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Published in:
Atmospheric environment

DOI:
[10.1016/j.atmosenv.2017.08.063](https://doi.org/10.1016/j.atmosenv.2017.08.063)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Ni, H., Tian, J., Wang, X., Wang, Q., Han, Y., Cao, J., Long, X., Chen, L-W. A., Chow, J. C., Watson, J. G., Huang, R-J., & Dusek, U. (2017). PM2.5 emissions and source profiles from open burning of crop residues. *Atmospheric environment*, 169, 229-237. <https://doi.org/10.1016/j.atmosenv.2017.08.063>

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PM_{2.5} emissions and source profiles from open burning of crop residues

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HIGHLIGHTS

- Source profiles and EFs of crop residue open burning specific to China were determined.
- No significant differences existed in profiles for the same crop from different producing areas.
- No significant differences were found in profiles among different type of crops.
- Potassium and chloride were major ions emitted from crop residue burning.
- PM_{2.5} and its major component emissions from crop residue open burning for 2008 were estimated.

ARTICLE INFO

Article history:

Received 15 April 2017

Received in revised form

23 July 2017

Accepted 29 August 2017

Available online 31 August 2017

Keywords:

Source profiles
Emission factors
Emission rates
Crop residues
Biomass burning

ABSTRACT

Wheat straw, rice straw, and corn stalks, the major agricultural crop residues in China, were collected from six major crop producing regions, and burned in a laboratory combustion chamber to determine PM_{2.5} source profiles and speciated emission factors (EFs). Organic carbon (OC) and water-soluble ions (the sum of NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-}) are major constituents, accounting for $43.1 \pm 8.3\%$ and $27.4 \pm 14.6\%$ of PM_{2.5}, respectively. Chloride (Cl^-) and water-soluble potassium (K^+) are the dominant ionic species, with an average abundance of $14.5 \pm 8.2\%$ and $6.4 \pm 4.4\%$ in PM_{2.5}, respectively. The average K^+/Cl^- ratio is ~ 0.4 , lower than 2.8–5.4 for wood combustion. Similarity measures (i.e., Student's *t*-test, coefficient of divergence, correlations, and residual to uncertainty ratios) show the crop profiles are too similar for the species measured to be resolved from one another by receptor modeling. The largest difference was found between rice straw and corn stalk emissions, with higher OC and lower Cl^- and K^+ abundances (50%, 8%, and 3% of PM_{2.5}, respectively) for corn stalks; lower OC, and higher Cl^- and K^+ abundances (38%, 21%, and 10% of PM_{2.5}, respectively) for rice straw. Average EFs were $4.8 \pm 3.1 \text{ g kg}^{-1}$ for OC, $1.3 \pm 0.8 \text{ g kg}^{-1}$ for Cl^- and $0.59 \pm 0.56 \text{ g kg}^{-1}$ for K^+ . Flaming and smoldering combustions resulted in an average modified combustion efficiency (MCE) of 0.92 ± 0.03 , and low elemental carbon (EC) EFs ($0.24 \pm 0.12 \text{ g kg}^{-1}$). OC/EC ratios from individual source profiles ranged from 12.9 ± 4.3 for rice straw to 24.1 ± 13.5 for wheat straw. The average K^+/EC ratio was 2.4 ± 1.5 , an order of magnitude higher than those from residential wood combustion (0.2–0.76). Elevated emission rates were found for OC (387 Gg yr^{-1}) and Cl^- (122 Gg yr^{-1}), accounting for 44% and 14% of 2008 PM_{2.5} emissions in China.

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1. Introduction

China is a large agricultural country with the highest crop production in the world (Bi et al., 2009). As combustion is a simple and effective way to remove plant residues, open burning is a common practice during harvest seasons. Large amounts of gases and particulate matter (PM) (Andreae and Merlet, 2001; Cheng et al., 2013; Li et al., 2014; Streets et al., 2003) are emitted that affect local and regional air quality, with adverse effects on human health, visibility, and the Earth's radiation balance (Chow and Watson, 2011; Fiore et al., 2015; Yao et al., 2017). Zhang et al. (2016) estimate annual average PM_{2.5} Chinese straw burning emissions from 1997 to 2013 at 1036 Gigagram (Gg), based on crop yields and burning detection by satellites. Agricultural burning accounts for ~8% of anthropogenic PM_{2.5} emissions over the year and ~26% of PM_{2.5} during harvest seasons (Zhang et al., 2016). Long et al. (2016) reported a 34% increase in ambient PM_{2.5} concentrations from agricultural burning in the North China Plain. Cheng et al. (2014) attributed 37% of PM_{2.5} mass, 70% of organic carbon (OC), and 61% elemental carbon (EC) to crop burning in southern China. Li et al. (2014) estimated that wheat straw burning contributed to over 50% of PM_{2.5}, OC, EC, potassium (K), and chloride ion (Cl⁻) in eastern China.

The Chinese Ministry of Environmental Protection (MEP, 1999) has promulgated regulations to minimize crop burning and to seek constructive alternatives for using the residues as soil amendments, energy production, and animal feed (Liu et al., 2008). However, open burning is prevalent in spite of these measures (Huang et al., 2012b).

