Effect of the pollution control measures on PM$_{2.5}$ during the 2015 China Victory Day Parade: Implication from water-soluble ions and sulfur isotope[☆]

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ABSTRACT

Air pollution by particulate matter is a serious problem in Beijing. Strict pollution control measures have been carried out in Beijing prior to and during the 2015 China Victory Day Parade in order to improve air quality. This distinct event provides an excellent opportunity for investigating the impact of such measures on the chemical properties of particulate matter with an aerodynamic diameter ≤ 2.5 μm (PM$_{2.5}$). The water-soluble ions as well as sulfur and oxygen isotopes of sulfate in PM$_{2.5}$ collected between August 19 and September 18, 2015 (n = 31) were analyzed in order to trace the sources and formation processes of PM$_{2.5}$ in Beijing. The results exhibit a decrease in concentration of water-soluble ions in PM$_{2.5}$ including aerosol sulfate. In contrast, the mean values of $\delta^{34}S_{sulfate}$ (4.7 ± 0.8‰ vs. 5.0 ± 2.0‰) and $\delta^{18}O_{sulfate}$ (18.3 ± 2.3‰ vs. 17.2 ± 6.0) in PM$_{2.5}$ during the air pollution control period and the non-source control period exhibit no significant differences, which suggests that despite a reduction in concentration, the sulfate source remains identical for the two periods. It is inferred that the decrease in concentration of sulfate in PM$_{2.5}$ mainly results from variations in air mass transport. Notably, the air mass during the pollution control period originated mainly from north and northeast and changed to southerly directions thereafter. The sulfur and oxygen isotopes of the sulfate point to coal combustion as the major source of sulfate in PM$_{2.5}$ from the Beijing area.

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1. Introduction

In the past few years, Beijing is frequently suffering from haze events as do numerous cities in China (Chan and Yao, 2008; R.J. Huang et al., 2014; Li and Zhang, 2014; Wang et al., 2014; Gao et al., 2015; Wang et al., 2015; Chen et al., 2016) as well as globally (e.g., Cheng et al., 2016). Of particular concern is particulate matter with an aerodynamic diameter ≤ 2.5 μm (PM$_{2.5}$) having a significant impact on human health, global climate change and regional visibility (Pope and Dockery, 2006; IPCC, 2007; R.J. Huang et al., 2014). However, the sources and formation processes of PM$_{2.5}$ in the atmosphere are not well constrained and differ from region to region. Hence, detailed investigations of the chemical and physical characteristics of PM$_{2.5}$ advance our understanding of their sources and formation mechanisms (Yao et al., 2002; Guo et al., 2010; R.J. Huang et al., 2014).

Water-soluble ions are important components of PM$_{2.5}$ (Yao et al., 2002; Chan and Yao, 2008; Gao et al., 2015). It has been shown that NH_4^+, NO_3^- and SO_4^{2-} represent the major ions of PM$_{2.5}$ in the Beijing atmosphere accounting for 9.8%, 12.0% and 16% of the PM$_{2.5}$ mass (R.J. Huang et al., 2014). Zhang et al. (2016) reported that water-soluble ions contributed 60% of the PM$_{2.5}$ mass during the summer months in Beijing and found that PM$_{2.5}$ samples were significantly acidic during hazy days. Therefore, investigations on water-soluble ions of PM$_{2.5}$ could have important implications for understanding the formation processes of haze in Beijing.

Sulfate is a substantial fraction of PM$_{2.5}$ in the atmosphere (Yao et al., 2002), accounting for 16% in Beijing aerosol (R.J. Huang et al., 2014). Sulfur isotopes allow for the identification of the potential sources of atmospheric sulfate and for estimating of the relative contribution by these sources (Norman et al., 2006; Lin et al., 2012; Xiao et al., 2012; Q. Guo et al., 2016). Many investigations have been conducted in Europe (Sinha et al., 2008), China (Mukai et al., 2001; Guo et al., 2010; Xiao et al., 2011), Japan (Sakata et al., 2013) and Antarctica (Kunasek et al., 2010) to trace atmospheric sulfate sources using sulfur isotopes. Recently, Z. Guo et al. (2016) investigated the sulfur isotopic composition of PM$_{2.5}$ in Nanjing and identified the major sulfur sources of PM$_{2.5}$.

In addition to sulfur, the oxygen isotopic composition of sulfate ($\delta^{18}O_{sulfate}$) can provide additional evidence on source and/or formation processes (Norman et al., 2006; Proemse et al., 2012). $\delta^{18}O_{sulfate}$ is influenced by source variation and mixing (Holt & Kumar, 1991). Hence, paired sulfur and oxygen isotopes provide a powerful tool for constraining the source of sulfate (Schiff et al., 2005; Proemse et al., 2012). In addition, the stable isotopes have also been used to investigate the oxidation processes of SO$_2$ and transport pathways of sulfur in the atmosphere (Norman et al., 2006; Harris et al., 2012).

For the Victory Day, the 70th anniversary of the end of World War II, strict pollution control measures have been conducted between August 20 and September 4, 2015 in order to achieve a better air quality for the city of Beijing during that time. The specific measures include: (1) Dust: Construction sites were shut down and more sprinklers were used to spray water on the road; (2) Vehicles: The odd-even license plate number rule was imposed for all vehicles except public transport; (3) Industry: A decrease in production or a temporary suspension of operations were applied for coating, printing, petrochemical and furniture industry (People's Government of Beijing Municipality, 2015). We used this distinct opportunity to investigate the impact of these pollution control measures on the chemical properties of PM$_{2.5}$ in the local atmosphere during these days. In this work, water-soluble ions as well as sulfur and oxygen isotopes of sulfate in PM$_{2.5}$ from Beijing air collected during and after the V-Day Parade have been analyzed in order to obtain a better understanding of sources and formation processes of PM$_{2.5}$.

2. Materials and methods

2.1. Sampling

PM$_{2.5}$ samples were collected on a 24-h basis between August 19 and September 18, 2015 (n = 31) using a high volume air sampler (TH-1000H, Tianhong Wuhan) with a flow rate of 1.05 m^3 min^{-1}. The sampling site is located on the building roof (around 24 m above ground level) of the Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences between the North 4th and 5th Ring Roads of Beijing (Fig. 1), an urban office

Fig. 1. A map showing the PM$_{2.5}$ sampling site in Beijing, China (modified after Guo et al., 2013). The samples were collected on the roof (around 24 m above ground level) of the Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing.

site in the Chaoyang District of Beijing. No large buildings surround the sampling site which is located immediately west of Olympic Forest Park, a large urban park area. The sampling site is located around 11 km from the Tian'anmen Square in the city center, where the V-Day Parade has been held. The samples were collected on pre-combusted (450 °C for 6 h) quartz fiber filters (20 cm × 25 cm, Munktell, Sweden). After sampling, the filters were stored in a freezer at −20 °C until geochemical analyses.

The meteorological data during the sampling period were obtained from the National Meteorological Information Center (http://data.cma.cn/site/index.html, Fig. 2). The daily average values of air temperature, air humidity, atmospheric pressure and wind speed are computed on the basis of the observation data at 2.00 a.m., 8.00 a.m., 14.00 p.m. and 20.00 p.m. The detection limits for precipitation, air temperature, air humidity, atmospheric pressure and wind speed are 0.1 mm, 0.1 °C, 1%, 0.1 hPa and 0.1 m/s, respectively.

