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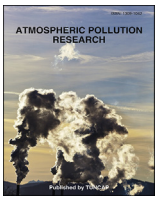

Biomass burning tracers in rural and urban ultrafine particles in Xi'an, China

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ABSTRACT

To investigate the impact of biomass burning emissions on ultrafine particles ($PM_{0.133}$: particulate matter with an aerodynamic diameter less than 0.133 μm), biomass burning tracers (including levoglucosan, mannonsan and K^+) were measured at a rural and an urban sites in Xi'an during winter heating period. The average levoglucosan concentrations of rural and urban $PM_{0.133}$ were 0.93 ± 0.32 μg m^{-3} and 0.29 ± 0.14 μg m^{-3}, respectively. Comparable $PM_{0.133}$ mannosan concentrations were observed in rural samples (0.16 ± 0.26 μg m^{-3}) and urban samples (0.17 ± 0.10 μg m^{-3}). Higher correlation between levoglucosan and K^+ was obtained for urban samples (R = 0.86) than that for rural samples (R = 0.72). The levoglucosan to K^+ ratio was found to be higher for rural samples (0.77 ± 0.39) compared to that for urban samples (0.32 ± 0.14). Levoglucosan to mannosan ratios averaged 7.86 and 2.83 for rural and urban samples, respectively. It can be concluded that the major source of rural biomass burning was the combustion of crop residuals and softwood. The contributions of biomass burning to OC ranged from 19% to 32%, with an average of 24% for rural samples. The results provide a better understanding on the rural and urban magnitude of levoglucosan and contributions of biomass burning in Xi'an.

1. Introduction

Biomass burning, associated with both open and domestic fires (for cooking and heating) is common in northern China (Cheng et al., 2013; Zhang et al., 2014). Its contribution to aerosol particles has been recognized to be substantial (Fine et al., 2001; Schauer et al., 2001; Venkataraman et al., 2005; Lee et al., 2008). Levoglucosan is considered as a highly specific tracer for biomass burning aerosols because it is relatively stable in the atmosphere (Simoneit et al., 1999; Puxbaum et al., 2007; Schkolnik et al., 2005). In recent years, however, 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 relative humidity conditions. Such conditions may be quite important for biomass burning particles in tropical areas and during long-range transport, but are expected to be of minor importance for our study in Xi'an under winter conditions when photooxidation is low (Hoffmann et al., 2010; Hennigan et al., 2010). The use of levoglucosan as biomass burning tracer has been preferred to the conventional water soluble potassium, since recent studies have evidenced that potassium has other significant sources, i.e., meat cooking, waste incinerators, coal usage (Duan et al., 2004; Caseiro et al., 2009). Several studies about levoglucosan in $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) have been conducted in Chinese cities, such as Beijing, Nanjing, Guangzhou, and Hong Kong (Wang and Kawamura, 2005; Wang et al., 2007; Zhang et al., 2008; Sang et al., 2011; Cheng et al., 2013), with concentration ranging from 0.030 μg m^{-3} to 0.950 μg m^{-3}. High concentrations of $PM_{2.5}$ levoglucosan were reported in winter and autumn in Xi'an with notable biomass burning contribution to OC (Zhang et al., 2014). Therefore, controls on biomass combustion could be an effective method to reduce pollutant emissions in northern China.

The Guanzhong plain is one of the major agricultural production areas for wheat and corn, surrounded by Qinling Mountains to the

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south and the Loess Plateau to the north. Xi'an is the largest city in the Guanzhong plain, where air pollution is a serious problem due to drastic enhancement of coal and biomass burning for house heating in winter (Huang et al., 2014; Zhu et al., 2016). Levoglucosan to K^+ ratios are capable of distinguishing the emissions of the crop residual burning from the wood burning. Levoglucosan to mannosan ratios can be applied to reliably distinguish hardwood burning from softwood burning (Cheng et al., 2013). The investigations of biomass burning types and contributions to ultrafine particles were scarce in Xi'an which can well be conducted by using the comparison of levoglucosan to K^+ ratio and levoglucosan to mannosan ratio.

