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TECHNICAL PAPER

Characterization and seasonal variations of levoglucosan in fine particulate matter in Xi'an, China

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$PM_{2.5}$ (particulate matter with an aerodynamic diameter <2.5 μm) samples (n = 58) collected every sixth day in Xi'an, China, from 5 July 2008 to 27 June 2009 are analyzed for levoglucosan (1,6-anhydro-β-D-glucopyranose) to evaluate the impacts of biomass combustion on ambient concentrations. Twenty-four-hour levoglucosan concentrations displayed clear summer minima and winter maxima that ranged from 46 to 1889 ng m^{-3}, with an average of 428 ± 399 ng m^{-3}. Besides agricultural burning, biomass/biofuel combustion for household heating with straws and branches appears to be of regional importance during the heating season in northwestern China. Good correlations (0.70 < R < 0.91) were found between levoglucosan relative to water-soluble K^+, Cl^-, organic carbon (OC), elemental carbon (EC), and glyoxal. The highest levoglucosan/OC ratio of 2.3% was found in winter, followed by autumn (1.5%). Biomass burning contributed to 5.1–43.8% of OC (with an average of 17.6 ± 8.4%).

Implications: $PM_{2.5}$ levoglucosan concentrations and the correlation between levoglucosan relative to other compounds during four seasons in Xi'an showed that the influence of biomass burning is maximum during the residential heating season (winter), although some important influences may be detected in spring (field preparation burnings) and autumn (corn stalks and wheat straw burning, fallen dead leaves burning) at Xi'an and surrounding areas. Household heating with biomass during winter was quite widespread in Guanzhong Plain. Therefore, the control of biomass/biofuel combustion could be an effective method to reduce pollutant emission on a regional scale.

Introduction

Biomass combustion, such as domestic biofuel combustion (stoves for cooking and heating etc.), agricultural burning (crop residues, leaves), and wildfires (Fine et al., 2001; Schauer et al., 2001; Venkataraman et al., 2005; Wang et al., 2006a; Lee et al., 2008), is an important source of carbonaceous aerosols that scatter and absorb incident solar radiation, thereby affecting the Earth's albedo as well as causing visibility impairment (Chow et al., 2002; Watson, 2002). Biomass burning is also an important primary source of many trace substances (HCN, CH_3CN) that are reactants in atmospheric chemistry and that can affect biogeochemical nitrogen cycle of ecosystems (Lobert et al., 1990; Simoneit et al., 1999). Polysaccharide cellulose and hemicellulose are the dominated constituents in biomass burning (Lee et al., 2008). As the major molecular marker for biomass/biofuel burning processes, levoglucosan (1,6-anhydro-β-D-glucopyranose) originates from the pyrolysis of cellulose (Rogge et al., 1998; Simoneit et al., 1999) and mainly presents in fine aerosol fraction (Maenhaut et al., 1996; Liu et al., 2000; Lara et al., 2005; Sullivan et al., 2008). It is chemically stable in the atmosphere, showing no decay over 8-hr exposures to ambient conditions and sunlight (Locker, 1988). With the biomass combustion increasingly being identified as a major contributor to air pollution, a series of studies has appeared investigating the PM levoglucosan in many East Asian countries, and specifically in China (Abas et al., 2004; Wang and Kawaruma, 2005; Wang et al., 2007a; Bi et al., 2008; Lee et al., 2008; Zhang et al., 2008; Sang et al., 2011).

Xi'an, the capital city of Shaanxi Province in northeast China, is located in the Guanzhong Plain area with a topographic basin

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surrounded by Qinling Mountains to the south and the Loess Plateau to the north. Guanzhong Plain is one of the major agricultural production areas for wheat and corn. With a population of about 8.47 million, Xi'an is the largest city in northwestern China, where air pollution is significant, especially in winter due to drastic enhancement of coal and biomass burning for house heating. In addition, biomass burning practices in other seasons include a large variety of burning activities, such as field burning in preparation from agriculture planting (spring), post-harvest burning of crop residues (summer, autumn), fallen leaves burning (autumn), and so on. Several studies about levoglucosan in $PM_{2.5}$ (particles with an aerodynamic diameter $\leq$2.5 μm) have been conducted in China's well-developed cities, such as Beijing, Nanjing, Guangzhou, and Hong Kong (Wang and Kawaruma, 2005; Wang et al., 2007a; Zhang et al., 2008; Sang et al., 2011), with concentration ranged from 30 to 950 ng m^{-3}. But few measurements for $PM_{2.5}$ levoglucosan are available in northwestern China.

The objectives of this study are to (1) examine the seasonal variations of $PM_{2.5}$ levoglucosan, (2) investigate the relationship between levoglucosan and other chemical composition, and (3) estimate the biomass burning contribution to organic carbon (OC).

Experiments and Methods

Field sampling

The sampling station (34.23°N, 108.88°E) was located in Xi'an High-Tech Zone (see Figure 1), where there are no major industrial activities, or local fugitive dust sources. A more detailed description of this site can be found in Zhang et al. (2011). The air sampler was deployed on the rooftop of the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS), at ~10 m above ground level.

Twenty-four-hour $PM_{2.5}$ sampling was performed every sixth day (from 10:00 a.m. to 10:00 a.m. the next day, local standard time [LST]) using TE-6070MFC hi-vol $PM_{2.5}$ air sampler (Tisch, Cleveland, OH, USA) at a flow rate of 1.0 m^3 min^{-1} from 5 July 2008 to 27 June 2009 (Dai et al., 2012). Samples were collected on 203 mm × 254 mm quartz-fiber filters (Whatman QM/A, Clifton, NJ, USA), which were prefired at 800 °C for 3 hr before sampling in order to remove contaminants. After sampling, the filters were wrapped in prefired aluminum foils and stored in the freezer (less than −10 °C). Also, field blank filters were collected to subtract the positive artifacts due to adsorption of gas-phase organic components onto the filter during and/or after sampling.

