore, strengthening the control of nitrogen-containing compounds by reducing their potential to generate secondary atmospheric fine particles in Beijing is necessary in the future. The change trends of SNA were not synchronized with the change in their precursors' reduction amount, indicating that SNA precursors in Beijing were sufficient. Research on the collaborative control of SNA must be strengthened.

Keywords: Ammonium ion; Long-term trend; Nitrate ion; $PM_{2.5}$; Sulfate ion

***Corresponding author:** Weili Lin, College of Life and Environmental Sciences, Minzu University of China, Beijing, China, Tel: +86 1013661031210; E-mail: linwl@muc.edu.cn

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Introduction

Fine particulate matter ($PM_{2.5}$) refers to particles that are suspended in the atmosphere with an aerodynamic diameter (*D*p) smaller than or equal to 2.5 μm [1]. The aerodynamic diameter of 2.5 μm is usually considered the boundary between coarse and fine particles [2]. Atmospheric particles, especially $PM_{2.5}$, exert the effect of absorption or scattering of sunlight. Sulfate, nitrate, and other substances in particulate matter can reduce visibility by scattering light. Especially under higher relative humidity, sulfate, ammonium, and nitrate are more hygroscopic and deliquescent, which means that they have a much stronger light scattering effect and a more obvious visibility reduction [2]. Sulfate, ammonium, and nitrate play a key role in the formation of particulate matter pollution and acid rain [3]. At present, $PM_{2.5}$ is a major air pollutant in China and is a key material that causes haze.

$PM_{2.5}$ contains various chemical components, among which are water-soluble ions such as sulfate ions (SO_4^{2-}), nitrate ions (NO_3^-), and ammonium ions (NH_4^+) (collectively known as "SNA"). These ions significantly contribute to the mass concentration and composition of particulate matter, which generally constitutes the main body of aerosol inorganic components. Research has shown that SNA accounts for more than 50% of $PM_{2.5}$ mass concentration [4] and more than 80% of water-soluble ions in $PM_{2.5}$ in Beijing [5]. Water-soluble ions in $PM_{2.5}$ can be directly produced from primary emission sources, but mainly from secondary aerosol formation in gas: Particle transformation processes in the atmosphere, whose gaseous precursors mainly include acid or alkaline gases such as NH_3, NO_x (including NO and NO_2), and SO_2 [6]. In urban atmospheres, motor vehicle emissions, sewage treatment processes, and industrial and combustion processes are the main sources of NO_x, SO_2, and NH_3 [7,8].

NO_x and SO_2 can be oxidized to gaseous HNO_3 and H_2SO_4 by oxidants such as O_3, H_2O_2 and OH in the atmosphere. Under the action of ultraviolet light, O_3 is one of the most important photochemical oxidants that can produce the OH radical through photolysis and subsequent reaction with water vapor. The OH radical plays a critical role in the conversion of gaseous NO_x and SO_2 into nitrate and sulfate [9]. Homogeneous or heterogeneous chemical reactions between acidic substances and NH_3 can form water-soluble substances, including NH_4NO_3, $(NH_4)_2SO_4$, and NH_4HSO_4 [10]. The stability of $(NH_4)_2SO_4$ is obviously higher than that of NH_4NO_3. Once formed, $(NH_4)_2SO_4$ is stable in the atmosphere. Therefore, if sufficient NH_4^+ exists, H_2SO_4 will eventually transform into $(NH_4)_2SO_4$ in the atmosphere. NH_4NO_3 is greatly affected by atmospheric temperature and humidity because of its thermal instability, and gas-particle equilibrium exists between NH_3 and HNO_3. NH_4NO_3 is more abundant in particles in spring and winter [11]. The fluctuations of SNA might be closely related to the emission changes of their precursors such as SO_2, NO_x, and NH_3. Understanding the long-term variations of SNA in $PM_{2.5}$ in the

atmosphere may reveal the truth about the pollution characteristics at different periods under related emission control measures.

As one of the biggest megacities in the world, Beijing has been undergoing rapid economic growth, urbanization, and population growth. The aggravated air pollution has greatly challenged scientific research and the management of urban and regional air quality. Compared with other regions, there are more studies on the fine particulate pollution with a longer history in Beijing. But, most of them focus on the characteristics or source analysis of $PM_{2.5}$ in a specific period, year or season [4, 11-37]. In this paper, literatures about SNA seasonal and inter annual concentrations in $PM_{2.5}$ in Beijing from 2000 to 2016 are reviewed to obtain their trends and to evaluate the effect of pollution control measures, which would provide scientific information for the future pollution control on $PM_{2.5}$ in Beijing.