This paper documents laboratory combustion chamber measurements of wheat straw, rice straw, and corn stalks; residues of these types represent ~80% of the total agricultural burning in China. PM_{2.5} emission factors (EFs) and chemical source profiles containing OC, EC, water-soluble ions, and elements are obtained from these tests. Similarities and differences among profiles from different agricultural areas and crop types are investigated. PM_{2.5} EFs and profiles are compared with those from other anthropogenic sources.

2. Experimental section

2.1. Sample collection

Ni et al. (2015) document the fuel collection and processing. Wheat straw, rice straw, and corn stalks were obtained from six major crop-producing regions, Shaanxi, Anhui, Shandong, Henan, Jiangxi and Hebei provinces. Samples were stored at ambient temperature (~20 °C) and humidity (35–45%) for more than one month before the experiments. Dry mass carbon and nitrogen contents, as well as the moisture, ash, volatile matter, and fixed carbon content as received, were measured before each burn and are listed in Supplemental Table S1 (Liao et al., 2004). For each experiment, 0.1–0.2 kg of crop residues were weighed before being placed on a platform inside a custom-made combustion chamber (Tian et al., 2015). Emissions were drawn through a dilution sampler (Wang et al., 2012) connected to the chimney of the combustion chamber. Dilution with clean air at ambient temperatures better represents real-world emissions as it allows for condensation and equilibration of the PM_{2.5} prior to measurement. Based on pilot experiments, optimal dilution ratios of 5–15 and sampling durations of 30–50 min were applied for each test. Dilution ratios that are too low result in high concentrations that exceed the upper limits of real-time instruments, whereas high dilution ratios do not allow for sufficient PM mass to be collected on filters for gravimetric and chemical analyses. The sampling

duration of 30–50 min accounts for the entire burning cycle, including ignition, flaming, smoldering, and extinction. Twenty-one experiments were conducted, including nine wheat straws, seven rice straws, and five corn stalks.

2.2. Chemical analysis

PM_{2.5} samples were collected on three parallel channels located downstream of the residence chamber of the dilution sampler, with 5 L min⁻¹ drawn through each filter. Two 47 mm Whatman quartz microfiber filters (QM/A), which were pre-fired at 900 °C for 3 h to remove adsorbed organic vapors (Chow et al., 2010a; Watson et al., 2009), were used for OC, EC, and water-soluble ion analyses. One 47 mm Teflon-membrane filter (2 µm pore size, R2PJ047, Pall Life Sciences, Ann Arbor, MI, USA) was used for gravimetric and elemental analyses. The sampled filters were stored in airtight containers and refrigerated at -4 °C after sampling 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 a ±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 averages of pre-sampling from the post-sampling weights (Watson et al., 2017). Differences among the three repeated weights were <10 µg for blank filters and <20 µg for sampled filters.

OC and EC were analyzed following the IMPROVE_A thermal/optical protocol (Chow et al., 1993, 2007; 2011b). Water-soluble ions, including ammonium (NH₄⁺), sodium (Na⁺), potassium (K⁺), magnesium (Mg²⁺), calcium (Ca²⁺), Cl⁻, nitrate (NO₃⁻), and sulfate (SO₄²⁻), were determined by Ion Chromatography (Chow and Watson, 1999, 2016) (Dionex 600, Thermal Scientific-Dionex, Sunnyvale, CA, USA). Elemental species, including K, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Ba and Pb, were determined by Energy Dispersive X-ray fluorescence spectrometry (Watson et al., 1999) (Epsilon 5 ED-XRF, PANalytical B.V., the Netherlands). Details of these measurements are described in Zhang et al. (2011) and Xu et al. (2012).

2.3. Similarities and differences among profiles

Four measures (i.e., the Student's *t*-test, coefficient of divergence (CD), correlation coefficient (*r*), and residual (*R*) to uncertainty (*U*) ratios) are used to examine similarities and differences among the source profiles. The Student's *t*-test is used to estimate the statistical significance of differences between chemical fractions of PM mass. If *P* > 0.05, there is more than a 95% probability that the two profiles are not significantly different. The CD, a self-normalizing parameter, is used to compare the similarities and differences between the source profiles (Zhang et al., 2014):

$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2} \quad (1)$$

where *x_{ij}* represents the average concentration for a chemical component *i* from source *j*; *j* and *k* represent two different crop residues; and *p* is the number of chemical components.

A CD approaching zero supports the null hypothesis that the two types of samples are similar for the measured chemical species. The closer the CD is to unity, the greater are the differences between samples. Several studies use low CD values to infer similarity. Wongphatarakul et al. (1998) used a CD of 0.269 to show similarity between particles from two cities. Feng et al. (2007) found no significant differences in PM chemical composition between topsoil and deep soil profiles of the same subtype, with the CD values

ranging from 0.11 to 0.29. Similar CD values (0.11–0.25) were reported by Zhang et al. (2014) to demonstrate the similarity of fugitive dust profiles. Based on these prior studies, a $CD < 0.3$ is taken as an indicator of profile similarity.

