Source profiles of particulate organic matters emitted from cereal straw burnings

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Abstract

Cereal straw is one of the most abundant biomass burned in China but its contribution to fine particulates is not adequately understood. In this study, three main kinds of cereal straws were collected from five grain producing areas in China. Fine particulate matters (PM$_{2.5}$) from the cereal straws subjected to control burnings, both under smoldering and flaming status, were sampled by using a custom made dilution chamber and sampling system in the laboratory. Element carbon (EC) and organic carbon (OC) was analyzed. 141 compounds of organic matters were measured by gas chromatography-mass spectrum (GC-MS). Source profiles of particulate organic matters emitted from cereal straw burnings were obtained. The results indicated that organic matters contribute a large fraction in fine particulate matters. Levoglucosan had the highest contributions with averagely 4.5% in mass of fine particulates and can be considered as the tracer of biomass burnings. Methyloxylated phenols from lignin degradation also had high concentrations in PM$_{2.5}$, and contained approximately equal amounts of guaiacyl and syringyl compounds. β-Sitostrol also made up relatively a large fraction of PM$_{2.5}$ compared with the other sterols (0.18%–0.63% of the total fine particle mass). Normal alkanes, PAHs, fatty acids, as well as normal alkanols had relatively lower concentrations compared with the compounds mentioned above. Carbon preference index (CPI) of normal alkanes and alkanoic acids showed characteristics of biogenic fuel burnings. Burning status significantly influenced the formations of EC and PAHs. The differences between the emission profiles of straw and wood combustions were displayed by the fingerprint compounds, which may be used to identify the contributions between wood and straw burnings in source apportionment researches.

Key words: biomass burning; cereal straw; particulate organic matter; source profile

Introduction

As an important kind of primary pollution source, biomass burnings contribute much aerosol particular matters into the atmosphere, thus play significant roles in regional air pollution, and severely affect climate and human health (Charlson *et al.*, 1992; Crutzen and Andreae, 1990; Levine, 1996). Furthermore, pollutants emitted from biomass burnings can transport to a long distance and caused a global influences, even in the polar regions (Dibb *et al.*, 1996; Swap *et al.*, 1996).

There were many kinds of biomass burnings: savanna and forest fires were regarded as two major types of natural biomass burnings and have been discussed by numerous studies (Abas *et al.*, 2004, 1995; Allen and Miguel, 1995; Formenti *et al.*, 2003; Yamasoe *et al.*, 2000). Besides this, anthropogenic biomass burnings, both the

usages of biofuels and waste eliminations, also make up a large fraction of air pollutions. In the United States and Scandinavia in winter, wood fuels were widely used for heating, which could contribute 20%–30% of urban fine particles and even contributed more than 50% under some unfavorable meteorological conditions (Schauer and Cass, 2000; Schauer *et al.*, 1996; Yttri *et al.*, 2005). Differently, for some places lack of forest, especially in the developing counties, agricultural residual were more frequently used for domestic usage. In addition, agricultural residual often combusted in the field for seeding eliminations in some crop producing countries, such as Spain and China (Zarate *et al.*, 2000).

To understand the influences of biomass burnings, receptor-oriented chemical mass balance models were used to apportion the sources contributing to ambient fine particulate matters. In this case, as important input data to the model, source profiles were essential for reliable source apportionment results. Therefore, representative compounds as tracers should be accurately quantified both in the source emissions and in the ambient air (Zheng *et*

al., 2005a). In the previous researches, inorganic species especially water-soluble potassium (K^+) was widely used as tracers to identify the contributions of biomass burnings (Cachier *et al.*, 1995; Chow, 1995; Duan *et al.*, 2004; Zheng *et al.*, 2005b). However, as other anthropogenic sources of K^+ were identified in cities, the application of K^+ as tracer of biomass burning is suspected (Hildemann *et al.*, 1991; Sheffield *et al.*, 1994). Recently, emission characteristics of organic components were studied focusing on many kinds of wood burnings under different combustion conditions or burning status (smoldering and flaming). A series of particulate organic matters (POMs), such as monosaccharide derivatives (e.g. levoglucosan) and methoxylated phenols derived from cellulose, semi-cellulose and lignin were identified and regarded as tracers of biomass burnings for their unique concentrations or fingerprint characteristics. Minor POMs, such as polycyclic aromatic hydrocarbons (PAHs), lipids and terpenoids, can also serve as the fingerprint compounds to distinguish the contributions of different biomass sorts. Effects of these organic compounds were frequently discussed and the technique of source identification using organic components characterized by GC/MS got better used and has been well demonstrated (Cass, 1998; Fine *et al.*, 2002; Mochida and Kawamura, 2004; Rogge *et al.*, 1998; Schauer *et al.*, 2001; Simoneit *et al.*, 1999, 2000a; 2000b, 2003, 2004).

As a developing country, China has a large amount of crop straw yield, up to about 604×10^6 t/a (1997). 45%–47% of the crop straw was burned as energy source in rural regions and about 15% was burned to reduce cereal waste (1995). Crop straw burning may contribute significantly to ambient particle pollutions, but either the amounts of their contributions or the emission characteristics were still very poorly understood till now. In the present work, measurements were taken on the chemical composition of fine particulate matters (PM$_{2.5}$) directly emitted from three primary cereal straw combustions in China (wheat straw, corn straw and rice straw). On the basis of the emission profiles obtained, contributions of cereal straw burnings can separately be identified from the other biomass burnings.

