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One–year aerosol characterization study for PM$_{2.5}$ and PM$_{10}$ in Beijing

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ABSTRACT

A one–year–long aerosol characterization study was conducted from July 2002 through July 2003, in Beijing, China. Twenty–four hour PM$_{2.5}$ and PM$_{10}$ filter samples were collected, and about 50 aerosol samples of each type were obtained. Organic, elemental, and total carbon, levoglucosan and other organic compounds, and inorganic ionic species were measured. The overall mean PM mass concentrations were 99 and 175 μg/m^3 for PM$_{2.5}$ and PM$_{10}$, respectively. Total carbon was the main component in both PM$_{2.5}$ and PM$_{10}$, with overall mean concentrations of 21 and 30 μg/m^3, respectively. Of the organic compounds measured, levoglucosan exhibited the highest levels (overall mean of 0.31 ng/m^3 in PM$_{2.5}$ and of 0.40 ng/m^3 in PM$_{10}$). Sulfate was the most prominent inorganic ionic species, with overall mean levels of 15.6 and 17.0 μg/m^3 in PM$_{2.5}$ and PM$_{10}$, respectively. Most components measured were predominantly present in the PM$_{2.5}$ size fraction; the overall mean PM$_{2.5}$/PM$_{10}$ ratio was typically in the range of 0.7–0.8, but this ratio was only 0.55 for the PM mass and for Ca^{2+} it was as low as 0.19. In PM$_{2.5}$, total carbon exhibited relatively larger concentration levels (30 μg/m^3) in winter than in the other seasons. K$^+$ also exhibited a relatively high concentration level in the winter season, with 2.3 μg/m^3 in PM$_{2.5}$. The contribution from biomass burning to K$^+$ in PM$_{2.5}$ was estimated on the basis of the levoglucosan data and the minimum K$^+$/levoglucosan ratios obtained throughout the year; it was found that the contribution was largest in autumn, with 44%.

Keywords: PM mass, ionic characteristics, biomass burning, sources of K$^+$, levoglucosan

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1. Introduction

Beijing is the capital of China, with a population of 15 million since 2004 (China Statistical Yearbook, 2005). With rapid urbanization and corresponding increases in traffic and energy consumption, many pollutants are emitted and released inside the city (Chan and Yao, 2008). Air quality and environmental pollution of Beijing, especially its high PM levels, have attracted much attention, also worldwide, and many field studies have been conducted (He et al., 2001; Wang et al., 2002; Yao et al., 2002a; Liu et al., 2003; Lun et al., 2003; Dan et al., 2004; Wang et al., 2004; Chan et al., 2005; Guinot et al., 2007). There is a seasonal variation of PM concentration, however, and the highest PM$_{2.5}$ mass concentration was found in April (139 μg/m^3), because of the important impact of dust (51 μg/m^3 on average) (Zheng et al., 2005a). Besides desert dust, the principle PM sources in Beijing include industrial processes, coal combustion from energy plants and residential heating (during winter time), traffic emissions, and biomass burning, including burning in neighboring countries (He et al., 2001; Duan et al., 2004; Han et al., 2005; Yang et al., 2005; Zhang et al., 2008).

Biomass burning is regarded as one of the important air pollution sources in Beijing, and its effect on air pollution was studied by several research groups (Duan et al., 2001; Zheng et al., 2005b; Zhang et al., 2008). Among the first used tracers of biomass burning are soot carbon and excess fine potassium (Andreae, 1983), which served as indicators of long–range transport over the Atlantic Ocean of smoke from African savanna fires. Since over a decade, novel molecular markers, such as levoglucosan and related saccharidic compounds, are increasingly used as biomass burning tracers (Simoneit et al., 1999; He et al., 2005; Zhang et al., 2008). According to Cheng et al. (2013), the major source of biomass burning aerosol in Beijing is the combustion of crop residues, and positive matrix factorization (PMF) modeling indicated that 50% of the organic carbon and nearly 50% of the elemental carbon were associated with biomass burning.

In the present paper, results from a one–year long characterization of PM$_{2.5}$ and PM$_{10}$ in Beijing aerosols are presented and discussed. The seasonal variations in the PM mass and in the concentrations of the various aerosol components were examined and by looking at concentration ratios between some components, it is attempted to identify their major sources. Furthermore, what extent of water–soluble potassium can serve as an appropriate indicator for biomass burning in PM$_{2.5}$ in Beijing was investigated.

2. Methodology

In order to study the impact from biomass burning to the PM, a one–year–long study was conducted in Beijing from July 2002 through July 2003 within a co–operation of Chinese and European research groups.

2.1. Sampling site and meteorological information

The sampling site in Beijing for this study was at the Sino–Japan Friendship Centre for Environmental Protection (39°09′N, 116°04′E); it is situated in the close vicinity of the north–eastern fourth–ring avenue. The most important aerosol source is expected to be traffic–related emissions; besides, local or even regional biomass burning and dust storms may exert a strong influence from time to time.

Beijing is in a warm temperate zone and has a typical continental monsoon climate with four distinct seasons (Chan and Yao, 2008). During the year 2002–2003, the monthly average temperature was lowest in January with –3.2 °C and highest in July with 27.4 °C (China Statistical Yearbook, 2003; China Statistical Yearbook, 2004). The high temperatures and relative humidity (RH) in summer in Beijing are caused by subtropical anticyclones.

The air masses from the north–west with high wind speeds that carry dust to Beijing in spring, winter, and fall, give rise to elevated PM mass concentrations, but the levels decrease with increasing wind speed (He et al., 2001). Under the slow winds from the south and stagnant weather conditions, there is a build–up of pollutants in Beijing (Zhuang et al., 2001; Wang et al., 2005; Liu et al., 2010).

