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Emission characteristics of carbonaceous particles and trace gases from open burning of crop residues in China

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HIGHLIGHTS

- Custom-made combustion chamber was used to determine emission factors (EFs).
- EFs of crop residue open burning specific to China and elsewhere were compared.
- Increased moisture content decreased CO_2 and enhanced CO, $PM_{2.5}$ & OC emissions.
- Emission inventories for crop residue combustion in China were compiled for 2008.

ARTICLE INFO

ABSTRACT

Open burning of crop residue is an important source of carbonaceous pollutants, and has a large impact on the regional environment and global climate change. Laboratory burn tests were conducted using a custom-made combustion chamber to determine pollutants (i.e. CO_2, CO, $PM_{2.5}$, organic carbon (OC) and elemental carbon (EC)) emission factors (EFs) of wheat straw, rice straw and corn stalk; the three major agricultural crop residues in China. The average EFs were estimated to be 1351 ± 147 g kg^{-1} for CO_2, 52.0 ± 18.9 g kg^{-1} for CO, 10.6 ± 5.6 g kg^{-1} for $PM_{2.5}$, 4.8 ± 3.1 g kg^{-1} for OC and 0.24 ± 0.12 g kg^{-1} for EC. In addition, the effect of fuel moisture was investigated through the controlled burning of wheat straw. Increasing the moisture content decreased the CO_2 EF, and increased the EFs of CO, $PM_{2.5}$ and OC. Based on measurements from this study and nationwide statistics in crop type and area, pollutants emission inventories for crop residue combustion with $1° \times 1°$ resolution were compiled for 2008. Total emissions were 120 Tg CO_2, 4.6 Tg CO, 0.88 Tg $PM_{2.5}$, 0.39 Tg OC and 0.02 Tg EC.

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1. Introduction

Open burning of crop residue is a common practice in China for the elimination of waste during the harvesting, post-harvesting or pre-planting periods. In Asia, field burning has become a serious

concern due to its adverse environmental and health impacts (Bond et al., 2013; Fernandez et al., 2001; IPCC, 2013; Jacobson, 2001; Wei et al., 2015; Wu et al., 2013, 2012). Streets et al. (2003) estimated that open burning in China accounted for nearly half (~110 terragram [Tg]) of the total (250 Tg) crop residues burned in Asia in the mid-1990s. Huang et al. (2012a) reported a lower estimate of 40 Tg in 2006 due to the government's attempts to prohibit open burning in recent years. However, biomass burning emissions, including carbon dioxide (CO_2), carbon monoxide (CO), elemental carbon (EC), organic

carbon (OC), particulate matter (PM) and others (Andreae and Merlet, 2001; Jenkins et al., 1992), still have significant impacts on the local and regional environment (Huang et al., 2014, 2012b).

Emission factors (EFs), defined as the mass of a pollutant emitted per unit of fuel consumed, are used to compile emission inventories, as inputs to dispersion models, and to evaluate the effectiveness of pollutant control strategies. EFs strongly depend on the type of crop, and burning conditions, such as fuel load and moisture content (Chen et al., 2010; McMeeking et al., 2009; Reid et al., 2005). Previous studies have obtained many EFs for open burning of crop residue worldwide as summarized in Supplemental Table S1 (e.g. Andreae and Merlet, 2001; Dhammapala et al., 2006; Hays et al., 2005; Kim Oanh et al., 2011; Nguyen et al., 1994; Turn et al., 1997; U.S. EPA, 1995; Yokelson et al., 2011), but few of these studies have considered the effect of moisture content on EFs (Kim Oanh et al., 2011). A more recent study by Hayashi et al. (2014) determined EFs for open burning of rice straw, wheat straw and barley straw in Japan using a portable combustion hood, and evaluated the effects of fuel moisture content on the EFs. Hayashi et al. (2014) found that an increased moisture content enhanced the emissions of CO, CH$_4$ and particulate organic matter. In China, few EFs from open burning of crop residue are available (Table S1). Li et al. (2007) reported EFs of PM$_{2.5}$ (particles with aerodynamic diameters <2.5 μm) and trace gases from open burning of wheat straw and maize stover in a rural area in Shandong Province. Zhang et al. (2008) performed burn experiments on rice, wheat and corn straw in a test chamber and measured EFs of trace gases. More recently, Zhang et al. (2013) conducted chamber burning experiments on rice straw and sugarcane leaves, the two major crop residues in Southeast China. EFs for both gaseous pollutants and particles were reported, including CO$_2$, CO, non-methane hydrocarbons, oxygenated volatile organic compounds, PM$_{10}$ (particles with aerodynamic diameters <10 μm), PM$_{2.5}$, OC and EC. None of these studies considered the impacts of the fuel moisture content on pollutant emissions. Higher moisture often needs additional energy to vaporize the water and results in a lower combustion efficiency (CE) and higher pollutant emissions (Chen et al., 2010).

Given the limited availability of EFs in China, most emission inventories in China (e.g. Huang et al., 2012a; Streets et al., 2003; Yan et al., 2006) have used the EFs reported by Andreae and Merlet (2001) or Akagi et al. (2011). Biomass burning emissions are aggregated without specifying the fuel types or combustion conditions. This can cause large uncertainties when compiling emission inventories.