1 Experimental methods

1.1 Sampling

Three kinds of cereal straw were collected from grain producing areas in China (Table 1). These areas account for 81.5×10^6 hm^2, about 78.4% (18.2% for rice, 15.5% for wheat and 15.9% for corn) of all the sown areas of farm crops (2003). Five growing districts were selected from both North China (Beijing, Henan, Hebei) and South China (Sichuan, Zhejiang). At each place, each sample of cereal straw was collected at 15 random sampling points from 3 fields situated far away from strong anthropogenic pollution sources. Approximately 1.5–2 kg straw was collected for each sample and sealed in clean kraft paper bags.

A dilution chamber (Fig.1, Chinese patent number:

Table 1 Collection of cereal straw samples

Biomass type	Sample sites	Moisture content (%)	Combustion type
Wheat	Bejing	11.4	F
Wheat	Hebei	9.2	F
Wheat	Henan	8.5	F, S
Wheat	Sichuan	7.4	F, S
Corn	Hebei	5.3	F, S
Corn	Henan	7.3	F, S
Corn	Zhejiang	9.4	F, S
Corn	Sichuan	7.7	F, S
Rice	Zhejiang	8.1	F, S

F. flaming combustion; S. smoldering combustion.

2004100427465) was designed for simulated combustions of biomass burning in controlled conditions. It consists of four main parts: combustion chamber, dilution tunnel, residence chamber and PM$_{2.5}$ samplers. The combustion chamber was an L-shape stainless steel pipe with an adjustable electric heater placed horizontally inside the pipe at the bottom. Cereal straw was cut into small pieces (about 3–5 cm) and added to the heater gradually. An external voltage of 110 V was applied to burn the straw in smoldering condition, and 220 V in flaming condition. The combustion types of every kind of cereal straw are listed in Table 1. When the fuel burned, the hot smoke flowed through the pipe and got into the dilution tunnel, quickly but completely mixed with the dilution air and cooled down the system. Temperature was monitored and kept under 51°C in the middle of the dilution tunnel. The flow rate of the residence chamber was 48 L/min, and the excessive part was released outdoor through the vent and purge pipe. After a residence time of 96 s in the residence chamber, fine particles (<2.5 μm) were separated in the cyclone separator and flowed down-stream through two four-port flow splitters to get to the PM$_{2.5}$ samplers. The agreement of PM$_{2.5}$ mass loading from the eight samplers was tested to be within 1%. PM$_{2.5}$ samples were collected by 47 mm diameter quartz filters (QM-A, Whatman Co., of all the eight filters for one test, six were pre-baked at 550°C for 4.5 h for measurement of ions, OC/EC and organic analysis, two were for mass analysis). After collection, each filter was sealed in an air-tight petri dish with aluminum liner (pre-baked at 550°C for 4.5 h) and refrigerated under –25°C until analysis was performed.

1.2 Chemical analysis

Filters were weighed by a microbalance (Mettler AE 204) in clean room at 25°C and 50% relative humidity after equalized for at least 48 h before and after sampling. The weight of every filter was taken as the average of three continuous weights if they agree within 60 μg. The organic and element carbon (OC/EC) concentrations were measured using a thermal-optical method, Sunset Laboratory laboratory-based instrument (Sunset Laboratory Inc.) (NOISH, 1996).

Particulate organic matters (POMs) collected on the quartz fiber filters were analyzed using the updated method reported by He *et al.* (2004). The method consists of extraction and GC-MS analysis. The substrates
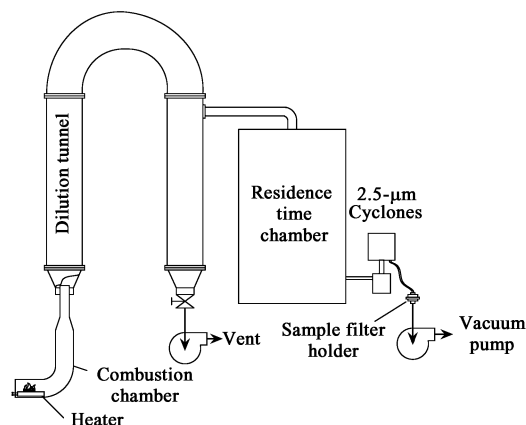
Fig. 1 Combustion instrument and sampler design.

used for organics analysis were spiked with a mixture of 26 deuterated compounds and 2 carbon isotope (^{13}C) substituted compounds (n-pentadecane-d$_{32}$, n-eicosane-d$_{42}$, n-tetracosane-d$_{50}$, n-triacontane-d$_{62}$, n-dotriacontane-d$_{66}$, n-hexatriacontane-d$_{74}$, cholesterol-2,2,3,4,4,6-d$_6$, decanoic acid-d$_{19}$, tetradecanoic acid-d$_{27}$, heptadecanoic acid-d$_{33}$, eicosanoic acid-d$_{39}$, tetracosanoic acid-d$_{47}$, phthalic acid-d$_4$, octanedioic acid-d$_4$, succinic acid-d$_4$, acenaphthene-d$_{10}$, pyrene-d$_{10}$, benz[a]anthracene-d$_{12}$, coronene-d$_{12}$, cholestane-d$_4$, anthracene-d$_{10}$, perylene-d$_{12}$, phenol-d$_5$, benzaldehyde-d$_6$, benzoic acid-d$_5$, hexanoic acid-d$_{11}$, galactosan-^{13}C and vanillin-^{13}C ring), then extracted three times with 30 ml dichloromethane/methanol (3:1, v/v) in thick wall sealed bottles (pre-baked at 550°C for 4.5 h) using an mild ultrasonic bath maintained at room temperature. The extracts were pooled and then reduced to about 5 ml using a rotary vacuum evaporator. Then, the extract was concentrated to 1 ml by mild nitrogen (ultra purified, >99.9%) blowing and was split into two fractions. One of the fractions was derivatized with BSTFA (BSTFA/TMCS, 99:1, Supelco) to substitute the active hydrogen with trimethylsilanized derivant. Both of the derivatized and underivatized fractions were analyzed using an Agilent GC-MS (6890-5973N) equipped with a DB-5MS column (60 meters length, 0.25 mm diameter, 0.25 μm film thickness, Agilent) and oven temperature