2.2. Chemical and isotopic measurements

Half of each filter was shredded and soaked in 200 ml of Milli-Q water for 30 min by ultrasonication (Norman et al., 2006). The filter was kept in the water overnight in order to thoroughly extract the water-soluble ions. Subsequently, 0.45 mm millipore filters were used to remove the quartz filter fibers through filtration. From the filtered solution, an aliquot of 10 ml was withdrawn for concentration measurements. The remaining solution was acidified with HCl to a pH to <2, heated up to boiling, and the dissolved sulfate was precipitated as barium sulfate by adding 25 ml of 8.5% $BaCl_2$ solution. The solution was kept at 80 °C for 3 h. Thereafter, 0.22 μm acetate millipore filters were used to collect the barium sulfate precipitate, which was rinsed with 150 ml Milli-Q water (Guo et al., 2010). The precipitates were dried in an oven at 45 °C for 48 h and later analyzed for their sulfur and oxygen isotopic compositions. Blank samples were analyzed accordingly.

The concentrations of water-soluble ions (SO_4^{2-}, NO_3^-, Cl^-, F^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) were measured by ion chromatography (Dionex ICS900), which is composed of a separation column (Dionex IonPac CS12A for cation and AS23 for anion), a guard column (Dionex IonPac CG12A for cation and AG23 for anion), a self-regenerating micro-membrane suppressor (Dionex CERS500 for cation and Dionex AERS 500 for anion) and an electrical conductivity detector (Dionex IonPac DS5). 4.5 mM Na_2CO_3 and 0.8 mM $NaHCO_3$ were used as the eluent for anions; 20 mM methansulfonic acid (MSA) was used as the eluent for cations. The recovery of each ion was in the range of 80−120%. The result of the reproducibility test show the relative standard deviation for each ion was less than 5%. The detection limits range from 0.01 to 0.04 $μg/m^3$ for cations and 0.03−0.07 $μg/m^3$ for anions, and results are corrected for blank values.

The sulfur ($δ^{34}S$) and oxygen ($δ^{18}O$) isotope measurements were performed at the Institute of Geographic Sciences and Natural
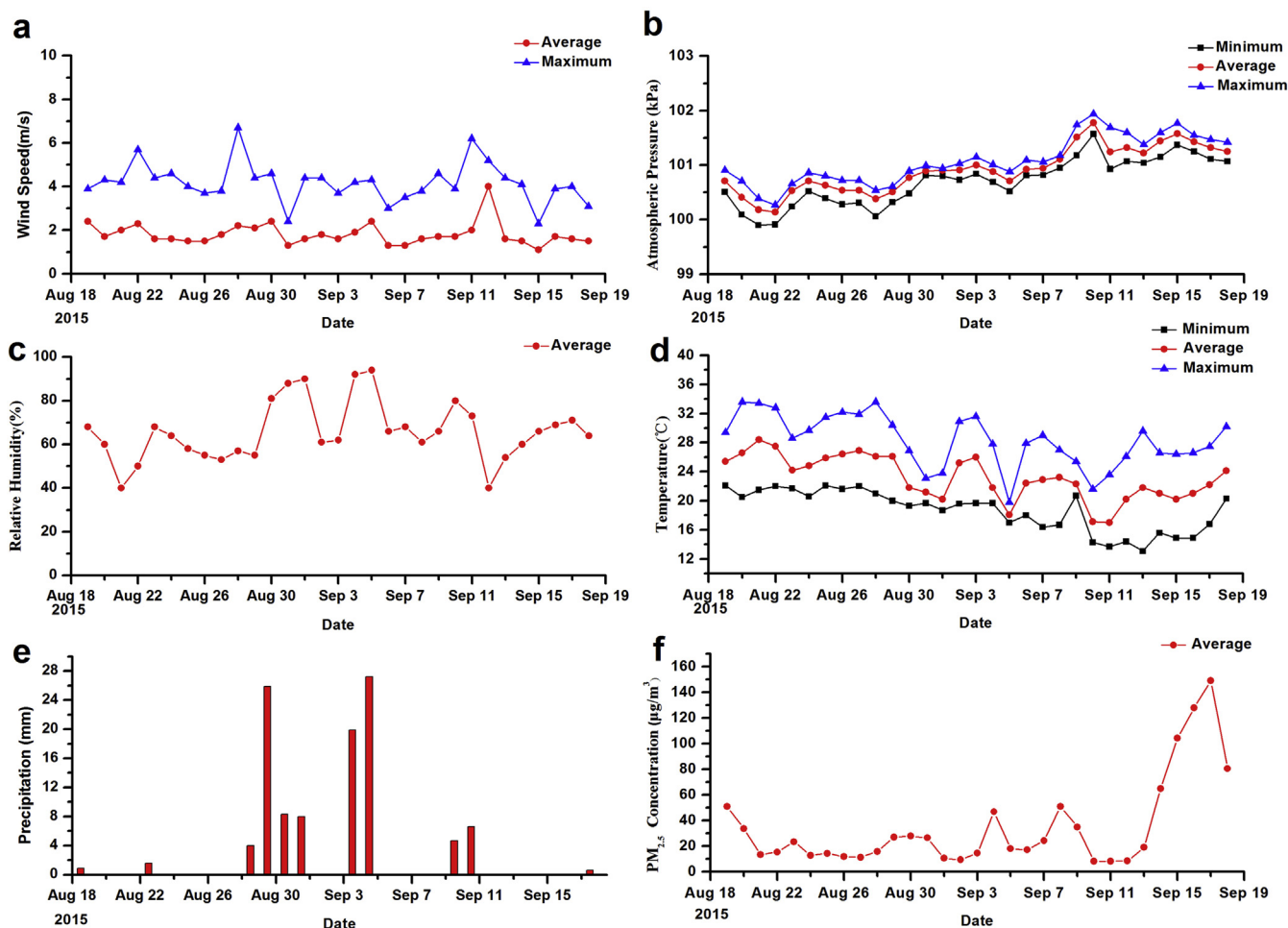

Fig. 2. Meteorological parameters and PM$_{2.5}$ concentrations during the sampling period (Meteorological data from National Meteorological Information Center, http://data.cma.cn/site/index.html; PM$_{2.5}$ data from China National Environmental Monitoring Centre, http://106.37.208.233:20035/).

Resources Research, Chinese Academy of Sciences. $\delta^{34}S_{sulfate}$ values were determined using an Elemental Analyzer (EA) coupled to a Delta V Advantage Isotope Ratio Mass Spectrometer (IRMS). The results are reported in the standard delta notation relative to the Vienna Canyon Diablo Troilite standard (V-CDT). The $\delta^{34}S$ measurements were calibrated against the reference materials NBS127 ($\delta^{34}S = 21.17 \pm 0.12‰$, n = 10) and IAEA−SO−5 ($\delta^{34}S = 0.5 \pm 0.2‰$, n = 7). The oxygen isotope values ($\delta^{18}O$) were measured using a Thermal Conversion Elemental Analyzer (TC/EA) interfaced to a Delta V Advantage isotope ratio mass spectrometer (IRMS). The results are expressed in the standard delta notation against the Vienna Standard Mean Ocean Water (V-SMOW). The calibration of $\delta^{18}O$ measurements was performed using the reference material NBS127 ($\delta^{18}O = 8.59 \pm 0.25‰$, n = 10).

2.3. Calculation of air mass trajectories

The hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model (Draxler and Rolph, 2003) was used for exploring the influence of the regional air mass transport on the $PM_{2.5}$ composition at the sample site during the V-Day Parade. 48-h back trajectories at 50 m, 200 m and 500 m arrival height above ground

level were calculated every 6 h during the investigation, respectively.

3. Results and discussion

3.1. Water-soluble ion composition of $PM_{2.5}$

The average concentration of $PM_{2.5}$ throughout the entire year 2015 is 80.1 ± 72.1 μg/m^3 (n = 365). During the time of pollution control (August 20 to September 4, 2015), $PM_{2.5}$ concentrations range from 9.4 to 46.8 μg/m^3 around a mean value of 19.6 ± 10.4 μg/m^3 (n = 16). This is in contrast to average $PM_{2.5}$ concentrations of 67.4 ± 36.4 μg/m^3 (n = 61) for a two months period (June 19, 2015−August 19, 2015) prior to and 68.8 ± 71.0 μg/m^3 (n = 61) for a two months period (September 5, 2015−November 4, 2015) after the pollution control interval. Thus, a significant decrease in $PM_{2.5}$ concentration is discernible for the period where pollution control measures were imposed.

