Chemical Characteristics and Source Apportionment of PM$_{2.5}$ during winter in South Urumqi, China

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Abstract

Urumqi, the administrative center of Xinjiang, suffers from severe atmospheric aerosol pollution; however, no study has comprehensively analyzed the local constituents and sources of fine particulate matter (PM$_{2.5}$). Characteristics of PM$_{2.5}$ in Urumqi in winter were observed after the energy switch from coal to natural gas. Enrichment factors, backward trajectories, the potential source contribution function (PSCF) model, and positive matrix factorization (PMF) were used to identify the source area and categories. The results showed that the mean concentration of PM$_{2.5}$ was 197.40 $\mu$g m$^{-3}$ and significantly decreased after the conversion from coal to natural gas. Although the concentration of NO$_3^-$ increased, SO$_4^{2-}$ and Cl$^-$ decreased 42.54% and 32.93%, respectively. Water-soluble ions (WSIs) were mainly present as NH$_4$HSO$_4$, CaSO$_4$, MgSO$_4$, Ca(NO$_3$)$_2$, Mg(NO$_3$)$_2$, and KCl. Elements such as Pb, Cr, and As decreased compared with before the fuel switch. There was a strong correlation between organic carbon and element carbon, and the mean concentration of secondary organic carbon was 18.90 $\mu$g m$^{-3}$. Pyr, Chr, BbF, BkF, IcdP, and BghiP were the most prevalent individual polycyclic aromatic hydrocarbons, and BaP exceeded health-based guidelines. Trajectory clustering and the PSCF method

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suggested that both inside and outside the city and the typical topography might be the main factors to form the heavy PM$_{2.5}$ pollution in south Urumqi. PMF identified five primary sources: secondary formation, biomass and waste burning, vehicle emissions, crustal minerals, and industrial pollution and coal combustion.

**Keyword:** Fine particulate matter; Chemical composition; Source apportionment; Urumqi
INTRODUCTION

Air pollution in China is increasingly severe because of rapid economic growth, urbanization, and industrialization. This problem seriously threatens human health and the environment. Atmospheric particulate matter (PM) originates from human and natural sources and also forms after the conversion of precursor gases into secondary particles through photochemical reactions (Chen et al., 2017a; Chen et al., 2017b). PM varies in shape, size, surface area, solubility, and chemical composition depending on the source and subsequent atmospheric chemical reactions; therefore, its characteristics differ by region (Hassan and Khoder, 2017). Numerous studies have demonstrated that PM can damage human health directly as well as indirectly through influence on climate and food security. Recently, atmospheric PM$_{2.5}$ (PM with aerodynamic diameter $< 2.5$ $\mu$m) has attracted worldwide attention because its small size can penetrate the human lungs (Jiang et al., 2018). The sum of major components, including trace elements, water-soluble ions (WSIs), organic carbon (OC), elemental carbon (EC), and polycyclic aromatic hydrocarbons (PAHs), accounts for more than 60% of PM$_{2.5}$ (Lonati et al., 2005).

Aust et al. (2002) reported that transition metals are a major toxic component of the toxicity of PM. EC is emitted from a variety of combustion processes and directly influences climate and causes atmospheric warming (Ramanathan and Carmichael, 2008). Consistent evidence demonstrates a causal relationship between PAHs and cancer risk, and the International Agency for Research on Cancer classified
benzo[a]pyrene (BaP) as a Group 1 carcinogen (Wei et al., 2010). Sun et al. (2014) found that WSIs promote haze formation during haze episodes.

PM$_{2.5}$ levels in many Chinese cities frequently exceed the National Ambient Air Quality Standards (NAAQS), especially in winter (Chen et al., 2017a; Chen et al., 2017b). Xinjiang is a developing province in China with the administrative center at Urumqi, which is undergoing rapid economic development, urbanization, population growth, and a critical increase in traffic. In recent years, Urumqi has experienced severe air pollution. In the 2011 World Health Organization (WHO) air quality rankings of 1083 cities, Urumqi ranked 1053, the third worst in China (Xia et al., 2016).

The rapid deterioration of the atmosphere in Urumqi is related to a variety of factors. Most influential are the excessive amount of anthropogenic pollutants and typical topography. Under the national energy relocation program and to promote regional economy, Xinjiang energy industries have been booming in the past decades (Dorian et al., 1999). With the rapid economic development and urbanization, the sources of air pollution in Urumqi have gradually shifted from conventional dust storms to a mixture of dust storms, coal-burning emissions, vehicle emissions, and industrial emissions. The urban area of Urumqi is located on the alluvial plain of the northern foothills of the central Tianshan Mountains (only one mouth facing north exists). The topography of Urumqi causes unique meteorological conditions characterized by a stable atmosphere and calm winds, which are extremely
unfavorable to the transmission and diffusion of air pollutants. Moreover, the 6-month heating period (October through March) enhances precursor gas accumulation. Furthermore, subject to the high pressure over Mongolia in winter, Urumqi frequently experiences foehns, and interactions between foehns and valley winds cause severe air pollution (Li et al., 2015). Daily concentrations of PM$_{2.5}$ reached 263.77 μg m$^{-3}$ in the winter of 2010–2011 in Urumqi, far exceeding the National Ambient Air Quality Standard (NAAQS-II, GB3095) of 35 μg m$^{-3}$ (Limu et al., 2013). In 2012, to rapidly reduce the air pollution caused by coal-fired heating, the municipal government implemented a heating energy structure adjustment strategy that uses natural gas instead of raw coal as fuel. However, Urumqi is still suffering heavy air pollution and haze during the wintertime. Thus, air pollution has been extensively studied in Urumqi (Li et al., 2008a; Mamtimin and Meixner, 2011; Ren et al., 2017; Song et al., 2015; Wang et al., 2017; Xia et al., 2016). These studies demonstrated that high concentrations of particulate matter, SO$_2$ and NOx in this city, making it one of the most polluted in the world. And Urumqi is located in source area of Asian dust and the mineral dust mixes with anthropogenic aerosol have a great impact on the regional environment and global climate change. Moreover, the chemical characteristics and formation mechanisms of air pollution are different from other cities in China. Thus, intensive environmental surveys in Urumqi would allow better assessing the impact of humans' activities on environment in Urumqi as well as other Chinese cities.

