

Chemical Composition of PM_{2.5} at an Urban Site of Chengdu in Southwestern China

TAO Jun¹ (陶俊), CHENG Tiantao*² (成天涛), ZHANG Renjian³ (张仁健),
CAO Junji⁴ (曹军骥), ZHU Lihua¹ (朱李华), WANG Qiyuan⁴ (王启元),
LUO Lei⁵ (罗磊), and ZHANG Leiming^{3,6} (张雷鸣)

¹South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou 510655

²Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention,

Department of Environment Science and Engineering, Fudan University, Shanghai 200433

³Key Laboratory of Regional Climate-Environment Research for Temperate East Asia,
Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029

⁴Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075

⁵Institute of Plateau Meteorology, China Meteorological Administration, Chengdu 610071

⁶Air Quality Research Division, Science and Technology Branch, Environment Canada, Toronto, Canada

(Received 30 July 2012; revised 22 September 2012; accepted 8 October 2012)

ABSTRACT

PM_{2.5} aerosols were sampled in urban Chengdu from April 2009 to January 2010, and their chemical compositions were characterized in detail for elements, water soluble inorganic ions, and carbonaceous matter. The annual average of PM_{2.5} was 165 $\mu\text{g m}^{-3}$, which is generally higher than measurements in other Chinese cities, suggesting serious particulate pollution issues in the city. Water soluble ions contributed 43.5% to the annual total PM_{2.5} mass, carbonaceous aerosols including elemental carbon and organic carbon contributed 32.0%, and trace elements contributed 13.8%. Distinct daily and seasonal variations were observed in the mass concentrations of PM_{2.5} and its components, reflecting the seasonal variations of different anthropogenic and natural sources. Weakly acidic to neutral particles were found for PM_{2.5}. Major sources of PM_{2.5} identified from source apportionment analysis included coal combustion, traffic exhaust, biomass burning, soil dust, and construction dust emissions. The low nitrate: sulfate ratio suggested that stationary emissions were more important than vehicle emissions. The reconstructed masses of ammonium sulfate, ammonium nitrate, particulate carbonaceous matter, and fine soil accounted for 79% of the total measured PM_{2.5} mass; they also accounted for 92% of the total measured particle scattering.

Key words: water soluble ions, carbonaceous matters, trace elements, enrichment factor, source apportionment, mass closure

Citation: Tao, J., T. T. Cheng, R. J. Zhang, J. J. Cao, L. H. Zhu, Q. Y. Wang, L. Luo, and L. M. Zhang, 2013: Chemical composition of PM_{2.5} at an urban site of Chengdu in southwestern China. *Adv. Atmos. Sci.*, **30**(4), 1070–1084, doi: 10.1007/s00376-012-2168-7.

1. Introduction

Atmospheric aerosols perturb Earth's radiation balance (Charlson et al., 1992) and play important roles in climate system (Ramanathan et al., 2001;

Rosenfeld, 2006). Aerosol effect remains one of the greatest sources of uncertainty in assessing global climate change (IPCC, 2007). Aerosol particles usually cause visibility reduction and surface incident solar radiation decline through scattering and absorbing light

*Corresponding author: CHENG Tiantao, ttcheng@fudan.edu.cn

(Dzubay et al., 1982), which could result in global and regional dimming or brightening (Wild et al., 2005; Wang et al., 2009). In addition, fine particle matter (PM_{2.5}, particles with diameters <2.5 μm) near the surface has strong and consistent correlations with adverse health effects (Pope III et al., 2002). Knowledge of chemical composition of PM_{2.5} is crucial for fully understanding and assessing its impacts on climate, air quality, and human health. Many studies have been conducted worldwide to characterize chemical properties of PM_{2.5} (Chow et al., 1996; Wittig et al., 2004; Qin et al., 2006; Haglera et al., 2007; Kim et al., 2007; Bahadur et al., 2009). Over the past several decades, China has experienced rapid economic growth and dense urbanization, which has led to a general decline in air quality due to heavy particulate pollution as a result of human activities (Wang et al., 2001; Che et al., 2009; Tie and Cao, 2009). The most obvious evidence is the increase of low-visibility weather days (Che et al., 2007). Much attention has been given to particulate pollutions (e.g., haze) in several developed regions of China, such as the Yangtze River Delta (Fu et al., 2008; Du et al., 2011), the Pearl River Delta (Cao et al., 2003; Cheng et al., 2008; Deng et al., 2008), and the Beijing-Tianjin-Tangshan region (Sun et al., 2006; Hu et al., 2008). The in situ measurements of PM_{2.5} chemistry have been primarily conducted in several megacities, including Beijing, Guangzhou, Chongqing, Wuhan, Shanghai and Xi'an, and a few rural sites (Wei et al., 1999; Cao et al., 2005; Duan et al., 2006; Chan and Yao, 2008; Shen et al., 2009; Shen et al., 2010). These studies investigated soil dust, carbonaceous species, water-soluble ions, mixing, aerosol acidity, and aerosol hygroscopicity (He et al., 2001; Ye et al., 2003; Zhang et al., 2003a, b; Wang et al., 2005, 2006; Cao et al., 2007; Eichler et al., 2008). However, similar studies are scarce in southwestern China.

Chengdu is one of the most crowded megacities in China and in the world, having a population of more than 13 million. Topographically, Chengdu is located in the west part of the Sichuan Basin, surrounded by the Longquan Mountains on the east and the Qionglai Mountains on the west. It is thus a well-known city suffering serious air pollution because of unfavorable atmospheric diffusion conditions, relatively high humidity, and a large population. Industrial factories are concentrated in the northern suburbs of the city, ~20 km away from downtown. The number of vehicles reached 2.0 million in 2011, resulting in a large quantity of vehicular emissions. In recent years, the dramatic increase of energy consumption and thus pollutant emissions has exacerbated the air pollution problems of this inland city (Chang et al., 2009).

In this paper, we present the chemical analyses of PM_{2.5} samples collected at an urban site of Chengdu. In this study, we aimed to understand the pollution level, especially the PM_{2.5} level and its seasonal variations in this city, and to characterize the chemical composition and associated potential sources of PM_{2.5}.

2. Measurements and methodology

2.1 Observation site and data

PM_{2.5} concentrations, the aerosol scattering coefficient, and meteorological variables were measured continuously on the roof of one building ~15 m above the ground within the Institute of Plateau Meteorology (IPM) (30°39'N, 104°00'E) of the China Meteorological Administration (CMA) from April 2009 to January 2010. The site is located in an urban district of Chengdu (Fig. 1). Synchronously, SO₂ and NO₂ were measured at the Caotang environment monitoring station of Chengdu, ~1.4 km southeast of the IPM. Local LST was used in this study and was eight h ahead of UTC.

2.2 Aerosol sampling and chemical analysis

PM_{2.5} particles were sampled for 24 h using tactical air samplers (Model MiniVOI, Air Metrics Co.) with 47-mm Teflon (Whatman PTFE) and Quartz (Whatman QM-A) filters at a calibrated airflow rate, respectively. A total of 242 samples were collected at the IPM from 19 April to 17 May (representative of spring, MAM), 6 July to 6 August (summer, JJA), 26 October to 26 November (autumn, SON) in 2009 and 1 to 31 January (winter, DJF) in 2010. In addition, ~10 blank samples were collected and used for subtracting the positive artifact caused by filters. The operation of weighting and element analyzing has been described



Fig. 1. Location of Chengdu in southwestern China.

in detail by Xu et al. (2012). Overall, 29 elements such as sodium (Na), magnesium (Mg), aluminium (Al), silica (Si), phosphor (P), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), zinc (Zn), iron (Fe), lead (Pb), manganese (Mn), Molybdenum (Mo), copper (Cu), vanadium (V), arsenic (As), tin (Sn), bromide (Br), rubidium (Rb), nickel (Ni), selenium (Se), antimony (Sb), barium (Ba), chromium (Cr), chromium (Cd), cobalt (Co), and strontium (Sr) in PM_{2.5} samples were detected using X-ray fluorescence analysis (XRF, Epsilon5, PANalytical Company, Netherlands).

One-quarter of each sample was quartz filtered to determine water-soluble ion mass concentrations. Four anions (SO₄²⁻, NO₃⁻, Cl⁻, and F⁻) and five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) in aqueous extracts were detected using ion chromatography (IC, Dionex 600, Dionex Corp, CA), as described in Tao et al. (2012). The detection limits (DL) of Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, NO₃⁻, and SO₄²⁻ were 0.0203, 0.0041, 0.0045, 0.0032, 0.0049, 0.0381, 0.0352, 0.1037 and 0.1094 μg m⁻³, respectively. Standard Reference Materials (SRMs) obtained from the National Research Center for Certified Reference Materials, China, were analyzed for quality assurance purposes. Procedural blank values were subtracted from sample concentrations.

A 0.5-cm² punch from each quartz filter was analyzed for carbonaceous matter, based on the IMPROVE (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol using a DRI model 2001 carbon analyzer (Atmoslytic Inc., Calabasas, CA) (Chow et al., 2007). Intercomparison of the IMPROVE_TOR with the TMO (thermal manganese dioxide oxidation) has shown a difference of <5% for total carbon (TC) and <10% for organic carbon (OC) and elemental carbon (EC) (Chow et al., 1996; Cao et al., 2003). Four OC fractions (OC1, OC2, OC3, and OC4), an OP (pyrolyzed carbon) fraction, and three EC fractions (EC1, EC2, and EC3) were determined (Tao et al., 2009). The average mass in the field blanks were 1.85 μg m⁻³ and 0.53 μg m⁻³ for OC and EC, respectively.

