Source apportionment of PM2.5 in Beijing using principal component analysis/absolute principal component scores and UNMIX

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Abstract

Source apportionment of fine particulate matter (PM2.5, i.e., particles with an aerodynamic diameter of 2.5 µm or less) in Beijing, China, was determined using two eigenvector models, principal component analysis/absolute principal component scores (PCA/APCS) and UNMIX. The data used in this study were from the chemical analysis of 24-h samples, which were collected at 6-day intervals in January, April, July, and October 2000 in the Beijing metropolitan area. Both models identified five sources of PM2.5: secondary sulfate and secondary nitrate, a mixed source of coal combustion and biomass burning, industrial emission, motor vehicles exhaust, and road dust. On average, the PCA/APCS and UNMIX models resolved 73% and 85% of the PM2.5 mass concentrations, respectively. The results were comparable to previous estimate using the positive matrix factorization (PMF) and chemical mass balance (CMB) receptor models. Secondary products and the emissions from coal combustion and biomass burning dominated PM2.5. Such comparison among various receptor models, which contain different physical constraints, is important for better understanding PM2.5 sources.
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1. Introduction

Over the past 20 years, epidemiological studies have demonstrated that ambient particulate pollution is associated with mortality and morbidity (Dockery et al., 1993) and that the association may be stronger for PM2.5 (particles with an aerodynamic diameter of 2.5 µm or less; Schwartz et al., 1996). High concentrations of PM2.5 have been measured in Beijing, China. He et al. (2001) reported an annual average of PM2.5 concentration at 115 µg m^{-3} in Chegongzhuang and at 127 µg m^{-3} in Tsinghua between July 1999 and September 2000. Zheng et al. (2005) reported the average PM2.5 concentration of 101 µg m^{-3} at five monitoring sites in Beijing in 2000. The PM2.5 pollution level in

Beijing is very high compared to the concentrations in US and European cities where levels are typically several to tens of micrograms per cubic meter. While it is urgently necessary to reduce PM2.5 pollution in Beijing, a clearer understanding of potential PM2.5 sources is required to implement this reduction.

Potential sources of particulate matter in Beijing have been identified using chemical speciation data. Secondary formation, biomass burning, traffic, industry, dust storms, coal burning, and construction activities have been identified as potentially important PM2.5 sources (He et al., 2001; Dan et al., 2004; Chan et al., 2005; Wang et al., 2005). However, these results were based only on qualitative analysis, and quantitative results from receptor models are needed to shape policy.

More recently, Zheng et al. (2005) applied molecular markers in the chemical mass balance receptor (CMB) model to apportion organic carbon (OC) in fine particles, as well as the total PM2.5 mass. Using the positive matrix factorization (PMF) method, Song et al. (2006) obtained improved results based on the original inorganic data from the same set of samples analyzed in the CMB model by Zheng et al. (2005). To better understand PM2.5 sources, results from current multi-receptor models should be compared and evaluated. Only a few comparisons have been performed (Poirot et al., 2001; Anderson et al., 2002; Miller et al., 2002; Maykut et al., 2003; Ito et al., 2004), although Hopke et al. (2006) recently used six different models to analyze particulate composition data sets for Washington, DC, and Phoenix, AZ. Each model has its own advantages and disadvantages. For example, PMF is very complicated and time-consuming. With CMB, the measurements of source profiles can have a difficult methodology and are also time-consuming. The source profiles obtained from USA or Europe are not suitable for use in China. By contrast, both eigenvector models, principal component analysis/absolute principal component scores (PCA/APCS) and UNMIX (Miller et al., 2002) to be used in this study are relatively simple and easy to perform using common software packages.