Therefore, the present study collected PM$_{2.5}$ data during the winter of 2012–2013
(the first winter after the conversion from coal to gas) in Urumqi. The objectives of were (1) to determine the level of PM$_{2.5}$ after the switch to natural gas, (2) to reveal the chemical profile of PM$_{2.5}$ during winter in Urumqi, and (3) to analyze the various combinations of PM$_{2.5}$ chemical components to obtain potential sources. The results provide valuable information for more effective PM$_{2.5}$ control in Urumqi or other cities in northwest China during winter.

**METHODOLOGY**

**PM$_{2.5}$ sampling**

The sampling site was located on the roof (15 m above ground level) of the building of the Chemistry and Chemical Engineering College at Xinjiang University (43°77′ N, 87°61′ E) in Tianshan District. The sampling site was under the influence of residential, traffic, and construction emissions and representative of urban Urumqi. Daily PM$_{2.5}$ samples were collected from 10:00 a.m. to the following day 8:00 a.m. by using a high-volume air sampler (Wuhan Tianhong Instruments Co., Ltd., TH-1000) at a flow rate of 1.05 m$^3$ min$^{-1}$. A total of 38 aerosol samples, including 34 daily samples and 4 filed blank samples, were collected on 47-mm quartz microfiber (QMA, Whatman, Mainstone, UK) filters from October 16, 2012, to May 3, 2013. The filters were prebaked for 4 h at 480°C to remove organic and inorganic materials. Before and after sampling, the quartz filters were equilibrated for 48 h in a desiccator at a constant temperature of 25°C and relative humidity of 45%. Each filter was weighed at least three times. After sampling, the filters were wrapped in aluminum foil and
stored at −20°C to prevent evaporation of volatilized components. Daily meteorological data including wind speed, temperature, relative humidity, and visibility during the sampling period were obtained from a website (https://www.wunderground.com).

**Chemical analysis**

A punch was extracted from each filter and submerged in HNO₃ (10 mL, 69%) and HClO₄ (4 mL, 70%) in acid-cleaned glass test tubes. The mixtures were left overnight and heated progressively to 170°C in a heating digester for 4 h to near dryness. After the test tubes were cooled, the solutions were filtered into 50-mL volumetric flasks using 1% HNO₃ and then decanted into acid-cleaned polyethylene tubes. Cr, Co, Ni, Cu, Zn, Pb, and Mn metals were analyzed using an atomic absorption spectrometer; Hg and As were detected using a dual-channel atomic fluorescence photometer. The standard deviations of each element were less than 5%. Field and laboratory blanks were extracted and analyzed in the same manner as the field samples.

A punched-out section of the quartz filter was placed into a centrifuge tube and submerged in 10 mL of ultrapure water (resistivity = 18.25 MΩ cm). To completely dissolve all the WSIs, the tubes were shaken twice through ultrasound at a low temperature (< 10°C) for 20 min each time and subsequently centrifuged at 11,000 revolutions per minute for 12 min. The solution was filtered through a polytetrafluorethyylene membrane (Whatman, Middlesex UK) with a 0.22-μm pore
size, transferred to clean plastic bottles, and stored at 4°C in a refrigerator for analysis. Field and laboratory blanks were also analyzed in the same manner as samples.

Five cations (Ca\(^{2+}\), NH\(_4\)^{+}, Mg\(^{2+}\), K\(^{+}\), and Na\(^{+}\)) and four anions (NO\(_3\)^{−}, SO\(_4\)^{2−}, Cl\(^{−}\), and F\(^{−}\)) were analyzed through ion chromatography (IC, 883 Basic IC plus, Metrohm AG, Switzerland). The MagIC Net 2.0 workplace was used to calculate the concentration of WSIs. In this study the detection limits of the IC system were 0.0018, 0.006, 0.007, 0.006, 0.013, 0.007, 0.009, and 0.0105 mg L\(^{−1}\) for Ca\(^{2+}\), NH\(_4\)^{+}, Mg\(^{2+}\), K\(^{+}\), Na\(^{+}\), NO\(_3\)^{−}, SO\(_4\)^{2−}, Cl\(^{−}\), and F\(^{−}\), respectively. The recovery of each ion was 90%–105%.

A punch of each filter (0.5 cm\(^{2}\)) was analyzed for OC and EC using an Optical Carbon Analyzer (Desert Research Institute, DRI Model 2015, Sunset Laboratory Inc., USA). OC fractions were produced in a helium atmosphere, and EC fractions were produced in a 2% oxygen/8% helium atmosphere. The detection limits for OC and EC were 0.05 \(\mu\)g.