Continuous hourly average temperature, relative humidity (RH), wind speed, and wind direction were obtained from a local weather station (15 km north of the sampling site) (http://www.weather.com.cn). The monthly mean temperature (°C), RH (%), and wind speed (m sec^{-1}) are presented in Figure 2a. Summertime is hot and humid, with an average ambient temperature of 26 °C and relative humidity (RH) of 70%. Wintertime is cold and dry, with an average ambient temperature of −1.3 °C and RH of 50%. A typical wind rose is shown in Figure 2b. From the figure, it can be deduced that over 90% of the time the wind blows to the northeast-southwest at average speed of 1.5 m sec^{-1}, maximum speed of 3.6 m sec^{-1}.

Based on the meteorological characteristics and the typical residential heating period (mid-November through mid-March), the period from 15 November to 14 March was designated as winter, with allocated spring (15 March to 31 May), summer (1 June to 31 August), and autumn (1 September to 14 November) periods.

Analytical methods

$PM_{2.5}$ chemical species, including water-soluble inorganic ions (K^+, NH_4^+, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}), carbonaceous species (OC and elemental carbon [EC]), stable carbon isotope ($\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$), and levoglucosan (LG), were measured.

Ion chromatographic analyses. A portion of quartz-fiber filter (10.8 cm^2) was extracted with 10 mL of distilled deionized water. Typical extraction efficiencies for levoglucosan were 100% based on spiked standards followed by ultrasonic agitation/extraction. The extracts were filtered through 0.45-μm pore size microporous membranes to remove insoluble material. Levoglucosan were quantified by high-performance anion-exchange chromatography with pulsed amperometric detector (HPAEC-PAD) on a Dionex DX-600 ion chromatograph

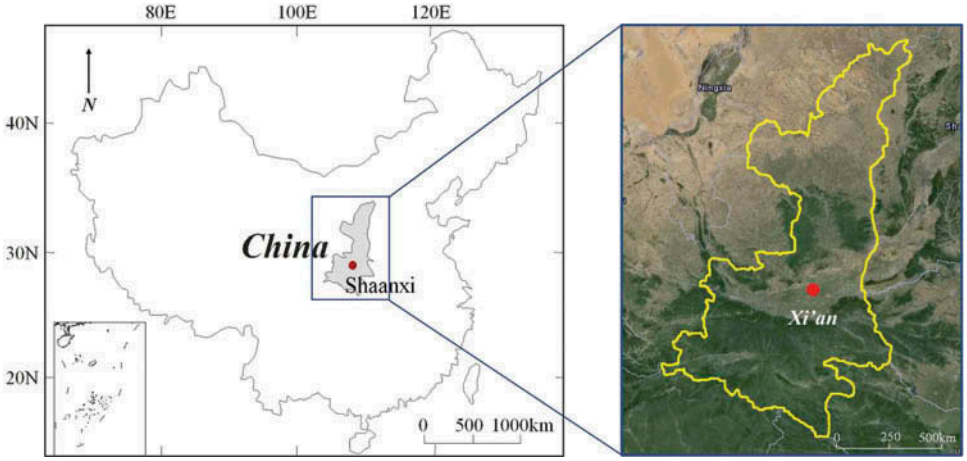

Figure 1. Geographical location of Xi'an sampling site in Shaanxi Province, China.

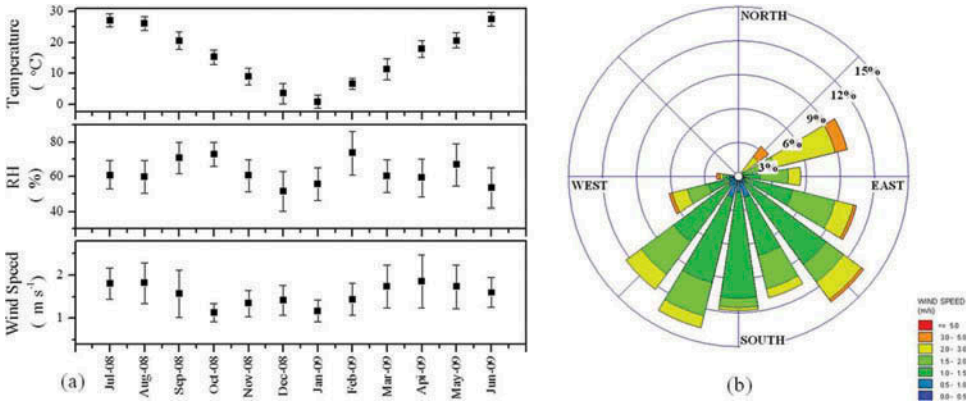

Figure 2. (a) Monthly average ambient temperatures, relative humidity (RH), and wind speeds and (b) wind rose in Xi'an.

