New field-based agricultural biomass burning trace gas, PM$_{2.5}$, and black carbon emission ratios and factors measured in situ at crop residue fires in Eastern China

Tianran Zhang $^a$, Martin J. Wooster $^{a,b,*}$, David C. Green $^c$, Bruce Main $^a$

$^a$ King’s College London, Earth and Environmental Dynamics Research Group, Department of Geography, Strand, London, WC2R 2LS, UK
$^b$ NERC National Centre for Earth Observation (NCEO), UK
$^c$ King’s College London, Environmental Research Group, MRC-PHE Centre for Environment and Health, London, SE1 9NH, UK

HIGHLIGHTS

- A new sampling system was designed to measure CO, CO$_2$, PM$_{2.5}$ and black carbon (BC) in situ during field based fires.
- A linear mixing model was generated to quantify the combustion phase contribution to the measurement of each species.
- New ‘fire averaged’ CO, CO$_2$, PM$_{2.5}$ and BC emission factors are reported for Chinese agricultural fires in different fuel types.
- Intense flaming processes with visible clouds of soot was found for the rapeseed residue bonfires in particular.

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ABSTRACT

Despite policy attempts to limit or prevent agricultural burning, its use to remove crop residues either immediately after harvest (e.g. field burning of wheat stubble) or after subsequent crop processing (e.g. “bonfires” of rice straw and rapeseed residues) appears to remain widespread across parts of China. Emission factors for these types of small but highly numerous fire are therefore required to fully assess their impact on atmospheric composition and air pollution. Here we describe the design and deployment of a new smoke measurement system for the close-range sampling of key gases and particles within smoke from crop residue fires, using it to assess instantaneous mixing ratios of CO and CO$_2$ and mass concentrations of black carbon (BC) and PM$_{2.5}$ from wheat stubble, rice straw, and rapeseed residue fires. Using data of our new smoke sampling system, we find a strong linear correlation between the PM$_{2.5}$ mass and BC, with very high PM$_{2.5}$ to BC emission ratios found in the smouldering phase (up to 80.7 mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$) compared to the flaming phase (2.0 mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$). We conclude that the contribution of BC to PM$_{2.5}$ mass was as high as 50% in the flaming phase of some burns, whilst during smouldering it sometimes decreased to little over one percent. A linear mixing model is used to quantify the relative contribution of each combustion phase to the overall measured smoke composition, and we find that flaming combustion dominated the total emission of most species assessed. Using time series of trace gas concentrations from different fire cases, we calculated ‘fire integrated’ trace gas emission factors (EFs) for wheat, rice and rapeseed residue burns as 1739 ± 19 g kg$^{-1}$, 1761 ± 30 g kg$^{-1}$ and 1704 ± 27 g kg$^{-1}$ respectively for CO$_2$, and 60 ± 12 g kg$^{-1}$, 47 ± 19 g kg$^{-1}$ and 82 ± 17 g kg$^{-1}$ respectively for CO. Where comparisons were possible, our EFs agreed well with those derived via a simultaneously-deployed open path Fourier transform infrared (OP-FTIR) spectrometer. These EFs, and the linear best fit relationships between both PM$_{2.5}$ and BC mass and the CO$_2$ and CO measurements, were used to generate particulate EFs, which varied over the 5.8 –20.3 g kg$^{-1}$ and 0.25 –2.89 g kg$^{-1}$ range respectively. We note a particularly high 2.89 g kg$^{-1}$ BC emission factor for the rapeseed bonfires, reflective of intense flaming combustion that gave off visible clouds of soot. These field-measured EFs offer a different perspective than is obtained when burning in laboratory combustion chambers, and are suitable for combining with landscape-scale fuel consumption estimates to provide atmospheric modelling inputs of emissions from these types of crop residue fires.

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1. Introduction

1.1. Agricultural residue burning

Agricultural residues (sometimes called agricultural waste) represent the by-products of crop production, for example the wheat stubble remaining after harvest, the rice straw cut at grain harvest, or the rapeseed material remaining after harvest and pressing. Methods to remove or dispose of these residues prior to the next harvest include their use as mulch for the succeeding crop, a substrate for composting, fuel for biogas or power generation, and use as animal feed or bedding (Ponnamperuma, 1984). However, the viability of these uses depend on local circumstances, and in many still developing economies agricultural residues are often removed via in situ burning, which in areas without well-developed large scale agricultural mechanisation is generally the quickest, simplest and cheapest approach, and also possibly provides some nutrients back into the soil prior to the next planting (Jiang et al., 2012; Smith et al., 2007). Though each individual crop residue burn may be quite limited in area, their widespread nature across extremely high numbers of fields worldwide means that such fires actually contribute significantly to the overall global landscape-scale burning totals (Akagi et al., 2011; Andreae and Merlet, 2001; Randerson et al., 2012), Korontzi et al. (2006) for example estimated that agricultural fires may constitute 30–40% of all fire detections made using the MODIS burned area products, though the true amount is highly uncertain since many of the individual agricultural burns maybe too small to detect using this particular Earth observation approach (Randerson et al., 2012). Smoke emissions from these agricultural fires have significant impacts however, particularly in areas such as East Asia where such burning appears extremely commonplace (Streets et al., 2003).

China has the largest agricultural enterprise worldwide (Frolking et al., 1999) and Xiao et al. (2003) estimate around 1.4 million km$^2$ of the country is given over to crop production. Until recently, crop residues have been the second largest industrial waste product produced in China (Qu et al., 2014). Whilst field burning of these residues has been largely forbidden in China since the late 1990’s, and there are state-sponsored efforts to collect and burn the material in power stations or otherwise recycle it, much of the material is still burned in situ. Indeed, such field-based burning of crop residues remains extremely widespread across large parts of China (Huang et al., 2012; Zhang et al., 2008), Streets et al. (2003) used total crop production figures to estimate that perhaps 110 million tonnes of agricultural residue is burned annually in China. This represents around 60% of the total biomass burned in the country (the remainder being primarily grassland and forest fires), and around half of all the agricultural burning believed to occur across Asia. However, all these figures remain very tentative estimates, due to uncertainties in the quantities of dry matter left after harvest, and the relatively poor current understanding of how much residue material is burnt in the field per unit of dry matter residue produced via the different agricultural practices (since, as stated above, some residues are used for other purposes). Whilst very accurate assessments of overall agricultural biomass burning totals may remain elusive therefore, inventories based on satellite remote sensing are continually improving (van der Werf et al., 2010) and it is clear that China remains one of the countries in which agricultural burning is most widespread.