2.3 Reconstruction of PM_{2.5} and Extinction

According to the IMPROVE method for calculating aerosol components and light extinction (Hand and Malm, 2006), we reconstructed PM_{2.5} and aerosol scattering coefficient using daily averages of aerosol species concentrations. PM_{2.5} concentration can be calculated using the following equation:

$$[\text{PM}_{2.5}] = [\text{AS}] + [\text{AN}] + [\text{POM}] + [\text{LAC}] + [\text{Soil}], \quad (1)$$

where [AS] is ammonium sulfate ([AS]=1.375[SO₄²⁻]), [AN] is ammonium nitrate ([AN]=1.29[NO₃⁻]), [POM] is particulate organic matter ([POM]=1.8[OC]), [LAC] is light absorbing carbon referred to as [EC], and [Soil] is soil concentration ([Soil]=2.2[Al]+2.49[Si]+1.63[Ca]+2.42[Fe]+1.94[Ti]). Assuming fine soil particles entirely scatter solar radiation, aerosol scattering (b_{sca}) coefficient of PM_{2.5} particles can be calculated using the following equation:

$$b_{\text{sca}} = 2.2 \times f_{\text{S}}(\text{RH}) \times [\text{SS}] + 4.8 \times f_{\text{L}}(\text{RH}) \times [\text{LS}] + 2.4 \times f_{\text{S}}(\text{RH}) \times [\text{SN}] + 5.1 \times f_{\text{L}}(\text{RH}) \times [\text{LN}] + 2.8 \times [\text{SOM}] + 6.1 \times [\text{LOM}] + 1.0 \times [\text{Soil}]. \quad (2)$$

where RH (relative humidity) growth curves of f_{S} and f_{L} of sulfate and nitrate can be referred to Pitchford et al. (2007). [SS] is small sulfate, [LS] is large sulfate, [SN] is small nitrate, [LN] is large nitrate, [SOM] is small organic mass, and [LOM] is large organic mass.

The calculated PM_{2.5} was closely correlated with the measured PM_{2.5} (Fig. 2); high linear correlation

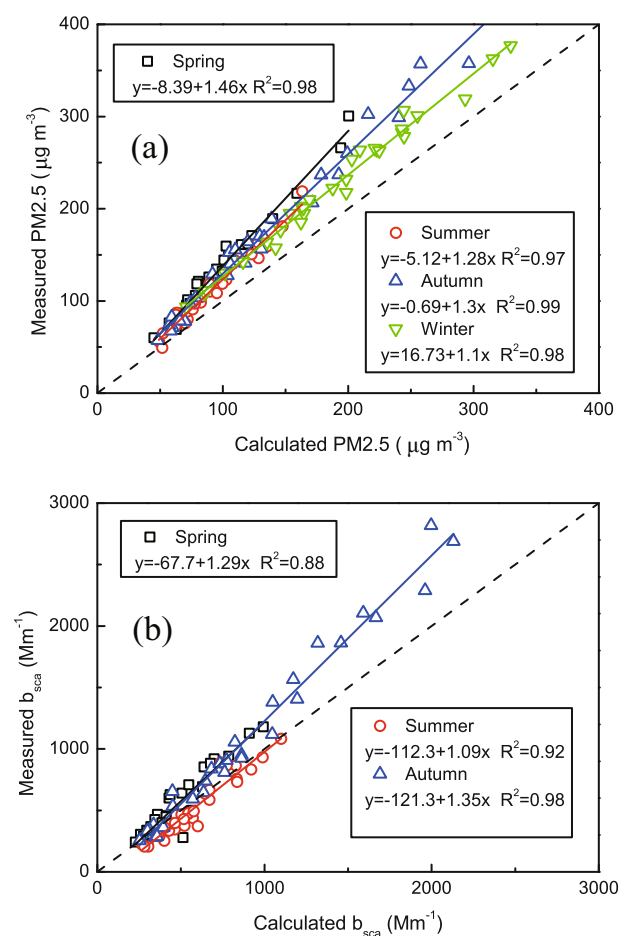


Fig. 2. Scatterplots of measured and calculated PM_{2.5} concentrations and scattering (b_{sca}) coefficients.

coefficients exceeded 0.97 for the four seasons. The differences were $\sim 16\%$ – 26% of the measured $PM_{2.5}$ and were from unidentified mass in $PM_{2.5}$ (hereafter referred to ‘remainders’), which consisted of water content and nonsoluble species (Hand and Malm, 2006). Similar to $PM_{2.5}$, the calculated b_{sca} was also highly correlated to the measured b_{sca} , with correlation coefficients exceeding 0.88 (Fig. 2). The bias between the calculated and the measured b_{sca} accounted for 7%–18% of the measured b_{sca} due to the impacts of remainders fraction in $PM_{2.5}$ on light scattering. This result indicates that POM, EC, water-soluble ions, and fine soil are major contributors of $PM_{2.5}$ in Chengdu. Furthermore, the IMPROVE equations are somewhat suitable for estimating $PM_{2.5}$ and b_{sca} using these chemical species.

3. Results and discussion

3.1 Overview of $PM_{2.5}$ Concentrations

Seasonal variations of $PM_{2.5}$ concentrations were distinct. On average, $PM_{2.5}$ was $\sim 133 \mu\text{g m}^{-3}$ in spring, $114 \mu\text{g m}^{-3}$ in summer, $188 \mu\text{g m}^{-3}$ in autumn, and $225 \mu\text{g m}^{-3}$ in winter. The highest $PM_{2.5}$ level in winter was most likely due to a combination of the relatively elevated emissions from fossil fuel (e.g., coal) combustion and biomass burning for heating, as well as stagnant meteorological conditions, such as low mixing or inversion layer, which limited the dilution and dispersion of pollutants. The lowest level in summer was attributed to the wet removal of aerosol particles by rain (Fig. 3 and Fig. 4). The climatic rainfall data show that JJA had the largest precipitation amount and DJF had the smallest precipitation amount. The annual mean $PM_{2.5}$ in Chengdu ($165 \mu\text{g m}^{-3}$) exceeded 10 times the US National Ambient Air Quality Standards (NAAQS; $15 \mu\text{g m}^{-3}$; US EPA, 2006). The annual value in Chengdu was also in the high end when

compared with measurements at other Chinese urban sites: $156 \mu\text{g m}^{-3}$ in Guangzhou, $127 \mu\text{g m}^{-3}$ in Beijing, $133 \mu\text{g m}^{-3}$ in Shanghai, $140 \mu\text{g m}^{-3}$ in Qingdao, $86 \mu\text{g m}^{-3}$ in Xiamen, and $130 \mu\text{g m}^{-3}$ in Chongqing (Wang et al., 2006; Cao et al., 2007; Andreae et al., 2008; Zhao et al., 2010; Zhang et al., 2012). Air pollution in this city is a serious issue.

Figure 3 shows the daily $PM_{2.5}$ and atmospheric visibility observed in the four seasons. The daily $PM_{2.5}$ exceeded the US 24-h $PM_{2.5}$ standard of $35 \mu\text{g m}^{-3}$ (US EPA, 2006) by 1.4 to 12.1 times on any given day. Overall, 74% of the measurement days exceeded $100 \mu\text{g m}^{-3}$, and 47% exceeded $150 \mu\text{g m}^{-3}$. These numbers suggest that particulate pollution, especially the fine particle pollution, is very serious in Chengdu. The daily $PM_{2.5}$ was highest during 6–10 November 2009 ($364 \mu\text{g m}^{-3}$), and the second highest during 16–19 January 2010 ($340 \mu\text{g m}^{-3}$); the visibility was also low ($<5 \text{ km}$) during these periods. Not surprisingly, high $PM_{2.5}$ generally matched with low atmospheric visibility, low wind speed, and high NO_2 and SO_2 levels, regardless of the level of relative humidity (Fig. 4). This synchronization revealed that $PM_{2.5}$ loading was closely linked with gaseous precursors emitted from human activities and local meteorological conditions.

3.2 Chemical Elements of $PM_{2.5}$ Particles

Enrichment factor (EF) is often used to compare chemical elements in aerosol particles with those in reference materials for qualitatively identifying their potential natural and/or anthropogenic sources (Taylor and McLennan, 1995). The EFs of $PM_{2.5}$ particles can be calculated as follows:

$$EF = \frac{(C_{ele}/C_{ref})_{aer}}{(C_{ele}/C_{ref})_{cru}}, \quad (3)$$

where C_{ele} and C_{ref} are the concentrations of focused

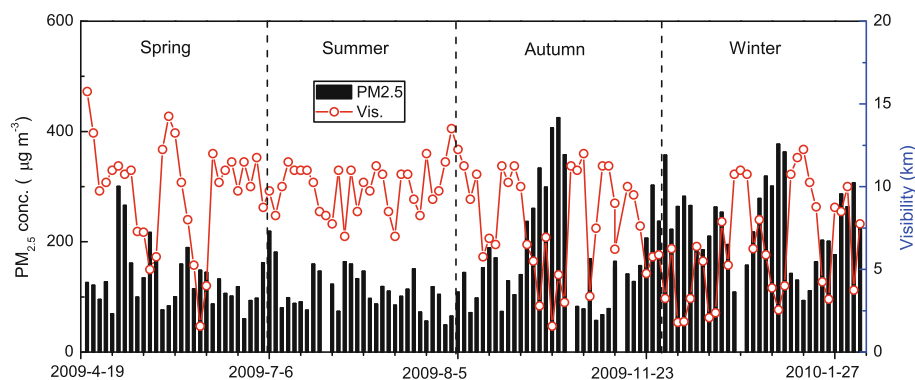


Fig. 3. Temporal variations of $PM_{2.5}$ concentrations and atmospheric visibility in spring, summer, autumn and winter.