Data Source

Data on $PM_{2.5}$ and its components SO_4^{2-}, NO_3^-, and NH_4^+ from 1999 to 2016 in Beijing were collected from published journals and reports released by the Beijing Municipal Ecological Environmental Bureau. The detailed data information is shown in table 1. Over 50 sample sites were identified, divided into urban and suburban sites, including the routine monitoring sites of the Beijing Municipal Environmental Monitoring Center, regional atmospheric background and city stations of the China Meteorological Administration, and field observation sites selected by different researchers. The specific sites range from university campuses to residential areas to industrial zones to high-traffic areas to pollution transport boundaries. Generally, limited amounts of data were collected from the early years than from the later years.

Sample Site/(Number*, Location)	Sample Period		Sample Number	$PM_{2.5}$	SO_4^{2-}	NO_3^{2-}	NH_4^+	Date Source
2; urban, suburb	1999~2000		-	129	16.9	9.9	6.5	Yao et al. [34]
2; urban	1999~2000		48	129	14.47	12.9	6.45	He et al. [20]
1; urban	1999.9-2000		-	127	14.1	9.9	6.5	He et al. [20]
1; urban	2001.8-2002.9		-	106.9	10.6	7.8	5.5	Duanet al. [18]
5; urban, suburb	2001~2003		334	154	17.07	11.52	8.72	Wang et al. [30]
5; urban, suburb	2001-2003	Spring	-	162.1	13.5	11.9	6.5	Wang et al. [30]
		Summer	-	93.3	18.4	11.2	10.1	
		Autumn	-	105.2	12.7	9.1	6.3	
		Winter	-	214.2	20.9	12.3	10.6	
3; urban, suburb	2002~2003		-	115.6	18.3	12.9	10.4	Sun et al. [11]
1; urban		Summer	20	77.3	16	12.2	10.4	Sun et al. [11]
		Winter	20	135.7	30.4	17	12.9	
1; suburb		Summer	22	82.2	19.2	13.3	11	
		Winter	20	140.8	23.1	13.5	13.3	
1; urban		Summer	21	75.4	19.7	13.2	9.75	
		Winter	20	182.2	29.9	19.3	20.3	
1; urban	2001-2004		Dust days(19)		15.61	4.79	4.06	Duan et al. [18]
			Haze days(18)		39.2	25.3	18.11	
			Clear days(89)		10.98	9.18	5.06	
1; suburb	2002.10-2003.5		-	92.4	8.44	6.72	4.54	
1; urban	2003.6-7		-	123.6	21.3	13.4	9.6	He et al. [20]
1; urban	2003.6-7		-	123.6	21.3	13.4	9.6	Cao et al. [12]
1; urban	2005.3-2006.2		43	118.49	15.77	10.06	7.3	Zhao [35]
1; suburb	2005.3-2006.2		42	68.44	12.71	6.41	5.96	
1; suburb	2005.6.29-8.2		--	68	22.6	9.9	4.7	Pathak et al. [27]
1; urban	2005.6-2006.5		27	99.65	16.71	7.03	5.62	Sun et al. [28]
1; urban			103	82.37	11.63	5.31	4.18	
1; suburb			24	52.52	10.52	3.01	4.39	
2; urban, suburb	2005~2007		105	102	29.5	18.6	-	Wang et al. [31]
1; urban	2006.3		-		10.77	10.42	9.63	Cui et al. [13]
1; urban	2006.6.16-6.18, 6.20-6.22		-		9.16	7.78	2.81	Cui et al. [14]
1; suburb	2008.7.9-8.25		683	41.83	20.78	10.32	7.15	Wang [32]
1; urban	2007.10-2008.1		-		21.3	7.6	7.22	Liu [25]
1; suburb			-		30.3	21.1	14.1	
1; urban	2008.6-2008.10		-		34.7	30.3	13.2	
1; suburb			-		21.1	17.8	10	
1; suburb	2008.7-2008.8		-		20.74	10.32	7.15	Hu et al. [21]

