



Contents lists available at ScienceDirect

Particuology

journal homepage: www.elsevier.com/locate/partic



Aerosol pollution in a megacity of southwest China inferred from variation characteristics of sulfate- $\delta^{34}\text{S}$ and water-soluble inorganic compositions in TSP

Zhou Yang^a, Xiaodong Li^{b,*}, Shilu Wang^c, Qinkai Li^b, Jun Huang^c, Gaoyang Cui^c

^a Department of Tourism and Geography, Tongren University, Tongren 554300, China

^b Institute of Surface-Earth System Sciences, Tianjin University, Tianjin 300072, China

^c State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guizhou 550081, China

ARTICLE INFO

Article history:

Received 15 August 2017
Received in revised form 9 February 2018
Accepted 2 March 2018
Available online xxx

Keywords:

Aerosol pollution
Variation characteristics
Sulfate- $\delta^{34}\text{S}$
Total suspended particle

ABSTRACT

Daytime and nighttime aerosol samples for total suspended particles (TSP) were collected in Chengdu from 12 to 23 January 2013 (winter) and 10 to 21 August 2014 (summer). The mass concentrations of TSP, major inorganic ions, and stable sulfur isotope ratios were determined. Clear winter–summer variation in TSP was observed; the mass concentrations of TSP in summer were below levels defined by the Chinese National Ambient Air Quality Standard (GB3095-2012), whereas winter TSP levels exceeded the standard by 2–4 times. Overall, the sum of SO_4^{2-} , NO_3^- , and NH_4^+ concentrations represented the highest contribution to water-soluble ionic components, which showed similar trends to TSP mass. According to correlations among major ions, the major compounds in TSP were likely to be $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , CaCl_2 , and KCl in both sampling times, and CaSO_4 and $\text{Ca}(\text{NO}_3)_2$ were also present in summer. The $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios ranged from 0.57 to 1.28 (average 0.85 ± 0.16) in winter and 0.5 to 0.93 (average 0.66 ± 0.11) in summer, indicating stationary source emissions (coal burning) were more important sources than the vehicle exhaust. The relationship between SO_4^{2-} and $\delta^{34}\text{S}$ indicated the sulfate sources were affected by the low sulfur isotope value of biogenic sulfur release in summer, and the high sulfur isotope value of coal in winter. As a whole, the mixture of coal burning and vehicle exhaust represent the major TSP sources in Chengdu in the study period, and biogenic sulfur also contributes to TSP in summer.

© 2018 Chinese Society of Particuology and Institute of Process Engineering, Chinese Academy of Sciences. Published by Elsevier B.V. All rights reserved.

Introduction

Total suspended particles (TSP; particulate matter with aerodynamic diameters less than $100\ \mu\text{m}$) significantly impact visibility, climate change, and human health (Chen & Kan, 2008; Han et al., 2012; Huang et al., 2014; Li et al., 2011; Osborne & Lambert, 2014; Wang et al., 2009, 2016). During periods of wintertime haze pollution in China, extremely high levels of airborne particles are associated with a wide range of human health effects. These effects are related to the physical properties and chemical components of the airborne particles (Beckerman et al., 2013; Perrone et al., 2013). Studies of the physical and/or chemical characteristics of the water-soluble ionic components (WSIC) of airborne particles and

the stable sulfur isotope ratios ($\delta^{34}\text{S}$) of their sulfates are useful for determining their sources and transformation mechanisms.

In most cases, sulfate is a major component of aerosol particles, derived either from primary emissions or oxidation of precursor gases such as SO_2 (Cheng et al., 2016; Wang et al., 2016). Typically, sulfate is of anthropogenic origin, related to fossil fuel and/or coal combustion (Huang et al., 2014). Many researchers have described chemical characteristics, sources, and spatial and temporal variations of TSP and $\text{PM}_{2.5}$ within cities all over the world, including Beijing (Guo et al., 2014; Ianniello et al., 2011), Tianjin (Han et al., 2012; Li, Bai, Liu, Chen, & Chen, 2009), Shanghai (Wang et al., 2006), Pune (Safai, Budhavant, Rao, Ali, & Sinha, 2010), Delhi (Srivastava, Gupta, & Jain, 2009), and Gosan (Kang, Kim, Ko, & Hong, 2009). To date, only a few studies have used $\delta^{34}\text{S}$ to explore the sources of sulfate in TSP in urban environments. Different sources of sulfate have distinctive $\delta^{34}\text{S}$ values, which suggests that sulfur isotopic values could be a potential tracer for various sulfate sources (Garbaras, 2008; Guo et al., 2010; López-Veneroni, 2009; Sharma et al., 2014;

* Corresponding author.

E-mail address: xiaodong.li@tju.edu.cn (Li Xiaodong).

Winterholler, Hoppe, Huth, Foley, & Andreae, 2008). This potential was explored in the current study, using Chengdu as an example.

Chengdu (30.67°N, 104.06°E, 500 m above sea level; Fig. 1), located in the west part of the Sichuan Basin, is one of the largest megacities in southwest China. It has quite severe air pollution because of its rapid urbanization, motorization, and energy consumption over the last decade. According to the Chengdu Economic and Social Development Statistics Bulletin, the mass concentrations of particulate matter in 2012 showed a 19% increase against values for 2011. This city has an annual mean particulate matter concentration of about 119 $\mu\text{g}/\text{m}^3$, which is twice the National Ambient Air Quality Standard of China (GB3095-2012). In winter, the air pollutants within Chengdu do not diffuse easily, given the bowl-shaped basin topography, coupled with low wind speeds and the stable atmospheric conditions of the Sichuan Basin. Therefore, Chengdu may be regarded as an ideal site to investigate the sources of sulfate in WSIC using stable sulfur isotope ratios of sulfate in TSP during haze-fog episodes.

The present study focuses on the winter–summer and day–night variation of WSIC and $\delta^{34}\text{S}$ values of sulfate-containing particles under various weather conditions. The main aims were: (1) to understand the diurnal variation of WSIC in TSP; (2) to use relationships among specific ions to trace sources of WSIC; and (3) to use stable isotopes to trace sulfate sources of TSP in Chengdu.

Materials and methods

Sample collection

Aerosol samples of TSP were continuously collected from 12 to 23 January 2013 and from 10 to 21 August 2014 in Chengdu, Sichuan province, Southwest China. Samples were separated to represent day and night 12-h time periods, using 08:00 local time (LT) and 20:00 LT, respectively. We used a high-volume air sampler to collect TSP, with an airflow rate of 0.8 m^3/min (Qingdao Laoshan Institute for Electronic Equipment, China). The sampler was placed on the rooftop (15 m above ground level) of a four-story building on the campus of Chengdu University of Technology, located in the north-eastern part of Chengdu (Fig. 1). Prior to use, all quartz-fiber filters were pre-combusted at 450 °C for 6 h to remove potential organic contamination and stored at 50% relative humidity (RH) and 25 °C for over 24 h. Filters were weighed before and after sampling. Field blanks were collected at the beginning and the end of the sampling campaign; these blank filters were placed in the sampler for 10 min, without pumping air through the filters. After sampling, all samples were sealed within an aluminum foil bag and stored at -4 °C prior to analysis. During this study, 48 TSP samples and 4 blank filters were collected.