The concentrations of water-soluble inorganic ions (WSII) in $PM_{2.5}$ during the sampling period are presented in Fig. 3 and Table 1. NO_3^-, SO_4^{2-} and NH_4^+ are the predominant ions in $PM_{2.5}$, and collectively account for ~90% of the WSII. During the pollution
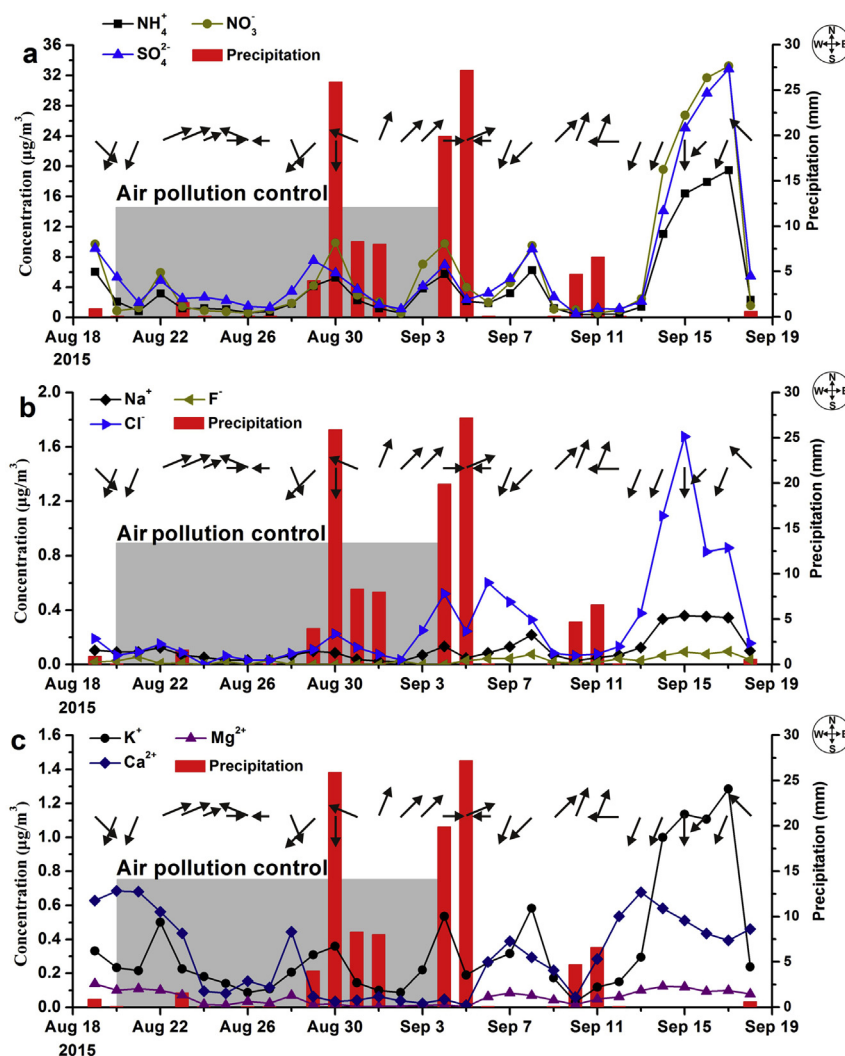

Fig. 3. Variations in precipitation, wind direction and concentrations of water-soluble ions in $PM_{2.5}$ from August 19 to September 18, 2015 in Beijing, China. Arrow represents direction of maximum wind.

Table 1
Concentrations of water-soluble inorganic ions and stable isotopes of sulfate in $PM_{2.5}$ in Beijing, China during summer months.

$PM_{2.5}$	Sampling period		Non-source control period		Period of pollution control measures		Aug. 4th-Sep. 3rd, 2012[a]		Olympic period (Jul. 1st-Sep. 20th, 2008)[b]		Jul. 1st-Sep. 20th of 2005–2007[b]		Summer of 2001–2003[c]	
	Mean ± SD	n	Mean ± SD	n	Mean ± SD	n	Mean ± SD	n	Mean ± SD	n	Mean ± SD	n	Mean ± SD	n
Ionic species														
Na^+ ($\mu g/m^3$)	0.11 ± 0.10	31	0.16 ± 0.12	15	0.07 ± 0.04	16	0.4 ± 0.6	31	0.19 ± 0.16	9	0.43 ± 0.22	26	0.24 ± 0.17	86
NH_4^+ ($\mu g/m^3$)	4.08 ± 5.17	31	6.04 ± 6.80	15	2.24 ± 1.69	16	10.5 ± 9.3	31	8.4 ± 2.5	9	8.0 ± 3.1	31	10.10 ± 6.97	86
K^+ ($\mu g/m^3$)	0.35 ± 0.33	31	0.48 ± 0.43	15	0.23 ± 0.14	16	0.9 ± 0.6	31	0.46 ± 0.22	9	1.5 ± 0.59	31	1.29 ± 1.25	86
Mg^{2+} ($\mu g/m^3$)	0.06 ± 0.04	31	0.08 ± 0.04	15	0.04 ± 0.04	16	0.3 ± 0.6	31	0.08 ± 0.04	8	0.22 ± 0.10	29	0.10 ± 0.07	86
Ca^{2+} ($\mu g/m^3$)	0.30 ± 0.23	31	0.38 ± 0.20	15	0.22 ± 0.25	16	1.2 ± 1.7	31	0.41 ± 0.19	6	1.5 ± 0.74	31	0.73 ± 0.60	86
F^- ($\mu g/m^3$)	0.03 ± 0.03	31	0.05 ± 0.03	15	0.01 ± 0.02	16	–		–		–		0.10 ± 0.09	86
Cl^- ($\mu g/m^3$)	0.29 ± 0.37	31	0.48 ± 0.46	15	0.12 ± 0.13	16	0.6 ± 0.6	31	0.47	1	0.39 ± 0.22	11	1.41 ± 1.31	86
NO_3^- ($\mu g/m^3$)	6.45 ± 9.09	31	9.92 ± 11.87	15	3.20 ± 3.23	16	13.7 ± 13.4	31	3.9 ± 1.5	9	1.5 ± 2.2	28	11.18 ± 10.37	86
SO_4^{2-} ($\mu g/m^3$)	6.47 ± 8.18	31	9.59 ± 10.91	15	3.56 ± 2.05	16	28.4 ± 27.3	31	13.1 ± 4.8	8	22.3 ± 11.3	31	18.42 ± 15.28	86
Stable isotopes														
$\delta^{34}S$ (‰)	4.9 ± 1.5	29	5.0 ± 2.0	14	4.7 ± 0.8	15	–		–		–		–	
$\delta^{18}O$ (‰)	17.9 ± 4.1	24	17.2 ± 6.0	10	18.3 ± 2.3	14	–		–		–		–	

SD: standard deviation; n: number; −: No data.
[a] Data from Zhang et al. (2016).
[b] Data from Okuda et al. (2011).
[c] Data from Wang et al. (2005).

control period, the concentrations of NO_3^-, SO_4^{2-} and NH_4^+ vary from 0.55 to 9.88 $\mu g/m^3$ (mean = 3.20 ± 3.23 $\mu g/m^3$, n = 16), from 1.12 to 7.54 $\mu g/m^3$ (mean = 3.56 ± 2.05 $\mu g/m^3$, n = 16) and from 0.56 to 5.76 $\mu g/m^3$ (mean = 2.24 ± 1.69 $\mu g/m^3$, n = 16), respectively. In contrast, the concentrations of NO_3^-, SO_4^{2-} and NH_4^+ are higher during the non-source control period, ranging from 0.61 to 33.28 $\mu g/m^3$ (mean = 9.92 ± 11.87 $\mu g/m^3$, n = 15), from 0.50 to 32.88 $\mu g/m^3$ (mean = 9.59 ± 10.91 $\mu g/m^3$, n = 15) and from 0.4 to 19.49 $\mu g/m^3$ (mean = 6.04 ± 6.80 $\mu g/m^3$, n = 15), respectively. The concentration of Cl-is very low during the pollution control period (0.00–0.52 $\mu g/m^3$), while it shows a significant increase during the non-source control period (0.07–1.68 $\mu g/m^3$). The concentrations of Na^+, Mg^{2+}, Ca^{2+} and F^- are lower than 0.7 $\mu g/m^3$ throughout the sampling period.