PCA/APCS is an effective tool to identify independent factors using the eigenvector decomposition of a matrix of pairwise correlations among compound concentrations (Miller et al., 2002). It was first applied in a study by Thurston and Spengler (1985) in Boston to estimate sources of particulate matter. UNMIX differs from PCA in that it uses a new transformation method based on the self-modeling curve resolution technique to derive meaningful factors (Miller et al., 2002). PCA/APCS and UNMIX have been successfully applied in numerous source apportionment study of air pollutants,

e.g., particulate matter (Baek et al., 1997; Poirot et al., 2001; Maykut et al., 2003; Almeida et al., 2005), volatile organic compounds (VOCs), and gaseous pollutants (Bruno et al., 2001; Anderson et al., 2002; Guo et al., 2004). In this study, the data used in PCA/APCS and UNMIX to apportion Beijing PM2.5 sources are the same data used previously in Song et al. (2006) for PMF analysis, and the results are compared to those from the CMB (Zheng et al., 2005) and PMF (Song et al., 2006) models.

2. Methods

2.1. Sampling and Chemical Analysis

In January, April, July, and October 2000, PM2.5 samples were collected simultaneously at five sites in Beijing for 24 h at 6-day intervals. The five sampling sites, shown in Fig. 1, were the Ming Tombs (OT), the airport (NB), Beijing University (BJ), Dong Si EPB (XY), and Yong Le Dian (CH). The OT site served as a background site, given that fewer people live there and it is far away from the downtown. The BJ and XY sites were located in urban areas, surrounded by heavy traffic, shops, and residential apartments. The NB site was close to the airport, surrounded by light industrial activities with little traffic. The CH site was near a street, surrounded by light industrial and residential activities. Three parallel filters (two Teflon filters and one quartz fiber filter, 47 mm in diameter) were collected during each 24-h sampling period. For each sample, the 24-h PM2.5 mass concentrations were measured. The chemical composition was analyzed for sulfate, nitrate, chloride, and ammonium ions by ion chromatography (IC) and for metals by X-ray fluorescence (XRF) spectroscopy using the Teflon filters. Elemental carbon (EC) and OC were determined following the National Institute of Occupational Safety and Health (NIOSH) thermal-optical procedures using the quartz fiber filter. Additional details of the sites, the particulate sampling procedures, and the analytical methods are given in Zheng et al. (2005).

Altogether, 100 samples were collected over 4 months. As indicated in Zheng et al. (2005) and Song et al. (2006), two dust storm (DS) events, which occurred on 7 and 25 April, were identified using backward trajectories and analysis of elemental data. The ten DS samples (five sites, two DS events) were excluded from this analysis for two reasons. First, after many tests, the contributions caused by DS events and local dust could not be distinguished by either the PCA or the UNMIX model, and the apportionment results were not well explained. Second, although DS events occur frequently in northern China during the
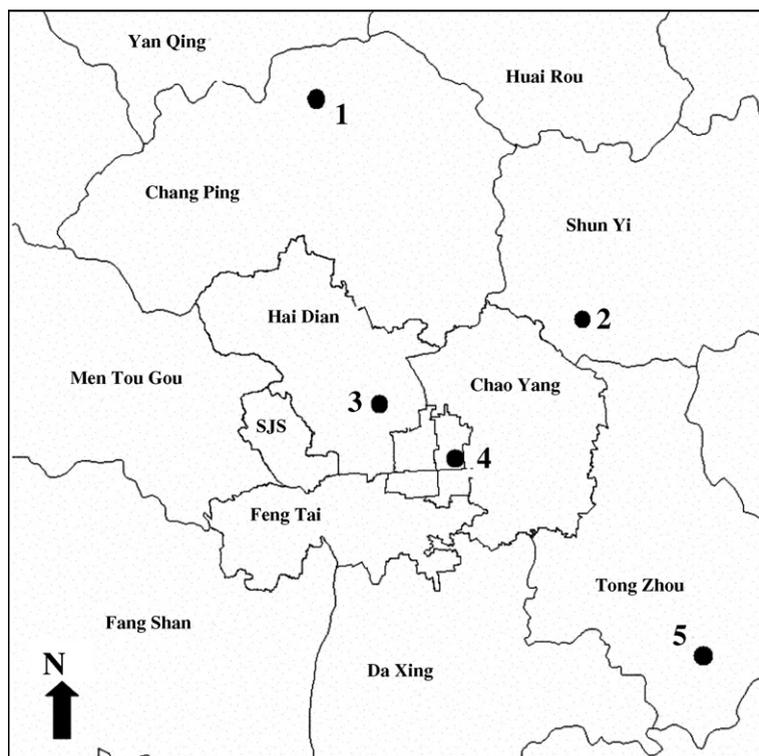
Fig. 1. The sampling site locations in Beijing: (1) the Ming Tombs (OT), (2) the airport (NB), (3) Beijing University (BJ), (4) Dong Si EPB (XY), and (5) Yong Le Dian (CH). "SJS" refers to the Shijingshan industrial area. The southwest corner is 39.586°N, 115.812°E, and the northeast corner is 40.425°N, 116.846°E.