Analytical procedures

All filters were analyzed for WSIC (SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , Ca^{2+} , K^+ , Na^+ , and Mg^{2+}) and $\delta^{34}\text{S}_{\text{sulfate}}$.

Analysis of water-soluble ionic components

To carry out analyses of WSIC, a quarter of the filter was cut into pieces and ultrasonically extracted with 40 mL of ultrapure water (Milli-Q; EMD Millipore, Merck KGaA, Germany) for 30 min. This ultrasonication was repeated with 30 mL of Milli-Q for 20 min, and finally with an additional 20 mL of Milli-Q for 10 min. The extracted samples were filtered with a 0.22 μm polytetrafluoroethylene syringe filter (Pall Co. Ltd, USA) and divided into two parts. One part was placed in a 15 mL centrifuge tube and stored in refrigerator at 4 °C for cation (Na^+ , K^+ , Mg^{2+} , Ca^{2+}), anion (Cl^- , NO_3^- , SO_4^{2-}), and NH_4^+ analyses, while the other part was used for stable sulfur isotope analyses. The concentrations of cations in

the extracted samples were measured using inductively coupled plasma-optical emission spectrometry (ICP-OES; MPX; Varian, Inc., Walnut Creek, CA, USA) and anions were analyzed using ion chromatography (ICS-90; Dionex Corp., Sunnyvale, CA, USA). The limits of detection were less than 0.005 mg/L for cations and 0.02 mg/L for anions. NH_4^+ was measured using a Skalar continuous flow analyzer (San^{++} ; Skalar, Holland) with a limit of detection of less than 0.005 mg/L. The background WSIC in the quartz-fiber filter was ignored in this study because the WSIC concentrations in blank filters were found to be below the detection limit.

Stable sulfur isotope ratios analyses

The remainder of the extracted sample was placed in a 50 mL bottle and acidified to $\text{pH} < 2$, using 2 mol/L HCl, as preparation for sulfur isotope analyses. The sulfate in this acidified extract was precipitated as BaSO_4 by adding 2 mL of a 10% BaCl_2 solution. The BaSO_4 precipitate was collected on a 0.45 μm Millipore filter (Toyo Roshi Kaisha, Ltd., Japan), and washed with ultrapure water to neutralize it. This filter was combusted in a muffle furnace to obtain pure BaSO_4 for sulfur isotope analyses. The $\delta^{34}\text{S}$ was determined using an elemental analyzer (Euro EA 1108; Thermo Fisher Scientific Inc., Waltham, MA, USA) coupled with isotope ratio mass spectrometry (IRMS; Delta C Finningan Mat; Isomass Scientific Inc., Calgary, Canada). The $\delta^{34}\text{S}$ was expressed in delta notation defined according to the following equation (VCDT: Vienna Canyon Diablo Troilite).

$$\delta^{34}\text{S}(\text{‰}) = \left[\left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{\text{sample}} / \left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{\text{VCDT}} - 1 \right] \times 1000.$$

The average standard deviation for duplicate analyses of a given sample was $\pm 0.2\text{‰}$ ($n = 18$). All measurements were carried out at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

Meteorological considerations

During the sampling period, the weather conditions were mainly misty, cloudy, sunny, or rainy. During this study, calm winds were frequently recorded in Chengdu; thus, the effects of wind direction and wind speed were ignored. Ambient temperatures ranged from -1 °C to 13 °C (mean = 5.7 °C ± 1.9 °C) in winter, and from 18 °C to 31 °C (mean = 23.5 °C ± 2.9 °C) in summer. RH varied from 28% to 92% (mean = 78% $\pm 8.9\%$) in winter, and from 50% to 98% (mean = 85% $\pm 12\%$) in summer (<http://sc.com.weather.cn/qxfw.shtml>).

The NOAA's HYSPLIT4 trajectory model (<http://www.arl.noaa.gov/hysplit.html>) was used to calculate 24-h backward trajectories for each sample. Summer air masses over Chengdu were transported northeasterly (towards Shanxi province) and southwesterly (towards Chongqing, Guizhou province). In contrast, air masses were mainly from the Sichuan Basin in winter. Thus, winter air pollution in Chengdu is mainly related to local sources within Sichuan province, while summer air masses are less obviously affected by local pollution sources.

Results and discussion

Variations of the mass concentrations of TSP

The mass concentrations of TSP ranged from 360 to 1423 $\mu\text{g}/\text{m}^3$ (mean = 643 ± 266 $\mu\text{g}/\text{m}^3$, $n = 24$) in winter, and from 90 to 283 $\mu\text{g}/\text{m}^3$ (mean = 160 ± 45 $\mu\text{g}/\text{m}^3$, $n = 24$) in summer. A clear winter–summer variation in TSP was observed in the samples. The low concentrations of TSP in summer were likely to be because of frequent rainfall, given that precipitation scavenging is an efficient way of removing particles from the atmosphere (Tao et al., 2013), in