1; urban	2008		-	109.6				Zhao [35]
1; suburb			-	66.8				
1; urban	2009.6.5-2009.8.31		z	129.7	26.1	12.7	9.1	Hu et al. [21]
1; urban	2009.6.5-2009.11.31			115.8	23	9.2	6.6	
1; urban	2009.8.1-2009.8.31		43	102.5/30 samples	26.9	16.1	15.8	Wang [32]
1; urban	2009~2010		121	135	13.6	11.3	6.9	Zhang et al. [36]
9; urban, suburb	2012.8~2013.7		486	89.8	19.4	20.3	13.5	Yang et al. [33]
8; urban, suburb	2012.8-2013.7		472	125	19.4	20.3	13.6	Liu et al. [26]
1; urban	2012.8.3-2012.8.16		126		12.2	9.07	6.71	Di et al. [17]
1; urban	2012.8-2013.7		-	114.75	18.8	19.3	12.5	Lin et al. [24]
1; suburb			-	82.25	15.9	14.1	10.2	
1; urban			-	121.25	16.5	20.4	12.1	
1; suburb			-	158	19.5	19.1	12.4	
1; suburb			-	144.25	23.3	22.9	15.5	
5; urban, suburb	2012.8-2013.7	Spring	-	107.8	16.3	26.8	12.5	
		Summer	-	106.8	17.9	15.9	11.6	
		Autumn	-	77	11.2	12.7	8.6	
		Winter	-	204.8	31.6	24.5	17.9	
1; urban	2013		-		24.92	11.92	9.58	Wang et al. [4]
	2014		-		17.97	16.99	17.61	
1; urban	2014.3-2015.2		94	-	5.39	13.9	5.37	Dao et al. [15]
unpublished data	2014		-		15	17.6	10.4	Ding et al. [16]
1; urban	2014.3-2015.2		-		7.24	9.89	9.15	Fang et al. [19]
	2014.3-2015.2	Spring	-		14.72	10.21	4.93	
		Summer	-		6.98	9.85	8.29	
		Autumn	-		9.25	11.21	5.63	
		Winter	-		9.95	11.08	7.27	
1; urban	2015.1.1-12.31		325	79	12.7	13.5	8.1	Ding et al. [16]
1; urban	2016.11.15-2016.12.31		19	114				Li et al. [23]
			Clear day 5d	59.08	4.65	4.35	2.42	
			Light polluted 4d	95.96	7.78	12.38	8.9	
			Moderately polluted 3d	140.75	14.99	20.84	9.1	
			Heavy polluted 4d	179.29	16.68	21.67	9.32	
			Severe polluted 3d	337.81	27.82	27.73	10.82	
1; urban	2014	Spring		90.8	7.6	12.6	8.7	Jia et al. [22]
		Summer		88.9	15.5	13.1	10.4	
		Autumn		91.5	9.1	16.6	9.2	
		Winter		101.4	13.3	14.8	9.1	
	2015	Spring		73.2	9.1	16.7	10.5	
		Summer		59.7	6.5	8	6.4	
		Autumn		65	4.2	9.6	4.4	
		Winter		94.8	11	16.8	11.1	
	2016	Spring		73.4	9.1	9.6	6.4	
		Summer		49.2	5.3	6.6	5.2	
		Autumn		87.6	14.9	14.5	10.2	
		Winter		67.4	10.6	11.1	8.8	

Table 1: Concentrations of $PM_{2.5}$ and SO_4^{2-}, NO_3^- and NH_4^+ in Beijing (units: μgm^{-3}).

*: the number of sites used to get the statistical data.

In the early years, the average annual concentrations of $PM_{2.5}$ were usually more than 100 μgm^{-3}; in more recent years, the values have fallen to below 100 μgm^{-3} following the intensification of pollution control of fine particles. Nevertheless, the average annual concentrations are still higher than the annual limit value (35 μgm^{-3}) and the daily limit value (75 $\mu g\ m^{-3}$) set by the National Ambient Air Quality Standard (GB3095-2012). The concentration of SO_4^{2-} is approximately 15 μgm^{-3}, NO_3^- is approximately 10 μgm^{-3} and NH_4^+ is below 10 μgm^{-3}. Prior to 2014, the concentration relationship of these three water-soluble ions was usually $[SO_4^{2-}] > [NO_3^-] > [NH_4^+]$, but in more recent years, the relationship has shifted to $[NO_3^-] > [SO_4^{2-}] > [NH_4^+]$.

Change in SNA Level in $PM_{2.5}$ in Beijing

Inter annual variation

Figure 1 shows the trends in the annual average concentration of SNA and $PM_{2.5}$ from 2000 to 2016 in Beijing and figure 2 shows the inter annual changes of SNA proportion in $PM_{2.5}$ and the ratio of $[NO_3^-]$ to $[SO_4^{2-}]$ from 2000 to 2016 in Beijing. For the 2008 Olympic Games, Beijing placed a considerable amount of attention on air pollution control; as a result, from 2000 to 2008, the mass concentration of $PM_{2.5}$ in Beijing sharply decreased at an average of -5.78 $\mu g\ m^{-3}$ per year. After 2008, a significant $PM_{2.5}$ pollution rebound was observed that peaked in 2010 (no data are available in 2009 and in 2011), following which $PM_{2.5}$ concentration again declined year by year. From 2012 to 2016, $PM_{2.5}$ concentration decreased by 22.7 % and the annual average concentration of $PM_{2.5}$ in 2016 began to fall below the lowest value even during 2000-2008.