spring, they seldom arrive in Beijing. Our analysis was therefore based on 90 samples, more than 50, the minimum of the sample number minus the number of selected species, recommended by Thurston and Spengler (1985) to obtain robust results. We excluded species that were frequently present at concentrations below the detection limit (BDL). The 24 species selected for our analysis were: OC, EC, NO_3^-, SO_4^{2-}, NH_4^+, Na, Al, Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Pb, and Mg. The few BDL points present in this data set were substituted with values of one-half the detection limit.

2.2. PCA/APCS and UNMIX

Assuming a linear relationship between the total mass concentration and the contributions of each species, PCA factors the data in several steps. First, the chemical composition data are transformed into a dimensionless standardized form:

$$Z_{ij} = \frac{C_{ij} - \bar{C}_j}{\sigma_j}, \tag{1}$$

where $i = 1, …, n$ samples; $j = 1, …, m$ elements; C_{ij} is the concentration of element j in sample i; and $\bar{C}_j$ and σ_j are the arithmetic mean concentration and the standard deviation for element j, respectively. The PCA model is expressed as

$$Z_{ij} = \sum_{k=1}^{p} g_{ik} h_{kj}, \tag{2}$$

where $k = 1, …, p$ sources, and g_{ik} and h_{kj} are the factor loadings and the factor scores, respectively. This equation is solved by eigenvector decomposition. Varimax rotation is often used to redistribute the variance and provide a more interpretable structure to the factors.

APCS is then used, based on the PCA factor scores, to derive quantitative estimates of source contributions and source profiles (Thurston and Spengler, 1985). Because the PCA results are based on normalized data, the true zero for each factor score should be calculated as

$$(Z_0)_j = \frac{0 - \bar{C}_j}{\sigma_j} = -\frac{\bar{C}_j}{\sigma_j}. \tag{3}$$

The rescaled scores are known as APCS. Finally, regression can be used to derive the source contributions, expressed as

$$M_i = \zeta_0 + \sum_{k=1}^{p} \zeta_k \text{APCS}_{ki}, \qquad (4)$$

where M_i is the measured mass concentrations in sample i. In general, M_i could be the sum of the mass concentrations of the chemical species or the total mass concentrations measured directly, such as by gravimetric filter weighing. APCS_{ki} is the rotated absolute component score for source k in sample i. $\zeta_k \text{APCS}_{ki}$ is the mass contribution in sample i made by source k. ζ_0 is the mass contribution made by sources unaccounted for in the PCA. Subsequently, the source profiles can also be obtained from the regression between C_{ij} and $\zeta_k \text{APCS}_{ki}$. The source contributions to individual species can be calculated from the source profiles and the mass contribution.

UNMIX uses the singular value decomposition (SVD) method to estimate the source number by reducing the dimensionality of data space m to p (Henry, 2003). The UNMIX model can be expressed as

$$C_{ij} = \sum_{l=1}^{p} \left(\sum_{k=1}^{p} U_{ik} D_{kl} \right) V_{lj} + \varepsilon_{ij}, \qquad (5)$$

where U, D, and V are $n \times p$, $p \times p$ diagonal, and $p \times m$ matrices, respectively; and ε_{ij} is the error term consisting of all the variability in C_{ij} not accounted for by the first p principal components. Geometrical concepts of self-modeling curve resolution are used to ensure that the results obey (to within error) the nonnegative constraints on source compositions and contributions. Additional constraints are also used to help determine the results. UNMIX normalizes the data matrix such that all the species are on the same scale with a mean of 1. The data are then projected to a plane perpendicular to the first axis of p-dimensional space. The edges represent the samples that characterize the source. Such edges in point sets are then used to calculate the vertices, which are used with the matrices decomposed by SVD to obtain the source profiles and contributions. The stand-alone EPA UNMIX version 5.0 was used in this study.