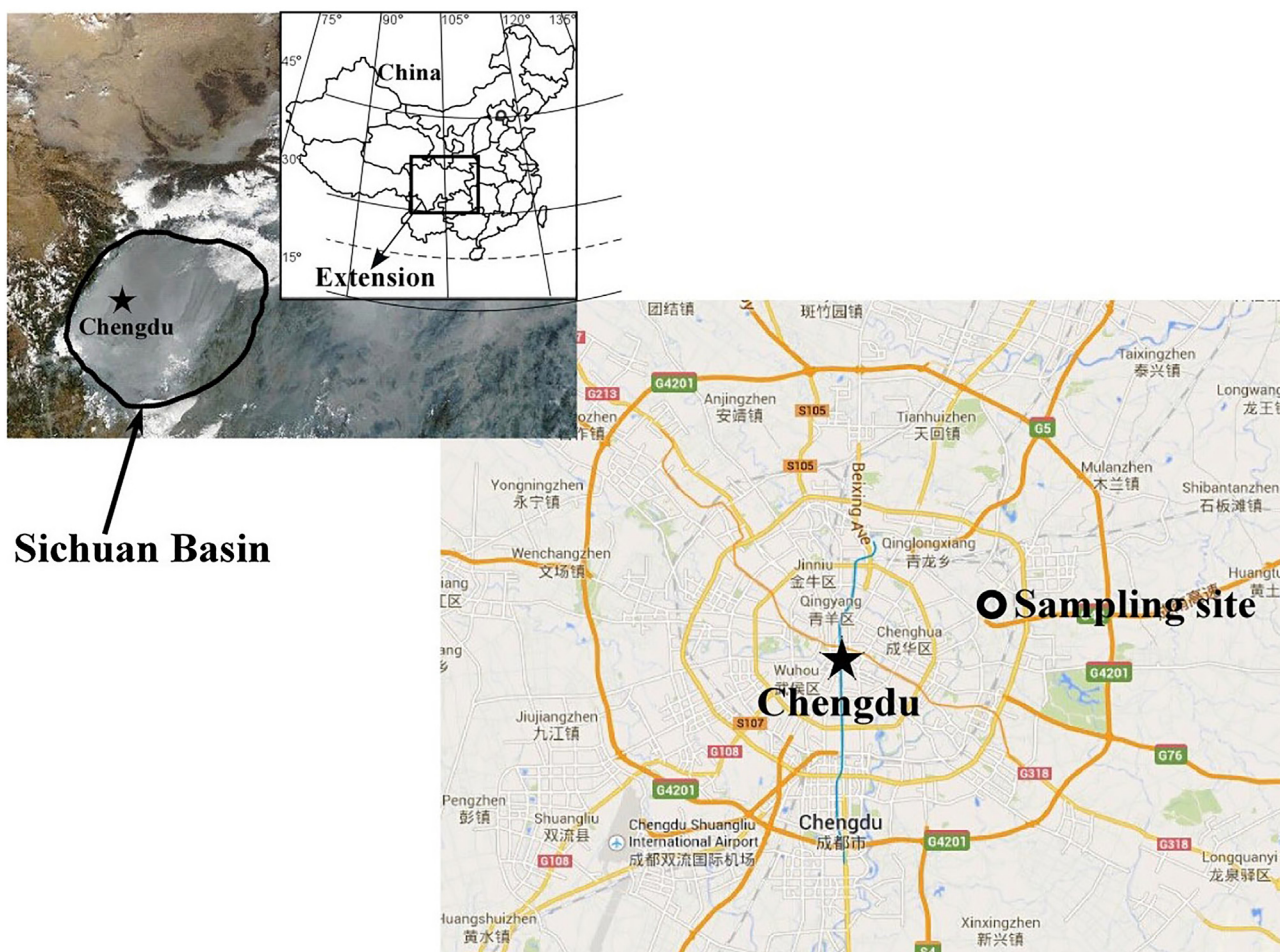


Fig. 1. Map showing the sampling site in Chengdu within the Sichuan Basin, Southwest China.

addition to the higher wind speed, which increases the diffusion of air pollutants, reducing local contributions from home stoves. High concentrations of TSP in winter reflect the meteorological setting, in which calm winds, inversion layers, and high RH occur within the basin topography. These conditions accelerate the accumulation and secondary formation of pollutants emitted from local sources, such as biomass burning, power plants, home stoves, and vehicles (Huang et al., 2014). Although the mass concentrations of TSP in summer were below levels defined by the Chinese National Ambient Air Quality Standard (GB3095-2012) ($300 \mu\text{g}/\text{m}^3$), winter TSP levels exceeded this limit by 2–4 times. These levels may also be related to more frequent and stronger fog-haze events in January of 2013 (Ho et al., 2016).

The mass concentrations of TSP varied from 360 to $1050 \mu\text{g}/\text{m}^3$ (mean = $643 \pm 231 \text{ mg}/\text{m}^3$, $n = 12$) in the daytime and from 483 to $1423 \mu\text{g}/\text{m}^3$ (mean = $740 \pm 289.3 \mu\text{g}/\text{m}^3$, $n = 12$) at nighttime during the winter period, respectively. In contrast, the mass concentrations of TSP varied from 110 to $224 \mu\text{g}/\text{m}^3$ (mean = $156 \pm 35.6 \mu\text{g}/\text{m}^3$, $n = 12$) in the daytime and from 94 to $283 \mu\text{g}/\text{m}^3$ (mean = $168 \pm 31.4 \mu\text{g}/\text{m}^3$, $n = 12$) at nighttime during the summer period. Day–night variation in the concentration of TSP clearly occurred during the two sampling periods, with higher concentrations occurring at nighttime. This may reflect the lower temperature and higher RH at night. High RH can cause absorption growth and reduce the residence time of TSP in the atmosphere. For example, under high RH and low temperatures after midnight, nitrate is present as NH_4NO_3 (Guo et al., 2010), and it may therefore

be less dissociated than other forms, resulting in an increase in TSP at nighttime.

Day–night variations of WSIC, SNA, and $\delta^{34}\text{S}$

In this study, we analyzed SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , K^+ , Na^+ , Ca^{2+} , and Mg^{2+} . Plots of their daytime versus nighttime concentrations (Fig. 2) show similarities to trends in the mass of TSP, although there were differences among various ions. The total mass concentrations of SO_4^{2-} , NO_3^- , and NH_4^+ (SNA) were the highest contributors to WSIC during the sampling time. They showed no clear variation in daytime and nighttime levels in winter (78%) or summer (86%). In both seasons (Table 1), the average concentrations of SNA in daytime samples were slightly higher than nighttime concentrations, but there was no clear variation pattern in Cl^- , Ca^{2+} , K^+ , Na^+ , and Mg^{2+} , which could be related to the sources and transformation pathways of these ions. Such sources may be responsible for formation of large amounts of secondary aerosols during the daytime (Guo et al., 2016), with primary emissions being relatively stable over time.

Variation in NH_4^+ was basically coincident with variations in SO_4^{2-} and NO_3^- (Fig. 2), indicating that it was largely related to the neutralization of ammonia by acidic species (Wang et al., 2006), such as H_2SO_4 or HNO_3 . Fig. 3 shows the linear relationships among mass concentrations of NH_4^+ , SO_4^{2-} , and NO_3^- over the sampling period. The relationships between NH_4^+ and SO_4^{2-} were similar during the daytime ($R^2 = 0.92$) and nighttime ($R^2 = 0.95$), suggesting that ammonium was associated with sulfate (as $(\text{NH}_4)_2\text{SO}_4$) in win-

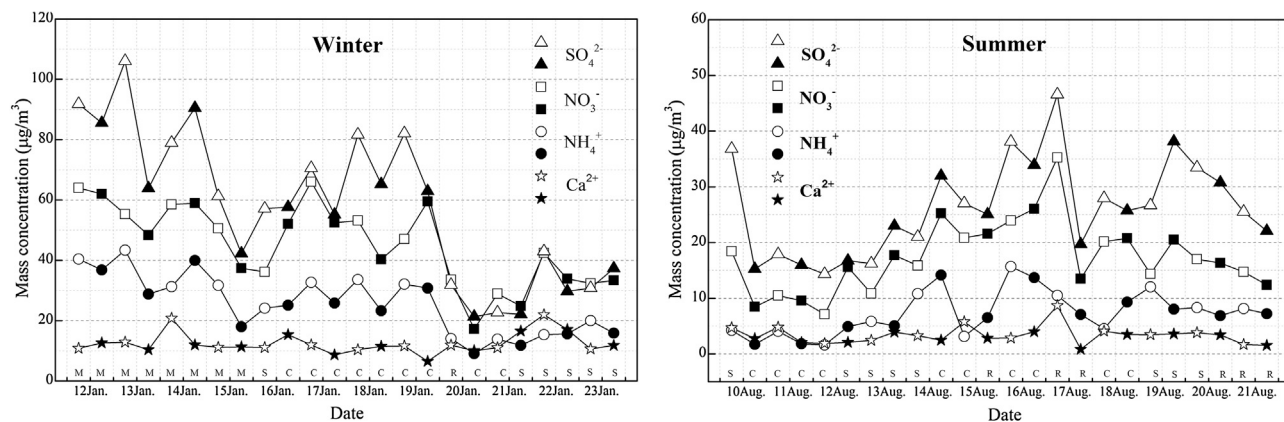


Fig. 2. Day–night variations of the mass concentrations of WSIC in winter and summer. Unfilled symbols: daytime, filled symbols: nighttime. M: misty, S: sunny, C: cloudy, R: rainy.

