Long-term trend of chemical composition of atmospheric precipitation at a regional background station in Northern China

Weiwei Pu^{a, b} Weijun Quan^b Zhiqiang Ma^{a, b*} Xuefeng Shi^c Xiujuan Zhao^{a, b} Linna Zhang^d Zhenfa Wang^e Wenyan Wang^e

^aInstitute of Urban Meteorology, China Meteorological Administration, Beijing 100089, China

^bEnvironmental Meteorology Forecast Center of Beijing-Tianjin-Hebei, China Meteorological Administration, Beijing 100089, China

^cChina Meteorological Administration, Beijing 100081, China

^dBeijing Municipal Meteorological Observatory 100081, China

^eMiyun Meteorology Administration, Beijing 101500, China

Abstract

Understanding the trend of chemical composition of precipitation is of great importance for air pollution control strategies in Northern China. A comprehensive study on the long-term chemical compositions of precipitation was carried out from 2003 to 2014 at the Shangdianzi (SDZ) regional background station in northern China. All samples were analyzed for pH, electrical conductivity and major ions (F^- , Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Mg^{2+} , Ca^{2+} , K^+ and Na^+). The average pH during this period was 4.53 ± 0.35 , which is considerably lower than those reported in other background stations in China (Linan, Waliguan and Longfengshan). NH_4^+ , SO_4^{2-} , Ca^{2+} and NO_3^- were the dominant ions in precipitation, with concentrations (volume-weighted mean) of $212.99 \mu eq L^{-1}$, $200.20 \mu eq L^{-1}$, $116.88 \mu eq L^{-1}$ and $98.56 \mu eq L^{-1}$, respectively. The ion concentrations at SDZ were much higher than those of other background stations and megacities in China. A significantly increasing trend was observed for NO_3^- ($7.26\% yr^{-1}$), and a decreasing trend was observed for SO_4^{2-}/NO_3^- , suggesting that the precipitation of SDZ evolved from a sulfuric acid type to a mixed type dominated by both sulfuric and nitric acid. The source identification indicated that SO_4^{2-} , NO_3^- , NH_4^+ and F^- were dominated by secondary sources, Mg^{2+} , Ca^{2+} and Na^+ mostly originated from natural sources, and K^+ and Cl^- probably associated with

*Corresponding author E-mail: zqma@ium.cn

anthropogenic sources. Long-range transport of air masses could influence the acidity, electrical conductivity and ion concentrations of precipitation at SDZ. The higher acidity and ion concentrations mainly occurred in the southerly and westerly trajectory pathways and partially in northwest pathways. Anthropogenic pollutants and crustal sources along these pathways were significant contributors to the chemical composition of precipitation in SDZ.

Keywords: Chemical composition; Precipitation; Source; Background station

1. Introduction

Precipitation has been considered as the most effective scavenging factor for removing particulate and dissolved gaseous pollutants from the atmosphere (Al-Khashman, 2005; Migliavacca et al., 2005). Scavenging of atmospheric pollutants affects the chemical composition and pH of precipitation. In China, the fast economic development and urbanization have resulted in severe air pollution problem. Due to the effect of long-range transport and local pollutant emissions, the pollution presented regional scale characteristics especially in megacity clusters, and acid rain become one of the important regional atmosphere environmental problems. Following Northeast America and Central Europe, China has become the third region in the world and seriously affected by acid rain during the past several decades.

Since the areas in south of the Yangtze River affected by acid rain at the end of 1970s (Tang et al., 2006), acid depositions expanded gradually due to the increasing fuel consumptions in China. According to the intensity of acid rain, the severe acid rain existed during 1993-1998. After the government implemented the ‘SO₂ and acid rain pollution control area’ program, the intensity of acid rain slightly decreased from 1999 to 2002, however, it enhanced again during 2003-2006 (Zhao et al., 2008). In China, large emissions were concentrated in the megacity clusters, such as Jing-Jin-Ji (the abbreviation for Beijing, Tianjin, and Hebei provinces in China), the Pearl River delta (PRD) and the Yangtze River delta (YRD) regions (Parrish et al., 2009). Jing-Jin-Ji is the important region in north China where the economic development is

1 most active. With the rapid economic development, population expansion and
2 urbanization, the local environment and the climate have changed in Jing-Jin-Ji region
3 in recent decades. Due to the air pollution problem in this region, the composition of
4 precipitation, which is determined by ‘in-cloud’ and ‘below-cloud’ scavenging
5 processes and incorporates both the gases and aerosols in the air, will be changed.
6 However, only a few studies have focused on the composition of precipitation in
7 Jing-Jin-Ji region in recent years (Xu et al., 2015; Wu et al., 2016; Li et al., 2010).

8 A systematic investigation on the emission sources and the precipitation chemical
9 composition is necessary to understand the consequences of pollution on ecosystems
10 (Arsene et al., 2007). The composition of precipitation varies from site to site, region
11 to region due to the difference of the emission sources. Even though there have been
12 some studies about chemical composition of precipitation in China (Zhang et al., 2007;
13 Huang et al., 2008; Zhang et al., 2012; Xu et al., 2015; Wu et al., 2016; Yang et al.,
14 2004), however, few studies focused on the background station. Tang et al. (2000)
15 investigated the chemical characteristics of precipitation at Waliguan background
16 station in 1997. Yang et al. (2002) and Li et al. (2010) discussed the chemical
17 characteristics of precipitation at Shangdianzi (SDZ), Longfengshan and Linan
18 background stations during 1985-1997 and 2005-2007, respectively. Xu et al. (2008)
19 analyzed the chemical characteristics of precipitation at SDZ background station,
20 basing on the observational data from the period of 1999-2004. In addition, U.S.
21 investigators, in collaboration with Chinese scientists, staged a long-term background
22 precipitation observation at a plateau station in Lijiang during 1991-1993, and
23 unveiled basic information about background precipitation in southwest China (Liu
24 and Keene, 1993). Most of the previous studies have only carried out a limited short
25 sample period. In comparison to North America and Europe, especially long-term and
26 comprehensive studies, the research on the chemical composition of precipitation is
27 relatively limited at background station of China.

28 In order to improve our understanding about the chemical composition of
29 precipitation at background station, we investigated the long-term trend of pH,
30 electrical conductivity and concentrations of chemical composition at SDZ regional

background station during 2003-2014. Moreover, we also identify the sources of the various compositions in precipitation by using the inter-relationship, enrichment factors and source contribution methods, and applied the cluster analysis to determine the impact of long-range transport on chemical compositions. These results would provide useful information for the environment protection in North China.

2. Experimental methods

2.1 Study area

The Shangdianzi station (SDZ, 40°39'N, 117°07'E, 293.9 m a.s.l) is one of the regional Global Atmosphere Watch (GAW) stations in China. This station is situated in the transitional region of the North China Plain (NCP) and the Yanshan mountain area (Fig. 1). It is approximately 100 km from urban areas and 55 km from the Miyun Township of Beijing, surrounding the core of Jing-Jin-Ji. Within 30 km of the site, there are only small villages in mountainous areas with sparse populations and insignificant anthropogenic emission sources. Therefore, the atmospheric pollution level at SDZ station can represent the background concentration of atmospheric pollutants in the economic developed regions of northern China. Due to the valley topography, the prevailing winds at SDZ are from the east–northeast and the west–southwest. Polluted air masses from urban areas in NCP can therefore be easily transported to SDZ by southwesterly winds, while relatively clean air masses arrive from other wind directions (Lin et al., 2008; Zhao et al., 2009).

Fig.1. The station location of SDZ (circle), Cheju (triangle), Ijira (square) and distribution of precipitation acidity during 2008 in China (The pH data was released by Centre for atmosphere watch and services of Chinese academy of meteorological sciences.)