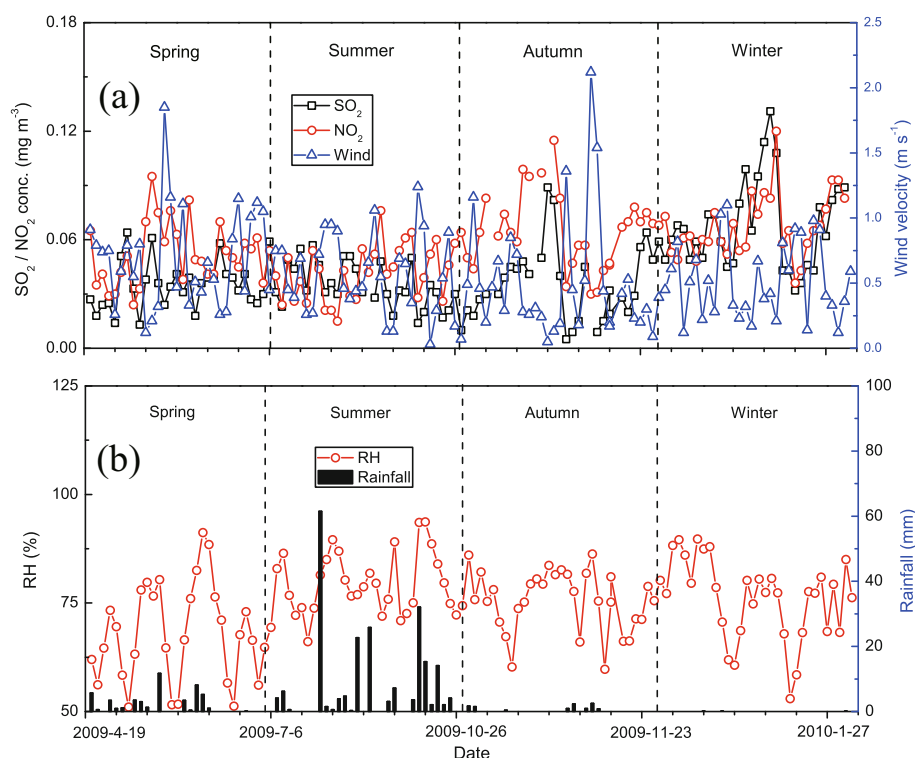


Fig. 4. Temporal variations of trace gases and meteorological factors in spring, summer, autumn and winter.

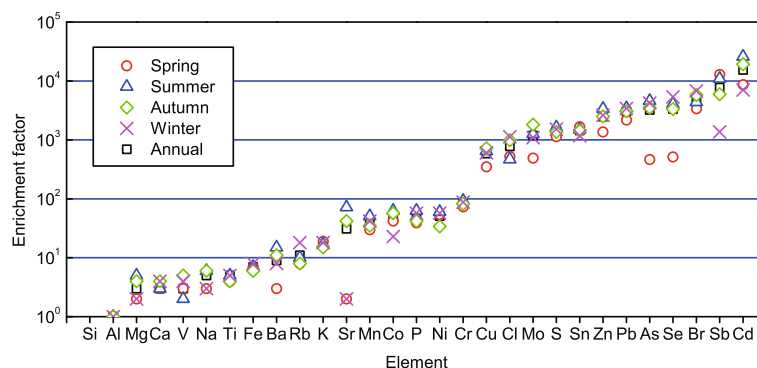


Fig. 5. Enrichment factors of particle chemical elements.

and reference elements, the subscript “aer” refers to aerosol, while “cru” refers to crust. In this study, Al was used as the reference element, and the crustal element concentrations were derived from the measurements of Wedepohl (1995).

The EFs of Si, Al, Mg, Ca, V, Na, Ti, Fe and Ba were <10 (Fig. 5), indicating that their major sources were undoubtedly dominated by crustal material (e.g., soil) (Zhang et al., 2010). The EFs of Cu, Cl, Mo, S, Sn, Zn, Pb, As, Se, Br, Cd, and Sb were >>600 (Fig. 5), indicating that these elements were emitted from anthropogenic sources and are mainly influenced by human activities (Zhang et al., 2010). The rest of

the elements (Rb, K, Sr, Mn, Co, P, Ni and Cr) had EFs in the range 10–100 (Fig. 5), implying that they were from both natural and anthropogenic sources. Compared with other elements, As, Se, Br, Ba, and Sr showed distinct seasonal variations in EF; in some cases this variation was >10 fold. This was especially the case for Sr, which had an EF value of 2 in spring and winter, 42 in autumn, and 72 in summer. The large seasonal variation in EF means that various or unstable sources affected the element emissions and caused a high variability in its atmospheric loading.

Annual average concentrations were >1.0 $\mu\text{g m}^{-3}$ for S, Cl, K, Fe, Si, Al, and >0.3 $\mu\text{g m}^{-3}$ for Ca, Zn,

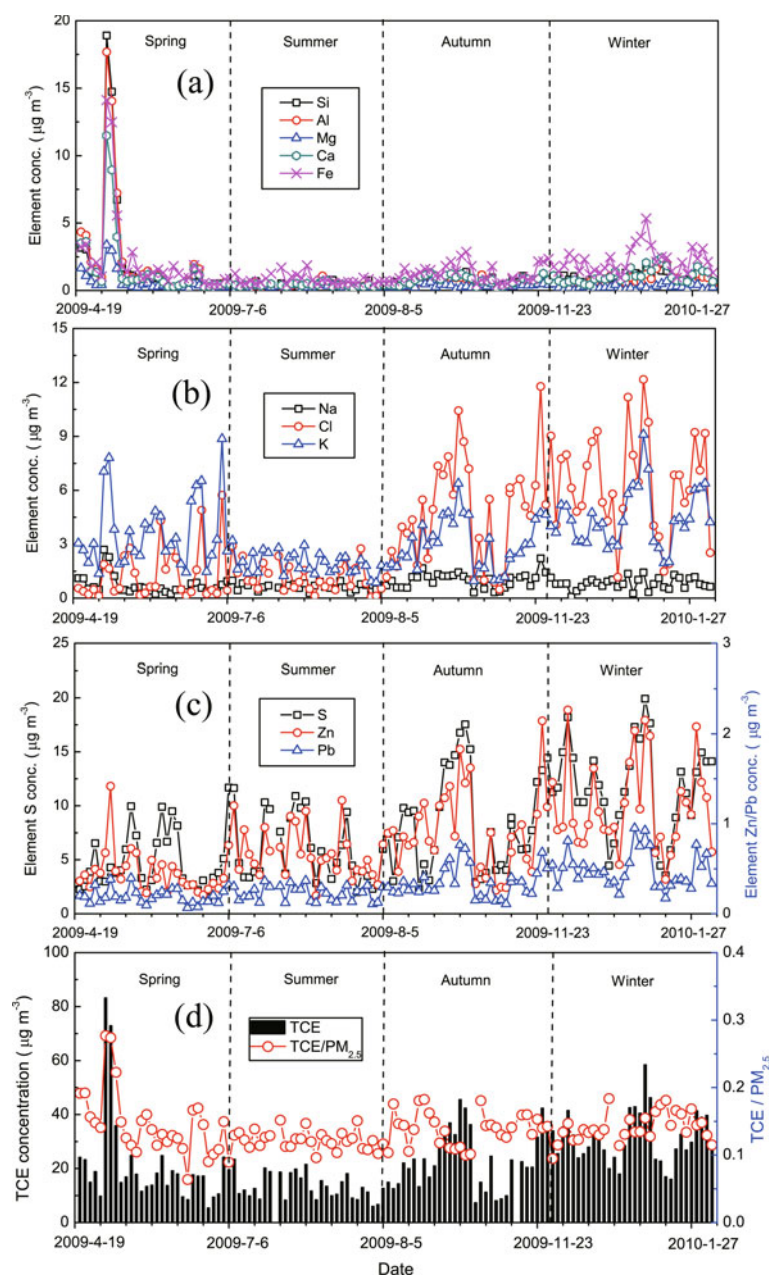


Fig. 6. Temporal variations of major chemical elements, total chemical elements (TCE) and their fractions in $PM_{2.5}$ particles.

Na, Mg, Pb, indicating that these elements were abundant in $PM_{2.5}$. Most crustal elements (e.g., Si, Fe, Al, Ca) followed the seasonal pattern of spring > winter > autumn > summer, and main pollution elements (e.g., S, Pb, Zn, Se, Cl) followed the pattern of winter > autumn > summer > spring (Fig. 6). *K* was associated with particles emitted from coal combustion and biomass burning and had a seasonal pattern of winter > spring > autumn > summer. Known human or animal carcinogens (e.g., As, Cd, Cl, Co, Cr, Mn, Ni, P, Pb, Sb and Se) are among the 188 hazardous air

pollutants (HAPs) identified by the US Environmental Protection Agency (EPA) in 1990. The concentrations of As, Cd, Co, Mn, and Pb ($3\text{--}319\text{ ng m}^{-3}$) in Chengdu in this study were higher than those in Shanghai (Chen et al., 2008) and Tokyo (Furuta et al., 2005), indicating serious metallic pollution of airborne particles in this city.