(Dionex Inc., Sunnyvale, CA, USA). The separation was carried on a Dionex CarboPac MA1 analytical column (4 × 250 mm) and a Dionex CarboPac MA1 guard column with sodium hydroxide solution (612 mM) as eluent at the flow rate of 0.4 mL min^{-1} (Engling et al., 2006; Iinuma et al., 2009). Aliquots of 100 μL of each extract were injected into the system, and the chromatographic run time was 1 hr for each measurement. Authentic standards were used for identifying and obtaining response factors of the individual anhydrosugars. The minimum detection limit (MDL) was estimated as the concentration visible in the chromatogram with the peak height at least 3 times the signal-to-noise ratio, which was found to be 1.3 ng mL^{-1}. Measurement precision for levoglucosan was 2.3% (1 relative standard deviation), based on replicate analyses of sample extracts ($n = 10$).

The major ionic species, including water-soluble potassium (K^+), ammonium (NH_4^+), calcium (Ca^{2+}), chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}), were also measured in the same extracts using a Dionex DX-600 ion chromatograph. IonPac CS12A and AS14A columns were used for the separation of cations and anions, respectively. For anion separation, an eluent of 8 mM Na_2CO_3 and 1 mM $NaHCO_3$ was used with a flow rate of 1 mL min^{-1}, whereas 20 mM methanesulfonic acid with a flow rate of 1 mL min^{-1} was utilized as eluent for cation separation. The MDLs were as follows: 0.001 μg mL^{-1} each for NH_4^+, K^+, and Ca^{2+}, 0.008 μg mL^{-1} for Cl^-, 0.025 μg mL^{-1} for NO_3^-, and 0.027 μg mL^{-1} for SO_4^{2-}. Data reported are the field blank corrected. Quality assurance/quality control (QA/QC) procedures are as described by Zhang et al. (2011).

Carbon and stable isotope analyses. A punch (0.526 cm^2) of quartz-fiber filter was analyzed for organic carbon (OC) and elemental carbon (EC) by the IMPROVE_A thermal/optical reflectance (TOR) protocol (Chow and Watson, 2002) using a Desert Research Institute (DRI, Reno, NV, USA) model 2001 thermal/optical carbon analyzer (Atmoslytic Inc., Calabasas, CA, USA). Detailed information on carbon analysis and required quality assurance and quality control are documented in Chow et al. (2011).

The stable carbon isotope composition ($\delta^{13}C_{OC}$ and $\delta^{13}C_{EC}$) was determined by combusting quartz-fiber filters using a Finnigan MAT-251 ratio mass spectrometer (Thermo Electron Corporation, Burlington, ON, Canada) (Ho et al., 2006a; Cao et al., 2011). Prior to isotopic analysis, carbonate was removed by treatment with hydrochloric acid. The carbon remaining on the substrates, which included both OC and EC, was then oxidized to CO_2 by dry combustion at 375 °C for 3 hr. A series of cold traps was used to collect the CO_2 produced from OC, and the CO_2 was quantified by manometry. The stable carbon isotopic composition of the CO_2 was determined as $\delta^{13}C_{OC}$. The carbon that remained on the filters was combusted at 850 °C for 5 hr and quantified as $\delta^{13}C_{EC}$. Samples were analyzed at least in duplicate, with a maximum difference in carbon isotopes of 0.3‰ between replicates.

$\delta^{13}C$ values, based on the international standard Vienna Pee Dee Belemnite (V-PDB), were calculated as follows:

$$\delta^{13}C = \left(\frac{^{13}C/C^{12}C_{sample}}{^{13}C/C^{12}C_{s\,tan\,dard}} - 1\right) \times 1000. \quad (1)$$

PDB is the primary reference material for measuring natural variations of ^{13}C, consisting of calcium carbonate from a cretaceous belemnite rostrum from the Pee Dee Formation in South Carolina, USA. Isotopic indications of naturally occurring ^{13}C are conventionally expressed in relation to V-PDB.

Fire count map from satellite observations

Fire count maps, displaying the active burning hot spots, were derived from MODIS (Moderate Resolution Imaging Spectroradiometer) satellite images. Data were analyzed using a standard MODIS MOD14 Fire and Thermal Anomalies Product algorithm (http://earthdata.nasa.gov/data/near-real-time-data/firms).

Results and Discussion

Characteristics of levoglucosan

Figure 3 shows the temporal variation of $PM_{2.5}$ levoglucosan concentrations, with 24-hr average ranging from 46 to 1889 ng m^{-3} and the average concentration of 428 ng m^{-3} from 5 July 2008 to 27 June 2009 (Table 1). Average levoglucosan concentration in winter (935 ± 443 ng m^{-3}) was 11 times higher than summer (85 ± 24 ng m^{-3}), with 370 ± 325 and 178 ± 125 ng

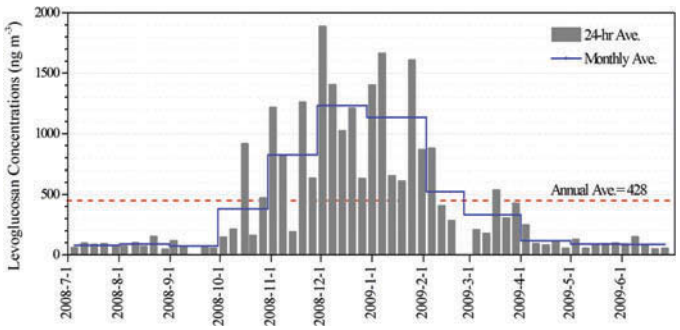

Figure 3. Temporal variation of levoglucosan mass concentrations (ng m^{-3}) from July 2008 to June 2009. The blue lines show the monthly average concentrations and red line shows the annual average concentration.

m^{-3} for autumn and spring, respectively. The summer minima and winter maxima phenomena were also found in Chongqing, Wuhan, and Guangzhou (Wang et al., 2006a). The seasonal variations of $PM_{2.5}$ chemical compositions are shown in Table 1, the concentrations and fractions of different constituents varied during the different seasons. The difference may be ascribed to (1) the change of emission sources (i.e., residential and commercial coal combustion, biomass burning, motor vehicle exhaust, soil dust, and so on); (2) chemical conversions of different compositions; and (3) different chemical compositions removal rates by deposition. Chemical conversions and deposition are all influenced by meteorological conditions (such as temperature, RH, wind speed, rainfall, and so on).