The correlation coefficient (r) between F_{i1}/σ_{i1} and F_{i2}/σ_{i2} is used to quantify the strength of association between paired profiles. Subscripts “1” and “2” refer to the two paired profiles. F_{i1} and F_{i2} are chemical species fractions of PM mass for species i from paired sources 1 and 2; σ_{i1} and σ_{i2} are the uncertainties for F_{i1} and F_{i2} , determined from the standard deviation of F_{i1} and F_{i2} for several representative samples, respectively. For this study, $r > 0.8$ is used to indicate similarity between the two profiles.

The distribution of weighted differences (residual/uncertainty $[R/U] = (F_{i1} - F_{i2}) / \sqrt{(\sigma_{i1}^2 + \sigma_{i2}^2)}$) indicates how many of the 21 reported chemical fractional abundances differ by more than a given number of uncertainty intervals for the profiles being compared. The chosen uncertainty intervals are $\pm 1\sigma$, $\pm 2\sigma$, and $\pm 3\sigma$ (herein σ is the standard deviation), corresponding to the normal probability density function of 68%, 95%, and 99%, respectively. When 80% of the R/U ratios are within $\pm 3\sigma$, with $P > 0.05$, $CD < 0.3$, and $r > 0.8$, the two profiles are considered to be similar, within the uncertainties of the chemical fractional abundances (Chow et al., 2003; Zhang et al., 2014). The variance (r^2) and the R/U ratio are performance measures of effective variance (Watson et al., 1984) solution to the chemical mass balance (CMB) receptor model (Watson et al., 2016) that quantify the agreement between measured receptor concentrations and those produced by the source profiles and source contribution estimates.

2.4. Emission factor (EF) calculation

PM mass EFs, expressed as grams of emission per kilogram of consumed dry fuel (g kg^{-1}), were determined by dividing the mass of pollutant emitted by the mass of the fuel consumed (Andreae and Merlet, 2001):

$$EF_{PM} = \left(\frac{m_{\text{filter}}}{Q} \frac{V_{\text{chimney}}}{m_{\text{fuel}}} \right) DR \quad (2)$$

where m_{filter} is the net mass collected on the filter (g); V_{chimney} is the volume of gas flowing through the chimney for each burn at standard temperature and pressure (m^3); Q is volume of sampled air drawn 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. DR is controlled by the flow balance of the dilution sampler, and can be determined by dividing total inflow (equals total outflow) by sample flow of the dilution sampler (Tian et al., 2015). The EF_{PM} are averaged for each fuel type j , to obtain $EF_{PM,j}$ and the uncertainty of this average is estimated as the standard deviation of the tests.

Country-wide emission estimates are obtained by multiplying the $EF_{PM,j}$ for each type of crop by the weights of the burned residues:

$$M_j = P_j \times R_j \times D_j \times W_j \times BE_j \quad (3)$$

where M_j is the weight of residue burned for crop type j ; P_j is the annual crop yield for type j ; R_j is the residue-to-crop ratio for crop j ; D_j is the dry fraction of crop residue; W_j is the proportion of residues burned in the field; and BE_j is the burn efficiency (the fraction of the fuel that is actually consumed through combustion). Ni et al. (2015) and references therein, estimated values for each of these variables, arriving at M_j of 24140.95 Gg of wheat straw, 34490.33 Gg of rice straw, 9305.52 Gg of corn stalks, and 18581.77 Gg of other

agricultural residues burned during 2008.

Total emissions for each $PM_{2.5}$ chemical species (E_i) are calculated by multiplying $EF_{PM,j}$ by M_j and by the fractional source profile abundances (F_{ij}) for each chemical species (Chow et al., 2011a; 2010b), termed *source-profiles-based method* (SP-based method):

$$E_i = \sum_{j=1}^4 EF_{PM,j} M_j F_{ij} \quad (4)$$

For wheat straw, rice straw, and corn stalks, source profiles from this study were used. Other types of crop residues (e.g., soybeans, tubers, cotton, peanut, canola, sesame, hemp, sugarcane, sugarbeet, and tobacco leaves) account for the remaining ~20% of total crop residue combustion and were included in previous emission inventory (e.g., Cao et al., 2008; Streets et al., 2003). For other crop residues, a composite profile was applied, as described by Ni et al. (2015).

3. Results and discussion

3.1. $PM_{2.5}$ source profiles

The combustion experiments were dominated by flaming and smoldering, with modified combustion efficiencies (MCE) ranging from 0.91 to 0.93 (see Supplemental Section S1), which are on the lower end of those for flaming-dominated combustion (0.9–1). This is also evident from the high OC to EC ratios (12–20) shown in Table S2, which are higher than OC/EC ratios derived from flaming-dominated crop residues reported elsewhere (Andreae and Merlet, 2001; Dhammapala et al., 2006; Li et al., 2007; Sahai et al., 2007; Turn et al., 1997). The reconstructed mass (Chow et al., 2015) accounts for $98 \pm 7\%$ (range 88–109%) of the gravimetric $PM_{2.5}$ mass, dominated by organic matter (OM; 52–96%) and inorganic ions (6–45%), as shown in Figure S1.