2.2. Aerosol samplings and analyses

Twenty–four hour $PM_{2.5}$ and PM_{10} sampling was carried out about once a week during a one–year period from July 2002 through July 2003. The aerosol samplers were placed on the top of the 11–floor building of the Sino–Japan Friendship Centre for Environmental Protection, 35 m above ground level. A filter sampler with a Gent PM_{10} inlet (Hopke et al., 1997) was used for 48 PM_{10} sample collections, while one with a $PM_{2.5}$ cyclone inlet (URG Corporation, USA) was employed for 52 $PM_{2.5}$ sample collections. The air flow rate for both samplers was 16.7 L/min. The aerosols were collected on quartz fiber filters (47 mm diameter, Pall Gelman Sciences, USA), which had been pre–fired at 850 °C for 3 h to remove any absorbed carbon.

PM mass concentrations were gravimetrically determined with a microbalance. Prior to weighing, the sample filters were placed for 24 h at room temperature and relative humidity of approximately 25%, and then weighted with an electronic balance (MT5, Mettler Toledo Inc.). Organic, elemental, and total carbon (OC, EC, and TC) were determined by using a two–stage thermal method (Cachier et al., 1989). The analyses for levoglucosan and other organic compounds were carried out by gas chromatography – flame ionization detection (GC–FID), as described in detail by Zhang et al. (2008). The analyses for inorganic ionic species were done with a Dionex 4500i ion chromatography (IC) instrument (Wang, 2010). The uncertainty of the PM mass determination and of the analyses for the carbonaceous and organic species is estimated at 10% maximum for concentrations well above the detection limit. For details on the uncertainties associated with the IC analyses, reference is made to Wang (2010).

3. Results and Discussion

The average concentrations and associated standard deviations of the PM mass and the carbonaceous, organic, and ionic species in $PM_{2.5}$ and PM_{10} are given in Table 1. For $PM_{2.5}$ data are given for each season and for the overall study period, whereas for PM_{10} data are only given for the overall period. Also given in the table are the overall average $PM_{2.5}/PM_{10}$ ratios and associated standard deviations.

3.1. PM mass characteristics

The overall mean PM_{10} mass concentration for our study period was 175 µg/m^3 and the median 167 µg/m^3. This level exceeded the national air quality standards set in 1996 (with annual PM_{10}<100 µg/m^3 of the Type II standard). As to the $PM_{2.5}$ mass, the annual mean and median concentrations were 99 and 87 µg/m^3, respectively. Our PM data are comparable with the ones of 100 µg/m^3 ($PM_{2.5}$) and 176 µg/m^3 (PM_{10}) in Beijing from January to April 2003 (Yu et al., 2004). Compared with those from other studies in Beijing (Table 2), our data for $PM_{2.5}$ are at the lower end of the various data sets, whereas those for PM_{10} are at the higher end, but overall, there is good agreement between our results and the published data.

There was quite some variability in our seasonally averaged $PM_{2.5}$ mass concentrations, i.e., from 64 µg/m^3 in fall to 152 µg/m^3 in summer 2003; the latter data is even higher than that of winter (115 µg/m^3). The PM_{10} mass concentration did not show substantial seasonal variation, ranging on average from 158 µg/m^3 in fall to 195 µg/m^3 in winter. The maximum daily $PM_{2.5}$ and PM_{10} mass concentrations were 400 µg/m^3 and 640 µg/m^3, respectively, and they were observed in winter.

The mass ratios of $PM_{2.5}$ to PM_{10} were around 0.5, the seasonally averaged ratios ranged from 0.39 to 0.59, except for the summer 2003, when it was 0.86. The high ratios of $PM_{2.5}/PM_{10}$ in summer 2003 may be associated with the high transformation efficiency into secondary aerosols. Our $PM_{2.5}/PM_{10}$ mass ratios from 0.39 to 0.59 are similar to the ratios for kerbside sites in Europe (Van Dingenen et al., 2004). When compared with previous studies in Beijing, our $PM_{2.5}/PM_{10}$ mass ratios are slightly lower than the 0.62 obtained by Duan et al. (2006), but similar to the annual ratio of 0.55 reported by Yang et al. (2002) during a similar sampling time in Beijing. Our low $PM_{2.5}/PM_{10}$ mass concentration ratios indicate that coarse particles are quite important in Beijing. So, the reduction of coarse particles can directly and substantially lead to a decrease in PM_{10} mass levels.

3.2. Carbonaceous aerosol characteristics

The overall mean PM_{10} OC and EC mass concentrations for this study were 21 µg/m^3 and 9.4 µg/m^3, respectively; as to $PM_{2.5}$, the overall mean concentrations were 13.7 and 7.4 µg/m^3, respectively. Our $PM_{2.5}$ OC mean concentration is smaller than the value of 21 µg/m^3 reported by Zheng et al. (2005a). The highest OC and EC levels were noted in winter for both $PM_{2.5}$ (see Table 1) and PM_{10}; a similar seasonal variation was observed by Dan et al. (2004). Coal combustion for domestic heating in winter (from November until March) was likely a large contributor to the regional OC and EC levels. Frequent thermal inversion in winter certainly plays a role in raising the levels of the PM and its constituents in winter, but the seasonal variation of OC and EC was much larger than that of the PM mass for both $PM_{2.5}$ and PM_{10}.

The overall mean OC/EC ratio is around 2.5 in both $PM_{2.5}$ and PM_{10}; this value is comparable to the 2.2 for $PM_{2.5}$ reported by Sun et al. (2004) at a site which is located between the second and third ring road and is heavily influenced by traffic emissions. The ratios at our site were elevated during the domestic heating period.