The majority of China’s agriculture is located in Eastern China, where the vast majority of crop residue burning also apparently occurs (Huang et al., 2012; Streets et al., 2003). Merged satellite and ground based aerosol optical depth (AOD) data show that Henan, Jiangsu and Anhui provinces are the three main sources of smoke soon after the spring harvest (e.g. Huang et al., 2012; Xue et al., 2014, Fig. 1). In these areas, most fields support at least two crops per year, for example with wheat being grown over winter, harvested in June and the stubble often burned before the fields are rapidly flooded via irrigation networks and rice is planted. The rice is harvested in October, and the fields are then drained, the rice straw often burned, and the fields prepared again for wheat (Huang et al., 2012). The intensity of this agricultural cycle, the difficulties and costs associated with crop residue collection in the many non-mechanised farming areas, the lack of other significant uses for certain of the residues types in many parts of the country, together with a sometimes unclear overall management plan to guide the large-scale alternative crop residue utilisation, leads to many farmers burning the residues in situ, as demonstrated in Fig. 1 (Qu et al., 2014).

1.2. Agricultural residue fire emissions

Agricultural residue burning releases smoke containing a wide variety of trace gases (e.g. CO$_2$, CO, CH$_4$, NH$_3$ and NO$_x$) along with BC and organic carbon (OC) aerosols. These can have significant environmental effects both locally and at large distances downstream of the fires, often affecting densely populated urban areas well outside of the agricultural areas themselves (Chan and Yao, 2008; Zhang et al., 2011). Simulation modelling of emissions transport in the Yangtze River Delta region attributed up to 37% of PM$_{2.5}$, 70% of OC and 61% of BC to the smoke from agricultural residue fires in neighbouring provinces, hundreds of km away (Cheng et al., 2014), and in Beijing for example, severe episodes of crop residue burning are estimated to contribute perhaps 50% of the OC aerosols making up the city-wide haze (Duan et al., 2004), worsening the existing air quality problems (Li et al., 2010; Du et al., 2011). There remains, however, an increasing need to better understand the exact gaseous and aerosol species makeup of smoke emitted from crop burning fires, so that their contributions can be better quantified in emissions inventories, and such impacts better assessed.

To estimate the total emissions of each smoke constituent, estimates of crop residue fuel consumption must be multiplied by an emissions factor (EF; g kg$^{-1}$) for each emitted species, representing the amount of that species emitted per unit of dry fuel burned (Andreae and Merlet, 2001). As with other biomass fires, the EFs of crop residue burns most likely depend on the physical properties of the fuel (e.g. packing density, fuel diameter, moisture content) and the fire characteristics (e.g. the relative proportions of flaming or smouldering phase combustion) (Andreae and Merlet, 2001; van der Werf et al., 2010; Wooster et al. 2011). Current knowledge regarding agricultural residue burning emissions factors has primarily been based on laboratory studies (e.g. Andreae and Merlet, 2001; Zhang et al., 2008), where fire behaviour can be somewhat different to those of real landscape-scale fires (Delmas et al. 1995; Wooster et al., 2011). Furthermore, field-based EFs measured in one region, for example a largely mechanized harvesting area in Mexico, may differ markedly from those appropriate to the more manually farmed areas in another country, even if the actual crop type (e.g. wheat) is the same (Akagi et al., 2011). Due to their major impact on air quality, there is a special concern on emitted particles, including the amount of black carbon as opposed to other aerosols (Cheng and Lin, 2013). Particulate emission from fires appears quite dependent on the amount of flaming and smouldering combustion occurring (Reid et al., 2005), so field measurements of emitted particles should ideally be performed in parallel with CO and CO$_2$ measurements in order to better quantify particulate emission factors during different fire phases (in which the ratio of these two key gases can vary markedly).
The work described here reports our recent work in developing and deploying a field-based smoke emissions measurement approach in eastern China, using this to assess the trace gas and particulate makeup, and ultimately the emissions factors, of smoke from the burning of wheat stubble, rice straw, and rape-seed residues, three of the most frequently burned crop residues in China. We compare results to simultaneous measurements obtained from an open path Fourier transform infrared (OP-FTIR) spectrometer, first used to derive such EFs in savannah regions (Griffith et al., 1991; Wooster et al., 2011). To our knowledge this is the first time these approaches have been used together on agricultural residue fires, and if proved viable such field-derived datasets representative of real in situ burning conditions can be expanded to other areas of agricultural burning.

Fig. 1. Fire activity in China during the period of the fieldwork, with the sites close to the cities of Changzhou and Tongling marked. (a) Aqua MODIS true colour composite of part of eastern China taken on 11 June 2014, with MOD14/MYD14 Terra and Aqua active fire detections of that day overlain in red and the fieldwork sites circled (Giglio et al., 2003). Smoke from the fires can be clearly seen in this image, which is adapted from the NASA Worldview system (b). Distribution of actively burning fires detected across China throughout June 2013, as detected by the same MODIS active fire products, and with the area imaged in (a) outlined along with the two fieldwork sites. The widespread nature of burning in both the fieldwork area and throughout much of China at this time is readily apparent. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)
2. Methodology

2.1. Sampling box design, build and test

For this work, we designed and deployed a new smoke sampling system for the close range, in situ measurement of the mixing ratios of CO and CO2 and the mass and BC content of PM2.5 in smoke from agricultural fires. The aim was that these measurements could then be used to calculate the emission ratios (ERs) and EFs of these species, disaggregated by combustion phase (flaming/smouldering), and also these could be combined to deliver a ‘fire integrated’ EF measure appropriate for the entire burn and for use with measures of fuel consumption to provide new estimates of the total emissions released (e.g. Andreae and Merlet, 2001; Wooster et al., 2011). Details of sampling system design and test are presented in the Supporting Information, and summarized below.