2.2 Sampling and analysis

A total of 599 rainwater samples were collected from March 2003 to December 2014. Rainwater samples were collected using an automatic wet deposition collector manufactured by M.I.C in Canada. The collector was approximately 1.5 m above the ground. The collected precipitation was divided into two parts: one for analyzing pH and conductivity, and the other for ion analysis. Values for pH and conductivity were measured using PHS-3B and DDS-307 instruments manufactured by Shanghai Leici instruments. After the analysis of conductivity and pH, the rain samples were removed to pre-cleaned polyethylene bottles and stored in a refrigerator at 4°C before being transported to the China Meteorological Administration's Key Lab of Atmospheric Chemistry for ion composition analysis.

A total of 438 rainwater samples were analyzed for F^- , Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Mg^{2+} , Ca^{2+} , K^+ and Na^+ , but 161 samples were used only for the determination of pH and conductivity due to limited samples from the low rainfall event. The rain samples were filtered through microporous membranes (pore size, 0.45 μ m) to remove the insoluble substances before the analysis of ion concentrations. The analytical method of anions and cations were the same as Li et al. (2010).

2.3 Data quality

Electrical conductivity (EC) of precipitation is a primary parameter in acid rain/precipitation chemistry monitoring. As the conductivity of ions in precipitation is an additive quantity, the conductivity data is commonly used in the quality check/assessment on the analysis data of ionic components in precipitation by comparing the measured EC with the calculated EC from the ionic concentration data obtained from the chemical analysis. This method is normally referred to as the conductance percent difference (GPD) method and is widely used (Tang et al., 2008). The criteria used by Tang and Li (Li et al., 2010) were used for the quality control of

1 the samples, and abnormal samples were rejected. Moreover, the chemistry laboratory
2 of the China Meteorological Administration was included in the WMO-GAW Acid
3 Rain Performance Survey and participated in the semi-annual inter-laboratory
4 comparison studies. The laboratory passed all of the examinations and the relationship
5 with lab values and target values shown in Fig. 2. Graphical and tabular results of past
6 studies are available at <http://www.qasac-americas.org/>. In this study, the ratio
7 between mean $\sum \text{anions}$ ($\text{F}^- + \text{Cl}^- + \text{NO}_3^- + \text{SO}_4^{2-}$) and mean $\sum \text{cations}$
8 ($\text{NH}_4^+ + \text{Mg}^{2+} + \text{Ca}^{2+} + \text{K}^+ + \text{Na}^+$) was 0.87. It seems generally acceptable if the
9 concentration ratio of measured anions to cations in rain water samples is within the
10 range of 1 ± 0.25 (Zhang et al., 2000).

Fig.2. Results of WMO-GAW Acid Rain Performance Survey from 2000 to 2014.

2.4. Backward trajectories modeling

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, version 4) model, developed jointly by National Oceanic and Atmospheric Administration (NOAA) and Australia's Bureau of Meteorology (ABOM) (<http://www.arl.noaa.gov/ready/hysplit4.html>), is adopted for calculation of airflow trajectories and cluster analysis. The meteorological input data is FNL global analysis data generated by the National Centers for Environmental Prediction(NCEP) model

1 and processed by the Global Data Assimilation System(GDAS),
2 (<http://www.rl.noaa.gov/ss/transport/archives.html>). 3-day back trajectories were
3 calculated in this study with the starting time of each rain event during 2006~2014.
4 Considering the winds to be at 1500 m should be a good approximation of the mean
5 transport wind; the starting height of the trajectory was selected as 1500 m asl in this
6 study.

7 To determinate the optimum number of clusters, the total spatial variance (TSV),
8 the sum of all the cluster spatial variances, was calculated. Based on the percent
9 change in TSV vs. number of clusters, the large increase in the change of TSV gave
10 the final number of clusters (cf. HYSPLIT4 user's guide).

12 3. Results and discussion

13 3.1. Variations of pH and electrical conductivity (EC)

14 To give a preliminary understanding of the characteristics of precipitation during
15 the whole study period from 2003 to 2014, the basic statistics of pH
16 (volume-weighted mean), EC (volume-weighted mean) and precipitation were
17 presented in Fig. 3. The average precipitation of SDZ was 526.4 mm, and ranged from
18 429.1 to 705.9 mm. As the pH of the unpolluted natural water in equilibrium with
19 atmospheric CO₂ is 5.6, the rainwater, in which the pH is less than 5.6, is considered
20 to be acid rain (Seinfeld, 1986). The volume-weighted mean pH of SDZ during
21 2003-2014 was 4.53, and the annual average pH at SDZ ranged from 4.20 to 4.95,
22 which indicated that SDZ had suffered acid rain pollution for a long time and became
23 a stable acid rain area in northern China. The yearly variation of pH could be divided
24 into two parts.

25 From 2003 to 2007, the pH showed an obvious decreasing trend with the average
26 rate of $-2.58\% \text{ yr}^{-1}$ ($r=0.91$, $p<0.01$). On the contrary, the pH presented an increasing
27 trend from 2008 to 2014. Gottald and Bovensmann (2011) found that SO₂ column
28 concentration over China from The Global Ozone Monitoring Experiment (GOME) /
29 Scanning Imaging Absorption Spectrometer for Atmospheric Chartography
30 (SCIAMACHY) had a clear increasing trend from 2000 to 2007; since 2007, which

1 was a turning point, SO₂ emissions from China experienced a sharp reduction. The
 2 SO₂ concentration variation tendency mentioned above was in accordance with the
 3 pH at SDZ during 2003-2007. However, the SO₂ concentration is directly related to its
 4 emission. In terms of China Statistical Yearbook, the SO₂ emissions during 2003-2014
 5 experienced an increasing stage in early 2000s and a reducing period from 2007 to
 6 2014 (Fig.4), which had a negative correlation with the pH at SDZ ($r=-0.78$, $p<0.01$).
 7 This might indicate that the SO₂ emissions in China have highly effect on the acid
 8 rain pollution. Moreover, the rapid increase in motor vehicles in NCP, which
 9 associated with the high NO_x emissions, had led to an increase in acidic ions in
 10 precipitation during 2003-2007. From 2008 to 2014, the government of Beijing
 11 carried out several measures, including coal pollution control, energy saving and
 12 emission reduction, and adoption of the Euro-III standards of vehicles, resulting in
 13 the decrease of the concentrations of fine particulate matter and acid gases in the
 14 atmosphere. In addition, provinces around Beijing also carried out a series of air
 15 pollution control measures to reduce the emissions of pollution sources in recent years.
 16 Due to the measures mentioned above, the pH presented an increasing trend after
 17 2007, but the annual pH values were still below 5.6.

18

19 Fig.3.Temporal variations of pH, conductivity and annual precipitation at SDZ from2003 to 2014.

Fig.4. SO₂ emissions of China and pH at SDZ during 2003~2014.

Fig. 5 showed the long-term variation of pH at the SDZ, Cheju (33°18'N, 126°10'E) and Ijira(35°34'N, 136°41'E) stations. Cheju and Ijira are both the EANET sites, which are located in South Korea and Japan (Fig.1), respectively (Data of Cheju and Ijira are available at <http://www.eanet.asia/index.html>). As shown in Fig. 5, except for 2010, the pH of SDZ was lower than that of Cheju and Ijira during 2003- 2011 but higher than that of Ijira after 2011. The variation characteristics of pH at the Cheju and Ijira stations were similar to that of SDZ and also showed the decreasing trend in early years and an increasing trend in later years. This might suggest that the acid rain pollution in East Asia decreased in recent years.