The objective of this study was to quantify EFs for gaseous and particle pollutants (i.e. CO$_2$, CO, PM$_{2.5}$, OC and EC) from major crop residues (i.e. wheat straw, rice straw and corn stalk) in China, using a laboratory combustion chamber. The impact of fuel moisture content on pollutant emissions was assessed because measured EFs are sensitive to moisture in the fuel. The results were compiled to produce an statewide emission inventory for 2008 with 1° × 1° resolution.

2. Experimental section

2.1. Crop residue collection and processing

Wheat straw, rice straw and corn stalk were collected from five major crop producing regions (i.e. Shaanxi, Anhui, Shandong, Henan and Hebei Provinces). Samples were stored at ambient temperature (~20 °C) and humidity (35%—45%) for at least 1 month before the experiments. Ultimate analyses for the carbon (C) and nitrogen (N) content in dry mass, as well as proximate analyses for the moisture, ash, volatile matter, and fixed C content as received (Liao et al., 2004), were conducted (Table S2). When studying the effect of different moisture contents on emissions, we rehydrated

the crop residues by adding ultrapure water to obtain fuels with different moisture levels (~10%, 28% and 50%), and then sealed the wet fuel in plastic bags for 1—2 days before combustion (Chen et al., 2010). The moisture content was tested before each burn.

2.2. Sampling and analysis

A combustion chamber was set up to simulate open burning of biomass at the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS) in collaboration with the Desert Research Institute (DRI), USA. The chamber was a large cuboid container (1.8 (L) × 1.8 (W) × 2.2 m (H)) with a volume of approximately 8 m^3, with 3 mm-thick aluminum walls to withstand high temperatures. The combustion chamber was equipped with a thermocouple, a thermoanemometer, an air purification system and a sampling line to connect with a dilution sampler (Wang et al., 2012). The crop residues were first weighed with a balance (0.1—0.2 kg for each test) and then burned on a platform inside the combustion chamber. The smoke emitted from these laboratory burns was sampled by the dilution sampler and on-line instruments. The dilution ratios ranged from 5 to 15 in this study. The details of this biomass burning simulation system are described in Tian et al. (submitted manuscript, 2015). A total of 21 tests were conducted: nine for wheat straw, seven for rice straw, and five for corn stalk. The sampling periods typically lasted from 30 to 50 min.

PM$_{2.5}$ samples were collected from three parallel channels located downstream of the residence chamber of the dilution sampler, with a flow rate of 5 L min^{-1} per channel. Two 47 mm Whatman quartz microfiber filters (QM/A), which were pre-heated at 900 °C for 3 h before sampling to remove any residual carbon, were used for the carbon analysis, and one 47 mm Teflon-membrane filter (2 μm pore size, R2PJ047, Pall Life Sciences, Ann Arbor, MI, USA) was collected for gravimetric analyses. The sampled filters were stored in a refrigerator at ~4 °C before chemical analysis to minimize the evaporation of volatile components. Before and after sampling, the Teflon-membrane filters were conditioned for 24 h at ~25 °C and 35% relative humidity, and weighed using a microbalance with ±1 μg sensitivity (Sartorius, Göttingen, Germany). Each filter was weighed at least three times before and after sampling, and the net mass was obtained by subtracting the average of pre-sampling weights from the average of the post-sampling weights. The difference among the three repeated weights was less than 10 μg and 20 μg for a blank filter and a sampled filter, respectively. The OC, EC and their carbon fractions were analyzed following the IMPROVE_A thermal/optical protocol (Chow et al., 2007). Real-time CO levels and PM$_{2.5}$ mass concentrations were monitored by a CO analyzer (Model 48i, Thermo Scientific Inc., Franklin, MA, USA) and a DustTrak (Model 8532, TSI Inc., Shoreview, MW, USA) (Wang et al., 2009), respectively. Three nondispersive infrared (NDIR) CO$_2$ analyzers (Model SBA-4, PP System, Amesbury, MA, USA) were used to measure background CO$_2$, and CO$_2$ in stack and diluted emissions.

2.3. Determination of EFs

EFs were calculated by dividing the emission by the mass of the fuel consumed, and expressed as grams of emission per kilogram of consumed dry fuel (g·kg^{-1}) (Andreae and Merlet, 2001). For particulate pollutants (i.e. PM$_{2.5}$, OC and EC), the EFs were calculated as:

$$EE_P = \frac{m_{filter}}{Q} \frac{V_{Total-chimney}}{m_{fuel}} DR \tag{1}$$

where EF_p is the EF of particulate pollutants for the specific crop

residue; m_{filter} is the mass of pollutants collected on the filter; $V_{Total-chimney}$ is the total volume of exhaust flowing through the chimney during the experiment (m^3) at standard temperature and pressure; Q is the sampling volume through the filter (m^3) at standard temperature and pressure; m_{fuel} is the mass of burned fuel (kg, dry basis); and DR is the dilution ratio in the dilution sampler, which was determined using the measured stack, diluted, and background CO_2 concentrations (i.e. $CO_{2,Stk}$, $CO_{2,Dil}$ and $CO_{2,Bkg}$, respectively), where:

$$DR = \frac{CO_{2,Stk} - CO_{2,Bkg}}{CO_{2,Dil} - CO_{2,Bkg}} \qquad (2)$$

For CO_2 and CO, the EFs were calculated using online monitored concentrations as follows:

$$EF_x = \frac{V_{Total-Chimney}}{m_{fuel}} \frac{C_{x,Dilute}}{V_x} M_x DR \qquad (3)$$

where $C_{x,Dilute}$ is the average concentration (molar fraction) measured in the dilution sampler; V_x is the molar volume of gas at standard temperature and pressure (0.0224 m^3) and M_x is the molecular weight of species x (g·mol^{-1}).

2.4. Methodology used to compile the emission inventory

Emissions were estimated as the product of the amount of crop residues burned in the field and the corresponding EF measured in this study. For crop residues other than wheat straw, rice straw and corn stalk, the average EF from the three crops was assumed.

The amount of crop residue burned in the field was calculated as:

$$M = P \times R \times D \times W \times E \qquad (4)$$

where M is the total mass of crop residue burned in the field in gigagrams [Gg], P is the yield of crop in Gg, R is the residue-to-crop ratio, D is the dry fraction of crop residue, W is the proportion of residue burned in the field, and E is the fraction of the fuel that is actually consumed through combustion (i.e. burn efficiency). The parameters R, D and E are listed in Table S3 (He et al., 2011; Streets et al., 2003; Xie et al., 2011). The P values were taken from an official statistical yearbook (NBS, 2009), and the W values on a provincial basis were taken from Wang and Zhang (2008). A geographical information system (GIS) was applied to allocate pollutants from open burning of crop residues to $1° \times 1°$ grid using the product of agricultural land cover and fire counts as a proxy (Bond et al., 2004). The monthly variation of emissions was also presented using the Moderate Resolution Imaging Spectroradiometer (MODIS) Thermal Anomalies/Fire product (MOD/MYD14A1) fire counts in croplands.

3. Results and discussion

3.1. Modified combustion efficiency (MCE) and pollutants emission

Flaming and smoldering combustion can be differentiated by their CE, i.e. the fraction of carbon in fuel emitted in the form of CO_2 (Ward and Hardy, 1991). When only CO_2 and CO were measured, the MCE was reported (e.g. Kim Oanh et al., 2011; McMeeking et al., 2009; Ward and Radke, 1993):

$$MCE = \frac{\Delta[CO_2]}{\Delta[CO] + \Delta[CO_2]} \qquad (5)$$

where $\Delta[CO_2]$ and $\Delta[CO]$ are the excess molar mixing ratios of CO_2

and CO, respectively. The MCE is usually close to 1 during the flaming phase due to near-stoichiometric combustion. For the smoldering phase, the MCE is reported to be 0.7–0.9 (Hao and Ward, 1993; Reid et al., 2005; Yokelson et al., 1996). In this study, the MCE with natural fuels (i.e. without rehydration) was higher than 0.9, suggesting the dominance of the flaming phase. Fig. 1 shows the time series of MCE and the concentrations of CO_2, CO and $PM_{2.5}$, emitted from a unit mass of wheat straw (Fig. 1a), rice straw (Fig. 1b) and corn stalk (Fig. 1c). The concentrations increased rapidly after ignition (0 s), with a more pronounced increase in CO_2. The MCE gradually decreased but remained above 0.9 (flaming), except for the final phase when the flame extinguished, resulting in a slow increase in CO. CO_2 concentrations reached a peak first, followed by CO and $PM_{2.5}$. After the fire extinguished, pollutant concentrations decreased gradually to the background levels.