A single inlet design using a PM2.5 size selective impaction inlet (BGI miniPM® inlet 5011, 5 l min⁻¹) provided both gas and aerosol samples to a range of different instruments all housed in a wheeled peli case (see Fig. 2). A flow splitter (TSI 3708) isokinetically divided the airstream and aerosols into three pathways. Pathway 1 was drawn by a TSI Dustrak; and the eluent flow, now particle-free, was used to provide the CO and CO2 gas sensors with an ambient sample. Pathway 2 was drawn by a Casella Apex Pro pump; and PM2.5 then collected on a filter. Pathway 3 was drawn by a combination of a Casella Apex pump and a microAeth AE51 (Cheng and Lin, 2013) to measure black carbon.

Electrochemical and NDIR sensors are typically characterised by non-zero response ‘lag’ times, generally specified via a T90 metric (Roberts et al., 2012), and these details are provided in the Supporting Information. To minimise measurement impacts from the combination of lag times and the rapidly changing trace gas mixing ratios experienced during in situ smoke plume measurements (Reid et al., 2005), the outputs from the gas sensors were averaged over 20s for trace gas emission ratio (ER) derivation. This averaging period was further increased to 120s when comparing the gas and aerosol measurements, and such averaging is commonly used in plume investigations when relying on different instruments to target diverse species whose concentrations will later be used to derive emissions ratios (e.g. Reid and Hobbs (1998); Roberts et al., 2014).

2.2. Sampling approach

Fieldwork took place in Eastern China in June 2014, coinciding with the main harvest and burning time in this part of China (Fig. 1a), which the MODIS Active Fire product (Giglio et al., 2003) confirms (Fig. 1b). Smoke emissions from in situ burning were measured in four different fields close to the two cities marked in Fig. 1, Changzhou City (31.75°N, 121.11°E) and Tongling City (30.84°N, 117.65°E). Wheat, rice and rapeseed residues were used, burned in their most common way (spreading fire for wheat and bonfires for the other two fuels; Fig. 3). Each burn took 6–30 min to complete, depending on the field size and shape, fuel load, and wind velocity (Table 1). Though wheat is normally burned as stubble in spreading fires, samples of wheat stubble of ~5 kg mass were also burned as a bonfire to help assess the specific emissions related to the flaming and smouldering phases of its combustion (see Table 1, Fire 3a and Fire 3b).

During the spreading fires, smoke was mostly advected horizontally, allowing the sampling system described in Section 2.1 to appropriately capture the ground-level plume. For the bonfires, the inlet of the sampling box was fit into one end of a 100 mm pipe attached to a pump that drew smoke into the pipe a significant distance ahead of the sampling box inlet. The pipe inlet end was linked to a >5 m long lightweight pole that was easily controlled to allow the pipe to capture smoke from the vertically rising smoke (Fig. 3b).

A portable MIDAC open-path Fourier transform infrared (OP-FTIR) spectrometer and IR emitting lamp was deployed co-incident with the smoke sampling system on some of the fires, in order provide comparison trace gas assessments based on the methods described in Wooster et al. (2011). Further details of all measurement approaches employed are provided in the Supporting Information.

![Fig. 2. Design of the smoke sampling system developed and deployed herein with (a) flow rates, and (b) completed sampling system contained in its peli case shown.](image-url)
2.3. Emission factor calculation methodology

The EFs (g kg\(^{-1}\)) of the trace gases present in the smoke were calculated using the carbon mass balance method used by Yokelson et al. (1999) and many others:

\[
EF_x = \frac{1000 F_c \times MM_x \times C_x}{MM_C \times C_t} \tag{1}
\]

Where \(F_c\) is the mass fraction of carbon in the fuel (0.5 ± 0.05; Yokelson et al., 1999), \(MM_x\) is the molecular mass of trace gas species \(x\) (limited to CO and CO\(_2\) when considering data from the small gas sensors present in the smoke sampling system of Fig. 2, but expandable to other gases when considering the data from the FTIR system [as per Wooster et al., 2011]), \(MM_C\) is the molecular mass of carbon (0.012 kg mol\(^{-1}\)), and where \(C_x\) is the ratio of the number of moles of species \(x\) divided by the total number of moles of carbon (assessed over key emitted carbon containing species). Further details of this calculation are provided in the Supporting Materials. We also calculated the modified combustion efficiency (MCE), commonly used as an indicator of the relative magnitude of flaming and smouldering phase combustion (Ward and Radke, 1993):

\[
MCE = \frac{1}{1 + ERCO/CO_2} \tag{2}
\]

To derive the EFs of the aerosol components (\(EF_{PM2.5}\) and \(EF_{BC}\); g kg\(^{-1}\)) we developed a new approach using the EF of a reference gas and the abundance ratio of the aerosol and gas in question (\(S_{particle/gas};\) mg m\(^{-3}\) ppm\(^{-1}\)), derived from the slope of the linear best fit between the excess mass concentration measures of the aerosol species (PM\(_{2.5}\) or BC) and the excess mixing ratio of the reference gas (either CO\(_2\) or CO) recorded in the same sample over the same averaging period:

\[
EF_{aerosol} = a S_{aerosol/gas} EF_{gas} \tag{3}
\]

where \(a\) is a factor included for unit conversion (having the value of 0.909 ppm (mg m\(^{-3}\))\(^{-1}\) when using CO\(_2\) as the reference gas, and 0.556 ppm (mg m\(^{-3}\))\(^{-1}\) when using CO).
3. Results

3.1. Gas and aerosol measurements

The mean trace gas and aerosol abundances in the smoke recorded by the sampling system for each fire are listed in Table 1, expressed as excess measures via subtraction of the pre-fire values. The recorded excess trace gas mixing ratios, $\Delta$CO$_2$ and $\Delta$CO, varied between 138–1317 ppm and 1–89 ppm respectively, whilst the mean excess mass concentrations of PM$_{2.5}$ and BC varied between 1.1–13 mg m$^{-3}$ and 0.06–0.89 mg m$^{-3}$ respectively. Since the inlet of the sampling system was always located within 20 m of the fire emissions source, these values are directly representative of the agricultural burning, uninfluenced by any other emissions source and without any major atmospheric processing. The abundances appear significantly higher than those obtained at greater distances from the source fire (e.g. Yang et al., 2008; Zhang et al., 2013).