Figure 6 shows the temporal variations of major aerosol chemical elements, the sum of total chemical elements (TCE), and their fractions in $PM_{2.5}$ concentrations. The mean TCE was $21\text{ }\mu\text{g m}^{-3}$ in spring

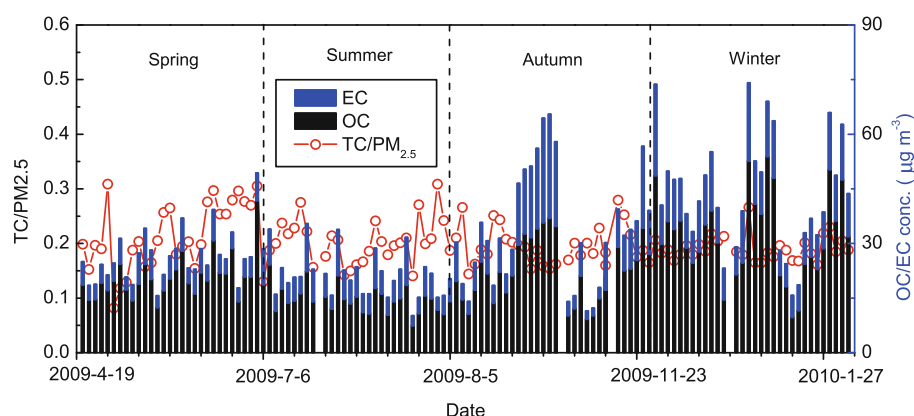


Fig. 7. Temporal variations of elemental carbon (EC), organic carbon (OC), total carbon (TC=EC+OC) fractions in PM_{2.5} particles.

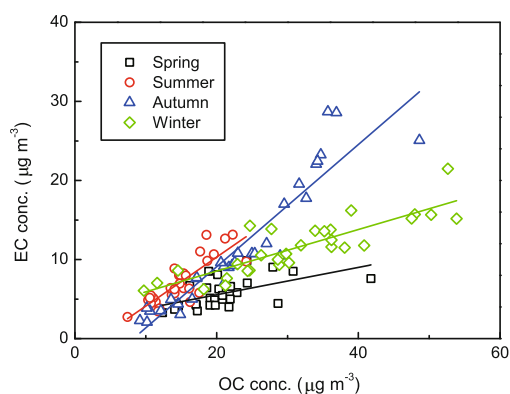


Fig. 8. Scatterplots of elemental carbon (EC) vs. organic carbon (OC) and their linear relationships in the four seasons.

(i.e., 15.8% of PM_{2.5} mass), 13.7 $\mu\text{g m}^{-3}$ in summer (i.e., 12% of PM_{2.5} mass), 23.7 $\mu\text{g m}^{-3}$ in autumn (i.e., 12.6% of PM_{2.5} mass), and 31.3 $\mu\text{g m}^{-3}$ in winter (i.e., 14.9% of PM_{2.5} mass). The maximum TCE appeared during 24–26 April 2009 (64 $\mu\text{g m}^{-3}$) and contributed 25.8% of the total PM_{2.5} (243 $\mu\text{g m}^{-3}$). During the same period, Si, Al, Fe, Ca concentrations were also the highest with 8–14 $\mu\text{g m}^{-3}$. The most likely explanation is a dust storm sweeping over Chengdu, during which event a large amount of dust particles transported from northwestern China caused high PM_{2.5} and crustal elements (Zhao et al., 2010). Compared with crustal elements, Cl, Zn, and Pb, S elements mainly emitted from anthropogenic pollution were notably higher in autumn and winter than in spring and summer, implying potential impacts of coal combustion and household energy consumption on aerosol loadings in these seasons at low temperatures.

3.3 Carbonaceous mass of PM_{2.5} particles

Figure 7 presents the temporal variations of EC and OC, and the ratio of TC (TC=EC+OC) to PM_{2.5}.

The mean EC and OC were 5.7 and 20.7 $\mu\text{g m}^{-3}$, respectively, in spring, 7 and 15 $\mu\text{g m}^{-3}$ in summer, 11.7 and 23.3 $\mu\text{g m}^{-3}$ in autumn, and 11.6 and 31.5 $\mu\text{g m}^{-3}$ in winter. Compared with other measurements, the annual mean EC (9 $\mu\text{g m}^{-3}$) in Chengdu was higher than in Beijing (7 $\mu\text{g m}^{-3}$) and Shanghai (8 $\mu\text{g m}^{-3}$), but lower than in Guangzhou (14 $\mu\text{g m}^{-3}$). The annual mean OC (22.3 $\mu\text{g m}^{-3}$) was lower than that in Beijing (27 $\mu\text{g m}^{-3}$), Shanghai (29 $\mu\text{g m}^{-3}$), Guangzhou (41 $\mu\text{g m}^{-3}$), and Chongqing (31 $\mu\text{g m}^{-3}$) (Cao et al., 2007; Andreae et al., 2008; Zhao et al., 2010). The daily EC and OC concentrations were commonly higher in winter and autumn than in spring and summer, with the maximum OC (54 $\mu\text{g m}^{-3}$) on 18 January 2010 and the maximum EC (29 $\mu\text{g m}^{-3}$) on 8 and 9 November 2009. The daily TC: PM_{2.5} ratio ranged from 8% to 31%, but the seasonal averaged ratio narrowly changed (19%–22%). The annual average of the total carbonaceous aerosols (TCA=POM+EC) was 49.7 $\mu\text{g m}^{-3}$, which roughly contributed to 32.0% of PM_{2.5}, indicating that carbonaceous aerosol was one of the major components of urban aerosol fine particles.

An OC: EC ratio provides a valuable tool to indicate the sources and formation for the carbonaceous particles (Cao et al., 2003). In Chengdu, the OC: EC ratio ranged from 1.2 to 6.4, with seasonal averages of 3.8 in spring, 2.2 in summer, 2.5 in autumn and 2.7 in winter. These values were comparable to measurements (2.7–3.6) in Guangzhou (Cao et al., 2003; Andreae et al., 2008). The maximum OC: EC ratios appeared during 12 May (OC: EC = 5.4) and 13 May 2009 (OC: EC = 6.4). Good correlations between EC and OC in autumn ($R^2=0.87$) and winter ($R^2=0.72$) were found (Fig. 8), indicating that OC and EC were possibly emitted from the same sources such as coal combustion. The poor linear correlation ($R^2=0.32$) in spring revealed an evident difference of OC and EC

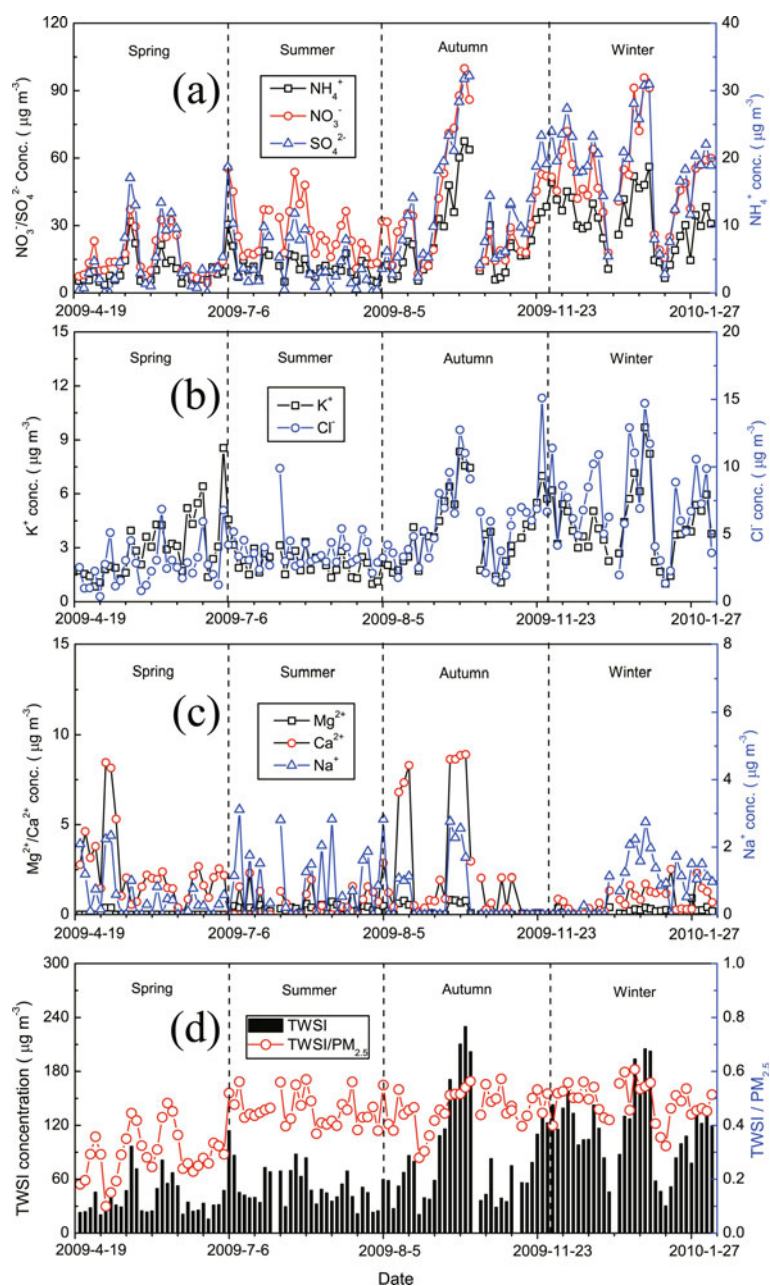


Fig. 9. Temporal variations of major water soluble ions, total water-soluble ions (TWSI) and their fractions in $\text{PM}_{2.5}$ particles.

sources in this season. For example, OC was mainly emitted from biomass burning and coal combustion, while EC was mainly emitted from coal combustion and vehicle. Vehicle emission was the most important contributor to EC loading in the summer ($R^2=0.69$). The slopes of fitted linear functions between EC and OC were 0.17 in spring, 0.62 in summer, 0.77 in autumn, and 0.26 in winter. These values suggest that EC increment depended on OC changes. In general, EC and primary OC are emitted directly from com-

bustion, while secondary OC is produced by gas-to-particle conversion or chemical reaction (Cao et al., 2005). The strong correlation between K^+ , SO_4^{2-} , and NO_3^- and between OC and EC also implies that biomass burning, coal combustion, and vehicle exhaust were major contributors to $\text{PM}_{2.5}$ carbon in Chengdu.