3. Results and discussion

3.1. Chemical species in PM2.5

The average mass concentrations of the 24 species and the total measured PM2.5 concentrations are listed in Table 1. OC, often emitted from burning sources, e.g.,

coal combustion and biomass burning, or transformed from VOCs by photochemical reactions, was the biggest contributor (22 μg m^{-3}, 23%) to PM2.5. SO_4^{2-}, NO_3^-, and NH_4^+ together contributed 37 μg m^{-3}, or 39% of the total PM2.5. These secondary products are primarily derived from the gaseous precursors SO_2 and NO_x. Strong solar radiation, high ambient temperature, and high relative humidity enhance photochemical processes (Seinfeld and Pandis, 1998), and these factors may have been responsible for the higher summer concentrations of SO_4^{2-}. Ammonium nitrate is semi-volatile at high temperatures, so NO_3^- concentrations should not be high in the summer. These patterns were also observed in Beijing by Yao et al. (2003). In order to be comparable with previous results by PMF and CMB, the PM2.5 mass concentrations used in the regression equation were reconstructed by multiplying the levels of OC by 1.4 to obtain the mass of organic matter, and the oxygen associated with minerals was also included to estimate the mass attributable to crustal materials.

3.2. Source identification

Sensitivity analysis was conducted in PCA and those results were found to be relatively stable. Unusually high

Table 1
Average concentration (μg m^{-3}) of chemical species in PM2.5

	January (n=25)	April (n=15)	July (n=25)	October (n=25)	Mean (n=90)	S.D.
Mass	60.93	134.15	98.96	105.55	96.09	54.43
OC	23.40	23.17	16.37	24.87	21.82	9.77
EC	2.03	3.67	3.06	4.01	3.14	1.38
NO_3^-	5.03	22.35	5.51	17.91	11.63	13.46
SO_4^{2-}	8.46	24.35	28.49	15.12	18.52	13.31
NH_4^+	3.41	12.16	7.40	7.19	7.03	6.33
Na	0.33	0.59	0.60	0.78	0.57	0.28
Al	0.40	0.74	0.56	0.39	0.50	0.36
Si	0.99	2.18	1.87	1.51	1.58	1.41
Cl	1.99	3.15	0.11	2.09	1.69	1.74
K	1.38	2.84	2.38	2.83	2.30	1.35
Ca	0.47	1.15	1.20	0.75	0.86	1.09
Ti	0.02	0.05	0.05	0.03	0.04	0.05
V	0.00	0.00	0.01	0.00	0.00	0.00
Cr	0.01	0.01	0.04	0.02	0.02	0.03
Mn	0.03	0.09	0.07	0.10	0.07	0.05
Fe	0.58	1.08	0.97	0.89	0.86	0.54
Ni	0.01	0.01	0.04	0.02	0.02	0.02
Cu	0.02	0.04	0.05	0.04	0.03	0.03
Zn	0.28	0.87	0.51	0.63	0.54	0.38
As	0.02	0.04	0.03	0.03	0.03	0.02
Se	0.00	0.01	0.01	0.01	0.01	0.01
Br	0.01	0.04	0.00	0.02	0.02	0.02
Pb	0.14	0.44	0.30	0.39	0.30	0.24
Mg	0.06	0.15	0.11	0.15	0.12	0.11

or unusually low concentrations were not found in individual samples, but V and Cr were removed from the analysis because there was not much change of their levels in different samples and they were not sensitive to PCA. The lowest eigenvalue for extracted factors was restricted to more than 1.0. UNMIX also uses some strict criteria to determine sources (e.g., explained variation is more than 0.8 and the signal-to-noise ratio is less than 2). Both PCA and UNMIX extracted five sources as shown in Table 2.