In general, acid rain has always existed in southern China, and the intensity of acid rain in northern China was not as severe as the southern areas. The pH level at SDZ obtained by this study was relatively low in northern China and close to that of the site in southeastern China, Jinhua (4.54), which is located in Zhejiang province (Zhang et al., 2007). It was lower than those of Tianjin (5.4) (Guo, 2007), Shenzhen (5.02) (Huang et al., 2008), Guangzhou (4.62) (Xie, 2002) and Hong Kong (4.55) (Tanner and Wong, 2000) but higher than that of Shanghai (4.49) (Huang et al., 2008) (Table 1) due to the difference in the chemical composition of precipitation and the neutralizing capacity of alkaline aerosols. In comparison to other background stations of China, the pH of SDZ was higher than that of the Linan background station (4.25)

1 (Li et al., 2010), which represents the background atmosphere of the economically
2 developed YRD, and lower than that of the Longfengshan background station (4.60)
3 (Li et al., 2010) and the Waliguan background station (6.38) (Tang et al., 2000), which
4 represent the background atmosphere of northeastern China and the northern Tibetan
5 Plateau, respectively. This indicated that the acid rain pollution of NCP was severe in
6 China. In comparison to the cities of neighboring countries, the pH of SDZ was lower
7 than that of Korea (4.70) (Lee et al., 2000) and similar to that of Japan (4.52) (Okuda
8 et al., 2005). In addition, the pH of SDZ in this study was lower than those of the
9 periods 1985-1997 (5.33) (Yang et al., 2002) and 1999-2004 (4.82) (Xu et al., 2008),
10 suggesting that the intensity of the precipitation acidity of NCP was enhanced than
11 that of in the earlier period.

12 The EC of precipitation ranged from 45.5 to 82.01 $\mu\text{S cm}^{-1}$, with a volume-weighted
13 mean of 65.03 $\mu\text{S cm}^{-1}$. The EC was mainly attributed to the total soluble ions of
14 precipitation and indirectly reflected the cleanliness of precipitation. Compared to the
15 other background stations, the average EC of SDZ was much higher than that of the
16 Waliguan background station (14.8 $\mu\text{S cm}^{-1}$) (Tang et al., 2000), the Linan background
17 station (51.93) and the Longfengshan background station (25.00) (Li et al., 2010).
18 This could indicate that the precipitation of SDZ was much more polluted by air
19 pollution than other background areas in China. It is worth noting that the EC value of
20 2008 was much lower in the period of 2005-2010, with a value of approximately
21 63.0 $\mu\text{S cm}^{-1}$. This could be due to the special air pollutant control measures
22 implemented for the 2008 Beijing Olympics. The control measures were not only
23 applied in Beijing but also extended to surrounding areas, such as the Tianjin
24 municipality, Inner Mongolia and Hebei, and Shanxi and Shandong provinces. Wang
25 et al. (2009) found that the daily average concentrations of SO_2 and NO_y during the
26 Olympics decreased by 61% and 21%, respectively. Wang et al. (2010) showed that
27 ambient concentrations of NO_x and VOCs at an urban site in Beijing dropped by 25%
28 and 20-45% during the 2008 Olympics. Therefore, the significant decrease of EC in
29 2008 is closely related with air pollution control measures.

Fig.5.Temporal variations of pH at SDZ, Cheju and Ijira stations.

3.2. Chemical composition of precipitation

3.2.1. Ion composition of precipitation

The data statistics of the precipitation compositions were listed in Table 1. These results clearly showed that the average concentration (volume-weighted mean) of ion species in precipitation at SDZ during 2003-2014 followed the order of $\text{NH}_4^+ > \text{SO}_4^{2-} > \text{Ca}^{2+} > \text{NO}_3^- > \text{Mg}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{K}^+ > \text{F}^-$. Among these ions, NH_4^+ , SO_4^{2-} , Ca^{2+} and NO_3^- were the dominant ones, accounting for 30.28%, 28.46%, 16.62% and 14.01% of total ions, respectively. SO_4^{2-} was the anion with the highest concentration ($200.20\mu\text{eqL}^{-1}$) because coal was the major fuel consumption source in China (Zhang et al., 2007). NO_3^- had a contribution approximately half of that of the SO_4^{2-} ion, with a concentration of $98.56\mu\text{eqL}^{-1}$, and is mainly derived from the burning of fossil fuels, power plants and emissions from vehicles (Huang et al., 2008). NH_4^+ had the highest concentration among the cations ($212.99\mu\text{eqL}^{-1}$), which is likely from fertilizers in agriculture activities and biomass burning (Chan et al., 2008; Yang et al., 2004). In addition, Pan et al. (2016) demonstrated that fossil fuel emissions and NH_3 slip from power plants are important sources of NH_3 during haze pollution periods in urban Beijing. Therefore, the agricultural sources, fossil fuel consumptions and industry activities could lead to the high level of NH_4^+ in precipitation. Ca^{2+} contributed 30.91% to the total cations measured, with a concentration of $116.88\mu\text{eqL}^{-1}$, and it may be

1 derived from the dissolution of minerals (Mouli et al., 2005).

2 Compared to the previous studies during 1985-1997 (Yang et al., 2002) and
3 1999-2004 (Xu et al., 2008), the average concentrations of SO_4^{2-} , NO_3^- and NH_4^+ in
4 this study increased obviously, while the concentration of Ca^{2+} decreased to a certain
5 extent, which indicated that the emissions of SO_2 , NO_x and NH_3 of NCP increased in
6 recent years due to economic development and agricultural activities. Jin et al. (2006)
7 showed that due to the comprehensive control of dust content in Beijing, the
8 concentration of coarse mode particles in the atmosphere decreased, and the level of
9 Ca^{2+} which existed in the 30-100 μm aerosols also decrease. Therefore, the
10 concentration of Ca^{2+} in precipitation declined. The concentrations of SO_4^{2-} and NO_3^-
11 at SDZ were approximately 2.5 to 11 times higher, respectively, than those of Linan,
12 Longfengshan and Waliguan background stations. The values for NH_4^+ and Ca^{2+} at
13 SDZ were also more than approximately 2 times higher than those of the other three
14 background stations. These results indicated that compared to the YRD area,
15 northeastern China and the northern Tibetan Plateau, the precipitation of NCP was
16 much more affected by anthropogenic activities. Compared with the megacities of
17 Shanghai and Shenzhen, the concentrations of SO_4^{2-} , NO_3^- and NH_4^+ of SDZ were
18 higher than those of the cities, while Cl^- and Na^+ concentrations were much lower. Cl^-
19 and Na^+ likely originated from the same source, i.e., sea salt. Both Shanghai and
20 Shenzhen are typical coastal cities and could easily be affected by the marine source.
21 Compared to the sites located in the acid rain control zone in China, such as
22 Chongqing and Hunan, the ionic concentration of SDZ was also much higher.
23 Compared with Tokyo, Seoul and Mexico City, one of the most polluted cities in the
24 world (Báez et al., 2007), SDZ showed the highest ion levels among the four cities in
25 the majority of ionic concentrations. As mentioned above, the ionic concentrations of
26 SDZ were much higher than those of other sites, especially for SO_4^{2-} , NO_3^- and NH_4^+ .

27 Precipitation of SDZ mainly occurs between May and September, and 70% of the
28 precipitation transport pathways come from the southeast and southwest (Xu et al.,
29 2011). Previous studies showed that emissions from the southerly direction made
30 significant contributions to the air pollution of SDZ (Pu et al., 2015; Meng et al.,

2009). Therefore, the air masses transported from the south of the NCP areas and the rapid increase in the abundance of vehicles resulted in high concentrations of air pollutants. Through in-cloud and/or below-cloud scavenging processing, more acidic ions, such as SO_4^{2-} and NO_3^- , dissolved in precipitation attributed to severe acid rain at SDZ.