3.4 Water soluble ions of $\text{PM}_{2.5}$ particles

Seasonal averages of the sum of the total water soluble ions (TWSI) in $\text{PM}_{2.5}$ were $38.9 \mu\text{g m}^{-3}$ in spring,

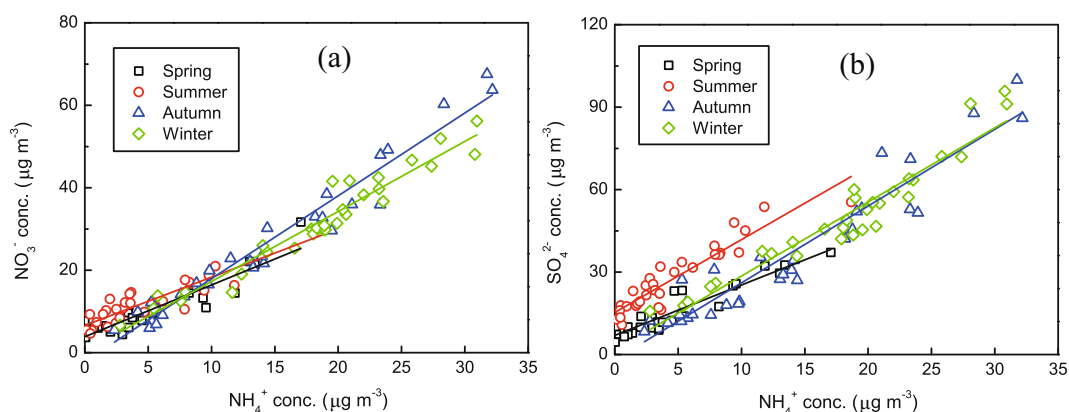


Fig. 10. Linear relationships of NH_4^+ vs. NO_3^- and NH_4^+ vs. SO_4^{2-} in the four seasons.

$52.9 \mu\text{g m}^{-3}$ in summer, $89.4 \mu\text{g m}^{-3}$ in autumn, and $113.7 \mu\text{g m}^{-3}$ in winter, accounting for 29%, 47%, 48% and 50% of PM_{2.5} mass, respectively. Apparently, the soluble ions were crucial portions of urban aerosol fine particles. The annual concentrations of the individual ions showed SO_4^{2-} ($33 \mu\text{g m}^{-3}$) > NO_3^- ($20 \mu\text{g m}^{-3}$) > NH_4^+ ($10.4 \mu\text{g m}^{-3}$) > Cl^- ($5 \mu\text{g m}^{-3}$) > K^+ ($3.4 \mu\text{g m}^{-3}$) > Ca^{2+} ($1.6 \mu\text{g m}^{-3}$) > Na^+ ($0.7 \mu\text{g m}^{-3}$) > F^- ($0.3 \mu\text{g m}^{-3}$) > Mg^{2+} ($0.2 \mu\text{g m}^{-3}$). SO_4^{2-} , NO_3^- , and NH_4^+ were the dominant ions in PM_{2.5}, and they also had the same seasonal pattern: winter > autumn > summer > spring. However, seasonal patterns of Cl^- , K^+ , Ca^{2+} , Na^+ and Mg^{2+} were different from each other, and they were also different from their corresponding individual elements (Fig. 9).

Figure 9 shows the temporal variations of water soluble (WS) ions, TWSI, and TWSI/PM_{2.5}. SO_4^{2-} and NO_3^- showed relatively higher variabilities (SD/AV) than other ions, especially in autumn (0.7) and winter (0.6). The highest seasonal variability appeared in spring for NH_4^+ , K^+ and Cl^- , in autumn for Na^+ (2.1), Ca^{2+} (1.3), and F^- (0.8), and also in spring for Mg^{2+} (3.7). The highest daily values appeared from 8 to 10 November 2009 and 16 to 19 January for SO_4^{2-} and NO_3^- , and from 4 to 10 November 2009 and 15 to 19 January 2010 for NH_4^+ , K^+ , and Cl^- . The seasonal ratio of TWSI/PM_{2.5} narrowly changed, especially from summer to autumn, and to winter.

Figure 10 shows the linear relationships of NH_4^+ vs. NO_3^- and NH_4^+ vs. SO_4^{2-} in the four seasons. NH_4^+ was strongly correlated with NO_3^- and SO_4^{2-} , having correlation coefficients exceeding 0.81 in all seasons. This indicates that ammonium was associated with both sulfate [as $(\text{NH}_4)_2\text{SO}_4$] and nitrate (as NH_4NO_3). K^+ was strongly correlated with Cl^- and SO_4^{2-} , having correlation coefficients of 0.70–0.87 in autumn and winter (Fig. 11), indicating that the possibility of the existence of K_2SO_4 and KCl . NH_4^+ and Cl^- were correlated in autumn (0.67), and K^+ and NO_3^- were cor-

related in autumn (0.84), summer (0.68) and winter (0.66) (Fig. 11), indicating that ammonium chloride and potassium nitrate were possible chemical components of PM_{2.5} in these periods.

Water soluble ions usually link with the formation, growth, aging, and surface chemical reactions of particles (Wang et al., 2006). Na^+ , Mg^{2+} , and Ca^{2+} are known to mainly originate from road and construction dust, SO_4^{2-} , NO_3^- , and NH_4^+ originate from secondary particles produced by the transformation of SO_2 , NO_2 , and NH_3 precursors, and K^+ and Cl^- are from biomass burning particles (Dibb et al., 1995; Dabell et al., 2004; Hsu et al., 2009). The high correlation coefficients between NH_4^+ and SO_4^{2-} , and between NH_4^+ and NO_3^- revealed that $(\text{NH}_4)_2\text{SO}_4$ and/or NH_4HSO_4 , and NH_4NO_3 were major sulfate and nitrate salts (Sun et al., 2006). Ammonia was believed to be neutralized first by sulfuric acid to form ammonium sulfate or ammonium bisulfate, and the excess NH_3 could react with nitric acid to form NH_4NO_3 and with hydrochloric acid to form NH_4Cl (McMurry et al., 1983; Yuan et al., 2003; Wang et al., 2005; Du et al., 2010). The scatterplots between ammonium versus sulfate in PM_{2.5} (Fig. 10) showed that NH_4^+ was almost neutralized by SO_4^{2-} , especially in autumn and winter, with higher correlation coefficients close to one and lower intercepts close to zero. However, in spring and summer, SO_4^{2-} seemed to exceed NH_4^+ and was likely neutralized by other actions in particles. The strong correlation between K^+ and Cl^- implies that K^+ was abundantly present in the form of KCl (Fig. 11), a phenomenon that was demonstrated in the haze pollution influenced by biomass burning emissions (Du et al., 2011).

Figure 12 shows the temporal variations of sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR), where available SOR and NOR were calculated using the equations $\text{SOR} = \text{SO}_4^{2-} / (\text{SO}_4^{2-} + \text{SO}_2)$ and $\text{NOR} = \text{NO}_3^- / (\text{NO}_3^- + \text{NO}_2)$ (Du et al., 2010). The

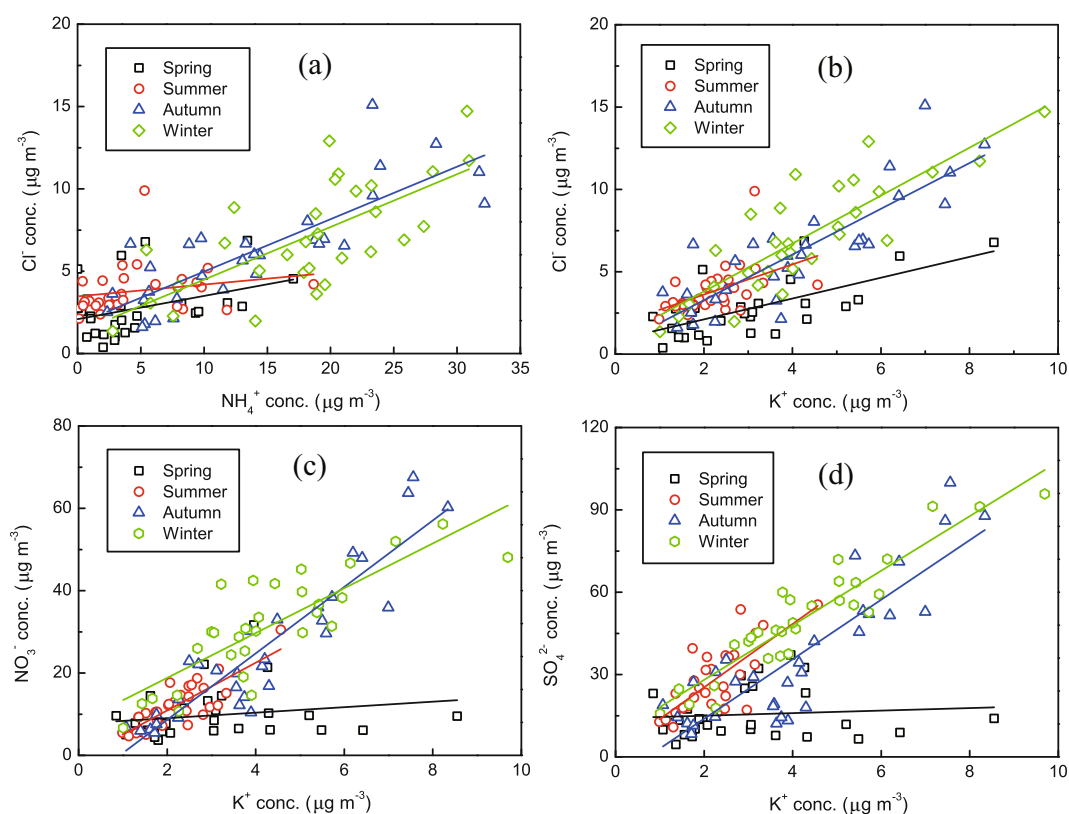


Fig. 11. Linear relationships of K^+ vs. Cl^- , NH_4^+ vs. Cl^- , and K^+ vs. NO_3^- and SO_4^{2-} in the four seasons.

