Characterization of the chemical components and bioreactivity of fine particulate matter produced during crop-residue burning in China☆

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ABSTRACT

Five types of crop residue (rice, wheat, corn, sorghum, and sugarcane) collected from different provinces in China were used to characterize the chemical components and bioreactivity properties of fine particulate matter (PM$_{2.5}$) emissions during open-burning scenarios. Organic carbon (OC) and elemental carbon (EC) were the most abundant components, contributing 41.7%—54.9% of PM$_{2.5}$ emissions. The OC/EC ratio ranged from 8.8 to 31.2, indicating that organic matter was the dominant component of emissions. Potassium and chloride were the most abundant components in the portion of PM$_{2.5}$ composed of water-soluble ions. The coefficient of divergence ranged from 0.27 to 0.51 among various emissions profiles. All samples exposed to a high PM$_{2.5}$ concentration (150 μg/mL) exhibited a significant reduction in cell viability (A549 lung alveolar epithelial cells) and increase in lactic dehydrogenase (LDH) and interleukin 6 levels compared with those exposed to 20 or 0 μg/mL. Higher bioreactivity (determined according to LDH and interleukin 6 level) was observed for the rice, wheat, and corn samples than for the sorghum straw samples. Pearson's correlation analysis suggested that OC, heavy metals (chromium, manganese, iron, nickel, copper, zinc, tin, and barium), and water-soluble ions (fluoride, calcium, and sulfate) are the components potentially associated with LDH production.

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1. Introduction

Biomass burning is defined as the burning of vegetation caused by natural wildfires, agricultural fires, or residential combustion (e.g. cooking and heating) (Hays et al., 2005; Qin and Xie, 2011). These activities have long been recognized as prominent sources of air pollutants in the atmosphere (Andreae and Merlet, 2001; Streets et al., 2003) that may contribute to the effects of respiratory diseases through inhalation exposure. The majority of biomass is used for combustion in small-scale processes (e.g. household heating) and agricultural operations (e.g. land clearing) (Shen et al., 2011). In Asia, emissions from biomass burning have had significant effects on regional air quality. Streets et al. (2003) estimated that regions with a high amount of biomass burning are primarily located in Central and East China, Southeast Asia, and South Asia. In China, the open burning of crops and agricultural residue is a common farming practice because of its many benefits (e.g. grass cleaning) (Cheng et al., 2013; Li et al., 2014). Farmers often perform these procedures to eliminate excess straw and thereby reduce the overall production of solid waste. These actions typically lead to a large open-burning area, and pollutant emissions have

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consequently become a serious health concern for local residents.

Source apportionment studies have revealed that biomass burning is a key source of particulate matter (PM) (Hagler et al., 2006; Zheng et al., 2011). One study reported that the majority of particles generated from biomass burning are composed primarily of fine particulate matter (PM$_{2.5}$; PM with aerodynamic diameter < 2.5 μm) (Hays et al., 2002). Another study determined that the different emission factors of PM$_{2.5}$ from open biomass burning were in the range 3.41–16.8 g/kg (Shen et al., 2010), whereas further research discovered the emission factors of organic carbon (OC) and elemental carbon (EC) to be in the ranges 0.35–2.34 g/kg and 0.49–2.64 g/kg, respectively, with the concentration varying according to fuel type, water content, combustion phase, and environmental conditions (Reid et al., 2005). Biomass burning was estimated to contribute approximately 40% of the global annual average submicron black carbon aerosol emissions and 65% of primary OC emissions (Bond et al., 2013). Numerous studies have demonstrated that OC sometimes contains carcinogenic components that cause adverse human health conditions (Chen et al., 2005; Daher et al., 2014; Ho et al., 2016; Niu et al., 2017). Furthermore, EC is a potential carrier of toxic components in human and animal respiratory systems (Kuenzi et al., 2013; Reed et al., 2006). The burning of agricultural residue was proven to exacerbate the symptoms of respiratory diseases among humans (Long et al., 1998). A 29% increase in patients suffering from asthma attacks during rice-straw burning in the daytime was reported (Jacobs et al., 1997) as well as an increase in the number of patients admitted to hospitals when temporarily exposed to wildfire smoke in comparison with smoke-free periods (Kunzli et al., 2006; Mott et al., 2005). A time-series study of urban and rural areas in Australia affected by bushfire smoke revealed an association between smoke-derived PM and treatment for asthma in hospitals (Chen et al., 2006).