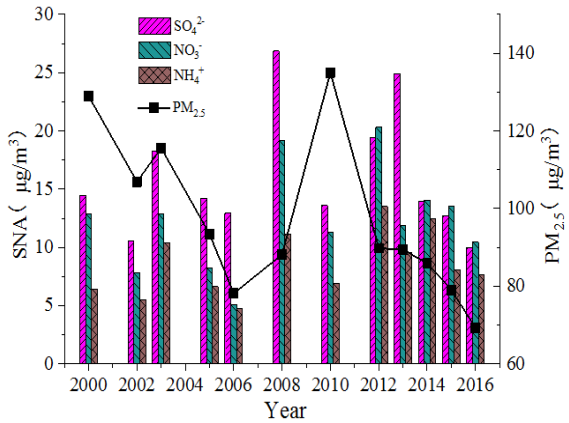

Figure 1: Trends of annual mean of SNA in $PM_{2.5}$ and $PM_{2.5}$ from 2000 to 2016.

(In 2008, the annual concentration of SNA was only based on the average of two periods: From October 2007 to January 2008 and from June 2008 to October 2008).

The mass concentration of SO_4^{2-} fluctuated from 2000 to 2013 and peaked at 24.92 μgm^{-3} in 2013 (26.85 μgm^{-3} in 2008 with no available data from February to May), with an average value of 17.26 μgm^{-3}. Although the mass concentration of $PM_{2.5}$ dropped to its lowest value in 2008, SO_4^{2-} did not decline during that same time. After the Olympic Games ended, the mass concentration of SO_4^{2-} increased significantly by 50.2 %. Then, the mass concentration of SO_4^{2-} decreased year by year from 2013 onward, which is consistent with the decreasing trend of $PM_{2.5}$. Studies [38,39] have indicated that the emissions of SO_2 in northern China began to decline in 2006 and that the concentration of this material was declining in urban areas. However, the mass concentration trend of SO_4^{2-} in $PM_{2.5}$ was not synchronized with the trend of emission and concentration of SO_2 in the air, revealing a lagging effect for many years. This may indicate that the primary emission of $PM_{2.5}$ was largely controlled in the early years, as SO_4^{2-} mainly existed in the secondary fine particles. It should also be noted there was sufficient SO_2 in the air for many years, which provided abundant amounts to meet the needs of the transformation to SO_4^{2-} in $PM_{2.5}$. With the intensification of SO_2 emission control measures in recent years (e.g., the implementation of measures like "replacing coal with gas" and "replacing coal with electricity" in Beijing and surrounding areas), the content of SO_2 in the atmosphere had dropped rapidly and the mass concentration of SO_4^{2-} in $PM_{2.5}$ began to decrease. As is evident from the proportion change of SO_4^{2-} in $PM_{2.5}$ (Figure 2), the mass concentration of SO_4^{2-} has been decreasing since 2013, as has its proportion in SNA. Sulfur control measures seemed to have achieved good results in recent years in Beijing and its surrounding areas.

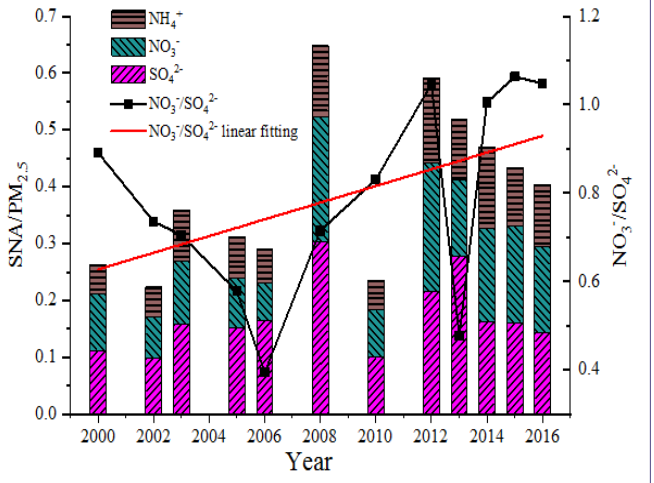

Figure 2: Inter annual changes in the proportion of SNA in $PM_{2.5}$ and NO_3^-/SO_4^{2-} in Beijing from 2000 to 2016.