Table 1 Volume-weighted mean of Chemical composition in precipitation

at various sites (μeqL^{-1})

Area	Time	Type	pH	SO_4^{2-}	NO_3^-	Cl^-	F^-	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+
SDZ (This study)	2003-2014	Background station	4.53	200.20	98.56	19.88	6.58	10.23	10.61	116.88	27.46	212.99
SDZ ^a	1985-1997	Background station	5.33	90.00	88.55	38.59	34.21	12.02	9.57	144.50	22.21	115.56
SDZ ^b	1999-2004	Background station	4.82	158.53	72.68	16.28	--	12.11	14.59	162.07	28.76	181.33
Linan ^c , China	2007	Background station	4.25	80.72	44.62	10.90	3.84	8.89	10.26	71.08	45.97	63.23
Longfengshan ^c , China	2007	Background station	4.60	81.82	31.46	7.28	4.54	4.37	7.24	30.03	8.42	69.53
Waliguan ^d , China	1997	Background station	6.38	24.00	8.30	6.10	--	3.8	8.7	34.0	12.10	45.50
Shanghai ^e , China	2005	Megacity	4.49	199.59	49.80	58.34	--	14.89	50.11	203.98	29.64	80.68
Shenzhen ^f , China	1986-2006	Megacity	5.02	74.30	22.10	37.90	4.50	7.20	40.30	77.70	9.70	35.20
Chongqing ^g , China	2003	Forest	4.10	184.00	35.00	11.00	5.00	8.00	3.00	58.00	9.00	76.00
Hunan ^g , China	2003	Inland	4.33	155.00	60.00	11.00	7.00	10.00	7.00	60.00	10.00	112.00
Tokyo ^h , Japan	1990-2002	Megacity	4.52	50.20	30.50	55.20	--	2.90	37.00	24.90	11.50	40.40
Seoul ⁱ , Korea	1996-1998	Megacity	4.70	70.90	29.9	18.2	--	3.50	10.50	34.90	6.90	66.40
Mexico City ^j , Mexico	2001-2002	Megacity	5.08	61.94	42.62	9.56	--	2.16	7.00	26.44	2.46	92.35

^a Yang et al. (2002); ^b Xu et al. (2008); ^c Li et al. (2010); ^d Tang et al. (2000); ^e Huang et al. (2008); ^f Zhang et al. (2007); ^g Aas et al. (2007); ^h Okuda et al. (2005); ⁱ Lee et al. (2000); ^j Báez et al. (2007).

3.2.2. Temporal variations of ion concentrations

Fig. 6 showed the annual variations of ionic constituents of precipitation (volume-weighted mean) at SDZ during 2003-2014. The SO_4^{2-} concentrations in the precipitation of SDZ fluctuated during the study period and are directly associated with SO_2 emissions. Due to improving the combustion and pollution control measures in Beijing and surrounding areas, such as coal-fired plant closures, heating boiler renovation and industrial coal reduction, SO_2 emissions from industrial exhaust decreased dramatically. Moreover, urban residents have used natural gas instead of coal as fuel for winter heating. According to the China Statistical Yearbook, SO_2

1 emissions in Beijing decreased from 2.24×10^5 tons in 2000 to 1.52×10^5 tons in
2 2007, but the emissions from energy consumption of provinces around Beijing, such
3 as Hebei (1.32×10^6 - 1.49×10^6 tons) and Shanxi (1.20×10^6 - 1.38×10^6 tons),
4 increased. Yan (Yan et al., 2005) and Xu (Xu et al., 2005) also reported that SO_2
5 emissions in Beijing decreased in the last decade; however, more than 20% of the
6 ground SO_2 in Beijing was estimated to be transported from the surrounding areas.
7 Under the influence of external sources, although the emissions of SO_2 in Beijing
8 were reduced, the long-term SO_4^{2-} variation did not decrease obviously. Okuda et al.
9 (2005) and Huang et al. (2008) also found similar trends in the concentration of SO_4^{2-}
10 in precipitation in the Tokyo metropolitan area during 1990-2002 and in Shenzhen
11 from 1986 to 2006, respectively.

12 The concentration of NO_3^- showed a significantly increasing trend ($r=0.69$,
13 $p=0.01$), with a rate of $7.26\% \text{ yr}^{-1}$ over time. This result suggested that the
14 contribution of NO_3^- to acidification has become more and more important due to the
15 dramatically increasing number of motor vehicles and increased fuel combustion.
16 Similarly, the trend of NO_3^- in precipitation was directly associated with NO_x
17 emissions in northern China. Beijing was typical of the rapid increase in vehicle
18 numbers in China. The number of mobile vehicles in Beijing was 2,124,000 in 2003
19 and reached nearly 5,371,000 in 2014 (Beijing Statistical Bureau, 2015); this could
20 result in the increasing trend of NO_3^- in recent years.

21 The tendency of $\text{SO}_4^{2-}/\text{NO}_3^-$ significantly declined during the study period
22 ($r=-0.95$, $p<0.01$) (Fig. 6-j), but the ratio was still above 1. This indicated that sulfuric
23 acid was more significant than nitric acid as an acidifying species, which means that
24 SO_2 emissions are still the major contributor to NCP. Nevertheless, due to the SO_2
25 emission control and the increasing NO_x emissions in northern China, the ion
26 concentration of NO_3^- was more similar to that of SO_4^{2-} . This suggested that the
27 contribution of nitrogen as an acidifying species in precipitation increased, and the
28 precipitation of SDZ evolved from a sulfuric acid type to a mixed type dominated by
29 both sulfuric and nitric acids in recent decades.

30 Among cations, K^+ showed a significant decreasing trend ($r=-0.59$, $p=0.04$) during

1 the study period (Fig. 6-e). K^+ could be the tracer species of biomass burning
2 (Andreae et al., 2001) and could also be the trace element of crop straw burning in
3 China (Duan et al., 2004). Combustion of the crop straw after harvest is a common
4 phenomenon in rural areas of China. A previous study showed that the crop straw
5 burning of areas surrounding Beijing could make non-negligible contributions to the
6 high level of K^+ in Beijing (He et al., 2011). In recent years, to control the pollution
7 from biomass burning, the government implemented many measures to control
8 biomass burning, which resulted in a decrease in K^+ . Generally, there are two major
9 sources of terrestrial Ca^{2+} in precipitation: (1) the local and long-range transport of
10 dust and/or carbonate weathering; (2) anthropogenic pollution, such as cement
11 factories. Usually, three transport pathways of dust storms (north-north westerly
12 direction, northwesterly direction, and westerly direction) that pass through Beijing
13 were identified (Zhou et al., 2002; Sun et al., 2001). Based on the chemical
14 composition analyses (Sun et al., 2005; Wang et al., 2005b), dust storms can be
15 further classified as Ca^{2+} enriched when the air mass comes from the west and passes
16 through the Loess plateau of China. On the other hand, rapidly increasing
17 urbanization has led to increased open areas and construction sites, which act as
18 sources of particles. Thus, we would deduce that the high level of Ca^{2+} in
19 precipitation is mainly due to the contribution of the long-range transport of dust
20 storms and urban expansion. NH_4^+ in precipitation was certainly related to the
21 emission of NH_3 , which was mainly from plants, fertilizer use, industrial processes
22 and on-road vehicular emissions. The high NH_4^+ concentration (Table 1) indicated that
23 there were strong sources of NH_3 in NCP, and the decreasing trend of NH_4^+ suggested
24 that the NH_3 emission around SDZ declined in recent years but was still at a high
25 level in comparison to other areas.

26

Fig.6. Temporal variations of ionic concentrations (volume-weighted mean) (a-i) and $\text{SO}_4^{2-}/\text{NO}_3^-$ in precipitation during 2003-2014. Blue lines denote the linear regression.

3.2.3. Neutralization capacity

Kulshrestha et al. (1995) suggested neutralization factor (NF) to describe the interaction between cations and anions, and were calculated by the following equation:

$$NF_{NH_4^+} = \frac{NH_4^+}{NO_3^- + SO_4^{2-}}, NF_{Ca^{2+}} = \frac{Ca^{2+}}{NO_3^- + SO_4^{2-}}, NF_{Mg^{2+}} = \frac{Mg^{2+}}{NO_3^- + SO_4^{2-}}$$

The equivalent concentrations of the ions were used in this calculation. To verify which cation (NH_4^+ , Ca^{2+} and Mg^{2+}) plays the most important role for the neutralization in precipitation, a triangular diagram was drawn, showing the relative proportion of these three NFs (Fig.7). The NF triangle result revealed that both NH_4^+ and Ca^{2+} were the predominant neutralizers in precipitation contributing about 55.1% and 36.4% for neutralization, respectively, and only 8.5% of the neutralization was by Mg^{2+} . The NF values for NH_4^+ , Ca^{2+} and Mg^{2+} with an average value were 0.67, 0.48 and 0.11 during 2003 to 2014, respectively. This result was different from Wu et al. (2016) and Zhang et al. (2012). Their study showed that the strong acid neutralization in Hebei province and Lijiang were mainly brought about by Ca^{2+} and followed by NH_4^+ and Mg^{2+} .

