

### Source Characterization and Apportionment of PM<sub>10</sub> in Panzhihua, China

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### ABSTRACT

A total of 258 particulate matter ( $PM_{10}$ ) filter samples and 69 source samples applicable to receptor model source apportionment were collected and chemically analyzed from February to August 2007 in Panzhihua, China. Contributive sources were identified and the chemical profiles were reported for resuspended dust, paved and unpaved road dust, coal-fired power plant exhaust, emissions from coking plants and other industrial sources in Panzhihua. All samples were analyzed for 19 elements (Na-Pb), two ions (NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) and organic and total carbon. Elevated abundances of geological components (Al, Si, Ca and Fe) from fugitive dust materials and elements (Ti, Cr, Mn, Cu and Zn) from special industry plants were found in the profiles. The contributions to the ambient  $PM_{10}$  levels at six sites in three seasons (spring, summer and winter) were estimated using a chemical mass balance receptor model. The concentration of  $PM_{10}$  was high (150 µg/m<sup>3</sup>) on winter days and low in summer and spring (133 and 129 µg/m<sup>3</sup>, respectively). Apportionment results indicate that coal combustion ash, iron and steel industry dust, vehicle exhaust and secondary  $SO_4^{2-}$  were major contributors, accounting for about 70% of  $PM_{10}$ . More attention should be paid to particulate matter emitted by iron and steel manufacturing facilities in view of high contribution and potentially toxic metals.

Keywords: Chemical mass balance; Particulate matter; Source apportionment.

### INTRODUCTION

Particulate matter is generated by various natural processes and human activities, such as soil dust, resuspended dust, coal combustion fly ash, vehicle exhaust, secondary aerosols and particulate matter produced by other industrial processes (Voutsa et al., 2002; Machemer, 2004; Sun et al., 2004; Han et al., 2005). Source apportionment of ambient particulate matter is widely conducted using chemical mass balance (CMB) model. The CMB model infers source contributions by determining the best-fit combination of emission source chemical composition profiles needed to reconstruct the chemical composition of ambient samples (Waston et al., 1991). Hundreds of source profiles have been compiled and estimations of source contributions have been determined by using the CMB model (Waston et al., 1994; Abu-Allaban et al., 2002; Chio et al., 2004; Samara, 2005). The CMB source apportionment have been also applied in

several urban areas in China to develop pollution control strategies (Bi *et al.*, 2007; Feng *et al.*, 2007; Zhang *et al.*, 2007).

Panzhihua, a highly industrialized city in southwest China, has poor air quality mainly because of the high concentration of PM<sub>10</sub> in the atmosphere. The area has suffered from high particulate matter (PM) and heavy metals. In recent years, most power plants were equipped with electrostatic precipitators with high retention efficiency (>99.9%), however considerable amounts of fine fly ash particles and heavy metals were emitted to the atmosphere because of the high rate of coal combustion and various metallurgical industries. Furthermore, Panzhihua locates in Pan-Xi Rift Valley and the urban area is surrounded by high mountains, which aggravates particulate pollution. In this study, the concentrations of PM<sub>10</sub> at six monitoring sites were investigated, and profiles of sources and receptors that include 19 elemental species, two water-soluble ions, total carbon (TC) and organic carbon (OC) were acquired by chemical analysis. Potential major contributors were identified on the basis of factor analysis and local environmental background information. Source contributions to ambient PM<sub>10</sub> were estimated using a CMB receptor model.

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### METHODS

### Description of the Study Area

Panzhihua is an industrialized city with over 1 million inhabitants in an urban area of 54 km<sup>2</sup>. With a longitude of  $108^{\circ}08'E-102^{\circ}15'E$  and latitude of  $26^{\circ}05'N-27^{\circ}21'N$ , Panzhihua lies in southwest China (Fig. 1(a)) where Sichuan Province borders Yunnan Province and the Yalung River merges into the Jinshajiang River.

