Study on time variations of elemental composition and source of PM2.5 in Beijing

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Chemical elements are major components of PM2.5 and crucial tracers to identify the source of aerosol particles using source apportionment models such as Positive Matrix Factorization (PMF) model and Chemical Mass Balance (CMB) model. In this study, PM2.5 samples were collected hourly from November 28, 2016, to May 30, 2017 in a chosen location within Beijing. Mass concentration and elemental composition were detected using an X-ray fluorescence-based online elemental analyzer (PX-375, Horiba, Kyoto, Japan). PM2.5 concentration ranged between 3.4 μg/m^3 and 763 μg/m^3 and had an average of 91.2 μg/m^3 A total of twenty elements were detected and investigated. Among them, Ni had the lowest average concentration at 0.0038 μg/m^3, and S had the highest average concentration at 5.82 μg/m^3. The levels of Si, Ca, Fe, Mn, Cu, and K were found to be lower than their corresponding values from 2001 and 2006 reported in the literature. PMF model was employed to identify the main source of PM2.5. Based on the PMF source analysis, the primary sources of PM2.5 during the observation period in Beijing, in descending order of contribution to PM2.5, were secondary particles (44.0%), coal burning (28.3%), vehicle emission (17.2%), dust (7.9%), and fireworks (2.5%). The hourly variation trends of the three main sources are similar in winter due to atmospheric diffusion. PM2.5 concentration seemed positively corre-lated to each of the sources. In particular, vehicle emission and secondary particles appeared highly correlated during the winter. The model results also revealed that during different pollution episodes, excluding fireworks during festivals and dust storms, the contribution of secondary particles rose especially quickly, suggesting that the formation of the secondary particles was the crucial instigator in the explosive increase of PM2.5 concentration in Beijing during winter.

Introduction

Due to the rapid urbanization and industrialization of China, air pollution is increasingly becoming a focal point in environmental studies. Particulate matter PM2.5 is one of the primary air pollutants. Chemical elements, which are major components of PM2.5, are harmful to human health and the environment.[1-5] For example, heavy metals such as Pb, As, Cr, Cd, and Hg are toxic and carcinogenic, and once inhaled by humans, they may enter human tissues such as alveoli, causing multiple diseases.[5-8] Studies have shown that trace elements in marine ecological systems have pronounced harmful effects on planktons.[9-11] In addition, many heavy metal pollutants, such as Pb, have global effects since they can diffuse from land to sea and even the polar regions.[9, 12] PM2.5 tends to stay longer in the air than heavier particulates because it is smaller and harder to degrade, and the longevity of PM2.5 is detrimental to ecological systems and environmental health. Studying the chemical components of PM2.5 through source emission analysis is a crucial way to identify the source of aerosol particles.[13-16] Previously, positive matrix factorization (PMF) analysis have identified six major sources of PM2.5 in Beijing: dust, the burning of coal, the burning of biomass, vehicle emission and the burning of trash, industrial emission, and secondary inorganic aerosol.[14] Also, cooking, metal processing, dust storm, and specifically timed fireworks contribute to the pool of PM2.5.[4, 17-22] Therefore, studying the elemental components in PM2.5 with PMF analysis will provide granular insights to PM2.5 -driven pollutions.

Traditionally, in the study on the elemental components in the air, aerosol particles are first collected from a large volume of air on filters, and then the samples are analyzed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Particle-induced X-ray emission (PIXE), or Energy Dispersive X-ray Fluorescence (EDXRF) offline.[23-26] However, because the traditional process is time- and labor-intensive, researchers can only collect samples once a day or every few days. Therefore,

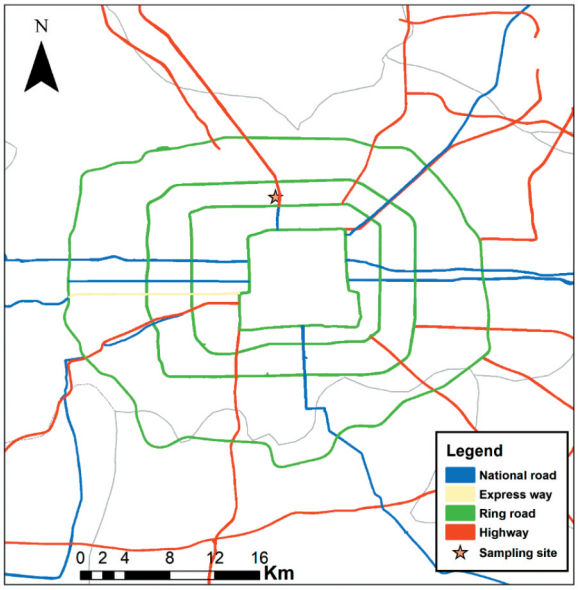

Figure 1 Sampling site.

the resulting analysis has a low temporal resolution, which will not be suitable for the study of transient pollutions that last only a few days. There have been efforts to increase the temporal resolution of the traditional method, whereas in a study of the pollution of aerosol metals in the air before and after fireworks during a festival in Taiwan, the researchers increased the frequency of sample collection to twice a day.[27] Despite the increase in efforts and workload, such offline analytical methods still cannot provide the temporal resolution demanded by researchers. Therefore, there is a need to develop an online analytical system that can continually monitor the changes in the chemical composition of pollutants over time.

In recently years, the Chinese government has implemented many policies to address the increasingly severe problem of air pollution. While air quality has been improved significantly, to the populace, it is still far from ideal.[28-32] Beijing is the capital of China with a population of over 21.7 million. In recent years, there has been growing public concern over Beijing's PM2.5-induced, poor air quality during winter.[22, 32-35] A study of the heavy smog that occurred in Beijing during January of 2013 showed that Beijing had a PM2.5 daily average concentration up to 159 μg/m^3, which was twice the national average standard of 75 μg/m^3 and far above the international average standard of 35 μg/m^3.[19] During the two of the most polluted periods, PM2.5 hourly concentration even reached 680 and 530 μg/m^3, respectively.[36] In addition, through the monitoring and analytical modeling of winter air pollution in Northern China, researchers found that local diffusion and unusual weather had a tremendous impact on the spread of local pollutants.[19, 37, 38] In other words, smog occurs when the release of massive pollutants by winter heating coincides with weather conditions that are adverse to the diffusion of contaminants. Also, fireworks during the Chinese Lunar New Year and the Lantern Festival may trigger smog.[17, 20, 21, 32, 39, 40] Moreover, the frequent sandstorms sweeping through Northern China every spring is another special factor that causes air pollution in Northern China.[26, 41] Elements are a crucial chemical component of the aerosol particles that cause smog. Until now, the change in the chemical composition of the pollutants in Beijing during winter and spring has not been analyzed using a high-resolution online elemental analyzer.

Therefore, from November 28, 2016, to May 30, 2017, in a chosen location within Beijing, we detected the mass concentration of PM2.5 in hourly collected samples continuously using an X-ray fluorescence-based online elemental analyzer (PX-375, HORIBA, Ltd., Kyoto, Japan) and analyzed the elemental composition of the pollutant. Our study covered a part of a period when Beijing residents used heating as well as when the residents did not. Some smog episodes occurred within the period of sampling. The Lunar New Year, which had a high volume of emission from the fireworks, fell within the period of monitoring. In addition, a dust storm occurred in the last month of the surveillance. We analyzed the specific changes as well as the overall trend in the chemical components of PM2.5 during each of the above characteristic periods of the pollution. Lastly, we also used Positive Matrix Factorization (PMF) to determine the sources of the captured pollutants.

Methodology

Sampling site

The sampling site was on the campus of Institute of Atmospheric Physics, Chinese Academy of Sciences, which located in the Northern part of Beijing and between the 3rd Ring Road and the 4th Ring Road (**Figure 1**). There is a two-way, four-lane city road 100 meters north to the sampling site, and there is a two-way, six-lane expressway 300 meters east of the sampling site. In addition, there are some residential areas and small city parks around the sampling site. Therefore, the sampling site is a typical location within Beijing.

Instrumentation

An online elemental analyzer (PX-375, Horiba, Kyoto, Japan) was used from November 28, 2016, to May 30, 2017, to obtain and analyze PM2.5 mass concentrations and elemental components online. A total of 20 elements were detected during the detection: Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd, Hg, Pb, Al, Si, S, K, Ca, P, and Cl.