Analysis of PAHs followed the method described by Gao et al. (2012) and Yu et al. (2016). Before solvent extraction, a mixture of three isotopes of labeled PAH compounds (phenanthrene-d10, chrysene-d12, and perylene-d12), tetracosane-d50, and levoglucosan-\(^{13}\)C\(_{6}\) were added as surrogates prior to extraction. The quartz was ultrasonically extracted twice for 20 min under a low temperature (<10°C) with a mixed solvent of dichloride methane (DCM)/hexane (1:1, vol/vol), then extracted twice with a mixed solvent of DCM/methanol (1:1, vol/vol). The extracts were
purified by an anhydrous sodium sulfate column to remove potentially interfering compounds. The extracts of each sample were combined. The samples were concentrated to a volume of approximately 2 mL with a rotary evaporator and further concentrated to a volume of 0.5 mL through nitrogen blow-down. Subsequently, 200 μL of DCM, 10 μL of methanol, and 300 μL of freshly diazomethane were added and maintained at room temperature for 1 h. The extracts were then analyzed for PAHs using a gas chromatography–mass spectrometry system (Agilent, 6890-5973N) equipped with a DB-5MS column (50 m, 0.32 mm, 0.17 μm). Concentrations of 17 PAHs were quantified in this study, with the following elution order: naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), BaP, indeno[1,2,3-cd]pyrene (IcdP), benzo[g,h,i]perylene (BghiP), dibenz[a,h]anthracene (DahA), and coronene (Cor).

The field and laboratory blanks were analyzed using the same method, and none of the target compounds were detected. Recoveries for all compounds were higher than 90%. The aforementioned measurement procedures underwent strict quality control and quality assurance to avoid possible contamination of the samples.

Pollution pathways and source area

Transport pathways and source regions can influence local air quality (Zhang et al., 2013; Tan et al., 2017). To address this, both trajectory clustering and the potential
source contribution function (PSCF) method were used. The 48-h air mass back trajectories were investigated using the hybrid single-particle Lagrangian integrated trajectory (Hysplit) model. The meteorological field was obtained from National Oceanic and Atmospheric Administration’s Air Resources Laboratory (ARL) archives, and the model was run at a height of 100 m above ground level with a time interval of 1 h. The total trajectories were used for cluster analysis in the geographic information system-based software TrajStat.

The PSCF model has been widely used to identify potential source areas of pollutants. In the current study, this model was implemented using TrajStat based on the results of the Hysplit. The study domain was 20.00–60.00° N, 65.00–100.00° E with a horizontal resolution of 0.5° × 0.5°. The weighting function \( W_{ij} \) was adopted to accurately reflect the uncertainty in cells with a small number of endpoints that fall within cell \( ij \). In this study, the daily average PM\(_{2.5}\) concentration standard (75 µg m\(^{-3}\)) was treated as the pollution threshold (Zhang et al., 2013; Zhao et al., 2015).

\[
W_{ij} = \begin{cases} 
1.00, & 80 < n_{ij} \\
0.70, & 20 < n_{ij} \leq 80 \\
0.42, & 10 < n_{ij} \leq 20 \\
0.05, & n_{ij} \leq 10 
\end{cases} \quad (1)
\]

Source apportionment analysis

Source apportionment analysis is vital to developing effective control strategies for PM\(_{2.5}\). Positive matrix factorization (PMF) is an effective mathematical receptor model recommended by the US Environmental Protection Agency (EPA) and has been used worldwide for source apportionment for PM\(_{2.5}\). The principle of PMF is
minimizing the objective function $Q$, which was determined as follows:

$$Q = \frac{m}{n} \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]$$  \hspace{1cm} (2)

In this function, $x_{ij}$ and $u_{ij}$ are the concentration (Con) and uncertainty (Unc) of the $j$th species in the $i$th sample, $f_{kj}$ is the fraction of the $j$th species from the $k$th source, $g_{ik}$ indicates the contribution of the $k$th source to the $i$th sample, $p$ is the number of sources, and $m$ and $n$ are the total number of species and samples, respectively.

Detailed description can be found in other studies (Paatero and Tapper, 1994; Hopke, 2016).

This model required Con and Unc input data. Values below the method detection limit (MDL) were substituted with half the MDL, and missing data were substituted with the median Con. Unc is calculated by the following equation if the concentration is higher than the MDL:

$$Unc = \sqrt{(ErrorFraction \times Con)^2 + (0.5 \times MDL)^2} \hspace{1cm} (3)$$

If the concentration is less than or equal to the MDL,

$$Unc = \frac{5}{6} MDL \hspace{1cm} (4)$$

In this study, PMF5.0 was employed for source apportionment. The input data included PM$_{2.5}$, OC, EC, Ca$^{2+}$, NH$_4^+$, Mg$^{2+}$, K$^+$, Na$^+$, NO$_3^-$, SO$_4^{2-}$, Cl$^-$, F$^-$, Cr, Co, Ni, Cu, Zn, Pb, Mn, and As. PM$_{2.5}$ was set as the total variable. In this section, the extra modeling uncertainty of PMF was 10%. To determine the proper number of source factors, three to eight source factors were separately run with different Fpeak values.
for optimum results. When the changes in $Q$ values become smaller, and the $Q$ (Robust) and $Q$ (True) values are closed, it can suggest that it could be an optimal solution.

**Quality assurance/quality control and statistical analyses**

All analytical procedures were monitored with strict quality assurance (QA) and quality control (QC) measures. Both pre- and post-sampling and chemical analysis strictly guaranteed that the filter was intact and undamaged, and the cracked filters were excluded. To reduce the uncertainties in chemical and statistical analyses created by sample size, we made large efforts (e.g. combined principal component analysis (PCA) and PMF model for source apportionment) to offset the defect.