Fig. 1 shows the distribution of fire counts recorded in 2008 using the Moderate Resolution Imaging Spectroradiometer (MODIS) Thermal Anomalies/Fire product (MOD/MYD14A1) (NASA, 2017). Open fire counts mainly occurred in the central and south-eastern regions, accounting for >40% of the total fire counts, with sparse fire counts in western China. The spatial emissions distribution is related to economic activities and rural population densities. Regions with higher gross domestic product (GDP) and denser rural populations tend to contain more field burns (Cao et al., 2008; Yan et al., 2006). Monthly variation of fire counts in Table S3 demonstrate that most agricultural fires occur between March and June, consistent with agricultural planting and harvest activities (Huang et al., 2012a; 2012b).

Mass fractions of major $PM_{2.5}$ species for three fuel types in six provinces are also shown in Fig. 1. For wheat straw, OC is most abundant, ranging from 32.8% in Hebei to 45–46% of $PM_{2.5}$ in Shandong, Anhui, and Henan provinces. Chloride (Cl^-) is most abundant in rice straw, ranging from 20 to 27% of $PM_{2.5}$; Cl^- is most variable in wheat straw (from 7.9% in Anhui to 20.7% of $PM_{2.5}$ in Hebei). Large variations are also found for K^+ in wheat straw, ranging from 2.9% in Anhui to 11.1% of $PM_{2.5}$ in Hebei. Water-soluble ion abundances (i.e., sum of NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-}) are lowest for corn stalks, ranging 7.6–24.7% of $PM_{2.5}$. Student's t -tests (Table S4) show no significant difference at the 95% confidence level for crops collected from different provinces ($P > 0.05$), despite the large variabilities. Table S1 shows greater similarity among the three crops.

Distributions of $PM_{2.5}$ chemical abundances along with individual and composite source profiles are summarized in Fig. 1, Table 1 and Table S2. The most abundant species is OC, ranging from

Fig. 1. Chemical composition of PM_{2.5} from wheat straw, rice straw, and corn stalk burns in Shaanxi, Anhui, Shandong, Henan, Hebei and Jiangxi Provinces. The map shows locations where crop residues were produced and collected. Histograms show abundances of major chemical components in PM_{2.5} emissions from burning each residue. The map also shows the locations of agricultural fires (22,586 for 2008) as identified by NASA (2017) (see Supplemental Table S3). ^a Other measured ions, Na⁺, NH₄⁺, Mg²⁺, Ca²⁺, and NO₃⁻, have PM_{2.5} abundances <3%. ^b With the exception of K, measured elements have abundances <1%.

Table 1
Distribution of chemical abundances in PM_{2.5} mass (wt % of PM_{2.5} mass).

	Species in PM _{2.5} mass abundance (%)				
	<0.01%	0.01–0.1%	0.1–1%	1–10%	>10%
wheat straw	Mn, Ni, As	Mg ²⁺ , Ti, Cr, Fe, Cu, Zn, Br, Pb	Na ⁺ , Ca ²⁺ , NO ₃ ⁻ , Ba	EC, NH ₄ ⁺ , K ⁺ , SO ₄ ²⁻ , K	OC, Cl ⁻
rice straw	Ti, Cr, Mn, Ni, Cu, As, Pb	Fe, Zn, Br, Ba	Mg ²⁺ , NO ₃ ⁻	EC, Na ⁺ , NH ₄ ⁺ , Ca ²⁺ , SO ₄ ²⁻	OC, K ⁺ , Cl ⁻ , K,
corn stalk	Ti, Cr, Mn, Ni, Cu, Zn	Mg ²⁺ , Fe, As, Br, Ba, Pb	Ca ²⁺ , NO ₃ ⁻	EC, Na ⁺ , NH ₄ ⁺ , K ⁺ , Cl ⁻ , SO ₄ ²⁻ , K	OC

38.2 ± 4.0% of PM_{2.5} for rice straw to 50.5 ± 5.7% of PM_{2.5} for corn stalks. Water-soluble ions account for 40.9 ± 11.4% of PM_{2.5} for rice straw, a factor of two higher than their average abundances for wheat straw (22.7 ± 11.9%) and corn stalks (17.0 ± 9.6%). The largest variation in the averages is found for Cl⁻, ranging from 8.4 ± 6.4% of PM_{2.5} in corn stalks to 21.2 ± 7.3% in rice straw. The average K⁺ abundances are less than 50% of Cl⁻ abundances, ranging from 2.9 ± 2.1% for corn stalks to 10.1 ± 3.6% for rice straw. These abundances are consistent with those from previous studies (Hays et al., 2005; Li et al., 2007; Sillapapiromsuk et al., 2013; Turn et al.,

1997) as seen in Table S5. Previous studies found high abundances of Cl⁻ and K⁺ from agricultural burning, with emissions and abundances varying with fuel composition and fire temperatures (Christian et al., 2003; Hays et al., 2005; Keene et al., 2006; Khalil and Rasmussen, 2003; Knudsen et al., 2004; McMeeking et al., 2009; Oanh et al., 2011). Among the three types of crop residues, rice straw has the lowest OC/EC ratios and highest Cl⁻ and K⁺ abundances (Table S2), possibly due to their higher combustion temperature. This and prior studies (Table S5) show high Cl⁻ (6–27%) and K⁺ (3–25%) abundances in PM_{2.5} from crop burning,

5–20 times higher than residential wood combustion abundances ($0.13\text{--}1.5\%$ Cl^- and $1.4\text{--}4.2\%$ K^+).