OC sources in Beijing include fossil fuel combustion from traffic (Yao et al., 2002b), coal combustion in power plants and industries (He et al., 2001) and for domestic heating, biomass burning (Duan et al., 2004; Zheng et al., 2005b), and other sources.

3.3. Levoglucosan and biomass burning

A detailed description of the use of levoglucosan to assess the impact from biomass burning during our study is given by Zhang et

Table 1. *Concentrations and associated standard deviations in $PM_{2.5}$ and PM_{10} for the PM mass and inorganic and organic species and means and associated standard deviations for some ratios during 2002–2003 in Beijing. For $PM_{2.5}$ both seasonal and overall mean data are given, for PM_{10} only overall mean data. The last column presents the overall mean $PM_{2.5}/PM_{10}$ ratios and associated standard deviations*

	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	PM_{10}	$PM_{2.5}/PM_{10}$
	Summer 2002	Fall 2002	Winter 2002–03	Spring 2003	Summer 2003	All	All	All
	(N=8)	(N=13)	(N=12)	(N=12)	(N=7)	(N=52)	(N=48)	(N=48)
PM mass ($\mu g/m^3$)	82±38	64±35	115±116	103±42	152±66	99±71	175±106	0.55±0.19
OC ($\mu g/m^3$)	6.8±4.2	13.0±9.7	20±20	15.0±8.6	9.6±2.8	13.7±12.0	21±18	0.69±0.17
EC ($\mu g/m^3$)	9.2±5.3	5.4±3.2	10.1±12.9	5.4±3.8	8.1±3.3	7.4±7.0	9.4±8.3	0.74±0.26
NH_4^+ (ng/m^3)	10 500±5 200	5 200±3 800	10 100±11 100	8 700±7 300	16 500±12 100	9 500±8 600	8 300±10 000	1.14±0.19
NO_3^- (ng/m^3)	10 800±6 900	5 800±4 000	9 600±10 300	11 600±7 700	15 300±8 300	10 100±7 800	10 900±9 200	0.91±0.19
SO_4^{2-} (ng/m^3)	19 400±8 300	7 500±4 500	16 800±18 300	14 700±11 200	26 000±15 200	15 600±13 500	17 000±15 500	0.85±0.14
Cl^- (ng/m^3)	1 100±770	2 400±2 600	4 100±4 200	2 000±1 330	680±380	2 300±2 700	2 800±3 100	0.79 ± 0.21
Na^+ (ng/m^3)	520±63	610±171	1 240±750	2 500±490	1 090±1 220	1 240±960	1 570±1 090	0.82±0.16
K^+ (ng/m^3)	1 250±500	1 220±870	2 300±3 800	1 460±980	1 590±780	1 340±1 950	1 890±2 400	0.86±0.18
Mg^{2+} (ng/m^3)	100±7.7	143±39	210±169	300±89	144±71	189±119	600±300	0.34±0.14
Ca^{2+} (ng/m^3)	600±70	870±210	750±510	2 100±550	1 050±730	1 100±710	6 500±2 900	0.19±0.10
Levo. (ng/m^3)	159±116	410±390	410±470	290±320	133±63	310±340	400±430	0.81±0.09
Mannosan (ng/m^3)	35±19	51±30	65±76	60±73	31±21	51±52	66±66	0.73±0.28
Mannitol (ng/m^3)	4.1±1.0	12.8±42	9.9±10.1	16.2±14.6	25±32	13.2±19.1	30±21	0.39±0.33
Levo./OC (%)	2.5±1.8	2.9±1.1	1.71±0.72	1.73±0.87	1.39±0.42	2.1±1.1	1.72±0.87	
K^+/OC (%)	19.7±11.6	9.7±6.0	9.9±14.6	9.7±5.7	16.4±6.9	12.2±9.6	8.8±6.4	

Table 2. Annual and seasonal mean $PM_{2.5}$ and PM_{10} mass concentrations ($\mu g/m^3$) for different sites in Beijing

Site	Sampling Period	PM Conc.	Reference
$PM_{2.5}$			
Fourth Ring road	2002–2003	99±71	This study
Second Ring road	2001–2002	96.5	Duan et al. (2006)
Second Ring road	1999–2000	129	He et al. (2002)
Forth Ring road	1999–2000	145	He et al. (2002)
Between Second and Third Ring road	2001–2003	154±146	Wang et al. (2005)
Between Second and Third Ring road	2002–2003 winter	136±97	Sun et al. (2004)
	2002–2003 summer	77±56	
Five urban and rural sites	2000	101	Zheng et al. (2005a)
PM_{10}			
Fourth Ring road	2002–2003	175±106	This study
North Fourth Ring road	2006 summer	133	van Pinxteren et al. (2009)
Between Second and Third Ring road	2002–2003 winter	184±131	Sun et al. (2004)
	2002–2003 summer	172±102	
Between Second and Third Ring road	Jan. 2003–Aug. 2004	105	Guinot et al. (2007)

al. (2008). Although, Hoffmann et al. (2010) and Hennigan et al. (2010) have published cautionary articles on the stability of levoglucosan, especially at high OH levels and under high RH conditions, levoglucosan still is a unique indicator for biomass burning aerosol. Kessler et al. (2010) estimated that the heterogeneous oxidation lifetime of levoglucosan is 10.6 days, which is near the estimated depositional lifetimes (5–12 days).