3.2. EFs of pollutants

The average EFs from five to nine tests per crop are shown in Table 1. Average CO_2 EFs ranged from 1311 ± 181 g kg^{-1} for wheat
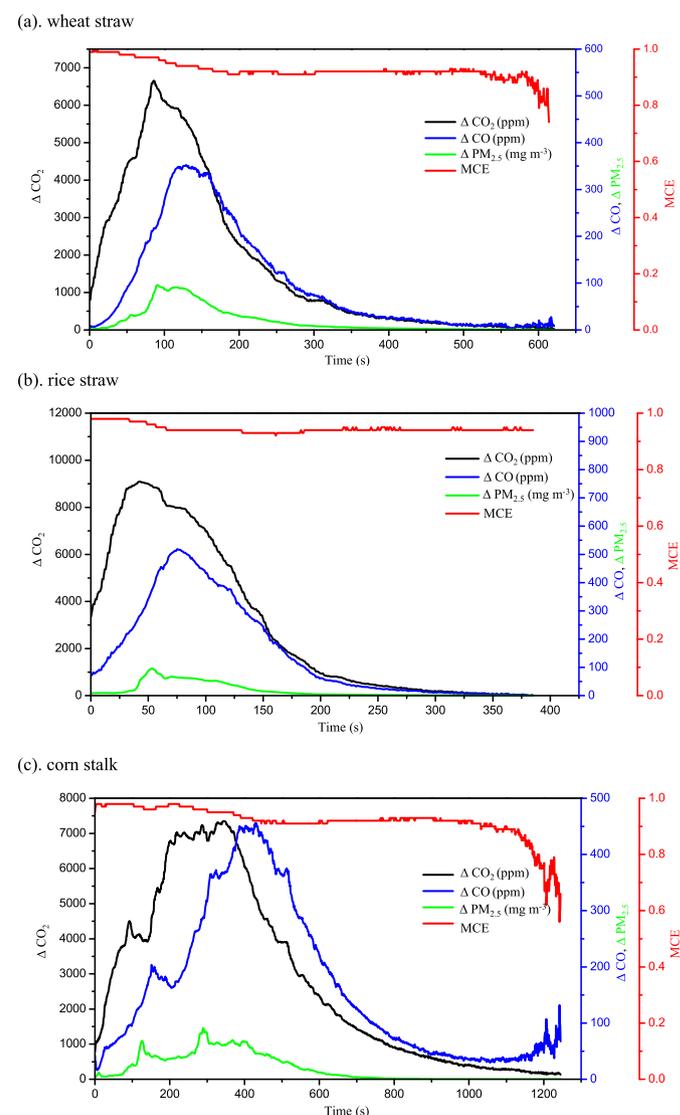

Fig. 1. Time series of modified combustion efficiency (MCE), $PM_{2.5}$ mass, CO_2, and CO concentrations during combustion per unit mass of: (a) wheat straw, (b) rice straw, and (c) corn stalk. Time resolution is 1 s.

straw, to 1393 ± 91 g kg^{-1} for rice straw. The CO EFs were 47.9 ± 13.5 g kg^{-1} for wheat straw, 57.2 ± 26.0 g kg^{-1} for rice straw. These levels are in reasonable agreement with published values, which are mostly in the range of 911–1558 g kg^{-1} for CO_2, and 53–141 g kg^{-1} for CO (Cao et al., 2008; Dhammapala et al., 2006; Kim Oanh et al., 2011; Li et al., 2007; Miura and Kanno, 1997; Zhang et al., 2008; See Table S1). Rice straw yielded the highest EFs for CO_2 and CO, despite having the lowest C content (~43%, lower than those of wheat straw and corn stalk, Table S2). The differences in the EFs could be attributed to the fuel properties, such as bulk densities, size and moisture, which could affect burning conditions, and further affect the EFs (ASI, 2003; Chen et al., 2010; McMeeking et al., 2009).

The EFs of $PM_{2.5}$ were similar for wheat straw and corn stalk, but differed from those of rice straw, with a range of 8.5–12.0 g kg^{-1} for the three crop residues. The average $PM_{2.5}$ EF for rice straw was 8.5 ± 6.7 g kg^{-1}, lower than the 12.95 g kg^{-1} reported by Hays et al. (2005), and the 15.4 g kg^{-1} by Watson et al. (2011), but comparable to the 8.3 ± 2.7 g kg^{-1} reported by Kim Oanh et al. (2011). The average EF for corn stalk of 12.0 ± 5.4 g kg^{-1} was also comparable to the 11.7 ± 1.0 g kg^{-1} reported by Li et al. (2007). However, the $PM_{2.5}$ EFs in Table 1 are a factor of 2–3 higher than the 3.9 g kg^{-1} for agricultural residues reported by Andreae and Merlet (2001).

The OC and EC EFs were 3.3–6.3 and 0.2–0.3 g kg^{-1}, respectively, which was consistent with values reported by Andreae and Merlet (2001), i.e. 3.3 and 0.69 g kg^{-1} for OC and EC, respectively. These values fall within the range (0.29–8.94 g kg^{-1} for OC, and 0.17–1.2 g kg^{-1} for EC) reported for similar fuels with comparable moisture content (e.g. Cao et al., 2008; Dhammapala et al., 2006; Hays et al., 2005; Li et al., 2007; Sahai et al., 2007; Turn et al., 1997; See Table S1).

The carbon emissions were dominated by CO_2, which on average accounted for 74%, 85%, and 81% of carbon in wheat, rice and corn, respectively. Emissions of CO accounted for 4%–5% of the carbon, with OC accounting for 0.7–1.7% and EC accounting for 0.04–0.07%. The remaining carbon was either emitted as trace gases, such as CH_4 and C2–4 hydrocarbons, or remained in the ash.

