**Chemical composition, sources and secondary processes of aerosols in
Baoji city of northwest China**

Y. C. Wang^{a,b}, R.-J. Huang^{a,d,e,*}, H. Y. Ni^a, Y. Chen^a, Q. Y. Wang^a, G. H. Li^a, X. X. Tie^a, Z.
X. Shen^f, Y. Huang^a, S. X. Liu^a, W. M. Dong^h, P. Xue^g, R. Fröhlich^e, F. Canonaco^e, M.
Elser^e, K. R. Daellenbach^e, C. Bozzetti^e, I. El Haddad^e, A. S. H. Prévôt^e, M. R.
Canagaratna^h, D. R. Worsnop^h, J. J. Cao^{a,c,*}

^a Key Laboratory of Aerosol Chemistry & Physics, State Key Laboratory of Loess and Quaternary Geology,
Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an 710049, China

^d Centre for Atmospheric and Marine Sciences, Xiamen Huaxia University, Xiamen 361024, China

^e Laboratory of Atmospheric Chemistry, Paul Scherrer Institute (PSI), 5232 Villigen, Switzerland

^f Department of Environmental Sciences and Engineering, Xi'an Jiaotong University, Xi'an, 710049, China

^g Baoji Environmental Monitoring Central Station, Baoji 721000, China

^h Aerodyne Research, Inc., Billerica, MA, USA

E-mail address: R.-J. Huang (rujin.huang@ieecas.cn) and J.J. Cao (cao@loess.llqg.ac.cn)

Abstract

Particulate air pollution is a severe environmental problem in China, affecting visibility, air quality, climate and human health. However, previous studies focus mainly on large cities such as Beijing, Shanghai, and Guangzhou. In this study, an Aerodyne Aerosol Chemical Speciation Monitor was deployed in Baoji, a middle size inland city in northwest China from 26 February to 27 March 2014. The non-refractory submicron aerosol (NR-PM₁) was dominated by organics (55%), followed by sulfate (16%), nitrate (15%), ammonium (11%) and chloride (3%). A source apportionment of the organic aerosol (OA) was performed with the Sofi (Source Finder) interface of ME-2 (Multilinear Engine), and six main sources/factors were identified and classified as hydrocarbon-like OA (HOA), cooking OA (COA), biomass burning OA (BBOA), coal combustion OA (CCOA), less oxidized oxygenated OA (LO-OOA) and more oxidized oxygenated OA (MO-OOA), which contributed 20%, 14%, 13%, 9%, 23% and 21% of total OA, respectively. The contribution of secondary components shows increasing trends from clean days to polluted days, indicating the importance of secondary aerosol formation processes in driving particulate air pollution. The formation of LO-OOA and MO-OOA is mainly driven by photochemical reactions, but significantly influenced by aqueous-phase chemistry during periods of low atmospheric oxidative capacity.

Keywords: ACSM, chemical composition, organic aerosol, source apportionment, secondary formation processes

1. Introduction

Aerosols scatter and absorb solar radiation, and affect cloud formation, thereby influencing visibility and radiative forcing of the Earth's atmosphere (Watson, 2002; Forster et al., 2007). The exposure to ambient aerosols is associated with increased respiratory and cardiovascular diseases (Pope and Dockery, 2006; Cao et al., 2012a). In China, aerosol pollution is a serious environmental problem (Cao et al., 2012b). A study by Chang et al. (2009) on the visibility trends between 1973 and 2007 revealed a substantial decrease in visibility in five out of six Chinese megacities. Tie et al. (2016) found that the reduction of solar irradiance caused by the aerosol pollution leads to 2% decrease in the rice production and 8% decrease in the wheat production in China. Lelieveld et al. (2015) investigated the link between some emission sources and premature mortality, and it was estimated that 1.3 million premature deaths were caused by outdoor air pollution in China in 2010. These effects are associated with the aerosol properties, such as the concentration and chemical composition (Zhang et al., 2015a).

Numerous field studies have been conducted to identify the composition, sources and processes of aerosols in China. Most of the studies are based on the analyses of filter samples collected on a daily basis (Chan et al., 2008; Cao et al., 2012c; Huang et al., 2014). Recently, several measurements of submicron aerosol composition with high time-resolution have been conducted in Chinese cities using online aerosol mass spectrometry. The studies with high time-resolution mainly focus on megacities such as Shanghai and Beijing (Huang et al., 2012; Sun et al., 2013a; Elser et al., 2016) and big cities such as Shenzhen, Nanjing, Xiamen (He et al., 2011; Zhang et al., 2015b; Yan et al., 2015), Xi'an and Lanzhou (Xu et al., 2014; Elser et al., 2016). However, middle size ordinary cities (with population of around 1 million) constitute the main portion (~70%) of Chinese cities and also suffer from serious aerosol pollution. The Chinese MEP (Ministry of Environmental Protection) reported that 5 middle size ordinary cities ranked the top 10 most polluted cities in China in 2014. Since the Chinese government is committed to reducing the urban $PM_{2.5}$ mass concentration by at least 10% in 2017 compared to 2012 levels ("Atmospheric Pollution Prevention and Control Action Plan")

issued by Chinese State Council in 2013), and aerosol pollution in ordinary cities may affect nearby major cities through transport (Sun et al., 2010; Sun et al., 2014; Huang et al., 2014), it is necessary to study aerosol properties, sources and processes in ordinary prefecture cities for effective emission control strategies. Compared to megacities the middle size cities in China, on the other hand, may have different characteristics in chemical nature and sources and thus require more studies.

Baoji is a typical ordinary middle sized city in China (Wu et al., 2004; Xie et al., 2009; Xiao et al., 2014). There are a few studies based on filter samples to characterize the aerosol composition and its influence on visibility in Baoji (Xie et al., 2009; Wang et al., 2010; Xiao et al., 2014). Xie et al. (2009) have illustrated that aliphatic alkanes and polycyclic aromatic hydrocarbons (PAHs) in PM₁₀ were much higher in Baoji than those in Chinese megacities. Xiao et al. (2014) concluded that ammonium sulfate contributed mostly (32.0%) to visibility impairment in Baoji in 2012. However, the filter samples are limited by the low temporal resolution and filter sample artifacts (Ng et al., 2011a). In this study, measurements with an aerosol chemical speciation monitor (ACSM) were conducted at Baoji with 30-minute time resolution, and the objectives were: (1) to characterize the temporal evolution, mass fractions and diurnal variations of non-refractory PM₁ (NR-PM₁) species; (2) to study the sources and formation processes of organic aerosol; and (3) to identify the main causes of aerosol pollution in Baoji.