The main energy source for cooking and heating in rural China are biofuels, including crop residues and fuel wood (Wang et al., 2006a; Yan et al., 2006). Biomass burning started after agriculture harvest in Xi'an and its surrounding areas, and household heating with straw and branch burning took place from November to March the following year. Meteorological conditions during winter were characterized by stagnation with a low inversion layer, which intensify levoglucosan levels through accumulation of air pollutants.

Besides, several episodic events with dramatic increases were clearly observed in spring. Elevated levoglucosan concentrations reached 538 and 429 ng m^{-3} on 17 and 29 March 2009, respectively, accompanied by substantial increase in OC (34 and 25 μg m^{-3}) and K^+ (2 μg m^{-3}) concentrations. This might have been affected by agricultural burning activities and dry weather. In spring, field preparation burnings occurred at Xi'an and surrounding areas, with monthly average RH of 60% (March), 59% (April), and 66% (May).

Biomass burning activities were apparent in Guanzhong Plain, as shown by satellite-derived fire counts (Figure 4). Extensive biomass burning activities occurred in summer as compared with winter. Farmers in Guanzhong Plain started field preparation during June and July and burned crop residues (e.g., corn and wheat), resulting in sporadic emissions of biomass burning smoke. However, the meteorological conditions were favorable for dilution and diffusion of pollutants in summer. Summer monsoons from the southeast carried an abundance of rainfall to Xi'an, leading to high precipitation in summer (Shen et al., 2012). The average wind speed was also relatively high (1.8 m sec^{-1}). Although the fire counts were relatively low in winter, average levoglucosan concentrations were the highest, suggesting that larger domestic biofuel burning sources (not shown in the MODIS fire counts map) during the winter coupled with a more stagnant air mass led to the elevated levoglucosan levels.

Correlation of levoglucosan with other compounds

Table 2 shows that relatively high correlation coefficients ($0.70 < R < 0.92$) were found between levoglucosan and K^+, Cl^-, OC, EC, and glyoxal, indicative of biomass burning.

Elevated K^+ have been found in biomass burning emission and has been applied in several source apportionment studies (Cachier et al., 1991; Chow, 1995; Duan et al., 2004). However, K^+ was also reported in fireworks (Wang et al., 2007b; Chang et al., 2011). In addition to, it suffers from the fact that it has also contributions from sea salt, meat cooking, refuse incinerators, and, particularly, all combustion (Hildemann et al., 1991; Sheffield et al., 1994; Zhang et al., 2008). Figure 5a shows that the correlation between levoglucosan and K^+ was highest in spring ($R = 0.77$), followed by winter ($R = 0.75$; excluding Chinese New Year's firework events), and low in other seasons.

Table 1. Statistical summary of 24-hr $PM_{2.5}$ chemical composition for samples acquired over spring, summer, autumn, and winter periods in Xi'an, China

		Seasonal Concentration		
Pollutant	Annual Concentration Avg. ± SD	Spring Avg. ± SD	Summer Avg. ± SD	Autumn Avg. ± SD	Winter Avg. ± SD
Levoglucosan (ng m^{-3})	428 ± 399	178 ± 125	85 ± 24	370 ± 325	935 ± 443
NH_4^+ (μg m^{-3})	4.5 ± 3.0	4.9 ± 1.1	2.8 ± 2.4	7.3 ± 6.4	9.1 ± 5.6
K^+ (μg m^{-3})	1.4 ± 0.8	0.8 ± 0.3	0.7 ± 0.2	1.5 ± 0.8	2.2 ± 0.7
Ca^{2+} (μg m^{-3})	2.5 ± 1.2	2.2 ± 0.7	2.9 ± 0.9	1.3 ± 0.7	3.3 ± 1.7
Cl^- (μg m^{-3})	2.6 ± 1.6	2.1 ± 1.5	1.0 ± 0.5	2.6 ± 1.2	4.4 ± 1.3
SO_4^{2-} (μg m^{-3})	16.7 ± 7.8	18.2 ± 2.4	13.4 ± 7.1	19.1 ± 11.4	26.9 ± 14.3
NO_3^- (μg m^{-3})	9.1 ± 5.8	9.1 ± 4.1	4.6 ± 2.5	13.8 ± 10.9	16.7 ± 8.3
OC (μg m^{-3})	21.5 ± 13.4	12.8 ± 6.3	10.9 ± 3.5	19.2 ± 10.5	38.1 ± 15.1
EC (μg m^{-3})	7.6 ± 2.4	5.7 ± 1.8	6.3 ± 1.6	8.4 ± 2.5	9.6 ± 2.2