Source 1 was interpreted as road dust because both high factor loadings in the PCA results and high composition in the UNMIX results were found for crustal elements, e.g., Al, Si, Ca, Ti, Fe, and Mg (Watson and Chow, 2001; Almeida et al., 2005), most of which were also high in PMF (Song et al., 2006). Considerable levels of OC and SO_4^{2-} were found in the UNMIX profile, as well as in the PMF output, possibly from the deposition of particulate matter, e.g., coal ashes rich in OC and SO_4^{2-}.

Source 2 was explained by motor vehicle exhaust, as Pb and Zn were enriched in both the PCA and UNMIX results. In China, Pb had been used as an important antidetonator in gasoline, and Zn is emitted from lubricant oil, brake linings, and tires (Zhou et al., 2004). High factor loadings for EC in the PCA results were probably from tailpipe exhaust and attributable to poor vehicle maintenance in Beijing (Dahl, 2005). High levels of SO_4^{2-}

in UNMIX suggest that secondary sulfate was mixed in this source. The other high factor loadings, Mn, Cu, and As, in PCA could be explained by the mixing of this source with other unclear sources. The ratio of OC/EC in UNMIX in this source was 3.36, a bit higher than the 2.05 found by Cadle et al. (1999) in fresh gasoline exhaust. The number of gasoline-powered vehicles accounted for 95% of all vehicles in Beijing in 2000.

Source 3 may have been a mixture of coal combustion and biomass burning because both PCA and UNMIX showed high levels for OC, Cl, and K. High OC and EC (relatively high in the UNMIX results) levels can be found in combustion emissions (Zheng et al., 2005). Both the chemical analysis of ambient PM2.5 samples (Duan et al., 2006) and source profiles measured in the laboratory (Zheng et al., 2005) have indicated that Cl can be considered an elemental tracer for coal combustion in Beijing. Moreover, in accordance with the PMF results (Song et al., 2006), high levels of K were found, indicating that biomass burning was occurring (Watson and Chow, 2001). High nitrate source was found in PCA and UNMIX. Combustion sources actually emit few nitrates, but they emit large quantities of NO_x, which could rapidly form nitric acid regardless of the meteorological conditions (Harrison et al., 1997). Therefore, the nitrate in this source could represent the local emission of precursor pollutants. Similar results were also

Table 2
PCA factor loadings (only those with values ≥ 0.5 are listed) and UNMIX source compositions (mass fractions) for PM2.5

	PCA factor loadings					UNMIX source composition				
	F1	F2	F3	F4	F5	S1	S2	S3	S4	S5
OC			0.79			0.196	0.235	0.426	0.069	0.371
EC		0.63				0.043	0.070	0.051	0.006	0.049
NO_3^-			0.65	0.59		−0.049	0.029	0.200	0.287	−0.049
SO_4^{2-}				0.81		0.191	0.351	−0.098	0.394	0.340
NH_4^+				0.78		0.003	0.054	0.040	0.172	0.056
Na						0.011	0.012	0.005	0.004	0.009
Al	0.96					0.030	0.005	0.006	0.001	0.002
Si	0.98					0.111	0.015	0.012	0.006	0.002
Cl			0.83			−0.008	0.002	0.078	0.000	−0.009
K			0.54			0.034	0.043	0.039	0.009	0.031
Ca	0.97					0.082	0.004	0.003	0.003	−0.001
Ti	0.95					0.004	0.000	0.000	0.000	0.000
Mn		0.60				0.001	0.002	0.001	0.001	0.001
Fe	0.92					0.041	0.008	0.009	0.003	0.011
Ni					0.79	0.000	0.000	0.000	0.000	0.002
Cu		0.75				0.000	0.002	0.000	0.000	0.000
Zn		0.70				0.004	0.012	0.012	0.001	0.007
As		0.60		0.55		0.000	0.001	0.000	0.000	0.000
Se					0.62	0.000	0.000	0.000	0.000	0.000
Br			0.72			0.000	0.000	0.001	0.000	0.000
Pb		0.83				0.002	0.012	0.004	0.002	0.001
Mg	0.69					0.006	0.002	0.002	−0.001	0.001

observed by Almeida et al. (2005). The contribution of secondary sulfate was often very high in summertime, while contribution of coal burning especially for heating was low, and secondary sulfate contribution was low in wintertime while coal burning was high in wintertime. Sulfate appears low in the combustion source. High Br could be related to coal burning, as with Cl.