NH_4^+ and SO_4^{2-} contribute 1–3% of $\text{PM}_{2.5}$, about tenfold higher than NO_3^- (Table 1 and Table S2), consistent with past studies cited above. Variations in nitrogen- and sulfur-containing particles (NH_4^+ , SO_4^{2-} , and NO_3^-) could be partly explained by the different fuel nitrogen and sulfur contents and combustion conditions (Turn et al., 1997). The anion/cation ratio is 1.22 ± 0.09 , consistent with more acidic compounds (Supplemental Section S3) such as hydrochloric acid (HCl) (Keene et al., 2006). This is consistent with a pH value of 5 reported by Sillapapiromsuk et al. (2013) for water extracts of rice straw, maize residue, and leaf litter smoke. By contrast, the anion/cation ratios for fugitive dust are often more alkaline, due to abundant Ca^{2+} (Wang et al., 2015; Zhang et al., 2014).

K is mostly water-soluble, as indicated by the K^+/K ratios averaging 0.77 ± 0.13 . This is consistent with findings of Watson et al. (2001), in which K^+/K ratios ranged from 0.1 in geological material to 0.9 in vegetative burning. Abundances of all other elements are below 0.1%, with the exception of barium (Ba, $0.28 \pm 0.30\%$) in wheat straw (Table S2). Although in the range of hundredths of one percent, Table S2 shows that several other trace elements (e.g., Ti, Cr, Cu, and Zn) are tenfold higher for wheat straw than for other crop residues.

Diagnostic ratios of chemical species can be used as source indicators (Arimoto et al., 1992; Cao et al., 2012). OC/EC ratios have been used to distinguish among different combustion sources (Han et al., 2016). Biomass burning usually has higher OC/EC ratios (3–10) (Cao et al., 2008; Li et al., 2009; Sun et al., 2017; Zhang et al., 2007, 2012) than those for coal combustion (1.6–3) (Chen et al., 2015; Shen et al., 2012; Zhi et al., 2008), and engine exhaust (0.5–1.3) (Gelencser et al., 2007; He et al., 2008; Huang et al., 2006). Based on the individual profiles, OC/EC ratios in this study ranged from 12.9 ± 4.3 for rice straw to 24.1 ± 13.5 for wheat straw (Table S2), lower than those reported by Sun et al. (2017), with OC/EC ratios of ~35 for household maize straw burning dominated by the smoldering phase. OC/EC ratios also depend on the analysis protocol applied to the samples (Chow et al., 2001, 2004; Han et al., 2016).

K^+/EC ratios have been used to assess biomass burning contributions (Srinivas and Sarin, 2014). Table 2 shows that K^+/EC ratios vary by threefold, from 1.1 ± 0.7 for corn stalks to 3.5 ± 2.0 for rice straw, comparable to the K^+/EC ratios of 1–3 reported elsewhere (Hays et al., 2005; Li et al., 2007). These ratios are higher than those found for herbaceous and wood burning (0.19) (Turn et al., 1997) and household wood burning (0.76) (Zhang et al., 2012).

Elevated K^+ and Cl^- abundances in PM have been reported for biomass burning, with K^+/Cl^- ratios ranging from 0.3–1 for crop residues to 2.8–5.4 for wood burning (Table S5). K^+/Cl^- ratios close

to unity were also reported for straw burning in an inland Chinese city (Shen et al., 2009). The average K^+/Cl^- of ~0.4 for this study falls within the range of published values.

The fact that these profiles have high t -statistics ($0.55 < P < 0.96$), low CD values ($0.1 < \text{CD} < 0.23$), high correlations ($0.77 < r < 0.87$), and are within $\pm 2\sigma$ for R/U ratios (Table 3) indicates that they will probably be collinear (Henry, 1992; Lowenthal et al., 1992) in source apportionment applications.

3.2. Speciated $\text{PM}_{2.5}$ emission factors (EFs)

EFs of $\text{PM}_{2.5}$ mass and chemical components are summarized in Table 4. The largest EF is found for OC, ranging from $3.3 \pm 2.8 \text{ g kg}^{-1}$ for rice straw to $6.3 \pm 3.6 \text{ g kg}^{-1}$ for corn stalk burning, and accounting for 38–51% of $\text{PM}_{2.5}$ emissions. EC EFs range from 0.2 to 0.3 g kg^{-1} . OC and EC EFs are consistent with those reported by Andreae and Merlet (2001) for similar fuels (3.3 g kg^{-1} for OC, 0.69 g kg^{-1} for EC). High OC EFs ($17.7 \pm 0.74 \text{ g kg}^{-1}$) were reported for smoldering-dominated maize straw burning in household stoves by Sun et al. (2017), which is ~28 times the $0.62 \pm 0.65 \text{ g kg}^{-1}$ reported by Shen et al. (2012) for flaming-dominated household wood burning. Higher EC EFs ($1.38 \pm 0.70 \text{ g kg}^{-1}$) for crop residues burned in a household stove was reported (Shen et al., 2010), as opposed to open burning.