The air was introduced from the air sample inlet at a flow rate of 16.7 L/min, then a sizing device sorted the particles with the diameter less than 2.5 μm and the particles were sampled on a reel-to-reel polytetrafluoroethylene filter tape with a time resolution of 1 hour. For the collected samples, firstly, the mass concentration of the collected PM2.5 sample was measured with beta attenuation analysis; secondly, the sample was analyzed by

Table 1 Concentrations of PM2.5 and element species (unit: μg/m^3)

	This study		Beijing 2000 (winter to spring) [61]	Beijing 2006 (4th to 27th Dec.) [62]	
	Ave.	S.D.	Ave.	Ave.	S.D.
PM2.5	87.9	103.6	132.25	142.3	46
S	5.6848	7.0333	6.275		
Cl	1.9986	3.4595	2.74		
Al	1.9281	3.5567	1.055	1.1125	0.2821
K	1.7405	5.3902	2.905	2.3135	0.8118
Si	1.4287	4.1967	3.16	2.073	0.2451
Fe	0.5281	1.0960	1.345	1.5042	0.1666
Ca	0.5047	1.0858	1.38	2.4828	0.5564
Zn	0.1432	0.1711	0.5185	0.4628	0.1741
Pb	0.0702	0.1411	0.33	0.26681	0.10105
P	0.0698	0.0775	0.045	0.00374	0.0012
Ti	0.0640	0.2427	-	0.1001	0.0204
Cd	0.0467	0.0160	-	0.00531	0.0016
Mn	0.0327	0.0380	0.095	0.1271	0.0332
Cu	0.0278	0.1317	0.0395	0.0616	0.0276
V	0.0070	0.0611	-	0.00686	0.00178
As	0.0083	0.0181	-	0.04204	0.0254
Se	0.0117	0.0096	0.0085	0.00783	0.00353
Cr	0.0088	0.0176	-	0.0329	0.008
Hg	0.0076	0.0065	-	0.00023	0.0002
Ni	0.0037	0.0030	0.0035	0.0176	0.0018

XRF for the identification of the element components. The instrument was calibrated by Micromatter and SRM2783(NIST) standards every month. Each sample was analyzed for 500 s. The detection limits (in ng/m^3) of each element were: Ti(9.6), V(47.9), Cr(3.6), Mn(2.2), Fe(5.2), Ni(1.6), Cu(1.9), Zn(2.3), As (5.6), Cd(8.8), Hg(10.7), Pb(6.3), Al(88.7), Si(11.8), S(4.1), K(11.9), Ca(9.8), P(5.1) and Cl(7.0). 10 times, blank filters were analyzed for element components by XRF. The blank corrected data was used in this report.

PMF analysis

Positive Matrix Factorization (PMF), proposed by Paatero and Tapper in 1993, is an effective method of data analysis.[42] First, with weighted calculation, PMF analysis identifies the error in the compositional value of each chemical component in the aerosol particle. Then PMF calculates the source type and source contribution of the pollutants with the least square method. Comparing to other methods of emission source analysis, PMF does not require the composition apportionment of the source or the share rate of matrix component to be non-negative. In addition, PMF can be optimized with the standard deviation of data and handle missing data or inaccurate data. PMF has enabled the identification of aerosol particle sources in studies conducted in Hong Kong, Beijing, Thailand, the United States, Finland, and Australia. The primary source apportionment obtained by PMF is very similar to the data collected from actual monitoring. Therefore, PMF has the highest accuracy amongst source emission analyses.

Assuming X is n*m matrix, where n is the sample size and m is the number of chemical components. Then the matrix X can be broken down to matrix G and matrix F, where G is n*p matrix of particle emission source contribution, F is p*m matrix of pollution source component apportionment, and p is number of the main source of pollutants. The relationship between X, G, F, and E is defined as follows:

$$X = GF + E \quad (1)$$

E is the residual matrix, indicating the difference between X and GF.

The goal of PMF analysis is to minimize Q, and Q is defined as:

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

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \quad (3)$$

i=1, 2, ..., n; j=1, 2, ..., m; k=1, 2, ..., p.

In the equation, S is the standard deviation of X: x_{ij}, g_{ik}, f_{kj} and e_{ij} are elements in the X, G, F, and E matrix, respectively. When $g_{ik} \geq 0$ and $f_{kj} \geq 0$, Q could be calculated using minimized iteration, then both the relative value of G (pollutant source) and F (the relative concentration of chemical component in the pollutant) can be determined.

Results and discussion

Concentrations of PM2.5 and element

Table 1 contains a list of PM2.5 mass concentrations and the mass concentration of each of the chemical components from this study. Comparable values from 2001 and 2006 reported in the literature are also included in the table.

The mass concentration of PM2.5 measured in this study ranged between 3.4 μg/m^3 and 763 μg/m^3 and had an average of 91.2 μg/m^3, which was lower than the comparable values from the winter and spring of 2000 and December of 2006 reported in the literature. From 2000 to 2015, the PM2.5 concentration in Beijing had been decreasing at a rate of 1.5 μg/m^3 annually.[43] This study also showed that, among the identified elements, Ni had the lowest average concentration of 0.0038 μg/m^3, and S had the highest concentration of 5.82 μg/m^3. A previous study has shown that the level of predominant elements in aerosol particles, such as Si, Ca, Fe, Mn, Cu, and K, has been decreasing on an annual basis from 2000 to 2010.[43] Wherein Si and Ca mainly come from construction and road dust, and Fe, Mn, and Cu come from industrial emission.[44] Because K comes mostly from biomass burning, it is often used as the designated marker for biomass burning.[45] In this study, the concentrations of the elements mentioned above were respectively lower than their respective levels in 2001 and 2006 reported in the literature. For example,

Table 2 Concentrations of PM2.5 and element species during each episode (unit: μg/m^3)

		Ep1	Ep2	Ep3	EpF1	EpF2	Ep4	EpD	heating	no heating
PM2.5	Max.	525	564	404	763	363	381	433	763	433
	Ave.	185	269	200	327	273	154	138	111	54.1
S	Max.	41.3	51.6	25.9	32.6	22.8	17.4	5.35	51.6	14.7
	Ave.	12.1	20.5	10.7	15.6	14.3	6.92	2.07	7.19	3.44
Cl	Max.	19.2	10.6	11.5	41	10.8	18.2	1.16	41	6.8
	Ave.	5.86	4.27	5.57	17.7	4.91	7.74	0.276	3	0.498
Al	Max.	8.7	6.64	6.9	53.9	5.39	23.9	27.9	53.9	27.9
	Ave.	3.07	3.19	3.04	20.7	3.53	6.51	8.86	2.18	1.55
K	Max.	5.78	4.82	7.33	103	5.49	46.2	8.28	103	8.28
	Ave.	2.29	2.42	2.87	36.2	3.7	9.65	2.61	2.28	0.931
Si	Max.	3.16	2.37	1.78	11	1.61	4.94	61.4	11	61.4
	Ave.	1.28	1.2	0.93	4.27	1.11	1.84	19.4	0.841	2.31
Fe	Max.	1.99	3.7	0.675	0.946	1.04	1.88	18.4	3.7	18.4
	Ave.	0.823	0.747	0.365	0.46	0.672	0.624	4.86	0.395	0.727
Ca	Max.	1.23	0.785	0.86	9.81	0.728	4.29	16.1	9.81	16.1
	Ave.	0.531	0.405	0.402	3.44	0.488	1.06	4.52	0.381	0.689
Zn	Max.	1.6	0.669	0.456	0.798	0.481	1.29	0.566	2.16	0.747
	Ave.	0.436	0.345	0.197	0.328	0.265	0.251	0.0903	0.175	0.0957
P	Max.	0.409	0.385	0.272	0.766	0.238	0.353	0.532	0.766	0.532
	Ave.	0.14	0.174	0.122	0.321	0.135	0.135	0.183	0.082	0.0516
Pb	Max.	0.377	0.353	0.352	3.38	0.243	0.777	2.19	3.38	0.142
	Ave.	0.139	0.171	0.125	0.852	0.133	0.245	0.08	0.0938	0.035
Mn	Max.	0.192	0.122	0.0672	0.444	0.0777	0.166	0.389	0.444	0.389
	Ave.	0.0717	0.0584	0.0302	0.148	0.0512	0.0707	0.112	0.0338	0.0311
Cu	Max.	0.263	0.103	0.111	2.89	0.07	0.843	0.0663	2.89	0.103
	Ave.	0.0584	0.0401	0.0316	0.796	0.0418	0.166	0.0151	0.0386	0.0117
Cd	Max.	0.101	0.131	0.0804	0.116	0.0759	0.0703	0.176	0.131	0.115
	Ave.	0.0552	0.0648	0.0501	0.0598	0.0549	0.0453	0.0628	0.0447	0.0497
Ti	Max.	0.113	0.104	0.208	4.88	0.129	1.54	1.44	4.88	1.44
	Ave.	0.047	0.042	0.0601	1.48	0.0873	0.34	0.404	0.0679	0.0582
As	Max.	0.119	0.16	0.0709	0.194	0.0805	0.0895	0.0303	0.194	0.133
	Ave.	0.0388	0.0253	0.0123	0.018	0.0331	0.0157	0.00377	0.0119	0.0028
Se	Max.	0.0526	0.0474	0.0406	0.11	0.0576	0.0401	0.0367	0.11	0.0367
	Ave.	0.0224	0.0243	0.0193	0.0386	0.0252	0.0199	0.0105	0.0131	0.00957
Hg	Max.	0.041	0.0392	0.0255	0.0537	0.0267	0.0238	0.0326	0.0537	0.0326
	Ave.	0.0161	0.0185	0.0127	0.0196	0.0137	0.011	0.00727	0.00919	0.0052
Cr	Max.	0.0398	0.0319	0.0202	0.357	0.0216	0.118	0.0697	0.357	0.0697
	Ave.	0.0147	0.0119	0.00796	0.111	0.0126	0.0285	0.0215	0.00996	0.00714
Ni	Max.	0.0189	0.0144	0.00981	0.0276	0.0132	0.00907	0.0327	0.0276	0.0327
	Ave.	0.00677	0.00618	0.00429	0.0101	0.00832	0.00496	0.00935	0.00392	0.00346
V	Max.	0.00345	0.0074	0.0499	1.3	0.0353	0.419	0.069	1.3	0.069
	Ave.	0.0000584	0.00022	0.00641	0.388	0.0175	0.0787	0.0158	0.0106	0.00154