2. Materials and methods

2.1. Site description

Baoji is located in the semi-arid region of northwest China (Supplementary Fig. S1). It is an ordinary prefecture city of inland China with a population of 1.02 million and 199 thousand vehicles. An ACSM and other supporting instruments were deployed in the Baoji environmental monitoring station (34°21'18.4"N, 107°08'34.7"E). This site is classified as a residential and business area. The instruments were installed on the top of a fourth-floor building (~15 m high). During the measurement period (26 February-27 March 2014), the average temperature and RH were 10.6 ± 5.3 °C (1.0-29.1 °C) and $50.2 \pm 20.7\%$ (13.2-94.5%), respectively. The meteorological condition was very stable with average wind speed of $0.63 (\pm 0.56)$ m s⁻¹.

2.2. Instrumentation

The quadrupole aerosol chemical speciation monitor (Q-ACSM, Aerodyne Research Inc., Billerica, Massachusetts) with unit mass resolution (UMR) and time steps of ~30 min was deployed for the continuous measurement of non-refractory submicron aerosol species (organics, sulfate, nitrate, ammonium and chloride). The ambient aerosol was drawn through a 3/8 in. stainless steel tube at a flowrate of ~3 L min⁻¹, and coarse particles were removed by an URG cyclone (Model: URG-2000-30ED) with a size cut of 2.5 µm in front of the sampling inlet. The sample was dried by a nafion dryer (MD-110-48S; Perma Pure, Inc., Lakewood, NJ, USA) to reduce uncertainties in the collection efficiency (CE) caused by particle bounce for different phase states with different aerosol water content. Detailed descriptions of the operational principles and calibration procedures of the ACSM are presented elsewhere (Ng et al., 2011a). Briefly, the submicron aerosol (~40–1000 nm vacuum aerodynamic diameter) was subsampled into the ACSM with a flow rate of 85 cc min⁻¹. The air was sampled through a 100 µm-diameter critical aperture and then focused by the aerodynamic lens. The focused particle beam was transmitted to the vaporizer (~600 °C), and the vaporized species were detected and characterized by 70 eV electron impact quadrupole mass spectrometry. The combination of an atomizer (Model 9302, TSI Inc., Shoreview, MN, USA), a differential mobility analyzer (DMA, TSI model 3080) and a condensation particle counter (CPC, TSI model 3772) was used for the ionization efficiency (IE) calibration and to calculate the ACSM response factor (RF). Monodisperse ammonium nitrate (NH₄NO₃) particles were generated and are used for the calibration due to the complete vaporization of NH₄NO₃ (Ng et al., 2011a).

Hourly mass concentration of PM_{2.5} were measured with a micro-oscillating balance (TEOM®1405-DF; Thermo Scientific, Waltham, MA, USA). Hourly average ozone (O₃) concentrations were measured by a UV photometer (Model 49i Ozone Analyzer, Thermo Scientific). The hourly meteorological data, including temperature, relative humidity (RH), precipitation, wind speed and wind direction, were measured by an automatic weather station (MAWS201, Vaisala, Vantaa, Finland) and a wind sensor (Vaisala Model QMW101-M2).

2.3. Data analysis

2.3.1. ACSM data analysis

The ACSM DAQ software version 1.4.4.5 (Aerodyne Research Inc., Billerica, Massachusetts, USA) was used for data acquisition. The ACSM local tool version 1.5.3.5 (Aerodyne Research Inc., Billerica, Massachusetts, USA) for Igor Pro (WaveMetrics, Inc., Lake Oswego, Oregon USA) was used for ACSM data analysis and export of PMF (positive matrix factorization) matrices. Standard relative ionization efficiencies (RIEs) were used for organics, nitrate and chloride (i.e. 1.4 for organics, 1.1 for nitrate and 1.3 for chloride) (Canagaratna et al., 2007) and were estimated from the IE calibrations for ammonium (7.2). The RIE_{SO_4} was estimated from IE calibration using NH_4SO_4 before and after the measurement campaign, which provided the RIE_{SO_4} value of 1.19 and 1.24, respectively, very similar to the default value of 1.2 (Canagaratna et al., 2007). We therefore expected that the RIE_{SO_4} was rather stable during the entire campaign period and the value of 1.2 was used. Decreases in the CE are mainly related to the bounce of particles when they impact the vaporizer (Middlebrook et al., 2012). The CE is influenced by the aerosol acidity, composition and particle phase water content. Because aerosols were dried before entering the ACSM, and particles are overall neutralized, the influences of particle phase water and acidity are expected to be negligible. Therefore, CE was determined as $CE_{dry} = \max(0.45, 0.0833 + 0.9167 \times ANMF)$ (Middlebrook et al., 2012), where ANMF represents the mass fraction of ammonium nitrate in NR-PM₁.

2.3.2. Source apportionment

Commonly used receptor models for organic aerosol (OA) source apportionment include PMF (Paatero and Tapper, 1994; Paatero, 1997), multilinear engine (ME-2) (Paatero., 1999) and chemical mass balance (CMB, Watson et al., 1997). PMF is a bilinear unmixing model that represents the input data as a linear combination of static factor profiles and their corresponding time series:

$$\mathbf{X} = \mathbf{GF} + \mathbf{E} \quad (1)$$

where $\mathbf{X}$ ($m \times n$) refers to the organic spectral matrix containing m organic mass spectra (rows) with n ion fragments each (columns), $\mathbf{F}$ ($p \times n$) contains the factor profiles (being p the number of profiles) and $\mathbf{G}$ ($m \times p$) the corresponding time series. The matrix $\mathbf{E}$ ($m \times n$)

contains the model residuals, and scaled residuals are minimized. The model utilizes a least squares approach to iteratively minimize the quantity Q , defined as the sum of the squared residuals (e_{ij}) weighted by their respective uncertainties (σ_{ij}):

$$Q = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{e_{ij}}{\sigma_{ij}} \right)^2 \quad (2)$$

PMF requires no *a priori* information about factor profiles or time series. In contrast, ME-2 is used to introduce *a priori* information as an additional model input. With the *a* value approach one or more factor profiles can be constrained as follows:

$$f_{j,solution} = f_j \pm a \cdot f_j \quad (3)$$

where f refers to a row of the matrix $\mathbf{F}$. j represents the mass to charge ratio (m/z) of the ions, and the a value determines the extent to which the output profiles can differ from the model inputs and it ranges from 0 to 1.

The PMF receptor model has been widely utilized for the OA source apportionment in recent years (Lanz et al., 2009; Ulbrich et al., 2009; Jimenez et al., 2009; Ng et al., 2010; He et al., 2011; Huang et al., 2012; Dall'Osto et al., 2013; Sun et al., 2013b; Xu et al., 2014; Zhang et al., 2015b; Yan et al., 2015). However, it is pointed out that the PMF receptor model has difficulties in separating the factors with similar profiles (e.g. cooking and traffic, Mohr et al., 2009) or time series (Fröhlich et al., 2015). This problem can be solved by the ME-2 or CMB, which introduces *a priori* information (profiles) for the factors (Canonaco et al., 2013; Crippa et al., 2014; Fröhlich et al., 2015).