Cl^- EFs range from $0.81 \pm 0.42 \text{ g kg}^{-1}$ for corn stalks to $1.7 \pm 1.2 \text{ g kg}^{-1}$ for rice straw, comparable to $1.54 \pm 0.34 \text{ g kg}^{-1}$ by McMeeking et al. (2009) and $1.14 \pm 0.59 \text{ g kg}^{-1}$ by Zhang et al. (2013). These levels are higher than those of other studies, which ranged from 0.05 to 0.89 g kg^{-1} (Hayashi et al., 2014; Hays et al., 2005; Jenkins et al., 1998; Oanh et al., 2011; Sillapapiromsuk et al., 2013; Turn et al., 1997). The Cl^- EF for wheat straw burning ($1.3 \pm 0.5 \text{ g kg}^{-1}$) is higher than previously reported data which is in the range of $0.12\text{--}1.20 \text{ g kg}^{-1}$ (Hayashi et al., 2014; Li et al., 2007; Turn et al., 1997) (Table S6). The Cl^- EF for corn stalks ($0.81 \pm 0.42 \text{ g kg}^{-1}$) is much lower than 1.3 g kg^{-1} by Turn et al. (1997) and $2.7 \pm 1.1 \text{ g kg}^{-1}$ by Li et al. (2007). The Cl^- fractions in total water-soluble ions were relatively constant among the three fuel types, ranging 50–57%, similar to those for other biomass burning experiments (Christian et al., 2003; Keene et al., 2006; McMeeking et al., 2009; Yokelson et al., 2008).

K^+ EFs of are ~34–53% of Cl^- EFs, ranging from $0.28 \pm 0.12 \text{ g kg}^{-1}$ for corn stalks to $0.90 \pm 0.87 \text{ g kg}^{-1}$ for rice straw. The rice straw K^+ EF is twice the 0.45 g kg^{-1} reported by Turn et al. (1997), and much higher than the 0.047 g kg^{-1} EF of Sillapapiromsuk et al. (2013). The wheat straw K^+ EF ($0.53 \pm 0.25 \text{ g kg}^{-1}$) is comparable to the 0.58 g kg^{-1} reported by Li et al. (2007), but 40% lower than the 0.89 g kg^{-1} of Turn et al. (1997). For corn stalk burning, the K^+ EF ($0.28 \pm 0.12 \text{ g kg}^{-1}$) is

Table 2

Average ratios of K/EC and K^+/EC for crop residue emissions from this study compared to similar measurements reported elsewhere.

Type of fuel	Measurement approach	PM size	K/EC ratio	K^+/EC ratio	References
wheat straw	chamber	$\text{PM}_{2.5}$	2.85 ± 1.36	2.26 ± 0.80	this study
rice straw	chamber	$\text{PM}_{2.5}$	4.68 ± 2.49	3.45 ± 1.90	this study
corn stalk	chamber	$\text{PM}_{2.5}$	1.48 ± 0.79	1.12 ± 0.68	this study
wheat straw	field measurement	$\text{PM}_{2.5}$	0.94	1.18	Li et al., 2007
wheat straw	chamber	$\text{PM}_{2.5}$	2.9	2.2	Hays et al., 2005
corn stalk	field measurement	$\text{PM}_{2.5}$	2.29	2.86	Li et al., 2007
biomass	source dominated sampling	TSP	0.1	/	Andreae et al., 1988 ^a
wood	wind tunnel	PM_{10}	0.2	0.19	Turn et al., 1997
wood	field measurement	$\text{PM}_{2.5}$	0.47	0.76	Zhang et al., 2012
wood	field measurement	$\text{PM}_{2.5}$	0.01–0.26	/	Fine et al., 2001
wood	field measurement	$\text{PM}_{2.5}$	0.03–0.46	/	Fine et al., 2004

^a EC was measured as soot by light absorption.

Table 3

Similarity statistics for chemical profiles from different agricultural fuels.

Profile#1	Profile#2	<i>t</i> -statistics ^a ; <i>P</i> values	CD ^b	Correlation coefficient (<i>r</i>) ^c	Percent distribution ^d		
					<1σ	<2σ	<3σ
wheat straw	rice straw	0.56	0.23	0.86	48%	96%	100%
wheat straw	corn stalk	0.96	0.21	0.77	60%	96%	100%
rice straw	corn stalk	0.55	0.10	0.87	68%	96%	100%

^a If *P* > 0.05, there is more than a 95% probability that the two profiles did not differ significantly.^b The coefficient of divergence (CD) is a self-normalizing parameter, ranging between zero and unity. The closer the CD to zero, the more similar between the two profiles.^c *r* between the two fractional source profile species *i* in sources ₁ and ₂ (i.e., *F*_{1*i*} and *F*_{2*i*}) divided by their associated uncertainties (*σ*_{1*i*} and *σ*_{2*i*}) quantifies the strength of association between paired profiles.^d Fraction of chemical abundances that differ by less than multiples of the precision of the difference as determined from residual to uncertainty (*R/U*) ratios, where $R/U = (F_{1i} - F_{2i}) / \sqrt{(\sigma_{1i}^2 + \sigma_{2i}^2)}$.**Table 4**Emission factors of PM_{2.5} mass and chemical components for each crop and for the average of all three crops.