Source 4 was characterized by high sulfate, nitrate, and ammonium that could be identified as a mixture of secondary sulfate and secondary nitrate. These secondary products are often formed from the oxidation of SO_2 and NO_x and the neutralization of NH_3 (Seinfeld and Pandis, 1998). It was surprising that the secondary sulfate and secondary nitrate were not separated by factor methods as in other research (Li et al., 2004; Song et al., 2006) because they usually have opposing seasonal patterns, as high temperatures can accelerate sulfate formation and render secondary nitrates unstable (Seinfeld and Pandis, 1998). Rather, we found that sulfate and nitrate exhibited distinct opposite trends only in July 2000, although their concentrations were highly correlated in the other 3 months (the correlation coefficient reached 0.9). Secondary sulfate formation in other seasons was not as efficient as in summer. Firstly, the weaker solar radiation could reduce the photochemical activity. Secondly, the lower air temperatures and lower relative humidity could lead to reduced efficiency by in-cloud processing (Yao et al., 2003). In contrast, secondary nitrate was conserved under lower air tempera-

tures and was found to form by deposition onto existing fine mode sulfates in Beijing (Yao et al., 2003). The high correlation between secondary sulfate and secondary nitrate resulted in these components not being distinguished by the PCA and UNMIX models, as they were in previous studies (Baek et al., 1997; Almeida et al., 2005; Yuan et al., 2006).

Source 5 suggested an industrial source because of high factor loadings by the heavy metal element Ni, which was also high in the PMF industry source. Some metal manufacturing plants still exist in Beijing, including those in the Shijingshan and Fatou industrial areas, and these could probably affect the sampling sites, as the average concentrations of Ni were relatively high at the two sites close to the industrial areas, BJ and XY. The highest concentration of Ni was found at NB in Shunyi and may reflect the presence of car manufacturers in the area.

3.3. Source contributions

Before estimating the source contributions, we evaluated the performance of PCA/APCS and the UNMIX model. Table 3 compares the calculated values with the measured concentrations for each species. The mean differences indicate that UNMIX results were closer to the measurements than the APCS results. Large uncertainties in APCS, such as 63% for NO_3^-, may have been caused by the model itself (e.g., uncertainties in

Table 3
A comparison among measured, APCS-calculated, and UNMIX-calculated concentrations ($\mu g\ m^{-3}$) of chemical species in PM2.5

Species	Measured	APCS-modeled	APCS R^2	APCS uncertainty	UNMIX-modeled	UNMIX R^2	UNMIX uncertainty
OC	21.82	14.11	0.72	35	20.25	0.48	7
EC	3.14	2.58	0.74	18	3.02	0.64	4
NO_3^-	11.63	18.90	0.88	−63	13.12	0.91	−13
SO_4^{2-}	18.52	16.18	0.86	13	20.30	0.81	−10
NH_4^+	7.03	8.11	0.93	−15	7.03	0.94	0
Na	0.57	0.47	0.61	18	0.55	0.55	4
Al	0.50	0.35	0.94	30	0.48	0.91	5
Si	1.58	1.59	0.97	−1	1.56	0.97	1
Cl	1.69	1.72	0.83	−2	1.86	0.81	−10
K	2.30	2.42	0.66	−5	2.27	0.57	1
Ca	0.86	1.17	0.95	−36	0.91	0.96	−5
Ti	0.04	0.04	0.91	−11	0.04	0.93	−5
Mn	0.07	0.10	0.75	−44	0.07	0.75	−6
Fe	0.86	0.82	0.94	4	0.85	0.94	1
Ni	0.02	0.02	0.68	10	0.02	0.68	−9
Cu	0.03	0.04	0.64	−4	0.04	0.64	−4
Zn	0.54	0.56	0.65	−4	0.55	0.65	−2
As	0.03	0.02	0.73	39	0.03	0.73	6
Se	0.01	0.01	0.70	−22	0.01	0.70	2
Br	0.02	0.02	0.65	−17	0.02	0.65	−23
Pb	0.30	0.36	0.85	−20	0.32	0.85	−4
Mg	0.12	0.13	0.63	−16	0.14	0.63	−21