Located in the southern central part of the Pan-Xi Rift Valley, Panzhihua lies in a denuded mountainous area, which features high mountains and deep valleys intersected with basins and canyons. The terrain inclines from the northwest to the southeast and the mountain range runs almost from north to south. The relative altitude difference is 3258.5 m, with the highest altitude being 4195.5 m and the lowest 937 m. Most of the terrain of Panzhihua (92% of the urban area) is mountainous. The terrain is shown in detail in Fig. 2.

Panzhihua is dominated by the south subtropical-north temperate zone with a vertical climatic distribution, which is characterized by a long summer, abrupt daily temperature changes, indistinct seasons, dry air, concentrated rainfall and diverse microclimates. The rainy season is usually from early June to October, while the dry season is from November to May. Valley wind is significant in Panzhihua. Every district has a distinct wind direction depending on various partial landforms. Near-ground temperature inversion occurs frequently and the largest difference in temperature is 3°C in winter. Such topography and meteorology make it difficult for particulate pollutants to disperse and thus they have adverse health effects.

According to the database of the Panzhihua Environmental Protection Agency, industrial emissions were considerable in 2007 and included  $8.2 \times 10^3$  t of coal combustion fly ash,  $9.36 \times 10^3$  t of industrial dust and  $112 \times 10^3$  t of SO<sub>2</sub>. Iron and steel manufacturing is the major industrial activities to potentially impact on the ambient air quality, and the airborne release of particulate matter may have adverse effects on human health (Machemer, 2004). Particulate matter and sulfur dioxide exhausted in manufacturing accounted for 78% and 72.3% of total emissions respectively.

Considering various anthropogenic activities, such as construction, vehicle movement on paved and unpaved roads, quarrying of coal, fugitive dust is another important potential particulate source. Furthermore, vehicle exhaust is thought to be a considerable source in view of the large number of vehicles.

### **Sampling Procedures**

Ambient sampling. Ambient  $PM_{10}$  samples were collected at six sites shown in Fig. 1(b), Fig. 2 and Table 1. Hemenkou (HMK), Nongnongping (NNP), Bingcaogang (BCG), Tailong (TL) and Jinjiang (JJ) were located in urban areas in which there were different types of anthropogenic activity, while Renhe (RH) was a background site. Site HMK was located in the west of the study area in one of the main industrial parks in Panzhihua. Near the site, anthropogenic activity, such as energy generation, V and Ti industry, construction activity, mining and the quarrying of coal and other raw materials, contributes particles to the ambient air. Site NNP was located in another significant industrial park, which has typical iron and steel industry and is the location of the



Fig. 1. Maps (a, b) of the study area of Panzhihua and locations of ambient sampling sites.



Fig. 2. Terrain of Panzhihua and six ambient sampling sites.

Table 1. Ambie	nt PM <sub>10</sub> san	pling sites.
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No.	Site Name	Latitude, Longitude	Elevation <sup>a</sup> (m)	Site Description
1	HMK	26°35'28.70"N, 101°34'37.30"E	1123	Mixed Industrial area
2	NNP	26°34'11.50"N, 101°41'40.95"E	1163	Iron and steel industrial area
3	BCG	26°35'8.95"N, 101°43'1.32"E	1127	Commercial and inhabited area
4	TL	26°35'8.95"N, 101°43'1.32"E	1207	Identical with BCG site
5	JJ	26°32'56.50"N, 101°50'54.20"E	1026	Traffic and inhabited area
6	RH	26°30'2.76"N, 101°44'13.44"E	1108	A background site

<sup>a</sup> Above mean sea level

Panzhihua Iron and Steel Group Corporation. Sites BCG and TL were located in central urban areas where there were busy roads and residential buildings. The two sites had identical locations but different sampling heights (Table 1). Site JJ was located in the eastern urban area, with the Panzhihua New Technology Zone to the south. The background site RH, around which there were no evident particulate emitters, was about 9 km south of site BCG.

At each site, two precalibrated samplers (TH-150, Wuhan Tianhong Intelligence Instrument Facility, China) collected  $PM_{10}$  samples. One sampler contained polypropylene filters (90 mm in diameter, Beijing Synthetic Fiber Research Institute, China) and the other quartz-fiber filters (90 mm in diameter, 2500QAT-UP, Pall Life Sciences). All samples were collected at a flow rate of 100 L/min and in a 24-hr period. A total of 258  $PM_{10}$ ambient filters were acquired for three periods (February 7–14, April 19–26 and August 23–30 in 2007).