the concentration of K had decreased by 40% since 2001 and 25% since 2006, respectively. While the overall trend predicts a certain decrease in the level of PM2.5 and its elements, winter pollution remains a matter of great concern. During this study, the highest level of PM2.5 was 763 μg/m^3, which was ten times the PM2.5 daily average limit of 75 μg/m^3 specified in the China's ambient air quality standards (GB3095-2012), suggesting that the small particulate pollution in Beijing is still a deleterious problem.

Temporal variations of PM2.5 and element

This study spanned nearly six months and covered both winter and spring when the most serious particulate pollutions occur. In addition, seasonal episodes that are specific to Beijing during winter and spring were captured in the study. All these pollution episodes will be discussed below.

In Northern China, local governments start to supply coal-powered central heating to their residents from November 15 every year to March 15 of the following year. Such activity is characteristics of Northern China and has major impact on the regional air quality.[46-48] According to the above heating period, the period of observation in this study can be divided into the heating period, November 28, 2016, to March 15, 2017, and the non-heating period, March 16, 2017, to May 27, 2018. The average hourly concentration of PM2.5 during the heating period was 111 μg/m^3, which was 2.1 times of the PM2.5 concentration during the non-heating period (**Table 2**). The disparity in PM2.5 concentrations indicates a tremendous effect of winter heating on air quality. At the level of elements, during the heating period, Cl and S had the highest contributions at 2.2% and 7.8%, respectively, which reflects the typical characteristics of coal combustion emissions and is consistent with the high contents of Cl and S in the burnt coal.[49, 50] In addition, during the non-heating period, the contribution of Cl and S was 0.6%, and 6.8%

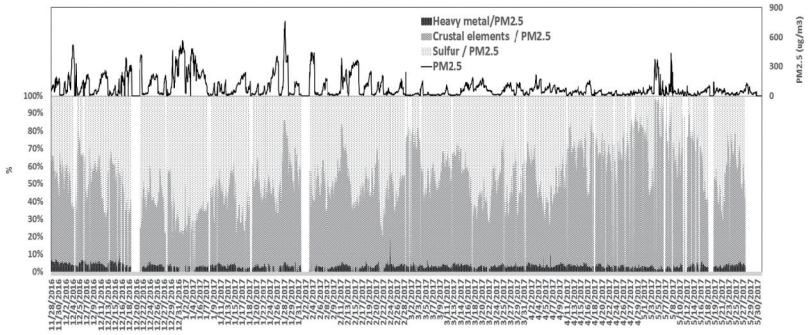

Figure 2 Time series of concentrations of PM2.5 and element detected (Heavy metal elements include Ti, V, Cr, Mn, Ni, Cu, Zn, As, Se, Cd, Hg, Pb, crustal elements include Fe, Al, Si, K, Ca and P)

respectively, which was significantly lower than the contribution during the heating season, and compared with the heating period, the contribution from crustal elements such as Si, Ca, Al and Fe increased significantly to 2.58%, 0.66%, 0.32% and 0.72%, respectively, suggesting the occurrence of dust storms. Dust events will be discussed in detail in the last paragraph of this section.

In recent years, air pollution has been serious in Beijing, particularly during the heating period, when heavy pollution episodes of varying lengths occurred.[51, 52] Here, several particularly severe pollution episodes that occurred during the observation period of this study will be discussed.

Episode 1 (Ep1), occurred on December 1, 2016, was the first serious pollution incident observed during this study. From 4 PM on December 1 to 0 AM on December 2, PM2.5 concentration had risen rapidly from 15.0 μg/m^3 to 143 μg/m^3. Although the level of PM2.5 started to decrease afterward, only after about a dozen hours it began to rise again at 3 PM on December 2, reaching 239 μg/m^3 at 8 PM before subsiding. At 10 AM on December 3, the concentration of PM2.5 dropped to 61.9 μg/m^3 and rose sharply for the third time to 509.0 μg/m^3 at 2 AM on December 4, eventually lowering to 6.3 μg/m^3 at 11 AM on December 5 (**Figure 2**).

Episode 2 (Ep2) was the most prolonged episode of pollution observed in this study. It lasted almost ten days, from 10 AM on December 29, 2016, to 5 AM on January 8, 2017, had an average PM2.5 concentration of 269 μg/m^3 and peaked at 2 PM on January 1, 2017, at 564 μg/m^3. In Ep1 and Ep2, the level of S reached 41.3 μg/m^3 and 51.6 μg/m^3, respectively (with an average concentration of 12.1 μg/m^3 and 2.5 μg/m^3 respectively), which also happened to be the highest concentrations of S observed in the entire study. S and PM2.5 had a very positive correlation in Ep1 and Ep2, with a correlation coefficient of 0.95 and 0.99, respectively; this was consistent with the composition characteristics of PM2.5 during winter heating in Northern China, indicating that these two pollution episodes were significantly affected by coal combustion emission. In comparison, although one of the indicators for coal combustion emission, Cl, had a positive correlation with PM2.5 (correlation coefficients of 0.92 and 0.74 respectively) in Ep1 and Ep2. Cl had significantly lower concentrations with the maximum concentration of 1.92 μg/m^3 and 10.6 μg/m^3 respectively and the average concentration of 5.86 μg/m^3 and 4.27 μg/m^3 respectively in Ep1 and Ep2. On the other hand, Cl had the highest observed concentration at 5 AM on January 28, 2017, at 40.5 μg/m^3, which was about two- and four-fold of the concentration of Cl in Ep1 and Ep2, respectively. Such inconsistency might be because Cl was a crucial element in fireworks. The lighting of fireworks is a Chinese tradition during the Lunar New Year and thus becomes a unique contributor to air pollution. The impact of fireworks on air pollution will be discussed below.

According to Chinese tradition, the lighting of fireworks mainly happens during the Lunar New Year and the Lantern Festival. During this study, the Lunar New Year and the Lantern Festival was on January 28, 2017, and February 11, 2017, respectively. Transient episodes of pollution also occurred on these dates, where the concentration of PM2.5 quickly peaked within several hours and then subsided within several hours. For the ease of discussion, the Lunar New Year will be termed EpF1, and the Lantern Festival will be termed EpF2.