In this study, three biomass burning tracers (including levoglucosan, mannosan, and K^+) for rural and urban ultrafine particles were quantified. The goal is to gain a better understanding on the magnitude of biomass burning tracers, biomass burning types and contributions in Xi'an.

2. Methods

2.1. Aerosol sampling

Sampling was conducted at a rural site (34.12 °N, 108.62 °E), and an urban site (34.21°N, 109°E) at Xi'an, China. In the rural area, it is common for residents to use coal and biomass for cooking and heating in winter. The site is on the rooftop of a private house in a village of Huxian county. The urban sampling site is located at Xi'an, China (in the Institute of Earth Environment, Chinese Academy of Sciences).

$PM_{0.133}$ samples (Dp $\leq$ 0.133 μm, particulate matter with an aerodynamic diameter less than 0.133 μm) were collected using personal active nanoparticle samplers (PENS) operating at 1.5 L/min (Tsai et al., 2012; Zhu et al., 2016). The sampling periods are from 17 to 26 January 2014 at the rural site and from 8 December 2013 to 14 January 2014 at the urban site, respectively. Rural samples were collected on 37 mm Whatman quartz microfibre filters (QM/A) (n = 10) and Teflon microfibre filters (n = 10), simultaneously. Urban samples were collected on 37 mm Teflon microfibre filters (n = 12). Whatman quartz microfibre filters were pre-heated at 900 °C for 3 h and then stored in aluminum foils. The samples were stored in a refrigerator at about −20 °C immediately to prevent the evaporation of volatile components after sampling.

2.2. Measurement of OC, EC, and K^+

The rural quartz microfibre filters were analyzed for carbon fractions by using a Thermal/Optical Carbon Analyzer (DRI Model 2001; Atmoslytic Inc., Calabasas, CA, USA). Carbon fractions were obtained following the IMPROVE-A (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol (Chow et al., 2007). Temperature defined carbon fractions are: OC1-OC4 (OC evolved from the filter punch in a pure helium atmosphere at 140 °C, 280 °C, 480 °C, and 580 °C, respectively), OP (a pyrolyzed carbon fraction, determined when reflected laser light attained its original intensity after oxygen was added to the combustion atmosphere), and EC1-EC3 (EC evolved from the filter in a 2% oxygen/98% helium atmosphere at 580 °C, 740 °C, and 840 °C, respectively). The protocol defined OC as OC1+OC2+OC3+OC4+OP and EC as EC1+EC2+EC3-OP. Replicate analyses were conducted once every ten samples. Blank sample was also analyzed and used to correct the sample results. The detailed quality assurance/quality control procedures have been described elsewhere (Cao et al., 2003; Chow et al., 2011). No urban OC and EC data were acquired because quartz microfibre filters were not available.

The concentrations of K^+ were obtained by using a Dionex-600 Ion Chromatograph equipped with an IonPacCS12A column (20 mM methanesulfonic acid as the eluent) to analyze the cations (Dionex Inc., Sunnyvale, CA, USA). The detection limit is 0.001 μg/mL for K^+. The reported K^+ concentrations are corrected using the field blank sample. The experimental uncertainty is ±0.01 for K^+. Standard reference materials produced by the National Research Center for Certified Reference Materials (Beijing, China) were analyzed for quality assurance/quality control purposes.

2.3. Measurement of levoglucosan, and mannosan

The rural and urban Teflon microfibre filters were analyzed for levoglucosan and mannosan using the high-performance anion exchange chromatography with pulsed amperometric detection method (HPAEC-PAD). The detailed description of the analytical method can be found elsewhere (Engling et al., 2006). The HPAEC-PAD method is developed and validated for simultaneous determination of atmospherically relevant sugar alcohols, monosaccharides, and monosaccharide anhydrides (Engling et al., 2009; Zhang et al., 2013). The method detection limits of levoglucosan and mannosan are 0.008 μg/mL and 0.005 μg/mL, respectively. The absolute values measured by HPAEC-PAD were slightly higher than those obtained by GC/MS methods for organic compounds (e.g., levoglucosan), which might be attributed to the uncertainties arising from the steps involved in GC/MS analysis (Engling et al., 2006).