3. Results and discussion

3.1. Concentrations and chemical composition of NR-PM₁

Fig. 1a shows the time series of mass concentrations of NR-PM₁ chemical species. The variation of OA mass concentration has short-term fluctuations and shows a distinct diurnal profile. The increase rates are 7.3 (3.0-13.3) $\mu\text{g m}^{-3} \text{ h}^{-1}$ from the early morning to the morning rush hour (5:00-10:00 Local time, LT) and 17.7 (4.0-38.2) $\mu\text{g m}^{-3} \text{ h}^{-1}$ from afternoon to the evening (16:00-22:00 LT). The higher mass increase rate from late afternoon could be a consequence of decreasing boundary layer and increasing emissions during this period. The relative contribution of the aggregated primary OA (POA,

including HOA, BBOA, COA and CCOA) to total OA is generally high in the morning and evening peaks ($62 \pm 11\%$ for the morning peak, $70 \pm 11\%$ for the evening peak) and low ($49 \pm 12\%$ for the morning valley, $38 \pm 14\%$ for the evening valley) for the corresponding valleys. Therefore, the high mass increase rates of OA could be associated with the enhanced primary emissions. Most of the OA events are not correlated with inorganic events, which do not have many short term fluctuations and appear to be more regional. Fig. 1b represents the relative contribution of each constituent to the NR-PM₁ mass during the entire study period. On average, NR-PM₁ consists of 55% (31-88%) organic, 16% (3-35%) sulfate, 15% (2-45%) nitrate, 14% (0-32%) ammonium and 2% (0-20%) chloride. The average mass concentration of total NR-PM₁ species is $54 (\pm 28) \mu\text{g m}^{-3}$. As shown in Fig. 2a, the time series of NR-PM₁ correlates strongly with PM_{2.5} ($R^2=0.77$), yielding a regression slope of 0.71. This indicates the dominance of NR-PM₁ in PM_{2.5}. Fig. 2b summarizes the NR-PM₁ mass concentrations from AMS (aerosol mass spectrometer) or ACSM measurement at five cities in Asia during springtime. NR-PM₁ concentrations measured in Tokyo and Hong Kong are less than $15 \mu\text{g m}^{-3}$, while those measured in inland China (Beijing, Nanjing and Baoji) exceed $25 \mu\text{g m}^{-3}$. The highest concentration is found in Baoji, which is comparable to the highly aerosol polluted city – Beijing (Sun et al., 2015), more than 2 times higher than in Nanjing (Wang et al., 2016), and ~4 times higher than in Hong Kong (Li et al., 2015) and Tokyo (Takegawa et al., 2006). The higher NR-PM₁ concentration in Baoji emphasizes the heavily polluted air in this city.

In order to obtain the information about the NR-PM₁ sources and formation, the diurnal variation of NR-PM₁ species is discussed. As shown in Fig. 3, OA exhibits two major peaks. The first one appears at 8:00-10:00 LT coinciding with the morning traffic rush hour and the enhanced OOA concentrations (as described in Sect.3.2), while the second one, which is ~2 times higher, at 20:00 LT. The evening peak is due to the PBL change, enhanced primary emissions and the effect of relative humidity, as discussed in the next section. Sulfate shows peaks in the late morning, likely due to the enhance of SO₂ oxidation from increased atmospheric oxidative capacity. Nitrate presents an evident increase from $7.6 \mu\text{g m}^{-3}$ at 8:00 LT to $10.0 \mu\text{g m}^{-3}$ at 10:00 LT, which is probably due to

the enhanced production of nitric acid (HNO_3). Indeed, the NO_2 concentration is enhanced in the morning traffic rush hour. Nitrous acid (HONO) is accumulated at night and photolyzed in the morning after sunrise producing OH and NO (Alicke et al., 2003; Li et al., 2010). HNO_3 is produced from the photochemical reactions of $\text{NO}_2 + \text{OH}$. Nitrate shows a valley between 13:00 and 16:00 LT, indicating that the photochemical production of nitrate cannot overcome the vertical dilution from PBL development. By contrast, the variation of sulfate is rather flat in the afternoon, indicating the large production of sulfate which compensates for the dilution from PBL development.

3.2. Sources of organic aerosol

In the PMF solutions from 2 to 8 factors, the 6-factor solution is most interpretable, which includes HOA, BBOA, COA, CCOA, LO-OOA and MO-OOA. BBOA is mixed with other factors in PMF solutions with a lower number of factors and is splitted into two factors of similar profiles in the 7-factor PMF solutions (Supplementary Fig. S2). Further separation of factors does not enhance the interpretation of the data, as the new factor cannot be associated with distinct sources or processes. In the 6-factor solutions, the BBOA profile is characterized by the presence of signals at m/z 60 and m/z 73. The time series of BBOA is highly correlated with m/z 60 ($R^2 > 0.85$) and m/z 73 ($R^2 > 0.83$). Although the BBOA profile is well-defined in PMF solutions, the mixing between other sources is obvious (Supplementary Fig. S2). Specifically, HOA profile contains rather high contributions at the PAH-related m/z 's, such as m/z 77, 91 and 115, indicating the mixing between HOA and CCOA. COA profiles contains a higher than expected contribution at m/z 44 (CO_2^+), indicating the mixing between COA and OOAs.

To separate HOA from CCOA in ME-2, we constrained the HOA profile from Ng et al. (2011b), which is the average over 15 sites all over the world (including China, Japan, Europe and United States). Although the vehicle in China and European are different, e.g. the vehicle is dominated by gasoline in China and diesel in Europe, the HOA spectra from Europe and China are similar (Ng et al., 2011b; Elser et al., 2016), indicating that traffic emissions from different type of vehicles have similar profiles. To decrease the influence of OOA on the appointment of COA, the COA profile from Paris (Crippa et al., 2013) was constrained. While some variabilities are expected between Chinese and European

cooking activities, high similarities are found between the COA profile from Paris and four COA profiles from different types of Chinese cooking (He et al., 2010; Crippa et al., 2013; Elser et al., 2016). To minimize the effect of non-local input profiles (both HOA and COA), a value approach was used to adjust the input profiles in a certain extent. For ME-2 results with constrained HOA and COA profiles, one unconstrained factor was always present and was characterized by high signals at m/z 43, m/z 44, m/z 60 and m/z 73, indicating the mix of OOA with BBOA (Supplementary Fig. S3). To separate BBOA from OOA, we constrained BBOA profile from the 6-factor PMF solution in Baoji with a value of 0. The BBOA profile is totally constrained because it is a well-defined local profile as discussed above. 121 possible results can be obtained by limiting a values for HOA and COA profiles between 0 and 1 with an interval of 0.1.

A set of three criteria for optimization of OA source appointment are as follows:

(1) *The COA diurnal pattern.* In the urban area, COA usually has peaks in the mealtimes.

This diurnal pattern can be used for the identification of COA.

