



Source Profiles of Volatile Organic Compounds from Biomass Burning in Yangtze River Delta, China

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ABSTRACT

The volatile organic compounds (VOCs) associated with biomass burning were characterized in the Yangtze River Delta of China, including two types of burning conditions (stove burning and field burning) and five typical kinds of biomass (straws of rice, wheat, bean and rape, and wood). According to the results, the VOC emission factors of straw burning ranged from 2.08 g/kg to 6.99 g/kg with an average of (4.89 ± 1.70) g/kg, compared to 0.98 g/kg for wood burning. Some differences in VOC composition were observed with the burning of different biomasses. Oxygenated VOC (o-VOC) were the largest contributors to the mass concentration of measured VOCs from straw burning, with a proportion of 49.4%, followed by alkenes 21.4%, aromatics 13.5%, alkanes 10.6% and halogenated VOC (x-VOC) 5.0%. More aromatics and x-VOC were emitted from wood burning compared with straw burning. Field burning emitted more o-VOC due to more air being supplied during the burning test compared with stove burning. Further examination of the detailed VOC species showed the most abundant VOC species from biomass burning were o-VOC, C₂–C₃ alkenes and C₆–C₇ aromatics. The ozone formation potential (OFP) of VOCs from straw burning was in the range of 13.92–33.24 g/kg, which was much higher than that of wood burning (4.30 g/kg). Alkenes and o-VOC were the largest contributors to OFP of VOCs from biomass burning. The top five contributors of OFP were ethene, n-hexanal, propylene, acetaldehyde and methyl vinyl ketone, the sum of which accounted for 77% of total OFP. The ratio of ethylbenzene to m,p-xylenes from biomass burning was significantly higher than those from other VOC sources, and thus this could be seen as the fingerprint of biomass burning.

Keywords: Biomass burning; Volatile organic compounds; Emission factor; Source profile; Yangtze River Delta.

INTRODUCTION

Biomass was widely used as a biofuel in the rural of China. It was reported that more than 550 million tons of biomass was burned in China in year of 2005 (National Bureau of Statistics, 2006). Biomass burning is known as a significant source of gaseous and particulate pollutants to the atmosphere, which causes serious local and regional air pollution (Levine *et al.*, 1995; Andreae *et al.*, 2005; Koppmann *et al.*, 2005; Bo *et al.*, 2008; Li *et al.*, 2008; Wei *et al.*, 2008; Zhang *et al.*, 2011). Moreover, some of the emissions with hazardous pollutants have adverse impacts on human health (Johnson *et al.*, 2005).

Compared with some other emission sources, emissions from biomass burning presented significant variations among different seasons. Taking the Yangtze River Delta (YRD) as an example, Huang *et al.* (2011) reported that the volatile organic compounds (VOCs) emission amount from biomass burning accounted for ~3.5% of total VOCs in YRD. Though it did not play a significant role on an annual scale, biomass burning mostly occurred in the harvest season (i.e., in June and October) and usually caused serious regional air pollution (Li *et al.*, 2009a). However, it still had some uncertainties in estimating the VOC emission from biomass burning due to the lack of local emission factors and source profiles of VOCs (Huang *et al.*, 2011). Wang *et al.* (2009) and her group studied the characterization of VOCs from typical biomass burning in northern China (Li *et al.*, 2007; Li *et al.*, 2009b; Li *et al.*, 2011). As reported in these studies, VOC emission factors of biomass burning ranged over two orders of magnitude, which were affected by the ambient temperature and the types of the biomass (Wang *et al.*, 2009).

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The YRD region locates in the southeast of China, and the meteorological conditions and the types of biomass are different from those in northern China (National Bureau of Statistics, 2006). Furthermore, Jiangsu and Anhui, two large provinces in YRD, are both among the top five provinces which have abundant biomass burning (Li *et al.*, 2009b). However, there have been few reports about the characterization of VOCs from biomass burning in YRD. It is necessary to get better understanding on the emission characteristics of VOCs from local biomass burning in YRD. In this study, two types of burning tests, namely field burning and stove burning, were conducted to study the characterization of VOCs from typical biomass burning in YRD, as discussed in section *Emission factors and Source profiles*. The ozone formation potential (OFP) of VOCs from biomass burning was estimated in section *The OFP of VOCs from biomass burning*. The characterization of VOCs from biomass burning in different studies was compared in section *Comparison with other studies*. In section *Comparison with other VOC sources*, the characterization of VOCs from biomass burning was compared with those from other VOC sources and the potential fingerprint of biomass burning was identified. The uncertainty of VOC characterization from biomass burning was discussed in section *Uncertainty analysis*.

EXPERIMENTS AND MATERIALS

Biomass Burning Tests and Sampling

A burning chamber was employed to simulate the field biomass burning, which included a smoke collecting unit, a smoke aging unit, and a sampling unit, as shown in Fig. 1 (left). The pre-weighted biomass was directly burnt on the farmland, and the flue gas was drawn into the collecting unit by the ventilator settled at the end of the burning chamber. Notably, the flow of the ventilator might influence the normal burning if the air velocity at the chamber inlet was larger than the indoor air velocity, namely as 0.25 m/s (Guo, 2011). Thus, the chamber inlet should be large enough. In

this study, the air velocity at the chamber inlet was designed as about 0.12 m/s. The weather was windless (< 2 m/s) with the temperature of about 25–30°C during the field test, which has limited impact on the burning process.

After short aging process, the flue gas was sampled into the dilution system (Dekati Fine Particle Sampling (FPS) 4000) by an isokinetic sampling inlet in the sampling unit. The dilution rate was set ~ 15 , and under this condition the temperature of flue gas could be decreased to the ambient temperature and no condensed water could be observed. A gas sampler was connected to the dilution system. The flue gas from the dilution system went through a Teflon filter to remove the particles, and then was pumped into a clean and vacuumed Teflon bag (20 L) by a membrane pump at controlled flow rates (10–100 L/h). PFA tubes were used to connect each part as its low adsorption. After sampling was completed, a portion of the flue gas was immediately transferred from the Teflon sample bag to a 6-L stainless steel, vacuumed SUMMA canisters (Entech Inc.) for the stable storage of gaseous VOCs. Carbon monoxide (CO) in the flue gas was measured by a CO analyzer (Ecotech9830B) simultaneously with a particle-filter removing the particles.

For stove burning, the biomass was directly burnt in stove. The experiment was similar to the “Water Boiling Test (WBT)”. In WBT, the testers use a pre-weighted bundle of biomass to raise the temperature of a specific quantity of water from room temperature to boil, and then keep the water boiling for approximately 40 minutes (Wang *et al.*, 2009). The sampling inlet was inserted to the chimney, and the sampling process was similar to that of field burning, as shown in Fig. 1 (right).