3. Results and discussion

3.1. Variations of levoglucosan, mannosan, and K^+

As shown in Table 1, the concentrations of levoglucosan, and K^+ in rural $PM_{0.133}$ were 0.93 ± 0.32 μg m^{-3}, and 2.0 ± 1.1 μg m^{-3}, respectively. The values were much higher than those in urban $PM_{0.133}$ levoglucosan (0.29 ± 0.14 μg m^{-3}), and K^+ concentrations (1.1 ± 0.9 μg m^{-3}), respectively. The concentration of rural mannosan (0.16 ± 0.26 μg m^{-3}) was found to be comparable with that of urban samples (0.17 ± 0.10 μg m^{-3}). Levoglucosan coincided well with K^+ of most rural samples, while the variation of urban levoglucosan was different from that of K^+ (Fig. 1).

Daily levoglucosan concentrations varied by three times from 0.53 μg m^{-3} to 1.53 μg m^{-3}, which was comparable with the variation of K^+ (range: 0.7–4.5 μg m^{-3}) of rural samples. Fig. 1 shows that the daily levoglucosan values of urban samples varied by nearly sevenfold, from a low of 0.07 μg m^{-3} to 0.49 μg m^{-3}. A strong variation was observed in the daily urban K^+ concentration, ranging from 0.2 μg m^{-3} to 2.9 μg m^{-3} during the study period. Therefore, higher levoglucosan and K^+ were observed for rural samples than those for urban samples.

The urban $PM_{2.5}$ levoglucosan concentrations in Xi'an measured by Zhang et al. (2014) (averaging 0.94 μg m^{-3} in winter) were much higher than those for $PM_{0.133}$ levoglucosan obtained in the present study. Compared with American and European cities, Xi'an was characterized by rather high levoglucosan concentrations, especially in winter. Previous results showed that the annual average levoglucosan concentration was 0.142 μg m^{-3} and 0.11 μg m^{-3} in

Table 1
Average concentrations of rural and urban $PM_{0.133}$ chemical components in winter (μg m^{-3}).

Site	Levoglucosan	Mannosan	OC	EC	K^+
Rural	0.93 ± 0.32	0.16 ± 0.26	48.9 ± 18.1	0.4 ± 0.3	2.0 ± 1.1
Urban	0.29 ± 0.14	0.17 ± 0.10	N.A.[a]	N.A.	1.1 ± 0.9

[a] No data.

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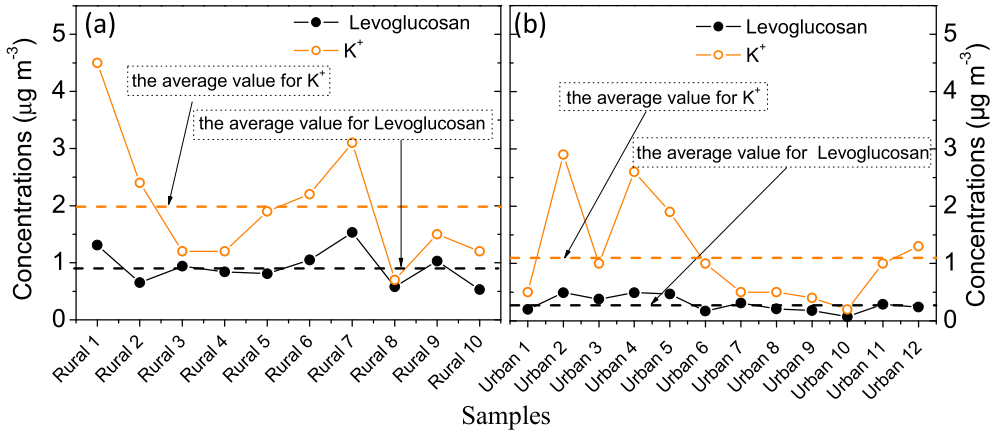