As discussed above, NH_4^+ and Ca^{2+} as the main neutralization components of rain, while SO_4^{2-} and NO_3^- were the main acidifying components of precipitation. To assess the balance between acidity and alkalinity, the equivalent ratio of $(NH_4^+ + Ca^{2+}) / (SO_4^{2-} + NO_3^-)$ was calculated. The average value of $(NH_4^+ + Ca^{2+}) / (SO_4^{2-} + NO_3^-)$ was 1.33 during study period, and ranged from 1.03 to 2.60.

Fig.7. Triangular diagrams of NF of predominant alkaline ions.

3.3. Sources of ions in precipitation

3.3.1. Inter-relationship

To identify possible relations among ions in precipitation and obtain a quick overview on the possible sources of ions, a Pearson correlation analysis was performed, the results of which were presented in Table 2. Since the acidity of the precipitation was 4.53, pH was more sensitive to alkaline ions than acidic ions. Therefore, pH had significant correlation with Na^+ , Ca^{2+} and Mg^{2+} , and nonsignificant correlation coefficients existed between pH and other ions, especially the major acidic ions.

SO_4^{2-} and NO_3^- had a good correlation ($r=0.88$), which may be due to the similarity in their behavior in precipitation and their co-emission (fossil fuel combustion) of their precursors SO_2 and NO_x (Kaya et al., 1997; Mphepya et al., 2004). There were also strong correlations between NH_4^+ and SO_4^{2-} ($r=0.88$) and between NH_4^+ and NO_3^- ($r=0.80$). Association of NH_4^+ , SO_4^{2-} and NO_3^- was attributed to atmospheric chemical reactions with each other. NH_3 generally reacts with H_2SO_4 and HNO_3 in the atmosphere to generate $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 and NH_4NO_3 aerosols by homogeneous or heterogeneous processes (Pathak et al., 2009). The correlation of NH_4^+ and SO_4^{2-} was higher than that of NH_4^+ and NO_3^- , indicating that NH_3 will first react with H_2SO_4 , and then the remaining NH_3 will be taken up by HNO_3 (Seinfeld, 1986), and sulfur

compounds could be predominant in the atmosphere. F⁻ showed significant correlations with SO₄²⁻ (r=0.85), NO₃⁻ (r=0.78) and NH₄⁺ (r=0.80), which indicated that most of these ions had the same origin, such as anthropogenic sources. A high relationship between Ca²⁺ and Mg²⁺ (r=0.86), K⁺ and Cl⁻ (r=0.87), Na⁺ and Cl⁻ (r=0.76) suggested common source of crustal origin, anthropogenic pollution and sea of these ions, respectively.

There were high correlations between acidic anions and dust-derived cations, such as SO₄²⁻ and Ca²⁺ (r=0.72), SO₄²⁻ and Mg²⁺ (r=0.64), NO₃⁻ and Ca²⁺ (r=0.68), NO₃⁻ and Mg²⁺ (r=0.62) and Cl⁻ and Ca²⁺ (r=0.64). This result could indicate that acid pollutants might be absorbed by the particulate matter and react with alkaline cations. It has been demonstrated that aqueous SO₂ oxidation by NO₂ can be an important pathway for sulfate and nitrate formation on the particulate matter surface in the presence of sufficient neutralizing agents (Wang et al., 2016). Thus, Ca²⁺ and Mg²⁺, the major alkaline neutralizing agents, showed high correlation with SO₄²⁻ and NO₃⁻.

Table2 Pearson correlation coefficients for major ions

	pH	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	F ⁻	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
pH	1.00									
SO ₄ ²⁻	-0.07	1.00								
NO ₃ ⁻	-0.03	0.88*	1.00							
Cl ⁻	-0.02	0.76*	0.78*	1.00						
F ⁻	0.04	0.85*	0.78*	0.64*	1.00					
K ⁺	-0.07	0.67*	0.62*	0.87*	0.55*	1.00				
Na ⁺	0.15*	0.61*	0.56*	0.76*	0.55*	0.65*	1.00			
Ca ²⁺	0.22*	0.72*	0.68*	0.64*	0.70*	0.50*	0.74*	1.00		
Mg ²⁺	0.21*	0.64*	0.62*	0.65*	0.60*	0.54*	0.74*	0.86*	1.00	
NH ₄ ⁺	-0.03	0.88*	0.80*	0.62*	0.80*	0.56*	0.39*	0.52*	0.48*	1.00

N=438

*Significant at 0.01 level.

3.3.2 Source identification by principal component analysis

Principal component analysis (PCA) was applied to identify the sources of the

chemical compositions in precipitation. As shown in Table 3, three principal components were extracted from the precipitation samples, which explained 90.3% of total variance. The communalities for all species were higher than 0.85, suggesting that the three factors identified were reasonable. PC1 had high loadings of NH_4^+ , SO_4^{2-} , F^- and NO_3^- , indicating a secondary source taking up approximately 37% of the total data variance. PC2 accounting for around 29.1% of total data variance, had high loadings of Mg^{2+} , Ca^{2+} and Na^+ , indicating a source of crustal origin, for instance soil or dust. PC3 occupying for approximately 24.2% of total variance had high loadings for K^+ and Cl^- . K^+ mainly originated from biomass burning. Although Cl^- major came from seawater, anthropogenic pollution such as coal combustion and steel production also sources of it (Zhang et al., 2006; Zhang et al., 2007). Therefore, PC3 was likely associated with the anthropogenic pollution source, such as biomass burning.

Table 3 Rotated factor matrix of rainwater samples at SDZ

Variable	PC1	PC2	PC3	Communalities
NH_4^+	0.91	0.13	0.25	0.92
SO_4^{2-}	0.82	0.37	0.37	0.94
F^-	0.81	0.41	0.19	0.85
NO_3^-	0.77	0.34	0.38	0.86
Mg^{2+}	0.30	0.86	0.26	0.89
Ca^{2+}	0.42	0.85	0.17	0.93
Na^+	0.15	0.73	0.57	0.94
K^+	0.33	0.22	0.88	0.87
Cl^-	0.43	0.38	0.78	0.93
Contribution (%)	37.0	29.1	24.2	

3.3.3. Source identification by air mass transport pathway

Investigation of the variation of atmospheric composition with the air mass transport pathways in background areas is a common way to understand the influence of the long-range transport of pollutants on the atmospheric environment (Das and Jayaraman, 2012; Tang et al., 2014). Cluster analysis in this study was applied to rainy days, which resulted in five clusters (Fig. 8). The number of trajectories in the five

clusters was 21, 42, 53, 144 and 60, respectively. Clusters 1, 2 and 3 were composed of trajectories originating from a wide range of north. According to the relatively long pathway of clusters 1 and 2, these two clusters corresponded to fast-moving trajectories. In addition, the move altitude of these trajectories was high, with the mean trajectory higher than 1800 m. Clusters 4 and 5 came from the south and west, respectively, with a low trajectory altitude (Fig. 9). The mean trajectory altitudes of clusters 4 and 5 were approximately 1200 m, indicating a transport pattern below the boundary level.

By comparing the pH, EC and ions concentrations of the five clusters (Table 4), the characteristics of each cluster could be identified. According to the pH and EC, cluster 4 corresponded to the most acidic and polluted pathway among the five clusters, with a pH under 4.5, achieving the strong acid level, suggesting the air masses along this pathway were affected by more anthropogenic emissions than that of other pathways. The pH of other clusters was above 4.5 but still under 5.6, indicating that air masses from different directions could result in acid rain of SDZ.