3.3. The OC/EC ratio, and carbon fractions

The OC/EC ratio can be used to distinguish between different combustion sources (Novakov et al., 2000). The abundance of the carbon fraction is shown in Fig. 2 and the OC/EC ratios are shown in Table 2. In this study, the OC/EC ratios from open burning of wheat straw, rice straw and corn stalk were 24.7 ± 13.4, 15.6 ± 5.9 and 21.4 ± 6.0, respectively. These ratios were two to ten times higher than those reported for similar fuels combusted in household stoves (Cao et al., 2008; Li et al., 2009). This could be explained by a more complete combustion of household biofuels leading to a higher EC emission. A factor of 3 higher OC/EC ratio (52.6) for open
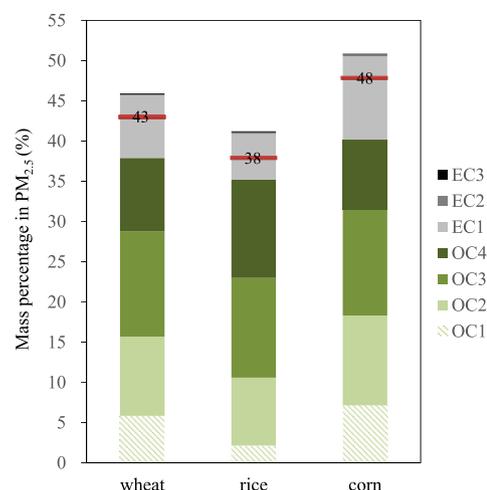

Fig. 2. Mass percentage of thermally resolved carbon fractions in $PM_{2.5}$ following IMPROVE_A protocol (Chow et al., 2007). OC1 to OC4 are OC evolved in 100% helium atmosphere, EC1 to EC3 are EC evolved in 98% helium/2% oxygen atmosphere. The numbers on the red bar indicate the mass percentage of OC. Pyrolyzed OC (the gray area below the red bar) is the difference between OC and OC1 + OC2 + OC3 + OC4. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Comparison of OC/EC ratios from this study and values reported in the literature.

	This study	Literature reported	
	Open burning	Open burning	Burning in household stove
Wheat straw	24.7 ± 13.4*		6.3–12.5[a],**,8.2[b],**
Rice straw	15.6 ± 5.9*	52.6[c],***	4.1[b],**
Corn stalk	21.4 ± 6.0*	11.2[d],**	4–4.8[a],**, 10 ± 12.5[a],**, 2.4[b],**

Data are from: a. Li et al., 2009; b. Cao et al., 2008; c. Hays et al., 2005; d. Li et al., 2007. The asterisks (*) indicate the different protocals used to determine OC and EC: IMPROVE_A* used in this study, IMPROVE** (Chow et al., 1993), and NIOSH*** (Birch and Cary, 1996).
Comparison of different protocols (IMPROVE and NIOSH) has shown that the difference in OC/EC ratio can be up to over 3 times (Chow et al., 2001). The reflectance and transmittance corrections can cause the biggest OC/EC ratio difference (up to 2.5 times). This might be the reason for the highest OC/EC ratio measured with the NIOSH method that applies the transmittance corrections. The difference in OC/EC ratio between IMPROVE and IMPROVE_A can be up to 2 times (Chow et al., 2007).

burning of rice straw was reported by Hays et al. (2005), which was attributed to its prolonged smoldering combustion.

Table S4 shows that OC accounted for 38%–49% of the $PM_{2.5}$ mass, with minor contributions (2%–3%) from EC. These levels are comparable to those reported by Li et al. (2007), in which OC accounted for 38.5 ± 16.0% and 33.6 ± 13.8% of the $PM_{2.5}$ mass from open burning of wheat straw and corn stalk, with the EC fraction

Table 1
EFs from open burning of crop residue with the corresponding MCE.

	EFs[a] (g·kg^{-1})					MCE[b]
	CO_2	CO	$PM_{2.5}$	OC	EC	
Wheat straw (n = 9)	1311 ± 181	47.9 ± 13.5	11.4 ± 4.9	5.1 ± 3.0	0.24 ± 0.12	0.91 ± 0.03
Rice straw (n = 7)	1393 ± 91	57.2 ± 26.0	8.5 ± 6.7	3.3 ± 2.8	0.21 ± 0.13	0.93 ± 0.03
Corn stalk (n = 5)	1363 ± 154	52.1 ± 17.7	12.0 ± 5.4	6.3 ± 3.6	0.28 ± 0.09	0.93 ± 0.02
Average	1351 ± 147	52.0 ± 18.9	10.6 ± 5.6	4.8 ± 3.1	0.24 ± 0.12	0.92 ± 0.03

[a] Dry fuel mass basis. The results are given as average EF and standard deviation.
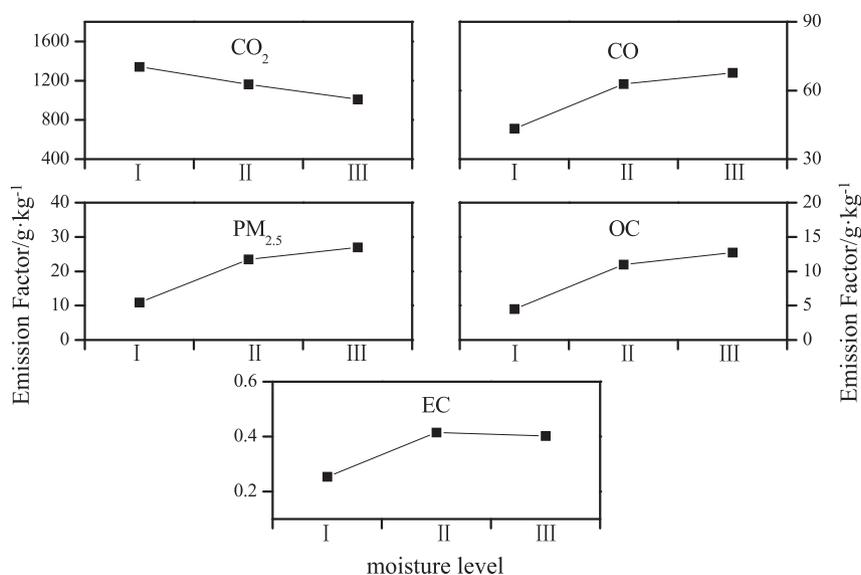[b] MCE, modified combustion efficiency.