(2) *Minimization of m/z 60 and 115 in HOA.* The threshold for the maximal fractional contributions is derived from multiple ambient data sets (mean + 2σ) (Ng et al., 2011b). The upper limit of fractional contribution of m/z 60 and 115 in HOA is 0.006 and 0.004, respectively.

(3) *The consistency of unconstrained factors with previous studies.* Specifically, CCOA should present high signals at PAH-related m/z 's, such as m/z 77, 91 and 115. OOAs should have abundant peaks at m/z 44 and have lower signals at PAH-related m/z 's than CCOA.

8 solutions conform to the criteria above. The final profiles and time series of individual factors are the average from these 8 solutions. Error bars are the standard deviation of each m/z . An overview of the time series and mass spectrometric profile of each factor is shown in Fig. 4, including HOA, BBOA, COA, CCOA and two oxygenated OA factors (i.e., LO-OOA and MO-OOA). The diurnal profiles and mass fractions of individual OA factors are shown in Fig. 5. The characteristics of each factor are discussed in detail in this section.

The average concentration of HOA is $5.7 (\pm 5.0) \mu\text{g m}^{-3}$, and the mass fraction of HOA

in OA is 20%. The Baoji HOA spectra is highly correlated with the mass spectra of organic particles emitted from diesel ($R^2 = 0.94$) (Canagaratna et al., 2004) and gasoline vehicles ($R^2 = 0.92$) (Mohr et al., 2009). As shown in Supplementary Fig. S4, HOA co-varies closely with the C_nH_{2n-1} and C_nH_{2n+1} ions, particularly m/z 41, 43, 55, 57, 69, 71, 83, 85, 97 and 111. Further, HOA contributes 25.5–47.2% of the signal in these m/z 's, higher than the contribution from other OA components. The diurnal pattern of HOA displays a peak in the morning rush hour (8:00) and the other peak in the evening rush hour (20:00).

The average mass concentration of COA is $4.0 (\pm 3.2) \mu\text{g m}^{-3}$, and it contributes 14% of total OA mass. The correlations in the mass spectra between the Baoji COA and the COA factors identified in previous studies are high ($R^2 = 0.81, 0.93$ and 0.94 for the COA factors determined in Barcelona, Paris and Beijing, respectively) (Mohr et al., 2012; Crippa et al., 2013; Elser et al., 2016). The mass spectra of COA is characterized with high m/z 41/43 ratio (1.7) and m/z 55/57 ratio (1.9) which have been shown to be robust markers for COA (He et al., 2010; Mohr et al., 2012; Crippa et al., 2013; Elser et al., 2016). The enhanced signals at m/z 41 and 55 can be from the heating of seed oil (Allan et al., 2010). The COA diurnal cycle shows peaks during morning (7:00), noon (12:00) and early evening (20:00), consistent with the breakfast, lunch and dinner time.

The average BBOA mass concentration is $3.9 (\pm 4.2) \mu\text{g m}^{-3}$ with a contribution of 13% to total OA mass. The correlations in the mass spectra between the Baoji BBOA and the BBOA from Ng et al (2011b) are high ($R^2 = 0.83$). This factor shows high signals at m/z 60 ($C_2H_4O_2^+$) and 73 (95% of which is $C_3H_5O_2^+$) (Lanz et al., 2008; Mohr et al., 2009). These two ions ($C_2H_4O_2^+$ and $C_3H_5O_2^+$) are well-known fragments of levoglucosan and mannosan, which are products of incomplete combustion and pyrolysis of cellulose and hemicelluloses from biomass burning (Alfarra et al., 2007). BBOA contributes 47 % of m/z 60 and 45 % of m/z 73, much higher than the contributions from other factors (Supplementary Fig. S4). The time series of BBOA correlates very well with that of m/z 60 ($R^2 = 0.90$) and m/z 73 ($R^2 = 0.85$). It also has a high correlation with COA ($R^2 = 0.63$, Supplementary Table S1), indicating that some cooking activities may use wood or straw for combustion. The diurnal variation of BBOA is consistent with that of chloride, both of

which shows morning (9:00) and evening (20:00) peaks. The two peaks are associated with increased heating and cooking activities.

The average mass concentration of CCOA is $2.6 (\pm 2.3) \mu\text{g m}^{-3}$, accounting for 9% of the total OA mass. The CCOA contribution is lower compared to BBOA, which is similar to previous study in a nearby city Xi'an during the wintertime heating season (Elser et al., 2016). The CCOA mass spectra is dominated by unsaturated hydrocarbons. It is correlated well with the ambient CCOA mass spectra in Beijing and Xi'an ($R^2 = 0.66$) (Elser et al., 2016). The signal of m/z 44 in Baoji CCOA is similar with those observed in 2014 winter Beijing (Elser et al., 2016; Sun et al., 2016), but much lower than those in 2010 winter Beijing (Hu et al., 2016) and 2014 winter Lanzhou (Xu et al., 2016). The spectral differences were probably due to different burning conditions and aging processes. Zhou et al (2016) found that the change in burning types of coals can produce different CCOA spectra, particularly for m/z 44 and 73. The mass spectra of CCOA can be further validated by the high signals at PAH-related m/z , such as m/z 77, 91 and 115 (Dall'Osto et al., 2013; Hu et al., 2013). Not surprisingly, the temporal variation of CCOA correlates well with m/z 77, 91 and 115, with correlation coefficient $R^2 > 0.65$ (Supplementary Fig. S4). It should be noted that CCOA presents the highest contributions to (PAH)-related ions (Supplementary Fig. S4). The diurnal of CCOA shows a peak (not the maximum) at 8:00 LT, which might be associated with the breakfast cooking activities which often use coal, particularly for the on-street breakfast cooking. The CCOA morning peak was also observed in other locations, e.g., Beijing and Xi'an (Elser et al., 2016). CCOA started increase in the evening and reached the maximum at the midnight, consistent with enhanced emissions from residential coal combustion at night.

Two oxygenated OA factors were resolved, i.e., LO-OOA and MO-OOA, which account for 23% and 21% of the total OA mass, respectively. The sum of OOAs correlates well with SIAs (secondary inorganic aerosols, including sulfate, nitrate and ammonium) ($R^2 = 0.82$), indicating likely a more regional nature due to the difference in their formation rates (Huang et al., 2014). The correlation of time series between LO-OOA and MO-OOA is low ($R^2 = 0.39$, Supplementary Table S1), but the resulting linear combination indicates the evolution of secondary OA (SOA). The most abundant

peaks in the mass spectra of the OOAs are at m/z 44 and 43. LO-OOA contributes 36% of m/z 43 and 31% of m/z 44 signals, while MO-OOA contributes 3% of m/z 43 and 60% of m/z 44 signals. Ion intensities at m/z 44 and 43 (representing SOA) were retrieved by removing the POA contribution from the measured m/z 44 and 43 following the approach described in Canonaco et al. (2015). LO-OOA is highly correlated ($R^2 = 0.97$) with SOA m/z 43 (an indicator of less oxidized oxygenated organics), while MO-OOA is well correlated ($R^2 = 0.90$) with SOA m/z 44 (an indicator of more oxidized oxygenated organics). The diurnal cycle of two OOAs peaks in the morning (10:00 LT) and increases in the evening (18:00-20:00). The peak in the morning is likely due to the enhanced production of OH radicals from e.g. HONO, H_2O_2 and CH_3OOH after sunrise (Alicke et al., 2003; Li et al., 2010). The increase in the evening is likely due to the decrease of PBL height and the effect of regional transport. Besides, both f_{LO-OOA} (the mass fraction of LO-OOA in OA) and f_{MO-OOA} (the mass fraction of MO-OOA in OA) are positively correlated with RH when $RH > 60\%$ (Supplementary Fig. S5), indicating that the formation of LO-OOA and MO-OOA is also influenced by relative humidity (RH) in the nighttime.