Chemical species	Wheat straw	Rice straw	Corn stalk	Composite average ± standard deviations
PM _{2.5} (g kg ⁻¹)	11.4 ± 4.9	8.5 ± 6.7	12.0 ± 5.4	10.6 ± 5.6
OC (g kg ⁻¹)	5.1 ± 3.0	3.3 ± 2.8	6.3 ± 3.6	4.8 ± 3.1
EC (g kg ⁻¹)	0.24 ± 0.11	0.21 ± 0.13	0.28 ± 0.09	0.24 ± 0.12
NH ₄ ⁺ (g kg ⁻¹)	0.18 ± 0.09	0.14 ± 0.10	0.12 ± 0.12	0.15 ± 0.10
Na ⁺ (g kg ⁻¹)	0.09 ± 0.08	0.17 ± 0.09	0.15 ± 0.13	0.13 ± 0.10
K ⁺ (g kg ⁻¹)	0.53 ± 0.25	0.90 ± 0.87	0.28 ± 0.12	0.59 ± 0.56
Mg ²⁺ (g kg ⁻¹)	0.0067 ± 0.0055	0.016 ± 0.011	0.011 ± 0.008	0.011 ± 0.009
Ca ²⁺ (g kg ⁻¹)	0.082 ± 0.072	0.077 ± 0.03	0.088 ± 0.043	0.081 ± 0.052
Cl ⁻ (g kg ⁻¹)	1.30 ± 0.46	1.7 ± 1.2	0.81 ± 0.42	1.3 ± 0.8
NO ₃ ⁻ (g kg ⁻¹)	0.022 ± 0.011	0.029 ± 0.015	0.021 ± 0.012	0.024 ± 0.013
SO ₄ ²⁻ (g kg ⁻¹)	0.086 ± 0.079	0.24 ± 0.16	0.24 ± 0.07	0.17 ± 0.13
K (g kg ⁻¹)	0.56 ± 0.31	1.20 ± 1.12	0.38 ± 0.14	0.76 ± 0.72
Ti (mg kg ⁻¹)	2.0 ± 2.6	0.08 ± 0.08	0.27 ± 0.32	1.0 ± 2.0
Cr (mg kg ⁻¹)	1.1 ± 1.5	0.076 ± 0.097	0.17 ± 0.37	0.60 ± 1.12
Mn (mg kg ⁻¹)	0.29 ± 0.37	0.56 ± 0.58	0.62 ± 0.50	0.47 ± 0.47
Fe (mg kg ⁻¹)	1.2 ± 1.6	1.5 ± 0.7	2.0 ± 1.5	1.5 ± 1.3
Ni (mg kg ⁻¹)	0.79 ± 0.87	0.21 ± 0.17	0.27 ± 0.32	0.51 ± 0.66
Cu (mg kg ⁻¹)	3.3 ± 4.2	0.31 ± 0.24	0.33 ± 0.10	1.8 ± 3.2
Zn (mg kg ⁻¹)	4.4 ± 5.5	1.1 ± 0.8	1.1 ± 1.3	2.7 ± 4.1
As (mg kg ⁻¹)	ND ^a	0.084 ± 0.16	3.9 ± 5.3	0.96 ± 2.92
Br (mg kg ⁻¹)	1.1 ± 0.9	3.4 ± 1.1	5.3 ± 4.9	3.0 ± 2.9
Ba (mg kg ⁻¹)	21.9 ± 27.3	1.4 ± 1.3	4.1 ± 5.0	11.9 ± 20.9
Pb (mg kg ⁻¹)	2.3 ± 2.5	0.86 ± 0.81	7.8 ± 10.3	3.3 ± 5.6

^a ND denotes not detected or lower than background level.

within the range 0.13–0.43 g kg⁻¹ reported by [Andreae and Merlet \(2001\)](#), but it is lower than the 0.67 g kg⁻¹ of [Turn et al. \(1997\)](#) and the 1.0 ± 0.65 g kg⁻¹ of [Li et al. \(2007\)](#). EFs for other ions are low, in the range of 6.7×10^{-3} to 0.18 g kg⁻¹.

The sum of trace element EFs excluding K (i.e., Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Ba, and Pb) is low, ranging from 0.15 ± 0.07 g kg⁻¹ for rice straw to 0.45 ± 0.48 g kg⁻¹ for wheat straw. EFs for toxic elements, such as As, Cr, Pb, Mn, and Ni, are low, with the sum being 0.06 ± 0.09 g kg⁻¹ on average.

EFs from burning of air-dried crop residues (~10% moisture content) in the laboratory chamber may differ from the real-world combustion, where the moisture content can be as high as 26% ([Oanh et al., 2011](#)), and environmental conditions are not as well controlled ([Zhang et al., 2013](#)). Higher moisture content can enhance emissions of PM_{2.5}, OC, and some ions (e.g., NH₄⁺, Cl⁻ and SO₄²⁻) ([Chen et al., 2010](#); [Hayashi et al., 2014](#); [Ni et al., 2015](#)).