programming (60°C for 10 min to 300°C for 38 min at 6°C/min). Multipoint calibrations were conducted using authentic standards spiked with the same final concentrations of internal standards as used in the samples. The quantification standards included sugars, methoxylated phenols, polycyclic aromatic hydrocarbons (PAHs), n-alkanes, n-alkanols, sterols, and so on.

Laboratory blanks (performed same as the POM analysis processes with a blank filter) were added into the analytical batches to evaluate the possible contamination in analysis processes. In this study, laboratory blanks measurement in organic analyses produced results that only n-octadecanol and n-eicosanol were detected from one of six blanks at a very low concentration level (totally less than 0.18 ng on the filter), thus they could be ignored in organic analysis. Spiked filters were analyzed to determine the overall efficiency and accuracy of the measurements. Average recoveries and deviations of the spike samples were 67.9%–103.3% and 5.1%–16.3%, respectively, which met the accuracy requirement of this study. The coefficients of correlation (R^2) of standard compounds calibration curves were 0.990±0.017. The target compounds were not quantified if the single to noise ratio (peak area) was less than 10. Method detection limit of the target compounds in this study was 0.1–4 ng/μl (1 μl splitless injection of total 1 ml extractions).

2 Results and discussion

OC, EC and totally 12 class organic compounds in PM$_{2.5}$ were measured. The concentrations of individual organic compounds in fine particulates are listed in Table 2.

2.1 OC/EC and bulk chemical compositions

Generally, smoke emitted from biomass burnings was characterized by high concentration of organic carbon (OC). In this study, the percentage of OC for different cereal straws in different burning status ranged from 0.438 to 0.619 mg/mg PM$_{2.5}$, averagely 0.546±0.060 mg/mg PM$_{2.5}$. Element carbon (EC) is a byproduct of incomplete combustion of OC (Chu, 2005), usually formed under conditions in which insufficient oxygen is present for

Table 2 Mass fractions of organic compounds in fine particles from cereal straw burnings (Units: ng/mg of PM$_{2.5}$)

Compound	Conc. in PM$_{2.5}$	Compound	Conc. in PM$_{2.5}$	Compound	Conc. in PM$_{2.5}$
n-Alkanes					
n-Hexadecane	128.0±112.0	n-Heptadecane	13.7±16.1	n-Octacosane	20.2±15.2
n-Octadecane	9.8±8.3	n-Nonadecane	17.3±7.7	n-Triacontane	19.4±18.7
n-Eicosane	23.0±13.8	n-Heneicosane	31.9±11.1	n-Dotriacontane	7.8±11.2
n-Docosane	39.3±15.0	n-Tricosane	31.7±12.3	n-Nonacosane	492.3±607.0
n-Heptacosane	124.1±125.1	n-Tritriacontane	79.1±50.2	n-Tetracosane	24.1±11.0
n-Pentacosane	29.6±17.2	n-Hentriacontane	441.3±492.8	n-Hexacosane	16.6±9.0
Total class	1549.2±1289.3				
n-Alkanols					
n-Tetradecanol	5.6±1.5	n-Pentadecanol	4.3±1.8	n-Octacosanol	1696.7±2569.7
n-Hexadecanol	6.1±2.1	n-Heptadecanol	1.9±1.2	n-Triacontanol	724.9±1021.1
n-Octadecanol	16.8±6.6	n-Nonadecanol	3.2±1.8	n-Pentacosanol	11.1±8.6
n-Eicosanol	56.6±31.8	n-Henicosanol	6.9±3.6	n-Heptacosanol	21.5±26.4
n-Docosanol	58.5±27.0	n-Tricosanol	9.5±4.7	n-Nonacosanol	20.4±13.6
Tetracosanol	176.9±172.8	n-Hexacosanol	189.9±236.7		
Total class	3010.8±2773.2				

Table 2 (Continued)