The majority of studies on the health effects of PM combustion have focused on equivalent toxicity of polycyclic aromatic hydrocarbons (PAHs) or assessing the exposure to PM (Bostrom et al., 2002; Dorne et al., 2011; Zhang et al., 2009). Several *in-vitro* studies have demonstrated that exposure to biomass PM combustion could cause the generation of reactive oxygen species, DNA damage, lipid peroxidation, and the release of proinflammatory cytokines in lung cells (Danielsen et al., 2009; Kocbach et al., 2008; Leonard et al., 2007). Danielsen et al. (2009) reported that PM in wood smoke could lead to DNA damage in A549 cells. Lin et al. (2013) suggested that several PAHs could exert proinflammatory effects in human cells. However, studies have only investigated the association between PM exposure and bioreactivity and (or) elected species (e.g. PAHs). Few systematic studies have been conducted on the chemical and bioreactivity properties of PM$_{2.5}$ (Brook et al., 2010).

China has one of the fastest growing economies worldwide (>7.0% annual GDP growth for the past 20 years) (National Bureau of Statistics of China, 2012). The country is suffering from serious problems related to environmental pollution, such as frequent haze days (Zheng et al., 2011). The purpose of the present study was to 1) evaluate the potential health effects and corresponding health outcomes of exposure to the open burning of crop residue and 2) identify the chemical components of PM$_{2.5}$ to further characterize the relationship between PM$_{2.5}$ chemical properties and bioreactivity.

2. Materials and methods

2.1. Sample collection and analysis of particulate matter

The emissions of five types of straw were tested, namely those from rice, sugarcane, sorghum, wheat, and corn. These types of straw represent the majority of agricultural residue in China (Sang et al., 2012). All straw was collected from major crop-producing regions in China, and further details are provided in Table S1 (Supplementary Material). All collected samples were stored at an ambient temperature (~20 °C) with controlled relative humidity (~35%−40%) prior to analysis. Initial analyses were performed to characterize the samples as received conditions. The carbon and nitrogen content in the dry mass, moisture, ash, volatile matter, and fixed C content were determined and are listed in Table S2 (Supplementary Material). Experiments on biomass burning emissions were performed in a fully-enclosed, stainless steel environmental chamber designed for measuring source emissions. Further details of the combustion chamber apparatus were described in another study (Tian et al., 2015). The size of the chamber was $1.8 \times 1.8 \times 2.2$ m^3 (length × width × height), with a volume of approximately 8 m^3. Biomass fuels were burned on a plate in the chamber to simulate a realistic open-burning scenario. Each sampling duration of 30−50 min accounted for the entire burning cycle, including ignition, flaming, smoldering, and extinction, which were also simulated in accordance with realistic conditions (Ni et al., 2015). All rubber, plastic, grease, and oil were removed to minimize organic contamination. High-efficiency particulate air filters (3M Company, St Paul, MN, USA) (nominal filtration efficiencies of 95%) for PM (>0.3 μm) and an air blower were installed in front of the combustion air inlet. Exhaust was purged through a diameter exhaust duct (0.15 m) under controlled conditions. The crop residues were weighed (0.1−0.2 g in each test) and subsequently burned on a combustion platform inside the chamber. The emitted PM was sampled using a dilution sampler and detected with online instruments, which are listed in Table S3 (Supplementary Material). The dilution ratios were in the range 5−15. Further details of the biomass burning tests are provided in Tian et al. (2015) and Ni et al. (2015).

PM$_{2.5}$ samples were collected from three parallel channels (one for quartz filter sampling and the other two for Teflon filter sampling) that were located downstream from the residence chamber in a dilution sampler, with a flow rate set at 5 L/min in each channel. Prior to beginning the experiment, the 47-mm quartz filters (QM/A) were preheated to 900 °C for 3 h to remove any residual carbon. The Teflon filters ($\Phi = 47$ mm, 2-mm pore size, R2PJ047, Pall Life Sciences, Ann Arbor, MI, USA) used in the analysis were assessed to ensure that no particles would leak from the edge of the Teflon filter during the sampling period. All Teflon filters were preconditioned at a temperature of 25 °C ± 0.5 °C and relative humidity of 35% ± 5% for 48 h prior to and following the sample-weighing procedure. Each filter was weighed on a microbalance (±1 mg precision, Sartorius AG MC5, Germany) before and after sample collection. The mass concentrations of the collected PM$_{2.5}$ sample filters were calculated by subtracting from the blank filters to ensure the absence of gas-adsorption artifacts.