Source sampling. A total of 69 samples of nine potential source categories according to the Panzhihua emitter inventory were collected in and around urban areas. Resuspended dust was sampled with a brush from long time uncleaned windowsills or plat floors in urban areas (Zhao et al., 2006). The resuspended dust sampling sites were uniformly selected to cover the entire urban area and five subtypes were established on the basis of different districts. Road dust was swept from representative portions of major paved and unpaved road surfaces or parking lots at 14 locations with a plastic brush and dustpan. Coal combustion fly ash was divided into three subtypes (MGSMY, PPMY and SMMY) on the basis of the characteristic of the fuel and dedusting facilities. Samples were collected from fly ash storage piles, dust precipitators, briquette-burning residuals (residential and coal combustion) by grab sampling. Other industrial dust samples were collected with corresponding source sampling methods (Gordon et al., 1984; Chow et al., 1988; Ahuja et al., 1989; Hildemann et al., 1989). Detailed descriptions of major sources are summarized in Table 2.

Resuspended dust, paved and unpaved road dust, fly ash and other industrial source samples were sieved through a 150-mesh sieve, suspended in a resuspension chamber and sampled using a  $PM_{10}$  size-selective cutter with Xue et al., Aerosol and Air Quality Research, 10: 367–377, 2010

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Mnemonic	Source category	Description
R D <sup>a</sup>	Resuspended dust (including 5 subtypes: BCGRD,	Composite of 26 resuspended dust sampled in
itte	HMKRD, NNPRD, JJRD, RHRD)	Panzhihua
DL	Road dust	Composite of 14 paved and unpaved road dust
MGSMV	Gangue coal-fired nower plant fly ash	2 grab samples of bottom ash from Panzhihua
	Gangue coal-filed power plant fly ash	coal gangue fueled power plant
PPMV	Coal-fired power plant fly ash	3 grab samples of bottom ash from Panzhihua
1 1 101 1	Coal-filed power plant fly ash	coal-fueled power plant
SMMY	Residential coal combustion	Composite of 4 samples from residential coal
	Residential coal compastion	combustion
CP	Coking plant	Composite of 6 samples from coking plants
GVV	V industry	Composite of 2 samples collected at V2O3
UIV	v-industry	manufacture
GVTi	Ti industry	Composite of 2 samples collected at 4 Ti-
0111	11-mdustry	manufactories
GYCE	Cement manufacture	Composite of 10 grab samples
UICE		Composite of 10 grad samples

Table 2. Descriptions of PM sources in Panzhihua, China.

<sup>a</sup> RD: RD refers to dust that is continually raised into the surrounding atmosphere by natural forces or human activity after being initially deposited in urban areas. RD samples were collected at five sites: BCG, HMK, NNP, JJ and RH.

polypropylene and quartz-fiber filters, which was similar to ambient sampling (Chow *et al.*, 1994). The resuspended samples were stored in silica gel desiccators to ensure moisture equilibrium as for other samples.

### **Chemical Analysis Procedures**

Inductively coupled plasma analysis (ICP 9000 N+M, Thermo Fisher Scientific Inc., USA) was employed to determine concentrations of Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Hg and Pb in samples collected on polypropylene-fiber filters and in dust samples. Water-soluble ions ( $NO_3^-$ ,  $SO_4^{2-}$ ) were determined by ion chromatography (DX-120, Dionex Ltd., USA) after sample extraction with deionized water. TC and OC were measured using an element analyzer (Elementar Analysensysteme GmbH VarioE1, Germany). A set of standard reference materials—Sediments Standard Series (GSD1-GSD12), Soil Standard Series (GSS1-GSS8), Rock Standard Series (GSR1-GSR12), coal fly ash (82201), and cement (GBW 03201) was used in the quantitative analysis. Blanks and duplicate sample analyses were carried out for nearly 10% of samples.