The air masses of cluster 4 originated from the border of the Jiangsu and Shandong provinces and passed through Hebei province, Tianjin municipality, before arriving at SDZ. The trajectories of cluster 4 were similar to those of the south cluster given by Pu et al. (2015), which corresponded to the highest $PM_{2.5}$ and scattering coefficient and was referred to as the polluted pathway. According to the ionic concentrations of each cluster, the highest concentrations of SO_4^{2-} , NH_4^+ and K^+ existed in cluster 4. In addition, cluster 4 also had high NO_3^- levels among all clusters. Using the CMB model, Zheng et al. (2005) estimated that secondary sources from Beijing (the sum of SO_4^{2-} , NO_3^- and NH_4^+) accounted for 33%. Because the NCP region is one of the highest $PM_{2.5}$ emission regions in China (Zhang et al., 2009) and there are high concentrations of SO_4^{2-} , NO_3^- and NH_4^+ in $PM_{2.5}$, when in-cloud and/or below-cloud scavenging processes start, secondary inorganic ions dissolved in precipitation contribute to high ionic concentrations at SDZ. K^+ was associated with biomass burning and crustal sources. Of all source emissions, biomass burning has the highest abundance of both total potassium and soluble potassium (Watson and Chow, 1998).

1 Around Beijing, such as in Hebei, Tianjin and Shandong provinces, biomass burning
2 is widely present and contributes to the high abundance of K^+ , especially in summer
3 and autumn. Therefore, when air masses pass through these provinces, it could result
4 in a high K^+ level at SDZ. Moreover, the low moving altitude of the trajectories of
5 cluster 4 (under the boundary level) could easily uptake anthropogenic pollutants
6 from the ground when passing by the southern part of the NCP region.

7 Air masses of cluster 1 passed through Gobi areas in Mongolia and Inner Mongolia
8 before arriving at SDZ, corresponding to the highest ion concentrations of NO_3^- , Cl^- ,
9 Na^+ , Ca^{2+} and Mg^{2+} among all the clusters. According to Sun et al. (2010), the air
10 masses of cluster 1 passed through the Western Dust Region and Northern Dust
11 Region and could be affected by the dust source. Wu et al. (2013) showed that the
12 ratio of Ca^{2+} plus Mg^{2+} to the total cation concentration is the highest in spring in
13 Lanzhou, which is located in the Northern Dust Region. The high levels of crustal
14 species (Ca^{2+} and Mg^{2+}) from the northwest direction indicated the impact of
15 long-range transport of dust storms, which mainly occurred in the spring. The highest
16 concentration of NO_3^- , the second highest concentration of SO_4^{2-} and the third level of
17 NH_4^+ among all clusters were observed in cluster 1. Studies have shown that SO_4^{2-} and
18 NO_3^- could also be from crustal sources, in addition to the secondary sources near
19 dust source regions (Sun et al., 2005). Sun et al. (2010) investigated the Asian dust
20 and its impact on aerosol chemistry over northern China in the spring of 2004. The
21 result of spatial variations of water-soluble ions in $PM_{2.5}$ showed that the
22 concentrations of SO_4^{2-} , NO_3^- and NH_4^+ at Yulin, which is located in Northern Dust
23 Region, were higher than those of Duolun in the Northeastern Dust Region. Cluster 1
24 mostly passed through the Northern Dust Region; therefore, the high levels of these
25 three ions might be attributed to the local emission sources in the dust region. The ion
26 concentrations of cluster 5 were lower than those of clusters 1 and 4 but higher than
27 those of clusters 2 and 3. The airflows in cluster 5 had mainly come from the west,
28 which might correspond to the emissions from the Inner Mongolia, Shanxi and Hebei
29 province, which are the key coal mining, steel production and power generation
30 regions of China. Pollutants emitted from these regions were carried to SDZ by the

1 low and slow airflows.

2 In contrast to clusters 1, 4 and 5, clusters 2 and 3 represented the relatively clean
 3 trajectory pathways. The air masses of cluster 2 originated from Mongolia and then
 4 traveled through Inner Mongolia. The trajectories of cluster 3 originated from the east
 5 of Inner Mongolia and passed through the west of Liaoning province, Tianjin
 6 Municipality, before arriving SDZ. In comparison to the distribution of anthropogenic
 7 emissions in northern China and East Asia (Zhao et al., 2012; Zhang et al., 2009), the
 8 regions through which the air masses of clusters 2 and 3 traveled had low emissions.
 9 The low ion levels of the two clusters could be attributed to the less-polluted airflows
 10 over the north direction and its higher moving altitude and velocities.

11

12

13

Fig.8.Mean 72h backward trajectories of the five clusters

14

15

16

Fig.9.Average altitudes of the five trajectory clusters for SDZ

17

18

Table 4 Volume-weighted mean concentrations (μeqL^{-1}) of ions from five clusters

Type	No.	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	F ⁻	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
Cluster 1	21	4.75	60.88	228.95	123.02	25.25	6.22	10.45	13.92	170.24	41.96	234.50
Cluster 2	42	4.65	44.43	156.58	96.51	19.11	5.86	7.65	7.78	92.28	22.39	202.16
Cluster 3	53	4.75	53.37	160.18	80.27	15.58	5.45	7.29	8.79	102.92	24.90	172.02
Cluster 4	144	4.41	75.77	236.12	121.33	24.15	7.69	11.17	11.52	132.34	31.28	253.18
Cluster 5	60	4.57	62.10	216.12	117.85	21.51	7.50	9.93	10.36	114.30	26.58	247.57

1

2 4. Conclusion

3 An investigation of the chemical composition of atmospheric precipitation was
4 carried out at the SDZ regional background station during the period of 2003-2014.
5 The average pH during this period was 4.53, which is considerably lower than those
6 reported in other WMO background stations (Linan, Waliguan and Longfengshan),
7 many other cities in China, and other cities around world. The pH value showed a
8 significantly decreasing trend during 2003-2007, while in 2008-2014, it showed an
9 increasing trend. The annual pH values during 2003-2014 were below 5.6, which
10 indicated that SDZ had suffered acid rain pollution for a long time and became a
11 stable acid rain area in northern China. Compared to the previous studies, the pH
12 value of this study was lower than that of the past two decades, suggesting that the
13 intensity of precipitation acidity of NCP was enhanced compared to the earlier period.
14 The EC of precipitation with a volume-weighted mean of 65.03 μ S cm⁻¹ was much
15 higher than those of the Linan (4.25), Longfengshan (4.60) and Waliguan (6.38)
16 background station.

17 NH₄⁺, SO₄²⁻, Ca²⁺ and NO₃⁻ were the dominant ion species, and NH₄⁺ was the
18 predominant neutralizer in precipitation, contributing approximately 55.1% for
19 neutralization. The concentrations of SO₄²⁻, NO₃⁻ and NH₄⁺ increased obviously,
20 while Ca²⁺ decreased to a certain extent in comparison to the previous studies of SDZ.
21 The ionic levels of SDZ were much higher than those of other sites, including
22 domestic and foreign country sites, especially for SO₄²⁻, NO₃⁻ and NH₄⁺, suggesting
23 that the NCP has been affected by the pollution from anthropogenic sources and has

1 been a severely polluted area in China. A significantly increasing tendency of NO_3^-
2 and a decreasing tendency of $\text{SO}_4^{2-}/\text{NO}_3^-$ were observed during study period, and the
3 precipitation of SDZ evolved from a sulfuric acid type to a mixed type dominated by
4 sulfuric and nitric acid.

5 The source identification indicated that SO_4^{2-} , NO_3^- , NH_4^+ and F^- were dominated
6 by secondary sources, Mg^{2+} , Ca^{2+} and Na^+ mostly originated from natural sources, and
7 K^+ and Cl^- probably associated with anthropogenic sources.