**RESULTS AND DISCUSSION**

**PM$_{2.5}$ mass concentration**

The time series of the metrological parameters during the sampling period is shown in Fig. 1. Affected by the temperate continental climate, the first sampling period experienced high temperature, low humidity, high visibility, and sensitive wind speed. However, from November, the temperature, visibility, and wind speed decreased slightly, and the humidity rose. The average temperature, relative humidity and wind speed were $-8.4^\circ$C, 70.7%, and 1.5 m s$^{-1}$.

From October 2012 through March 2013, the mean concentration of PM$_{2.5}$ in Urumqi was 197.40 $\mu$g m$^{-3}$; the highest value was recorded on January 8 (481.43 $\mu$g m$^{-3}$), and the lowest value was recorded on February 14 (55.78 $\mu$g m$^{-3}$). All samples
far exceeded the NAAQS-II (35 μg m\(^{-3}\)) during the sampling period. The mass concentrations in urban Urumqi were higher than in most coastal cities in China, such as Guangzhou (89.30 μg m\(^{-3}\), Tao et al., 2014) and Shanghai (62.88 μg m\(^{-3}\), Tao et al., 2017), and other inland cities such as Lanzhou (120.5 μg m\(^{-3}\) in winter), illustrating the severity of PM\(_{2.5}\) pollution in winter in Urumqi. The low temperature and high humidity might favor the growth of aerosol particles and PM\(_{2.5}\) formation, and the low wind speed might be unfavorable to diffusion and transport of pollutants. Moreover, the typical valley and basin topography of Urumqi, which is surrounded by hills and mountains on three sides, blocks the flow of air and suppresses the transport of pollutants.

However, the concentration of PM\(_{2.5}\) in this study was lower than those measured at Urumqi before substituting natural gas for coal, such as from September 2010 through March 2011 (263.77 μg m\(^{-3}\)) observed by Limu et al., (2013). The concentration of PM\(_{2.5}\) has obviously decreased since the switch to natural gas, indicating that this project (shifting coal to natural gas) was successful, which is a crucial finding for the control of air pollution.

**Chemical composition of PM\(_{2.5}\)**

The compositions measured in this study (WSIs, metal elements, OC, EC, and PAHs) accounted for 66.21% of PM\(_{2.5}\) mass concentration on average (Fig. 1), and a large unidentified mass accounted for 33.79% (on average) in Urumqi in winter. The measured masses explained the majority of the composition of PM\(_{2.5}\) in Urumqi.
Table 1 lists the main WSIs, including Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, NO₃⁻, and SO₄²⁻, and their concentrations in the PM$_{2.5}$ in Urumqi during the sampling period. On average, the total WSI concentration was 58.08 μg m⁻³, accounting for 33.72% of PM$_{2.5}$ mass, which is approximately 20% lower than that observed in Urumqi before the switch from coal to gas (Li et al., 2008a). The concentrations of WSIs in PM$_{2.5}$ in Urumqi were, in order, SO$_4^{2-}$ > NH$_4^+$ > NO$_3^-$ > Cl⁻ > Ca$^{2+}$ > Na$^+$ > K$^+$ > F⁻ > Mg$^{2+}$, with mean concentrations of 26.66, 8.99, 8.52, 5.09, 4.05, 3.25, 0.81, 0.22, and 0.21 μg m⁻³, respectively. SO$_4^{2-}$, NH$_4^+$ and NO$_3^-$ were the three most prevalent WSIs, and the sum of their concentrations was 44.45 ± 20.64 μg m⁻³, or approximately 76.52% of the total WSIs; this finding is consistent with those from Taiyuan (75.21%) (He et al., 2017) and Lanzhou (73%) (Tan et al., 2017) but lower than those from megacities such as Beijing (88%) (Zhang et al., 2013). It is well known that SO$_4^{2-}$ and Cl⁻ are originated from coal combustion, and the coal was the sole energy source for domestic heating, power and industries in Urumqi before 2012. However, considerable efforts have been made by local government to alter the energy structure so as to improve the air quality in Urumqi, such as change coal to nature gas in 2012 (Wang et al., 2017). Therefore, in this study the concentrations of SO$_4^{2-}$ and Cl⁻ decreased approximately 42.54% and 32.93%, respectively, compared with the concentrations measured in 2007 (before the switch to gas) in Urumqi by Li et al., (2008a).
Generally, sulfuric acid and nitric acid react with ammonia to form salts (Hewitt, 2001). NH₃ preferentially reacts with H₂SO₄ to form NH₄HSO₄ when NH₃ is inadequate and transforms into (NH₄)₂SO₄ when NH₃ is abundant (Hassan and Khoder, 2017; Zhou et al., 2018). Therefore, the aforementioned mechanisms as well as the correlation (0.779) and molar ratio (0.091) of NH₄⁺ to SO₄²⁻ (Fig. 2a) indicated that NH₄HSO₄, rather than (NH₄)₂SO₄, was the dominant chemical species in Urumqi in winter. Fig. 2b illustrates that the NH₄⁺ to SO₄²⁻ + NO₃⁻ ratios ranged from 0.01 to 0.96 (all lower than unity), suggesting that some SO₄²⁻ and NO₃⁻ may be present in chemical forms other than NH₄HSO₄, (NH₄)₂SO₄, and NH₄NO₃. Li and Shao (2008) demonstrated that heterogeneous reactions between NOₓ, SO₂ (and its products, such as N₂O₅, HNO₃, and H₂SO₄), and dust carbonate often occur in northern China. Accordingly, we examined the correlation between NH₄⁺ + Ca²⁺ + Mg²⁺ and SO₄²⁻ + NO₃⁻ (Fig. 2c), given that a strong correlation between Ca²⁺ and Mg²⁺ (Fig. S1) suggests the dominant source of Mg²⁺ is mineral dust, mainly carbonate minerals. These ions were strongly correlated ($R^2 = 0.827$), and the mean molar ratio was 0.98 (the regression lines near unity), indicating that SO₄²⁻ and NO₃⁻ were present partly in CaSO₄, MgSO₄, Ca(NO₃)₂, and Mg(NO₃)₂. Fig. 2d shows that strong correlations between K⁺ and Cl⁻ were observed, whereas K⁺ and SO₄²⁻ were not significantly correlated (Fig. S2), indicating that KCl was the main form of potassium, consistent with earlier studies (Zhang et al., 2013; Zhou et al., 2018).