### Coefficient of Divergence for Colinearity Analysis of Source Profiles

The coefficient of divergence (CD), as an indicator of similarity between two profiles, was used in this study. The spread of data points for two datasets can be described by the CD, which is a self-normalized parameter. The CD is defined as

$$CD_{AB} = \sqrt{\frac{1}{P} \sum_{i=1}^{P} \left(\frac{x_{Ai} - x_{Bi}}{x_{Ai} + x_{Bi}}\right)^2}$$
(1)

where  $x_{Ai}$  and  $x_{Bi}$  are the abundances for chemical species i in profiles A and B respectively and P is the number of investigated chemical species.  $CD_{AB}$  ranges from 0 to 1. If  $CD_{AB}$  approaches zero, sources A and B are similar, whereas

they differ when  $CD_{AB}$  approaches 1 (Wongphatarakul *et al.*, 1998; Feng *et al.*, 2006).

### **RESULTS AND DISCUSSION**

#### **Ambient PM Concentration Data**

All concentrations of ambient  $PM_{10}$  and chemical species are summarized in Table 3. The concentrations of  $PM_{10}$  at the five urban sites exceeded 100 µg/m<sup>3</sup> to some extent, whereas the concentration at the background site RH did not. Annual concentrations exceeded the mandatory annual limit for  $PM_{10}$  by a factor of about 1.4 at sites NNP, BCG, TL and JJ and by a factor of about 1.8 at site HMK. The annual average was highest at site HMK and lowest at site RH. The  $PM_{10}$  level in Panzhihua was similar to levels in some cities in northern China, such as Urumqi (141 µg/m<sup>3</sup>), Yinchuan (133 µg/m<sup>3</sup>), Taiyuan (186 µg/m<sup>3</sup>), Anyang (145 µg/m<sup>3</sup>), Tianjin (123 µg/m<sup>3</sup>) and Jinan (115 µg/m<sup>3</sup>) (Bi *et al.*, 2007).

Determined chemical species accounted for about 67% of the total mass concentration, ranging between 53% and 85%. Geological (Al, Si, Ca and Fe), carbon (TC and OC) and ion  $(NO_3^-, SO_4^{2^-})$  species were the most abundant constituents in ambient samples, accounting for about 90% of the total mass of determined species. These findings are similar to those of previous particulate source apportionment studies conducted in Cairo, Egypt (Abu-Allaban *et al.*, 2002) and Madrid, Spain (Salvador *et al.*, 2004).

Remarkable abundances of trace metal elements were also observed in PM10, which indicates that the ambient receptor was significantly contaminated by various local industries. Highly elevated abundances of Cr (0.12%, ranging from 0.03% to 0.26%) and Mn (0.24%, ranging from 0.07% to 0.44%) were observed in ambient PM10, indicating considerable iron and steel industrial emissions by various manufacturers in urban areas. The pollution level of the two species in Panzhihua is more serious than in other study areas, such as Madrid (Spain) (Salvador *et al.*, 2004)