APCS parameters) and the data quality. The correlation coefficients were often high, suggesting acceptable results. The APCS were estimated from the factor scores. The source contributions were then obtained by regression. EPA UNMIX can provide the source contributions in the output window. The source contributions from PCA/APCS and UNMIX and comparisons with CMB and PMF results are shown in Table 4.

The sum of secondary sulfate and secondary nitrate determined by PCA/APCS and UNMIX was 23.3 and 28.3 µg m^{-3}, respectively, and the secondary products apportioned by CMB and PMF were 34.2 and 31.4 µg m^{-3}, respectively. Apportioning the secondary products was problematic. The total sulfate contained primary emissions from coal combustion (found in the chemical profile used in CMB) and secondary products from photochemical reactions. The CMB model used only sulfate, nitrate, and ammonium in the secondary profiles; however, in the factor analysis results, the secondary source often included other components, especially secondary OC. Furthermore, some sulfate and nitrate was often attributable to the combusting sources by factor analysis models, as gaseous precursors such as NO$_x$ and SO$_2$ are often emitted by combustion. High sulfate levels were associated with vehicle exhaust in the primary PMF run and UNMIX results, and as shown in this study, nitrate was found in vehicle exhaust and combustion sources (Harrison et al., 1997).

The contributions of coal combustion and biomass burning were 26.7 and 23.5 µg m^{-3} in the PCA/APCS

and UNMIX results, respectively, and close to 26.2 µg m^{-3} in the PMF and higher than 14.8 µg m^{-3} in the CMB results. Coal is the major energy source in Beijing, accounting for 64.3% of total energy consumption in 2000 (nearly 2.7×10^7 t of a total 4.2×10^7 t of energy consumed), and was a very commonly provided seasonal heating source before 2000. Agrarian cultivation is still extensive in the Beijing suburbs, and in the fall, the incineration of fallen leaves throughout the city contributes to biomass burning numbers (Dan et al., 2004). Biomass burning contributions in the PMF and CMB results were similar. However, coal combustion contributions were much higher in the PMF (16 µg m^{-3}) than in the CMB figures (6.4 µg m^{-3}). One reason for the difference was that the source profile of coal burning in the CMB model only represented residential coal burning in winter, and did not include high-efficiency low-organic coal combustion. The ratio of OC/EC in the CMB source profile was 1.8, very close to the ratio of 1.5 for PM10 emitted from coal burning in winter (Duan et al., 2005). The other reason was that the CMB profile contained only primary organics, but the profile extracted by PMF probably included secondary organics. The contributions from PCA/APCS and UNMIX may also contain the secondary organics.

PCA/APCS extracted a level of 6.0 µg m^{-3} from motor vehicle contributions, close to the CMB and PMF results of 6.6 and 5.6 µg m^{-3}, respectively. UNMIX appointed a higher contribution to motor vehicle contributions, at 10.9 µg m^{-3}; however, as noted previously, secondary sulfate could be mixed in the UNMIX results. Such mixing also occurred in the primary PMF run, and a parameter (FKEY) was used to force it to zero in the final PMF run. However, the contribution by motor vehicles, even as appointed by the other three models, was still very high compared to that in New York City (Li et al., 2004), where the vehicle contribution was only 0.52 µg m^{-3} in July 2001. However, the number of household motor vehicles in New York City, 2.98 million in 2000 (www.rightofway.org/research/5borocars2000.htm), exceeded the total number of vehicles in Beijing in 2000 (1.5 million). Recent testing showed that 40% of the cars and 70% of the taxis in Beijing failed to meet Western emission standards (Dahl, 2005) and indicates that motor vehicles in Beijing are poorly maintained. We should point out the appointment results could be the fresh fine particles emitted from the tailpipes. They also emitted lots of NO$_x$ and VOCs, which could be transferred to secondary nitrate and secondary organic carbon (SOC) by photochemical reactions. If such particles were considered, the total contributions from motor vehicles to PM2.5 could be much higher.