Fig. 1. Variations of levoglucosan and K^+ for (a) rural and (b) urban sites.

the Pearl River Delta, China and southeastern US, respectively (Wang et al., 2015; Zhang et al., 2010). Much lower levoglucosan concentration was observed in Pittsburgh, PA (in the northeastern US), with an annual average of 0.02 μg m^{-3} (Robinson et al., 2006). Low concentration of levoglucosan was also reported in Europe (Caseiro and Oliveira, 2012). The results showed that strategies to improve urban air quality also need to consider the advection from extra rural emission sources in the Guanzhong plain.

3.2. Relationship between biomass burning tracers and carbonaceous aerosols

During this period, linear regression of levoglucosan on K^+ resulted in a slope of 0.2 and an intercept of 0.53 (R = 0.72) for rural samples. Levoglucosan showed an apparent dependence on K^+ for urban samples, and there was more K^+ in comparison to levoglucosan with a slope of 0.14 and an intercept of 0.13 (R = 0.86) (Fig. 2).

Fig. 3 shows scatter plots of levoglucosan versus OC and EC for rural samples. Levoglucosan are highly correlated with OC and EC, with R values of 0.96 and 0.87, respectively. These good correlations suggest that biomass burning in rural areas is an important source of organic carbon (Fig. 3a). The values of K^+ are weakly correlated with OC and EC, with R values of 0.66 and 0.62, respectively (Fig. 3c and d). As for other sources of K^+ besides biomass burning, sea salt should be negligible, since Xi'an is an inland city. Thus, crustal material is the most likely additional source of K^+. However, influence of crustal material to K^+ is difficult to estimate.

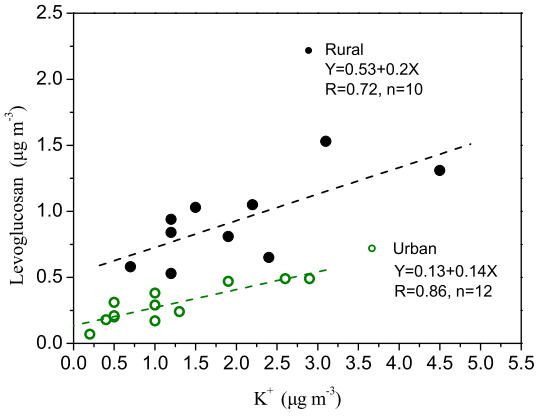

Fig. 2. Correlations between levoglucosan and K^+ for rural and urban site.

3.3. Major sources of biomass burning aerosol

The ratios of levoglucosan to K^+ and levoglucosan to mannosan were used to track possible sources of biomass burning in this study. Fig. 4 shows the plot of levoglucosan to K^+ ratios (Levo./K^+ ratio) and levoglucosan to mannosan ratios (Levo./manno. ratio) of biomass burning aerosols measured in source and ambient samples. The ratios were obtained from studies by Fine et al. (2001, 2002, 2004a, 2004b) for hardwoods; from Fine et al. (2001, 2002, 2004a, 2004b), and Cheng et al. (2013) for softwoods; from Sullivan et al. (2008) for US needle; from Sullivan et al. (2008) for grass; from Sullivan et al. (2008) for US duff; from Sullivan et al. (2008), Sheesley et al. (2003), and Cheng et al. (2013) for Asian crop residue; from Cheng et al. (2013) for wheat straw, corn straw, pine wood, and poplar wood.