	IMIK				Ē	Table 3	. Sumn	BC BC	ambie 2G	ent PM <sub>10</sub>	measu	TI	/βn) s	n <sup>3</sup> )ª.		Г				RH		
Sum		Ann	Win	Spr	Sum	Ann	Win	Spr	Sum	Ann	Win	Spr	Sum	Ann	Win	Spr	Sum	Ann	Win	Spr 5	m	Ann
1 147	0	9 178.88	148.84	112.86	130.57	130.71	164.5 ]	125.11	148.67	146.76	163.78	132.75	135.4	141.74	144.46	121.79	148.37	140.85	71.85	78.26 9	6.61 8	5.98
-	-51	2.59	2.2	1.76	1.62	1.8	2.33	2.36	2.3	2.32	3.84	2.46	2.01	2.57	1.89	1.94	1.58	1.74	0.91	0.94 (	.98 (	0.95
-	54	2.18	2.74	2.18	1.77	2.11	4.51	3.11	2.41	3.1	4.64	2.72	1.91	2.78	2.49	2.24	0.77	1.56	1.67	1.22	0.6	L.02
1	.32	12.96	9.04	8.43	6.44	7.57	13.73	12.12	7.41	10.13	12.12	11.59	6.69	9.23	12.62	13.85	7.27	10.21	5.33	5.59 -	1.68	5.06
	9.87	14.22	11.68	5.78	8.73	8.73	13.72	6.66	9.5	9.84	10.42	10.01	8.87	9.53	10.31	8.41	10.03	9.7	3.77	4.2	.62	4.81
	1.25	2.64	3.05	1.17	1.24	1.67	з	1.57	1.34	1.8	2.81	1.81	1.55	1.92	1.94	1.43	1.42	1.55	0.88	1.06 (	.87 (	0.92
10	10.38	14.23	11.46	9.21	5.72	7.99	11.47	9.47	5.31	7.86	10.35	11.48	5.15	8	10.36	8.73	4.12	6.79	6.73	8.04	1.35	5.85
	0.27	0.33	0.51	0.3	0.29	0.34	0.58	0.39	0.31	0.4	0.61	0.45	0.26	0.39	0.34	0.33	0.18	0.26	0.14	0.14 (	.19 (	).16
	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	•
	0.29	0.18	0.21	0.06	0.34	0.24	0.27	0.11	0.29	0.24	0.23	0.16	0.29	0.24	0.12	0.05	0.08	0.08	0.04	0.05 (	.09	0.06
-	0.31	0.29	0.65	0.16	0.53	0.47	0.47	0.25	0.62	0.49	0.46	0.33	0.54	0.47	0.21	0.22	0.53	0.37	0.11	0.08	.07 (	0.08
10	2.65	3.21	2.36	1.57	2.57	2.27	2.18	2.03	2.64	2.37	2.7	1.84	2.76	2.52	1.95	1.69	2.77	2.3	1.13	1.04	669.	L.39
	0.01	0.02	0.01	0.01	0.01	0.01	0.05	0.03	0.01	0.02	0.02	0	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.01	01 (	0.01
	0.16	0.1	0.02	0.03	0.11	0.07	0.07	0.03	0.12	0.08	0.05	0.04	0.08	0.07	0.03	0.04	0.01	0.02	0.03	0.03 (	.03 (	0.03
	0.03	0.04	0.01	0.06	0.05	0.04	0.03	0.04	0.04	0.04	0.09	0.06	0.05	0.06	0.02	0.05	0.02	0.03	0.04	0.04 (	.02	0.03
	0.65	0.53	0.33	0.27	0.44	0.37	0.35	0.21	0.36	0.32	0.42	0.17	0.37	0.33	0.3	0.3	0.23	0.26	0.16	0.09	.21 (	0.17
	0	0	0.01	0	0	0	0.01	0	0.07	0.04	0	0	0	0	0.01	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	0.29	0.18	0.09	0.03	0.14	0.1	0.07	0.02	0.12	0.09	0.06	0.02	0.13	0.09	0.05	0.02	0.06	0.05	0.03	0.01	.07 (	0.05
5	47.41	51.97	50.87	24.61	47.16	42.51	54.4	26.35	46.54	43.5	48.86	25.01	44.5	40.77	40.58	18.18	39.54	34.53	28.28	20.88 2	7.53 2	6.08
6	27.31	29.33	27.9	15.06	29.4	25.5	29.28	14.92	26.44	24.3	30.33	14.82	25.45	24.03	24.14	10.64	23.04	20.25	17.45 ]	1.94 2	0.071	7.42
	2.52	2.31	1.84	2.63	2.68	2.46	1.74	2.53	2.57	2.35	1.27	2.06	2.1	1.89	1.04	1.83	1.87	1.65	1.27	2.06	2.1	L.89
00	11.62	11.62	10.37	10.1	10.24	10.24	13.98	13.71	13.85	13.85	8.79	8.52	8.66	8.66	6.96	69.9	6.83	6.83	8.76	8.49	3.63	3.63
(D)	rage; S	pr = spr	ing aver	age; S	nm = su	ummer a	werage	; Ann	= annu	al avera	ge = (V	$Vin \times 9$	$0 + S_p$	$r \times 90 +$	- Sum >	(185)	365					

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and Jiaozuo (China) (Feng *et al.*, 2007). The annual average abundances of Cr at BCG, NNP and TL sites were 3–4 times abundances at the other sites due to large-scale industrial manufacturing in these areas. Except for site JJ, the sites simultaneously had highest concentrations of Cr on summer days, which is possibly due to temporal meteorological condition and seasonal characteristics of local source emitters. Geological components (Al and Si) are potential markers of soil dust and coal combustion fly ash. In comparison with Jiaozuo (China) (Feng *et al.*, 2007), the higher mass percentage of Al and lower level of Si indicate a different pattern of pollution contributed by geological dust and fly ash.