From 2000 to 2016, the average mass concentration of NO_3^- was 12.31 μgm^{-3}. The lowest value was 5.12 μgm^{-3} in 2006 and the highest values were 19.20 μgm^{-3} in 2008 and 20.30 $\mu g\ m^{-3}$ in 2012; changes were modest in the other years. This may indicate that the pollution control measures on nitrate in $PM_{2.5}$ have had little effect in recent years. Notably, the mass concentration of SO_4^{2-} in $PM_{2.5}$ was usually higher than that of NO_3^- prior to 2012, but NO_3^- mass concentrations have been equal to or higher than that of SO_4^{2-} since then (except in 2013), which suggests that the relative importance of NO_3^- in $PM_{2.5}$ and in SNA had changed. According to the results of environmental monitoring, the concentration of SO_2 has decreased greatly in recent years, but NO_x has decreased minimally in Beijing (Figure 3). The number of motor vehicles (the primary emission source of NO_x but not SO_2) keeps increasing, which appears to be countering the emission control efforts of NO_x from fixed sources or coal burning to some extent. Therefore, with the control of SO_2 now effective, more attention should be paid to NO_x control.

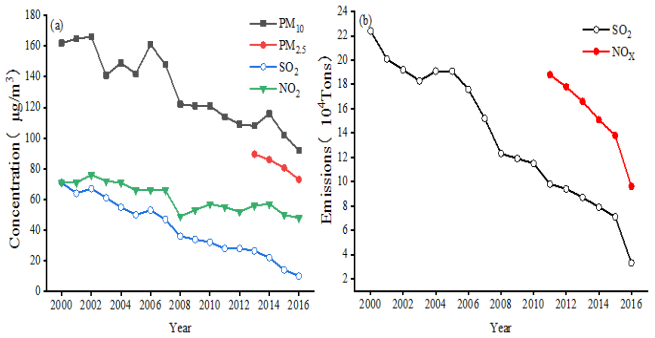

Figure 3: Annual concentration changes of four air pollutants (a) and emissions changes of SO_2 and NO_x (b)

Data source: Beijing Municipal Ecology and Environment Bureau.

$[NO_3^-]/[SO_4^{2-}]$ is often used to characterize the relative contribution of mobile sources and fixed sources to atmospheric fine particles [4]. Taken as a whole, the values of $[NO_3^-]/[SO_4^{2-}]$ showed an upward trend from 2000 to 2016 (Figure 2), indicating that the contribution of mobile sources (such as automobile exhaust gases) has gradually increased, whereas those of fixed sources (such as coal burning and other factory emissions) has gradually decreased. Upon closer examination, the value of $[NO_3^-]/[SO_4^{2-}]$ manifested a significant downward trend from 2000 to 2006, but since 2006, it has been increasing year by year (except 2013) and the ratio exceeded 1 in 2012. This may indicate that the emission control of coal burning and other factories was relatively weak in Beijing during a period of vigorous economic development before 2006. Since 2006, Beijing has gradually intensified its control of atmospheric particulate matter. Green production, "coal to gas", factory relocation and other measures have effectively reduced the contribution of fixed sources to atmospheric particulate matter. However, the number of vehicles in Beijing has been increasing year by year and thus the impact of mobile sources emission on $PM_{2.5}$ in the atmosphere must be considered more closely.

The mass concentration of NH_4^+ remained relatively stable from 2000 to 2016, with an average concentration of 8.58 μgm^{-3} and slightly higher levels in 2008 (11.13 μgm^{-3}) and 2014 (12.44 μgm^{-3}). In general, it seems that the recent emission reduction measures in Beijing have had little effect on NH_4^+ in $PM_{2.5}$. The average mass concentration of 10.25 μgm^{-3} after 2010 has increased compared with the value of 7.39 μgm^{-3} during the previous years and the mass concentration proportion of NH_4^+ in $PM_{2.5}$ and SNA has also increased significantly since 2008. As an important cation in $PM_{2.5}$, NH_4^+ combines with SO_4^{2-} and NO_3^- to form ammonium salt, which occupies a critical proportion in the mass composition of secondary fine particles. The NH_4^+ in $PM_{2.5}$ is mainly generated from gaseous NH_3 transformation, but the control measures of NH_3 have not yet received much attention. In the future, NH_3 emission control for $PM_{2.5}$ reduction should be the main focus.