Previous studies (Arimoto et al., 1996; Hassan and Khoder, 2017) have reported
that ion mass concentration ratios such as NO$_3^−$/SO$_4^{2−}$ could be used as an indicator of the relative importance of WSI sources (i.e., of stationary vs. mobile sources). In the present study, the value of NO$_3^−$/SO$_4^{2−}$ ranged from 0.06 to 1.60, with an average of 0.41, theoretically indicating that the WSIs originated from a stationary source. However, the ratio has a wide range. Li et al. (2008) reported that surface soil from the Junggar Basin (agricultural area, where chemical fertilizer is used widely) and salt flats (salt water lake) contained high concentrations of sulfates, and they could be transported into atmosphere by wind and human activity. Therefore, transported soil dust and anthropogenic aerosols were the major sources of WSIs in Urumqi in winter.

Trace elements

Table 2 shows a statistical description of the concentrations of trace elements obtained from Urumqi and other cities around the world. The total concentration of trace elements was 9.12 $±$ 8.21 μg m$^{-3}$, accounting for 4.5% of the PM$_{2.5}$ mass concentration. The mean concentrations of atmospheric Pb, Cr, and As (elements linked to coal combustion) were 87.60, 83.48, and 34.99 ng m$^{-3}$ in Urumqi in 2012 and respectively decreased by 27.72%, 62.82%, and 14.71% compared with winter 2009, which demonstrated that substituting natural gas for coal was useful in controlling these elements. However, the elements of Ni, Cu, and Mn respectively increased 6.24, 2.40, and 1.75 times after the natural gas substitution. Previous studies have observed that particles from traffic emissions are rich in Cu, Mo, Ca and Mn, these metals are linking to non-exhaust sources such as brake and tire wear debris,
and traffic-related dusts, and Ni could be obtained from diesel vehicular exhausts (Hsu et al., 2016). Thus, the rising trend of some PM$_{2.5}$-bound elements suggests that the increase of emissions and vehicles might outweigh the urban pollution control efforts. The concentration of atmospheric Cd was 22.43 ng m$^{-3}$, nearly four times higher than the NAAQS of China (GB3095-2012) and the WHO limit of 5 ng m$^{-3}$. The concentration of Zn was much higher than in other cities, indicating severe atmospheric Zn pollution in Urumqi. Studies have shown that Cd and Zn are carcinogenic (Duan and Tan, 2013; Huang et al., 2015); therefore, the municipal government should strengthen the control of metal pollution.

Compared with other cities, the concentration of Pb was higher than those in Seoul and New York but lower than that in New Delhi and other cities in China. The Cd concentration was much higher than that in Lanzhou, New York, and Korea; similar to that in New Delhi; and lower than that in Nanjing. Cr, Zn, Ni, Cu, and Fe concentrations were much higher than those other cities and NAAQS of China and the WHO limit. The concentration of Arsenic was similar to those of other Chinese cities and that in New Delhi but higher than those in Korea and the NAAQS and WHO limits.

To examine the preliminary sources of elements, the EF method was employed to distinguish man-made from natural sources (Han et al., 2015; Hsu et al., 2016). The EF values of ten elements were calculated based on Fe as a crustal reference (Han et al., 2015). The EF value Mn was <10 (Fig. S3), indicating that the element was
present mostly from natural process. By contrast, the EF values of As, Cr, Hg, Pb, Cu, Zn, Ni, and Cd were >10, suggesting that they were mostly from anthropogenic sources.

Carbonaceous species

Fig. 3 illustrates the daily variation in carbonaceous species among PM$_{2.5}$ during winter in Urumqi. OC and EC had similar daily variation patterns during the sampling period. The concentrations of OC and EC ranged from 7.66 to 106.24 μg m$^{-3}$ and from 2.89 to 31.19 μg m$^{-3}$, with mean values of 33.98 and 10.84 μg m$^{-3}$, respectively. Total carbonaceous aerosols (TCA = 1.6 × OC + EC) accounted for 34.02% of PM$_{2.5}$, suggesting that carbonaceous species were a substantial fraction of the PM$_{2.5}$ in Urumqi in winter but were lower than the proportions (>40%) found in megacities such as Beijing, Guangzhou, Zhengzhou, and Lanzhou (Zhang et al., 2013; Tan et al., 2017). Generally, the OC/EC ratio is a useful tool for identifying sources of carbonaceous aerosols (Li et al., 2009). The OC/EC ratio fell mostly within 2.0–5.5, with a mean ratio of 3.21, in Urumqi in winter (Figs. 3 and S4). Generally, OC/EC ratio has a great distinction between coal combustion (0.3–7.6), vehicle emission (0.7–2.4), and biomass burning (4.1–14.5) (Watson et al., 2001). In this study, the high OC/EC ratio and strong correlation ($R^2 = 0.748$) indicated that OC and EC originated from similar sources, such as fossil fuel combustion and biomass burning.