### Source Apportionment Modeling

Nested chemical mass balance (NCMB) (Feng *et al.*, 2002) was employed to estimate the contributions of major source categories, namely geological dust, construction materials, vehicle exhaust, iron and steel industry exhaust, coal combustion ash, SOC, secondary  $NO_3^-$  and secondary  $SO_4^{2^-}$ .

## Source Characterization and Apportionment of Ambient PM

Source categories that potentially have contributed to ambient  $PM_{10}$  in the Panzhihua urban area were identified, including geological dust (resuspended dust, paved and unpaved road dust), construction materials, coal combustion fly ash, vehicle exhaust dust, industrial sources and secondary ionic aerosols. Detailed source profile information is shown in Fig. 3.

The relative contributions of emission sources to the  $PM_{10}$  mass in different periods are illustrated in Fig. 4.

### Geological Sources

Two subtypes were selected for geological source categories: resuspended dust and paved and unpaved dust. In total, 26 samples were collected for resuspended dust and 14 for road dust. Al, Si, Ca and TC are abundant species in the two geological sources, accounting for about 80% of the analyzed mass and about 50% of  $PM_{10}$ .

The CDs for geological source profiles are summarized in Table 4. In this study, CDs for different geological profiles are all close to zero, with  $CD_{JJRD-DL} = 1.34 \times 10^{-2}$ being the highest value.

Al, Si and TC have similar abundances in the two geological sources (approximately 8%, 18.6% and 11% respectively), while the abundance of Ca in resuspended dust is higher than that in road dust (12.2% and 8.5% respectively). Although both resuspended dust and road dust are mixed sources, resuspended dust may be more affected by construction activity because Ca is a marker of construction materials (McGee *et al.*, 2003; Tullio *et al.*, 2008). OC/TC ratios observed for the two geological materials (0.16–0.67) are similar to those obtained in our previous research conducted in Jiaozuo, China (Feng *et al.*, 2007). Generally, Cr is a trace element in fugitive dust, accounting for approximately 0.01% of PM<sub>10</sub> except in heavy-industry cities (Watson and Chow, 2001; Zhao *et al.*, 2006; Bi *et al.*, 2007; Feng *et al.*, 2007). However, Cr in

resuspended dust and road dust in Panzhihua is significantly elevated, reaching 0.28% and 0.16% respectively, which indicates that the iron and steel industry in Panzhihua has a great influence on the ambient air.

Fig. 5 shows that most species in resuspended dust have high abundance with low variability. The results of profile comparisons indicate that there is no significant difference in the chemical composition among the five subtypes of resuspended dust and road dust and the geological sources can be regarded as a single-source category in the CMB model (Waston *et al.*, 2000).

There was no significant variation in the vegetation cover in Panzhihua among seasons. Therefore, it is reasonable that the  $PM_{10}$  mass contributed by geological sources varied only slightly among the different periods, ranging from 5.9 to 11.66% or 7.9 to 15.1 µg/m<sup>3</sup>.

### Cement Manufacturing Dust

Construction materials are another source contributing to the ambient receptor because of municipal works in urban areas. Construction material samples were collected from cement kilns of two cement plants because cement is the most basic and typical composition of dust related to construction activities. In the cement manufacturing profile, Ca has the highest abundance (about 40%) with low variability. Al (5.96–8.21%), Si (1.48–7.05%) and TC (0.29–12.91%) as other major constituents have different abundance patterns.

Construction materials contributed less than 3.3% to the PM<sub>10</sub> mass, which may be a result of the little construction activity during the receptor sampling period.