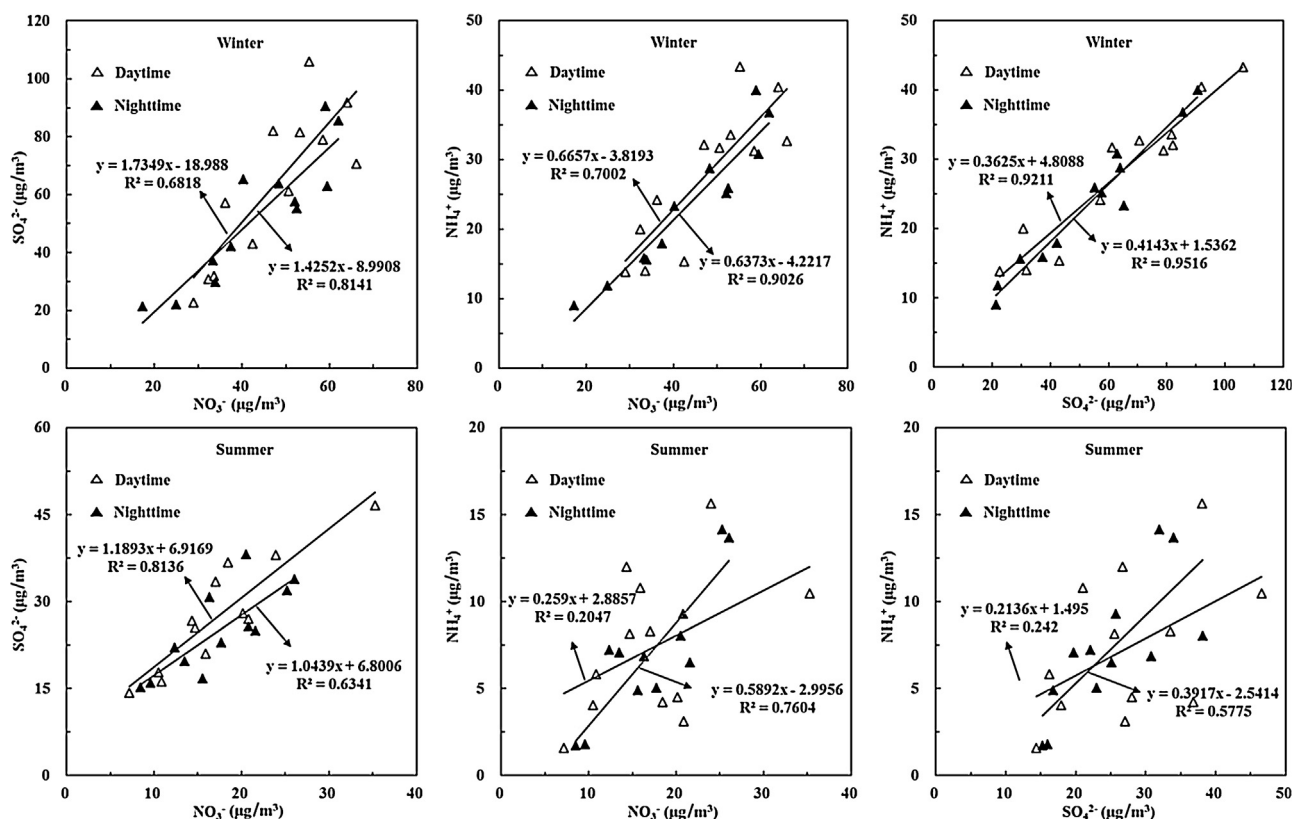


Fig. 3. Correlations among NH_4^+ , SO_4^{2-} , and NO_3^- ions in winter and summer.

ter (Tao et al., 2013). Guo et al. (2010) reported that when RH was between 50% and 70%, NH_4NO_3 could partly dissociate, whereas when RH was over 70%, NH_4NO_3 was relatively stable. In our study, NH_4^+ was more strongly correlated with NO_3^- during the nighttime than the daytime, indicating more NH_4NO_3 was present at night. This is related to high RH after midnight (>70%). The correlation coefficients between SO_4^{2-} and NO_3^- were higher for nighttime samples ($R^2 = 0.81$) than for daytime samples ($R^2 = 0.63$), suggesting that the precursors of these species were released from similar emission sources, such as coal burning or industrial sectors during the night (Zhang et al., 2011). This suggests that their sources were different during daytime hours. In summer, there is good correlation between SO_4^{2-} and NH_4^+ , and SO_4^{2-} and Ca^{2+} for both daytime and nighttime samples, indicating that $(\text{NH}_4)_2\text{SO}_4$ and CaSO_4 are likely to be the main species present in the urban atmosphere.

The correlation between NH_4^+ and NO_3^- was better for nighttime samples ($R^2 = 0.76$) than daytime samples ($R^2 = 0.21$), with similar results observed in winter samples. Moreover, Ca^{2+} was better correlated with NO_3^- in daytime samples ($R^2 = 0.58$) than in nighttime samples ($R^2 = 0.29$), suggesting that the presence of $\text{Ca}(\text{NO}_3)_2$ during daytime hours was probably related to human activities.

In the present study, the $\delta^{34}\text{S}$ values of sulfate in TSP ranged from +3.4‰ to +6.4‰ (mean = +5.0‰, $n = 12$) in daytime samples, and from +4‰ to +7.1‰ (mean = +5.6‰, $n = 12$) in nighttime samples in winter (Fig. 4). The $\delta^{34}\text{S}$ values of sulfate in daytime samples were lower than nighttime values, indicating different oxidation pathways for the source SO_2 between daytime and nighttime. The RH was lower than 80% in daytime, favoring gas–particle conversion. In contrast, the main foggy weather in nighttime, when the RH was above 90%, favored heterogeneous oxidation to the forma-

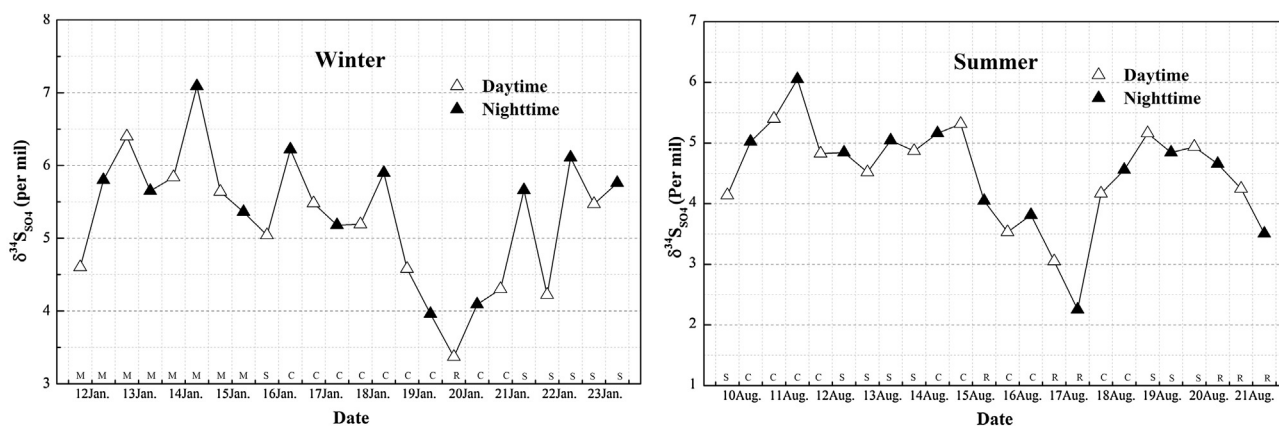


Fig. 4. Day–night variations of $\delta^{34}\text{S}$ in winter and summer. Unfilled symbols: daytime, filled symbols: nighttime. M: misty, S: sunny, C: cloudy, R: rainy.