Compound	Conc. in PM$_{2.5}$	Compound	Conc. in PM$_{2.5}$	Compound	Conc. in PM$_{2.5}$
***n*-Alkanoic acids**					
n-Hexanoic acid	95.5±29.1	*n*-Heptanoic acid	58.4±39.6	*n*-Tetracosanoic acid	633.8±405.5
n-Octanoic acid	37.8±15.1	*n*-Nonanoic acid	31.7±6.2	*n*-Hexacosanoic acid	141.6±80.7
n-Decanoic acid	10.9±18.1	*n*-Undecanoic acid	5.7±6.9	*n*-Octacosanoic acid	333.1±273.7
n-Dodecanoic acid	89.2±45.7	*n*-Tridecanoic acid	4.6±4.9	*n*-Triacontanoic acid	371.8±294.0
n-Tetradecanoic acid	185.4±85.3	*n*-Pentadecanoic acid	86.0±46.6	*n*-Tricosanoic acid	249.8±144.5
n-Hexadecanoic acid	3782.8±1802.6	*n*-Heptadecanoic acid	84.5±41.8	*n*-Pentacosanoic acid	55.6±36.8
n-Octadecanoic acid	1052.3±878.3	*n*-Nonadecanoic acid	37.3±27.6	*n*-Heptacosanoic acid	7.1±4.5
n-Eicosanoic acid	309.9±167.0	*n*-Henicosanoic acid	29.9±16.7	*n*-Nonacosanoic acid	8.3±10.7
n-Docosanoic acid	399.8±112.7				
Total class	8102.7±2397.1				
Unsaturated fatty acids					
Palmitoleic acid	171.6±163.9	Oleic acid	1703.9±1964.9	Linolenic acid	207.5±141.5
Linoleic acid	1202.3±733.6				
Total class	3285.3±2748.7				
Dicarboxylic acids					
Succinic	572.2±181.9	Fumaric	76.1±30.5	Azelaic	78.4±51.0
Maleic	12.8±5.6	Glutaric	481.4±142.5	Sebacic	0.9±2.3
Pimelic	3.8±9.2				
Total class	1225.5±380.9				
Glycerides					
Monopalmitin	350.1±222.7	Monostearin	82.9±61.7	Monoolein	129.6±159.5
Total class	562.6±408.7				
Aeromatic acids					
Benzoic acid	169.7±71.9	Isophthalic acid	13.9±29.8	Phthalic acid	135.7±60.0
Methylphthalic acid	9.8±23.9	1,2,4-Benzene- tricaboxylic acid	0.4±1.0	Terephthalic acid	10.6±26.0
Total class	340.1±130.9				
PAHs					
1-Methylnaphthalene	0.6±1.5	Chrysene	12.2±17.3	Benzo[e]pyrene	6.9±10.8
1-Methyl pyrene	4.7±5.5	Coronene	1.9±4.7	Benzo[ghi]flouranthene	9.1±14.9
2-Methylnaphthalene	0.6±1.1	Cyclopenta[cd]pyrene	16.5±28.8	Benzo[ghi]perylene	6.5±10.9
2-Methylphenanthrene	15.3±4.0	Dibenzofuran	0.3±0.1	Benzo[k]fluoranthene	4.3±7.9
9-Methylanthracene	0.3±0.6	Fluoranthene	27.9±28.4	*n*-Dodecylbenzene	0.7±0.8
Acenaphthylene	5.5±3.6	Fluorene	0.7±1.7	Perylene	1.4±3.5
Acenaphthene	1.7±0.9	Indeno[1,2,3-cd]pyrene	7.2±12.2	Phenanthrene	40.7±19.2
Anthracene	12.4±4.0	2,6-Dimethylnaphthalene	0.4±0.6	Picene	0.0±0.0
Benzo[a]anthracene	10.8±16.0	Methyl-chrysene	0.9±1.8	Pyrene	27.4±32.2
Benzo[a]pyrene	13.5±21.9	Methyl-fluorene	19.5±6.7	Retene	1.5±2.8
Benzo[b]fluoranthene	13.0±22.5	Napthalene	5.1±2.3		
Total class	269.6±228.1				
Sugars					
Galactosan	51.1±61.4	Mannosan	812.1±341.4	Levoglucosan	45196.6± 13671.2
Total class	46059.8±13746.9				
Sterols					
Campesterol	1876.1±1217.2	Stigmasterol	1831.6±1455.7	β-Sitosterol	3271.4± 1754.0
Cholesterol	50.5±31.4	Stigmastenol	48.7±23.5		
Total class	7078.3±2910.4				
Methyloxylated phenols					
2-Methoxymethylphenol	118.1±104.8	iso-Eugenol[G]	30428.2±26416.7	Propylguaiacol[G]	67.9±92.1
3,5-Dimethoxyphenol	36.3±48.6	Methyl vanillate[G]	72.6±28.7	Homovanillic acid[G]	122.2±45.7
4-Hydroxy-3-methoxycin- namaldehyde[G]	16123.0±21302.8	Vanillic acid[G]	413.5±107.3	3,5-Dimethoxy-4-hydro- xyacetophenone[S]	2758.5± 951.5
Eugenol[G]	135.6±115.9	Vanillin[G]	1690.2±394.0	3,5-Dimethoxy-4-hydro- xycinnamaldehyde[S]	30416.7± 40106.3
Guaiacol[G]	76.7±110.8	Acetovanillone[G]	1216.8±397.3	Syringaldehyde[S]	3440.4± 1690.2
Ethylguaiacol[G]	146.7±143.4				
Total class	87263.3±87142.9				
Other Compounds					
Catechol	11139.6±3461.1	Pentadecylcyclohexane	2.3±4.3	Pristane	10.6±13.3
Phytane	1.2±1.9	Quinoline	8.3±9.5		
Total class	11162.1±3458.5				
OC (mg/mg PM$_{2.5}$)	0.546±0.060				
EC (mg/mg PM$_{2.5}$)	0.071±0.029				
Resolved organic matter (mg/mg PM$_{2.5}$)	0.168±0.094				

Concentration±standard deviation; *n*=6.

complete oxidation of carbonaceous fuel to CO_2 (fuel-rich) (Bond *et al.*, 2004). Since primary OC and EC were mostly emitted from the same combustion sources, the percentage of EC usually used to distinguish different combusting status and estimate the amounts of primary and secondary (Chu, 2005). In this study, the percentage of EC in fine particulates ranged from 4.7% to 11.6%. For the flaming and smoldering status, $EC/PM_{2.5}$ ratios were 0.058–0.116 and 0.047–0.053, respectively. A larger $EC/PM_{2.5}$ ratio at flaming combustions may be due to the fact that higher temperature of flaming has caused much more conversion of organic substances into EC.