The concentrations of WSII in Beijing $PM_{2.5}$ during the pollution control period are lower than those in Shanghai (Huang et al., 2014a,b), Xi'an (Wang et al., 2015) and Chengdu (Tao et al., 2014b) cities, China, but they are close to the concentration values from Guangzhou, China except the sulfate concentration (Table 2; Tao et al., 2014a). Under the condition of strict pollution control measures, the concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+} and Cl^- in Beijing $PM_{2.5}$ are lower than for Shenzhen city except the

concentrations of SO_4^{2-}, NO_3^- and NH_4^+ (Dai et al., 2013, Table 2). However, the concentrations of NO_3^- (3.20 ± 3.23 $\mu g/m^3$) and NH_4^+ (2.24 ± 1.69 $\mu g/m^3$) are still higher than for four European cities along the densely populated Mediterranean Sea (Barcelona, Marseille, Genoa, and Thessaloniki; cf. Salameh et al., 2015) or a central European rural site in the Czech Republic (Schwarz et al., 2016, Table 3).

The mass ratio of NO_3^-/SO_4^{2-} can provide an implication for the relative importance of mobile versus stationary sources of nitrogen and sulfur in the atmosphere (Arimoto et al., 1996; Yao et al., 2002). High values of NO_3^-/SO_4^{2-} ratio indicate a higher contribution from mobile pollutant sources than from stationary sources (Arimoto et al., 1996). In Beijing, emission factors of pollutants are 0.1 g/km of NO_x and 0.01 g/km of SO_2 for gasoline vehicles, and 0.8 g/km of NO_x and 0.1 g/km of SO_2 for diesel vehicles, both of which conform to European emission standard IV(Hao and Xie, 2010). Thus, the emission ratios of NO_x to SO_2 from gasoline and diesel vehicles are 10:1 and 8:1, respectively. The sulfur and nitrogen contents in Chinese coal range from 0.1 to 5.6 wt% and from 0.4 to 1.6 wt%, respectively (Xiao and Liu, 2011). It is estimated that the ratios of NO_x to SO_2 is less than 1.0 from coal combustion. The average ratio of NO_3^-/SO_4^{2-} is 0.80 during the period from August 20

Table 2
Concentrations of water-soluble inorganic ions in $PM_{2.5}$ from different areas in China.

$PM_{2.5}$	Beijing Pollution control period	Xi'an, 2010[a]	Guangzhou July, 2009[b]	Chengdu July, 2011[c]	Shenzhen July and August in 2009 and 2010[d]	Shanghai March and May, 2012[e]
Ionic species	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
n	16	366	31	30	55	58
Na^+ ($\mu g/m^3$)	0.07 ± 0.04	–	2.1 ± 0.3	0.5 ± 0.2	3.05 ± 1.13	0.99 ± 0.22
NH_4^+ ($\mu g/m^3$)	2.24 ± 1.69	8.3 ± 8.3	1.6 ± 1.2	9.0 ± 5.0	1.38 ± 0.41	4.26 ± 2.11
K^+ ($\mu g/m^3$)	0.23 ± 0.14	2.5 ± 1.7	0.3 ± 0.1	1.3 ± 0.6	1.50 ± 0.28	0.58 ± 0.37
Mg^{2+} ($\mu g/m^3$)	0.04 ± 0.04	0.4 ± 0.6	–	0.1 ± 0.0	0.29 ± 0.07	0.16 ± 0.04
Ca^{2+} ($\mu g/m^3$)	0.22 ± 0.25	3.6 ± 4.8	0.2 ± 0.1	0.3 ± 0.2	1.32 ± 0.34	0.43 ± 0.23
F^- ($\mu g/m^3$)	0.01 ± 0.02	–	–	0.0 ± 0.0	–	–
Cl^- ($\mu g/m^3$)	0.12 ± 0.13	5.0 ± 5.5	1.0 ± 0.7	0.4 ± 0.4	1.12 ± 0.20	1.15 ± 1.02
NO_3^- ($\mu g/m^3$)	3.20 ± 3.23	17.8 ± 15.9	2.0 ± 1.0	5.3 ± 3.2	1.98 ± 0.56	10.80 ± 5.70
SO_4^{2-} ($\mu g/m^3$)	3.56 ± 2.05	23.1 ± 16.6	9.2 ± 4.6	23.7 ± 13.5	3.72 ± 0.92	12.04 ± 3.62

SD: standard deviation; n: number; −: No data.
[a] Data from Wang et al. (2015).
[b] Data from Tao et al. (2014a).
[c] Data from Tao et al. (2014b).
[d] Data from Dai et al. (2013).
[e] Data from G. Huang et al., 2014.

Table 3
Concentrations of water-soluble inorganic ions in PM$_{2.5}$ from European areas.

PM$_{2.5}$	China	European mediterranean cities[a]																Central europe[b]
	Beijing Pollution control period	Barcelona 02/2011−12/2011			Marseille 07/2011−07/2012			Genoa 3/2011−09/2011			Venice 01/2011−12/2011			Thessaloniki 06/2011−05/2012			Koseice** 02/2009−04/2010
Ionic species	Mean ± SD	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean ± SD
n	16	68	68	68	216	216	216	184	184	184	312	312	312	149	149	149	70
Na$^+$ (μg/m^3)	0.07 ± 0.04	0.30	0.03	0.08	0.10	0.03	0.60	0.10	0.00	0.90	0.20	0.10	2.40	0.20	0.01	0.90	0.04 ± 0.03
NH$_4^+$ (μg/m^3)	2.24 ± 1.69	1.00	0.10	5.40	1.50	0.10	5.20	1.40	0.02	4.40	2.30	0.10	18.60	2.10	0.10	6.40	1.52 ± 1.03
K$^+$ (μg/m^3)	0.23 ± 0.14	0.13	0.02	0.45	0.23	0.06	0.61	0.10	0.02	0.38	–	–	–	0.43	0.00	1.77	0.09 ± 0.08
Mg^{2+} (μg/m^3)	0.04 ± 0.04	0.05	0.01	0.14	0.14	0.05	0.29	0.04	0.01	0.11	–	–	–	0.44	0.01	1.55	0.00 ± 0.01
Ca^{2+} (μg/m^3)	0.22 ± 0.25	0.15	0.02	0.40	1.09	0.03	4.35	0.11	0.01	0.46	–	–	–	2.04	0.03	6.99	0.00 ± 0.00
F$^-$ (μg/m^3)	0.01 ± 0.02	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cl$^-$ (μg/m^3)	0.12 ± 0.13	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.04 ± 0.04
NO$_3^-$ (μg/m^3)	3.20 ± 3.23	1.00	0.01	10.50	1.70	0.20	6.90	0.50	0.10	6.10	5.40	0.20	60.20	2.40	0.10	10.20	2.20 ± 2.34
SO$_4^{2-}$ (μg/m^3) *	3.56 ± 2.05	2.80	0.40	7.90	2.20	0.40	7.20	3.60	0.04	9.90	3.40	0.20	13.30	3.90	0.10	11.30	2.85 ± 2.05

SD: standard deviation; n: number; −: No data; *: nss-SO$_4^{2-}$; **:Central European rural site.
[a] Data from Salameh et al. (2015).
[b] Data from Schwarz et al. (2016).

to September 4 (Fig. 4a), which suggests the predominance of stationary pollutant sources over mobile sources, reflecting the impact of vehicle restrictions on the nitrate concentration.

SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ primarily originate from the transformation of SO$_2$ and NO$_2$ (Wang et al., 2005; Huang et al., 2014a,b). Strong correlations between NO$_3^-$ and NH$_4^+$ (r = 0.99), between SO$_4^{2-}$ and NH$_4^+$ (r = 0.99) and between NO$_3^-$ and SO$_4^{2-}$ (r = 0.97) (Table 4), respectively, have been found suggesting that (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ are the major ionic species in PM$_{2.5}$ (Wang et al., 2005). SO$_2$ and NO$_x$ are mainly derived from coal combustion and vehicle exhausts; NH$_3$ mainly originates from agricultural activities and livestock waste (Tao et al., 2014b). (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ can be formed by the oxidation of these precursor gases.

Ca^{2+} and Mg^{2+} as tracers of terrestrial sources are mainly derived from road dust, soil dust and construction dust (Wang et al., 2005). Ca^{2+} and Mg^{2+} concentrations of PM$_{2.5}$ are lower than 0.7

Fig. 4. Ratios of NO$_3^-$ to SO$_4^{2-}$ concentrations and equivalent ratios of the total cations to the total anions measured in PM$_{2.5}$.

and 0.2 μg/m^3 throughout the sampling period, respectively. Ca^{2+} and Mg^{2+} concentrations of PM$_{2.5}$ in Guangzhou, Chengdu and Shanghai are also very low (Table 2). Respective Ca^{2+} and Mg^{2+} concentrations in PM$_{2.5}$ are somewhat more variable for the four European Mediterranean cities but really low for the rural site in central Europe (Table 3). Furthermore, no significant differences in Ca^{2+} and Mg^{2+} concentrations of PM$_{2.5}$ between the pollution control period and the non-source control period could be observed indicating only a minor contribution of road and construction dust to the PM$_{2.5}$ mass concentrations during the summer period.

Water soluble potassium can be used as a tracer for the identification of biomass burning (Duan et al., 2004). Cheng et al. (2013) reported that K$^+$ is an acceptable indicator for biomass burning during the summer months in the Beijing area based on their data of levoglucosan (C$_6$H$_{10}$O$_5$, a unique tracer for biomass burning). The K$^+$ concentrations of PM$_{2.5}$ during the period of the V-Day Parade are lower than 0.6 μg/m^3, implying that the contribution of biomass burning to PM$_{2.5}$ is negligible. K$^+$ concentrations range from 1.0 to 1.29 μg/m^3 during the period from September 14 to 17, which is related to the air mass from the south of Beijing.

The Cl$^-$ and Na$^+$ concentrations are positively correlated (r = 0.88) (Table 4), suggesting they may have a common source. It has been reported that high Cl$^-$ concentration in Beijing PM$_{2.5}$ may be related to coal combustion (Yao et al., 2002). During combustion, complex changes in coal particles may cause the vaporization of volatile elements, including sodium (Clarke, 1993). Na$^+$ may be present in the gas phase or bound in PM$_{2.5}$ in the flue gases, which can be emitted to the atmosphere (Clarke, 1993).

The ion balance as an indicator of the acidity of the aerosols was calculated using the equivalent ratios of the total cations to the total anions in PM$_{2.5}$ samples (Wang et al., 2005). The equivalent ratios of cations/anions (C/A) during the sampling period range between 0.92 and 1.49 (Fig. 4b) around a mean value of 1.15 ± 0.14 (n = 31). The equivalent ratio of C/A is higher than 1.0 during non-haze days, which indicates that the PM$_{2.5}$ samples are alkaline. The higher ratios of C/A during non-haze days may be caused by a higher amount of carbonate and bicarbonate (Clarke and Karani, 1992).

The average concentrations of water-soluble inorganic ions in PM$_{2.5}$ in the Beijing atmosphere during the summer months of the period between the years 2001 and 2015 are shown in Fig. 5 and Table 1. The concentrations of water-soluble ions in PM$_{2.5}$ during time interval prior to and around the V-Day Parade of 2015 (the time of pollution control) were lower, when compared to the year of 2001−2003, 2005−2007 and 2012. This could be attributed to
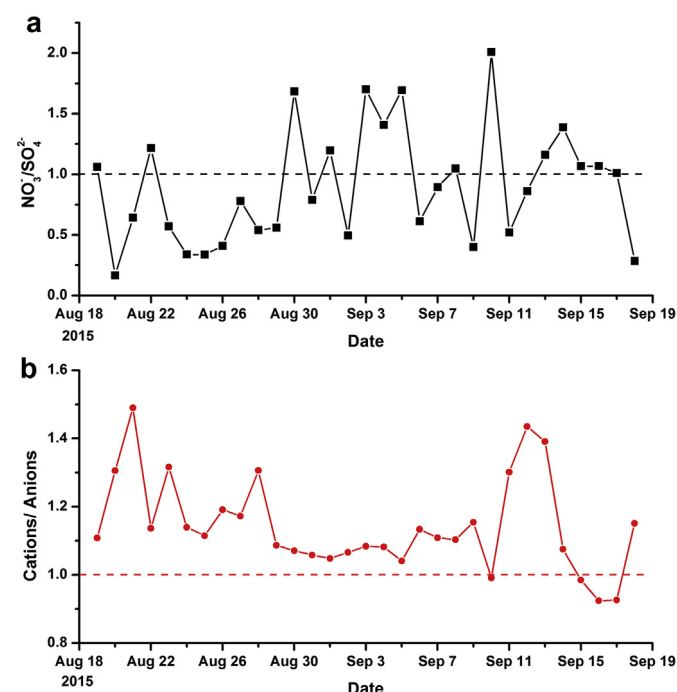
Table 4
Correlation coefficients for water-soluble ions and stable isotopes of PM$_{2.5}$ in Beijing.

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	$\delta^{34}S$	$\delta^{18}O$
Na^+	1.00										
NH_4^+	0.94**	1.00									
K^+	0.98**	0.97**	1.00								
Mg^{2+}	0.62**	0.47**	0.56**	1.00							
Ca^{2+}	0.43*	0.24	0.35	0.94**	1.00						
F^-	0.82**	0.72**	0.76**	0.62**	0.50**	1.00					
Cl^-	0.88**	0.84**	0.87**	0.49**	0.30	0.72**	1.00				
NO_3^-	0.93**	0.99**	0.96**	0.45*	0.22	0.71**	0.83*	1.00			
SO_4^{2-}	0.92**	0.99**	0.95**	0.49**	0.27	0.74**	0.79**	0.98**	1.00		
$\delta^{34}S$	−0.40*	−0.49**	−0.45*	−0.36	−0.21	−0.27	−0.25	−0.43*	−0.53*	1.00	
$\delta^{18}O$	−0.28	0.51**	0.37	−0.08	−0.28	0.07	0.22	0.51*	0.51*	−0.60**	1.00