Besides levoglucosan, other sugar–related compounds, including mannosan, galactosan and mannitol, were measured. There was a good correlation between levoglucosan and mannosan in $PM_{2.5}$, with R^2 of 0.75. There was a tendency for both levoglucosan and mannosan to exhibited higher levels in winter than in the other seasons, both in $PM_{2.5}$ and PM_{10}. The overall average ratio of levoglucosan to mannosan was 6.3; there was no evident seasonal variation in this ratio, but the highest mean ratio was observed in autumn, followed by the winter season.

As seen in Figure 1, there was a substantial sample–to–sample variation in the levoglucosan concentration. Although there is some coherence between the time series of the four species depicted in the Figure 1, levoglucosan was highly correlated with OC (R^2=0.80), but not with K^+ (R^2=0.36). Only when most of the K^+ is from biomass burning, it can be used as an appropriate biomass burning indicator. It should be kept in mind, though, that K^+ also has other important sources besides biomass burning, such as coal burning in our study; its use as biomass indicator in our data set seems to be jeopardized, as will be discussed below.
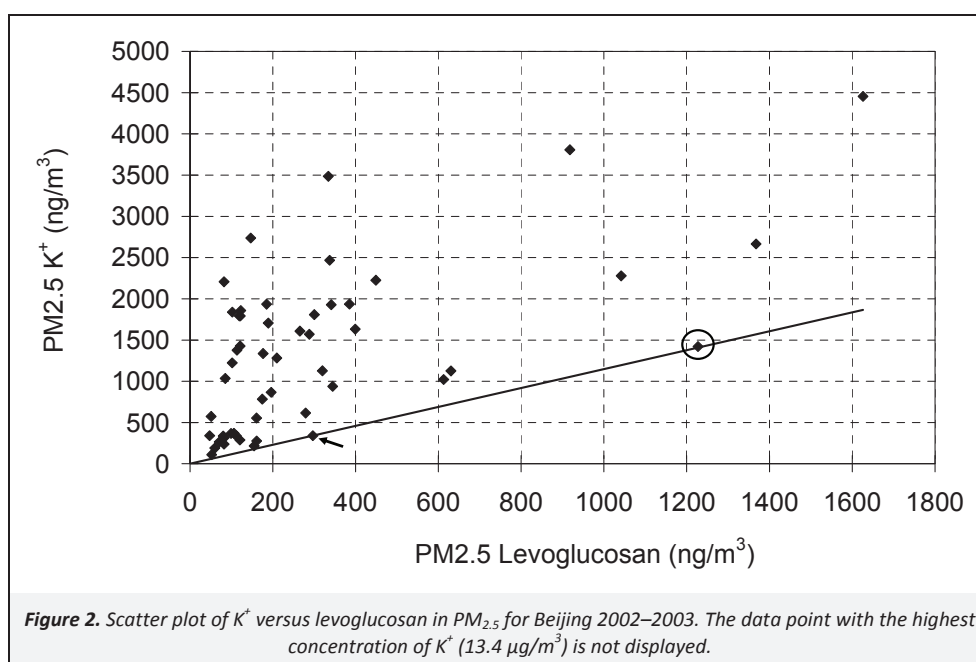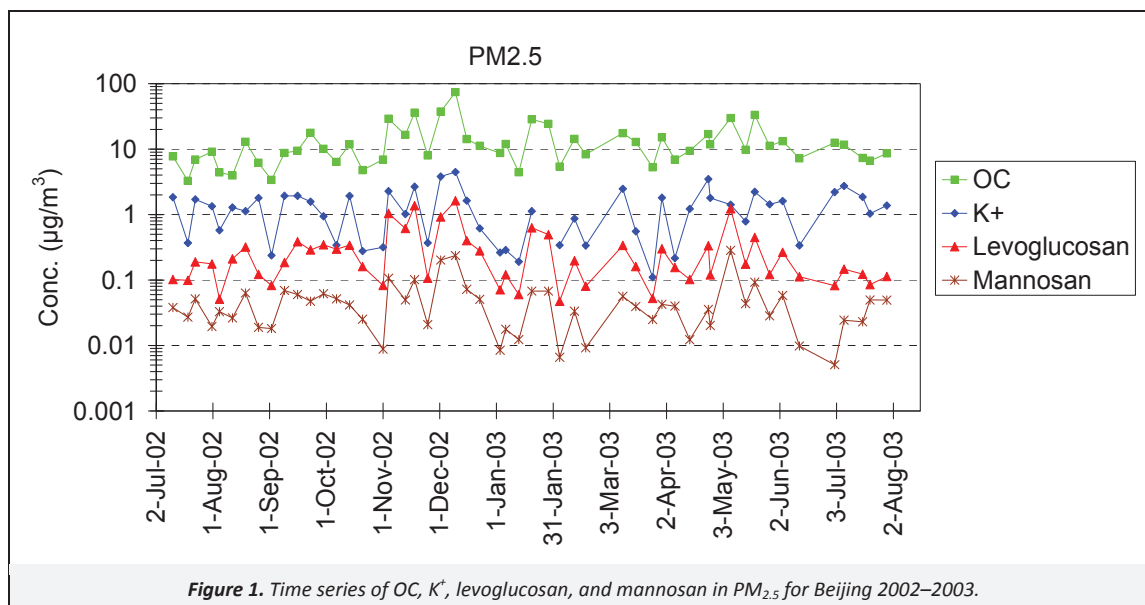
Figure 2 shows a scatter plot of K^+ versus levoglucosan in $PM_{2.5}$. The data point circled in the figure applies to the sample of 7 May 2003. This sample had the third highest levoglucosan concentration; it exhibited also a high OC level and high ratios of levoglucosan/OC (0.41) and levoglucosan/K^+ (0.86), but the $PM_{2.5}$ mass and K^+ concentration were only around average. By scrutinizing the Total Ozone Mapping Spectrometer (TOMS) Aerosol Index images, it became clear that forest fires occurred and went on during the period from 4 to 12 May 2003 in the border areas of China, Russia, and Mongolia. The prevailing winds were westerly during this period and the forest fire emissions were transported to the east, influencing the Far East of Russia and the Korean peninsula (Lee et al., 2005). However, the wind direction changed to northerly from 5 to 8 May 2003, which had the effect that the pollutants spread over the vast region of north–eastern China, arriving in Beijing, Tianjin, and Hebei province (Zhang et al., 2008).