Totally 141 organic compounds were quantified and classified into 12 classes. The total percentages of organic matters quantified were relatively small in Fig.2. The total fine particulates, which were ranging from 8.0% to 33.7%, mostly in 8%–13%. For every type of combustions, the dominant compositions were methyloxylated phenols and sugars, which consist 8.7% and 4.6% of fine particulates, respectively. Sterols, catechols and fatty acids were the secondary abundant compounds and averagely consist 0.7%–1.1% of total fine particulates. Moreover, other trace amount organic compound classes, such as PAHs, dicarboxylic acids and *n*-alkanols can also be identified from the fine particulates.

2.1.1 Sugars

In this study, three sugars, levoglucosan, galactosan and mannosan, were quantitatively analyzed. Among which levoglucosan had the highest concentrations (29787.2–64675.9 ng/mg $PM_{2.5}$, averagely 4.5% of fine particulates) in all the tests, followed with mannosan and galactosan. Sugars were generated from the pyrolysis of cellulose and hemicellulose, and often used as tracer compounds to identify the emission of biomass burnings. Levoglucosan

Fig. 2 Bulk chemical compositions of POMs from cereal straw burnings. F: flaming combustion; S: smoldering.

was reported in previous studies as an important tracer in tracking wood smoke in the atmosphere because of its high emission rate and uniqueness to wood combustions (Simoneit *et al.*, 1999). According to the literature, for wood burning in the fireplaces, levoglucosan is the most dominant compounds whose concentration in $PM_{2.5}$ ranged from 7.13% to 22.8% (Fine *et al.*, 2001; Schauer *et al.*, 2001), a little higher to the results of this study. These characteristics mean that levoglucosan could be the tracer compound to separate biomass burnings from other sources, but could not identify different biomass combustion sources from each other. Detailed fingerprint tracers should be measured to get comprehensive information to identify different biomass burnings. Galactosan and mannosan were isomers of levoglucosan, generated in a similar pyrolysis process with average concentrations of 51.1 and 812.1 ng/mg $PM_{2.5}$, respectively. The different concentrations of these three sugars attributed to not only the differences of cellulose and semicellulose portions of biomass fuels, but also the humidity, burning temperatures and the pyrolysis processes.

2.1.2 Methyloxylated phenols

Methyloxylated phenols were regarded as the thermal products of lignin pyrolysis during the combustion processes. Lignin is an irregular polymer of variously bonded hydroxy- and methoxy-substituted phenylpropane units. Lignin was mainly composed of three sorts of compounds: syringyl compounds, guaiacyl compounds and *p*-hydroxyphenylpropane, as well as their substitutes. Percentages of these three sorts of compounds differed from different biomass species. Softwood contains predominantly guaiacyl-type lignins and hardwood possesses a mixture of guaiacyl- and syringyl-type lignins, while most cereal straw lignins have significant amounts of *p*-hydroxyphenylpropane nuclei in addition to syringyl and guaiayl units. For wheat straws and rice straws, the proportions of syringyl- and guaiacyl-type lignins were roughly the same (Hu, 2002). Upon combustion, the lignin biopolymer emits breakdown products that include aromatic phenols, aldehydes, ketones, acids, and alcohols. According to the structures of emitted phenols and their substitutes, their chemical characteristics were related to the lignin of the biomass (Rogge *et al.*, 1998).

In this study, 16 methyloxylated phenols were measured (Table 2), including 11 guaiacyl- and 3 syringyl-type compounds (marked with G and S in Table 2, respectively). Among all the methyloxylated phenols, 4-hydroxy-3-methoxycinnamaldehyde, iso-eugenol and 3,5-dimethoxy-4-hydroxycinnamaldehyde had the dominant concentrations, which were 16123.0, 30428.2 and 30416.7 ng/mg $PM_{2.5}$, respectively. Fig.3 shows the concentrations of methyloxylated phenols in the fine particulates under different burning status. As can be seen from Fig.3, amounts of guaiacyl and syringyl compounds were approximately the same under each burning status except corn and rice straw in smoldering combustions. This may be caused of that some compounds belong to the guaiacyl or syringyl classes were not quantified and added into the compound
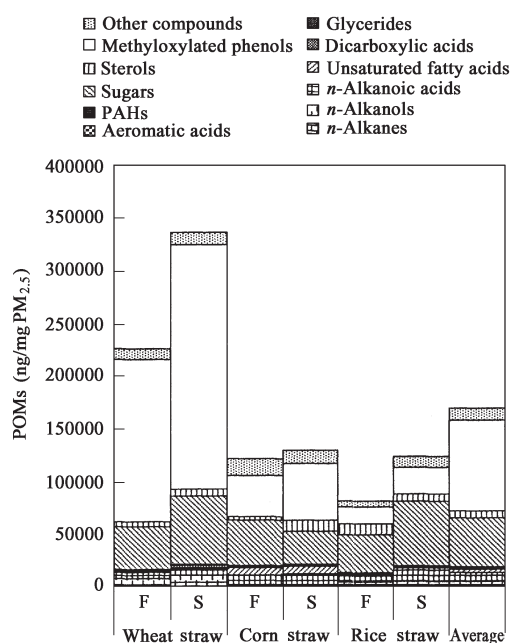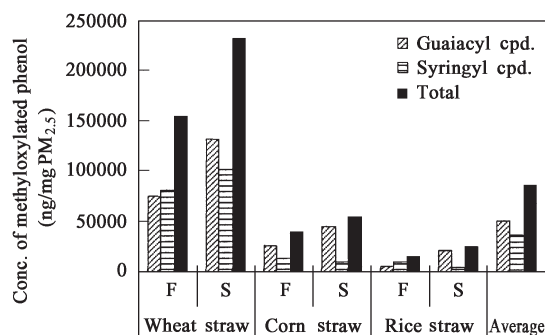
Fig. 3 Concentrations of methyloxylated phenols in the fine particulates. F: flaming combustion; S: smoldering.