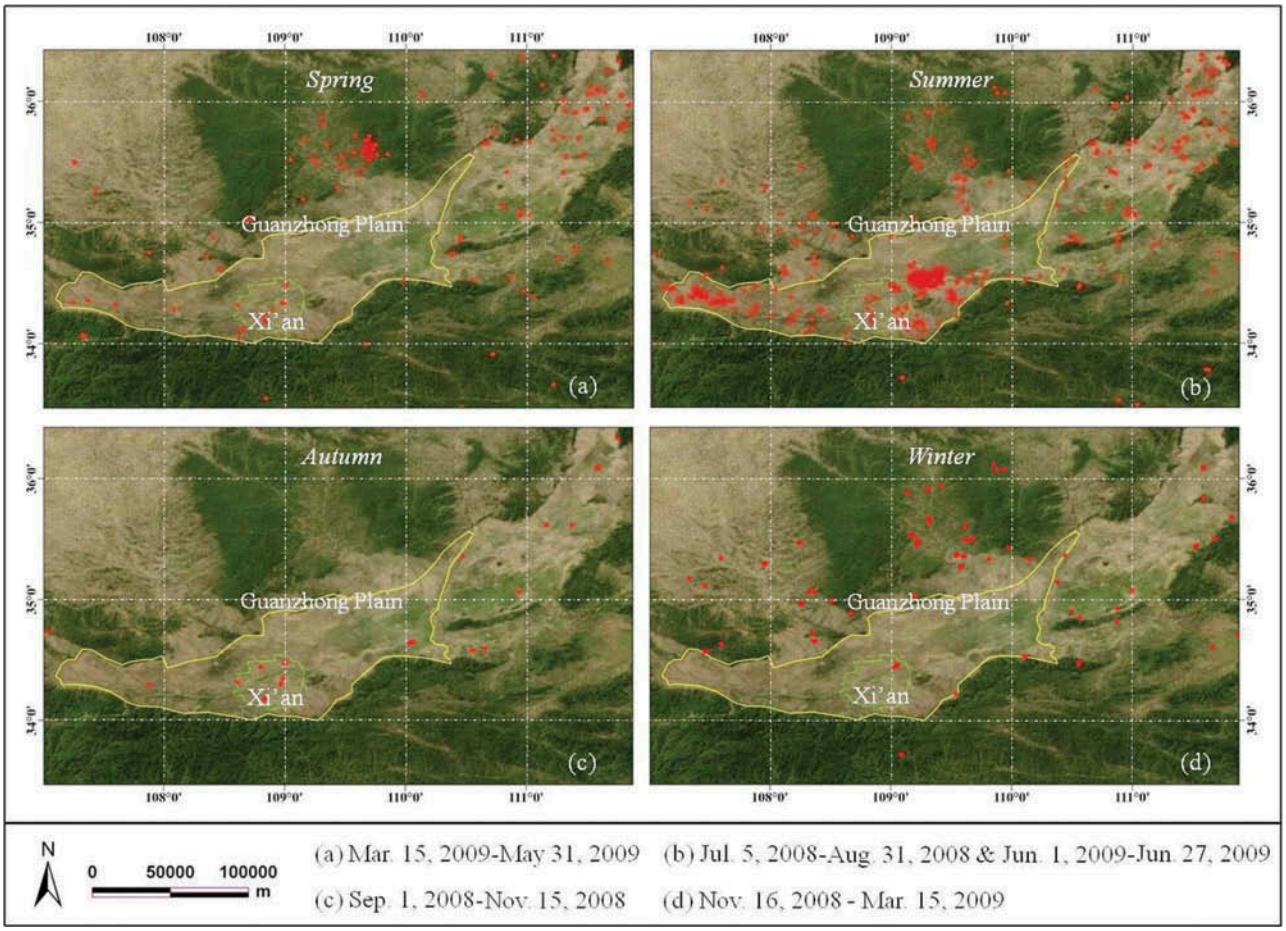

Figure 4. Fire counts (red points) during the period of 5 July 2008 to 27 June 2009.

Table 2. The correlation coefficients[a] between levoglucosan and other parameters

	NH_4^+	K^+	Ca^{2+}	Cl^-	SO_4^{2-}	NO_3^-	OC	EC	Glyoxal[b]
Levoglucosan	0.26 ($n = 58$)	**0.75** ($n = 57$)	0.32 ($n = 58$)	**0.79** ($n = 58$)	0.35 ($n = 58$)	0.33 ($n = 58$)	**0.91** ($n = 58$)	**0.70** ($n = 58$)	**0.80** ($n = 29$)

Notes: [a]Boldface indicates that the correlation coefficient is higher than 0.60. [b]Data from Dai et al. (2012).

Good OC/EC correlations with levoglucosan ($0.70 < R < 0.91$) were found, suggesting impacts from a combination of coal combustion (mostly residential), motor vehicle exhaust, and biomass burning (Streets et al., 2001; Zhang et al., 2001; Cao et al., 2005). Sullivan et al. (2008) suggest that the levoglucosan/OC ratio varies by fuel component, with the highest ratio found in branches, followed by straw, needles, and leaves. In this study, the highest levoglucosan/OC ratio of 2.3% was found in winter (the intercept of autumn was larger than winter) compared with other seasons, suggesting more straw was burned in winter. As can be seen in Figure 5b, the correlation between levoglucosan and OC was high in spring ($R = 0.91$), summer ($R = 0.73$), autumn ($R = 0.80$), and winter ($R = 0.86$). These good correlations suggest that biomass burning in spring and winter is an important source of organic carbon.