We use time series of measurements from two fires (Fire No. 4 and Fire No. 11) to demonstrate the performance of our smoke sampling system. In spreading wheat Fire No. 4 (Table 1), Fig. 4 indicates multiple peaks in the gas and aerosol time series, caused by the contributions of several discrete ‘plumes’ being sampled over the course of the fire (e.g. as the wind changed, the fire front spread across the field, and the sampling box was moved to keep well within the smoke). A clear difference in the width of the peaks between the gas and aerosol measurements can be seen in these time series, with the aerosol signals being noticeably sharper. As an example, several peaks can be seen before 17:14 h (local time) for all constituents, but are more distinguishable in the PM$_{2.5}$ and BC data than in the CO$_2$ and CO records. This difference is reflective of the significant lag times of the gas measurements compared to the particulate measurements, resulting from the combination of the T90 sensor response times and the placement of the gas sensors in the smoke sampling system measurement tube array (see Section 2.1 and Supporting Information). This lag effect delays the CO$_2$ and CO measurement peaks, changing their shape somewhat relative to the matching aerosol measures. For example, around the times of the multiple plumes sampled by the system in the last third of the time series, the PM$_{2.5}$ and BC data show five discrete spikes, ending around 17:25:13 h. By contrast, the CO electrochemical sensor shows a less well resolved response, with the individual plumes less discernible, whilst the faster response NDIR CO$_2$ sensor (K30) more clearly discerns at least three individual peaks. Thus the instantaneous aerosol and trace gas data cannot simply be combined as is, but rather must be time-averaged for use in ER and EF estimation, as discussed in Section 2.1. A somewhat similar approach was recently demonstrated by Roberts et al. (2014) when using different electrochemical sensors to derive emission ratios of volcanic plumes.

The second example, Fire No. 11 (piled rapeseed residue ‘bonfire’) at first showed intense flaming activity similar to that seen in Fig. 3b, and then smouldered for some time (changing its dominant combustion phase around 17:32 h local time in Fig. 5, when CO mixing ratios started to substantially increase). During the flaming phase of this burn, the modified combustion efficiency (MCE) is $\geq$ 0.95, indicating efficient and near complete combustion. The first four $\Delta$PM$_{2.5}$ measurement peaks are 39, 22, 21 and 39 mg m$^{-3}$, which each contain 7%, 10%, 12% and 6.6% of black carbon (peaks of 2.2–2.9 mg m$^{-3}$). After 17:32 h, BC abundance substantially reduces, with only a single plume exceeding 1 mg m$^{-3}$ after that time. However, PM$_{2.5}$ abundance shows increasing peak magnitudes after this time, up to 54 mg m$^{-3}$, and consequently the BC to PM$_{2.5}$ ratio of the smoke decreases to around 1% over this period. This indicates that high BC to PM$_{2.5}$ ratios are seen in the flaming stage, and generally much lower ratios characterise the smouldering phase, a finding which agrees with prior research indicating that the BC fraction of emitted aerosol differs between the phases of crop residue burns (Li et al., 2009). Reid and Hobbs (1998) report this effect more generally for biomass fires, and we find the effect to be more apparent in this crop residue bonfire (Fig. 5) than in the spreading fire (Fig. 4), since in the latter case whilst flaming combustion dominates in the moving headfire, a trailing ‘smoking zone’ is typically also present that is dominated by areas of still smouldering combustion (Wooster et al., 2011). Thus,

![Fig. 4. Time series of excess CO$_2$ and CO mixing ratio (ppmv), and PM$_{2.5}$ and BC mass concentrations (mg m$^{-3}$) for Fire No. 4, with the proportion of flaming combustion contributing to the BC mass concentrations being measured also shown (RF/[BC] from Equation 8)]. Wheat stubble was used as the fuel for this spreading fire, as shown in Fig. 3a.](image-url)
whilst the ground-level plume of a spreading fire typically contains a mix of smoke from both combustion phases (Lacaux et al., 1996; Wooster et al., 2011), the bonfire style of burning may more clearly commence with almost fully flaming combustion and end with almost solely smouldering activity.

### 3.2. Emission ratios and combustion phases

Section 3.1 has highlighted that different PM$_{2.5}$ to BC emission ratios are seen during the flaming and smouldering phases of the sampled agricultural residue fires. During the wheat residue bonfire (Fire No. 6) the abundances of BC and PM$_{2.5}$ during the flaming (Fire No. 6a) and smouldering (Fire No. 6b) phases of this fire were thus analysed individually (Fig. 6).

In both the flaming and smouldering phases (Fig. 6a and 6b respectively), we find strong positive correlations between PM$_{2.5}$ and BC. In the flaming phase, a PM$_{2.5}$ to BC mass concentration ratio of 2.0 mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$ is seen ($r = 0.97$), whilst for the smouldering phase the ratio is much higher at 80.7 mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$. The smouldering phase correlation coefficient is slightly lower ($r = 0.92$), possibly contributed to by the relative difficulty in sampling smoke from purely smouldering activity, since small pockets of flaming combustion still often exist close to the fuel surface during smouldering-dominated periods (Hays et al., 2005). This comparison of flaming and smouldering dominated burning presented in Fig. 6 nevertheless further highlights the very large difference in the emission ratio of PM$_{2.5}$ to BC for these two combustion phases, which can be also found in the