listed in Table 2. Comparing between flaming and smoldering status, total concentration of methyloxylated phenols always have higher values in smoldering combustions than that in flaming combustions, which demonstrated that the combustion temperature was an important parameter in the lignin degradations.

2.1.3 Sterols

Totally 5 sterols were detected in this study include campesterol, cholesterol, β-sitosterol, stigmasterol and stigmastenol. The results are shown in Fig.4. Among all the sterols detected, campesterol, stigmasterol and β-sitostrol had relatively high concentrations compared with the other sterols, which were ranged from 1830.1 to 6321.0 ng/mg $PM_{2.5}$ (0.18%–0.63% of the total fine particle mass). Contrastively, cholesterol had the lowest concentration less than 100 ng/mg $PM_{2.5}$. The differences were related to the compositions of cereal straws. Sterols in POMs were from the inherent sterols of biomass themselves. Campesterol, stigmasterol and β-sitostrol had vegetable origins. They were usually present in higher plant. Cholesterol was from alga and animal tissues, biosynthesized by higher animals and was found in all body tissues, especially in animal fats and oils (Rogge *et al.*, 1991). During the burning process, sterols evaporated and condensed on the surface of the particles, therefore, the characteristics of sterols in POMs and in biomass fuels were alike. In contrast, animality sterols, such as cholesterol was highly detected in the sources related to animality tissues, such as emissions from charbroilers and meat cooking operations (Rogge *et al.*, 1991).
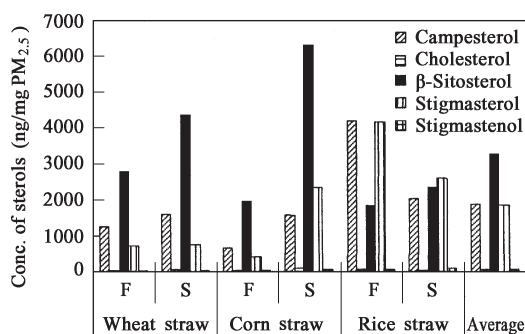

Fig. 4 Concentrations of sterols in the fine particulates. F: flaming combustion; S: smoldering combustion.

It should be pointed out that although β-sitostrol often had a relatively high concentrations in biomass burning emissions, it can be detected as the highest sterols in Chinese cooking emissions (He *et al.*, 2004). In this case, ratios between different sterols, but not just sterols themselves, may more suitable to be used to distinguish different emission sources.

2.1.4 *n*-Alkanes

Normal alkanes from C16 to C33 were measured in this study. Their concentrations are shown in Fig.5.

Normal alkanes had relatively lower concentrations among the organic species of the fine particulates, ranged from 0.4%–1.6% of $PM_{2.5}$. The maximum concentration species (C_{max}) were C29 and C31 with average concentrations of 492.3 and 441.3 ng/mg $PM_{2.5}$, respectively, and approximately 60% of the total alkane masses. Comparing with the analysis of the vegetable tissues, whose C_{max} were C29, C31 or C33 (Simoneit *et al.*, 1977), alkanes may come from the evaporation and condensation of alkanes in the cereal straws. Carbon preference index (CPI) was defined as the ratio of total masses of *n*-alkanes with odd carbon numbers to that with even carbon numbers. CPI could be used to distinguish the natural and fossil emissions. When CPI approximately equal to 1.0, that means fossil fuel combustion emissions was dominant (Rogge *et al.*, 1993a). In this study, the ratio ranged from 2.8 to 22.6, which were the prominent characteristics of biogenic fuel burnings.