3.3. Atmospheric processes of secondary aerosol

Fig. 6 shows the mass fractions of NR- PM_{10} species and OA sources in clean days, less-polluted days and polluted days. Here, the days with NR- PM_{10} daily average mass concentration below the 25th quartile (i.e., $43 \mu g m^{-3}$) are denoted as the clean days, within the 25-75th interquartile range (i.e., $43-75 \mu g m^{-3}$) as the less-polluted days, and higher than the 75th quartile (i.e., $75 \mu g m^{-3}$) as the polluted days. The mean concentration of NR- PM_{10} is $84.9 \mu g m^{-3}$ in the polluted days, about 3 times higher than in clean days. Organics account for 67% of NR- PM_{10} mass in clean days, but this fraction decreases to 56% in less polluted days and further to 48% in polluted days. In terms of the OA sources, while POA dominates OA in the clean days accounting for 65% of OA mass, its contribution decreases to 56% in less polluted days and to 48% in polluted days. The contribution of two OOAs increases correspondingly, i.e., from 16% in clean days to 24% in less polluted days and further to 29% in polluted days for LO-OOA, and from 19% in clean days to 20% in less polluted days and further to 23% in polluted days for MO-OOA.

Similar to LO-OOA and MO-OOA, the secondary inorganic species including sulfate, nitrate and ammonium also show increasing trends from clean days to polluted days (Fig. 6). It should be noted that the increase of two OOA fractions and SIA are accompanied with increased RH and decreased temperature and wind speed (Fig. 6), suggesting the important effects of meteorological conditions on the formation of secondary aerosol during particulate air pollution period in Baoji.

The strong increase of sulfate in polluted days is associated with high RH, suggesting aqueous-phase oxidation of SO_2 could be an important process for sulfate formation as reported in previous studies (Sun et al., 2013b; Elser et al., 2016). The large increase of nitrate from 9% during clean days to 18% during polluted days, however, is likely associated with the decrease of temperature which facilitates the gas-to-particle partitioning of semivolatile NH_4NO_3 . Compared to the SIAs, the formation of OOAs is still very uncertain, especially during particulate pollution period. Here the correlation of two OOAs with atmospheric oxidative capacity and meteorological conditions are further evaluated to better understand the factors governing SOA formation.

Data at the daily maximum solar radiation ± 2 h are analyzed to capture the period of highest photochemical activities. As shown in Fig. 7, the increases of $f_{\text{LO-OOA}}$ (the mass fraction of LO-OOA in OA) and $f_{\text{MO-OOA}}$ (the mass fraction of MO-OOA in OA) are accompanied with the increased odd oxygen ($\text{O}_x = \text{O}_3 + \text{NO}_2$) and solar radiation, indicating that the formation of OOAs is driven by the photochemical reactions. The fitted line for the $f_{\text{LO-OOA}}$ vs. O_x has a slope of 0.0019, while that for $f_{\text{MO-OOA}}$ vs. O_x is 0.0014. This suggests that the formation of LO-OOA is faster than MO-OOA, likely due to the enhanced emissions of volatile organic compounds (VOCs) in the pollution area which compete with the production of MO-OOA. Fig. 8 shows that the formation of LO-OOA and MO-OOA is also influenced by relative humidity (RH). When $\text{RH} > 60\%$ which is typical value during haze pollution events, both $f_{\text{LO-OOA}}$ and $f_{\text{MO-OOA}}$ are positively correlated with RH. In particular at low atmospheric oxidative capacity (i.e., $\text{O}_x = 40\text{--}70 \mu\text{g m}^{-3}$), $f_{\text{LO-OOA}}$ and $f_{\text{MO-OOA}}$ are linearly correlated with RH, suggesting the importance of aqueous-phase chemistry in the formation of SOA.

4. Conclusions

An Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc.) was deployed in Baoji from 26 February to 27 March 2014. The non-refractory submicron aerosol (NR-PM₁) is dominated by organics (55%), followed by sulfate (16%), nitrate (15%), ammonium (11%) and chloride (3%). Six OA factors were identified and classified as HOA, COA, BBOA, CCOA, LO-OOA and MO-OOA, which contributed 20%, 14%, 13%, 9%, 23% and 21%, to total OA respectively. The contribution of secondary components shows increasing trends from clean days to polluted days. The strong increase of sulfate in polluted days is associated with high RH, suggesting aqueous-phase oxidation of SO₂ could be an important process for sulfate formation. The large increase of nitrate is likely associated with the decrease of temperature which facilitates the gas-to-particle partitioning of semivolatile NH₄NO₃. The formation of LO-OOA and MO-OOA are mainly driven by photochemical reactions, but influenced by the aqueous-phase process particularly at low atmospheric oxidative capacity. Our study suggests the importance in reduction of the precursors of secondary aerosols to mitigate the PM pollution in Baoji. Further, due to the fact that middle size ordinary cities (e.g., Baoji) constitute the main portion (~70%) of Chinese cities, the measurement and data analysis techniques and even some results found in this study may be applicable to other middle size cities in China, potentially facilitating their efforts to design effective mitigation measures.

Acknowledgements

This research is supported by the National Science Foundation of China (No. 91644219, No. 41403110 and No. 41673134), the Shaanxi Government (2012KTZB03-01-01), projects from "Strategic Priority Research Program" of the Chinese Academy of Science (Grant No. XDB05060500 XDA05100401) and projects from Ministry of Science and Technology (2013FY112700).

References

Alfarra, M. R., Prévôt, A. S. H., Szidat, S., Sandradewi, J., Weimer, S., Schreiber, D., Mohr, M., Baltensperger, U., 2007. Identification of the mass spectral signature of organic aerosols from wood burning emissions. *Environ. Sci Technol.* 41, 5770–5777.

Aliche, B., Geyer, A., Hofzumahaus, A., Holland, F., Konrad, S., Pätz, H. W., Schäfer, J.,
 Stutz, J., Volz-Thomas, A., Platt, U., 2003. OH formation by HONO photolysis
 during the BERLIOZ experiment. *J. Geophys. Res.* 108 D4), 8247.