3.4. Ionic characteristics

The ion balance was studied for both $PM_{2.5}$ and PM_{10}, and it was found that the cations substantially over–weighted the anions in all samples. The missing anionic species are likely inorganic CO_3^{2-} and HCO_3^- and perhaps also organic acids; the latter have been detected in aerosol samples from Beijing (Yao et al., 2002b; Yao et al., 2003; Wang et al., 2005). The mean equivalent ratios of cations to anions were 1.86±0.68 in PM_{10} and 1.36±0.35 in $PM_{2.5}$. SO_4^{2-} and NO_3^- were fully neutralized by NH_4^+ in $PM_{2.5}$ with the $NH_4^+/(NO_3^- + SO_4^{2-})$ ratio of 1.00±0.27, but not in PM_{10} with the $NH_4^+/(NO_3^- + SO_4^{2-})$ ratio of 0.74±0.24.

In terms of mass concentrations, SO_4^{2-}, NO_3^-, and NH_4^+ were the dominant ionic species in $PM_{2.5}$; the overall average concentrations were 15.6 $\mu g/m^3$, 10.1 $\mu g/m^3$, and 9.5 $\mu g/m^3$, respectively, and they represented 37%, 23%, and 20%, respectively, of the total mass of water–soluble ions. These ionic mass concentration data are very similar as those obtained in Beijing for weekly samples in 1999–2000 by Yao et al. (2002a) and in 2001–2002 by Duan et al. (2006), and for daily samples in 2001–2003 by Wang et al. (2005). The individual percentage attributions of the major ions to the sum of all measured inorganic ions in this study are quite similar to the results reported by Wang et al. (2005) and Duan et al. (2006). As to PM_{10}, Ca^{2+} together with SO_4^{2-}, NO_3^-, and NH_4^+ were the dominant ionic species; as can be seen in Table 1, Ca^{2+} and Mg^{2+} were mostly associated with the coarse particles and all other ions mostly with the fine particles.

Na^+ and Mg^{2+} showed the maximum seasonally averaged concentrations in spring for both $PM_{2.5}$ and PM_{10}, which suggests that dust storms were an important source for these two ions. Ca^{2+} in $PM_{2.5}$ was high in spring and low in summer, and such seasonal variation was also observed by Wang et al. (2005). There was no obvious seasonal variation for Ca^{2+} in PM_{10} in this study. This may be due to the local construction activities, which can be regarded as another major source of Ca^{2+} in Beijing. Construction material is abundant in calcium [CaO or Ca(OH)$_2$] (Yang et al., 2005). Relatively low Ca^{2+} concentrations in PM_{10} in winter are consistent with a construction source as few construction works are performed in winter due to the cold temperatures in Beijing then. According to Guinot et al. (2007), construction works are an important source of local dust; elevated PM mass by construction activities was also observed by Zheng et al. (2005a). In $PM_{2.5}$, Mg^{2+} was well correlated with Na^+ (R^2=0.79) and Ca^{2+} (R^2=0.89), which suggests that they have the same source, which at least in spring is presumably long–range transported desert dust.

Figure 1. Time series of OC, K⁺, levoglucosan, and mannosan in PM₂.₅ for Beijing 2002–2003.

Figure 2. Scatter plot of K⁺ versus levoglucosan in PM₂.₅ for Beijing 2002–2003. The data point with the highest concentration of K⁺ (13.4 µg/m³) is not displayed.

It can be seen from Table 1 that the seasonally averaged concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ in PM₂.₅ were maximum in summer, followed by winter (except for NO_3^-), and were minimum in fall; a similar pattern was observed for SO_4^{2-} and NO_3^- in PM₁₀. In an earlier study in Beijing, SO_4^{2-}, NO_3^-, and NH_4^+ were maximum in winter, just slightly higher than in summer (Wang et al., 2005). NH_4^+ in Beijing may be mainly from the use of synthetic nitrogen fertilizers in agriculture in the suburb areas around Beijing (Bouwman et al., 1997), and it combines with NO_3^- and SO_4^{2-} under favorable conditions.

The high seasonal mass concentrations of SO_4^{2-} in winter and summer may be due to higher coal consumption and poor dispersion (shallow boundary layer) in winter and efficient photochemical reactions in summer; as to summer 2003, the quite high SO_4^{2-} level may be the result of oxidation in the liquid phase (Tang et al., 2006). SO_4^{2-} is regarded as a tracer for coal combustion and industrial activities and the formation mechanism of SO_4^{2-} in different seasons was discussed by Yao et al. (2002a). NO_3^- in Beijing is thought to originate mainly from traffic (Yao et al., 2002a; Wang et al., 2005).