2.1.5 PAHs

Polycyclic aromatic hydrocarbons (PAHs) can be formed by anthropogenic processes or be derived from natural sources. The mechanisms of PAHs formation during combustion processes of organic matters were not fully understood. It was reported that transformation of PAHs was related to free radical reactions, high temperature could generate more free radicals that increased the productivity of PAHs (Simoneit, 2002). In this study, totally 32 PAHs were measured and the yields of every burning types are shown in Fig.6. It can be seen that the total concentrations of PAHs under the flaming status were larger than that under the smoldering. Rice straw burning had the largest
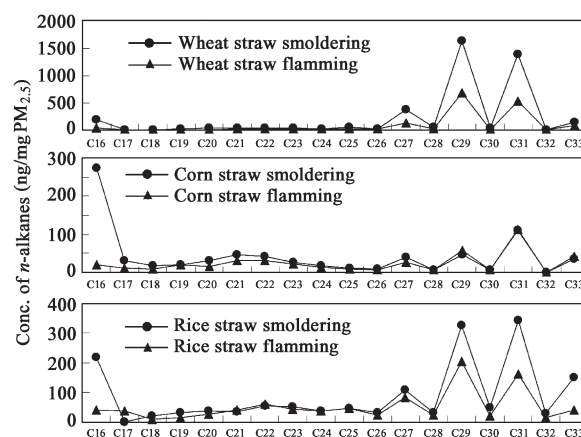

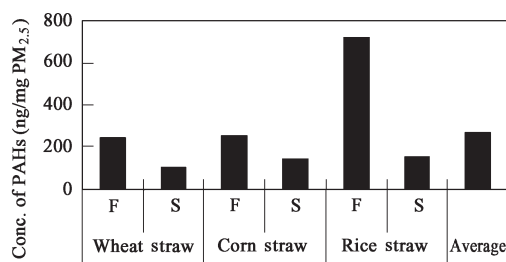Fig. 5 Concentrations of *n*-alkanes in the fine particulates.

Fig. 6 Concentrations of PAHs in the fine particulates. F: flaming combustion; S: smoldering combustion.

deviation between smoldering and flaming combustions. The total concentrations of PAHs were 719.6 and 154.8 ng/mg $PM_{2.5}$ under flaming and smoldering, respectively. Flaming combustions between wheat straw and corn straw had similar concentrations of 243.2 and 253.0 ng/mg $PM_{2.5}$. Among all the PAHs species, phenanthrene had the highest concentrations (averagely 40.7 ng/mg $PM_{2.5}$), secondary fluoranthene (averagely 27.9 ng/mg $PM_{2.5}$), followed by pyrene (averagely 27.4 ng/mg $PM_{2.5}$), and methyl-fluorene (averagely 19.5 ng/mg $PM_{2.5}$) (Table 2). Compared with the data of wood burnings from previous literature, similar tendency could be found for the PAHs distributions (Rogge et al., 1998; Schauer et al., 2001).

2.1.6 Fatty acids and dicarboxylic acids

In the previous researches, fatty acid can be detected in almost all the emission sources in various concentration levels (He et al., 2004; Rogge et al., 1994; Rogge et al., 1993a, 1993b, 1991; Schauer et al., 2001). In cooking emissions, fatty acids had the highest concentrations among all the organic matters (He et al., 2004). In this study, n-alkanoic acids from F6 to F30 were measured for different straw burning status and get similar results for each. n-Hexadecanoic acid and n-octadecanoic acid had the first and second high concentrations in the fine particulates which were 3782.8 and 1052.3 ng/mg $PM_{2.5}$, respectively. Even carbon predominance can be seen from Table 2 and Fig.7. The CPI even calculated from F6 to F30 was 11.3. Unsaturated fatty acids, include palmitoleic

acid (C16:1), oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3) were measured in this study. The concentrations of oleic acid (averagely 1703.9 ng/mg $PM_{2.5}$) were in the middle of n-hexadecanoic acid and n-octadecanoic acid. Dicarboxylic acids come from the oxidation of dialdehydes during the autoxidation process of unsaturated lipids (Rogge et al., 1991). In this study, 7 dicarboxylic acids were measured. The concentrations were very low compared with the fatty acids. Succinic acid and glutaric acid were the dominant species with concentrations of 572.2 and 481.4 ng/mg $PM_{2.5}$, respectively.

2.1.7 Other organic compounds

Catechol was abundantly detected in this study whose concentration ranged from 5438.1 to 11284.5 ng/mg $PM_{2.5}$. Catechol was generated from the process of lignin pyrolysis and can be detected in cigarette smoke (Rogge et al., 1994). As discussed in the above sections, concentrations of lignin pyrolysis products associated with the chemical components of the biomass, thus catechol can be a candidate tracer compound for the relatively high concentrations quantified.

The other quantified organic compounds such as normal alkanols, glycerides and quinoline etc. were measured and had relatively low concentrations in the fine particulates. The contributions of these compounds of cereal straw burnings to the ambient aerosols could be evaluated while further researches completed.