### Coal Combustion Ash

Coal combustion as a result of electricity generation, industrial processing and residential use is a significant particulate source category for ambient  $PM_{10}$ . Three subtype sources, namely MGSMY, PPMY and SMMY, were collected and the composite profile was constructed. MGSMY samples were collected at a power plant that uses gangue as fuel. PPMY and SMMY coal fly ash was emitted by coal-fired power plants and through residential use respectively. The three profiles for subtypes of coal combustion ash are all dominated by Al (6.3–17.9%), Si (9.8–10.3%) and TC (9–37.4%). The high variability of the three leading species indicates that subtypes of coal combustion ash can be chemically distinguished. This may be due to the use of different kinds of coal and different combustion patterns.

With regard to annual  $PM_{10}$ , coal combustion ash is found to be the major particulate contributor, accounting for 25.8% of the ambient concentration. Iron and steel industry dust is the next greatest contributor, accounting for 19.5% of annual  $PM_{10}$ . Vehicle exhaust and secondary  $SO_4^{2-}$  are the two other significant sources, accounting for 13.7% and 12.2% of  $PM_{10}$  respectively. The four source categories constitute the majority (about 70%) of ambient  $PM_{10}$ . Minor particulate categories include SOC (7.8%), geological dust (6.7%), construction dust (3.3%) and secondary  $NO_3^-$ , (2.7%). No more than 8.3% of  $PM_{10}$  mass was contributed by unknown sources. Fig. 4 shows that the percentage contribution of coal combustion to ambient  $PM_{10}$  was highest on winter days, accounting for 29.2% or 43.9  $\mu$ g/m<sup>3</sup>. This may be due to lots

of residential coal combustion and more temperature inversions on winter days, since coal consumption by power plants and other industries has no seasonal variation.



Fig. 3. Composite source profiles. The height of each bar indicates the average fractional abundance for the indicated chemical while the dot shows the standard deviation of the average.



Fig. 4. Seasonal and annual sources: (a) annual, (b) winter, (c) spring and (d) summer.

		1 abic 4. CD3 K	or geologiear source	e promes.		
	BCGRD	NNPRD	HMKRD	RHRD	JJRD	DL
BCGRD	0					
NNPRD	$2.00\times10^{-06}$	0				
HMKRD	$1.52\times10^{-04}$	$1.19\times10^{-04}$	0			
RHRD	$3.80 \times 10^{-03}$	$3.98\times10^{-03}$	$5.47  imes 10^{-03}$	0		
JJRD	$1.09\times10^{-03}$	$9.99  imes 10^{-04}$	$4.29  imes 10^{-04}$	$8.93  imes 10^{-03}$	0	
DL	$6.89 \times 10^{-03}$	$7.13 \times 10^{-03}$	$9.07 imes10^{-03}$	$4.61 \times 10^{-04}$	$1.34 \times 10^{-02}$	0

Table 4. CDs for geological source profiles.

### Metallurgical Industry

All metallurgical particulate samples were collected from the emissions of kilns and smelters, which are typical particulate emissions of the metallurgical industry in Panzhihua. The highly developed steel and metallurgical industry was a substantial particulate contributor to the ambient air. The coking plant profile was based on six chemically analyzed samples, which had similar species abundances. TC is the dominating substance, accounting for about 71% of all investigated species. There is highly elevated metal abundance in particle from V and Ti industry, including Ti, Cr and Mn abundances. Particle from the V industry is characterized by a high abundance of Ti (18%), Cr (5.35%) and Mn (4.23%). The Ti content in the dust profile for the Ti industry is much higher than that in the dust profile for the V industry, accounting for 27.8% of all investigated species. These significant characteristics were expected prior to chemical analysis and may fluctuate with material and manufacturing techniques.





Because Panzhihua is a city with highly developed heavy industry, iron and steel industry exhaust contributes a significant amount of particulate matter to ambient air According to the results of source apportionment, the  $PM_{10}$  concentration related to iron and steel manufacturing was 19.5% (26.9 µg/m<sup>3</sup>) and had little periodic variation. The high level of pollutant indicates poor ambient conditions and corresponds with the receptor and source profiles described above to a certain degree. Furthermore, the profiles of industry emissions were characterized by high abundances of several metals-V, Ti, Cr and Mn. Therefore, this unique source should be controlled and managed through special measurements.