Table 1

Average concentrations ($\mu\text{g}/\text{m}^3$) ($\pm 1\sigma$) of cations, and anions in TSP samples, and the average ratios ($\pm 1\sigma$) of selected measured species in ambient aerosols.

Species	TSP (n=48)			
	Winter		Summer	
	Day (n=12)	Night (n=12)	Day (n=12)	Night (n=12)
SO_4^{2-}	63.1 ± 26.6	52.8 ± 22.8	27.6 ± 9.7	24.8 ± 7.5
NO_3^-	47.3 ± 12.7	43.3 ± 14.4	17.4 ± 7.4	17.3 ± 5.7
Cl^-	13.5 ± 5.2	12.5 ± 3.6	2.3 ± 1.7	4.2 ± 1.3
NH_4^+	27.7 ± 10.1	23.4 ± 9.7	7.4 ± 4.2	7.2 ± 3.8
Ca^{2+}	13.2 ± 4.2	11.8 ± 3.1	4.1 ± 1.9	2.7 ± 1.1
K^+	4.1 ± 1.6	4.4 ± 1.3	0.7 ± 0.3	0.6 ± 0.2
Na^+	3.1 ± 1.7	2.6 ± 0.9	0.4 ± 0.4	0.4 ± 0.2
Mg^{2+}	0.8 ± 0.3	0.9 ± 0.4	0.2 ± 0.1	0.2 ± 0.1
WSIC ^a	172.8 ± 51.7	151.7 ± 48.6	60.2 ± 22.1	57.4 ± 17.2
SNA ^b	138.1 ± 47.4	119.5 ± 46.3	52.4 ± 19.1	49.3 ± 16
%WSIC ^c	27.7 ± 5.5	21.3 ± 5.4	38.4 ± 10.6	36.4 ± 7.7
%SNA ^c	22.1 ± 5.3	16.6 ± 5.4	33.8 ± 9.6	30.7 ± 8.2

^a WSIC: water-soluble inorganic component.

^b SNA: anthropogenic inorganic species (sum of SO_4^{2-} , NO_3^- , and NH_4^+).

^c Percentage contribution to TSP mass.

tion of secondary sulfates (Winterholler et al., 2008). Moreover, the NO_3^- formation pathway may contribute to sulfate formation in fog under polluted conditions (Cheng et al., 2016). Simultaneously, the mean $\delta^{34}\text{S}$ values of sulfate in nighttime samples were close to the average $\delta^{34}\text{S}$ (about +5.7‰) for foggy weather (Wu, 2010), indicating the formation of sulfate was dependent on heterogeneous oxidation in nighttime in winter. Furthermore, the $\delta^{34}\text{S}$ values of sulfate in TSP varied from +3.1‰ to +5.4‰ (mean = +4.5‰, $n=12$) in daytime samples, and from +2.3‰ to +6.1‰ (mean = +4.5‰, $n=12$) in nighttime samples in summer (Fig. 4). In this case, there were no obvious differences between day and night samples, and RH was under 70%, favoring gas–particle conversion in summer.

Winter–summer variations of WSIC, SNA, and $\delta^{34}\text{S}$

The mass of WSIC was consistently higher in winter ($72\text{--}224.3 \mu\text{g}/\text{m}^3$, average $162.3 \pm 50.3 \mu\text{g}/\text{m}^3$) than in summer ($28\text{--}110.2 \mu\text{g}/\text{m}^3$, average $59.2 \pm 19.6 \mu\text{g}/\text{m}^3$), showing a similar trend to mass concentrations of TSP during the sampling period. The mass concentrations of SNA accounted for 78% and 85% of the winter and summer total mass concentrations of WSIC, respectively. This indicates that sulfate and nitrogen were the major inorganic components of TSP during the sampling period. Likewise, they likely originated from secondary particles, produced through the transformation of precursor gases, such as SO_2 , NO_x , and NH_3 (DeBell et al., 2004; Hsu et al., 2009).

In this study, NH_4^+ was strongly correlated with SO_4^{2-} ($R^2=0.93$) and NO_3^- ($R^2=0.82$) in winter, but poorly correlated with SO_4^{2-} ($R^2=0.37$) and NO_3^- ($R^2=0.42$) in summer. This indicates that ammonium was associated with both sulfate (as $(\text{NH}_4)_2\text{SO}_4$) and nitrate (as NH_4NO_3) in winter, while only a small fraction of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 was present in summer. This indicates that the chemical components varied during each sampling period. This suggests that there must be other alkaline ions (such as Ca^{2+} and Mg^{2+}) present to neutralize acidic species (H_2SO_4 and HNO_3). Ca^{2+} and Mg^{2+} were more strongly correlated with SO_4^{2-} ($R^2=0.38, 0.46$, respectively) and NO_3^- ($R^2=0.41, 0.52$, respectively) in summer than in winter (no correlation). This further suggests that CaSO_4 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, and $\text{Mg}(\text{NO}_3)_2$ were chemical components of TSP in summer. Likewise, Ca^{2+} and Cl^- were correlated in winter ($R^2=0.58$), and summer ($R^2=0.51$), while K^+ and Cl^- were correlated in winter ($R^2=0.84$) and summer ($R^2=0.53$), indicating CaCl_2 and KCl were present in TSP during both sampling periods.

The ion balance can be used as an indicator of the acidity of the sampled aerosols. It can be calculated using the equivalent ratios of the total cations to the total anions (Wang et al., 2005, 2013) using these formulas:

$$\text{Cations} = \text{Na}^+/23 + \text{NH}_4^+/18 + \text{K}^+/39 + \text{Mg}^{2+}/12 + \text{NH}_4^+/18,$$

$$\text{Anions} = \text{F}^-/19 + \text{Cl}^-/18 + \text{NO}_3^-/62 + \text{SO}_4^{2-}/96.$$

The equivalent ratios of cations to anions (C/A) in samples of this study ranged between 1.18 and 1.75, with a mean value of 1.41 ± 0.12 ($n=24$) in winter, and from 0.51 to 1.25, with a mean value of 0.94 ± 0.21 ($n=24$) in summer. The equivalent C/A ratios were above 1.0 in winter and less than 1.0 in summer, indicating TSP samples are alkaline in winter, but faintly acid in summer. Thus, H_2SO_4 and HNO_3 were mainly neutralized by inorganic cations in winter but were not completely neutralized by inorganic cations in summer (Wang et al., 2013).