For quality assurance and quality control (QA/QC), all the Teflon bags and SUMMA canisters used in each test were cleaned with high-purity nitrogen ($> 99.999\%$) at least three times and evacuated in the laboratory. All the Teflon bags were solely used once to prevent cross contamination. The zero air from the dilution system was also collected as blank samples. The weight of the biomass for each test was kept at about several kilograms and the tests duration

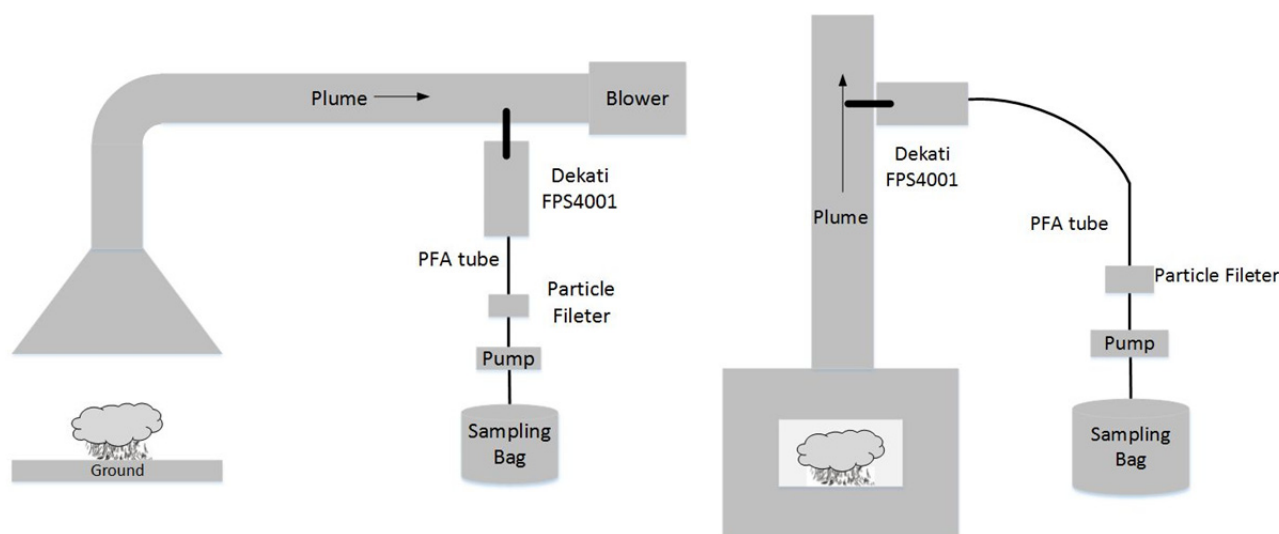


Fig. 1. The schematic of the sampling system for field burning (left) and stove burning (right).

ranged from 45 to 60 minutes. After each test, all the char and ash remaining was cleaned. Tests were repeated twice for each type of biomass burning to get reliable results. In total, 14 biomass/stove combinations were tested. After each test, a small bundle of biomass was sealed and brought to the laboratory for proximate analysis. The proximate analyses of the biomass were conducted according to the Chinese national standard methodologies (GB/T 212-2008) for proximate analysis of solid fuels.

The biomass selected for this study included straws of rice, wheat, bean and rape, and wood. Straws of rice, wheat, and bean were very important biofuels used for household energy in China (National bureau of Statistics, 2006). In particular, straws of rice, wheat, corn, rape, and bean were the five most abundant crop wastes in YRD region (Han *et al.*, 2002; Zhang *et al.*, 2008). In this study, maize straw was not included because it was unavailable in summer when the present study was conducted. More work is needed for the characterization of maize straw burning in future. In addition, one types of wood was selected for comparison with straws.

VOCs Analysis

VOC samples were analyzed by one Gas Chromatograph with a Mass Spectrometer and a Flame Ionization Detector (GC-MS/FID). Firstly, VOC samples were pumped into a cryogenic pre-concentrator (TH_PKU-300, Tianhong, China), and were concentrated at -150°C by two traps, respectively. The concentrated VOCs were desorbed at 100°C and were injected into the gas chromatograph (GC2010, Shimadzu, Japan). The C2–C5 hydrocarbons were separated on a PLOT capillary column (ϕ 0.32 mm \times 15 m, Dikma, USA) and were quantified by the FID. The C5–C10 hydrocarbons, halogenated VOCs (x-VOC), and oxygenated VOCs (o-VOC) were separated on a DB-624 (ϕ 0.25 mm \times 60 m, Agilent, USA) and were quantified using a quadrupole mass spectrometer (GCMS-QP2010E, Shimadzu, Japan). The source temperature in the MS was 200°C , with a scan mass ranging from 30 to 300 amu.

The VOC species were identified by their retention time and mass spectrums. A commercial standard gas (Spectra, USA) containing PAMS (Photochemical Assessment Monitoring System), o-VOC, and x-VOC was used to confirm compounds' retention time and identify compounds. In this study, 103 species including 28 alkanes, 11 alkenes, 16 aromatics, 16 o-VOC, 31 x-VOC and acetylene were identified, as listed in Table 1. The target species were quantified by using multipoint external calibration method. Calibration curves for all species were made before and after the analysis and had good linear regression ($R^2 > 0.99$). For every batch of 6 samples, a high-purity nitrogen sample and a standard sample (1 ppb) were spiked to assure the peak time and signal intensity. The method detection limits (MDLs) of the various VOC species ranged from 2 to 70 pptv (Liu *et al.*, 2009; Yuan *et al.*, 2012).

Determination of Emission Factors and Source Profiles

The emission factor was typically calculated by the carbon mass balance method (Zhang *et al.*, 2000; Dhammapala *et*

al., 2006; Wang *et al.*, 2009; Li *et al.*, 2011). In this method, all carbon was assumed to be emitted into the atmosphere as carbonaceous particles and carbonaceous gases, which required the complete measurement of the carbon both in the emissions and in the biomass and ash (Zhang *et al.*, 2000).

In this study, the emission factor of VOCs was determined by the measurement of the total VOC emission amount and the dry weight of biomass. The total VOC emission amount was calculated through multiplying the VOC concentration in the flue gas by the total volume of the flue gas which was equal to the product of the air velocity and the cross section area of chimney (or the burning chamber). The dry weight of the biomass was obtained according to the weight of the biomass and its moisture content.

For the comparison of VOC composition from different biomass burning, VOC source profiles of different biomass burning were obtained according to the mass percentage of each VOC group.

RESULTS AND DISCUSSIONS

Emission Factors

VOC and CO emission factors of different biomass burning were calculated by the method mentioned in section *Determination of emission factors and source profiles*, as shown in Fig. 2. For field biomass burning, VOC emission factors of straws were rape (2.90 ± 0.39) g/kg, rice (2.74 ± 0.10) g/kg, bean 2.55 g/kg, and wheat (1.98 ± 0.01) g/kg, respectively. In terms of stove burning, VOC emission factors were rice (6.98 ± 0.10) g/kg, rape (4.17 ± 0.33) g/kg, bean (3.06 ± 0.98) g/kg, and wood 0.98 g/kg respectively. CO emission factors of biomass burning showed similar variation trend with those of VOCs but were larger by one order of magnitude. CO emission factors of straw burning ranged from 17.47 to 66.32 g/kg, and the value of wood burning was 21.09 g/kg. Emission factors of VOCs were positively correlated with those of CO with the $R^2 = 0.57$ ($n = 14$), as shown in Fig. 3 (right). From Fig. 2, we can see that the emission factors of stove burning were a little larger than those of field burning, probably due to the incomplete collection of the flue gas by the burning chamber. We can also see that the emission factor of wood burning was significantly lower than that of straw burning (t-test, $p < 0.001$) because the dense structure of wood slowed down its emission of the volatile components and finally led to a more complete burning of the volatile components during the test (Li *et al.*, 2011). For emission factors of straw burning, those of rice and rape straws were generally higher than those of bean and wheat straws (t-test, $p < 0.001$).