Fig. 3. Emission factors (EFs) as a function of fuel moisture level (moisture contents are 10%, 28% and 50% of dry fuel mass for level I, II and III, respectively), based on the data presented in Table S5.

accounting for 7.7 ± 4.0% and 3.0 ± 0.7%, respectively. Seven carbon subfractions (OC1, OC2, OC3, OC4, EC1, EC2 and EC3) have been used in the source apportionment of carbonaceous aerosols, with different source types producing distinctly different abuandances of each carbon fraction (Cao et al., 2006, 2005; Chow et al., 2004; Han et al., 2010). All samples in this study were dominated by OC2, OC3 and OC4 (evaluated from 280 °C to 580 °C), as shown in Fig. 2. OC2 and OC3 represent low-volatility organic compounds with increasing molecular weights. The OC4 fraction is likely a mixture of high and/or polar molecular-weight organic compounds (Grabowsky et al., 2011; Joseph et al., 2012). Pyrolyzed OC is reported to be associated with water-soluble OC (Yang and Yu, 2002). EC was dominated by the EC1, with a very low EC2 fraction (i.e. 740 °C), as EC2 is most commonly found in diesel vehicle emissions (Han et al., 2007; Watson et al., 1994). These results are comparable with data reported by Chen et al. (2007).

3.4. The effect of moisture on carbon emissions

Wheat straws were prepared at different moisture levels (I, II and III). Level I was aired-dried fuel (~10% moisture of dry mass). Known amounts of water were added to known amount of fuels to achieve moisture contents of 28% (Level II) or 50% (Level III) of the dry mass. The Level II and III moisture levels were intended to simulate natural crop residues with high moisture content.

Dry and wet wheat straw resulted in different fire behaviors. Dry fuels ignited easily within 2 s, and the flame spread quickly with little ash remaining after combustion. The time required to ignite the wet fuel was much longer, because additional heat was required to vaporize the water before ignition. Wet fuels also left more unburnt residue than dry fuels. The MCE for the dry fuels was higher than both moisture levels of the wet fuels. Table S5 gives the average EFs at different moisture levels. As shown in Fig. 3, fuel

moisture decreased the CO_2 EF but increased the EFs of incomplete combustion products (e.g. CO, $PM_{2.5}$ and OC). This may be caused by the enhanced smoldering burn of wet fuels. The increased OC emissions due to an increase in moisture (from Level I to II, and from Level II to III) accounted for ~50% of the increase in $PM_{2.5}$ emissions. Hence, the increased emission of $PM_{2.5}$ could partly be attributed to the increased OC emission. Even though the EFs of EC did not decrease with increased moisture content (Table S5), the EC fraction in total carbon (TC) displayed a decreasing trend with increasing moisture content: 0.05, 0.04 and 0.03, respectively. This corresponds to EC being generated from a flaming phase that is intensified when the fuel is dry (Lobert and Warnatz, 1993).

Chen et al. (2010) also found increased EFs of CO, OC and $PM_{2.5}$ with increased fuel moisture contents in bitterbrush leaves. EFs increased from 112.6 to 215.6 g kg^{-1} for CO, from 9.1 to 393.6 g kg^{-1} for OC, and from 27.1 to 768.7 g kg^{-1} for $PM_{2.5}$, while moisture increased from <5% to as high as 84%. Hayashi et al. (2014) also reported that an increase in residue moistness enhanced the emissions of CO and OC. The EFs of CO increased from 27.2 to 59.4 g kg^{-1} for rice straw, from 41.8 to 77.3 g kg^{-1} for wheat straw, and from 46.9 to 93.3 g kg^{-1} for barley straw. The EFs of OC increased from 1.0 to 4.5 g kg^{-1}, from 9.3 to 13.5 g kg^{-1}, and from 1.8 to 3.0 g kg^{-1} for rice straw, wheat straw and barley straw, respectively, when the moisture content increased from ~10% to 20%. The differences in the EFs for fuel with different moisture levels suggests that the effect of moisture content should be considered when estimating emissions from for open burning of biomass.

3.5. Estimates of carbonaceous emissions from open burning of crop residues

Emissions from open burning of crop residues were estimated by the product of the burned mass (Table S6, estimated from Equation (4)) and the corresponding EFs measured in this study (Table S7). In 2008, the total amounts of agricultural crop residue burned in the field were 24.1, 34.5, and 9.3 Tg for wheat straw, rice straw and corn stalk, respectively. In China, these three crops account for nearly 80% of the total crop residue burned in the field.