Glyoxal is produced during the oxidation of many anthropogenic and biogenic volatile organic compounds (VOCs) (Ho et al., 2006b; Fu et al., 2008; Myriokefalitakis et al., 2008). Even if there is only a small fraction of glyoxal partitioning onto particles, it can still affect the global secondary organic aerosol (SOA) budget significantly. Dai et al. (2012) reported an average $PM_{2.5}$ glyoxal concentration of 0.7 $\pm$ 0.4 ng m^{-3} during same sampling period at Xi'an, with the highest concentration of 1.1 ng m^{-3} in winter. As shown in Table 1, there was a strong correlation between levoglucosan and glyoxal ($R = 0.80$) concentrations. The results are consistent with other studies and are suggestive of biomass burning being a glyoxal source (Fu et al., 2008; Akagi et al., 2011). Figure 5c shows the relationship between levoglucosan and glyoxal during four seasons, with the relatively high correlation in spring ($R = 0.98$) and winter ($R = 0.64$). There was no correlation between levoglucosan and glyoxal in summer and autumn, which may due to the limited

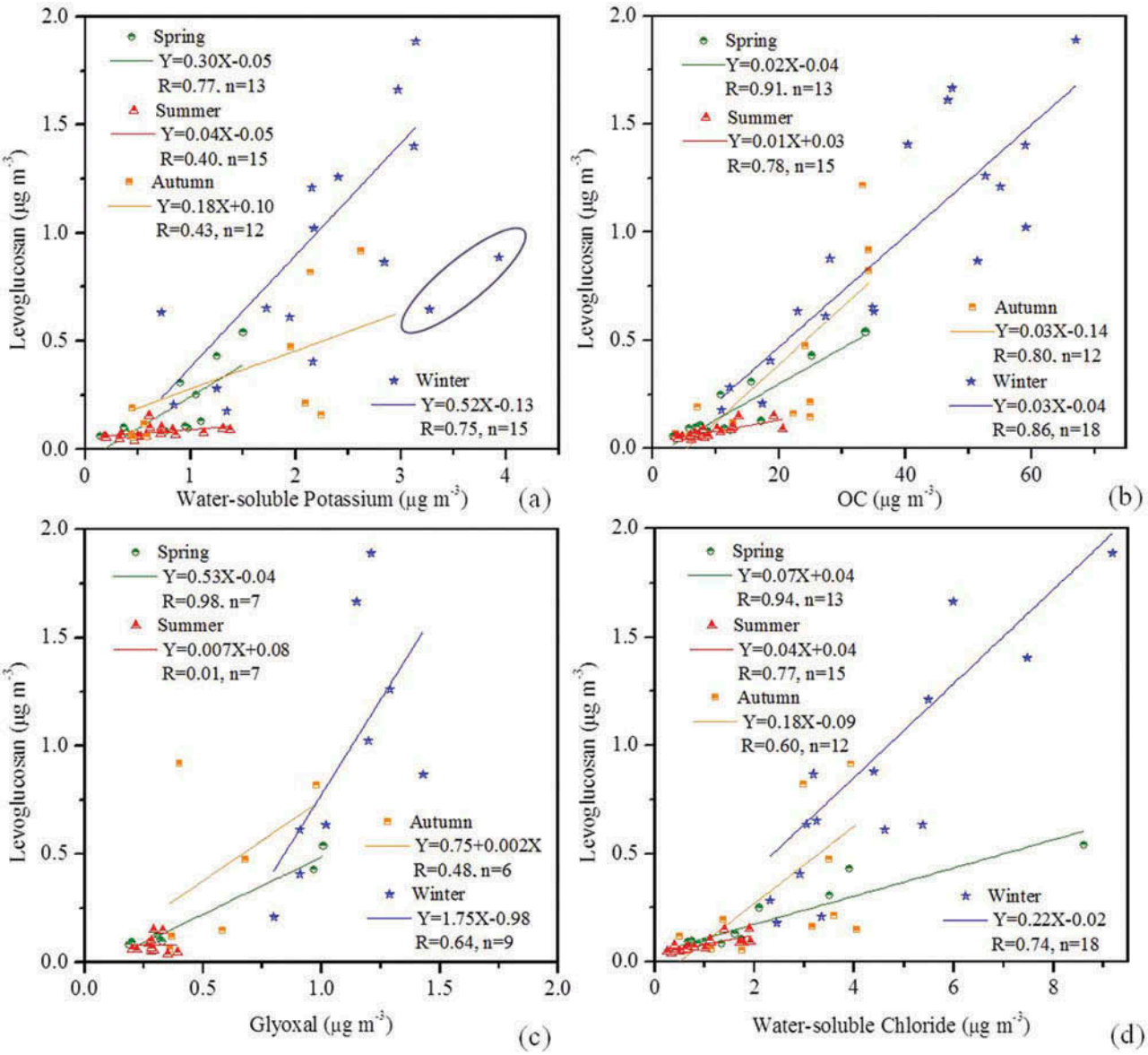

Figure 5. Correlations between levoglucosan and (a) K^+, (b) OC, (c) glyoxal, and (d) Cl^-. Green: spring; red: summer; yellow: autumn; blue: winter. The encircled components demonstrate fireworks during the Chinese New Year's firework events.

measurement and very low concentrations. In addition, the correlations between levoglucosan and other carbonyls were very low.

As Xi'an is far inland, marine influences on the urban aerosol particles should be minimal. Previous studies showed that Cl^- is also associated with the vegetative and coal burning activities during the cold seasons (Wang et al., 2006b; Deshmukh et al., 2011). Shen et al. (2009) reported that the high Cl^- is more likely from straw combustion emission in Xi'an. Therefore, levoglucosan is well correlated with Cl^- ($R = 0.79$), as shown in Table 1, implying its association with biomass burning.