Many factors might influence the VOC emission factor, such as the biomass types or the burning conditions as mentioned above. Additionally, the calorific value of the biomass might also influence the VOC emission factors. As indicated in Fig. 3 (left), VOC emission factors were negatively correlated with calorific values of the biomass with a correlation coefficient over 0.9 ($R^2 = 0.9213$, $n = 4$) for stove burning. However, no significant correlations were observed between VOC emission factors and the calorific values in field burning. Probably, the underestimation of

VOC emission factors in field burning due to the incomplete collection of flue gas might be the major reason of the poor correlations.

Source Profiles

The composition of VOCs from different biomass burning displayed some similarity as shown in Fig. 4. o-VOC were

Table 1. VOC species obtained in this study.

Alkane		Alkene		o-VOC		x-VOC	
C2	ethane	C2	ethene	C2	acetaldehyde	C1	chloromethane
	acetylene*	C3	propylene		Acetonitrile		Bromomethane
C3	propane	C4	tran-2-butene	C3	acrolein		Bromomethane
C4	isobutane		1-butene		Propanal		Iodomethane
	n-butane		cis-2-butene		Acetone		Chloroform
C5	cyclopentane		1,3-Butadiene		1-propanol		Carbontetrachloroide
	2-methylbutane	C5	1-Pentene		2-Propanol		Bromodichloromethane
	pentane		trans-2-Pentene	C4	Methacrolein		bromoform
C6	2,2-Dimethylbutane		Isoprene		n-Butanal	C2	Freon114
	2,3-Dimethylbutane		cis-2-Pentene	C5	MTBE		Vinylchloride
	2-Methylpentane	C6	1-Hexene		2-Pentanone		Chloroethane
	3-Methylpentane				n-Pentanal		Freon113
	n-Hexane		Aromatic		3-Pentanone		1,1-dichloroethylene
	Methylcyclopentane	C6	Benzene	C6	n-Hexanal		MethyleneChloride
	Cyclohexane	C7	Toluene				1,1-Dichloroethane
C7	2,4-Dimethylpentane	C8	Ethylbenzene				cis-1,2-Dichloroethylene
	2-Methylhexane		m/p-Xylene				1,1,1-Trichloroethane
	2,3-Dimethylpentane		o-Xylene				1,2-Dichloroethane
	3-Methylhexane		Styrene				1,1,2-Trichloroethane
	n-Heptane	C9	Isopropylbenzene				Tetrachloroethylene
	Methylcyclohexane		n-Propylbenzene				1,2-Dibromoethane
C8	2,2,4-Trimethylpentane		m-Ethyltoluene				1,1,2,2-tetrachloroethane
	2,3,4-Trimethylpentane		p-Ethyltoluene			C3	Trichloroethylene
	2-Methylheptane		1,3,5-Trimethylbenzene				1,2-Dichloropropane
	3-Methylheptane		o-Ethyltoluene				trans-1,3-Dichloropropene
	Octane		1,2,4-Trimethylbenzene				cis-1,3-Dichloropropene
C9	n-Nonane		1,2,3-Trimethylbenzene			C6	Chlorobenzene
C10	n-Decane	C10	m-Diethylbenzene				1,3-Dichlorobenzene
C11	Undecane		p-Diethylbenzene				1,4-dichlorobenzene
							1,2-Dichlorobenzene
						C7	Benzylchloride

*, included in C2 alkane

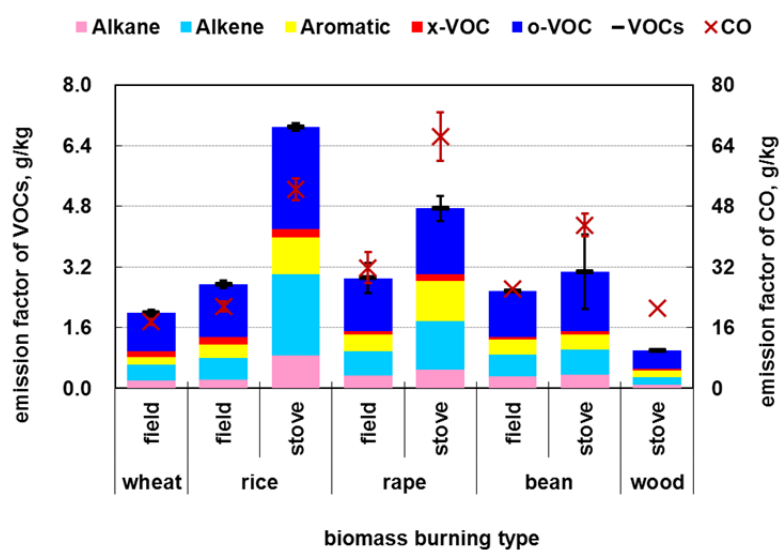


Fig. 2. Emission factors of VOCs and CO from different biomass burning.

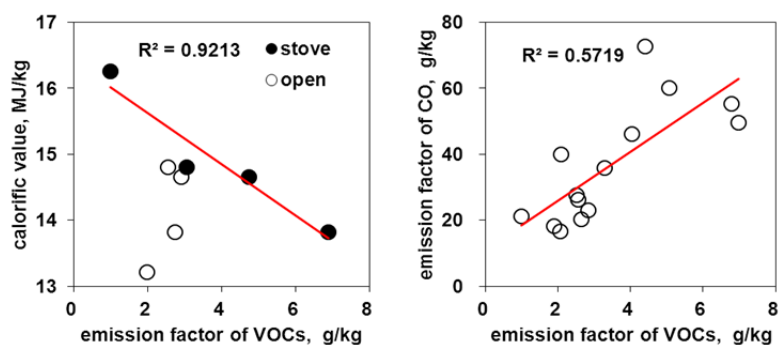


Fig. 3. Correlations between emission factors of VOCs and calorific values of the biomass (left) and emission factors of CO (right).