3.3. PM_{2.5} speciated emission rates

As summarized in [Table 5](#), PM_{2.5} emissions were 875 Gg in 2008, including 274.2 Gg from wheat straw burning (31% of PM_{2.5}), 292.1 Gg from rice straw (33%), 111.6 Gg from corn stalks (13%) and 197.2 Gg from other crops (23%). OC has the largest emissions

(387.3 Gg yr⁻¹), accounting for 44% of the total. OC emissions vary by the type of residue, ranging from 58.4 Gg yr⁻¹ for corn stalks to 123.6 Gg yr⁻¹ for wheat straw. The sum of the water-soluble ion emissions is 229.9 Gg yr⁻¹, accounting for 26% of the total. These ions can take up atmospheric moisture and act as cloud condensation nuclei ([Petters et al., 2009](#); [Rissler et al., 2006](#)). The two highest ion emissions are Cl⁻ (121.6 Gg yr⁻¹) and K⁺ (57.5 Gg yr⁻¹), constituting 53% and 25% of total ion emissions, respectively. This is consistent with ambient observations. [Park et al. \(2004\)](#) reported that Cl⁻ and K⁺ concentrations increased when agricultural waste burning occurred in Korea. [Shen et al. \(2009\)](#) also found high Cl⁻ and K⁺ loadings during crop burning episodes, in contrast to haze days with enriched secondary species (e.g., NH₄⁺, NO₃⁻, and SO₄²⁻) and dust storms events with elevated Ca²⁺ abundances in Xi'an, China.

These results are compared ([Table S7](#)) to those of the 2006 INTEX-B inventory ([Zhang et al., 2009](#)), which reports Chinese anthropogenic PM_{2.5} emissions, without agricultural burning of 1474 Gg yr⁻¹ from power generation, 6932 Gg yr⁻¹ from industry, 4461 Gg yr⁻¹ from residences, and 398 Gg yr⁻¹ from transportation. The 875 Gg yr⁻¹ for open agricultural burning estimated here constitutes more than half of the power generation and more than twice the transportation emissions included in the INTEX-B inventory.

Table 5

Estimates of 2008 annual emissions (Gg) from crop residues burning in China.

	PM _{2.5} ^a	OC ^b	EC ^b	NH ₄ ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl [−]	NO ₃ [−]	SO ₄ ^{2−}	K	Other Elements ^c
wheat straw	274.2	123.6	5.79	4.34	2.17	12.8	0.16	1.98	31.3	0.53	2.07	17.3	1.23
rice straw	292.1	114.2	7.24	4.83	5.87	31.1	0.55	2.66	58.6	1.00	8.28	40.5	0.43
corn stalk	111.6	58.4	2.61	1.12	1.40	2.6	0.10	0.82	7.5	0.20	2.23	4.3	0.30
others ^d	197.2	91.1	4.46	2.79	2.42	11.0	0.20	1.51	24.2	0.45	3.16	16.4	0.60
total	875.1	387.3	20.1	13.1	11.9	57.5	1.02	6.96	121.6	2.17	15.8	78.5	2.56

^a PM_{2.5} emissions were estimated as the product of the amount of crop residues burned in the field and the corresponding EFs as shown in Eq. (4).^b Emissions of OC and EC were presented in Ni et al. (2015).^c Other elements included all the elements list in Table 1 except for K.^d Other type of crop residues included straw of soybean, tubers, cotton, peanut, canola, sesame, hemp, sugarcane, sugarbeet, and tobacco leaf; for other types of crop residues, composite source profiles in Table S2 are used.

4. Conclusions

PM_{2.5} chemical source profiles and speciated EFs (i.e., OC, EC, water-soluble ions, and elements) from the combustion of crop residue (i.e., wheat straw, rice straw, and corn stalks) were investigated and compared with data from the literature. OC and water-soluble ions (sum of NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl[−], NO₃[−], and SO₄^{2−}) are major constituents, accounting for an average of $43.1 \pm 8.3\%$ and $27.4 \pm 14.6\%$ PM_{2.5} mass, respectively. Cl[−] and K⁺ are the dominant water-soluble ions, ranged $14.5 \pm 8.2\%$ and $6.4 \pm 4.4\%$ in PM_{2.5}, respectively. Source profiles within a fuel type were too similar for the measured species to be separated by receptor models, but they probably differ enough from other source types to be separated from them. Species with the highest EFs are OC (4.8 ± 3.1 g kg^{−1}), followed by Cl[−] (1.3 ± 0.8 g kg^{−1}), and K⁺ (0.59 ± 0.56 g kg^{−1}). Majorities of the elemental potassium are water soluble, with an average K⁺/K ratio of 0.77 ± 0.13 . Average K⁺/EC ratios in crop residues was 2.4 ± 1.5 , much higher than those derived from residential wood combustion (0.2 – 0.76) by Fine et al. (2001, 2004), indicating K⁺/EC ratio could be used as indicator to distinguish the source subtype contributions from biomass burning. Total emissions were estimated for 2008, with 387.3 Gg OC, 121.6 Gg Cl[−], and 57.5 Gg K⁺. To develop effective pollutant control strategies, comprehensive emission inventories including major biomass combustion are needed.

Acknowledgment

This work was jointly supported by the Ministry of Science and Technology (2013FY112700), the Chinese Academy of Sciences (XDA05100402, KZZD-EW-04, SKLLQG1417 and SKLLQG1529), the National Science Foundation (NSF) of China (41273140 and 41473119), and the National Basic Research Program of China (2010CB833403 and 2013CB955900).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2017.08.063>.

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