OC originates either directly as primary OC or from photochemical conversion as secondary OC (SOC). Additionally, the stable atmosphere, low temperatures, and
high relative humidity in winter accelerate the condensation of volatile organic
compounds on PM (Sheehan and Bowman, 2001). Moreover, the OC/EC was higher
than 2.0 in all sampling periods (Fig. S4). Therefore, in this work, SOC was estimated
using the EC tracer method \[\text{SOC} = \text{OC} - \text{EC} \times (\text{OC/EC})_{\min}\] (Cabada et al., 2004).
The time series of SOC is illustrated in Fig. 4. The estimated SOC in this study was
0–62.85 \(\mu\text{g m}^{-3}\), with a mean concentration of 18.90 \(\pm\) 12.92 \(\mu\text{g m}^{-3}\), and the SOC/OC
ratio was 0.53 \(\pm\) 0.13. The high levels of SOC and SOC/OC can be attributed to
domestic heating in winter enhancing emissions of SOC precursor gases. Additionally,
a low planetary boundary layer and thermal inversion height frequently occur in
winter in Urumqi and facilitate the accumulation of atmospheric pollutants.
Furthermore, the high relative humidity and low temperature in winter (Fig. 1) also
accelerate the adsorption or condensation of volatile organic compounds on PM.

Cor and 16 priority PAHs recommended by the US EPA were measured in this
study. Mean concentration of the total PAHs was 829.81 \(\pm\) 185.30 ng m\(^{-3}\) (Fig. 4 and
Table S1), which was higher than that observed in Urumqi in 2010 (54.11 ng m\(^{-3}\)) by
Limu et al. (2013). Pyr, Chr, BbF, BkF, IcdP, and BghiP were the most prevalent
individual PAH compounds, accounting for 54.94\% of the total PAHs. In the present
study, BaP ranged from 0.40 to 16.67 ng m\(^{-3}\), and the mean concentration was 6.15 \(\pm\)
4.3 ng m\(^{-3}\), which exceeded the health-based guideline of the NAAQS (GB
3095-2012) and indicated a high contribution to cancer risk in winter in Urumqi.

To facilitate further analysis, PAHs were divided into three types: low molecular
weight (LMW, two- and three-ringed PAHs), middle molecular weight (MMW, four-ringed PAHs), and high molecular weight (HMW, PAHs with five or more rings). HMW PAHs were the predominant compounds in present study, accounting for 49.78% ± 6.60% of total PAHs, whereas MMW and LMW PAHs only accounted for 32.65% ± 4.50% and 17.57% ± 4.31%, respectively (ternary plots in Fig. 4). The high contribution of HMW PAHs was caused by the many conversions of volatile compounds from the gas phase into particles in winter (Yu et al., 2016). The ratios of IcdP/(BghiP + IcdP), Flu/(Flu + Pyr), and BaA/(Chr + BaA) were 0.42–0.64, 0.34–0.61, and 0.21–0.52, respectively (Fig. S5), which suggested that combustion (e.g., grass, wood, coal, petroleum, or natural gas combustion) was the major source of PAHs in Urumqi in winter.

Pollution pathways, source area distribution, and source apportionment

Pollution pathways and source area distribution

All transport trajectories of PM$_{2.5}$ were clustered into three clusters (different colors representing different origins of air masses), and the concentrations of PM$_{2.5}$ and chemical species of different clusters are shown in Fig. 5(a). Affected by the cold Siberian current, west winds prevail in Urumqi in winter (Li et al., 2008b). Therefore, airflow trajectories from the west are dominant. Moreover, the valley topography facilitates the enrichment of pollutants. Clusters 1 (C1), 2 (C2), and 3 (C3) accounted for 67.55%, 21.18%, and 11.27% of the total trajectories, respectively. C1 represented the airflow from western Xinjiang (surrounding western area of Urumqi) and
exhibited higher load values of PM$_{2.5}$, OC, SO$_4^{2-}$, EC, and metals. C2 and C3 were the long-range transport from eastern Kazakhstan, which then passed through Karamay, Kuitun, and Dushanzi. These areas include numerous petrochemical facilities. Therefore, the PM$_{2.5}$ and relative components maintained a high concentration despite long-distance transport and high-wind-speed dilution of contaminants.

Earlier studies on PM$_{2.5}$ in Urumqi have reported that the typical topography (surrounded on three sides by Tianshan Mountains, and only one open mouth facing north, where is the pollution source area) could accelerate the accumulation of gas phase pollutants such as SO$_2$, NO$_2$ and volatile organic compounds (VOCs), then these gas phase components undergo heterogeneous reactions with mineral dust particles in the atmosphere and enhance the haze formation (Li et al., 2008a; Li et al., 2008b; Ma et al., 2012; Wang et al., 2017). Moreover, in order to find the sources of highly enriched elements in PM$_{2.5}$, Li et al., (2008a) collected the surface soil samples on the ground of Urumqi and the surrounding areas over Xinjiang, which could transport aerosols to the city, and found that the surface soil samples of Urumqi city contain as high as 6.6, 7.6, 303.8 and 7.8 times of concentration of Pb, As, Cd, and S compared to their crustal abundance, which could be from the deposition of these elements in the early years. Thus, in this study using backward trajectories, the PSCF was applied to explore the likely regional sources and transport pathways of PM$_{2.5}$ in south Urumqi. Fig. 5(b) shows that the north (the Midong-Wujiaqu industrial zone)
and the western (Junggar Basin, Gobi and Taklamakan deserts) of the city might play a vital sources area of air pollution in south Urumqi. Therefore, the anthropogenic aerosols (from inside city) and transported mineral dust (from outside city) are the main sources of PM in Urumqi.