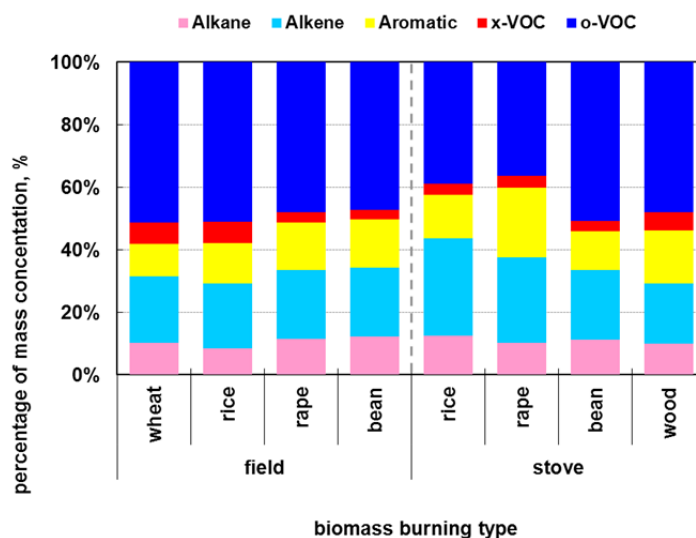


Fig. 4. The composition of VOCs from different biomass burning.

the primary contributors to VOCs from straw burning in the field, with a contribution of 49.4%, followed by alkenes (21.4%), aromatics (13.5%), alkanes (10.6%), x-VOC (5.0%). Compared with VOC composition of field straw burning, the contribution of o-VOC from stove burning decreased to 42.1%, and by contrast the contribution of alkenes and aromatics was relative high. This was mainly because of the more complete oxidation of volatile components with more air supplied in field burning. Some variations were identified between VOC compositions from different biomass burning. Taking the stove burning as an example, alkenes accounted for 19.3% of VOCs in wood burning, compared to 26.9% in straw burning, while the contribution of aromatics and x-VOC was relative high in wood burning, as indicated in Fig. 4.

The VOC species obtained from this study were categorized into 30 groups by the carbon number and chemical function group, as listed in Table 1. VOC source profiles of different biomass burning were obtained according to mass percentages of these groups in total VOC mass concentration. VOC source profiles of field straw burning were shown in Fig. 5(a), and there were no significant differences among VOC source profiles of different straw burning (Friedman test, $p > 0.05$). The top ten abundant groups were o-VOC ($15.7 \pm 5.0\%$), ethylene ($14.6 \pm 0.9\%$),

C3 o-VOC ($13.3 \pm 3.4\%$), C2 o-VOC ($9.7 \pm 4.2\%$), C4 o-VOC ($5.7 \pm 1.1\%$), C5 o-VOC ($5.3 \pm 1.7\%$), ethane ($5.2 \pm 2.0\%$), propene ($5.1 \pm 0.7\%$), benzene ($4.8 \pm 0.6\%$), and toluene ($2.7 \pm 0.5\%$), the sum of which contributed more than 82% of the total VOC mass concentration. Of the x-VOC, C3 x-VOC was the primary contributor with a proportion of ($2.4 \pm 0.6\%$).

Compared with VOC source profiles of field straw burning, those of stove burning had less o-VOC, as indicated in Fig. 5(b). The largest contributors were C6 o-VOC and ethylene, accounting for more than 43% of total VOCs together. The other eight groups listed in the top ten abundant groups were benzene ($8.7 \pm 3.9\%$), C3 o-VOC ($6.7 \pm 1.1\%$), ethane ($5.8 \pm 0.8\%$), propene ($4.9 \pm 1.3\%$), C5 o-VOC ($4.8 \pm 1.3\%$), C2 o-VOC ($4.6 \pm 1.2\%$), C4 o-VOC ($3.2 \pm 0.7\%$), and C4 alkanes ($2.9 \pm 1.4\%$) in sequence. VOC source profiles of stove wood burning showed some similarity with those of stove straw burning but with a higher contribution of C6 o-VOC, as shown in Fig. 5(b).

In summary, there were no significant differences among VOC source profiles of biomass burning in the same burning condition. o-VOC, C2–C3 hydrocarbons and C6–C7 aromatics were the major VOC species from biomass burning. The contribution of o-VOC was larger in source

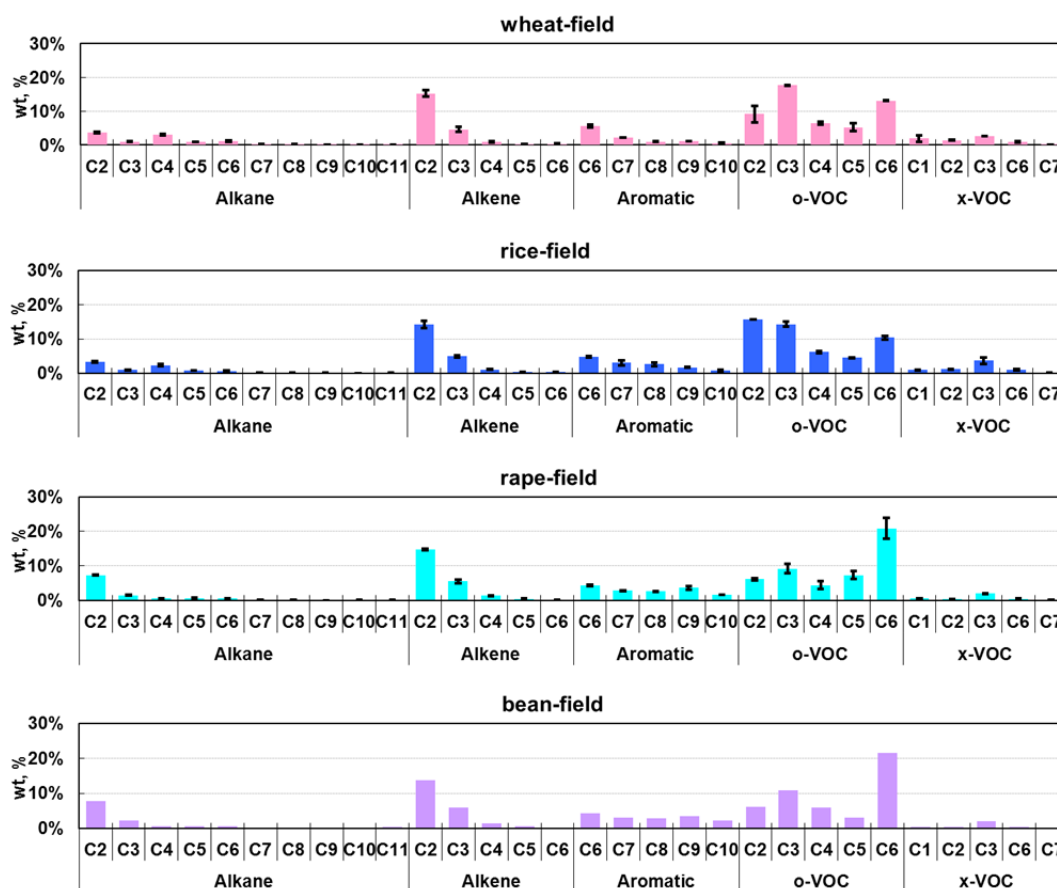


Fig. 5(a). Source profiles of VOCs from different biomass burning in the field.

profiles of field burning than those of stove burning. Our results displayed some similarity with the previous studies. As reported by Wang *et al.* (2009), C6–C7 aromatics, propylene, C2–C3 o-VOC were the major VOC species from typical biomass burning in northern China. Of the hydrocarbons, C2–C3 hydrocarbons and C6–C7 aromatics were abundant both in Liu *et al.* (2008) and Tsai *et al.* (2003) study. Nevertheless, significant variations of the specific proportions of VOC species were identified between this study and previous studies. For example, proportions of benzene and propylene were the largest with the values of $(17.3 \pm 8.1)\%$ and $(11.3 \pm 3.5)\%$ in Wang *et al.* (2009) study, respectively, compared to $(6.4 \pm 2.9)\%$ and $(4.8 \pm 1.0)\%$ in this study. Variations of measured VOC species in different studies played an important role in the variations of VOC source profiles of biomass burning.