In recent years, the average annual concentrations of PM_{10}, NO_2, SO_2 and $PM_{2.5}$ in Beijing has shown an obvious downward trend (Figure 3), which reflects the gradual improvement of ambient air quality and the effectiveness of controlling the primary emission of atmospheric particulates, such as dust removal from power plants, road dust and building dust. Indeed, the concentration of SO_2, NO_2 and PM_{10} decreased by 85.9 %, 32.4 % and 43.2 %, respectively, from 2000 to 2016 and $PM_{2.5}$ declined 18.9 % from 2013 to 2016. The annual total emission of SO_2 and NO_x also declined (Figure 3) by 72.9 % and 49.5 %, respectively, from 2011 to 2016. The total emissions of SO_2 and NO_x show similar decreasing patterns with that of their annual average concentrations, making it clear that the strict control of the total emission of atmospheric primary pollutants can effectively lower their concentrations.

Against the backdrop of decreasing $PM_{2.5}$ mass concentration in Beijing, the total emission and annual average concentration of SO_2 has been decreasing more significantly than that of NO_x and NH_3. As shown in figure 2, the total mass concentration proportion of SNA in $PM_{2.5}$ fluctuated from 2000 to 2012, peaking in 2012 (SNA in 2008 was not considered here) and gradually declining after 2012. The proportion of the mass concentration of SO_4^{2-} in $PM_{2.5}$ in particular had decreased significantly after 2012. However, the overall proportion of SNA in $PM_{2.5}$ and each element in SNA after 2012 were higher than the values from 2000 to 2011. The variations of SNA in $PM_{2.5}$ suggests that the reduction of $PM_{2.5}$ in Beijing in recent years might be mainly because of primary emissions (e.g., dust and factory emissions), but be limited for secondary $PM_{2.5}$. With continued reduction of the precursors, the proportion of SNA in the secondary fine particles has declined, although the ratios are still higher than they were in the earlier years. Therefore, the contribution of secondary $PM_{2.5}$ to PM pollution is becoming increasingly important in Beijing and forms the key focus regarding the control of PM pollution in the coming years. It is necessary to consider synthetic reduction measures of SNA precursors to reduce secondary particulate matter pollution.

Seasonal variation

The average seasonal changes of SNA and $PM_{2.5}$ were calculated using the complete data from 2013 to 2016, as shown in figure 4. The average change in the proportions of SNA to $PM_{2.5}$ in different seasons is shown in figure 5.

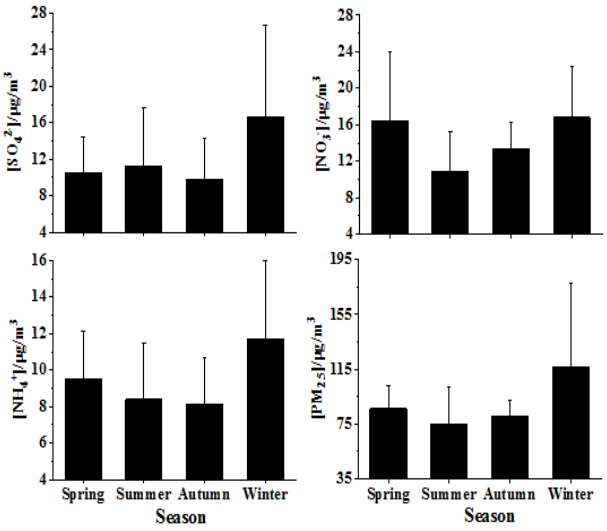

Figure 4: Seasonal variation of the mass concentration of SNA and $PM_{2.5}$ in $PM_{2.5}$ in Beijing from 2013 to 2016.

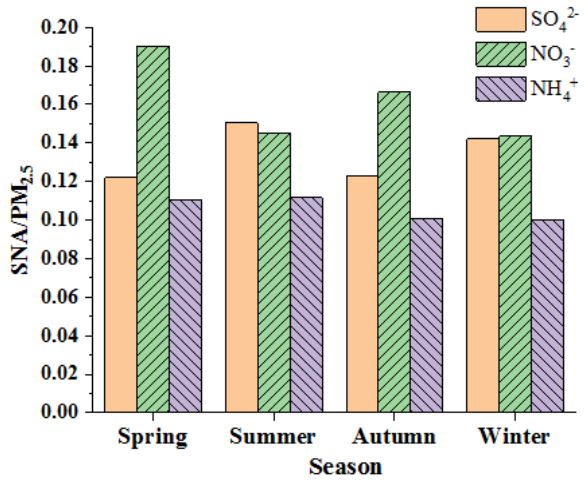

Figure 5: Seasonal variation of the mass concentration proportion of SNA in $PM_{2.5}$ in Beijing from 2013 to 2016.