Table 4
A comparison among PCA/APCS, UNMIX, PMF, and CMB models of average source contributions (µg m^{-3}) to PM2.5 mass concentrations

Identified sources	CMB	PMF	PCA/APCS	UNMIX
Secondary sulfates	16.9	16.2		
Secondary nitrates	10.8	15.2	23.3	28.3
Secondary ammonium	6.5			
Coal combustion	6.4	16.0	26.7	23.5
Biomass aerosols	8.4	10.2		
Motor vehicles	6.6	5.6	6.0	10.8
Road dust	12.4[a]	7.1	7.2	8.4
Industry		4.7	6.6	11.0
Cigarette smoke	1.3			
Vegetative detritus	1.0			
Other organic matter	11.3			
Others	15.5	18.3	26.4	14.1
Total[b]	101	93	96	96

[a] Averaged in January, July, and October as a different dust signature used during April in CMB.
[b] CMB: an average of the measured PM2.5 mass concentrations in 100 samples; PMF: the contributions of apportioned dust storms were subtracted from the CMB value (101 µg m^{-3}); PCA/APCS and UNMIX: averages of 90 samples (excluding 10 dust storm samples).

The road dust contribution was 7.2 and 8.4 µg m^{-3} in PCA/APCS and UNMIX, respectively, close to 7.1 µg m^{-3} in the PMF, and lower than 12.4 µg m^{-3} (the average for January, July, and October because a different dust profile was used in April samples) in the CMB results. However, the road dust profile used in the CMB model was measured from samples collected in the United States and would not be applicable to Beijing.

PCA/APCS and UNMIX appointed industry contributions of 6.6 and 11.0 µg m^{-3}, respectively, in comparison with the 4.7 µg m^{-3} found by the PMF model. The CMB model did not apportion PM2.5 to industry due to the lack of a source profile.

In total, the PCA/APCS and UNMIX methods resolved 73% and 85% of the PM2.5 mass concentrations, respectively. PMF resolved 82%. Although the CMB model indicated that 88% of the PM2.5 was apportioned, it included a category of other organic matter, most likely due to the secondary organic aerosol formation.

4. Conclusions

Receptor models are often used to identify source contributions. To date, several such models have been popular based on their physical assumptions and constraints. However, comparisons among the results of different models are important to better understand source apportionment. In the present study, PCA/APCS and the UNMIX model were used to distinguish among PM2.5 sources based on chemical species concentration data collected in 2000. Both the PCA/APCS and the UNMIX results resembled previous PMF results and were comparable to those from the CMB model. The present results reconfirmed that secondary aerosols and coal and biomass burning were dominant mass contributors to PM2.5 in Beijing. Road dust, motor vehicles, and industry also contributed significantly to the PM2.5 mass concentration. In general, UNMIX explained a higher percentage of PM2.5 than PCA/APCS, but sources with similar attributes, e.g., secondary sulfate and secondary nitrate or coal combustion and biomass burning, could not be distinguished by either model. To obtain primary results, the PCA or UNMIX were recommended because they could be run feasibly and easily on some statistical software.

PM2.5 pollution is a serious problem in Beijing. Shifting the city's principal energy source from coal to a clean source is necessary. Gasoline quality should also be improved to reduce emissions of NO$_x$ and OC. Moreover, watering and road washing practices could prevent the resuspension of road dust. These proposed measures should be carried out to reduce PM2.5 pollution in Beijing. While a large number of sampling sites is not crucial to improving the understanding of PM2.5 sources, a long-term monitoring system should be implemented in the near future.

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