The OFP of VOCs from Biomass Burning

The OFP of VOCs from different biomass burning was calculated based on VOC emission factors and source profiles combining with the maximum incremental reactivity (MIR) of each species by Eq. (1) below:

$$OFP = \sum_{i=1}^n (p_i \times MIR_i) \times EF \quad (1)$$

where, *OFP* is the ozone formation potential of VOCs

emitted from per unit of biomass burning, g/kg; p_i is the mass percentage of VOC_i in total VOCs, %; MIR_i is the MIR of VOC_i , g O_3 /g VOC_i ; *EF* is the VOC emission factor, g/kg. The *MIR* values can be cited in Carter (2008).

The OFP of VOCs from different biomass burning, and the contribution of each chemical group to the total OFP were shown in Fig. 6. Generally, the OFP could be categorized into three groups. The first group was the OFP of field straw burning whose values ranged from 8.06 to 12.20 g/kg, and these values were slightly higher than that of Li *et al.* (2009b) with an average of 7.0 ± 0.85 g/kg. The reason might be that the o-VOC and x-VOC were not included in the study of Li *et al.* (2009b). The second group was the OFP of stove straw burning which was 13.92–33.24 g/kg. The third group was the OFP of wood burning with the lowest value of 4.30 g/kg. The OFP of different biomass burning was mostly influenced by the various VOC emission factors.

From Fig. 6, we can see that alkenes and o-VOCs were the largest contributing species to the OFP, and their percentages were 41–61% and 28–42%, respectively, followed by aromatics 7–14%. The contribution of both alkanes and x-VOC to the OFP was lower than 2%. Further examination showed that the top five abundant species of the OFP were ethylene (36%), n-hexanal (17%), propene (13%), acetaldehyde (6.4%), and methyl vinyl ketone (3.8%). Of the aromatics, toluene was the most important species of the OFP with the percentage of 2.3%.

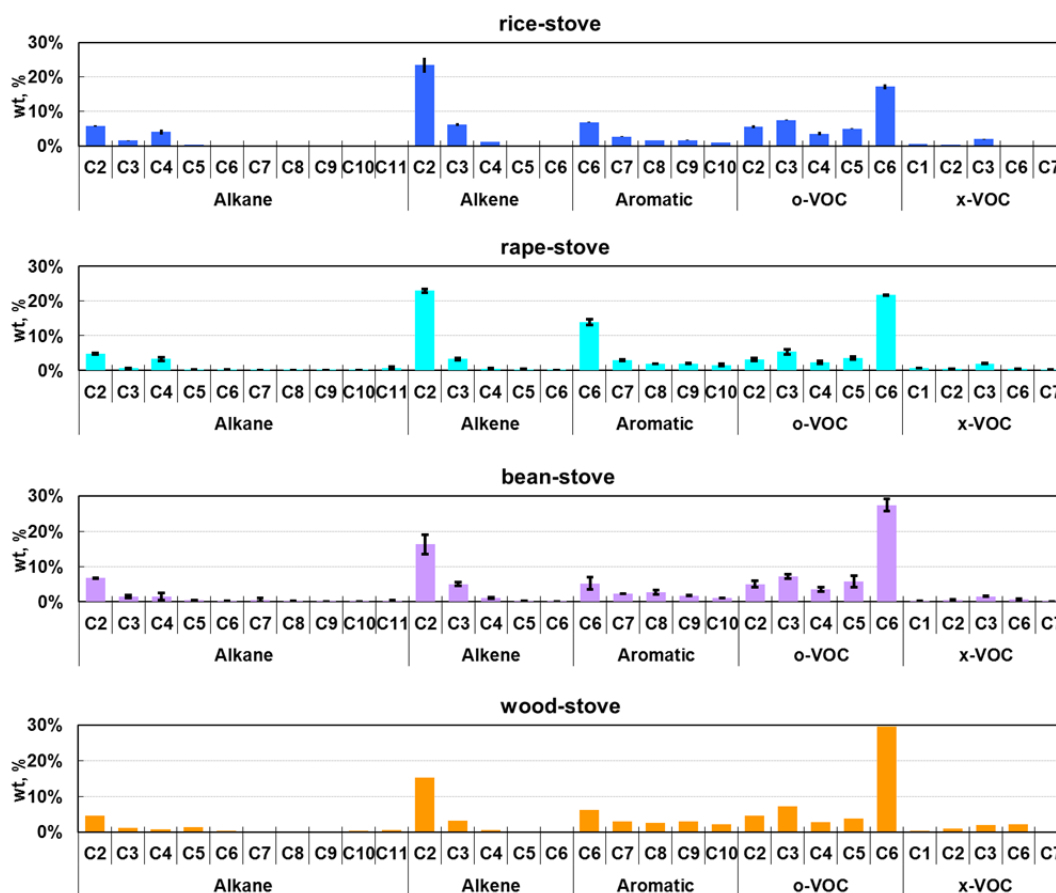


Fig. 5(b). Source profiles of VOCs from different biomass burning in stove.

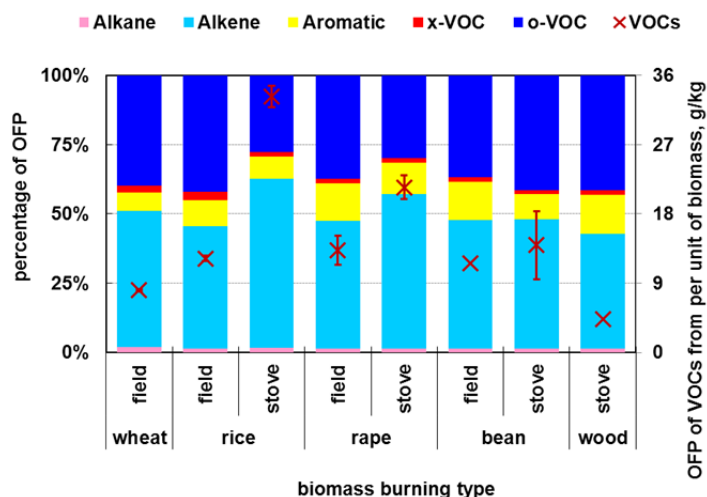


Fig. 6. OFP of VOCs from different biomass burning and the contribution of each VOC group to total OFP.