Allan, J. D., Williams, P. I., Morgan, W. T., Martin, C. L., Flynn, M. J., Lee, J., Nemitz, E.,
 Phillips, G. J., Gallagher, M. W., Coe, H., 2010. Contributions from transport, solid
 fuel burning and cooking to primary organic aerosols in two UK cities. *Atmos. Chem.*
Phys. 10, 647–668.

Canagaratna, M. R., Jayne, J. T., Ghertner, D. A., Herndon, S., Shi, Q.,
 Jimenez, J. L., Silva, P. J., Williams, P., Lanni, T., Drewnick, F., Demerjian, K. L.,
 Kolb, C. E., Worsnop, D. R., 2004. Chase studies of particulate emissions from in-use
 New York City vehicles. *Aerosol Sci. Tech.* 38, 555–573.

Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q.,
 Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R.,
 Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P.,
 Worsnop, D. R., 2007. Chemical and microphysical characterization of ambient
 aerosols with the aerodyne aerosol mass spectrometer. *Mass Spectrom Rev.* 26(2),
 185–222.

Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., Prévôt, A. S. H., 2013. SoFi,
 an Igor based interface for the efficient use of the generalized multilinear engine
 (ME-2) for source apportionment: application to aerosol mass spectrometer data.
Atmos. Meas. Tech. 6 3649–3661.

Canonaco, F., Slowik, J. G., Baltensperger, U., Prévôt, A. S. H., 2015. Seasonal
 differences in oxygenated organic aerosol composition: implications for emissions
 sources and factor analysis. *Atmos. Chem. Phys.* 15, 6993–7002.

Cao, J., Xu, H., Xu, Q., Chen B., Kan H., 2012a. Fine particulate matter constituents and
 cardiopulmonary mortality in a heavily polluted Chinese city. *Environ. Health*
Perspect. 120(3), 373–378.

Cao, J. J., 2012b. Pollution status and control strategies of PM_{2.5} in China. *J. Earth*
Environ. 3, 1030–1036.

Cao, J. J., Shen, Z. X., Chow, J. C., Watson, J. G., Lee, S. C., Tie, X. X., Ho, K. F., Wang,
 G. H., Han, Y. M., 2012c. Winter and summer PM_{2.5} chemical compositions in

fourteen Chinese cities. *J. Air Waste Manag. Assoc.* 62(10), 1214-1226.

Chan, C. K., Yao, X., 2008. Air pollution in mega cities in China. *Atmos. Environ.* 42(1), 1–42.

Chang, D., Song, Y., Liu, B., 2009. Visibility trends in six megacities in China 1973–2007. *Atmos. Res.* 94, 161–167.

Crippa, M., DeCarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., Nicolas, J. B., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J. Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J.-L., Prévôt, A. S. H., Baltensperger, U., 2013. Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris. *Atmos. Chem. Phys.* 13(2), 961–981.

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis, D., Dall’Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A.-M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O’Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U., Prévôt, A. S. H., 2014. Organic aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach. *Atmos. Chem. Phys.* 14, 6159– 6176.

Dall’Osto, M., Ovadnevaite, J., Ceburnis, D., Martin, D., Healy, R. M., O’Connor, I. P., Kourtchev, I., Sodeau, J. R., Wenger, J. C., O’Dowd., 2013. Characterization of urban aerosol in Cork city (Ireland) using aerosol mass spectrometry. *Atmos. Chem. Phys.* 13, 4997–5015.

Elser, M., Huang, R.-J., Wolf, R., Slowik, J. G., Wang, Q., Canonaco, F., Li, G., Bozzetti, C., Daellenbach, K. R., Huang, Y., Zhang, R., Li, Z., Cao, J., Baltensperger, U., El-Haddad, I., Prévôt, A. S. H., 2016. New insights into PM_{2.5} chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry. *Atmos. Chem. Phys.* 16, 3207-3225.

Forster, P., et al., 2007. Changes in atmospheric constituents and in radiative forcing, in Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change edited by S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, and H. L. Miller. Cambridge University Press, New York, NY.

Fröhlich, R., Crenn, V., Setyan, A., Belis, C. A., Canonaco, F., Favez, O., Riffault, V., Slowik, J. G., Aas, W., Aijälä, M., Alastuey, A., Artiñano, B., Bonnaire, N., Bozzetti, C., Bressi, M., Carbone, C., Coz, E., Croteau, P. L., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Jayne, J. T., Lunder, C. R., Minguillón, M. C., Mocnik, G., O'Dowd, C. D., Ovadnevaite, J., Petralia, E., Poulain, L., Priestman, M., Ripoll, A., Sarda-Estève, R., Wiedensohler, A., Baltensperger, U., Sciare, J., and Prévôt, A. S. H., 2015. ACTRIS ACSM intercomparison–Part 2: Intercomparison of ME-2 organic source apportionment results from 15 individual, co-located aerosol mass spectrometers. *Atmos. Meas. Tech.* 8, 2555–2576.

He, L.-Y., Lin, Y., Huang, X.-F., Guo, S., Xue, L., Su, Q., Luan, S.-J., Zhang, Y.-H., 2010. Characterization of high-resolution aerosol mass spectra of primary organic aerosol emissions from Chinese cooking and biomass burning. *Atmos. Chem. Phys.* 10, 11535–11543.

He, L.-Y., Huang, X.-F., Xue, L., Hu, M., Lin, Y., Zheng, J., Zhang, R., and Zhang, Y.-H., 2011. Submicron aerosol analysis and organic source apportionment in an urban atmosphere in Pearl River Delta of China using high-resolution aerosol mass spectrometry. *J. Geophys. Res. Atmos.* 116, D12304.

Hu, W. W., Hu, M., Yuan, B., Jimenez, J. L., Tang, Q., Peng, J. F., Hu, W., Shao, M., Wang, M., Zeng, L. M., Wu, Y. S., Gong, Z. H., Huang, X. F., He, L. Y., 2013. Insights on organic aerosol aging and the influence of coal combustion at a regional receptor site of central eastern China. *Atmos. Chem. Phys.* 13, 10095-10112.

Hu, W., Hu, M., Hu, W., Jimenez, J.-L., Yuan, B., Chen, W., Wang, M., Wu, Y., Chen, C., Wang, Z., Peng, J., Zeng, L., Shao M., 2016. Chemical composition, sources, and aging process of submicron aerosols in Beijing: Contrast between summer and winter. *J. Geophys. Res. Atmos.* 121, 1955–1977.

538 Huang, R.-J., Zhang, Y.L., Bozzetti, C., Ho, K.-F., Cao, J.J., Han, Y.M., Daellenbach, K.R.,
 539 Slowik, J.G., Platt, S.M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S.M., Bruns, E.A.,
 540 Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G.,
 541 Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad,
 542 I.E., Prévôt, A. S. H., 2014. High secondary aerosol contribution to particulate
 543 pollution during haze events in China. *Nature* 514, 218-222.