The NO_3^-/SO_4^{2-} mass ratio can be used to assess the relative importance of mobile versus stationary sources, whereby high ratios indicate a prevalence of mobile sources over stationary ones (Arimoto et al., 1996; Yao et al., 2002a; Wang et al., 2005). The seasonally averaged NO_3^-/SO_4^{2-} ratios for this study are given in Table 3 together with ratios from the literature. The overall average NO_3^-/SO_4^{2-} ratio in this study was 0.65; this value is very similar to the ratios of 0.67 of Wang et al. (2005) and 0.70 of Duan et al. (2006), and slightly larger than that of 0.58 of Yao et al. (2002a). Some seasonal variations in the NO_3^-/SO_4^{2-} are observed, with a low seasonally averaged ratio in winter and high ones in fall and spring. During the residential heating period, more SO_2 is emitted and then transformed to SO_4^{2-}, which results in a decrease in NO_3^-/SO_4^{2-} ratios in winter. At our study site, there was a strong impact from traffic emissions because the site was near a busy main road (northern fourth ring road). In the other seasons than winter, the weather conditions are suitable for the formation of both NO_3^- and SO_4^{2-}. So, the seasonal variation of NO_3^-/SO_4^{2-} in our study is not as large as in the study of Wang et al. (2005).

Table 3. Mass ratios for NO_3^-/SO_4^{2-} and Cl^-/NO_3^- in $PM_{2.5}$ samples collected in Beijing

Reference	Sampling Period	Ratio	Summer	Fall	Winter	Spring	All
This study	2002–2003	NO_3^-/SO_4^{2-}	0.57±0.28 (2002) 0.60±0.26 (2003)	0.72±0.24	0.52±0.17	0.78±0.27	0.65±0.26
		Cl^-/NO_3^-	0.10±0.03 (2002) 0.05±0.03 (2003)	0.48±0.28	0.50±0.21	0.23±0.13	0.31±0.26
Yao et al. (2002a)	1999–2000	NO_3^-/SO_4^{2-}		1.5			0.58
Wang et al. (2005)	2001–2003	NO_3^-/SO_4^{2-}	0.63	0.93	0.49	0.84	0.67
Guinot et al., 2007	Jan. 2003–Aug. 2004	NO_3^-/SO_4^{2-}	0.42–0.62				
Duan et al. (2006)	2001–2002	NO_3^-/SO_4^{2-}	0.40	0.85	1.09	0.69	0.70 (CGZ site) 0.74 (THU site)
		Cl^-/NO_3^- [a]	0.06	0.11	0.37	0.24	0.24 (CGZ site) 0.27 (THU site)

CGZ site: Chegongzhuang site (near the north-west Second ring road), THU site: Tsinghua University site (near the north-west Forth ring road)

[a] *Cl from XRF*

The residential heating period lasts from late fall to early spring in Beijing, and since much heating is produced from coal combustion, this leads to elevated levels of some inorganic ions in $PM_{2.5}$, including SO_4^{2-}, NO_3^-, Cl^-, and K^+ (He et al., 2001; Wang et al., 2005; Duan et al., 2006). Sea salt is not important as a source of Cl^- like it is also not important for Na^+. The overall average mass concentrations of Cl^- were 2.3 µg/m³ in $PM_{2.5}$ and 2.8 µg/m³ in PM_{10}; Cl^- was thus mostly associated with the fine size fraction, suggesting that it originated mainly from anthropogenic emissions. High seasonal mean Cl^- concentrations were observed in the winter season, with 4.1 µg/m³ in $PM_{2.5}$; the highest daily concentration in $PM_{2.5}$ was 13.4 µg/m³ in a winter sample. In summer 2003, the seasonal mean Cl^- concentration was as low as 0.68 µg/m³ in $PM_{2.5}$. The seasonal mean data are comparable to the data reported by Duan et al. (2006) for 2001–2002 and by Wang et al. (2005) for 2001–2003 in Beijing. The high mass concentration of Cl^- in winter is not only due to the shallow boundary layer; also the contribution from coal combustion for residential heating during the cold period has to be taken into account.

The mass ratio Cl^-/NO_3^- has been successfully used to estimate the pollution level from coal burning for heating during cold periods and/or for industrial activities in Beijing in previous studies (Yao et al., 2002a). Although our mass ratios were smaller than those of Yao et al. (2002a) and higher than those of Duan et al. (2006), the seasonal variation is the same, high in winter and low in summer. There is no doubt that the increase of the Cl^-/NO_3^- mass ratio in winter is due to increased Cl^- emissions from burning for residential heating.

3.5. K^+ from biomass burning and other sources

Our overall mean mass concentrations for K^+ are 1.34 µg/m³ in $PM_{2.5}$ and 1.89 µg/m³ in PM_{10}, and K^+ is mostly present in the fine size fraction. Our overall mean value in $PM_{2.5}$ is very similar to the 1.55 µg/m³ of Wang et al. (2005) and the 1.44 µg/m³ and 1.70 µg/m³ at two sites in Beijing of Duan et al. (2006), but substantially lower than the 2.2 µg/m³ of Yao et al. (2002a). Except that elevated mean levels were observed in winter, with 2.3 µg/m³ in $PM_{2.5}$ and 2.8 µg/m³ in PM_{10}, the seasonally averaged K^+ mass concentrations for the other three seasons in this study were similar.

The highest concentrations of K^+ in both $PM_{2.5}$ and PM_{10} were observed on 29 January 2003, with 13.5 µg/m³ and 15.4 µg/m³, respectively, but other components, such as Cl^-, NH_4^+, SO_4^{2-}, NO_3^-, OC, EC and levoglucosan, did not exhibit as elevated levels as K^+. The sampling date with that high K^+ concentration was just two days before the Chinese Spring Festival. It seems therefore that the highly elevated levels of K^+ in both $PM_{2.5}$ and PM_{10} on that date may have been related to fireworks and cooking (Wang et al., 2007, Cheng et al., 2013).