Field burning emissions were estimated to be 120 Tg CO_2, 4.6 Tg CO, 0.88 Tg $PM_{2.5}$, 0.39 Tg OC and 0.02 Tg EC (Table S8). The

Table 3
Comparison of the emissions (Tg·yr^{-1}) from open burning of crop residues.

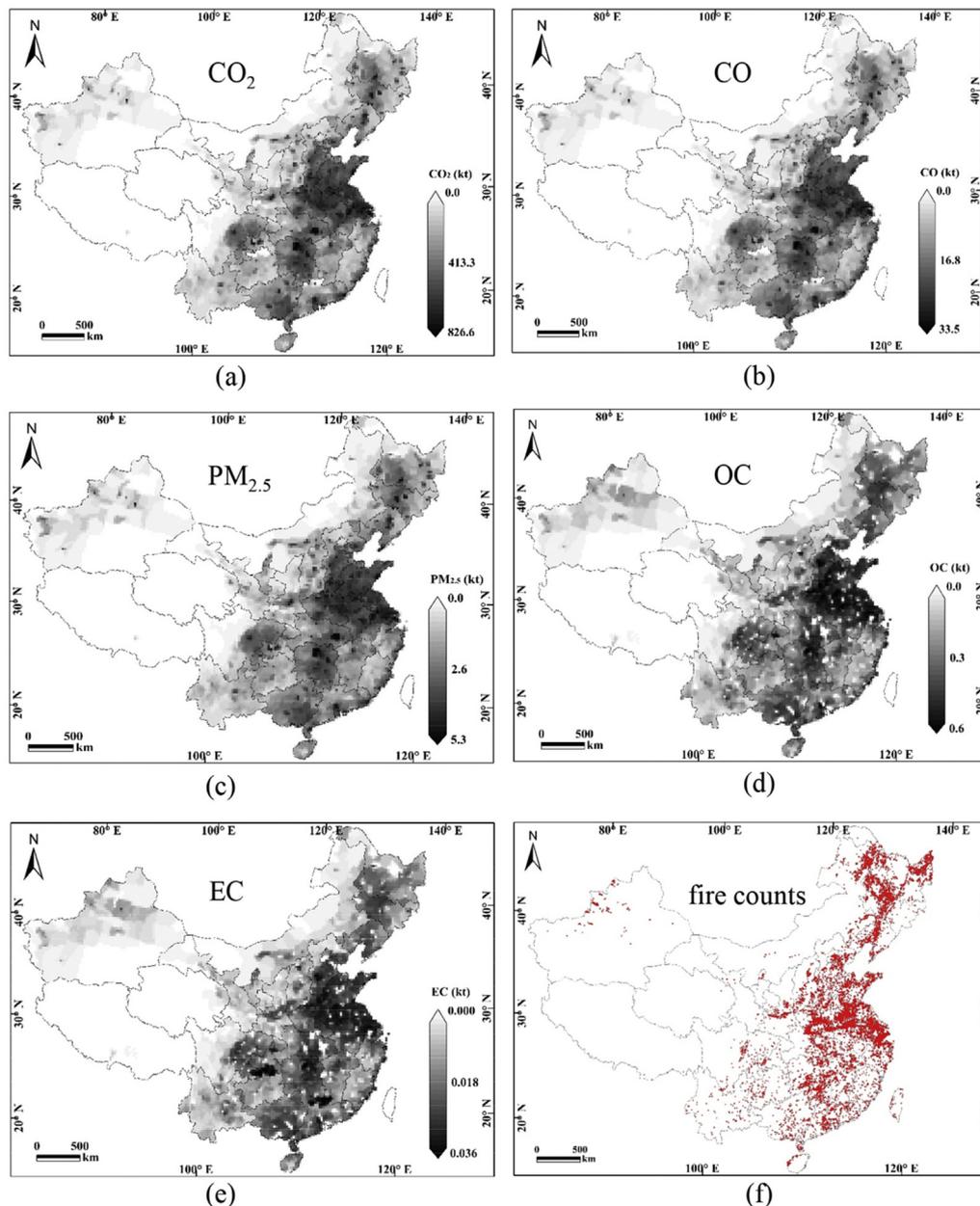|	Year	CO_2	CO	$PM_{2.5}$	OC	EC
This study	2008	120	4.6	0.88	0.39	0.02
Streets et al. (2003)	2000	167	10.0		0.36	0.08

Fig. 4. Spatial distribution of carbonaceous pollutants and agricultural fire counts in 2008: (a) CO_2 emissions, (b) CO emissions, (c) $PM_{2.5}$ emissions, (d) OC emissions, (e) EC emissions, and (f) the distribution of fire counts.

emissions of CO_2, CO and EC estimated in this study for 2008 were 72%, 46% and 25%, respectively, of those estimated by Streets et al. (2003) for the mid-1990s (Table 3). The lower emissions found in this study are caused by both the differences in EFs and the decrease in the practice of open burning of crop residues from the mid-1990s to 2008 (Table S7). Streets et al. (2003) adopted the EFs from Andreae and Merlet (2001), which did not include measurements from China. In addition, Streets et al. (2003) reported the amount of crop residue burned in the field was 110 Tg for the mid-1990s, while this study estimated 86 Tg for 2008. The decrease in the amount of fuel burned was attributed to a series of burning bans implemented in recent years.