**Source identification and apportionment**

Using the PMF model with the obtained full data set as input data, five main sources were identified: crustal minerals, vehicle emissions, biomass and waste incinerator burning, industrial pollution and coal combustion, and secondary formation. The concentrations and sources profiles modeled for each identified main source are shown in Fig. 6, and the relative contributions from each identified source to PM$_{2.5}$ are illustrated in Fig. 7.

Crustal materials were characterized by high levels of Mg$^{2+}$, Ca$^{2+}$, Fe, and Mn. Ca$^{2+}$ content was higher than that of other components, indicating Ca-rich dust (Zhang et al., 2013). This source also contained nearly 20% trace elements such as Cd, Cr, Zn, and Cu, suggesting that some trace elements in the PM$_{2.5}$ in Urumqi may not only have anthropogenic sources but also include resuspended road dust and transported soil from the Gobi Desert and Junggar Basin; this finding agrees with that of Li et al., (2008). Crustal minerals accounted for 18.94% of PM$_{2.5}$, which was higher than the proportion for other cities in China (Zhang et al., 2013; Tan et al., 2017).

Vehicle emissions are characterized by high Ni (88.78%), Zn (43.05%), Pb (42.10%), Cu (32.63%), OC (33.01%), and EC (27.64%) content. Ni, OC, and EC are
major pollutants originating from diesel and gasoline combustion (Du et al., 2017; Hsu et al., 2016; Liu et al., 2017). Cheng et al., 2010 reported that zinc is a common additive in lubricating oil for engines, and Cu and Pb are linked to brake wear. The contribution of this source to PM$_{2.5}$ was 20.87%. It is likely to be an influential source of PM$_{2.5}$ in Urumqi because the number of automobiles has been increasing in recent years.

Another source was characterized by high levels of K$^+$ (52.71%), F$^-$ (39.68%), and Cl$^-$ (36.36%). K$^+$ is an excellent tracer of biomass burning (Zhang et al., 2013; Yu et al., 2016) and Wang et al., (2016) demonstrated that F$^-$ and Cl$^-$ are released from not only coal but also waste incineration. Thus, this source was identified as biomass and waste burning, and the contribution of this source to PM$_{2.5}$ was 21.42%, constituting the second largest source of PM$_{2.5}$. Xinjiang is a large agricultural area, and the high contribution of biomass and waste burning is probably caused by open burning of straw during the harvest season in addition to the domestic usage of straw in winter, which releases atmospheric particles that are then transported to Urumqi.

Another source was represented by high loadings of As (83.76%), Cd (43.27%), Cr (36.44%), SO$_4^{2-}$ (31.95%), and Cl$^-$ (32.95%), which are closely related to industrial pollution and coal combustion (Hsu et al., 2016; Liu et al., 2017). Thus, this source was identified as industrial pollution and coal combustion. The contribution of this source to PM$_{2.5}$ was 10.46%. Despite Urumqi replacing coal with natural gas, the air from surrounding areas like Midong-Wujiaqu Industrial Zone, Karamay, Kuitun,
and Dushanzi, areas characterized by large-scale petrochemical and oil-refining facilities and coal-fired power plants, could enter Urumqi (as shown in Fig. 5). This indicates that comprehensive improvement of the atmosphere requires regional cooperation.

The remaining source was dominated by NH$_4^+$ (91.84%), SO$_4^{2-}$ (45.64%), NO$_3^-$ (37.08%), and Na$^+$ (65.13%), which are related to secondary formation (Tao et al., 2014; Liu et al., 2017). Studies have suggested that NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ are formed through reactions of SO$_2$, NO$_x$, and NH$_3$ and transformed from a gaseous state into particles (Zhang et al., 2013; Tao et al., 2014; Liu et al., 2017). This source was identified as secondary formation, and the contribution of this source to PM$_{2.5}$ was 28.31%. Secondary formation was the largest contributor to the PM$_{2.5}$ in Urumqi; this result is probably attributable to the common secondary reactions in Urumqi caused by its high concentrations of precursor gas, high humidity, and low wind speed, which are favorable to photochemical reactions.

Overall, secondary formation was the source contributing most to PM$_{2.5}$ in south Urumqi in winter, followed by biomass and waste burning, vehicle emissions, crustal minerals, and industrial pollution and coal combustion; their mean contributions to PM$_{2.5}$ were 28.31%, 21.42%, 20.87%, 18.94%, and 10.46%, respectively (Fig. 7). Other sources were not identified, because sources of PM are diverse and complicated, especially those of open sources such as agricultural production, catering oil fumes, and so forth. Regional transportation of atmospheric pollution may contribute
substantially to the atmospheric PM in Urumqi (Fig. 5). According to source
apportionment, biomass burning, vehicle exhaust, and soil dust should be managed
and controlled effectively. Additionally, regional cooperation should be implemented
to reduce PM$_{2.5}$ pollution in Urumqi.