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**Fig. 6.** Linear relationship between PM$_{2.5}$ and BC mass concentrations for (a) pure flaming phase combustion (Fire No. 6a) and (b) pure smouldering phase combustion (Fire No. 6b). Fire details are listed in Table 1, and wheat stubble is the fuel in both cases, burned as a bonfire. The blue line represents the least squares linear best-fit, which is then taken as the PM$_{2.5}$ to BC emission ratio for the ‘pure’ combustion phases in this fuel type, along with the 95% confidence intervals on the slope (grey filled polygon) and on the prediction (dashed line). These slopes are thus taken as the emission ratio for wheat undergoing flaming combustion [$S_f$; mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$] and smouldering combustion [$S_s$; mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$] respectively. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)
spreading fire data shown in Fig. 4 as discussed above. Our data indicate that the contribution of BC to PM$_{2.5}$ rises high as 50% during the flaming phase, whilst during smouldering phase it can decrease to little over one percent. Prior studies have indicated that, in general, vegetation fires with more intense flaming combustion, generating higher temperatures, are more likely to be oxygen limited and can thus produce much larger amounts of soot-based (BC) aerosols than does smouldering dominated burning (Martins et al., 1998; Reid and Hobbs (1998); 2005; Chakraborty et al., 2006). Our findings imply that, even though total PM$_{2.5}$ abundances appear higher in the smouldering phase plume, most of the BC may be emitted from agricultural residue fires during the flaming phase, particularly so since in these types of fine fuels most of the fuel consumption often occurs during flaming activity when combustion rates are much higher than in the (perhaps longer duration) smouldering phase (as discussed for savannahs by e.g. Wooster et al., 2011).

Using our finding of a very significantly different PM$_{2.5}$ to BC emission ratio for flaming combustion [$S_f$, mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$] from Fig. 6a] and smouldering combustion [$S_s$, mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$] from Fig. 6b] allows us to develop a simple linear mixing model to quantify the relative amounts of each combustion phase contributing to the smoke being sampled. We assume that the ratios represented in Fig. 6a and b represent that from the pure flaming and pure smouldering phase activity respectively, and that these ratios are valid for all the wheat residue fires assessed. Details of the mixing model can be found in the Supporting Information, and are summarized below.

For both BC and PM$_{2.5}$, we assume that the total excess mass concentration measured ($\Delta M_i$; mg m$^{-3}$) is a linear combination of the instantaneously measured excess mass concentration due to flaming ($\Delta M_f$; mg m$^{-3}$) and smouldering ($\Delta M_s$; mg m$^{-3}$) phase combustion:

$$\Delta M_i(\text{PM}_{2.5}) = \Delta M_f(\text{PM}_{2.5}) + \Delta M_s(\text{PM}_{2.5})$$

and

$$\Delta M_i(\text{BC}) = \Delta M_f(\text{BC}) + \Delta M_s(\text{BC})$$

And we relate the excess mass concentration of each aerosol type produced from flaming and smouldering combustion using the emission ratios $S_f$ and $S_s$, taken from Fig. 6a and 6b:

$$\Delta M_f(\text{PM}_{2.5}) = S_f \Delta M_f(\text{BC})$$

$$\Delta M_s(\text{PM}_{2.5}) = S_s \Delta M_s(\text{BC})$$

Then, for BC, the instantaneous flaming phase fraction $R_f$ (BC) [mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$] representing (at any particular time) the proportion of total sampled BC mass that has come from flaming phase combustion [i.e. $\frac{\Delta M_f(\text{BC})}{\Delta M_f(\text{BC}) + \Delta M_s(\text{BC})}$] can be expressed as a function of four known quantities, namely the total sampled excess mass concentration of PM$_{2.5}$ and BC, $\Delta M_f(\text{PM}_{2.5})$ and $\Delta M_s(\text{BC})$ respectively, and the PM$_{2.5}$ to BC emission ratios for flaming and smouldering combustion ($S_f$ and $S_s$ respectively):

$$R_f(\text{BC}) = \frac{S_f - \frac{\Delta M_f(\text{PM}_{2.5})}{\Delta M_f(\text{BC})}}{S_f - S_s}$$

Where the term in square brackets equates to the instantaneous ratio of the excess amount of PM$_{2.5}$ and BC, which can easily be derived from the measured timeseries (e.g. those shown in Figs. 4 and 5 for Fire No. 4 and 11 respectively for example). Exactly same approach can be used to derive the PM$_{2.5}$ instantaneous flaming phase fraction, $R_f$ (PM$_{2.5}$), and also the flaming phase fractions of the gases CO and CO$_2$.

However, when analysing rice and rapeseed fires, unlike for wheat we did not directly collect samples of pure flaming and pure smouldering smoke for these fuels from which we could directly obtain the flaming and smouldering emission ratios, $S_f$ and $S_s$. However, Fig. 7 plots the excess mass concentration of PM$_{2.5}$ and BC for our spreading wheat fires, and based on the observation of clear flaming and smouldering boundaries in these data, which appear quite well characterised by the PM$_{2.5}$ to BC flaming and smouldering ERs ($S_f$ and $S_s$ respectively) derived from the wheat bonfire data shown in Fig. 6a and 6b (and plotted on Fig. 7 as red and blue lines respectively), we applied a ‘boundary detection’ approach to the spreading wheat fire measurements. The idea here is to pilot use of this approach for the derivation of $S_f$ and $S_s$, such that it can be applied in cases where obviously “pure” samples of flaming and smouldering smoke are unavailable, for example in the case of the rice and rapeseed residue burns sampled here. Based on 95% confidence intervals, the highest and lowest 2.5% of the PM$_{2.5}$ to BC ratio shown in Fig. 7 were selected, and a linear best fit applied to these ‘boundary’ data to estimate the PM$_{2.5}$ to BC emission ratios for flaming and smouldering combustion of wheat, at 1.9 mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$ and 58.1 mg m$^{-3}$ (mg m$^{-3}$)$^{-1}$ respectively (yielded with correlation coefficients ($r$) of 0.82 and 0.88 respectively; Table 2). These particulate ERs are close to those obtained via our sampling of explicit flaming and smouldering smoke (with a scaling factor of 1.3) from wheat combustion separately (i.e. those shown in Fig. 6a and 6b respectively), thus demonstrating the viability of the ‘boundary detection’ approach (See Supporting Information for more details of this comparison). The same ‘boundary detection’ approach was then applied to the rice and rapeseed residue aerosol data (Fig. 8), and was also used with the CO$_2$ and CO data of all three agricultural residue fuels (Fig. 9) to derive a flaming and smouldering phase emission ratio (ppmv/(ppmv)$^{-1}$) for each trace gas (reported in Table 2). An averaging period of 120 s was selected to compare the aerosol and trace gas data, as discussed in Section 2.1, and the derived flaming phase fractions, $R_f(x)$, of the two flaming-dominated compounds (CO$_2$ and BC) were found to show similar trends (Fig. 10).