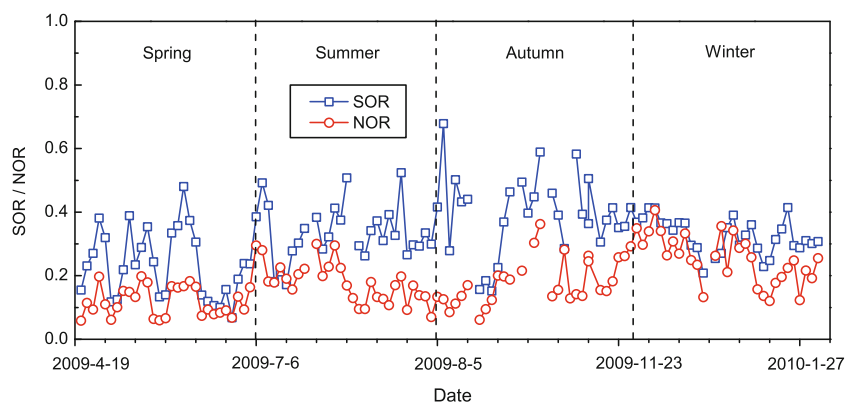


Fig. 12. Temporal variations of sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR).

average SOR and NOR values were 0.23–0.38 and 0.12–0.25, respectively, in the four seasons. Yao et al. (2002) reported that SOR was <0.1 under conditions of primary source emissions, while SOR was >0.1 when sulfate was mainly produced through the secondary transformation of SO_2 oxidation. Daily SORs were relatively higher in autumn and summer with a maximum (0.68) on 6 August 2009, and daily NORs were commonly higher in winter and autumn with a maximum

(0.41) on 3 January 2010. It is worth to point out that except precursor gases (i.e. SO_2 and NO_x), oxidants, cloud, surface area availability, temperature and RH also exerted some influences on these temporal variations of SOR and NOR (Du et al., 2010). Anyway, this result indicates that aerosol secondary transformation was responsible for a large quantity of secondary sulfate and nitrate particles in $PM_{2.5}$ in Chengdu.

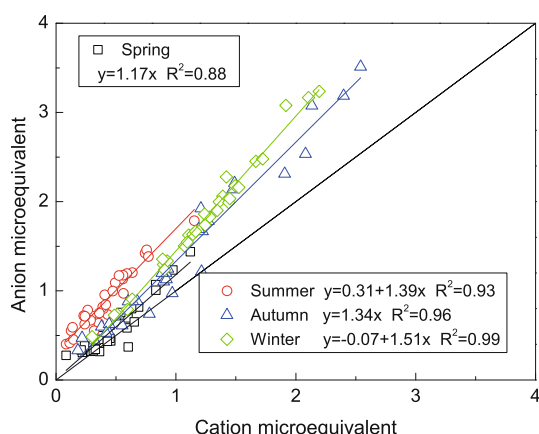


Fig. 13. Scatterplots between total cation microequivalent and total anion microequivalent and their linear relationships in the four seasons.

The mass ratio of NO_3^- : SO_4^{2-} has been used as a qualitative indicator to evaluate the relative importance of stationary and mobile sources for sulfur and nitrogen in the atmosphere (Arimoto et al., 1996). The seasonal average ratio of NO_3^- : SO_4^{2-} was 0.63 in spring, 0.44 in summer, 0.7 in autumn, and 0.62 in winter. These values are comparable to the values (0.4–0.7) measured in Shanghai and Nanjing (Yao et al., 2002). The low ratios in the present study suggest that stationary emissions were more important sources than vehicle emissions in Chengdu.

Ion balance is a common method used for evaluating the acid-base balance of aerosol particles. The cation:anion balance of PM_{2.5} was calculated using the ion mass concentrations in microequivalents using these formulas:

$$[\text{cation}] = \text{Na}^+/23 + \text{NH}_4^+/18 + \text{K}^+/39 + \text{Mg}^{2+}/12 + \text{Ca}^{2+}/20, \quad (4)$$

$$[\text{anion}] = \text{F}^-/19 + \text{Cl}^-/35.5 + \text{NO}_3^-/62 + \text{SO}_4^{2-}/48, \quad (5)$$

Fig. 13 shows scatterplots between total cation microequivalent and total anion microequivalent. Strong correlations between anion and cation equivalents of PM_{2.5} were clearly found in the four seasons with correlation coefficients of 0.88–0.99. The slopes of regression lines were >1.0, indicating a slight acidity of these particles.

3.5 Source Apportionment of PM_{2.5}

Table 1 summarizes the factor analysis of chemical composition in PM_{2.5} particles, which was calculated using the principal component analysis (PCA) method to deduce PM_{2.5} source (Zhang et al., 2011). Overall,

Table 1. Principle components analysis of aerosol chemical composition.

Chemical species	Factor 1	Factor 2	Factor 3	Factor 4
Na	0.17	0.27	0.75	−0.10
NH ₄ ⁺	0.94	−0.08	−0.02	−0.13
K ⁺	0.83	0.00	0.00	−0.06
Mg ²⁺	0.11	0.02	0.90	0.09
Ca ²⁺	0.01	0.43	0.63	−0.16
F [−]	0.40	0.35	−0.04	0.25
Cl [−]	0.90	0.03	0.08	0.02
NO ₃ [−]	0.92	−0.06	0.09	−0.07
SO ₄ ^{2−}	0.90	−0.08	0.23	−0.11
OC	0.86	0.13	−0.08	−0.18
EC	0.86	−0.02	0.20	0.06
Al	−0.14	0.97	0.07	−0.03
Si	−0.07	0.97	0.08	−0.04
Ca	−0.02	0.97	0.08	−0.05
Ti	0.11	0.97	0.08	−0.04
Cr	0.82	0.31	−0.02	−0.05
Mn	0.69	0.54	0.15	−0.09
Fe	0.20	0.94	0.11	−0.12
Ni	0.47	0.30	−0.07	−0.04
Zn	0.88	0.14	0.09	0.02
As	0.88	−0.01	0.14	−0.08
Br	0.93	0.02	0.05	−0.04
Rb	0.69	0.43	0.03	−0.14
Sr	0.03	−0.23	0.23	0.60
Mo	0.50	−0.01	0.24	0.14
Cd	0.05	−0.05	0.04	0.74
Sb	−0.04	0.06	−0.08	0.15
Ba	0.29	0.58	0.18	0.05
Pb	0.94	0.09	0.07	−0.08
Cu	0.86	0.14	0.07	0.09
% Variance	41.5	18.8	6.1	4.4

Note: bold fonts represent higher loadings chemical composition of factors.

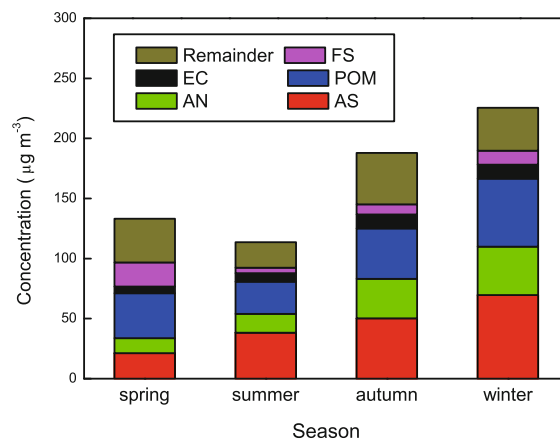


Fig. 14. Calculated ammonium sulfate (AS), ammonium nitrate (AN), particulate organic matter (POM), elemental carbon (EC), fine soil (FS), and remainders in PM_{2.5}.

four factors were reasonable for identifying PM_{2.5} sources, accounting for 41.5%, 18.8%, 6.1%, and 4.4%, respectively, of the total variance. In the first factor group, NH₄⁺, K⁺, Cl⁻, NO₃⁻, SO₄²⁻, OC, EC, Cr, Zn, As, Br, Pb, and Cu showed higher loadings, indicating that these species mostly originated from anthropogenic sources. NH₄⁺, NO₃⁻, and SO₄²⁻ are strongly linked with secondary reaction of primary pollutants such as SO₂ and NO_x. OC, EC, Cr, Zn, As, Br, Pb, and Cu relate to coal combustion and traffic exhaust (Vejahati et al., 2010). However, K⁺ and Cl⁻ relate to biomass burning. Thus, the most important sources of PM_{2.5} in Chengdu have been characterized as coal combustion, traffic exhaust, and biomass burning emissions. For the second factor, Al, Si, Ca, Ti, and Fe had highest loadings, indicating that these elements mainly originated from crust sources in particulate soil dust. For the third factor, Na⁺, Mg²⁺, and Ca²⁺ had higher loadings, suggesting that these ions were mainly related to construction dust. For the fourth factor, Sr and Cd had higher loadings, indicating that these two elements possibly originated from gaseous and particulate pollutants emitted from metallurgical industries.