In addition, there was the episode of PM2.5 pollution before the Lunar New Year (termed Ep3), and the episode of PM2.5 pollution after the Lantern Festival (termed Ep4). Ep3 lasted three days, where PM2.5 concentration peaked at 400 μg/m^3 at 5 AM on January 25, 2017, and fell rapidly to 11.6 μg/m^3 in only 13 hours due to weather-accelerated diffusion. January 27 was the Lunar New Year's Eve, and the lighting of fireworks already started in the afternoon. The concentration of PM2.5 began climbing at about 5 PM quickly and reached the maximum value of 763 μg/m^3 at 4 AM on January 28, which also happened to be the highest PM2.5 concentration observed during the entire study. At about 11 PM on January 28, PM2.5 reached another peak at 412 μg/m^3 and then dropped, due to weather-accelerated diffusion, to 8.0 μg/m^3 at 5 AM on January 29. On the other hand, during EpF2, PM2.5 concentration peaked at 381 μg/m^3 at 12 AM on February 12, 2017. However, due to the weather, this pollution did not dissipate until 5 PM on February 13, when the

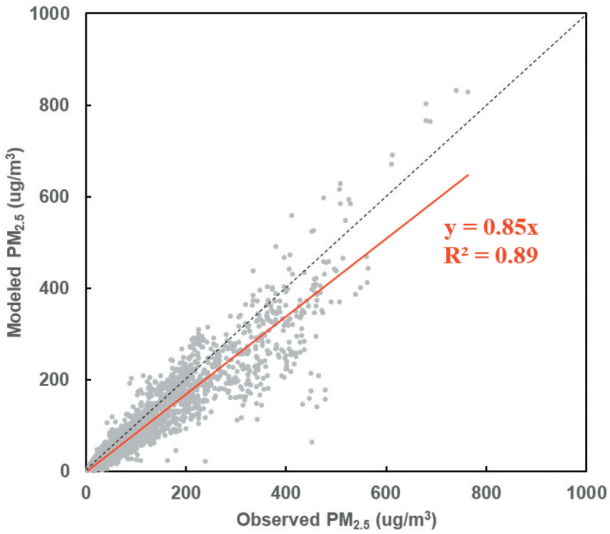

Figure 3 Correlation between observed and model predicted concentration of PM2.5

PM2.5 concentration receded to 11.8 μg/m^3. Later, during Ep4, PM2.5 level rose rapidly again, reaching the maximum value of 348 μg/m^3 at 6 AM on February 16, and due to weather-accelerated diffusion, dropped rapidly to 19.6 μg/m^3 at 12 PM on February 16.

Although EpF1 and Ep3, and EpF2 and Ep4, respectively, occurred close together, they had distinctively different sources of pollutants from the perspective of changes in elemental composition. During EpF1 and EpF2, the concentration of S, Al, K, Cu, V, P, Cr, Pb, Ca, and Cl rose significantly, which was consistent with the trend of PM2.5. These elements are ingredients of fireworks, of which Cu, Al, Ca, Pb, P, and V provide color or flash effects, K and Cr are ingredients in oxidants, S is the ingredient of an explosive, and Cl mentioned above is the ingredient contained in a blasting agent delivering sound effect and an oxidant[21, 27, 53-55]. One thing worth noting here is that while the concentration of S also rose significantly during EpF1 and EpF2, its concentration was comparable to those in adjacent Ep3 and Ep4. In fact, the average level of S was even higher during Ep4 than during EpF2 by 107%. The concentration of other characteristic elements of firework also had significantly higher concentration during EpF1 and EpF2 than in other episodes. For example, the respective average levels of Cu and K during EpF1 were higher than their respective concentrations during Ep3 by 24.2 fold and 11.6 fold, respectively.

During the non-heating period, from 3 AM on May 4 to 11 PM on May 8, 2017, we observed an episode of pollution (termed EpD), during which PM2.5 concentration spiked intermittently to an average concentration of 138 μg/m^3 and the highest value of 433 μg/m^3. According to PMF source apportionment results in Section 3.2, we determined the source of this to be dust. Dust storms often occur in Northern China during spring and cause severe air pollutions.[56, 57] From the change in element concentration, the four crustal elements, Fe, Al, Si and Ca all showed the same trend as PM2.5, indicating that their sources have high consistency. During EpD, the above four crustal elements all exhibited high levels with the average concentration of 4.86 μg/m^3, 8.86 μg/m^3, 19.4 μg/ m^3, and 4.52 μg/m^3, respectively. The results were consistent with previous data reported in other literatures.[47, 56, 57]

Source apportionment

This study used PMF modeling to analyze the hourly concentrations of PM2.5 and inorganic elements; the predicted results of PM2.5 were relatively consistent and correlated with the observed values (**Figure 3**; slope=0.85, R^2 = 0.89). The profile and time-series modeling of five main source factors of PM2.5 are shown in **Figure 4**.

Factor 1 was secondary particles and, at 44.0%, the largest contributor to the concentration of PM2.5. The primary elements in factor 1 were S (82.8%), P (43.3%), Se (31.1%), Cd (30.3%), Hg (28.1%) and Al (24.6%) (the percentage represents the fraction of the element in factor 1 contributed to the total concentration of this element). Secondary particles form when gaseous and granular pollutants from coal burning, traffic emission, and dust mix and react chemically.[58] Secondary particles usually contain a high concentration of secondary inorganic ions such as SO_4^{2-}, NO_3^-, and NH_4^+; in the particles, SO_4^{2-} is the main form of S, and more than 85% of S is in the form of SO_4^{2-}.[59] Therefore, in this study it can be determined from the high contribution of S that the source should contain more SO_4^{2-}. Secondary particles contributed 43.9 μg/m^3 to the total concentration of PM2.5 during the heating season, which was about 2.1 times of the contribution, at 21.3 μg/m^3, during the non-heating season.

Factor 2 was the burning of coal, which contributed 28.3% of the total PM2.5 concentration. The predominant elements in burnt coal included Cl (100%), Pb (66.2%), Cd (54.9%), Se (47.7%), Hg (47.4%), and Ni (46.1%) (the percentage represents the fraction of the element in factor 2 contributed to the total concentration of this element).

In source analysis, while Cl is usually regarded as the tracer element of coal burning, Ni, Pb, Se, Hg, and Cd are also the main elements.[60] Coal burning made seasonal contribution to PM2.5 concentration: 33.6 μg/m^3 during the heating season and about 5.4-fold less at 6.2 μg/m^3 during non-heating season. In addition, coal burning made a significant contribution to the spike of PM2.5 in the Lunar New Year on January 28, 2017. While coal burning may increase during the holiday, the spike might also be because the PMF model did not distinguish coal burning and the lighting of fireworks and determined part of the lighting of the fireworks to be coal burning.

Factor 3 was vehicle emission, which contributed 17.2% of the total concentration of PM2.5. The dominant elements of vehicle emission included Cu (49.6%), Zn (45.6%), Mn (33.7%), and Fe