Comparison with Other Studies

VOC emission factors of biomass burning in different studies were summarized in Fig. 7. For straw burning, VOC emission factors ranged from 1.98 to 9.62 g/kg in different studies with an average of (4.02 ± 2.21) g/kg, except those performed in Jan and April by Wang *et al.* (2009). As reported by Wang *et al.* (2009), VOC emission factors of straw burning were greatly influenced by the ambient temperature,

and the values were 0.23–1.48 g/kg in Jan and 7.36–26.57 g/kg in April, respectively, which were significantly different from those in other studies (*t*-test, $p < 0.001$). In terms of the results from the other studies, there were no significant differences among the emission factors of different straws burning (Kruskal-Wallis test, $p > 0.05$). The present study was conducted in late June and early July which was the typical harvest season in YRD. The other two studies did

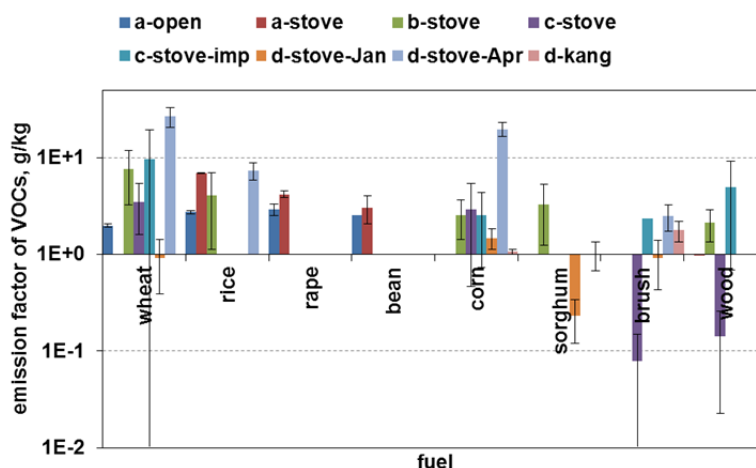


Fig. 7. Comparison of VOC emission factors of biomass burning in different studies. (a, this study; b, Li *et al.*, 2011; c, Zhang *et al.*, 2000; d, Wang *et al.*, 2009; stove-imp, improved stove; Jan, result in January; Apr, result in April; kang, a commonly used stove in northern China for heating bed).

not report the season or the ambient temperature of the experiments (Zhang *et al.*, 2000; Li *et al.*, 2011). The effect of the ambient temperature on VOC emission factors of straw burning needs further more studies.

VOC emission factors of wood burning were significantly lower than those of straw burning (t-test, $p < 0.001$), ranging from 0.08 to 4.95 g/kg with the average of (1.76 ± 1.41) g/kg, as shown in Fig. 7. Our value was 0.98 g/kg and fell in the range. VOC emission factors of wood burning ranged over one order of magnitude in the studies listed in Fig. 7. This large variation might result from different types of wood studied in those studies.

In addition to the differences of emission factors, variations of VOC composition were also observed among different studies. As shown in Fig. 8, the percentages of o-VOC and alkenes were much larger than those of aromatics and alkanes in the present study. While, according to the study of Wang *et al.* (2009) and her group (Li *et al.*, 2011),

the contribution of aromatics to total VOCs was dominant. It should be pointed out that specific VOC species measured in those studies were not always same, as shown in Table 2, which was probably one important reason of variations of the VOC composition.

Comparison with Other VOC Sources

The ratios of specific VOC pairs were usually used as the fingerprint for distinguishing or identifying VOC emission sources. For example, the ratio of toluene to benzene (T/B) was recognized as the characteristic of vehicle emissions with a value of 1.5–2.0 (Schauer *et al.*, 2002). The ratios of T/B and ethylbenzene to m,p-xylenes (E/X) in major VOC combustion sources were summarized in Fig. 9 (Liu *et al.*, 2008; Wang *et al.*, 2009; Li *et al.*, 2011; Qiao *et al.*, 2012). For the ratio of T/B, gasoline vehicle exhausts had the highest value, followed by the gasoline evaporation and diesel vehicle exhausts. The ratios of T/B were the lowest

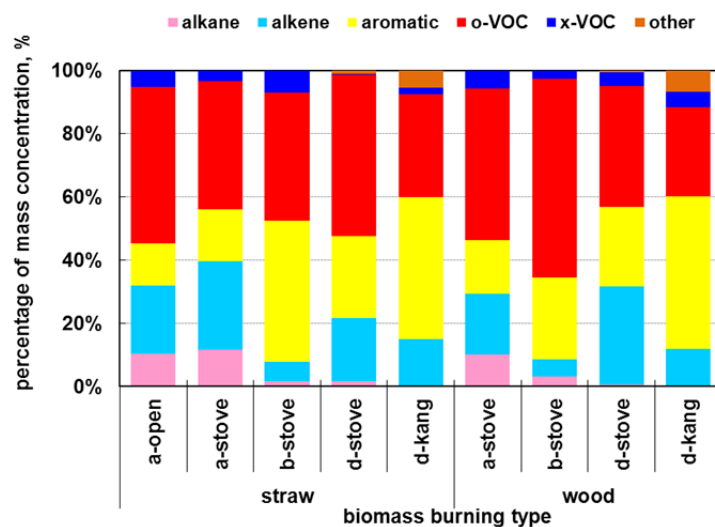


Fig. 8. Comparison of the VOC composition from biomass burning among different studies (a, this study; b, Li *et al.*, 2011; d, Wang *et al.*, 2009).

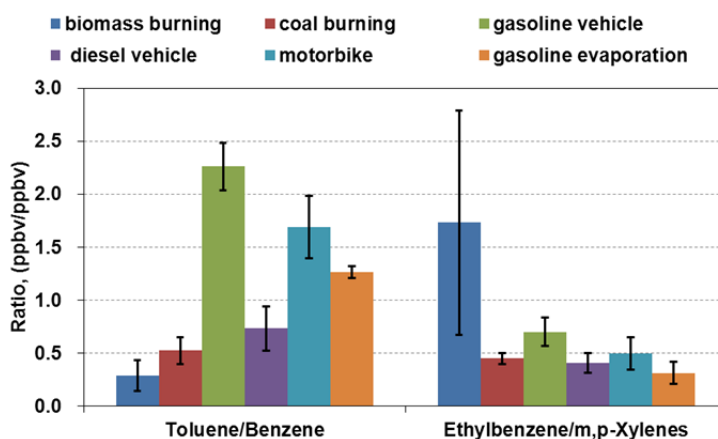


Fig. 9. Comparisons of ratios of T/B and E/X in different emissions (biomass burning: this study, Li *et al.* (2011), Wang *et al.* (2009); coal burning: Liu *et al.* (2008); gasoline vehicle: Qiao *et al.* (2012); diesel vehicle: Qiao *et al.* (2012); motorbike: Qiao *et al.* (2012); gasoline evaporation: Liu *et al.* (2008)).

for the emissions from coal burning and biomass burning, the difference between which was not significant. Thus, the ratio of T/B was not suitable to distinguish coal burning emissions from biomass burning emissions.