*Significant at 0.05 level; **Significant at 0.01 level.
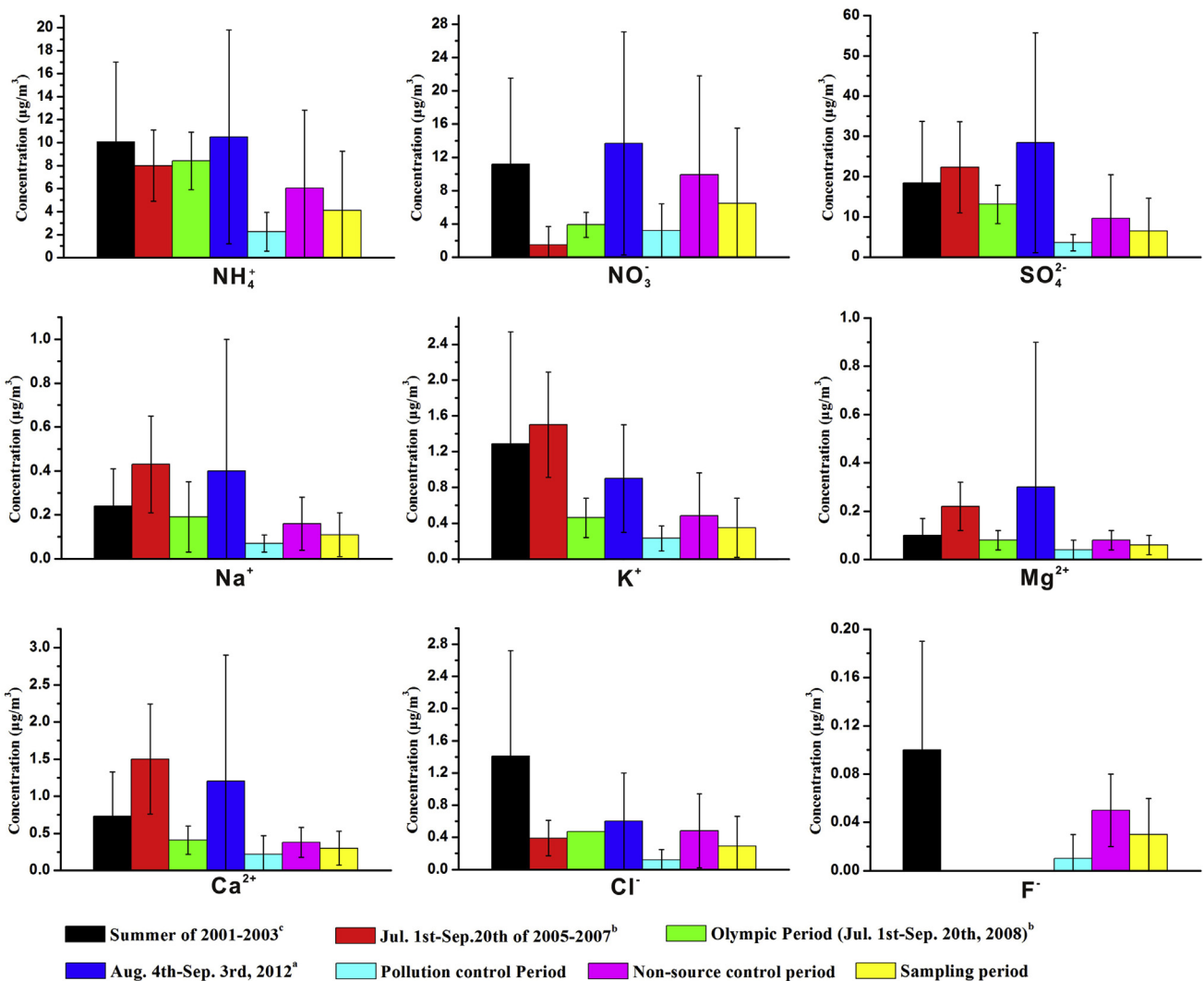
Fig. 5. Average concentrations of water-soluble inorganic ions in PM$_{2.5}$ for Beijing. a data from Zhang et al. (2016); b data from Okuda et al. (2011); c data from Wang et al. (2005).

the pollution control measures. Comparable pollution control measures were imposed during the 2008 Beijing Olympic Games, and similar concentrations, e.g. of NO_3^- and Ca^{2+} in PM$_{2.5}$ have been measured for both periods, indicating an effect on the concentration of both ionic species through, e.g., traffic regulations and construction sites' shut-down.

It seems that there is a significant difference in PM$_{2.5}$ between the pollution control period and the non-source control period. In addition to consequence of strict pollution control measures, meteorological parameters have to be considered as well. Air mass back trajectories show that the air mass during the period of the air pollution control measures mainly originated from north and northeast, except the period from August 29 to August 31, 2015 as well as on September 4, 2015 when the air mass were derived from the south and southeast (Fig. 6a, b and c). It has been reported that the air mass from the north is significantly cleaner than from the
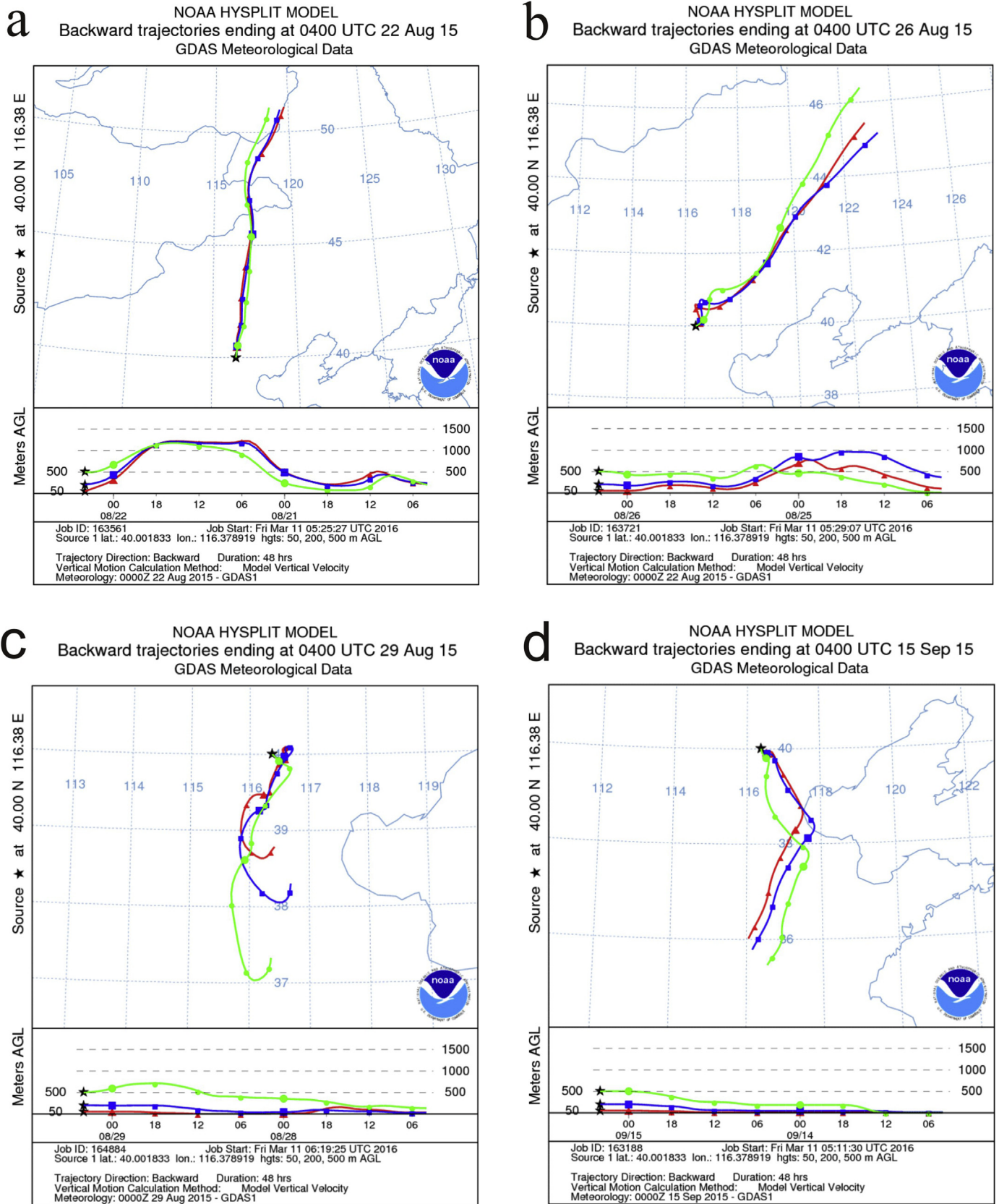
Fig. 6. Back trajectories of air masses for 4 events selected for the sampling period: a and b show that the air masses during the period of air pollution control measures mainly originated from north and northeast, respectively; c shows that the air masses derived from the south and southeast (heavily polluted area) during the period from August 29 to August 31, 2015 and on September 4, 2015 (air pollution control period); d shows that the air masses originated from the south and southeast (heavily polluted area) during the period from September 14 to September 17, 2015 (the non-source control period).
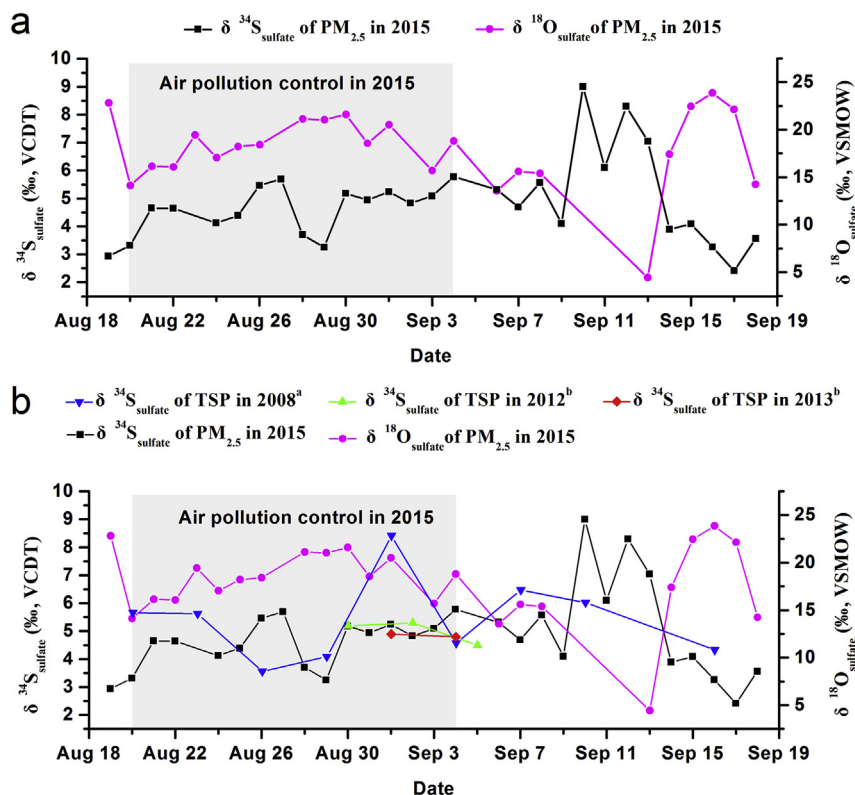
Fig. 7. Variations in $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ values of sulfate in $PM_{2.5}$ from August 19, 2015 to September 18, 2015 in Beijing, China. a data from Guo et al., 2014; b data from unpublished paper.