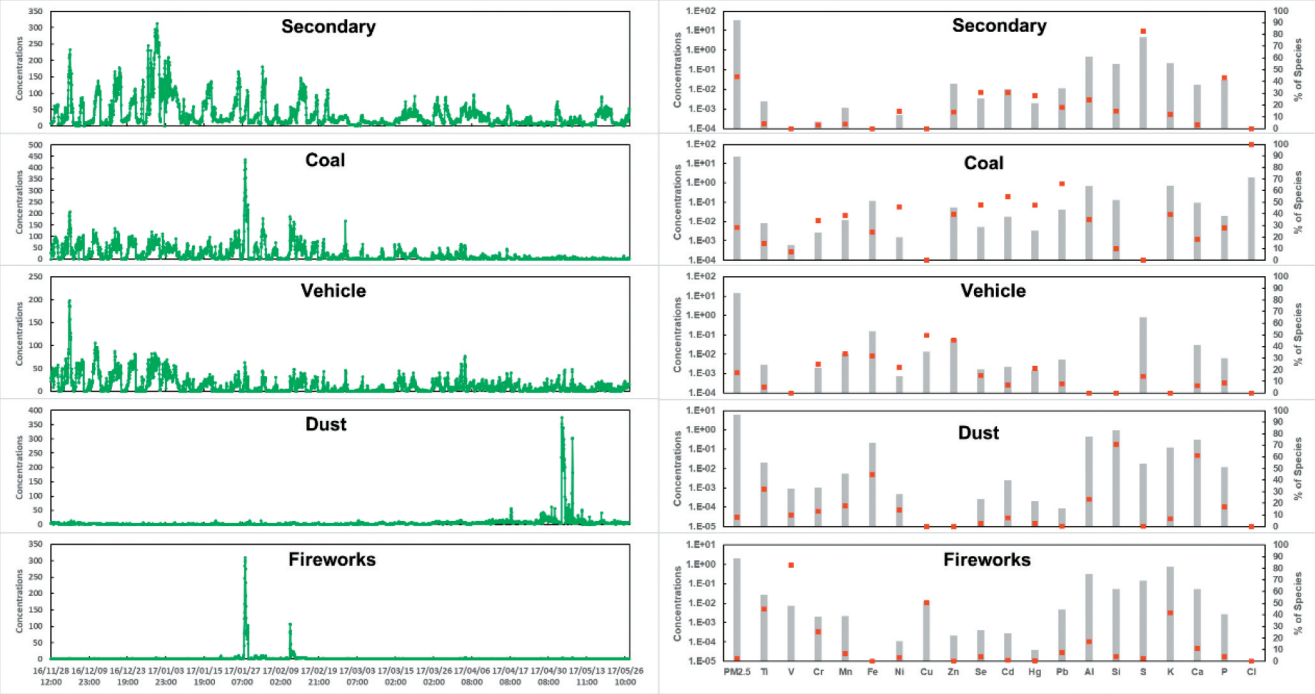

Figure 4 Factor profiles predicted from PMF model for PM2.5 samples obtained at Beijing

(31.5%) (the percentage represents the fraction of the element in factor 3 contributed to the total concentration of this element). Cu, Zn, Mn, and Fe are tracer elements for vehicle emission because they are usually present in the additives of engine oil or brake dust caused by the wear of brake pads of motor vehicles.[60] Affected by the weather, vehicle emission contributed 16.9 μg/m^3 to the total PM2.5 concentration during the heating season, which was slightly higher than the 9.2 μg/ m^3 during the non-heating season.

In addition, this study performed source analysis on two special types of pollutions, which were sandstorm and firework. These two pollutants are easily distinguishable from other pollutants due to their time-dependent variations (**Figure 4**).

Factor 4 was dust, which contributed 7.9% of the total PM2.5 concentration. The predominant elements in dust included Si (70.8%), Ca (61.3%), Fe (44.6%), and Ti (32.1%) (the percentage represents the fraction of the element in factor 4 contributed to the total concentration of this element). Because these elements are common in the Earth's crust, they are used as tracer elements for dust. Dust contributed significantly more to the total PM2.5 concentration in April and May than in other months because dust storm occurred most frequently during these months; the level of dust reached above 350 μg/m^3 during one known dust storm.

Factor 5 was fireworks, which contributed 2.5% of the total PM2.5 concentration. The main elements of fireworks included V (82.9%), Cu (50.4%), Ti (44.7%), K (42.0%) and Cr (25.2%) (the percentage represents the fraction of the element in factor 5 contributed to the total concentration of this element). The above elements are all ingredients contained in the raw materials for manufacturing the fireworks, in which Cu, Ti, and V provide color or flash effect, while K and Cr are ingredients of the oxidants.[21, 27, 53-55] The contribution from fireworks to the total PM2.5 concentration was significant during the Lunar New Year and the Lantern Festival and negligible in other periods. One thing worth noting is that, while Cl is the ingredient contained in a blasting agent delivering sound effect and an oxidant and often categorized as a tracer element for fireworks, it was categorized with coal burning (factor 2) in this study. Therefore, the contribution of coal burning to total PM2.5 concentration might be overestimated, and the contribution of fireworks might be underestimated.

From the monthly variation of the five sources, the contributions to PM2.5 from secondary particles (factor 1), coal burning (factor 2), and vehicle emission (factor 3) trended down from December 2016 to May 2017, and the contribution to PM2.5 from dust (factor 4) trended up in March 2017 and peaked during April to May 2017 (**Figure 5**). The hourly variation of secondary particles (factor 1), coal burning (factor 2), and vehicle emission (factor 3) demonstrated uniformity in December 2017 - low during daytime with the lowest point at about 11 AM, and high during nighttime with the highest point at about 11 PM, suggesting that, during December, the particulates from all three sources were influenced by atmospheric diffusion. However, after December such uniformity became less noticeable. From January to February 2017, the hourly variation of coal burning (factor 2) and fireworks (factor 5) showed similar trend, in particular, both peaking between 0 to 6 AM, indicating a lack of clear distinction between coal and fireworks in PMF modeling.

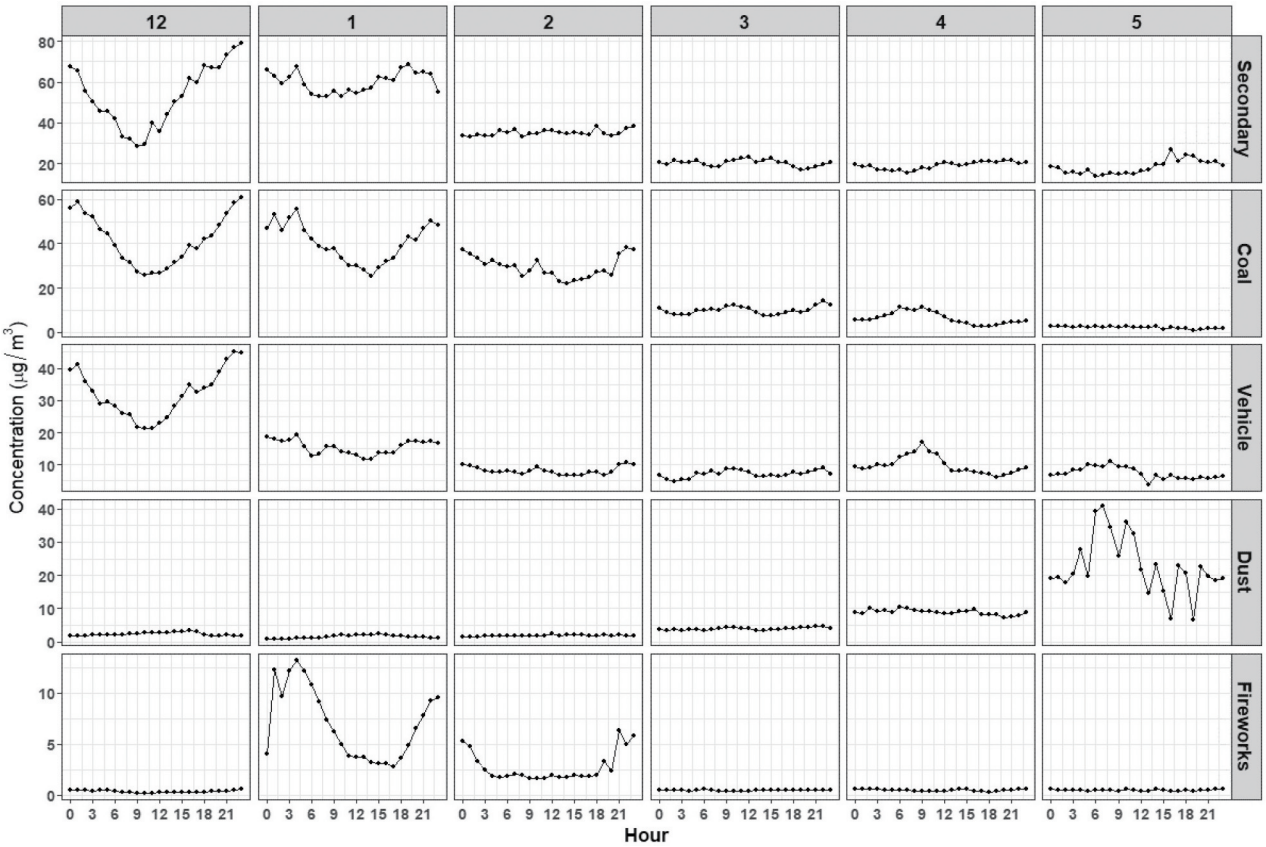

Figure 5 Monthly and hourly distribution of source factors from PMF model for PM2.5 at Beijing

There were seven episodes of severe pollution (**Figure 6**) observed in this study. In Ep1 to Ep4, the level of pollution increased as the concentration of secondary particles (factor 1) rose while other factors made smaller contributions, demonstrating that the formation of secondary particles was the chief instigator in the explosive increase of particles in heavy pollution episodes in Beijing during winter. In EpF1 and EpF2 fireworks (factor 5) made the most significant contribution to PM2.5 concentration, while in EpD, the most significant contributor, dust (factor 4), made more than 60% or even more than 90% to the total PM2.5 concentration.