The two ratios were used together to obtain new insights on biomass burning source identification. Previous results show that emissions from the combustion of crop residuals such as rice straw, wheat straw and corn straw exhibit comparable levoglucosan to K^+ ratios, typically below 1.0 (Fig. 4, Group I). Higher levoglucosan to K^+ ratios were observed from wood burning and US needle than those for cereal straw (Fig. 4, Group II, IV). The average levoglucosan to mannosan ratios of wheat straw and corn straw were 12.71 ± 1.53 and 19.48 ± 3.37, respectively (Cheng et al., 2013). The ratios of levoglucosan to mannosan for US hardwood, US grass, and cereal straw (Fig. 4, Group I, II) were higher than those of softwood, US needle, poplar wood, and pine wood (Fig. 4, Group IV).

The averages of levoglucosan to K^+ ratios in our study were 0.77 ± 0.39 and 0.32 ± 0.14 for rural and urban samples, respectively, which is comparable to the ratios for corn straw (0.21 ± 0.08) and Asian rice straw (0.62 ± 0.32) (Cheng et al., 2013). These ratios are much lower than those reported for wood. The levoglucosan to mannosan ratios decreased moderately to 7.86 ± 7.13 and 2.83 ± 2.77 for rural and urban samples, respectively, making most of the samples appear in the Group III region (Fig. 4). Therefore, the influence of softwood (poplar wood) and/or other materials from softwood (such as branches and needles) should be larger during winter, although emissions from crop residuals are still expected to be dominant due to the low levoglucosan to K^+ ratios. With a combination of levoglucosan to K^+ ratios and levoglucosan to mannosan ratios, it can be concluded that the major source of biomass burning in Xi'an is the combustion of crop residues and softwood.

Compared with the rural samples, the urban samples were characterized by lower ratios of levoglucosan to K^+ and levoglucosan to mannosan. There are several possible factors responsible

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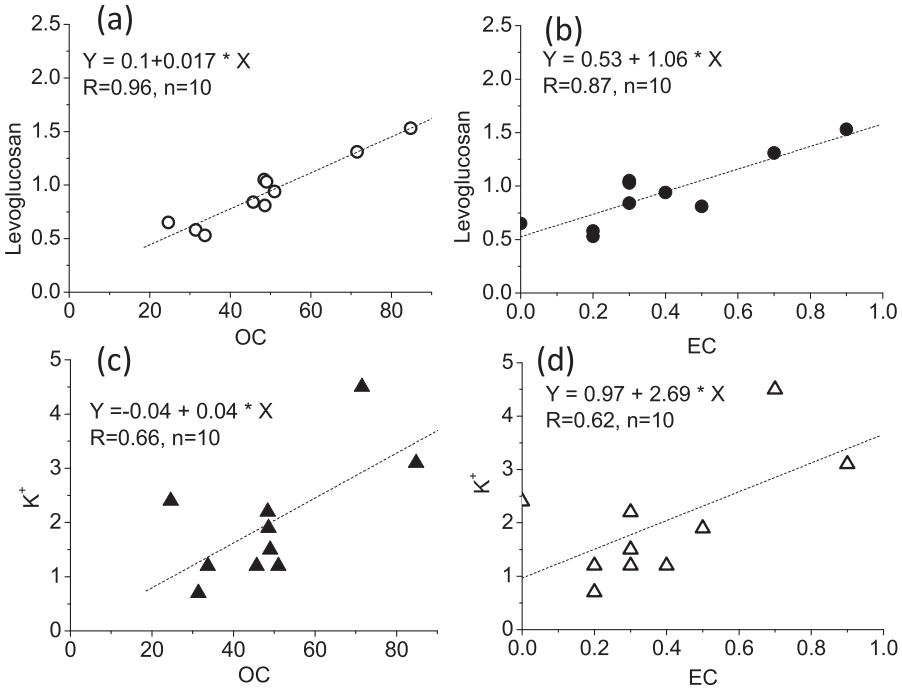

Fig. 3. Correlations between levoglucosan and (a) OC, (b) EC, and those between K^+ and (c) OC, (d) EC at the rural site.