544 Huang, X. F., He, L. Y., Xue, L., Sun, T. L., Zeng, L. W., Gong, Z. H., Hu, M., Zhu, T.,
 545 2012. Highly time-resolved chemical characterization of atmospheric fine particles
 546 during 2010 Shanghai World Expo. *Atmos. Chem. Phys.* 12(11), 4897-4907.

547 Jimenez, J. L. , Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J.
 548 H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S.,
 549 Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K.
 550 R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T.,
 551 Rautiainen, J., Vaattovaara, P., Ehn, M. Kulmala, M., Tomlinson, J. M., Collins, D.
 552 R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R.,
 553 Williams, P. I., Bower, K. Kondo, Y. Schneider, J. , Drewnick, F., Borrmann,
 554 S. , Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A.,
 555 Miyoshi, T., Hatakeyama, S., Shimojo, A. Sun, J. Y., Zhang, Y. M., Dzepina, K.,
 556 Kimmel, J. R. Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L.
 557 R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., Worsnop, D. R.,
 558 2009. Evolution of organic aerosols in the atmosphere, *Science* 326 (5959),
 559 1525–1529.

560 Lanz, V. A., Alfarra, M., Baltensperger, U., Buchmann, B., Hueglin, C., Szidat, S.,
 561 Wehrli, M., Wacker, L., Weimer, S., Caseiro, A., Puxbaum, H., Prévôt, A., 2008.
 562 Source attribution of submicron organic aerosols during wintertime inversions by
 563 advanced factor analysis of aerosol mass spectra. *Environ. Sci. Technol.* 42, 214–220.

564 Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A.
 565 S. H., 2009. Source apportionment of submicron organic aerosols at an urban site by
 566 factor analytical modelling of aerosol mass spectra, *Atmos. Chem. Phys.* 7,

1503-1522.

Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., Pozzer, A., 2015. The contribution of outdoor air pollution sources to premature mortality on a global scale, *Nature* 525, 367–371.

Li, G., Lei, W., Zvala, M., Volkamer, R., Dusanter, S., Stevens, P. S., Molina, L. T., 2010. Impacts of HONO sources on the photochemistry in Mexico City during the MCMA-2006/MILAGO campaign. *Atmos. Chem. Phys.* 10, 6551–6567.

Li, Y. J., Lee, B. P., Su, L., Fung, J. C. H., Chan, C.K., 2015. Seasonal characteristics of fine particulate matter (PM) based on high resolution time-of-flight aerosol mass spectrometric (HR-ToFAMS) measurements at the HKUST Supersite in Hong Kong. *Atmos. Chem. Phys.* 15, 37–53.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., Canagaratna, M. R., 2012. Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data. *Aerosol Sci. Tech.* 46(3), 258-271.

Mohr, C., Huffman, J. A., Cubison, M. J., Aiken, A. C., Docherty, K. S., Kimmel, J. R., Ulbrich, I. M., Hannigan, M., Jimenez, J. L., 2009. Characterization of primary organic aerosol emissions from meat cooking, trash burning, and motor vehicles with high-resolution aerosol mass spectrometry and comparison with ambient and chamber observations. *Environ. Sci. Technol.* 43, 2443–2449.

Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Peñuelas, J., Jiménez, J. L., Crippa, M., Zimmermann, R., Baltensperger, U., Prévôt, A. S. H., 2012. Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data. *Atmos. Chem. Phys.* 12, 1649–1665.

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y., Worsnop, D. R., 2010. Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry. *Atmos. Chem. Phys.* 10, 4625–4641.

597 Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B.,
 598 Sueoer, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., Jayne, J. T., 2011a. An Aerosol
 599 Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and
 600 mass concentrations of ambient aerosol. *Aerosol Sci. Technol.* 45(7), 770–784.

601 Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Zhang, Q., Ulbrich, I. M., Worsnop, D. R.,
 602 2011b. Real-time methods for estimating organic component mass concentrations
 603 from aerosol mass spectrometer data. *Environ. Sci. Technol.* 45, 910–916.

604 Paatero, P., Tapper, U., 1994. Positive Matrix Factorization: a nonnegative factor model
 605 with optimal utilization of error estimates of data values. *Environmetrics* 5, 111–126.

606 Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis,
 607 *Chemometr. Intell. Lab.* 37, 23–35.

608 Paatero, P., 1999. The multilinear engine: A table-driven, least squares program for
 609 solving multilinear problems, including the n-way parallel factor analysis model. *J.*
 610 *Comput. Graph. Stat.* 8, 854–888.

611 Pope, C. A., D. W. Dockery., 2006. Health effects of fine particulate air pollution: Lines
 612 that connect. *J. Air Waste Manage. Assoc.* 56, 709–742.

613 Sun, J. Y., Zhang, Q., Canagaratna, M. R., Zhang, Y. M., Ng, N. L., Sun, Y. L., Jayne, J. T.,
 614 Zhang, X. C., Zhang, X. Y., , Worsnop, D. R., 2010. Highly time- and size-resolved
 615 characterization of submicron aerosol particles in Beijing using an Aerodyne Aerosol
 616 Mass Spectrometer. *Atmos. Environ.* 44(1), 131–140.

617 Sun, Y. L., Wang, Z. F., Fu, P. Q., Yang, T., Jiang, Q., Dong, H. B., Li, J., Jia, J. J., 2013a.
 618 Aerosol composition, sources and processes during wintertime in Beijing, China.
 619 *Atmos. Chem. Phys.* 13(9), 4577–4592.

620 Sun, Y. L., Wang, Z., Fu, P., Jiang, Q., Yang, T., Li, J., Ge, X., 2013b. The impact of
 621 relative humidity on aerosol composition and evolution processes during wintertime
 622 in Beijing, China. *Atmos. Environ.* 77, 927–934.

623 Sun, Y., Jiang, Q., Wang, Z., Fu, P., Li, J., Yang, T., Yin, Y., 2014. Investigation of the
 624 sources and evolution processes of severe haze pollution in Beijing in January 2013. *J.*
 625 *Geophys. Res. Atmos.* 119, 4380–4398.

626 Sun, Y. L., Wang, Z. F., Du, W., Zhang, Q., Wang, Q. Q., Fu, P. Q., Pan, X. L., Li, J.,

Jayne, J., Worsnop, D. R., 2015. Longterm real-time measurements of aerosol particle composition in Beijing, China: seasonal variations, meteorological effects, and source analysis. *Atmos. Chem. Phys.* 15, 10149–10165.

Sun, Y., Du, W., Fu, P., Wang, Q., Li, J., Ge, X., Zhang, Q., Zhu, C., Ren, L., Xu, W., Zhao, J., Han, T., Worsnop, D. R., Wang, Z., 2016. Primary and secondary aerosols in Beijing in winter: sources, variations and processes. *Atmos. Chem. Phys.* 16, 8309-8329.

