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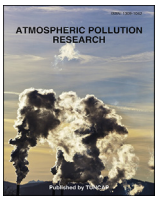

Biomass burning tracers in rural and urban ultrafine particles in Xi'an, China

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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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