8 By comparing the levels of pH, EC and ions in each cluster, relatively polluted
9 (clusters 1, 4 and 5) and clean (clusters 2 and 3) transport pathways were identified.
10 The trajectories in cluster 4 mainly consisted of 'short' and 'low' trajectories and were
11 affected by the high anthropogenic pollutants when airflows passed through the key
12 $\text{PM}_{2.5}$ emission source in the NCP. The air masses of cluster 1 originated from
13 northeastern China, passing through the dust regions, and were affected by the crustal
14 sources, sea-salt sources and local emission sources. The airflows in cluster 5 came
15 mainly from the west and corresponded to the anthropogenic pollutants, such as the
16 emissions from key coal mining, steel production and power generation of China. The
17 trajectories of clusters 2 and 3 mostly originated from clean areas and transported to
18 SDZ along pathways without or with fewer emissions.

20 Acknowledgements

21 The authors would like to acknowledge the staff of SDZ station for their support in
22 the data collection. This work was supported by the
23 Ministry of Science and Technology of the People's Republic of China (Grand No. 20
24 16YFC0201902 and 2016YFC0201901) and National Science Foundation of China
25 (41475135) and Beijing Natural Science Foundation (8161004).

27 References

- 28 Aas W, Shao M, Jin L, Larssen T, Zhao D, Xiang R, Zhang J, Xiao J, Duan L. Air
29 concentrations and wet deposition of major inorganic ions at five non-urban sites in China,
30 2001-2003. *Atmospheric Environment* 2007; 41:1706-1716.
31 Al-Khashman AO. Study of chemical composition in wet atmospheric precipitation in Eshidiya

area, Jordan. *Atmospheric Environment* 2005;39:6175-6183.

Andreae MO, Merlet P. Emission of trace gases and aerosols from biomass burning. *Global Biogeochem. Cycles* 2001;15(4):955-966.

Arsene C, Olariu RI, Mihalopoulos N. Chemical composition of rainwater in the northeastern Romania, Iasi region (2003-2006). *Atmospheric Environment* 2007; 41: 9452-9467.

Báez A, Belmont R, García R, Padilla H, Torres MC. 2007. Chemical composition of rainwater collected at a southwest site of Mexico City, Mexico. *Atmospheric Research* 2007; 86:61-75.

Chan C.K, Yao XH. Air pollution in mega cities in China. *Atmospheric Environment*, 2008;42:1-42.

Das SK, Jayaraman A. Long-range transportation of anthropogenic aerosols over eastern coastal region of India: investigation of sources and impact on regional climate change. *Atmos. Res.* 2012;118:68–83.

Delmas, R., 1981: Contribution à l'étude des forêts équatoriales comme sources naturelles de dérivés soufrés atmosphériques, PhD Thesis, Université Paul Sabatier de Toulouse, Toulouse, France.

Duan FK, Liu XD, Yu T, Cachier H. Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing. *Atmos. Environ.* 2004; 38(9):1275-1282.

Gottwald, M. and Bovensmann, H. (Eds.): *SCIAMACHY: Exploring the Changing Earth's Atmosphere*, 1st Edn., Springer, ISBN 978-9-481-9895-5, 2011.

Guo J. Variational Characteristics of Acid Rain and Its Affecting Factors in Tianjin. *Urban Environmental & Urban Ecology* 2007;20(4):34-37.

He KB, Yang FM, Duan FK, Ma YL. *Atmospheric particulate matter and regional compound pollution*. Science Press. 2011.

Huang K, Zhang GS, Xu C, Wang Y, Tang AH. The chemistry of the severe acidic precipitation in Shanghai, China. *Atmospheric Research* 2008;89:149-160.

Huang YL, Wang YL, Zhang LP. Long-term trend of chemical composition of wet atmospheric precipitation during 1986-2006 at Shenzhen City, China. *Atmospheric Environment* 2008;42:3740-3750.

Jin L, Xu Q, Lin AG, Lu HF. Trend analysis of wet deposition between 1987~2004 in Beijing City. *Acta Scientiae Circumstantiae* 2006; 26(7):1195-1202.

Kaya G, Tuncel, G. Trace element and major ion composition of wet and dry deposition in Ankara, Turkey. *Atmospheric Environment* 1997;23:3985-3998.

Kulshrestha UC, Sarkar AK, Srivastava SS, Parashar DC. Wet-only and bulk deposition studies at New Delhi (India). *Water, Air and Soil Pollution* 1995;85,:2137-2142.

Lee BK., Hong SH, Lee DS. Chemical composition of precipitation and wet deposition of major ions on the Korean peninsula. *Atmospheric Environment* 2000;34:563-575.

Li Y, Yu XL, Cheng HB, Lin WL, Tang J, Wang SF. Chemical characteristics of precipitation at three Chinese regional background stations from 2006 to 2007. *Atmospheric Research* 2010;96:173-183.

Lin WL, Xu XB, Zhang XL, Tang J. Contributions of pollutants from North China Plain to surface ozone at the Shangdianzi GAW Station. *Atmos. Chem. Phys.* 2008;8:5889 – 5898.

Liu JQ, Keene WC, Study of the precipitation in Lijiang, China. *China Environmental Science* 1993;13 (4): 246-250. (in Chinese)

Meng ZY, Xu XB, Yan P, Ding GA, Tang J, Lin WL, Xu XD, Wang SF. Characteristics of

trace gaseous pollutants at a regional background station in Northern China. *Atmos. Chem. Phys.* 2009;9:927-936.

Migliavacca D, Teixeira EC, Wiegand F, Machado ACM, Sanchez J. Atmospheric precipitation and chemical composition of an urban site, Gual'ba Hydrographic Basin, Brazil. *Atmospheric Environment* 2005;39:1829-1844.

Mouli PC, Mohan SV, Reddy SJ. Rainwater chemistry at a regional representative urban site: influence of terrestrial sources on ionic composition. *Atmos. Environ* 2005;39:999-1008.

Mphopya JN, Pienaar JJ, Galyacaux C, Held G, Turner CR. Precipitation chemistry in semi-arid areas of Southern Africa: a case study of a rural and an industrial site. *Journal of Atmospheric Chemistry* 2004;47:1-24.

Okuda T, Iwase T, Ueda H, Suda Y, Tanaka S, Dokiya Y, Fushimi K, Hosoe M. Long-term trend of chemical constituents in precipitation in Tokyo metropolitan area, Japan, from 1990 – 2002. *Science of the Total Environment* 2005;339:127-141.

PanYP, TianSL, LiuDW, FangYT, ZhuXY, ZhangQ, ZhengB, MichalskiG, WangYS. Fossil Fuel Combustion-Related Emissions Dominate Atmospheric Ammonia Sources during Severe Haze Episodes: Evidence from 15N-Stable Isotope in Size-Resolved Aerosol Ammonium. *Environmental Science and Technology* 2016;50(15): 8049-8056.

Parrish DD, Zhu T. Clean Air for Megacities, *Science* 2009;326:674-675.

Pathak RK, Wu WS, Wang T. Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere. *Atmos.Chem.Phys.* 2009, 9:1711-1722.

Pu WW, Zhao XJ, Shi XF, Ma ZQ, Zhang XL, Yu B. Impact of long-range transport on aerosol properties at a regional background station in Northern China. *Atmospheric Research* 2015;153:489-499.

Seinfeld JH, *Atmospheric Chemistry and Physics of Air Pollution*. John Wiley & Sons 1986, New York.

Sun J, Zhang M, Liu T. Spatial and temporal characteristics of dust storms in China and its surrounding regions, 1960–1999: Relations to sources area and climate, *J. Geophys. Res.*, 2001;106(10):325–10,333.

Sun YL, Zhuang GS, Huang K, Li J, Wang QZ, Wang Y, Lin YF, Fu JS, Zhang WJ, Tang AH, Zhao XJ. Asian dust over northern China and its impact on the downstream aerosol chemistry in 2004. *J. Geophys. Res.* 2010;115:D00K09.

Sun YL, Zhuang GS, Wang Y, Zhao XJ, Li J, Wang ZF, An ZS. Chemical composition of dust storms in Beijing and implications for the mixing of mineral aerosol with pollution aerosol on the pathway. *J. Geophys. Res.* 2005;110: D24209..