The seasonal variation of K^+ as seen from Table 1 is exactly the same as in previous studies (Yao et al., 2002a; Wang et al., 2005; Duan et al., 2006), with relatively high levels in winter. This seasonal pattern is somewhat different from that of the other water–soluble ions. The high concentrations of K^+ in Beijing suggest that this species originates from multiple sources in the local environment.

Potassium was first proposed as a tracer for biomass burning by Andreae (1983); and water–soluble potassium worked well as a tracer for biomass burning in the tropics, such as in parts of Africa (Andreae et al., 1988; Maenhaut et al., 1996) and India (Tiwari et al., 2008). Within a biomass burning plume (altitude >2 km asl), K^+ was highly correlated with NO_3^-, NH_4^+, and SO_4^{2-}, all with R^2 higher than 0.9; within the boundary layer pollution plume (altitude <2 km asl), NH_4^+ was correlated with SO_4^{2-} (R^2=0.80), but not with K^+ or NO_3^- (Ma et al., 2003).

In our study, the overall mean K^+/OC ratio in $PM_{2.5}$ is 0.12±0.55, with a higher ratio in summer (0.18) than in the other seasons (0.10). Zheng et al. (2005b) distinguished typical biomass–burning aerosol samples from other samples on the basis of relatively high K^+/OC ratios (0.09–0.21). However, it does not seem suitable to assess the biomass burning contribution by this method in our study. In Beijing, OC has multiple sources, including from combustion processes and non–combustion processes, such as humic acid in soil dust and tire debris (Zheng et al., 2005b). K^+ also has many sources, such as biomass burning, coal/charcoal burning, soil dust, and even traffic exhaust emissions in small amounts (Andreae and Merlet, 2001; Song et al., 2006). Most residents in the suburb areas of Beijing are used to burning biomass and tree branches for daily cooking (Zhang et al., 2007). On the other hand, waste emissions from coal–fired industries/plants in Beijing may also elevate the local K^+ concentration levels. Substantial emission of K from coal combustion was observed, with a K/Al ratio of 0.0158 in the coal fly ash (Zhu and Bai, 1995). Besides, potassium fertilizer is widely used in agricultural activities in China, and K is present in high concentrations in crops and also in their residues (Duan et al., 2004).

The diverse sources of K^+ make it therefore difficult to use water–soluble K^+ as a tracer for biomass burning in city aerosols, especially in our study. Also the seasonal $K^+/PM_{2.5}$ percentage mass ratios given in Table 4 are of not much help for that purpose. In using levoglucosan for this purpose, we assumed that both levoglucosan and pyrogenic K^+ originated throughout the year from a dominating biomass burning source, which is in our case the burning of crop (mainly including wheat and corn) residues (Cheng et al., 2013). Another assumption is that the ratio of levoglucosan

to K^+ from biomass burning is relatively constant throughout the year in the suburbs of Beijing and the neighboring provinces. Equation (1) was used to estimate the water–soluble potassium in $PM_{2.5}$ emitted from biomass burning:

$$K^+_{Biomass\ Burning}\ (\mu g/m^3)=levoglucosan\ (\mu g/m^3)\times(K^+/levoglucosan)_{min} \quad (1)$$

In deriving this equation the same reasoning was followed as is commonly followed for deducing secondary OC (e.g., Salma et al., 2004), where primary OC is obtained by multiplying EC by $(OC/EC)_{minimum}$. On 7 May 2003 (circled data point in Figure 2), the second lowest K^+/levoglucosan ratio was obtained (i.e. 1.16); as discussed above, the smoke aerosol on this date was long–range transported from forest fires. Incidentally, this ratio is comparable to that reported for boreal smoke aerosol by Saarikoski et al. (2007). The lowest K^+/levoglucosan ratio (i.e., 1.15) was observed on 7 October 2002 (data point marked with an arrow in Figure 2); the latter sample was likely heavily affected by the local biomass burning of crop residues after the autumn harvest. That biomass burning of the autumn harvest is important in the suburban areas of Beijing was already indicated by Zheng et al. (2005b). Low K^+/levoglucosan ratios of 1.72 and 1.67 were also obtained on 21 October and 13 November 2002, respectively; crop residue burning was probably also substantial on those dates. The lowest K^+/levoglucosan ratio (i.e., 1.15) was used as $(K^+/levoglucosan)_{minimum}$ in Equation (1). The K^+ data from biomass burning calculated in this way, together with the percentages of total K^+ attributable to pyrogenic sources, are given in Table 4; both overall mean and seasonal mean results are given. Instead of using the lowest K^+/levoglucosan ratio (of 1.15) as $(K^+/levoglucosan)_{minimum}$, calculations were also done by making use of the average of the K^+/levoglucosan ratios for the 7 October, 21 October, and 13 November samples as minimum ratio (that average was 1.51±0.32). The resulting overall mean K^+ concentration from biomass burning (in $\mu g/m^3$) was then 0.46±0.52 instead of 0.35±0.40 and the fraction of total K^+ attributable to biomass burning 0.41±0.31 instead of 0.31±0.23.