south (Zhang et al., 2014), which results in lower background concentrations of $PM_{2.5}$ during the V-Day Parade. The contribution from coal combustion to $PM_{2.5}$ of Beijing is very significant (R.J. Huang et al., 2014). The air mass from the south and southeast of Beijing passed the Hebei province, one of the largest coal-consuming provinces in China, which leads to an increase in $PM_{2.5}$ concentrations in Beijing air (Sun et al., 2010; Zhang et al., 2014). Still, the $PM_{2.5}$ concentrations during the period from August 29 to August 31, 2015 and on September 4, 2015 were lower than 50 $\mu g/m^3$. It is inferred that the lower concentrations of $PM_{2.5}$ during these four days could be caused by frequent rainfall (Fig. 3). Rainfall can substantially reduce the concentration of particulate matter (Giri et al., 2008). In addition, the air mass during the period of September 9 to 11, 2015 mainly originated from north and northeast (Fig. 3) could have led to a lower concentration of WSII in $PM_{2.5}$ after V-Day Parade (September 9 to September 12). A sharp increase in the $PM_{2.5}$ concentration during the period from September 14 to September 17, 2015, can be observed, which may be related to the air mass from the south and southeast with a higher content of particulate matter (Fig. 6d). It has been observed that the concentrations of water-soluble ions in $PM_{2.5}$ may increase when the wind are from the south, southeast and southwest of Beijing (Fig. 3). Consequently, in addition to the strict pollution control measures, the origin of the air masses exert a significant control on the Beijing air quality, as was also suggested for the reduction in $PM_{2.5}$ pollution during the 2008 Olympic Games (Schleicher et al., 2012).

3.2. Sulfur and oxygen isotopes in sulfate

The sulfur isotopic composition of sulfate ($\delta^{34}S_{sulfate}$) in $PM_{2.5}$ during the sampling period between August 19 and September 18, 2015 ranges from 2.4 to 9.0‰ (mean = 4.9 ± 1.5‰, n = 29) and the

respective $\delta^{18}O_{sulfate}$ values vary from 4.4 to 23.9‰ around a mean value of 17.9 ± 4.1‰ (n = 24). The $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ values exhibit a limited variability, except for the period from September 10th to 13th. The average values of $\delta^{34}S_{sulfate}$ in $PM_{2.5}$ during the air pollution control period and the non-source control period are 4.7 ± 0.8‰ (n = 15) and 5.0 ± 2.0‰ (n = 14), respectively. The mean values of $\delta^{18}O_{sulfate}$ in $PM_{2.5}$ during the air pollution control period and the non-source control period are 18.3 ± 2.3‰ (n = 14) and 17.2 ± 6.0‰ (n = 10), respectively. While the variability increases during the non-source control period, no significant differences in the mean $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ values between both time intervals are discernible (Fig. 8).

Previous studies revealed comparable isotope results. The mean value of $\delta^{34}S_{sulfate}$ in total suspended particulates (TSP) in Beijing between August 20 and September 16, 2008 (the period of the Olympic Games) was 5.4 ± 1.5‰ (n = 9; Guo et al., 2010), despite significant pollution control measures (People's Government of Beijing Municipality, 2015). Also, a mean $\delta^{34}S_{sulfate}$ value of 4.9 ± 0.3‰ (n = 5) was recorded in TSP from Beijing air for the period from August 30 to September 4 of 2012 and 2013, a time without any air pollution control measures in place (from unpublished paper) (Fig. 7). Thus, although a decrease in sulfate concentration was observed during V-Day time, no apparent impact on the sulfate source of $PM_{2.5}$ is discernible.

In order to guarantee blue skies for the V-Day Parade, a series of measures, such as construction sites' shut-down, traffic control measures, and industrial suspensions were imposed in order to reduce the emission of air pollutants (People's Government of Beijing Municipality, 2015). For example, around 9000 construction sites in Beijing were halted to reduce the impact of dust pollution (Zeng, 2015). In addition, more sprinklers were used to spray water onto the roads, in order to decrease air pollution by road dust. However, Ca^{2+} and Mg^{2+} concentrations of $PM_{2.5}$

$(Ca^{2+}<0.7$ and $Mg^{2+}<0.2$ μg/m^3) show lower values throughout the sampling period, indicating that dust is only a minor contributor to the sulfate pool of $PM_{2.5}$.