3.6 Chemical apportionment of PM_{2.5} mass and scattering

Based on the measured aerosol chemical components, the reconstructed PM_{2.5} mass concentrations calculated by the IMPROVE equations (section 2.3) are shown in Fig. 14. On average, the calculated PM_{2.5} was 96.7 μg m⁻³ in spring, 92.4 μg m⁻³ in summer, 145 μg m⁻³ in autumn, and 190 μg m⁻³ in winter. These values account for ~72.6%, 81.4%, 77.1% and 84.2% of the respective seasonal average measured PM_{2.5}. The calculated ammonium sulfate (AS), ammonium nitrate (AN), particulate organic matter (POM), EC, and fine soil accounted for 16.3%–33.2%, 9.7%–17.3%, 24.6%–30.7%, 4.5%–6.3%, and 4.1%–12.4%, respectively, of the measured seasonal PM_{2.5} mass. The calculated aerosol scattering coefficient (*b*_{sca}) was ~87.5%, 111.6%, and 82.2% of their seasonal averages measured in spring, summer, and autumn, respectively. The calculated AS, AN, POM and fine soil contributed to ~26.5%–55%, 15%–22.7%, 23.1%–42.3%, and 0.7%–3.7%, respectively, of the measured average *b*_{sca} in these three seasons. This result indicates that ammonium sulfate and organic carbon were major contributors to PM_{2.5} mass and particle scattering to light.

4. Conclusions

Chengdu has been undergoing rapid economic growth in recent years and experiencing significantly

increased particulate pollution. Analysis of the measured PM_{2.5} aerosol samples collected in this city from April 2009 to January 2010 provided a general knowledge of PM_{2.5} aerosol in this area, including its seasonal variations, major chemical components, and major emission sources contributing to each chemical component. The relative importance of each emission source to each individual chemical component was also investigated using various methods including enrichment factors, source apportionment analysis, and aerosol mass reconstruction method.

An annual average of PM_{2.5} reached 165 μg m⁻³ with seasonal variations up to a factor of two. Water-soluble ions, carbonaceous aerosols, and trace elements all contributed significantly to PM_{2.5}. Ammonium, sulfate, and nitrate were the dominant ions contributing to PM_{2.5}, and they also experienced the same seasonal variations. However, different seasonal patterns were identified for the majority of the other chemical components. Enrichment factor analysis separated all of the elements into three categories: those mainly originated from anthropogenic sources, those mainly from natural sources, or those from a combination of these two type of sources. Source apportionment using the principal component analysis identified four major factors, which represented different source types, contributing to PM_{2.5}. Major emission sources included coal combustion, traffic exhaust, and soil and construction dust emissions. The aerosol mass reconstruction method considering ammonium sulfate, ammonium nitrate, particulate carbonaceous matter, and fine soil explained 79% of the measured PM_{2.5} mass and 92% of the measured particle scattering. The results generated from this study are expected to be useful for making emission control policies to improve future air quality.

Acknowledgements. This study was supported by the Special Scientific Research Funds for Environment Protection Commonweal Section of China (Grant Nos. 201009001), the National Basic Research Program of China (Grant No. 2010CB428503), the Knowledge Innovation Program of the Chinese Academy of Sciences (Grant No. IAP09320), the National Natural Science Foundation of China (Grant Nos. 41075096 and 40975076), the Research and Development Special Fund for Public Welfare Industry (Meteorology) of the China Meteorological Administration (Grant No. GYHY201006047), the Ministry of Science and Technology of China (Grant No. 2010DFA22770), and the Innovation Method Fund of China (Grant No. 2008IM020500).

REFERENCES

Andreae, M. O., O. Schmid, H. Yang, D. L. Chan, J. Z.

- Yu, L. M. Zeng, and Y. H. Zhang, 2008: Optical properties and chemical composition of the atmospheric aerosol in urban Guangzhou, China. *Atmos. Environ.*, **42**, 6335–6350.
- Arimoto, R., and Coauthors, 1996: Relationships among aerosol constituents from Asia and the North Pacific during Pem-West A. *J. Geophys. Res.*, **101**, 2011–2023.
- Bahadur, R., G. Habib, and L. M. Russell, 2009: Climatology of PM_{2.5} organic carbon concentrations from a review of ground-based atmospheric measurements by evolved gas analysis. *Atmos. Environ.*, **43**, 1591–1602.
- Cao, J. J., S. C. Lee, K. F. Ho, X. Y. Zhang, S. C. Zou, K. Fung, J. C. Chow, and J. G. Watson, 2003: Characteristics of carbonaceous aerosol in Pearl River Delta Region, China during 2001 winter period. *Atmos. Environ.*, **37**, 1451–1460.
- Cao, J. J., and Coauthors, 2005: Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. *Atmos. Chem. Phys.*, **5**, 3127–3137.
- Cao, J. J., and Coauthors, 2007: Spatial and seasonal distributions of carbonaceous aerosols over China. *J. Geophys. Res.*, **112**, D22S11, doi: 10.1029/2006JD008205.
- Chan, C. K., and X. Yao, 2008: Air pollution in mega cities in China. *Atmos. Environ.*, **42**, 1–42.
- Chang, D., Y. Song, and B. Liu, 2009: Visibility trends in six megacities in China 1973–2007. *Atmospheric Research*, **94**, 161–167.
- Charlson, R. J., S. E. Schwartz, J. M. Hales, D. Cess, J. A. Coakley, and J. E. Hansen, 1992: Climate forcing by anthropogenic aerosols. *Science*, **255**, 423–430.
- Che, H. Z., X. Y. Zhang, Y. Li, Z. J. Zhou, and J. J. Qu, 2007: Horizontal visibility trends in China 1981–2005. *Geophys. Res. Lett.*, **34**, L24706, doi: 10.1029/2007GL031450.
- Che, H. Z., X. Y. Zhang, Y. Li, Z. J. Zhou, J. J. Qu, and X. J. Hao, 2009: Haze trends over the capital cities of 31 provinces in China, 1981–2005. *Theor. Appl. Climatol.*, **97**, 235–242.
- Chen, J., M. Tan, Y. Li, J. Zheng, Y. Zhang, Z. Shan, G. Zhang, and Y. Li, 2008: Characteristics of trace elements and lead isotope ratio in PM_{2.5} from four sites in Shanghai. *Journal of Hazardous Materials*, **156**, 36–43.
- Cheng, Y. F., and Coauthors, 2008: Aerosol optical properties and related chemical apportionment at Xinken in Pearl River Delta of China. *Atmos. Environ.*, **42**, 6351–6372.
- Chow, J. C., J. G. Watson, Z. Lu, D. H. Lowenthal, C. A. Frazier, P. A. Solomon, R. H. Thuillier, and K. Magliano, 1996: Descriptive analysis of PM_{2.5} and PM₁₀ at regionally representative locations during SJVAQS/AUSPEX. *Atmos. Environ.*, **30**, 2079–2112.
- Chow, J. C., J. G. Watson, L. W. Chen, M. C. Chang, N. F. Robinson, D. Trimble, and S. Kohl, 2007: The IMPROVE_A temperature protocol for thermal/optical carbon analysis: Maintaining consistency with a long-term database. *Journal of the Air & Waste Management Association*, **57**, 1014–1023.
- Dabell, L. J., R. W. Talbot, and J. E. Dibb, 2004: A major regional air pollution event in the northeastern United States caused by extensive forest fires in Quebec, Canada. *J. Geophys. Res.*, **109**, D19305.
- Deng, X., and Coauthors, 2008: Long-term trend of visibility and its characterizations in the Pearl River Delta (PRD) region. China. *Atmos. Environ.*, **42**, 1424–1435.
- Dibb, J. E., R. W. Talbot, S. I. Whitlow, M. C. Shipham, J. Winterle, J. McConnell, and R. Bales, 1995: Biomass burning signatures in the atmosphere and snow at summit Greenland: An event on 5 August 1994. *Atmos. Environ.*, **30**, 553–561.
- Du, H., and Coauthors, 2010: Insight into ammonium particle-to-gas conversion: Non-sulfate ammonium coupling with nitrate and chloride. *Aerosol and Air Quality Research*, **10**, 589–595.
- Du, H., and Coauthors, 2011: Insights into summertime haze pollution events over Shanghai based on online water-soluble ionic composition of aerosols. *Atmos. Environ.*, **45**, 5131–5137.
- Duan, F. K., K. B. He, Y. L. Ma, F. M. Yang, X. C. Yu, S. H. Cadle, T. Chan, and P. A. Mulawa, 2006: Concentration and chemical characteristics of PM_{2.5} in Beijing, China: 2001–2002. *Science of the Total Environment*, **355**, 264–275.
- Dzubay, T. G., R. K. Stevens, and C. W. Lewis, 1982: Visibility and aerosol composition in Houston, Texas. *Environ. Sci. Technol.*, **16**, 514–525.
- Eichler, H., and Coauthors, 2008: Hygroscopic properties and extinction of aerosol particles at ambient relative humidity in South-eastern China. *Atmos. Environ.*, **42**, 6321–6334.
- EPA, United States Code of Federal Regulations, 2006: Title 40, Subchapter C, Air Programs, National primary and secondary ambient air quality standards. [Available online at: <http://www.epa.gov/air/criteria.html>.]
- Fu, Q. Y., and Coauthors, 2008: Mechanism of formation of the heaviest pollution episode ever recorded in the Yangtze River Delta, China. *Atmos. Environ.*, **42**, 2023–2036.
- Furuta, N., A. Iijima, A. Kambe, K. Sakai, and K. Sato, 2005: Concentrations, enrichment and predominant sources of Sb and other trace elements in size classified airborne particulate matter collected in Tokyo from 1995 to 2004. *Journal of Environmental Monitoring*, **7**, 1155–1161.
- Haglera, G. S. W., and Coauthors, 2007: Local and regional anthropogenic influence on PM_{2.5} elements in Hong Kong. *Atmos. Environ.*, **41**, 5994–6004.
- Hand, J. L., and W. C. Malm, 2006: Review of the IMPROVE equation for estimating ambient light extinction coefficients. [Available online at: <http://vista.cira.colostate.edu/IMPROVE/Publications/>.]