Based on the time-series of $R_f(x)$ calculated for each sampled gas and aerosol species, the fire-integrated flaming-fraction $F(x)$ was also estimated, for each type of fire and each combustion product. For example, for wheat the fire-integrated fraction of black carbon
Table 2
Trace gas (CO/CO₂) and particulate (PM₂.₅/BC) emission ratios (ERs) for discrete flaming and smouldering phase combustion, as derived from the 95% confidence interval ‘boundary detection’ approach applied to the data of each fuel type (see Section 3.2). The correlation coefficients (r) for each linear best fit used in the calculation of the emissions ratios are also reported.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>PM₂.₅/BC ER (mg m⁻³/mg m⁻³)</th>
<th>PM₂.₅/BC r</th>
<th>CO/CO₂ ER (ppmv/ppmv⁻¹)</th>
<th>CO/CO₂ r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat</td>
<td>Flaming 1.9</td>
<td>0.82</td>
<td>0.0184</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Smouldering 58.1</td>
<td>0.88</td>
<td>0.46</td>
<td>0.98</td>
</tr>
<tr>
<td>Rice</td>
<td>Flaming 7.3</td>
<td>0.88</td>
<td>0.0043</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Smouldering 66.3</td>
<td>0.81</td>
<td>0.21</td>
<td>0.81</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>Flaming 0.50</td>
<td>0.90</td>
<td>0.0186</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>Smouldering 47.5</td>
<td>0.74</td>
<td>0.17</td>
<td>0.97</td>
</tr>
</tbody>
</table>

* Calculated from 20s averages to account for the different response times of the two trace gas sensors (Table 2).

Fig. 8. Scatterplot of PM₂.₅ and BC mass concentrations from (a) all rice, and (b) all rapeseed fires, with the PM₂.₅ to BC emission ratios for ‘pure’ flaming and ‘pure’ smouldering overlain (as derived from the 95% confidence interval method discussed in Section 3.2).

Fig. 9. Scatterplot of CO and CO₂ mixing ratio measures from (a) all wheat, (b) rice, and (c) rapeseed fires, with the CO and CO₂ emission ratios for ‘pure’ flaming and ‘pure’ smouldering overlain (as derived from the 95% confidence interval method discussed in Section 3.2).
emitted by flaming combustion was calculated as:

\[ F(BC) = \frac{\sum M_t(BC) R_f(BC)}{\sum M_t(BC)} \]  

Where \( M_t(x) \) is the mass concentration (for aerosol), or mixing ratio (ppmv) for gas, of the target species recorded over the 120 s averaging period. The corresponding fire-integrated fractional contribution of the smouldering phase to the production of the same species was then calculated as \([1 - F(x)]\). Table 3 presents the results of this calculation, where the flaming stage is confirmed to dominate in terms of BC (and CO2) production.

### 3.3. Emission factor determination

#### 3.3.1. Trace gases

The trace gas time series for each burn, discussed in Section 3.2 and consisting of \( n \) discrete measurements after the 120 s averaging, were used to calculate a timeseries of instantaneous emission ratios, \( E_f(x) \) and then emission factors, \( E_f(x) \). 'Fire integrated' EFs were then calculated by weighting each instantaneous EF by the corresponding instantaneous excess abundances \( \Delta CO_2 + \Delta CO \) of the two primary trace gases that make up more than 95% of the emitted carbon, used as a measure of the amount of smoke being produced by the fire at measurement time \( t \). This weighting approach has been used previously in laboratory burns, and was recently applied by Paton-Walsh et al. (2014) in an open burning situation. See Lacaux et al. (1996) and Wooster et al. (2011) for previous examples of such 'Fire integrated' trace gas EFs calculations:

\[ \text{Fire integrated EF}(\text{species } x) = \frac{\sum_{t=0}^{n} E_f(x)(\Delta CO_2 + \Delta CO)_t}{\sum_{t=0}^{n}(\Delta CO_2 + \Delta CO)_t} \] (10)

Our ‘fire integrated’ \( E_{FCO_2} \) (Table 4) for the spreading wheat residue fires is 1739 ± 19 g kg\(^{-1}\), somewhat higher than the 1470 g kg\(^{-1}\) and 1558 g kg\(^{-1}\) reported previously for Chinese wheat residues (Li et al., 2007; Zhang et al., 2008), though these latter measures are based on laboratory fires rather than field sampling. The difference may reflect the fact that laboratory fires usually comprise of piles of fuel that burn initially in flaming combustion, but which may have a longer and more significant smouldering phase than does a typical spreading fire measured in the field, and this supports the view that laboratory fires may behave differently to more ‘natural’ in situ combustion cases, and that care must be taken when combining and comparing these different types of measurement (Delmas et al., 1995; Wooster et al., 2011; Yokelson et al., 2013). Our field-measured fire integrated \( CO_2 \) emissions factors for wheat are, however, very close to the 1787 g kg\(^{-1}\) for wheat also measured in the field in an Indian agricultural area by Sahai et al. (2007). We also find that the fire integrated \( E_{FCO_2} \) for our field-measured rice and rapeseed burns are similar to that of our wheat burns, at 1761 ± 30 and 1704 ± 27 g kg\(^{-1}\) respectively. By contrast, our fire integrated carbon monoxide emissions factor varies quite widely amongst the three crop residues studied, with