SO_4^{2-} had the highest concentration (16.63 μgm^{-3}) in winter, a concentration of 11.30 μgm^{-3} in summer, a concentration of 10.53 μgm^{-3} in spring and the lowest concentration (9.85 μgm^{-3}) in autumn. The main source of SO_4^{2-} is the transformation of SO_2 emitted from burning fossil fuels. Thus, the emission of SO_2 in winter, the heating season, is much higher than that in other seasons. In addition to the primary emission source, the concentration of SO_4^{2-} is also determined by the transformation processes of gaseous SO_2 to particle SO_4^{2-} in the air, such as atmospheric photochemical reactions and liquid phase oxidation [19]. Because more radiation intensity occurs in summer, the stronger photochemical reaction facilitates an increasing concentration of SO_4^{2-}. Therefore, the proportion of SO_4^{2-} mass concentration in $PM_{2.5}$ was the largest in summer, followed by that in winter.

The concentration of NO_3^- was high in winter and spring, with average concentrations of 16.80 and 16.43 μgm^{-3}, respectively. In summer, the concentration of NO_3^- was at its lowest average concentration (10.90 μgm^{-3}) and in autumn, the concentration of NO_3^- was 13.35 μgm^{-3}. NO_3^- is mainly generated from the oxidation process of NO_x in the atmosphere, so NO_3^- and NO_x are closely related to meteorological factors. Temperature is a key factor affecting the concentration of NO_3^-, with NO_3^- mainly existing in the form of particles when the temperature is below 15°C and in the form of HNO_3(g) when the temperature is above 30°C [40]. Considering the slight change in annual motor vehicle exhaust emission intensity in Beijing, the seasonal variation of NO_3^- concentration may be mainly affected by temperature and other meteorological factors [41]. The lower temperature in winter is conducive to the transformation of HNO_3(g) into NO_3^-(s), making the concentration of NO_3^- higher in winter. In sum, the proportion of NO_3^- concentration in $PM_{2.5}$ in spring and autumn was significantly higher than that in summer and winter and the proportions in summer and in winter were similar.

The seasonal variation of NH_4^+ concentration was significantly higher in winter than in other seasons, with a concentration of 11.73 μgm^{-3} in winter, 9.53 μgm^{-3} in spring, 8.40 μgm^{-3} in summer and 8.10 μgm^{-3} in autumn. NH_4^+ in aerosols is mainly produced from the neutralization reaction between NH_3(g) and H_2SO_4 and HNO_3, generating granular NH_4^+ and NH_3 is mainly produced from livestock feeding, farmland emission and the degradation of organic matter [40]. Little difference in the proportions of NH_4^+ in $PM_{2.5}$ was noted among the four seasons, ranging only from 10.0 % to 11.0 %, with slightly higher values in summer and spring.

The seasonal variation of $PM_{2.5}$ concentration was similar to that of NH_4^+, with the highest concentration in winter (117.10 μgm^{-3}) and the lowest concentration in summer (75.15 μgm^{-3}). From 2013 to 2016, $PM_{2.5}$ concentrations as well as SO_4^{2-}, NO_3^- and NH_4^+ concentrations significantly decreased during summer (Figure 6). In spring and winter, $PM_{2.5}$ concentrations also showed a decreasing trend, but SO_4^{2-}, NO_3^- and NH_4^+ concentrations did not. In autumn, $PM_{2.5}$ and SNA consistently fluctuated in a zigzag pattern. Thus, in summer and autumn, the contributions of SNA to $PM_{2.5}$ were dominant, indicating a mainly secondary formation of $PM_{2.5}$. However, in winter and spring, the primary $PM_{2.5}$ also accounted for a notable percentage and the decrease in $PM_{2.5}$ concentration in winter and spring may be reflected largely in the reduction of primary $PM_{2.5}$.