The $\delta^{34}\text{S}$ values of sulfate varied from +3.4‰ to +7.1‰ (mean = +5.3‰, $n=24$) in winter, and varied from +2.3‰ to +6.1‰ (mean = +4.5‰, $n=24$) in summer. The $\delta^{34}\text{S}$ ratios in summer were lower than in winter, which could be affected by the presence of more biogenic sulfur and soil particles in summer (Mast, Turk, Ingersoll, Clow, & Kester, 2001), and the greater amount of coal combustion in winter. Li, Masuda, Kusakabe, Yanagisawa, and Zeng (2006) reported the $\delta^{34}\text{S}$ values of sulfur in the range -6.1% to $+7.4\%$ with average $+3.2\%$ for the coal samples, and Xiao et al. (2011) also reported raw coal in Chengdu mainly from Shanxi province, the average $\delta^{34}\text{S}$ about $+9.7\%$.

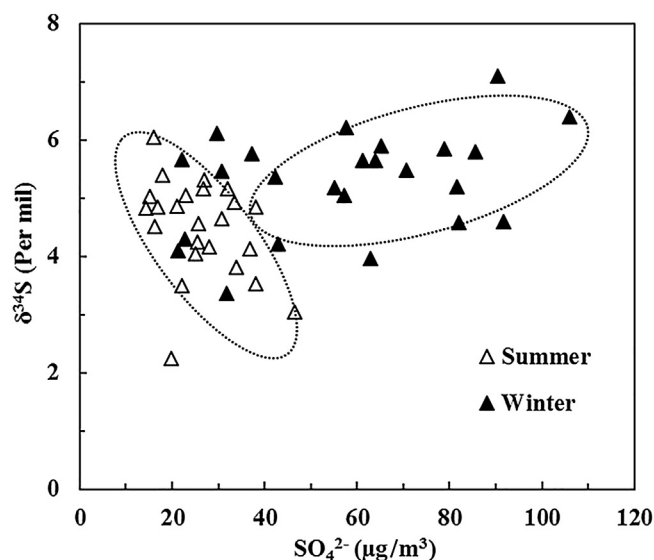


Fig. 5. Relationship between SO_4^{2-} concentrations and $\delta^{34}\text{S}$ values in winter and summer.

According to the relationship between SO_4^{2-} and $\delta^{34}\text{S}$ in the current study (Fig. 5), the sulfur isotopic composition of sulfate in the TSP reflects a mixture of sulfate sources, with high and low $\delta^{34}\text{S}$ values, indicating the sulfate was derived from different sources (Guo et al., 2010). A negative correlation was found between the mass concentrations of SO_4^{2-} and $\delta^{34}\text{S}$ in summer (Fig. 5), but these measures were positively correlated in winter. This indicates that the sources of sulfate were affected by low sulfur isotope values of biogenic sulfur released in summer, and the high sulfur isotope values of coal emitted in winter. Given that Chengdu is distant from the coast, the contribution of sea-salt would be very low; thus, sulfate from sea-salt can be ignored. Han et al. (2016) reported the emission rate of SO_2 from oil combustion is relatively constant, with almost no seasonal change, making sulfur isotopic ratios of SO_2 emissions from oil combustion a steady source of sulfate, with a relatively high $\delta^{34}\text{S}$ value. The $\delta^{34}\text{S}$ values in the present study were close to the sulfur isotopic ratios of $\text{PM}_{2.5}$ in Beijing (Han et al., 2016), indicating that SO_2 emissions from oil combustion could be another source of sulfate in TSP in Chengdu.

Change of WSIC, SNA, and $\delta^{34}\text{S}$ under different weather conditions

Fig. 2 shows variations in mass concentrations measured by an air ion spectrometer under different weather conditions (misty, cloudy, sunny, and rainy) during the sampling period in Chengdu. In winter, the mass concentrations of SNA under different weather conditions decreased in the order misty, cloudy, sunny, and rainy. Mass concentrations of SNA on misty days were 2–5 times higher than those for other weather conditions. This could be linked to calm winds, inversion layers, and higher RH on misty days in winter. In contrast, SNA concentrations under different weather conditions in summer decreased in the order cloudy, sunny, and rainy. The marked decreases related to rain are likely to reflect washout. Furthermore, mass concentrations of crustal elements (Ca^{2+} and Mg^{2+}) ranged from 7.2 to 23.2 $\mu\text{g}/\text{m}^3$ (mean = 13.3 \pm 3.7 $\mu\text{g}/\text{m}^3$, $n = 24$) in winter, and from 1.6 to 6 $\mu\text{g}/\text{m}^3$ (mean = 3.5 \pm 1.7 $\mu\text{g}/\text{m}^3$, $n = 24$) in summer. Clearly, the mass of crustal elements in winter was higher than in summer. This also suggests that the rain washed out airborne crustal material in summer. The total mass concentration of these crustal elements accounted for 1.7% \pm 0.8% of WSIC in winter, but 6% \pm 2.2% in summer, indicating that crustal sources, such as soil and re-suspended road dust contribute more to TSP in summer than

in winter. Alternatively, this pattern may simply reflect increases in ions other than Ca^{2+} and Mg^{2+} , related to fog-haze pollution in winter.

Our statistical analyses suggest that the average sulfur isotope ratios varied with weather conditions. In winter, the $\delta^{34}\text{S}$ values of sulfate under different weather conditions decreased in the order misty (+5.8%), sunny (+5.4%), and cloudy (+5.0%). This decrease may be related to heterogeneous oxidation reactions of SO_2 , which led to enrichment in heavy isotopes (^{34}S) on misty days, coupled with high water solubility of SO_2 under the low-temperature winter conditions. In summer, the $\delta^{34}\text{S}$ ratios were almost the same on cloudy (+4.8%) and sunny (+4.8%) days but decreased on rainy days (+3.6%), indicating rain wash caused the $\delta^{34}\text{S}$ values of sulfate in TSP to be negative, as most coarse particles (such as CaSO_4 and MgSO_4) were removed. The remaining fine particles of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 were from homogeneous oxidation of SO_2 in the atmosphere, related to photochemical oxidation. This process caused enrichment in lighter isotopes (^{32}S), while summer high temperatures reduced the water solubility of SO_2 .

Possible sources of sulfate in TSP

Several studies (Cheng et al., 2016; Sharma et al., 2014; Xiao & Liu, 2004; Yang, Li, Deng, & Wang, 2015) reported that the ratios of various chemical components, such as the $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio, in particulate matter may provide further information about its sources. The $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio has been used as an indicator of the relative importance of mobile versus stationary sources of sulfur and nitrogen in the atmosphere (Wang et al., 2006, 2013; Xiao & Liu, 2004; Yao et al., 2002). In Chengdu, the mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ in TSP samples ranged from 0.57 to 1.28 (mean = 0.85 \pm 0.16) in winter, and from 0.50 to 0.93 (mean = 0.66 \pm 0.11) in summer. These values were higher than in TSP sampled in Guiyang (0.01–0.38; mean = 0.13) (Xiao & Liu, 2004), as well as in TSP sampled from October 2001 to January 2003 in Chengdu (0.01–0.54; mean = 0.3) (Li, 2007). They are also similar to mass ratios in TSP from Shanghai (mean = 0.83 \pm 0.4) (Wang et al., 2006). These ratios suggest that stationary source emissions were important during the sampling periods, although the influence of vehicle exhaust emissions is increasing.