The month-by-month emission source analysis of the concentrations of PM2.5 and the corresponding contribution from different factors is illustrated in **Figure 7**. Overall, the concentration of PM2.5 most highly correlated with the

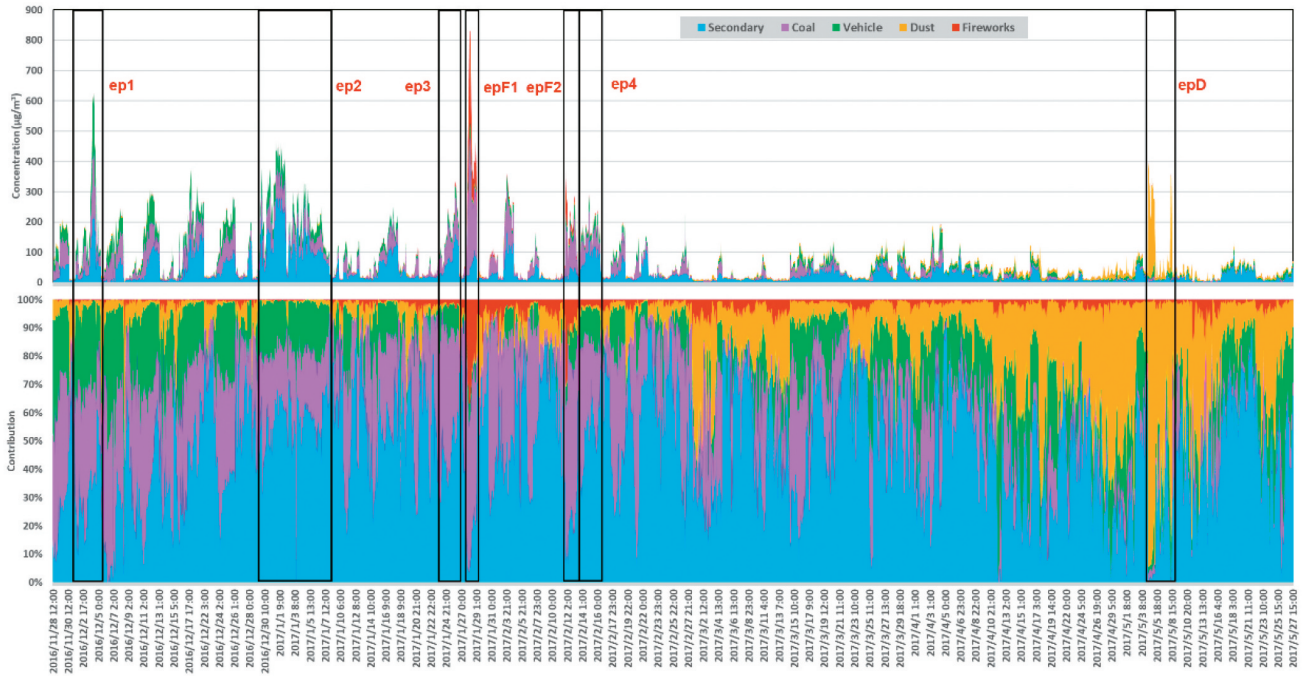

Figure 6 Time series of source factors from PMF model for PM2.5

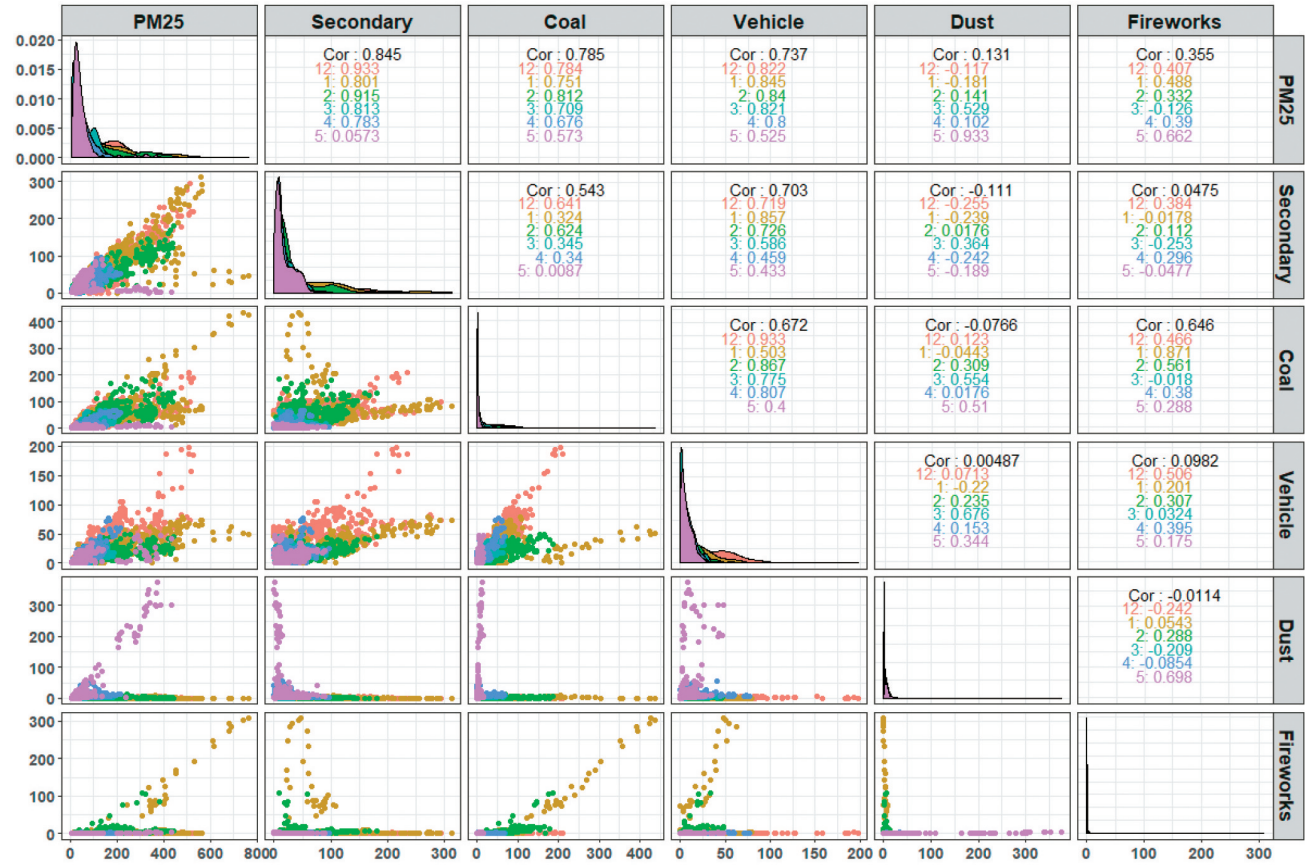

Figure 7 Monthly correlations between PM2.5 and different source factors

secondary particles (factor 1) with a correlation coefficient of 0.845. The correlation coefficient reached above 0.9 during December and February, but was significantly lower in April and May than in winter. Coal burning (factor 2) and vehicle emission (factor 3) had the second and third highest correlation, respectively, with PM2.5 concentration; both correlations had a coefficient of more than 0.7 (**Figure 7**). The level of PM2.5 was, in general, least correlated with dust (factor 4); their correlation coefficient was only 0.131. However, in May, dust and PM2.5 concentration became highly correlated at 0.933, confirming the positive correlation between PM2.5 and the various pollutant sources in this study. Vehicle emission (factor 3) and secondary particles (factor 1) were most correlated at a correlation coefficient of 0.703, which was higher than the correlation between coal burning (factor 2) and secondary particles (factor 1). Especially from December to February, vehicle emission (factor 3) and secondary particles (factor 1) had a correlation coefficient of more than 0.7, suggesting that vehicle emission made a significant contribution to the increase of secondary particles.

Conclusion

From November 28, 2016, to May 30, 2017, PM2.5 samples were collected hourly and analyzed with an online elemental analyzer. The mass concentration of PM2.5 was measured with beta-ray monitoring, and the concentration of the elements in each sample was measured with X-ray fluorescence. PM2.5 concentration ranged between 3.4 μg/m^3 and 763 μg/m^3 and had an average of 91.2 μg/m^3. A total of twenty elements were detected and investigated. Among them, Ni had the lowest average concentration at 0.0038 μg/m^3, and S had the highest average concentration at 5.82 μg/m^3. The levels of Si, Ca, Fe, Mn, Cu, and K were found to be lower than their corresponding values from 2001 and 2006 reported in the literature.