Relationship between $\delta^{13}C_{EC}$ and the EC/TC ratio

Cachier et al. (1989) uses the relationship between isotopic composition ($\delta^{13}C$) and C_{EC}/C_{TC} ratio to discriminate among combustion sources. TC (total carbon) was calculated as the sum of OC plus EC. The distributions of $\delta^{13}C_{EC}$ and EC/TC ratio during different seasons are shown in Figure 6 ($\delta^{13}C$ is replaced with $\delta^{13}C_{EC}$ because EC retains the isotopic information of the original emission sources whereas OC does not [Cao et al., 2011]).

Reasonable correlation ($R = 0.75$) was found between $\delta^{13}C_{EC}$ and EC/TC ratio, consistent with the association ($R = 0.70$) between levoglucosan and EC. As seen in Figure 6, $\delta^{13}C_{EC}$ was relatively light with increasing EC/TC ratios, it means biomass burning activities were relatively weak in summer. In contrast, when the $\delta^{13}C_{EC}$ was relatively heavy, the ratios of EC to TC decreased, this indicates that biomass burning was most active in winter. This result is consistent with the above dates.

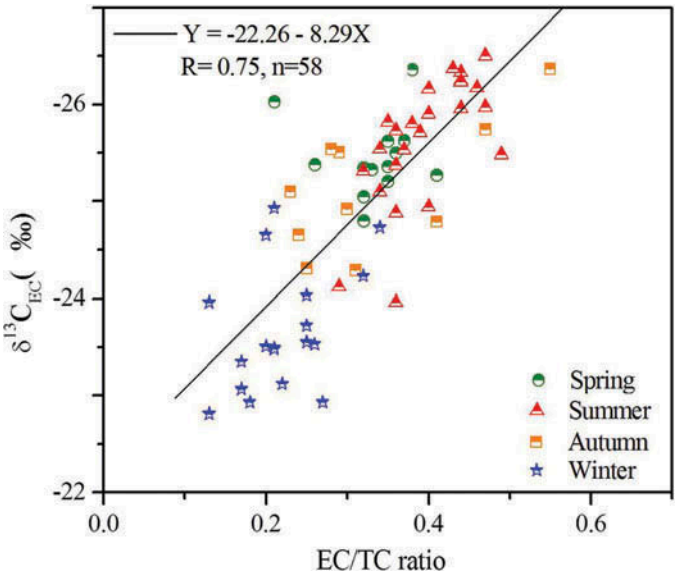

Figure 6. Scatterplot of $\delta^{13}C_{EC}$ versus EC/TC ratio in $PM_{2.5}$.

Impact of biomass burning on air quality

Levoglucosan to OC or $PM_{2.5}$ ratios have been used to estimate the effects of biomass burning (Zdrahal et al., 2002; Puxbaum et al., 2007; Wang et al., 2007a; Zhang et al., 2010, 2012; Sang et al., 2011). Sullivan et al. (2008) reported that the levoglucosan content in OC was 7.6% for rice straw burning in Taiwan. Zhang et al. (2007) reported an average of 8.2% (with a range of 5.4–11.8%) of levoglucosan in OC with cereal straw (corn, wheat, and rice) in China. Therefore, the contributions of biomass burning to OC (based on enrichment factor reception modeling approach) can be inferred as follows:

$$\text{Contributions of biomass burning to OC} = \frac{([\text{levoglucosan}]/[\text{OC}])_{\text{ambient}}}{([\text{levoglucosan}]/[\text{OC}])_{\text{source}}} \quad (2)$$

These characteristics mean that levoglucosan could be the tracer compound to separate biomass burnings from other sources, but could not distinguish different biomass combustion sources from each other. Due to the lack of source profiles for constituent ratio of different types biomass in different seasons under realistic ambient conditions, an average levoglucosan to OC ratios of 8.2% from combustion chamber study (Zhang et al., 2007) was adopted. Figure 7 shows that the contributions of biomass burning to OC were highest during January (30.2 ± 7.8%), with 26.4–30.2% for the remaining winter months, and lowest during June (7.6 ± 2.0%). These values are higher than those of 6.5–11% and 16–28% reported in Hong Kong (Sang et al., 2011) and Hainan (Zhang et al., 2012), respectively, but are closer to the upper range of 18–38% reported in Beijing (Zhang et al., 2008).

Comparison with other studies

Levoglucosan concentrations and levoglucosan/OC ratios acquired from rural, suburban, and urban areas in China are summarized in Table 3. Average concentrations of levoglucosan in Xi'an were similar to those in northern cities such as Beijing (Zhang et al., 2008) and Baoji (Xie et al., 2010). The seasonal tendency of levoglucosan concentrations between Xi'an and Beijing was also similar, with winter maxima and summer minima. In southern cities, levoglucosan levels were lower, such as Nanjing (Wang and Kawaruma, 2005), Guangzhou (Wang et al., 2007a), and Hong Kong (Sang et al., 2011). Levoglucosan concentrations were low in the range of 30–95 ng m^{-3} at the rural sites (e.g., Hok Tsui, Hong Kong; Jianfengling, Hainan; Mt. Hua, Shaanxi). Average levoglucosan concentrations in winter generally were around 2–5 times higher than these in summer. Emissions from biomass/biofuel combustion for domestic cooking and heating, together with wintertime stagnation and low inversion layers, most likely resulted in elevated levoglucosan, especially in the northern cities. The ratios of levoglucosan/OC were relatively high in northern cities and relatively low in southern cities. Moreover, the ratios were higher in winter than those in summer, which was attributed to winter/summer ratio of levoglucosan extremely higher than winter/summer ratio of OC. Compared with the data of levoglucosan and OC from previous literature, similar tendency could be found (Cao et al., 2007; Wang et al., 2006). We also compared the concentrations of levoglucosan measured in other countries available in the literature (Table 3). The concentrations of levoglucosan reported for different sampling locations ranged between hundreds and thousands of ng m^{-3} in winter and tens of ng m^{-3} in summer in various urban and rural locations.