Takegawa, N., Miyakawa, T., Kondo, Y., Jimenez, J. L., Zhang, Q., Worsnop, D. R., Fukuda, M., 2006. Seasonal and diurnal variations of submicron organic aerosol in Tokyo observed using the Aerodyne aerosol mass spectrometer. *J. Geophys. Res. Atmos.* 111.

Tie, X., Huang, R.-J., Dai, W.-T., Cao, J. J., Long, X., Su, X. L., Zhao, S. Y., Wang, Q. Y., Li, G. H., 2016. Effect of heavy haze and aerosol pollution on rice and wheat productions in China. *Sci. Rep.* 6, 29612.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., Jimenez, J. L., 2009. Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, *Atmos. Chem. Phys.*, 9, 2891-2918.

Watson, J. G., Robinson, N. F., Lewis, C., Coulter, T., Chow, J. C., Fujita, E. M., Lowenthal, D., Conner, T. L., Henry, R. C., Willis, R. D., 1997. Chemical Mass Balance Receptor Model Version 8 (CMB8) User's Manual, Prepared for US Environmental Protection Agency, Research Triangle Park, NC, by Desert Research Institute, Reno, NV.

Watson, J. G., 2002. Visibility: Science and regulation. *J. Air Waste Manag. Assoc.* 52 (6), 628–713.

Wang, G., Xie, M., Hu, S., Gao, S., Tachibana, E., Kawamura, K., 2010. Dicarboxylic acids, metals and isotopic compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal burning emission and secondary aerosol formation. *Atmos. Chem. Phys.* 10, 6087–6096.

Wang, J., Ge, X., Chen, Y., Shen, Y., Zhang, Q., Sun, Y., Xu, J., Ge, S., Yu, H., Chen, M., 2016. Highly time-resolved urban aerosol characteristics during springtime in Yangtze

River Delta, China: insights from soot particle aerosol mass spectrometry. *Atmos. Chem. Phys.* 16, 9109-9127.

Wu, D., 2004. Demographics of the County and City in China. Department of the Ministry of Public Security, China. Qunzhong Press Beijing, pp. 91–106.

Xiao, S., Wang, Q.Y., Cao, J.J., Huang, R.J., Chen, W.D., Han, Y.M., Xu, H.M., Liu, S.X., Zhou, Y.Q., Wang, P., Zhang, J.Q., Zhan, C.L., 2014. Long-term trends in visibility and impacts of aerosol composition on visibility impairment in Baoji, China. *Atmos. Res.* 149, 88–95.

Xie, M., Wang, G., Hu, S., Han, Q., Xu, Y., Gao, Z., 2009. Aliphatic alkanes and polycyclic aromatic hydrocarbons in atmospheric PM10 aerosols from Baoji, China: Implications for coal burning. *Atmos. Res.* 93, 840–848.

Xu, J., Zhang, Q., Chen, M., Ge, X., Ren, J., Qin, D., 2014. Chemical composition, sources, and processes of urban aerosols during summertime in northwest China: insights from high-resolution aerosol mass spectrometry. *Atmos. Chem. Phys.* 14(23), 12593-12611.

Xu, J., Shi, J., Zhang, Q., Ge, X., Canonaco, F., Prévôt, A. S. H., Vonwiller, M., Szidat, S., Ge, J., Ma, J., An, Y., Kang, S., Qin, D., 2016. Wintertime organic and inorganic aerosols in Lanzhou, China: sources, processes, and comparison with the results during summer, *Atmos. Chem. Phys.*, 16, 14937-14957.

Yan, J., Chen, L., Lin, Q., Li, Z., Chen, H., Zhao, S., 2015. Chemical characteristics of submicron aerosol particles during a long-lasting haze episode in Xiamen, China. *Atmos. Environ.* 113, 118-126.

Zhang, R., Wang, G., Guo, S., Zamora, M. L., Ying, Q., Lin, Y., Wang, W., Hu, M., and Wang, Y., 2015a. Formation of urban fine particulate matter. *Chem. Rev.* 115, 3803–3855.

Zhang, Y. J., Tang, L. L., Wang, Z., Yu, H. X., Sun, Y. L., Liu, D., Qin, W., Canonaco, F., Prévôt, A. S. H., Zhang, H. L., Zhou, H. C., 2015b. Insights into characteristics, sources, and evolution of submicron aerosols during harvest seasons in the Yangtze River Delta region, China. *Atmos. Chem. Phys.* 15(3), 1331–1349.

Zhou, W., Jiang, J., Duan, L., Hao, J., 2016. Evolution of submicron organic aerosols

during a complete residential coal combustion process. Environ. Sci. Technol. 50,
7861–7869.

Fig. 1. (a) Time series of NR-PM₁ species, (b) relative contributions of NR-PM₁ species for the entire study period. The number on the top of the pie chart is the average mass concentration of total NR-PM₁ species.

Fig.2. (a) Comparison of $PM_{2.5}$ and $NR-PM_1$ mass concentrations in this study, (b) $NR-PM_1$ mass concentrations at five cities in Asia during springtime. The data of other cities are taken from Takegawa et al. (2006), Li et al. (2015), Sun et al. (2015) and Wang et al. (2016).

Fig.3. Diurnal variations for NR-PM₁ species. Data of sulfate, nitrate and ammonium are multiplied by a factor of 3, data of chloride is multiplied by a factor of 10.

Fig. 4. Mass spectrums (left) and time series (right) of six resolved OA sources. Error bars of mass spectrums represent the standard deviation of each m/z over all accepted solutions..

Fig. 5. (a) Diurnal variations of OA sources, (b) mass fractions of OA sources.

Fig. 6. Mass fractions of NR-PM₁ species and OA sources in (a) clean days, (b) less-polluted days and (c) polluted days. We denote the days with NR-PM₁ daily average mass concentration below the 25th quartile as the clean days, within the 25-75th interquartile range as the less-polluted days, and higher than the 75th quartile as the polluted days.

898

899 **Fig. 7.** (a) Scatter plots of f_{LO-OOA} versus O_x concentration at the daily maximum solar radiation ± 2 h,
900 (b) Scatter plots of f_{MO-OOA} versus O_x concentration at the daily maximum solar radiation ± 2 h. Data
901 are color coded according to the solar radiation ($W M^{-2}$).

902

903

904

905

906

907

908

909

910

911

912

913

914

915

916

917

918

919

920

921

922

923

924

925

Fig. 8. (a) Scatter plots of $f_{\text{LO-OOA}}$ versus RH (>60%) in the daytime (8:00-18:00), (b) Scatter plots of $f_{\text{MO-OOA}}$ versus RH (>60%) in the daytime (8:00-18:00). Data are color coded according to the O_x concentration ($\mu\text{g m}^{-3}$). The black lines fit over data with low O_x (40-70 $\mu\text{g m}^{-3}$).