### Table 3

<table>
<thead>
<tr>
<th>Fuel</th>
<th>( CO_2 )</th>
<th>( CO )</th>
<th>PM(_{2.5})</th>
<th>BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat</td>
<td>Flaming (F)</td>
<td>0.93</td>
<td>0.36</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>Smouldering (1-F)</td>
<td>0.07</td>
<td>0.64</td>
<td>0.41</td>
</tr>
<tr>
<td>Rice</td>
<td>Flaming (F)</td>
<td>0.88</td>
<td>0.13</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>Smouldering (1-F)</td>
<td>0.12</td>
<td>0.87</td>
<td>0.04</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>Flaming (F)</td>
<td>0.60</td>
<td>0.14</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Smouldering (1-F)</td>
<td>0.40</td>
<td>0.86</td>
<td>0.25</td>
</tr>
</tbody>
</table>
wheat (60 ± 12 g kg⁻¹) and rice (47 ± 19 g kg⁻¹) having a lower EF_CO than rapeseed (82 ± 17 g kg⁻¹). From the information discussed in Section 3.2, and from Table 3, the CO from the rapeseed residue bonfires indeed appears to be sourced from a higher proportion of smouldering combustion (0.86) than does that from the spreading wheat fires (0.64), which may help explain the higher EF_CO of rapeseed compared to wheat. However, the rice residue bonfires have an even lower EF_CO than rapeseed residue, but are reported to have had a very similar smouldering combustion contribution (0.87). The explanation for this requires further study, but may result from differences in combustion rates between the same combustion phase of different burns, and a similar pattern was observed in previous research (Zhang et al., 2008). Overall, our fire integrated EF_CO values appear comparable to the 60 g kg⁻¹ obtained for wheat (laboratory combustion) by Li et al. (2007), but significantly lower than those reported by some another laboratory studies (141 g kg⁻¹ for wheat and 64 g kg⁻¹ for rice; Zhang et al., 2008).

Our FTIR data allowed the determination of EFs for one of the spreading wheat residue fires using a completely independent approach to the smoke sampling system (Fire No. 7, with Equation (2)) adjusted to take in account of the increased number of carbonaceous gases (CO₂, CO, methane [CH₄] and formaldehyde [CH₂O]) easily available to be probed using the IR spectroscopy. The OP-FTIR method samples a transect through the plume, representing at any one time a significantly larger proportion of the total smoke production compared to the point based smoke sampling system (Fig. 3a), and also suffers no lag time effects between the measurements of different gases (Wooster et al., 2011). The OP-FTIR derived fire integrated EFs of 1723 g kg⁻¹ for CO₂ and 66 g kg⁻¹ for CO, included in Table 4, are close to the values derived from the smoke sampling system for the same wheat fuel and well within the reported uncertainty ranges derived from those data. We obtain fire integrated EFs for CH₄ and CH₂O as 2.1 and 12 g kg⁻¹, respectively using the OP-FTIR method, with these gases accounting for less than 1% of all gaseous emitted carbon and thus indicating the validity of deriving CO₂ and CO EFs from measurements of only those two gases when using the smoke sampling system and Equation (2). The FTIR method can be used to probe many more gaseous species than just these four, though the relatively short pathlengths and thus low abundances of lesser species make this more difficult in this case, and we focus here on the main carbonaceous gases only.

Table 4

<table>
<thead>
<tr>
<th>Sampling box species emissions factor (g kg⁻¹)</th>
<th>EF₁</th>
<th>EF₁ uncertainty</th>
<th>OP-FTIR EF₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat CO₂</td>
<td>1739</td>
<td>19</td>
<td>1723</td>
</tr>
<tr>
<td>Wheat CO</td>
<td>60</td>
<td>12</td>
<td>66</td>
</tr>
<tr>
<td>Rice CO₂</td>
<td>1761</td>
<td>30</td>
<td>–</td>
</tr>
<tr>
<td>Rice CO</td>
<td>47</td>
<td>19</td>
<td>–</td>
</tr>
<tr>
<td>Rapeseed CO₂</td>
<td>1704</td>
<td>27</td>
<td>–</td>
</tr>
<tr>
<td>Rapeseed CO</td>
<td>82</td>
<td>17</td>
<td>–</td>
</tr>
</tbody>
</table>

3.3.2. Particulates

To estimate aerosol EFs, linear best fit relationships between both PM₂.₅ and BC and CO₂ and CO were derived from two minute averages of the smoke sampling system measures, as discussed in Section 2.1. Fig. 11 shows the results for wheat (and Figs. 52 and 53 in the Supporting Information for rice and rapeseed residues), and these aerosol-to-trace gas ERs were used alongside the EFs of the relevant gases in Equation (3) to derived the particulate emissions factors.

The particulate EF calculations were undertaken based on both the aerosol-to-CO₂ and aerosol-to-CO emission ratios shown in Fig. 11. We determine EF_PM₂.₅ for wheat as 10.0 ± 1.2 g kg⁻¹ when using CO₂ as the reference gas, and 6.1 ± 1.3 g kg⁻¹ when using CO. For comparison to other measurements derived using a similar technique to that used here, Cachier et al. (1995) recorded simultaneous CO₂ and total particulate matter (TMP) abundances in smoke from savannah fires, and using these data estimated EF_PM₂.₅ for flaming processes as 5.7 ± 2.3 g kg⁻¹, with more than 90% of the mass of TPM being sub-micron in size. This value is comparable with our findings. Cachier et al. (1995) found a considerably higher smouldering phase EF_PM₂.₅ (34.5 ± 12.5 g kg⁻¹), but note that most fuel is burned in the flaming phase, as is the case with our spreading wheat fires.