Table 4. *Concentration ratios and K^+ from biomass burning (K^+_{BB}), all in $PM_{2.5}$*

Average	$K^+/PM_{2.5}$ (%)	Levo./K^+	K^+_{BB} ($\mu g/m^3$)	K^+_{BB}/K^+_{total}
2002 summer	1.63±0.63	0.15±0.09	0.18±0.10	0.17±0.10
2002 autumn	1.74±0.72	0.38±0.23	0.47±0.45	0.44±0.26
2002 winter	1.77±2.45	0.29±0.14	0.47±0.52	0.34±0.16
2003 spring	1.34±0.61	0.28±0.26	0.34±0.36	0.33±0.30
2003 summer	1.07±0.35	0.12±0.10	0.15±0.07	0.13± 0.12
Overall	1.55±1.32	0.27±0.87	0.35±0.40	0.31±0.23
Cheng et al. (2013)				
BB episode		0.11±0.06		
2011 summer		0.21±0.16		
2011 winter		0.51±0.15		

From Table 4 it appears that the levoglucosan/K^+ ratio is lower in summer than in the other seasons. A similar pattern of low ratios in summer (and high ones in winter) was found by Cheng et al. (2013). Table 4 further shows that the contribution of K^+ from biomass burning to total K^+ was largest in autumn 2002 (with 44%), which is in line with the largest levoglucosan/K^+ ratio in this season. The same season (together with winter) also exhibited the largest K^+ level from biomass burning. In North China, open biomass burning in the field after the corn/wheat harvest occurs normally in autumn every year. Zhang et al. (2007) also found that the biomass burning after the harvest of corn and other types of agricultural crops led to K^+ emissions.

The calculated seasonal mean concentration of K^+ from biomass burning in winter is of the same level (0.47 $\mu g/m^3$) as in

autumn (see Table 4), but the concentration of total K^+ was almost double in winter than in autumn (see Table 1). Beside temperature inversions and low boundary layers, there must be other causes for the high K^+ levels in winter, such as fire–works around the period of the Chinese Spring Festival (Cheng et al., 2013). As indicated above, the highest K^+ level in the present study was observed two days before the Chinese Spring Festival.

In summer, the average levoglucosan/K^+ ratio (Table 4) was close to the corresponding source ratio (0.10) of wheat straw burning (Cheng et al., 2013). In our summer samples, less than 20% of total K^+ was attributed to biomass burning, which indicates that there were other very important sources of K^+ in this season. So, K^+ cannot be used as a reliable tracer for biomass burning in Beijing during the summers of 2002–2003 sampling period, which is in contrast to what was concluded for Beijing 2011 summer by Cheng et al. (2013). This discrepancy might in part be due to the fact that the latter study was carried out at a different sampling site and almost a decade later. In any case, it is desirable to perform additional studies on the identification and quantification of the sources of K^+ in Beijing.

After our estimation of $K^+_{BiomassBurning}$ in Beijing, it can be concluded that coal combustion for energy production and residential heating is an as important source of K^+ as the biomass burning related to agricultural activities.

4. Conclusions

High $PM_{2.5}$ and PM_{10} mass concentrations were observed in our Beijing study, with overall means of 99 $\mu g/m^3$ and 175 $\mu g/m^3$, respectively. These results are in agreement with results from previous studies in Beijing. The $PM_{2.5}$ mass concentration exhibited its highest levels in both winter and summer. The high levels in winter are likely due to the increased coal combustion emissions for residential heating coupled with meteorological conditions of poor dispersion with a shallow boundary layer, and in summer they are the result of transport of polluted air from the south together with strong photochemistry.

Ion imbalance was observed in both $PM_{2.5}$ and PM_{10}; the missing anionic species are mainly CO_3^{2-} and HCO_3^-, which are related to crustal sources (dust from long–range transport, re–suspension, and construction). There was sufficient NH_4^+ in $PM_{2.5}$ to fully neutralize both SO_4^{2-} and NO_3^-.

SO_4^{2-}, NO_3^-, and NH_4^+ were the dominant ionic species; their overall average concentrations in $PM_{2.5}$ were 15.6 $\mu g/m^3$, 10.1 $\mu g/m^3$, and 9.5 $\mu g/m^3$, respectively, and they represented 37%, 23%, and 20%, respectively, of the total mass of water–soluble ions. High concentrations of SO_4^{2-} were observed in winter and in summer for the same reasons as given for the PM mass. There was no large seasonal variation for the NO_3^- concentration, which may be due to the year–round strong impact from traffic emissions near the sampling site.

Since the PM in Beijing is little influenced by maritime air masses, Na^+, Mg^{2+}, and Ca^{2+} in $PM_{2.5}$ are mainly attributable to long–range transport of desert dust aerosols. As for Ca^{2+} in PM_{10}, it seems that there was a large contribution from construction materials.

Coal combustion for heating in winter was the main source of the elevated Cl^- concentrations in $PM_{2.5}$; the seasonal mean for winter was 4.1 $\mu g/m^3$ and the maximum daily concentration in winter was 13.4 $\mu g/m^3$.

The overall mean K^+ concentrations were 1.34 $\mu g/m^3$ in $PM_{2.5}$ and 1.89 $\mu g/m^3$ in PM_{10}; potassium was thus mainly present in the fine size fraction. Although the seasonal mean concentration of K^+ exhibited a high value in winter, the contribution of K^+ from

biomass burning was highest in autumn in this year–round study, with 44%, followed with more than 30% in winter and spring, but around 17% for summer. Since K^+ has a diversity of sources in Beijing, including coal and biomass combustion, and is also influenced by various other types of anthropogenic activities, such as the wide use of potassium fertilizer during sowing in spring in the suburbs of Beijing, biomass burning from the summer and fall harvest, burning of fallen leaves in late fall or early winter, wood burning for cooking and heating, and so forth. As a consequence, K^+ was not very suitable for tracing biomass burning in Beijing, at least not in this study; but levoglucosan proved to be much better for this purpose. Based on the seasonal concentrations of levoglucosan, it is concluded that it is necessary to take effective measures in China to control not only the open fire biomass burning during harvest and winter–heating time, but also the biomass burning for cooking all year around.

Acknowledgments

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