Substantial traffic control measures were put into place in Beijing from August 20 to September 3, with almost half of vehicles banned from the roads at any time. Recently, Wu et al. (2016) investigated the emission factor of sulfate in $PM_{2.5}$ emitted from China III and China IV diesel trucks in Beijing, ranging from 0.12 to 1.14 mg/km. According to the data from the Beijing traffic Management Bureau, the total number of vehicles in Beijing was 5.59 million by the end of 2014. Wang et al. (2013) reported for the years 2012 and 2013 that private passengers in Beijing drive with their vehicles a daily distance of 33.5 km in average. Assuming that all of the vehicles are diesel trucks and the daily driving distance is 33.5 km, the estimation of sulfate emission from vehicles ranges from 8.2 to 77.9 tons/year (Table 5). It may be equivalent to 5.5–51.9 tons/year of SO_2 emissions. Compared to 78.9 thousand tons of SO_2 emitted to the Beijing air in 2014 (Beijing Municipal Environmental Protection Bureau, 2015), vehicles account for only 0.007–0.066% of the annual SO_2 emissions in Beijing (Table 5). Thus, the sulfate emissions from vehicles may play a very small role as a contributor to the atmospheric sulfate pool. Consequently, the traffic control measures during the V-Day Parade had only a minor effect on the reduction of the sulfate concentration in $PM_{2.5}$.

In order to lower industrial pollution, the production of around 10,000 companies in Beijing and its surrounding areas was limited or suspended during the V-Day Parade (Zeng, 2015). However, it is not easy to determine the sulfate emissions from these companies.

The sulfur isotopic composition of sulfate in $PM_{2.5}$ shows a mixture between sulfate sources with high and low $\delta^{34}S$ values (Fig. 8a), which indicates that the sulfate was derived from different sources or formation processes (Guo et al., 2010). It has been reported that sea salt sulfate is characterized by a $\delta^{34}S$ value of +21‰ (Tostevin et al., 2014). However, the contribution of sea-salt sulfate can be very low due to the long distance from Beijing to the Bohai Sea (~150 km). Furthermore, a significant contribution from sea salt is not very likely as suggested by the low concentration of Na^+(0.11 ± 0.10 μg/m^3, n = 31). The sulfur content in oil from North China ranges from 0.1% to 0.6% and its $\delta^{34}S$ value varies between 13.7‰ and 24.2‰ (mean = 20.5‰, n = 4) (Maruyama et al., 2000). The emission rate of SO_2 from oil combustion is relatively constant with almost no seasonal change in the consumption of petroleum. Therefore, the SO_2 emissions from oil combustion in the study area are a steady source of sulfate in $PM_{2.5}$ that is characterized by a relatively high $\delta^{34}S$ value.

Sulfur from coal combustion is an important source for

Fig. 8. $\delta^{34}S_{Sulfate}$ versus sulfate concentrations and $\delta^{34}S_{sulfate}$ versus $\delta^{18}O_{sulfate}$ in $PM_{2.5}$ during the sampling period. The data of sulfur isotope in the coal of North China are from Maruyama et al. (2000); the data of sulfur isotope in rain water of Beijing are from Zhu et al. (2015); the data of sulfur isotope in biogenic sulfur are from Mast et al. (2001).

atmospheric sulfur in China (Mukai et al., 2001; Guo et al., 2010). It is reported that the $\delta^{34}S$ values of atmospheric sulfate in different regions of China are associated with local coal combustion (Mukai et al., 2001). The mean $\delta^{34}S$ values of sulfate in coal from North China and suburban areas of Beijing are +6.6 ± 9.6‰ (n = 39) (Hong et al., 1993; Maruyama et al., 2000) and 8.0 ± 3.0‰ (n = 14) (from unpublished paper), respectively. The average $\delta^{34}S$ value for sulfate in $PM_{2.5}$ from Beijing (4.9 ± 1.5‰, n = 29) is close to those of coals used in North China as well as suburban areas of Beijing indicating that coal combustion is the dominant source of atmospheric sulfate (Mukai et al., 2001; Guo et al., 2010). In summer, biogenic sulfur released from wetlands and soils can be also a source for atmospheric sulfate (Mast et al., 2001). The $\delta^{34}S$ values of biogenic sulfur are generally negative, varying from −10 to −2‰ (Liu et al., 1996; Mast et al., 2001). Hence, a contribution of sulfur from biogenic sources cannot be ruled out but appears to be minor as concluded from the different sulfur isotopic compositions compared to $\delta^{34}S$ in $PM_{2.5}$.

4. Conclusion

Water-soluble ionic species in $PM_{2.5}$ collected during a distinct period around the V-Day Parade in mid-August to mid-September 2015 in Beijing exhibit a reduction in concentration during the pollution control period. We attribute this to a combined effect of air pollution control measures and air mass transport. No significant differences in $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ values between the air

Table 5
Estimation of annual SO_2 emission from vehicles in Beijing.

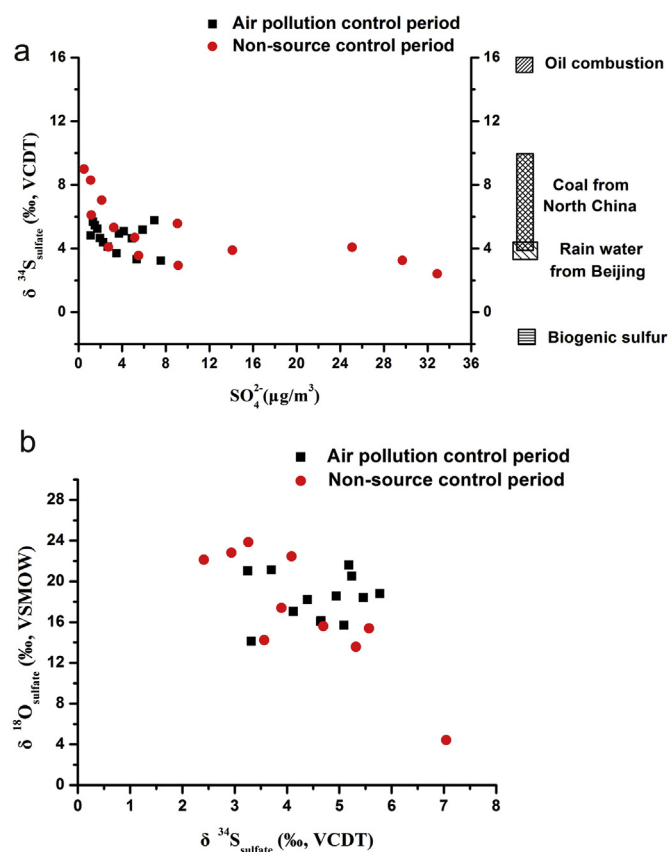| Species	Quantitative value	Reference
Number of vehicles (N)	5, 590, 000	Beijing traffic Management Bureau (2015)
Average of daily distance (D)	33.5 km	Wang et al. (2013)
Sulfate emission factor (F)	0.12−1.14 mg/km	Wu et al. (2016)
Period (P)	365 days	
Estimation of annual sulfate emission from vehicles (E) ($E = N \times D \times F \times P$)	8.2−77.9 tons/year	
Estimation of annual SO_2 emission from vehicles	5.5−51.9 tons/year	
Annual emissions of SO_2 in Beijing (2014)	78, 900 tons	Beijing Municipal Environmental Protection Bureau, 2015
Percentage of annual SO_2 emission from vehicles	0.007−0.066%	

pollution control period and the non-source control period are discernible, although the variability increases during the non-source control period. It reveals that the pollution control measures have only a minor impact on sulfate source of $PM_{2.5}$.

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