We suggest our EF_PM₂.₅ based on the CO measurement maybe more representative, since the correlation of PM₂.₅ was higher with CO rather than CO₂ (see Fig. 11). However, as discussed in Section 3.2, the flaming phase fraction (Rᶠ) of BC correlates better with CO₂ (Fig. 10) as they were both flaming phase dominated, and so the EF_BC based on CO₂ (0.70 ± 0.09 g kg⁻¹ for wheat) is considered a potentially better estimate. The US Environmental Protection Agency (EPA) quote EF_PM₂.₅ for wheat burning in the US as 6–10 g kg⁻¹, depending on burning conditions, as previous research found that PM₂.₅ emissions would decrease by over 80% as MCE increased from 92% to nearly 98% (Dhammapala et al., 2007). This EPA suggested range almost exactly brackets the EF_PM₂.₅ findings we report from our Chinese wheat residue field burns in Table 5, Akagi et al. (2011) summarizes global crop residue burning EFs from a variety of past studies, calculating an average EF_PM₂.₅ of 6.26 g kg⁻¹, and an average EF_BC of 0.75 g kg⁻¹ for different agricultural crop species, values again quite close to those reported here. Our EF_BC for wheat straw is, though, somewhat higher than that from some prior laboratory studies conducted in China (0.43–0.49 g kg⁻¹; Li et al., 2007; Zhang et al., 2008), and again may reflect the increased amount of flaming combustion seen in spreading field-based fires than in the typical 'pilled fuel' situations used within laboratories. Our field-based burns show an EF_BC of 0.56 g kg⁻¹ for rice residue, a little lower than for the spreading wheat fires, but the rapeseed residue fires developed a very high EF_BC of 2.89 g kg⁻¹ with a fraction of 0.96 contributed by flaming (Table 3), reflective of the intense flaming combustion processes involved (Fig. 3b) that gave off visible clouds of soot in the plume.

4. Summary and conclusions

Crop residue fires in eastern China are believed to contribute significantly to regional air pollution (Chan and Yao, 2008). To study closely the gas and particle emissions from these burns in the field during agricultural burning periods, we have developed and
deployed a new portable smoke sampling system for the simultaneous close range measurement of trace gases (CO and CO2) and aerosols (PM2.5 mass and BC). We have used the system to derive gas and particle emission ratios and emissions factors for a series of crop residue fires sampled in eastern China in June 2014. Most prior research on smoke from these types of fuels have either been based on laboratory measurements, and/or have relied on filter-based sampling that provides only the total sampled mass from whole combustion. Our system offers the advantage of allowing continuous in situ measurements of smoke generated by naturally behaving agricultural fires (e.g. fires spreading across agricultural fields and field-measured ‘bonfires’), which is important as field-burns may well behave quite differently to burns conducted under laboratory conditions (Delmas et al., 1995). Our sampling system allows us to study both inter and intra-fire variability between combustion phases and between different fires and fuels, and we use the data collected along with a new approach (summarised in Eq. (4)) to obtain ‘fire-integrated’ emission factors for particulates as well as gases.

We studied the combustion of three types of common Chinese agricultural residues (wheat, rice and rapeseed), both spreading fires and bonfires. For all we found quite different trace gas emission ratios during flaming and smouldering periods, and also different BC to PM2.5 mass ratios. BC represented a much higher proportion of the total PM2.5 generated by these burns during the flaming combustion phase, up to 10 × more in the case of rapeseed, and the CO to CO2 emission ratio was significantly lower, up to 50 × less in the case of rice residue. The full set of ERs are shown in Table 2, and using the carbon mass balance method we calculated the individual CO2 and CO trace gas ‘Fire integrated’ EFs for each fuel type (Table 4). Using these, and the measured ratios of aerosols (BC and PM2.5) to trace gases (CO2 and CO), we estimated the EFs for each type of particulate as well (Table 5). We also probed the wheat fires using open path FTIR spectroscopy (Wooster et al., 2011), and confirmed a very similar set of trace gas EFs for this fire type compared to those derived using our smoke sampling system (Table 4). We find our emission factors to be reasonably similar to those reported by prior studies, but our results from spreading wheat fires are characteristic of more flaming-dominated burning than are most previously reported laboratory measurements (Li et al., 2007; Zhang et al., 2008). This may reflect the increased amount of flaming combustion seen in more ‘natural’ spreading fires than in typical ‘piled fuel’ laboratory burns. Our rapeseed residue bonfires showed a very high EF for BC, at up to 2.89 g kg−1, reflective of the intense flaming combustion processes involved that gave off visible clouds of soot.

All our EFs are derived from measures made within 10–20 m of the fires themselves, which were burnt in the field as Chinese farmers do. They are therefore representative of fresh smoke without photochemical processing, and can be regarded as primary EFs for these types of fire. For the aerosols, chamber-based examination of photochemical processing is suggested for future work, since higher EFs maybe expected after hours of atmospheric processing (Akagi et al., 2011). We anticipate combining our EFs with estimates of the amounts of the various residues burned, producing updated agricultural emissions inventories for use in air quality modelling (e.g. Li et al., 2010; Cheng et al., 2014).

### Table 5

Particulate emission factors of PM2.5 and BC (with uncertainties), derived separately from the ratio of particles to the two measured trace gases (i.e. data of Figure 11) and the CO2 and CO emission factors listed in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>PM2.5 Emissions Factor (g kg⁻¹)</th>
<th>BC Emissions Factor (g kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Based on CO2</td>
<td>Based on CO</td>
</tr>
<tr>
<td>Wheat</td>
<td>10.0 ± 1.2</td>
<td>6.1 ± 1.3</td>
</tr>
<tr>
<td>Rice</td>
<td>20.3 ± 1.5</td>
<td>9.6 ± 4.3</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>16.9 ± 2.6</td>
<td>5.8 ± 1.3</td>
</tr>
</tbody>
</table>

*Based on CO2: For the aerosols, chamber-based examination of photochemical processing is suggested for future work, since higher EFs maybe expected after hours of atmospheric processing (Akagi et al., 2011). We anticipate combining our EFs with estimates of the amounts of the various residues burned, producing updated agricultural emissions inventories for use in air quality modelling (e.g. Li et al., 2010; Cheng et al., 2014).*
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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.05.010.

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