### Vehicle Exhaust

Vehicle exhaust is an important particulate contributor to ambient air in urban areas. However, in this study, no vehicle exhaust samples were collected. The composite vehicle exhaust profile used here was recorded in SPECIATE Version 3.2 (U.S. EPA, 2009), which was also used for source apportionment. The profile was characterized by high abundances of TC (89.87%), OC (51.67),  $SO_4^{2-}$  (3.87%), Fe (1.18%) and other species (less than 1%).

During the study period (February 2007 to August 2007), the number of vehicles in Panzhihua increased slightly. A lower contribution of vehicle exhaust on summer days may be due to stronger winds and the wind direction being parallel to Panzhihua Valley.

### Secondary Aerosols

The species mass balance is the principle premise of the CMB model. Therefore, some species determined in the receptor could not be identified or quantified in the source investigation. Because secondary aerosols, including secondary organic carbon (SOC),  $NO_3^-$  and  $SO_4^{2-}$ , can be generated by photochemical reactions in ambient air, the

mass balance of these components cannot be achieved between sources and receptors unless new sources are introduced or the amount of imbalance is removed from the receptor data.

For OC and TC mass balance between sources and receptors, SOC was subtracted from receptor data. The widely used "OC/EC minimum ratio" was used to quantify the SOC seasonally. The application and procedures are detailed in our previous work (Wu *et al.*, 2009). Seasonal and annual amounts of SOC are given in Table 5.

Many soluble ions, such as  $NO_3^-$  and  $SO_4^{2-}$  ions, can form through gas-to-particle transformation in ambient air and are not represented by primary-emission profiles (Watson *et al.*, 1994; Waston and Chow, 2002; Samara, 2005). Therefore, "pure" ammonium sulfate and ammonium nitrate were applied as sources of the two soluble ions, with profiles comprising 27%  $NH_4^+$  and 73%  $SO_4^{2-}$  and 23%  $NH_4^+$  and 77%  $SO_4^{2-}$  respectively.

Secondary aerosols, including secondary  $SO_4^{2-}$ ,  $NO_3^$ and OC, contribute steady mass fractions of approximately 21.0%, 24.3% and 26.3%, respectively, to  $PM_{10}$  during different seasons. This is reasonable considering the local topographic meteorological conditions and numerous manufacturers.

Table 5. Seasonal and annual SOC concentrations and mass fractions in  $PM_{10}$ .

	Concentration (µg/m <sup>3</sup> )	SOC/PM <sub>10</sub> (%)
Annual <sup>a</sup>	10.71	8.43
Winter	13.28	9.69
Spring	8.97	7.46
Summer	14.02	11.75

<sup>a</sup> Annual SOC was acquired by averaging the three seasonal values.

### CONCLUSIONS

In this study, high  $PM_{10}$  concentrations were observed at most sites in Panzhihua, with the spatially averaged annual concentration being 137.5 µg/m<sup>3</sup>. A higher  $PM_{10}$  average (187.1 µg/m<sup>3</sup>) was observed at site HMK.

Ambient  $PM_{10}$  profiles consisting of 23 major, minor and trace elements were determined for six receptor sites in Panzhihua. Chemical profiles were also created for particulate emissions from several urban, geological and industrial sources. Resuspended dust and road dust showed no significant difference in chemical composition and were regarded as single-source category, namely geological sources. The NCMB model was employed to estimate the contributions of major source categories.

Source apportionment modeling results indicate coal combustion ash as the major contributor to ambient PM levels. Other sources with significant contributions were iron and steel industry dust, vehicle exhaust and secondary  $SO_4^{2-}$ . The four major contributors mentioned above totally accounted for about 70% of PM concentration. All of the above findings help us understand the local sources and their contributions to serious particle pollution levels and also provide valuable insights for planning future monitoring and controlling strategies for airborne PM pollution in this area.

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