For the ratio of E/X, all VOC combustion sources except biomass burning showed similar values of (0.49 ± 0.12) which were much lower than that of biomass burning with the average of (1.73 ± 1.06) . Accordingly, we could easily identify VOC emissions of biomass burning from the other VOC combustion sources by the ratio of E/X. It should be pointed out that the ratio of E/X was usually used for estimating the photochemical age of the air mass (Mckeen *et al.*, 1996; Shao *et al.*, 2011), because ethylbenzene and m,p-xylenes had similar sources but different chemical reactivity in the atmosphere. Consequently, the possible influence of emissions from biomass burning should be taken into account on the estimation of the air mass photochemical age based on the ratio of E/X.

Uncertainty Analysis

Up to now, many studies were carried out to explore the characterization of VOCs from biomass burning. It seemed that the VOC emission factor of the straw burning was around several g/kg. Nevertheless, significant discrepancies of VOC emission factors were identified among different studies (compared in section *Comparison with other studies*) due to various burning conditions and measurement methods, as shown in Table 2. The discrepancy of VOC emission factors of wood burning among different studies was even more significant. Therefore, there might be two major sources of the uncertainty of VOC characterization from biomass burning.

One reason was the variability of emissions from different burning tests, largely associated with the variations in fire tending behavior (Tsai *et al.*, 2003). The burning cycle usually began with the ignition which was characterized by incomplete combustion, followed by a stable and complete combustion, and ended with combustion of the remaining charcoal. VOC characterization was different with firing processes (Wang *et al.*, 2009). Unfortunately, one entire burning cycle with three processes was almost impossible to

be completely repeated by each test, not to mention conducted by different testers. This may be the explanation for the discrepancy among different studies. In addition, the types of biomass also had influence on VOC emissions. Thus, more detailed combustion process should be conducted for better understanding VOC emissions from biomass burning.

The other reason of the uncertainty of VOC characterization might come from the measurements. In previous studies, VOC emission factors were usually determined by the carbon mass balance method, in which the accurate measurement of each part of carbon mass was very important. In this study, the emission amount of VOCs was obtained through multiplying the VOC concentration in flue gas by the total flue gas volume. Thus, the measurement of the flue gas volume was very crucial for this method and obviously this method underestimated emission factors of the field burning as the incomplete collection of the flue gas according to our results. In addition, the normative measurement of VOCs was also essential to study VOC characterization of different biomass burning. As shown in Table 2, detailed VOC species measured in different studies were not very similar. For example, in some studies o-VOC were not included, which were recognized as important VOC species from biomass burning. Even in some studies, VOCs were measured as the total non-methane hydrogen carbon (TNMHC). Accordingly, total VOCs were different as different VOC species were measured in those studies. It would be helpful to apply a similar list of the VOC species in future studies of VOC characterization of different sources, which would be also useful to identify the possible fingerprint of different VOC sources.

CONCLUSIONS

In this study, the characterization of VOCs emitted from biomass burning was investigated in YRD, including two types of burning conditions and five types of biomass. Based on the results, VOC emission factors of stove straw burning ranged from 2.08 to 6.99 g/kg with the average of (4.89 ± 1.70) g/kg and the OFP of VOCs emitted from per

Table 2. Tests conditions and measurement methods in different studies.

	Burning type	Biomass type	Sampling method	Sampling duration	VOC analysis	VOC species
This study	Improved stove field	rice, rape, bean, wood rice, wheat, rape, bean	Summa canister	45–60 min	GC-MS/FID	28 alkanes, 11 alkenes, 16 aromatics, 16 o-VOC, 31 x-VOC, acetylene
Li et al., 2011	improved stove	rice, wheat, maize, sorghum	Summa canister; DNPH tube	20 min	GC-MS	7 alkanes, 12 alkenes, 15 aromatics, 12 carbonyls, 3 x-VOC, 9 other o-VOC, propyne
Liu et al., 2008	improved stove	NP	Summa canister	NP	GC-MS/FID	38 alkanes, 35 alkenes, 2 alkynes, 17 aromatics
Zhang et al., 2000	stove improved stove	wheat, maize, brush, wood	Tedlar bag	35–60 min	FID	CH ₄ , TNMHC
Wang et al., 2009	improved stove kang	rice, wheat, maize, sorghum, brush maize, sorghum, brush	Summa canister	~40 min	GC-MS	TO-15

kilogram straw burning was 13.92–33.24 g/kg. The VOC emission factor was 0.98 g/kg for wood burning in stove and its OFP was 4.30 g/kg. Emission factors of field burning were easily underestimated due to the incomplete collection of the flue gas. VOC emission factors of wood burning ranged over one order of magnitude in different studies, and more studies are necessary in the future to investigate VOC emission factors of wood burning. Burning conditions and measurement methods should be paid much attention to because both of them might cause large uncertainty of VOC characterization of biomass burning.

Some differences of VOC composition were observed among different biomass burning. For field straw burning, the contribution of o-VOC was 49.4%, followed by alkenes (21.4%) > aromatics (13.5%) > alkanes (10.6%) > x-VOC (5.0%). The percentage of o-VOC from stove burning was lower than that from field burning due to more air supplied in field burning. Wood burning emitted more aromatics and x-VOC compared to straw burning. In terms of detailed VOC species, there were no large differences among the major contributing VOC species from different biomass burning. The most abundant groups were o-VOC, C2–C3 hydrocarbons, and C6–C7 aromatics in VOCs from biomass burning. Alkenes and o-VOC were the largest contributors of OFP, accounting for 41–61% and 28–42%, respectively. Ethylene, n-hexanal, propene, acetaldehyde, and methyl vinyl ketone were the top five contributing species of OFP, proportioning 77% of total OFP. VOC source profiles of biomass burning had significant large ratio of E/X with the value of (1.73 ± 1.06) which could be recognized as the fingerprint of VOCs from biomass burning.

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REFERENCES

- Andreae, M.O., Jones, C.D. and Cox, P.M. (2005). Strong Present-day Aerosol Cooling Implies a Hot Future. *Nature* 435: 1187–1190.
- Bo, Y., Cai, H. and Xie, S.D. (2008). Spatial and Temporal Variation of Historical Anthropogenic NMVOCs Emission Inventories in China. *Atmos. Chem. Phys.* 8: 7297–7316.
- Carter, W.P.L. (2008). Reactivity Estimates for Selected Consumer Product Compounds, Air Resources Board, California. Contract No. 06-408.
- Dhammapala, R., Claiborn, C., Corkill, J. and Gullett, B. (2006). Particulate Emissions from Wheat and Kentucky Bluegrass Stubble Burning in Eastern Washington and Northern Idaho. *Atmos. Environ.* 40: 1007–1015.
- Guo, S. (2011). Tracer-Based Method to Estimate Biogenic and Anthropogenic Secondary Organic Aerosol, Ph.D.