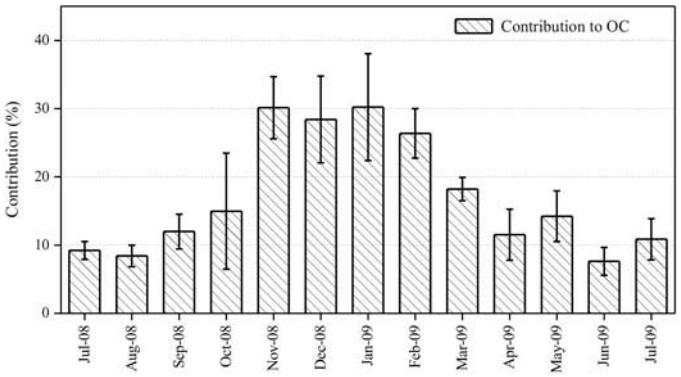

Figure 7. Monthly average contribution of biomass burning to OC.

Conclusion

Biomass burning is an important source of aerosol particles affecting local and regional air quality, but it was not recognized in western China. Annual average $PM_{2.5}$ levoglucosan concentration was 428 ± 399 ng m^{-3} from 7 July 2008 to 27 June 2009 in Xi'an. Average seasonal levoglucosan concentrations were highest during winter (934 ± 443 ng m^{-3}) and autumn (370 ± 325 ng m^{-3}) and low in spring (178 ± 125 ng m^{-3}) and summer (85 ± 24 ng m^{-3}), reflecting changes in biomass burning activities in the surrounding areas of Xi'an. The influence of biomass burning is maximum during the residential heating season (winter), with impacts during autumn field burning (corn stalks, wheat straw,

Table 3. Comparison of average levoglucosan concentrations and levoglucosan/OC ratios for different locations

Locations	Sampling Date	Site Type	Particle Size	Measurement Method	Levoglucosan Concentration (ng m^{-3})	LG/OC (%)	References
Xi'an	July 2008 to June 2009	Urban	$PM_{2.5}$	HPAEC-PAD	428 ± 399	1.44 ± 0.69	This study
Nanjing	July 2004 January 2005	Urban	$PM_{2.5}$	GC-MS	151 268	NA NA	Wang and Kawaruma, 2005
Hainan	April to May 2004	Rural	$PM_{2.5}$	HPAEC-PAD	42 ± 33	1.35	Zhang et al., 2012
Hong Kong	April to May 2004	Rural	$PM_{2.5}$	HPAEC-PAD	30	0.63	Sang et al., 2011
		Urban			36	0.5	
Guangzhou	October 2004	Suburban	$PM_{2.5}$	GC-MS	120–950	NA	Wang et al., 2007
		Urban			200–660	NA	
Beijing	July 2002 to July 2003	Urban	$PM_{2.5}$	GC-MS	307 ± 345	2.1	Zhang et al., 2008
14 Cities in China	Winter 2003 Summer 2003	Mixed	$PM_{2.5}$	GC-MS	700 ± 1015	1.94	Wang et al., 2006
Mt. Hua	January 2009	Rural	PM_{10}	GC-MS	123 ± 191 65 ± 30	0.77 1.1	Li et al., 2012
Baoji	February 2008 April 2008	Urban, Rural	PM_{10}	GC-MS	901 261	NA NA	Xie et al., 2010
Guangzhou	July 2006	Urban	PM_{10}	HPAEC-PAD	15–473	NA	Zhang et al., 2010
Tuscany, Italy	March 2009 to March 2010	Suburban	$PM_{2.5}$	HPLC/ESI-MS/MS	41.4 ± 64.1	0.04–8.7	Giannoni et al., 2012
		Urban			187 ± 332	0.13–9.75	
Slapanile, Czech Republic	Winter 2009 Summer 2009	Urban	$PM_{2.5}$	GC-MS	572 ± 71.3 55.6 ± 17.3	NA NA	Krumal et al., 2010
Brno, Czech Republic	Winter 2009 Summer 2009				326 ± 114 47.1 ± 26.4	NA NA	
Azores Islands, Portugal	July 2002 to July 2004	Rural coastal	$PM_{2.5}$	HPLC	517	3.23	Puxbaum et al., 2007
	July 2002 to May 2004	Rural continental			309	2.03	
Oslo, Norway	November to December 2001	Urban	PM_{10}	HPLC	166	0.79	Yttri et al., 2005
Elverum, Norway	January to March 2002	Suburban			407	2.17	
Seiffen, Germany	October, December 2007 and February 2008	Rural	PM_{10}	HPAEC-PAD	299	NA	Iinuma et al., 2009

dead leaves) and spring field burning in preparation for agriculture planting. Domestic biomass burning in northwestern China cannot be explored through the satellite fire counts. Reasonably good correlations were found between levoglucosan and water-soluble K^+ ($R = 0.75$), Cl^- ($R = 0.79$), OC ($R = 0.91$), EC ($R = 0.70$), and glyoxal ($R = 0.80$). Using a simplified receptor-based enrichment factor approach, biomass burning contributed to 5.1–43.8% of OC. Household heating with biomass during winter in Guanzhong Plain needs to be further investigated. Therefore, the control of biomass/biofuel combustion could be an effective method to reduce pollutant emissions on a regional scale in northwestern China.

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