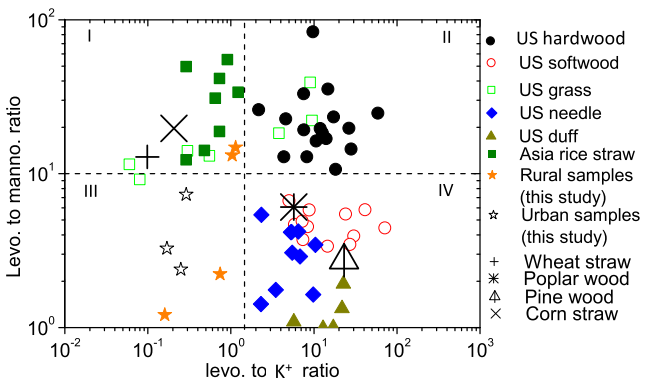

Fig. 4. Levoglucosan to K^+ ratios (Levo. to K^+ ratio) and levoglucosan to mannosan ratios (Levo. to manno. ratio) of biomass burning aerosols measured in source and ambient samples.

for the lower levoglucosan to K^+ ratios for urban samples, such as: (1) enhanced loss of levoglucosan due to atmospheric reactions (Hoffmann et al., 2010; Hennigan et al., 2010) and (2) contribution of K^+ by other sources besides biomass burning in transport. Xi'an is an inland city, crustal material is the most likely additional source of K^+. The previous study reported that the concentration of crustal material was usually higher during winter compared with other seasons in Xi'an (Cao et al., 2012). However, influence of crustal material on the levoglucosan to K^+ ratio is difficult to estimate.

3.4. The contribution of biomass burning to OC

The OC concentrations from biomass burning were estimated by using levoglucosan concentrations and levoglucosan to OC ratios. Zhang et al. (2007) reported an average levoglucosan to OC ratio of 0.082 for the main types of Chinese cereal straw (rice, wheat and corn) based on combustion chamber experiments. The ratio was used to estimate biomass burning contribution to OC in Beijing and Hong Kong (Zhang et al., 2008; Sang et al., 2011). Considering the main biomass types, the value for levoglucosan to OC ratio of 0.082 is used in this study. The conversion factor is comparable to the value of 0.09 from levoglucosan to wood smoke mass (Harrison et al., 2012), but is much lower than the value of 0.14 used to estimate biomass burning OC at background sites in Europe (Puxbaum et al., 2007). A conversion factor of 9.7 is also used to estimate the concentration of PM_{10} from softwood and hardwood in previous study (Maenhaut et al., 2012). Therefore, the biomass burning OC can be inferred as follows:

$$\text{Biomass burning OC} = \text{levoglucosan} \times 12.2 (= 1/0.082)$$

The contributions of biomass burning to $PM_{0.133}$ OC concentrations ranged from 19% to 32%, with an average of 24%, indicating that a large fraction of OC originated from biomass burning in the rural area during the sampling period. The contributions are higher than those of 6.5–11% in Hong Kong (Sang et al., 2011), 16–28% in Hainan (Zhang et al., 2012), and 18–38% in Beijing (Zhang et al., 2008), respectively, while the values are comparable to those of urban $PM_{2.5}$ in winter at Xi'an (Zhang et al., 2014).

4. Conclusions

In the present study, three biomass burning tracers were investigated for rural and urban ultrafine particles. The average levoglucosan concentrations were higher for rural samples (0.93 ± 0.32 μg m^{-3}) than that for urban samples (0.29 ± 0.14 μg m^{-3}). Higher ratio of levoglucosan to K^+ was found for rural samples (0.77 ± 0.39) compared to urban samples (0.32 ± 0.14). The average ratios of levoglucosan to mannosan were 7.86 and 2.83 for rural and urban samples, respectively. The major source of rural biomass burning was the combustion of crop residuals and softwood in winter. The biomass burning contributions to OC range from 19% to 32%, with an average of 24% for rural samples. Further work should be concentrated on rural biomass burning emissions due to a lack of reliable information on the sources and magnitudes in China.

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