Previous studies have shown coal burning is an important source for atmospheric sulfur in the urban environments of China (Guo et al., 2010; Mukai et al., 2001), and the $\delta^{34}\text{S}$ ratios of atmospheric sulfate in different regions in China depend on the extent of local coal burning (Mukai et al., 2001). In this study, the sulfur isotopic composition of sulfate in TSP was a mixture of sulfate with low and high $\delta^{34}\text{S}$ values (Fig. 5), indicating that sulfate was derived from different sources (Guo et al., 2010). Here, the average $\delta^{34}\text{S}$ value for sulfate (+5.3‰ in winter and +4.5‰ in summer) in TSP from Chengdu was close to the average sulfur isotope ratio (+3.7‰) for coal in northern China, which was close to values for vehicle exhaust (+5‰), indicating that coal burning and vehicle exhaust were the dominant sources of atmospheric sulfate. Liu, Hong, Piao, and Zeng, (1996) found that the $\delta^{34}\text{S}$ of size-segregated atmospheric particles (−1.49‰) were close to coal burning (−2.3‰) and soil (−2.2‰) in Guiyang, and deduced that the sulfur sources of atmospheric particles were mainly derived from coal burning and the soil in this city. Biogenic sulfur mainly arises as a combination of emissions from microorganisms that reduce SO_4^{2-} in water, and the product of microbial decomposition of sulfur-containing substances in land-based organic matter (Wu & Han, 2012, 2015). The $\delta^{34}\text{S}$ values of biogenic sulfur are negative, varying from −10‰ to −2‰ emitted from soil, lake, and swamp environments etc. (Liu et al., 1996; Mast et al., 2001). Biogenic sulfur as a source for sulfate in TSP in summer could explain the lower $\delta^{34}\text{S}$ ratios in summer than in winter (Mast et al., 2001). Therefore, a mixture of coal com-

bustion and vehicle exhaust is likely to be responsible for the major sources of sulfate in TSP in Chengdu during the sampling period with the contribution of biogenic sulfur in summer.

Conclusions

In Chengdu, the mass concentrations of TSP in winter exceeded the Chinese National Ambient Air Quality Standard (GB3095-2012) by about 2–4 times, which could be related to more frequent and stronger fog-haze events during winter periods. However, the mass concentrations of TSP in summer met this standard, suggesting rain washout and lower local emissions from coal combustion mitigate pollution in summer.

We found that sulfate and nitrate were the major inorganic components of TSP in Chengdu. According to correlations among water-soluble inorganic ions, the major compounds in TSP are likely to be $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , CaCl_2 , and KCl . CaSO_4 and $\text{Ca}(\text{NO}_3)_2$ are also likely to be present in TSP in summer.

The low mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ and $\delta^{34}\text{S}$ values of sulfate suggest that stationary source emissions (coal burning) may be more important than vehicle exhaust emissions. Sulfate isotopic ratios were affected by low sulfur isotope values from biogenic sulfur released in summer, and the high sulfur isotope values from coal burning in winter. Coal burning and vehicle exhaust emissions were the major sources of TSP in Chengdu during our sampling periods, with biogenic sulfur contributing more to TSP in summer than in winter.

Acknowledgments

This work was financially supported by the National Natural Science Foundation (Grant No. 41773006, 91644104), the West Light Foundation of the Chinese Academy of Sciences, the “Strategic Priority Research Program” of the Chinese Academy of Sciences (Grant No. XDB05030305), and Tongren University PhD Launches Fund (txyxDH1609). The authors would like to thank Mr. Ning An and Dr. Qixin Wu for their help during the sample analyses.