2.2 Comparison with wood combustion emissions

On the basis of the extraction-GC/MS analysis method, particulate organic matters from wood combustions have been adequately studied by many researchers for their considerable contributions to the ambient atmosphere (Nolte et al., 2001; Oros and Simoneit, 2001a, 2001b; Rogge et al., 1998; Schauer et al., 2001). In many reports, source profiles of wood burnings were frequently used to apportion the source contributions as of biomass burnings (Schauer and Cass, 2000; Zheng et al., 2005a). Compared with the profiles reported in the published literature, similar characteristics can be found. Sugars (mostly levoglucosan) and substituted phenols make up much larger fractions of the fine particle mass emitted from wood combustions. The portion of levoglucosan in the fine particulate matters ranged from 7.13% to 22.8% (Fine et al., 2001; Schauer et al., 2001). In the present study, we measured the percentage of levoglucosan in fine particulate matters was approximately 2.9%–6.5%. Bias of these values may because of the consisted ratio of cellulous and hamicellulose, also the burning status. As for the percentages of methyloxylated phenols, combustions of different woods gave different results. In the studies of different wood burnings, these differences in guaiacols versus substituted syringol emission rates were due to fundamental differences in the chemical composition of conifers and deciduous trees, as explained by Simoneit et al. (1993), and can be used to distinguish hardwood smoke from softwood smoke in the atmosphere. To better understand the differences, 5 methyloxylated phenols were
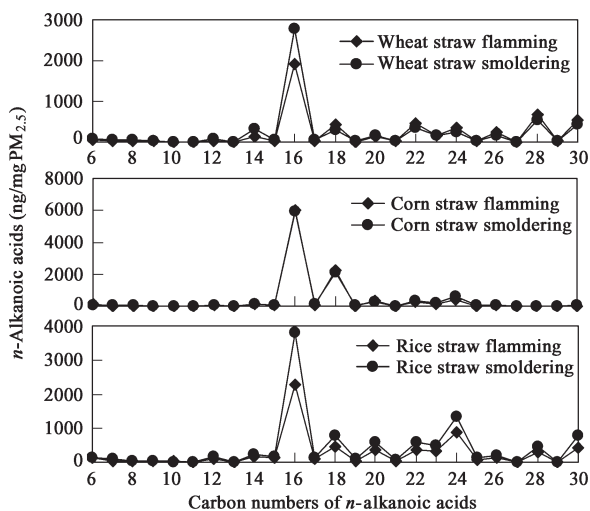

Fig. 7 Concentrations of n-alkanoic acids in the fine particulates.

Table 3 Ratio of selected syringyl-compounds to guaiacyl-compounds

Fuel	Burning status	S/G	Fuel	Burning status	S/G
Wheat straw	Flaming	0.16	Rice straw	Smoldering	0.06
Wheat straw	Smoldering	0.06	Pine wood[a]		0.00
Corn straw	Flaming	0.17	Oak wood[a]		6.43
Corn straw	Smoldering	0.07	Eucelptus wood[a]		19.41
Rice straw	Flaming	0.91			

[a]Schauer *et al.*, 2001

selected for they were all quantitatively detected in wood combustion study by Schauer *et al.* (2001) as well as in this study. They were guaiacol, iso-eugenol, vanillin, acetovanillone and syringaldehyde. The former 4 compounds were guaiacyl-phenols and the last was syringyl-phenol. The ratio of syringyl- to guaiacyl-compounds are listed in Table 3. The differences among hardwood, softwood and cereal straw combustions were obviously. In the presence of the data of this study, cereal straw burnings could be identified from wood combustions due to the fingerprint compounds of phenols.

Resin acids, such as abietic acid, dehydroabietic acid, pimaric acid and iso-pimaric acid, can be detected in the pine wood burnings. Even in other sorts of wood combustions, some special resin acids such as dehydroabietic acid can be detected in different concentration levels related to the chemical characteristics of fuel wood themselves (Schauer *et al.*, 2001). Contrastively, no resin acids were detected in the cereal straw burning in the present study. In this case, resin acids can be used as tracers to identify the emissions of hardwood and soft wood combustions, as well as cereal straw burnings and wood burnings.

Other compounds identified from wood combustions such as sterols and alkanes had the similar characteristics with that of cereal straw burnings, differed from other emission sources such as cigarette smoke and Chinese cooking emissions concerned above. Therefore, these compounds or characteristics could be regarded as the common tracers of all sorts of biomass burnings. Phenols could be valuable potential candidate tracers in the source apportionments.

3 Conclusions

As one of the most important biomass burning styles in China, cereal straw burning was widely performed for energy use or agricultural waste eliminations, and injects airborne particulate emissions into the atmospheric environment. In this study, combustions of three important cereal straws in China were simulated in the laboratory in smoldering and flaming burning status. Fine particulate matters ($PM_{2.5}$) emitted from the combustions were sampled. Mass, organic carbon, element carbon and individual extractive organic compounds were measured. Emission profiles of fine particulate organic matters of cereal straw burnings were obtained. The results show that in emitted fine particulates, organic carbon were averagely $(54.6\pm6.0)\%$, and for EC the values were 5.8%–11.6% and 4.7%–5.3% under flaming and smoldering status, respectively. Totally 141 organic compounds were quantified,

among which sugars and methyloxylated phenols were the predominant species. Levoglucosan had the highest concentrations (averagely 4.5% of fine particulates) in all the tests and can be the tracer of biomass burnings. Amounts of guaiacyl and syringyl compounds detected were approximately the same in most tests in this study. Compared with the wood combustions, the differences between syringyl and guaiacyl can be used to identify wood burning and straw burning. β-Sitostrol had relatively high concentrations compared with the other sterols ranged from 1830.1 to 6321.0 ng/mg $PM_{2.5}$. Normal alkanes show obvious odd carbon predominance, consists 0.4%–1.6% of $PM_{2.5}$. Concentrations of PAHs in fine particulates were related to the burning status, which were 719.6 and 154.8 ng/mg $PM_{2.5}$ for flaming and smoldering, respectively. The other compounds such as fatty acids and normal alkanols had relatively lower concentrations compared with the compounds mentioned above.

Compared with the source profiles of wood burnings, the main components of particulate organic matters from cereal straw burnings were alike, nevertheless the ratios of fingerprint organic compound species had big differences. These differences can provide information to apportion the contributions of wood and straw combustion sources. In this case, more organic compound species should be measured accurately to fit the requirements of precise source apportionments.

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