Based on the PMF source analysis, the primary sources of PM2.5 during the observation period in Beijing, in descending order of contribution to PM2.5, were secondary particles (44.0%), coal burning (28.3%), vehicle emission (17.2%), dust (7.9%), and fireworks (2.5%). Overall, the contribution from secondary particles, coal burning, and vehicle emission had been trending down month-bymonth. The hourly variation trends of the three main sources are similar in winter due to atmospheric diffusion. PM2.5 concentration seemed positively correlated to each of the sources. In particular, vehicle emission and secondary particles appeared highly correlated during the winter.

Analyses revealed that during different pollution episodes, excluding fireworks during festivals and dust storms, the contribution of secondary particles rose especially quickly, suggesting that the formation of the secondary particles was the crucial instigator in the explosive increase of PM2.5 concentration in Beijing during winter.

Prospect

This study was the first time that the PX375 online elemental analyzer made by HORIBA, Ltd. was used to study air pollution in Beijing. Since the instrument offers an hourly temporal resolution on the analysis of the PM2.5 concentration as well as the chemical elementary composition of PM2.5, it has a tremendous advantage over offline analytical technologies that only offers a daily temporal resolution. Hourly data enabled a detailed study on the source of PM2.5 in Beijing. At the same time, we think there is room for improvement:

1) During the observation period, there was a significant equipment-related loss of data. In particular, data loss during the heavy pollution episodes severely hampered data analysis and interpretation so that it became impossible to identify the source of the pollutant.
2) Even though we identified twenty compositional elements during the study, there were characteristic elements indicating the source of the pollutant that were still missing, such as Se, an important characteristic element of coal burning.
3) This study only covered winter and spring, which had pronounced episodes of pollution. However, Beijing also had serious pollution during spring and summer due to unfavorable weather conditions coinciding with industrial emission from cities surrounding Beijing. At the same time, since there is no heating-related emission during summer and autumn, studying pollution during these seasons will be helpful for targeted research on emissions from long-term industrial or residential air pollutants.

As to the first two items above, we intend to work closely with the research and development personnel at HORIBA to improve the performance of PX-375 according to the specific problems encountered in the actual use. For the third item above, we are planning one-year study of pollution in Beijing using PX-375 to perform online analysis of the chemical elementary composition of PM2.5 in different seasons. At the same time, we will compare the new data to existing data to explore the effectiveness of government policies on the air pollution in Beijing.

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References

[1] Kelly, J., Thornton, I., Simpson, P.R., 1996. Urban Geochemistry: a study of the influence of anthropogenic activity on the heavy metal content of soils in traditionally industrial and nonindustrial areas of Britain. Appl. Geochem. 11, 363e370.
[2] Nriagu, J.O., 1988. A silent epidemic of environmental metal poisoning. Environ. Pollut. 50, 139e161.
[3] Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace-metals. Nature 333, 134e139.
[4] Duan J, Tan J. Atmospheric heavy metals and Arsenic in China: Situation, sources and control policies[J]. Atmospheric Environment, 2013, 74(2): 93-101.
[5] Zhang N, Han B, He F, et al. Characterization, health risk of heavy metals, and source apportionment of atmospheric PM 2.5, to children in summer and winter: an exposure panel study in Tianjin, China[J]. Air Quality Atmosphere & Health, 2015, 8(4): 347-357.
[6] Donaldson K, Brown D, Clouter A, et al. The Pulmonary Toxicology of Ultrafine Particles[J]. J Aerosol Med, 2002, 15(2): 213-220.
[7] Limbeck A, Wagner C, Lendl B, et al. Determination of water soluble trace metals in airborne particulate matter using a dynamic extraction procedure with on-line inductively coupled plasma optical emission spectrometric detection[J]. Analytica Chimica Acta, 2012, 750(11): 111-119.
[8] Sato K, Tamura T, Furuta N. Partitioning between soluble and insoluble fractions of major and trace elements in size-classified airborne particulate matter collected in Tokyo[J]. Journal of Environmental Monitoring Jem, 2008, 10(2): 211-218.
[9] Gao, Y., Nelson, E.D., Field, M.P., Ding, Q., Li, H., Sherrell, R.M., Gigliotti, C.L., Van Ry, D.A., Glenn, T.R., Eisenreich, S.J., 2002. Characterization of atmospheric trace elements on PM2.5 particulate matter over the New York-New Jersey harbor estuary. Atmospheric Environment 36, 1077-1086.
[10] Nishikawa K, Yamakoshi Y, Uemura I, et al. Ultrastructural changes in Chlamydomonas acidophila, (Chlorophyta) induced by heavy metals and polyphosphate metabolism[J]. Fems Microbiology Ecology, 2003, 44(2): 253-259.
[11] Szivák I, Behra R, Sigg L. METAL-INDUCED REACTIVE OXYGEN SPECIES PRODUCTION IN CHLAMYDOMONAS REINHARDTII (CHLOROPHYCEAE)(1)[J]. Journal of Phycology, 2010, 45(2): 427-435.
[12] Hsu S C, Wong G T F, Gong G C, et al. Sources, solubility, and dry deposition of aerosol trace elements over the East China Sea[J]. Marine Chemistry, 2010, 120(1): 116-127.
[13] Song Y, Xie Z S, Zeng L, et al. Source apportionment of PM2.5 in Beijing by positive matrix factorization[J]. Atmospheric Environment, 2006, 40(8): 1526-1537.
[14] Zhang R, Jing J, Tao J, et al. Chemical characterization and source apportionment of PM2.5 in Beijing: seasonal perspective[J]. Atmospheric Chemistry & Physics, 2013a, 13(14): 7053-7074.
[15] Gao J, Tian H, Cheng K, et al. Seasonal and spatial variation of trace elements in multi-size airborne particulate matters of Beijing, China: Mass concentration, enrichment characteristics, source apportionment, chemical speciation and bioavailability[J]. Atmospheric Environment, 2014, 99: 257-265.
[16] Jin X, Xiao C, Li J, et al. Source apportionment of PM2.5 in Beijing using positive matrix factorization[J]. Journal of Radioanalytical & Nuclear Chemistry, 2016, 307(3): 2147-2154.
[17] Joly, A., Smargiassi, A., Kosatsky, T., Fournier, M., DabekZlotorzynska, E., Celo, V., Mathieu, D., Servranckx, R., D'amours, R., Malo, A., and Brook, J.: Characterisation of particulate exposure during fireworks displays, Atmos. Environ., 44, 4325-4329, 2010.
[18] Yu L. Characterization and Source Apportionment of PM2.5 in an Urban Environment in Beijing[J]. Aerosol & Air Quality Research, 2013, 13(2): 574-583.
[19] Huang R J, Zhang Y, Bozzetti C, et al. High secondary aerosol contribution to particulate pollution during haze events in China.[J]. Nature, 2014, 514(7521): 218-222.
[20] Jiang Q, Sun Y L, Wang Z, et al. Aerosol composition and sources during the Chinese Spring Festival: fireworks, secondary aerosol, and holiday effects[J]. Atmospheric Chemistry & Physics, 2014, 15(14): 20617-20646.
[21] Kong S, Li L, Li X, et al. The impacts of fireworks burning at Chinese Spring Festival on air quality and human health: insights of tracers,