A total of 22,586 fire counts were recorded in China in 2008. Fig. 4f shows the distribution of these fire counts. Open agricultural fires were mainly concentrated in Anhui, Henan, Heilongjiang, Jiangsu and Shandong Provinces, each of which had >1000 fire counts, accounting for 11.6%, 10.3%, 11.8% and 9.2% of the total, respectively. Fire counts were sparse in the western part of China, such as the Qinghai-Tibet Plateau (ten fire counts).

Emissions of CO_2, CO, $PM_{2.5}$, OC and EC in 2008 were allocated to $1° \times 1°$ resolution using the product of fire counts and agricultural land area as a proxy (Fig. 4a–e). The spatial and temporal distribution of emissions is consistent with that of the fire counts (Fig. 4f). Higher emissions were found in Eastern and Northeastern China, e.g. Jiangsu, Henan, Anhui and Shandong Provinces, all of which had high rural population densities and were experiencing rapid economic development (NBS, 2009). The lowest emissions were found in Inner Mongolia and western China, with low population densities and levels of economic activity. As shown in Fig. 5, the fire counts were mainly concentrated in the period from March to June, with a peak in June, followed by March and Octorber, and with the lowest records from November to Januray. The temporal
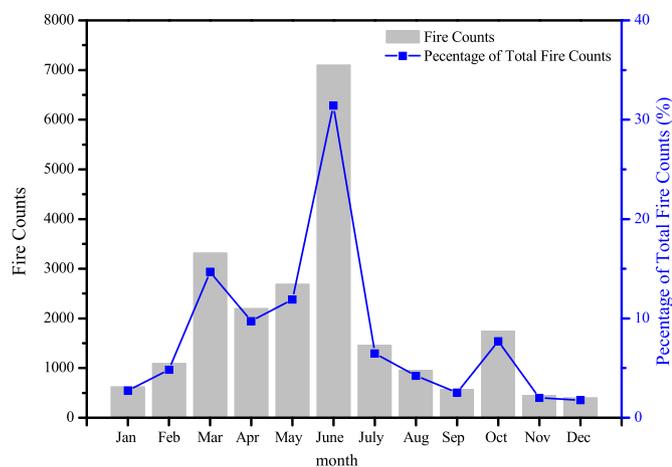
Fig. 5. Monthly variation of the fire counts in China in 2008. Data are from the Moderate Resolution Imaging Spectroradiometer (MODIS) Thermal Anomalies/Fire product (MOD/MYD14A1) fire counts in croplands.

distribution of emissions followed the same pattern as the agricultural sowing and harvesting times (CAAS, 1984; Huang et al., 2012b; Yan et al., 2006).

The emission uncertainty was related to the amount of crop residue burned in the field, namely the product of the yield of crop, residue-to-crop ratio, dry fraction of crop residue, proportion of crop residue burned in the field and burn efficiency (see details in Equation (4)) and the EFs (Streets et al., 2003). Given the large statistical uncertainties assumed to be associated with such datasets, expert judgment was used to estimate the uncertainty (20%) in the amount of crop residue burned in the field (Zhang et al., 2013). Uncertainties in the EFs were taken from the measured data and assumed to be normally distributed (Streets et al., 2003). The uncertainties in the amount of crop residue burned in the field and the EFs, which are independent random variables, were combined in quadrature (Streets et al., 2003). This caused the uncertainties in the emission estimates, measured as 95% confidence intervals, to be 87% for CO_2, 148% for CO, 215% for $PM_{2.5}$, 249% for OC and 188% for EC.

4. Conclusions

The EFs of trace gases (CO_2 and CO) and particles ($PM_{2.5}$, OC and EC) from open burning of agricultural crop residue in China were investigated using a combustion chamber. The OC/EC ratios from open burning of major crop residue (i.e. wheat straw, rice straw and corn stalk) were quantified, and can be applied to source identification; however, the results require careful consideration due to the variable burning conditions for the same fuel types. High temperature OC fractions (i.e. OC2, OC3, OC4) and low temperature EC fractions (i.e. EC1) are the most abundant fractions in combustion emissions. The effect of fuel moisture on emissions was investigated, with a decrease in CO_2 and an increase in CO, $PM_{2.5}$, and OC emissions found when there was a high moisture content. This suggests that the impact of fuel moisture content should be considered when estimating EFs of biomass burning. Emission inventories from open burning of crop residues in China for 2008, with $1° \times 1°$ resolution, were compiled. Total emissions were estimated to be 120 Tg CO_2, 4.6 Tg CO, 0.88 Tg $PM_{2.5}$, 0.39 Tg OC and 0.02 Tg EC. Jiangsu, Henan, Hunan, Anhui, and Shandong Provinces produced the highest crop-burning emissions. The temporal distribution of emissions followed the agricultural burn season, with the highest values in June.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.05.007.

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