References

- Beckerman, B. S., Jerrett, M., Serre, M., Martin, R. V., Lee, S. J., Van Donkelaar, A., et al. (2013). A hybrid approach to estimating national scale spatiotemporal variability of $\text{PM}_{2.5}$ in the contiguous United States. *Environmental Science & Technology*, 47(13), 7233–7241.
- Chen, B., & Kan, H. (2008). Air pollution and population health: A global challenge. *Environmental Health and Preventive Medicine*, 13(2), 94–101.
- Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., et al. (2016). Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. *Science Advances*, 2(12), e1601530.
- DeBell, L. J., Talbot, R. W., Dibb, J. E., Munger, J. W., Fischer, E. V., & Frolking, S. E. (2004). A major regional air pollution event in the northeastern United States caused by extensive forest fires in Quebec, Canada. *Journal of Geophysical Research: Atmospheres*, 109(D19), D19305.
- Garbaras, A. (2008). Tracing of atmospheric aerosol sources using stable carbon isotopes. *Lithuanian Journal of Physics*, 48(3), 259–264.
- Guo, S., Hu, M., Zamora, M. L., Peng, J., Shang, D., Zheng, J., et al. (2014). Elucidating severe urban haze formation in China. *Proceedings of the National Academy of Sciences*, 111(49), 17373–17378.
- Guo, Z., Jiang, W., Chen, S., Sun, D., Shi, L., Zeng, G., et al. (2016). Stable isotopic compositions of elemental carbon in $\text{PM}_{1.1}$ in north suburb of Nanjing Region, China. *Atmospheric Research*, 168, 105–111.
- Guo, Z., Li, Z., Farquhar, J., Kaufman, A. J., Wu, N., Li, C., et al. (2010). Identification of sources and formation processes of atmospheric sulfate by sulfur isotope and scanning electron microscope measurements. *Journal of Geophysical Research: Atmospheres*, 115(D7), D00K07.
- Han, S., Bian, H., Zhang, Y., Wu, J., Wang, Y., Tie, X., et al. (2012). Effect of aerosols on visibility and radiation in spring 2009 in Tianjin, China. *Aerosol and Air Quality Research*, 12, 211–217.
- Han, X., Guo, Q., Liu, C., Strauss, H., Yang, J., Hu, J., et al. (2016). Effect of the pollution control measures on $\text{PM}_{2.5}$ during the 2015 China Victory Day Parade: Implication from water-soluble ions and sulfur isotope. *Environmental Pollution*, 218, 230–241.
- Ho, K. F., Ho, S. S. H., Huang, R. J., Chuang, H. C., Cao, J. J., Han, Y., et al. (2016). Chemical composition and bioreactivity of $\text{PM}_{2.5}$ during 2013 haze events in China. *Atmospheric Environment*, 126, 162–170.
- Hsu, S. C., Liu, S. C., Huang, Y. T., Chou, C. C., Lung, S. C., Liu, T. H., et al. (2009). Long-range southeastward transport of Asian biomass pollution: Signature detected by aerosol potassium in northern Taiwan. *Journal of Geophysical Research: Atmospheres*, 114(D14), D14301.
- Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y., et al. (2014). High secondary aerosol contribution to particulate pollution during haze events in China. *Nature*, 514(7521), 218–222.
- Ianniello, A., Spataro, F., Esposito, G., Allegrini, I., Hu, M., & Zhu, T. (2011). Chemical characteristics of inorganic ammonium salts in $\text{PM}_{2.5}$ in the atmosphere of Beijing (China). *Atmospheric Chemistry and Physics*, 11(21), 10803–10822.
- Kang, C. H., Kim, W. H., Ko, H. J., & Hong, S. B. (2009). Asian dust effects on total suspended particulate (TSP) compositions at Gosan in Jeju Island, Korea. *Atmospheric Research*, 94(2), 345–355.
- Liu, G. S., Hong, Y. T., Piao, C. H., & Zeng, Y. Q. (1996). Study on sources of sulfur in atmospheric particulate matter with stable isotope method. *China Environmental Science*, 16(6), 426–429.
- Li, H. H. (2007). *Particulate matter pollution characteristics of east area of Chengdu City*. Master dissertation, China: Chengdu University of Technology (in Chinese).
- Li, J., Wang, G., Zhou, B., Cheng, C., Cao, J., Shen, Z., et al. (2011). Chemical composition and size distribution of wintertime aerosols in the atmosphere of Mt. Hua in central China. *Atmospheric Environment*, 45(6), 1251–1258.
- Li, W. F., Bai, Z. P., Liu, A. X., Chen, J., & Chen, L. (2009). Characteristics of major $\text{PM}_{2.5}$ components during winter in Tianjin, China. *Aerosol and Air Quality Research*, 9(1), 105–119.
- Li, X. D., Masuda, H., Kusakabe, M., Yanagisawa, F., & Zeng, H. A. (2006). Degradation of groundwater quality due to anthropogenic sulfur and nitrogen contamination in the Sichuan Basin, China. *Geochemical Journal*, 40(4), 309–332.
- López-Veneroni, D. (2009). The stable carbon isotope composition of $\text{PM}_{2.5}$ and PM_{10} in Mexico City Metropolitan Area air. *Atmospheric Environment*, 43(29), 4491–4502.
- Mast, M. A., Turk, J. T., Ingersoll, G. P., Clow, D. W., & Kester, C. L. (2001). Use of stable sulfur isotopes to identify sources of sulfate in Rocky Mountain snowpacks. *Atmospheric Environment*, 35(19), 3303–3313.
- Mukai, H., Tanaka, A., Fujii, T., Zeng, Y., Hong, Y., Tang, J., et al. (2001). Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. *Environmental Science & Technology*, 35(6), 1064–1071.
- Osborne, J. M., & Lambert, F. H. (2014). The missing aerosol response in twentieth-century mid-latitude precipitation observations. *Nature Climate Change*, 4(5), 374–378.
- Perrone, M. G., Gualtieri, M., Consonni, V., Ferrero, L., Sangiorgi, G., Longhin, E., et al. (2013). Particle size, chemical composition, seasons of the year and urban, rural or remote site origins as determinants of biological effects of particulate matter on pulmonary cells. *Environmental Pollution*, 176, 215–227.
- Safai, P. D., Budhavant, K. B., Rao, P. S. P., Ali, K., & Sinha, A. (2010). Source characterization for aerosol constituents and changing roles of calcium and ammonium aerosols in the neutralization of aerosol acidity at a semi-urban site in SW India. *Atmospheric Research*, 98(1), 78–88.
- Sharma, S. K., Mandal, T. K., Saxena, M., Sharma, A., Datta, A., & Saud, T. (2014). Variation of OC, EC, WSIC and trace metals of PM_{10} in Delhi, India. *Journal of Atmospheric and Solar-Terrestrial Physics*, 113, 10–22.
- Srivastava, A., Gupta, S., & Jain, V. K. (2009). Winter-time size distribution and source apportionment of total suspended particulate matter and associated metals in Delhi. *Atmospheric Research*, 92(1), 88–99.
- Tao, J., Zhang, L., Engling, G., Zhang, R., Yang, Y., Cao, J., et al. (2013). Chemical composition of $\text{PM}_{2.5}$ in an urban environment in Chengdu, China: Importance of springtime dust storms and biomass burning. *Atmospheric Research*, 122, 270–283.
- Wang, G., Zhang, R., Gomez, M. E., Yang, L., Zamora, M. L., Hu, M., et al. (2016). Persistent sulfate formation from London Fog to Chinese haze. *Proceedings of the National Academy of Sciences of the United States of America*, 113(48), 13630–13635.
- Wang, Q., Cao, J., Shen, Z., Tao, J., Xiao, S., Luo, L., et al. (2013). Chemical characteristics of $\text{PM}_{2.5}$ during dust storms and air pollution events in Chengdu, China. *Particology*, 11(1), 70–77.
- Wang, Y., Che, H., Ma, J., Wang, Q., Shi, G., Chen, H., et al. (2009). Aerosol radiative forcing under clear, hazy, foggy, and dusty weather conditions over Beijing, China. *Geophysical Research Letters*, 36(6), L06804.
- Wang, Y., Zhuang, G., Tang, A., Yuan, H., Sun, Y., Chen, S., et al. (2005). The ion chemistry and the source of $\text{PM}_{2.5}$ aerosol in Beijing. *Atmospheric Environment*, 39(21), 3771–3784.
- Wang, Y., Zhuang, G., Zhang, X., Huang, K., Xu, C., Tang, A., et al. (2006). The ion chemistry, seasonal cycle, and sources of $\text{PM}_{2.5}$ and TSP aerosol in Shanghai. *Atmospheric Environment*, 40(16), 2935–2952.
- Winterholler, B., Hoppe, P., Huth, J., Foley, S., & Andreae, M. O. (2008). Sulfur isotope analyses of individual aerosol particles in the urban aerosol at a central European site (Mainz, Germany). *Atmospheric Chemistry and Physics Discussions*, 8(3), 9347–9404.
- Wu, L. J. (2010). Sulfur distribution and source apportionment of atmospheric particles and precipitation in Chengdu. *Master thesis of Chengdu University of Technology*, pp. 39–42.
- Wu, Q. X., & Han, G. L. (2012). Isotopic composition and isotope tracing of sulfur in atmospheric precipitation at the Head Area of the Three Gorges Reservoir, China. *Environmental Science (Chinese)*, 33(7), 2145–2150.

- Wu, Q. X., & Han, G. L. (2015). Sulfur isotope and chemical composition of the rain-water at the Three Gorges Reservoir. *Atmospheric Research*, 155, 130–140.
- Xiao, H. Y., & Liu, C. Q. (2004). Chemical characteristics of water-soluble components in TSP over Guiyang, SW China, 2003. *Atmospheric Environment*, 38(37), 6297–6306.
- Xiao, H. Y., Tang, C. G., Zhu, R. G., Wang, Y. L., Xiao, H. W., & Liu, C. Q. (2011). Tracing sources of coal combustion using stable sulfur isotope ratios in epilithic mosses and coals from China. *Journal of Environmental Monitoring*, 13(8), 2243–2249.
- Yao, X., Chan, C. K., Fang, M., Cadle, S., Chan, T., Mulawa, P., et al. (2002). The water-soluble ionic composition of PM_{2.5} in Shanghai and Beijing, China. *Atmospheric Environment*, 36(26), 4223–4234.
- Yang, Z., Li, X. D., Deng, J., & Wang, H. Y. (2015). Stable sulfur isotope ratios and water-soluble inorganic compositions of PM₁₀ in Yichang city, central China. *Environmental Science Pollution Research*, 22, 13564–13572.
- Zhang, T., Cao, J. J., Tie, X. X., Shen, Z. X., Liu, S. X., Ding, H., et al. (2011). Water-soluble ions in atmospheric aerosols measured in Xi'an, China: Seasonal variations and sources. *Atmospheric Research*, 102(1–2), 110–119.