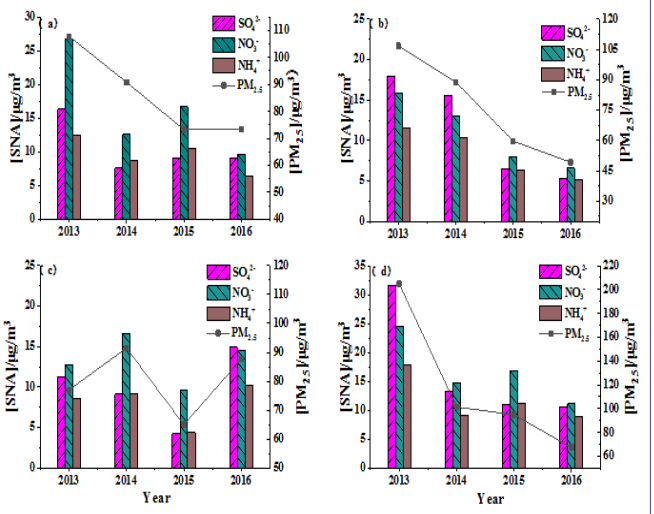

Figure 6: Trend of the mass concentration of $PM_{2.5}$ in spring (a), summer (b), autumn (c) and winter (d) and the mass concentration of SO_4^{2-}, NO_3^- and NH_4^+ in $PM_{2.5}$.

Conclusions and Discussion

Data on $PM_{2.5}$ and its three water-soluble inorganic ions (SO_4^{2-}, NO_3^- and NH_4^+ [SNA]) from 1999 to 2016 in Beijing were collected from the extant literature to analyze changes over time. The annual concentrations of $PM_{2.5}$ exhibited an obvious decreasing trend, whereas the overall level of SNA fluctuated in a "zigzag" shape. The concentrations of SO_4^{2-} dropped significantly after 2003, but NO_3^- and NH_4^+ concentrations stayed relatively constant. Nevertheless, the proportions of NO_3^- and NH_4^+ in $PM_{2.5}$ noticeably increased. This indicates that air pollution control measures have been effective against primary fine particulates and SO_4^{2-}, but have not been effective against NO_3^- and NH_4^+ in recent years.

$PM_{2.5}$ and SNA concentrations were usually high in winter, but the proportion of SNA in $PM_{2.5}$ varied from season to season. The SO_4^{2-} percentage in $PM_{2.5}$ was high in summer and the NO_3^- percentage was

high in spring and autumn, whereas the NH_4^+ percentage remained nearly the same across all four seasons. The SNA and $PM_{2.5}$ concentrations exhibited different trends in different seasons. From 2013 to 2016, $PM_{2.5}$ and SNA concentrations experienced a similar trend in summer and autumn, but not in winter and spring. It can therefore be concluded that SNA was the dominant contributor to $PM_{2.5}$ (mainly through secondary formation) in summer and autumn, whereas in winter and spring, the primary $PM_{2.5}$ also accounted for a considerable proportion.

The concentration levels of SO_4^{2-} and NO_3^- and their percentage in $PM_{2.5}$ were not aligned with the large decrease in their gaseous precursors, SO_2 and NO_x. For instance, a drop in both the emissions and ambient concentrations of SO_2 was found, yet the concentrations and percentage of SO_4^{2-} still increased before 2013. A continuous downward trend was observed after 2013, but the decreased levels of SO_4^{2-} concentrations remained the same or higher than that in the early years. NO_x emission control measures similarly exerted no obvious influence on the change of ambient NO_2 and NO_3^- concentrations. By contrast, NO_3^- accounted for a more prominent proportion in $PM_{2.5}$. NH_4^+ mass concentrations and its proportion in $PM_{2.5}$ and in SNA increased in later year in comparison with the earlier ones and thus, NH_3 emission control measures should be the focus for future PM control. SO_4^{2-}-NO_3^--NH_4^+ in atmospheric particulate matter is a complex equilibrium system, the establishment of which cannot be separated from the atmospheric chemical reactions of the precursor gases such as NH_3, SO_2 and NO_x [42,43]. From the perspective of the variation characteristics of SNA in $PM_{2.5}$, the gaseous precursors are still sufficient. Therefore, extensive research on SNA collaborative control strategiesis necessary.

The data in our paper were obtained from a wide range of literature, rather than systematic experimental results; therefore, there is a limitation in the data coverage of spatial and temporal distribution. Different type of sites, especially regarding urban and suburban sites, would certainly have different characteristics. However, the analysis in this paper did not separate them, considering the limited amount of data. Most of the data reported in the literature were mean values and the samples affected by extreme weather such as sandstorms (a large natural contribution source) could not be excluded, which might have impacted our trend analysis. The impact of transportation outside of Beijing was also not considered here. For example, the emission data of SO_2 only covered the statistical results of Beijing itself, but a large part of $PM_{2.5}$ measured in Beijing might be transported in from the surrounding areas, which would affect the matching degree of the trends between SO_4^{2-} and its precursor SO_2. Nevertheless, the conclusions of this work provide consequential information.

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