CONCLUSIONS

This study investigated the chemical composition, emission sources, and source
areas of PM in Urumqi in winter after the energy switch from coal to natural gas. The
average mass concentration of PM$_{2.5}$ was 197.40 $\mu$g m$^{-3}$, over five times the NAAQS
for annual PM$_{2.5}$ (35 $\mu$g m$^{-3}$). Although the atmospheric pollution was more severe,
PM$_{2.5}$ mass concentration decreased after the conversion. WSIs, metallic elements,
and carbonaceous species were the major components, accounting for 66.21% of the
total PM$_{2.5}$ mass. Among them, WSIs and carbonaceous aerosols were the dominant
fractions of PM$_{2.5}$ in Urumqi in winter, accounting for 33.72% and 34.02% of PM$_{2.5}$,
respectively. Carcinogenic substances, such as Pb, Cd, Cr, Zn, Ni, As, and BaP were
observed at hazardous levels in this study. Five main sources of PM$_{2.5}$ were identified:
secondary formation, biomass and waste burning, vehicle emissions, crustal minerals,
and industrial pollution and coal combustion. Transported soil dust from neighboring
areas and anthropogenic aerosols were the main sources of PM in Urumqi; therefore,
regional cooperation is recommended for reducing PM$_{2.5}$ pollution in Urumqi.
ACKNOWLEDGMENTS

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Table Captions

| Table1 | Concentrations of WSIs in PM$_{2.5}$ during the sampling period (μg m$^{-3}$) |
| Table2 | Concentration of elements in PM$_{2.5}$ in Urumqi and other cities (ng m$^{-3}$) |

<table>
<thead>
<tr>
<th>Table1</th>
<th>Concentrations of WSIs in PM$_{2.5}$ during the sampling period (μg m$^{-3}$)</th>
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<tbody>
<tr>
<td></td>
<td>PM$_{2.5}$</td>
</tr>
<tr>
<td>Mean</td>
<td>197.40</td>
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<tr>
<td>SD</td>
<td>81.79</td>
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<tr>
<td>Min</td>
<td>55.78</td>
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<tr>
<td>Max</td>
<td>481.43</td>
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SD: standard deviation

<table>
<thead>
<tr>
<th>Table2</th>
<th>Concentration of elements in PM$_{2.5}$ in Urumqi and other cities (ng m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>Pb</td>
</tr>
<tr>
<td>Urumqi $^a$ (2012-13, winter)</td>
<td>87.60</td>
</tr>
<tr>
<td>Urumqi $^b$ (2009-10, winter)</td>
<td>121.2</td>
</tr>
<tr>
<td>Lanzhou $^c$ (2012-13, winter)</td>
<td>1056</td>
</tr>
<tr>
<td>Beijing $^d$ (2010-11, winter)</td>
<td>112.7</td>
</tr>
<tr>
<td>Nanjing $^e$ (2013, winter)</td>
<td>393</td>
</tr>
<tr>
<td>New Delhi $^f$ (2013, winter)</td>
<td>600</td>
</tr>
<tr>
<td>Korea $^g$ (2012-13, winter)</td>
<td>29.2</td>
</tr>
<tr>
<td>New York $^h$</td>
<td>5</td>
</tr>
<tr>
<td>NAAQS $^i$ (GB3095-2012)</td>
<td>500</td>
</tr>
<tr>
<td>WHO $^i$</td>
<td>500</td>
</tr>
</tbody>
</table>

Note: $^a$ This study; $^b$ (YiLiMi-reABuDaLi-mu et al., 2012); $^c$ (Tan et al., 2017); $^d$ (Yu, 2013); $^e$ (Li et al., 2016); $^f$ (Pant et al., 2015); $^g$ (Han et al., 2015); $^h$ (Qin and Hopke, 2006); $^i$ (Duan and Tan, 2013);
Figure Captions

**Fig.1.** Temporal variations of PM$_{2.5}$, major components and meteorological parameters during winter in 2012-2013 in Urumqi.

**Fig.2.** Scatter plots of certain carions and anions: (a) NH$_4^+$ vs SO$_4^{2-}$, (b) NO$_3^-$ + SO$_4^{2-}$ vs NH$_4^+$, (c) NO$_3^-$ + SO$_4^{2-}$ vs NH$_4^+$ + Ca$^{2+}$ + Mg$^{2+}$, (d) Cl$^-$ vs K$^+$.

**Fig.3.** Time series of carbonaceous species in PM$_{2.5}$ in Urumqi.

**Fig.4.** PAHs profiles in Urumqi aerosol in winter.

**Fig.5.** 48-h air particle backward trajectory clusters (a) and PSCF (b) analysis in winter in Urumqi.

**Fig.6.** Factor profiles (% of species total) obtained from the PMF analysis.

**Fig.7.** Sources apportionment of PM$_{2.5}$ in winter in Urumqi.
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Fig. 2. Scatter plots of certain cations and anions: (a) $\text{NH}_4^+$ vs $\text{SO}_4^{2-}$, (b) $\text{NO}_3^- + \text{SO}_4^{2-}$ vs $\text{NH}_4^+$, (c) $\text{NO}_3^- + \text{SO}_4^{2-}$ vs $\text{NH}_4^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$, (d) $\text{Cl}^-$ vs $\text{K}^+$

Fig. 3. Time series of carbonaceous species in PM$_{2.5}$ in Urumqi
Fig. 4. PAHs profiles in Urumqi aerosol in winter

Fig. 5. 48-h air particle backward trajectory clusters (a) and PSCF (b) analysis in winter in Urumqi
Fig. 6. Factor profiles (% of species total) obtained from the PMF analysis.

Fig. 7. Sources apportionment of PM$_{2.5}$ in winter in Urumqi