- He, K., and Coauthors, 2001: The characteristics of PM_{2.5} in Beijing, China. *Atmos. Environ.*, **35**, 4959–4970.
- Hsu, S. C., S. C. Liu, Y. T. Huang, C. C. K. Chou, S. C. C. Lung, T. H. Liu, J. Y. Tu, and F. J. Tsai, 2009: Long-range southeastward transport of Asian biomass burning pollution: Signature detected by aerosol potassium in northern Taiwan. *J. Geophys. Res.*, **114**, D14301, doi: 10.1029/2009JD011725.
- Hu, M., Z. Wu, J. Slanina, P. Lin, S. Liu, and L. Zeng, 2008: Acidic gases, ammonia and water-soluble ions in PM_{2.5} at a coastal site in the Pearl River Delta, China. *Atmos. Environ.*, **42**, 6310–6320.
- IPCC, 2007: Summary for policymakers. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* S. Solomon et al., Eds., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 153–177.
- Kim, H. S., J. B. Huh, P. K. Hopke, T. M. Holsen, and S. M. Yi, 2007: Characteristics of the major chemical constituents of PM_{2.5} and smog events in Seoul, Korea in 2003 and 2004. *Atmos. Environ.*, **41**, 6762–6770.
- McMurry, P. H., H. Takano, and G. R. Anderson, 1983: Study of the Ammonia (Gas)–Sulphuric acid (aerosol) reaction rate. *Environ. Sci. Technol.*, **17**, 347–352.
- Pitchford, M., W. Malm, B. Schichtel, N. Kumar, D. Lowenthal, and J. Hand, 2007: Revised algorithm for estimating light extinction from improve particle speciation data. *Journal of the Air & Waste Management Association*, **57**, 1326–1336.
- Pope III, C. A., R. T. Burnett, M. J. Thun, E. E. Calle, D. Krewski, K. Ito, and G. D. Thurston, 2002: Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *The Journal of the American Medical Association*, **287**, 1132–1141.
- Qin, Y., E. Kim, and P. K. Hopke, 2006: The concentrations and sources of PM_{2.5} in metropolitan New York City. *Atmos. Environ.*, **40**, 312–332.
- Ramanathan, V., P. J. Crutzen, J. T. Kiehl, and D. Rosenfeld, 2001: Aerosols, climate, and the hydrological cycle. *Science*, **294**, 2119–2124.
- Rosenfeld, D., 2006: Aerosols, clouds, and climate. *Science*, **312**, 1323–1324.
- Shen, Z. X., and Coauthors, 2009: Ionic composition of TSP and PM_{2.5} during dust storms and air pollution episodes at Xi'an, China. *Atmos. Environ.*, **43**, 2911–2918.
- Shen, Z. X., J. J. Cao, R. Arimoto, Y. M. Han, C. S. Zhu, J. Tian, and S. X. Liu, 2010: Chemical characteristics of fine particles (PM₁) from Xi'an, China. *Aerosol Science Technology*, **44**, 461–472.
- Sun, Y. L., G. S. Zhuang, A. H. Tang, Y. Wang, and Z. S. An, 2006: Chemical characteristics of PM_{2.5} in haze-fog episodes in Beijing. *Environ. Sci. Technol.*, **40**, 3148–3155.
- Jun, T., K.-F. Ho, L. G. Chen, L. H. Zhu, J. L. Han, and Z. C. Xu, 2009: Effect of chemical composition of PM_{2.5} on visibility in Guangzhou, China, 2007 spring. *Particuology*, **7**(1), 68–75.
- Tao, J., Z. Shen, C. Zhu, J. Yue, J. Cao, S. Liu, L. Zhu, and R. Zhang, 2012: Seasonal variations and chemical characteristics of sub-micrometer particles (PM₁) in Guangzhou, China. *Atmospheric Research*, **118**, 222–231.
- Taylor, S. R., and S. M. McLennan, 1995: The geochemical evolution of the continental crust. *Rev. Geophys.*, **33**, 241–265.
- Tie, X., and J. Cao, 2009: Aerosol pollution in China: present and future impact on environment. *Particuology*, **7**, 426–431.
- Vejahati, F., Z. Xu, and R. Gupta, 2010: Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization—A review. *Fuel*, **89**, 904–911.
- Wang, K., R. E. Dickinson, and S. Liang, 2009: Clear sky visibility has decreased over land globally from 1973 to 2007. *Science*, **323**, 1468–1470.
- Wang, M., R. Zhang, and Y. Pu, 2001: Recent researches on aerosol in China. *Adv. Atmos. Sci.*, **18**(4), 576–586.
- Wang, Y., G. Zhuang, A. Tang, H. Yuan, Y. Sun, S. Chen, and A. Zhang, 2005: The Ion Chemistry of PM_{2.5} Aerosol in Beijing. *Atmos. Environ.*, **39**, 3771–3784.
- Wang, Y., G. Zhuang, X. Zhang, K. Huang, C. Xu, A. Tang, J. Chen, and Z. An, 2006: The ion chemistry, seasonal cycle, and sources of PM_{2.5} and TSP aerosol in Shanghai. *Atmos. Environ.*, **40**, 2935–2952.
- Wedepohl, H., 1995: The composition of the continental crust. *Geochimica et Cosmochimica Acta*, **59**, 1217–1239.
- Wei, F., E. Teng, G. Wu, W. Hu, W. E. Willson, R. S. Chapman, J. C. Pau, and J. Zhang, 1999: Ambient concentrations and elemental compositions of PM₁₀ and PM_{2.5} in four Chinese cities. *Environ. Sci. Technol.*, **33**, 4188–4193.
- Wild, M., and Coauthors, 2005: From dimming to brightening: decadal changes in solar radiative at Earth's surface. *Science*, **308**, 847–850.
- Wittig, A. E., S. Takahama, A. Y. Khlystov, S. N. Pandis, S. Hering, B. Kirby, and C. Davidson, 2004: Semi-continuous PM_{2.5} inorganic composition measurements during the Pittsburgh air quality study. *Atmos. Environ.*, **38**, 3201–3213.
- Xu, H. M., and Coauthors, 2012. Lead concentrations in fine particulate matter after the phasing out of leaded gasoline in Xi'an, China. *Atmos. Environ.*, **46**, 217–224.
- Yao, X., C. Chan, M. Fang, S. Cadle, T. Chan, P. Mulawa, K. He, and B. Ye, 2002: The water-soluble ionic composition of PM_{2.5} in Shanghai and Beijing, China. *Atmos. Environ.*, **36**, 4223–4234.
- Ye, B., X. Ji, H. Yang, X. Yao, C. Chan, S. Cadle, T. Chan, and P. A. Mulawa, 2003: Concentration and

- chemical composition of PM_{2.5} in Shanghai for a 1-year period. *Atmos. Environ.*, **37**, 499–510.
- Yuan, H., Y. Wang, and G. S. Zhuang, 2003: The simultaneous determination of organic acid, MSA with the inorganic anions in aerosol and rainwater by ion chromatography. *Journal of Instrumental Analysis*, **22**, 11–14.
- Zhang, F., L. Xu, J. Chen, Y. Yu, Z. Niu, and L. Yin, 2012: Chemical compositions and extinction coefficients of PM_{2.5} in peri-urban of Xiamen, China, during June 2009–May 2010. *Atmospheric Research*, **106**, 150–158.
- Zhang, R., M. Wang, X. Zhang, and G. Zhu, 2003a: Analysis on the chemical and physical properties of particles in a dust storm in spring in Beijing. *Powder Technology*, **137**(1), 77–82.
- Zhang, R., Y. Xu, and Z. Han, 2003b: Inorganic chemical composition and source signature of PM_{2.5} in Beijing during ACE-Asia period. *Chinese Science Bulletin.*, **48**(10), 1002–1005.
- Zhang, R., Z. Shen, T. Cheng, M. Zhang, and Y. Liu, 2010: The elemental composition of atmospheric particles at Beijing during Asian dust events in spring 2004. *Aerosol and Air Quality Research*, **10**, 67–75.
- Zhang, T., and Coauthors, 2011: Water-soluble ions in atmospheric aerosols measured in Xi'an, China: Seasonal variations and sources. *Atmospheric Research*, **102**, 110–119.
- Zhao, Q., and Coauthors, 2010: Dust storms come to central and southwestern China, too: Implications from a major dust event in Chongqing. *Atmos. Chem. Phys.*, **10**, 2615–2630.