source evolution and aging processes[J]. Atmospheric Chemistry & Physics Discussions, 2015, 14(21): 2167-2184.
[22] Li Y, Chang M, Ding S, et al. Monitoring and source apportionment of trace elements in PM2.5: Implications for local air quality management[J]. Journal of Environmental Management, 2017, 196: 16-25.
[23] Yatkin S, Bayram A. Elemental composition and sources of particulate matter in the ambient air of a Metropolitan City[J]. Atmospheric Research, 2007, 85(1): 126-139.
[24] Chow J C, Watson J G. Seasonal variations and sources of mass and chemical composition for PM_(10) aerosol in Hangzhou,China[J]. Particuology, 2009, 7(3): 161-168.
[25] Pan Y, Wang Y, Sun Y, et al. Size-resolved aerosol trace elements at a rural mountainous site in Northern China: importance of regional transport[J]. Science of the Total Environment, 2013, s 461-462(7): 761-771.
[26] Shen R, Schäfer K, Shao L, et al. Chemical characteristics of PM 2.5, during haze episodes in spring 2013 in Beijing[J]. Urban Climate, 2015.
[27] Do T M, Wang C F, Hsieh Y K, et al. Metals Present in Ambient Air before and after a Firework Festival in Yanshui, Tainan, Taiwan[J]. Aerosol & Air Quality Research, 2012, 12(5): 981-993.
[28] NPC, 2015. Law of Prevention and Control of Atmospheric Pollution. National People's Congress of China, Beijing.
[29] The Central People's Government of the People Republic of China, 2010. Guiding Opinions on Promoting the Joint Prevention and Control of Air Pollution to Improve Regional Air Quality, Beijing.
[30] The Central People's Government of the People Republic of China, 2013. Atmospheric Pollution Prevention and Control Action Plan.
[31] MEP, 2012. 12th Five-year Plan of Prevention and Control of Atmospheric Pollution in Key Areas, Beijing.
[32] Zhi G, Zhang Y, Sun J, et al. Village energy survey reveals missing rural raw coal in northern China: Significance in science and policy.[J]. Environmental Pollution, 2017, 223: 705-712.
[33] BJSTATS, 2016. http://www.bjstats.gov.cn/rkjd/.
[34] Gao M, Guttikunda S K, Carmichael G R, et al. Health impacts and economic losses assessment of the 2013 severe haze event in Beijing area[J]. Science of the Total Environment, 2015, 511: 553.
[35] Hao Y, Liu Y M. The influential factors of urban PM 2.5, concentrations in China: aspatial econometric analysis[J]. Journal of Cleaner Production, 2015, 112: 1443-1453.
[36] Wang Y S, Yao L, Wang L L, et al. Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China[J]. Science China Earth Sciences, 2014a, 57(1): 14-25.
[37] Wang Z F, Jie L I, Wang Z, et al. Modeling study of regional severe hazes over mid-eastern China in January 2013 and its implications on pollution prevention and control[J]. Science China Earth Sciences, 2014b, 57(1): 3-13.
[38] Zhang R H, Qiang L I, Zhang R N. Meteorological conditions for the persistent severe fog and haze event over eastern China in January 2013b[J]. Science China Earth Sciences, 2014b, 57(1): 26-35.
[39] Xiao Q, Ma Z, Li S, et al. The Impact of Winter Heating on Air Pollution in China[J]. Plos One, 2015, 10(1): e0117311.
[40] Liu J, Mauzerall D L, Chen Q, et al. Air pollutant emissions from Chinese households: A major and underappreciated ambient pollution source[J]. Proc Natl Acad Sci U S A, 2016, 113(28): 7756-7761.
[41] Guo J, Rahn K A, Zhuang G. A mechanism for the increase of pollution elements in dust storms in Beijing[J]. Atmospheric Environment, 2004, 38(6): 855-862.
[42] Paatero, P. and Tapper, U., 1993. Analysis of different modes of factor analysis as least squares fit problems. Chemometrics & Intelligent Laboratory Systems, 18 (2): 183-194.
[43] Jianlei Lang, Yanyun Zhang, Ying Zhou, Shuiyuan Cheng, Dongsheng Chen, Xiurui Guo, Sha Chen, Xiaoxin Li, Xiaofan Xing, Haiyan Wang, Trends of PM2.5 and Chemical Composition in Beijing, 2000-2015, Aerosol and Air Quality Research, 17: 412-425, 2017.
[44] Thurston, G.D., Ito, K. and Lall, R. (2011). A source apportionment of U.S. fine particulate matter air pollution. Atmos. Environ. 45: 3924-3936.
[45] Li, J.F., Song, Y., Mao, Y., Mao, Z.C., Wu, Y.S., Li, M.M., Huang, X., He, Q.C. and Hu, M (2014). Chemical characteristics and source apportionment of PM2.5 during the harvest season in eastern China's agricultural regions. Atmos. Environ. 92: 442-448.
[46] Oanh, N. T. K., Upadhuay, N., Zhuang, Y.-H., Hao, Z.-P., Murthy, D. V. S., Lestari P., Villarin, J. T., Chengchua, K., Co, H. X., Dung, N. T. and Lindgren, E. S.: Particulate pollution in six Asian cities: spatial and temporal distributions, and associated sources, Atmos. Environ., 40, 3367-3380, 2006.
[47] Chan, C. K. and Yao, X.: Air pollution in mega cities in China, Atmos. Environ., 42, 1352-2310, 2008.
[48] Yang, X. -Y. , Okada, Y., Tang, N., Matsunaga, S., Tamura, K., Lin, J. -M., Kameda, T. Toriba, A., and Hayakawa, K., 2007. Long-range transport of polycyclic aromatic hydrocarbons from China to Japan. Atmospheric Environment, 41, 2710-2718.
[49] Duan, F.K., He, K.B., Ma, Y.L., Yang, F.M., Yu, X.C., Cadle, S.H., Chan, T., Mulawa, P.A., 2006. Concentration and chemical characteristics of PM2.5 in Beijing, China: 2001e2002. Sci. Total. Environ. 355, 264e275.
[50] Westberg, H. M., Byström, M., and Leckner, B.: Distribution of potassium, chlorine, and sulfur between solid and vapor phases during combustion of wood chips and coal, Energy Fuel., 17, 18-28, doi: 10.1021/ef020060l, 2003.
[51] Duan,J.,Tan,J.,Hao,J.,Chai,F.,2014. Size distribution, characteristics and sources of heavy metals in haze episode in Beijing. J. Environ. Sci. (China) 26, 189-196.
[52] Zhang, Z.Z., Wang, W.X., Cheng, M.M., Liu, S.J., Xu, J., He, Y.J. and Meng, F. (2017). The contribution of residential coal combustion to PM2.5 pollution over China's Beijing-Tianjin-Hebei region. Atmos. Environ. 159: 147-161.
[53] Drewnick, F., Hings, S.S., Curtis, J., Eerdekens, G. and Williams, J. (2006). Measurement of Fine Particulate and Gas-Phase Species during the New Year's Fireworks 2005 in Mainz, Germany. Atmos. Environ. 40: 4316-4327.
[54] Moreno, T., Querol, X., Alastuey, A., Minguillon, M.C., Pey, J., Rodriguez, S., Miro, J.V., Felis, C. and Gibbons, W. (2007). Recreational Atmospheric Pollution Episodes: Inhalable Metalliferous Particles from Firework Displays. Atmos. Environ. 41: 913-922.
[55] Wang, Y., Zhuang, G., Xu, C., and An, Z. (2007). The Air Pollution Caused by the Burning of Fireworks during the Lantern Festival in Beijing. Atmos. Environ. 41: 417-431.
[56] Guo, J., Rahn, K., Zhuang, G., 2004. A mechanism for the increase of pollution elements in dust storms in Beijing. Atmos. Environ. 38, 855-862.
[57] Shen, R., Schäfer, K., Shao, L., Schnelle-Kreis, J., Wang, Y., Li, F., et al., 2016. Chemical characteristics of PM2.5 during haze episodes in spring 2013 in Beijing. Urban Clim. http://dx.doi. org/10.1016/ j.uclim.2016.01.003.
[58] Zhang, R., Jing, J., Tao, J., Hsu, S.-C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of PM2.5 in Beijing: seasonal perspective, Atmos. Chem. Phys., 13, 7053-7074, https:// doi.org/10.5194/acp-13- 7053-2013, 2013.
[59] Jiang, Z. Wang, A., 1982, Chemical state of sulfur in atmospheric suspended particulates in Beijing. Environ Chem. 1(4), 292-296.
[60] Yu L. Characterization and Source Apportionment of PM2.5 in an Urban Environment in Beijing [J]. Aerosol & Air Quality Research, 2013, 13(2): 574-583.
[61] He, K.B., Yang, F.M., Ma, Y.L., Zhang, Q., Yao, X.H., Chan, C.K., Cadle, S., Chan, T. and Mulawa, P. (2001). The characteristics of PM2.5 in Beijing, China. Atmos. Environ. 35: 4959-4970.
[62] Tan, J.H., Duan, J.C., Zhen, N.J., He, K.B. and Hao, J.M. (2016). Chemical characteristics and source of size-fractionated atmospheric particle in haze episode in Beijing. Atmos. Res. 167: 24-33.