- Thesis, Peking University (in Chinese).
- Han, L., Yan, Q., Liu, X., and Hu, J. (2002). Straw Resources and Their Utilization in China. *Trans. Chin. Soc. Agric. Eng.* 18: 87–91 (in Chinese).
- Huang, C., Chen, C.H., Li, L., Cheng, Z., Wang, H.L., Huang, H.Y., Streets, D.G., Wang, Y.J., Zhang, G.F. and Chen, Y.R. (2011). Emission Inventory of Anthropogenic Air Pollutants and VOC Species in the Yangtze River Delta Region, China. *Atmos. Chem. Phys.* 11: 4105–4120.
- Johnson, N.G., Bryden, M. and Xiao, A. (2005). Risk Analysis and Safety Evaluation of Biomass Cookstoves. Engineering/Technology Management 2005: Safety Engineering and Risk Analysis, Technology and Society, Engineering Business Management, Health and Safety, p. 185–192.
- Koppmann, R., von Czapiewski, K. and Reid, J.S. (2005). A Review of Biomass Burning Emissions, Part I: Gaseous Emissions of Carbon Monoxide, Methane, Volatile Organic Compounds, and Nitrogen Containing Compounds. *Atmos. Chem. Phys. Discuss.* 5: 10455–10516.
- Levine, J.S., Cofer, W.R., Cahoon, D.R. and Winstead, E.L. (1995). Biomass Burning: A Driver for Global Change. *Environ. Sci. Technol.* 29: 120–125.
- Li, L.J., Wang, Y., Zhang, Q., Li, J.X., Yang, X.G. and Jin, J. (2008). Wheat Straw Burning and Its Associated Impacts on Beijing Air Quality. *Sci. China, Ser. D Earth Sci.* 51: 403–414.
- Li, Q., Zhang, L., Wu, C., Sun, Z. and Liu, X. (2009a). Satellite-remote-sensing-based Monitoring of Straw Burning and Analysis of Its Impact on Air Quality. *J. Ecol. Rural Environ.* 25: 32–37 (in Chinese).
- Li, X.H., Wang, S.X., Duan, L., Hao, J.M., Li, C., Chen, Y.S. and Yang, L. (2007). Particulate and Trace Gas Emissions from Open Burning of Wheat Straw and Corn Stover in China. *Environ. Sci. Technol.* 41: 6052–6058.
- Li, X.H., Wang, S.X., Duan, L. and Hao, J.M. (2009b). Characterization of Non-methane Hydrocarbons Emitted from Open Burning of Wheat Straw and Corn Stover in China. *Environ. Res. Lett.* 4: 044015, doi: 10.1088/1748-9326/4/4/044015.
- Li, X.H., Wang, S.X. and Hao, J.M. (2011). Characteristics of Volatile Organic Compounds (VOCs) Emitted from Biofuel Combustion in China. *Environ. Sci.* 32: 3515–3521 (in Chinese).
- Liu, X.L., Zeng, L.M., Lu, S.H. and Yu, X.N. (2009). Online Monitoring System for Volatile Organic Compounds in the Atmosphere. *Acta Sci. Circumst.* 29: 2471–2477 (in Chinese).
- Liu, Y., Shao, M., Fu, L.L., Lu, S.H., Zeng, L.M. and Tang, D.G. (2008). Source Profiles of Volatile Organic Compounds (VOCs) Measured in China: Part I. *Atmos. Environ.* 42: 6247–6260.
- McKeen, S.A., Liu, S.C., Hsie, E.Y., Lin, X., Bradshaw, J.D., Smyth, S., Gregory, G.L. and Blake, D.R. (1996). Hydrocarbon Ratios during PEM-WEST A: A Model Perspective. *J. Geophys. Res.* 101: 2087–2109.
- National Bureau of Statistics (2006). China Energy Statistical Yearbook 2005, p. 142–144 (in Chinese).
- Qiao, Y.Z., Wang, H.L., Huang, C., Chen, C.H., Su, L.Y., Zhou, M., Xu, H., Zhang, G.F., Chen, Y.R., Li, L., Chen, M.H. and Huang, H.Y. (2012). Source Profile and Chemical Reactivity of Volatile Organic Compounds from Vehicle Exhaust. *Environ. Sci.* 33: 50–58 (in Chinese).
- Schauer, J.J., Kleeman, M.J., Cass, G.R. and Simoneit, B.R.T. (2002). Measurement of Emissions from Air Pollution Sources. 5. C-1-C-32 Organic Compounds from Gasoline-powered Motor Vehicles. *Environ. Sci. Technol.* 36: 1169–1180.
- Shao, M., Wang, B., Lu, S.H., Yuan, B. and Wang, M. (2011). Effects of Beijing Olympic Control Measures of Reducing Reactive Hydrocarbon Species. *Environ. Sci. Technol.* 45: 514–519.
- Tsai, S.M., Zhang, J.F., Smith, K.R., Ma, Y. and Khalil, M.A.K. (2003). Characterization of Non-methane Hydrocarbons Emitted from Various Cookstoves Used in China. *Environ. Sci. Technol.* 37: 2869–2877.
- Wang, S.X., Wei, W., Du, L., Li, G.X. and Hao, J.M. (2009). Characteristics of Gaseous Pollutants from Biofuel-stoves in Rural China. *Atmos. Environ.* 43: 4148–4154.
- Wei, W., Wang, S.X., Chatani, S., Klimont, Z., Cofala, J. and Hao, J.M. (2008). Emission and Speciation of Non-methane Volatile Organic Compounds from Anthropogenic Sources in China. *Atmos. Environ.* 42: 4976–4988.
- Yuan, B., Shao, M., de Gouw, J., Parrish, D.D., Lu, S.H., Wang, M., Zeng, L.M., Zhang, Q., Song, Y., Zhang, J.B. and Hu, M. (2012). Volatile Organic Compounds (VOCs) in Urban Air: How Chemistry Affects the Interpretation of Positive Matrix Factorization (PMF) Analysis. *J. Geophys. Res.* 117: D24302, doi: 10.1029/2012JD018236.
- Zhang, H.F., Ye, X.N., Cheng, T.T., Chen, J. M., Yang, X., Wang, L. and Zhang, R. Y. (2008). A Laboratory Study of Agricultural Crop Residue Combustion in China: Emission Factors and Emission Inventory. *Atmos. Environ.* 42: 8432–8441.
- Zhang, H.F., Hu, D.W., Chen, J.M., Ye, X.N., Wang, S.X., Hao, J.M., Wang, L., Zhang, R.Y. and An, Z.S. (2011). Particle Size Distribution and Polycyclic Aromatic Hydrocarbons Emissions from Agricultural Crop Residue Burning. *Environ. Sci. Technol.* 45: 5477–5482.
- Zhang, J., Smith, K.R., Ma, Y., Ye, S., Jiang, F., Qi, W., Liu, P., Khalil, M.A.K., Rasmussen, R.A. and Thorneloe, S.A. (2000). Greenhouse Gases and Other Airborne Pollutants from Household Stoves in China: A Database for Emission Factors. *Atmos. Environ.* 34: 4537–4549.

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