Tang AH, Zhuang GS, Wang Y, Yuan H, Sun YL. The chemistry of precipitation and its relation to aerosol in Beijing. *Atmospheric Environment* 2005;39:3397-3406.

Tang J, Xue HS, Yu XL, Cheng HB, Xu XB, Zhang XC, Ji J. The preliminary study on chemical characteristics of precipitation at Mt. Waliguan. *ActaScien. Circum.* 2000;20 (4):420 – 425. (in Chinese)

Tang L, Eugensson MH, Sjöberg K, Wichmann J, Estimation of the long-range transport contribution from secondary inorganic components to urban background PM10 concentrations in south-western Sweden during 1986–2010. *Atmos. Environ.* 2014;89:93–101.

Tang XY, Zhang YH, Shao M. *Atmospheric Environmental Chemistry*. Higher education press 2006.

- 1 Tanner PA, Won, AYS. Soluble trace metals and major ionic species in the bulk deposition and
2 atmosphere of Hong Kong. *Water, Air, and Soil Pollution* 2000;122:261-279.
- 3 Wang Gehui, Zhang Renyi, Gomez Mario E., Lingxiao Yang, Misti Levy Zamora. Persistent
4 sulfate formation from London Fog to Chinese haze. *PNAS* 2016.
5 www.pnas.org/cgi/doi/10.1073/pnas.1616540113
- 6 Wang T, Nie W, Gao J, Xue LK, Gao XM, Wang XF, Qiu J, Poon CN, Meinardi S, Blake D,
7 Wang SL, Ding AJ, Chai FH, Zhang QZ, Wang WX. Air quality during the 2008 Beijing
8 Olympics: Secondary pollutants and regional impact, *Atmos. Chem. Phys.*,
9 2010,10(16):7603–7615.
- 10 Wang XS, Li JL, Zhang YH, XieSD, Tang XY. Ozone source attribution during a severe
11 photochemical smog episode in Beijing, China. *Sci. China Ser. B: Chemistry*
12 2009,52(8):1270-1280.
- 13 Wang Y, Zhuang G, Sun Y, An Z. Water-soluble part of the aerosols in the dust storm
14 season-evidence of the mixing between mineral and pollution aerosols. *Atmospheric Environment*
15 2005b;39:7020-7029.
- 16 Watson JG, Chow JC. CMB8 applications and validation protocol for PM_{2.5} and VOCs. Desert
17 Research Institute. 1998.
- 18 Wu D, Wang SG, Xia JR, Meng XY, Shang KZ, Xie YY, Wang RB. The influence of dust
19 events on precipitation acidity in China. *Atmospheric Environment* 2013;79:138-146.
- 20 Wu Y, Xu ZF, Liu WJ, Zhao T, Zhang X, Jiang H, Yu C, Zhou L, Zhou XD. Chemical
21 compositions of precipitation at three non-urban sites of Hebei Province, North China: Influence
22 of terrestrial sources on ionic composition. *Atmospheric Research* 2016;181:115-123.
- 23 Xie M. The basic feature research of acid rain pollution in Guangzhou area during 1996-2000.
24 *Research of Environmental Sciences* 2002;15 (1):31 – 33 (in Chinese).
- 25 Xu J, Zhang XL, Xu XB, Ding GA, Yan P, Yu XL, Cheng HB, Zhou HG. Variations and
26 source identification of chemical compositions in wet deposition at Shangdianzi background
27 station. *Acta Scientiae Circumstantiae* 2008;28(5):1001-1006(in Chinese).
- 28 Xu JM, Xu XD, Liu Y, Ding GA, Chen HL, Hi JK, Zhang JC, Wu H, Li WL, He JH, Yang YQ,
29 Wang JH. Study of statistically correcting model CMAQMOS for forecasting regional air quality.
30 *Science in China Series D—Earth Science* 2005; 48 (S2):155 – 172.
- 31 Xu ZF, Wu Y, Liu WJ, Liang CS, Ji JP, Zhao T, Zhang X. Chemical composition of rainwater
32 and the acid neutralizing effect at Beijing and Chizhou city, China. *Atmospheric Research*
33 2015;164-165, 278-285.
- 34 Yan P, Huang J, Draxler R. The long-term simulation of surface SO₂ and evaluation of
35 contributions from the different emission sources to Beijing city. *Science in China Series D-Earth*
36 *Science* 2005;48:196 – 208.
- 37 Yang DZ, Zhou HG, Zhang ZH. Chemical characteristics of precipitation in regional air
38 pollution background stations of China. *Journal of applied meteorological science*
39 2002;13(4):430-439.(in Chinese).
- 40 Yang F, He K, Lei Y, Ma Y, Yu X, Tanaka S, Okuda T, Iwase T. Chemical characters of
41 atmospheric precipitation in Beijing in years of 2001 – 2003. *China Environ. Sci* 2004;24(5):
42 538-541 (in Chinese).
- 43 Zhang J, Chen N, Yu Zh, Zhang J. Ion balance and composition of atmospheric wet deposition
44 (precipitation) in Western Yellow Sea. *Marine Environmental Science* 2000;19(2):10–13.

1 Zhang K, Wang YS, Wen TX, Hu B, Liu GR. Water-soluble chloride in Aerosol PM10 in
2 Beijing. Environmental Science 2006;27(5):825-830 (in Chinese).

3 Zhang MY, Wang SJ, Wu FC, Yuan XH, Zhang Y. Chemical compositions of wet precipitation
4 and anthropogenic influences at a developing urban site in southeastern China. Atmos. Res.
5 2007;84: 311-322.

6 Zhang NN, He Y, Cao JJ, Ho k, Shen ZX. Long-term trends in chemical composition of
7 precipitation at Lijiang, southeast Tibetan Plateau, southwestern China. Atmospheric Research
8 2012;106:50-60.

9 Zhang Q, Streets DG, Carmichael GR, He KB, Huo H, Kannari A, Klimont Z, Park IS, Reddy S,
10 Fu JS, Chen D, Duan L, Lei Y, Wang LT, Yao ZL. Asian emissions in 2006 for the NASA
11 INTEx-B mission. Atmos. Chem. Phys. 2009;9:5131-5153.

12 Zhao B, Wang P, Ma JZ, Zhu S, Pozzer A, Li W. A high-resolution emission inventory of
13 primary pollutants for the Huabei region, China. Atmos. Chem. Phys. 2012;12:481 – 501.

14 Zhao XJ, Zhang XL, Xu XF, Xu J, Meng W, Pu WW. Seasonal and diurnal variations of
15 ambient PM_{2.5} concentration in urban and rural environments in Beijing. Atmos. Environ.
16 2009;43:2893 – 2900.

17 Zhao YX, Hou Q. An analysis on spatial/temporal evolution of acid rain in China(1993
18 -2006)and its causes. Acta Meteorologica Sinica 2008;66(6):1032-1042.(in Chinese)

19 Zheng M, Salmon LG, Schauer JJ, Zeng L, Kiang CS, Zhang Y, Cass GR. Seasonal trends in
20 PM_{2.5} source contributions in Beijing, China. Atmospheric Environment 2005;39:3967 – 3976.

21 Zhou XJ, Xu XD, Yan P, Weng YH, Wang JL. Dynamic characteristics of spring sandstorms in
22 2000. Sci. China, Ser. D 2002,32(4):921-930.

Type	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5
SO_4^{2-}	228.95	156.58	160.18	236.12	216.12
NO_3^-	123.02	96.51	80.27	121.33	117.85
Cl ⁻	25.25	19.11	15.58	24.15	21.51
F ⁻	6.22	5.86	5.45	7.69	7.5
K ⁺	10.45	7.65	7.29	11.17	9.93
Na ⁺	13.92	7.78	8.79	11.52	10.36
Ca ²⁺	170.24	92.28	102.92	132.34	114.3
Mg ²⁺	41.96	22.39	24.9	31.28	26.58
NH_4^+	234.5	202.16	172.02	253.18	247.57