2.2. Chemical analysis

2.2.1. Organic carbon and elemental carbon analysis

OC and EC on a small area of the quartz filter, obtained using a punch (0.526 cm^2), were analyzed by employing the thermal optical reflectance technique following the IMPROVE_A protocol on a thermal/optical carbon analyzer (DRI Model, 2001; Atmoslytic Inc., Calabasas, CA, USA). The EC and OC concentrations all exceeded the detection limit (1.0 μg/cm^2) of the instrument. One in every 10 samples was reanalyzed for quality-assurance purposes. The results yielded standard deviation errors within 10%. Details of the chemical analysis are provided by Pathak et al. (2011). The aforementioned procedure was repeated for all samples in a triplicate

analysis.

2.2.2. Analysis of water-soluble inorganic ions through ion chromatography

One quarter of each quartz filter was extracted with deionized water (10 mL), and the extractant was used for ion chromatographic (Dionex DX-600) analysis. IonPac CS12A and AS14A columns were used to separate cations and anions, respectively. An eluent solution mixture (Na_2CO_3 (8 mM) and $NaHCO_3$ (1 mM)) was used for anion separation (flow rate of 1 mL/min), and methanesulfonic acid (20 mM) was used for cation separation (flow rate of 1 mL/min). The extractants were filtered using microporous membranes (0.45-mm pore size) to remove any insoluble materials. Ions in the samples (Na^+, NH_4^+, K^+, SO_4^{2-}, NO_3^-, and Cl^-) were analyzed. The detection limits of Na^+, NH_4^+, K^+, SO_4^{2-}, NO_3^-, and Cl^- were 4.6, 4.0, 10.0, 0.5, 15.0, and 20.0 ppb, respectively. One in every 10 extractants was reanalyzed for quality-control purposes. Each analysis yielded results with standard deviation errors within 10%. Details of the chemical analysis are provided by Zhang et al. (2011). The aforementioned procedure was repeated for all collected quartz filters in a triplicate analysis.

2.2.3. Element analysis

Energy dispersive X-ray fluorescence (ED-XRF) spectrometry (Epsilon 5 ED-XRF, PANalytical B. V., The Netherlands) was used to determine the concentrations of elements collected on the $PM_{2.5}$ Teflon membrane filters (Steinhoff et al., 2000; Wasson and Guo, 2002). The three-dimensional polarizing geometry contained eleven secondary targets (i.e. CeO_2, CsI, Ag, Mo, Zr, KBr, Ge, Zn, Fe, Ti, and Al) and a barkla target (Al_2O_3). An acceptable signal-to-background ratio was achieved in the analysis. The ED-XRF spectrometer was calibrated using thin-film standards (MicroMatter Co., Arlington, WA, USA) prior to analysis. A total of 26 elements were identified in the analysis, and the detection limits for these elements are listed in Table S4 (Supplementary Material).

2.3. Bioreactivity analysis

2.3.1. $PM_{2.5}$ preparation

A $PM_{2.5}$ sample was removed from filter substrates using a two-stage sonication process in methanol followed by purging through nitrogen air. Details of the preparation are provided by Chuang et al. (2013). The $PM_{2.5}$ was then resuspended in a 1 mg/mL concentration of dimethyl sulfoxide (<0.01% vol in RPMI) and further used as a stock solution. Fresh samples remained at 4 °C and were consumed within 1 week of preparation.

2.3.2. Cell culture

Human A549 lung alveolar epithelial cells were obtained from the American Type Culture Collection (Manassas, VA, USA). Cells were seeded in surface-treated trans-wells (BD Biosciences, Oxford, UK) at a density of 10^5 cells/mL and then incubated for 24 h. They were then cultured in RPMI medium containing 10% fetal bovine serum, penicillin, and streptomycin before being incubated at 37 °C, 95% humidity, and 5% CO_2. Cells were then exposed to 0 (control), 20, or 150 µg/mL $PM_{2.5}$ samples (diluted with a serum-free RPMI cell medium from the stock solution) at 37 °C for 6 h in a humidified atmosphere with 5% CO_2. The $PM_{2.5}$ samples were diluted from the stock solution using phosphate-buffered saline to the levels 20 and 150 µg/mL, and the phosphate-buffered saline diluent alone was used as a control (Niu et al., 2017). These two doses were selected to represent two atmospheric conditions: normal conditions and conditions of serious pollution. The purpose was to compare and contrast bioreactivity in human lung cells and further reveal significant differences in bioreactivity under normal compared with

serious pollution conditions. Longer exposure could lead to a higher cell death rate, which ultimately causes a reduction in IL-6 level. Therefore, an exposure duration of 6 h was selected to ensure cell viability for follow-up experiments. Each experiment was conducted in a triplicate analysis. The concentrations of $PM_{2.5}$ in the biomass emissions were used to test for oxidative-inflammatory effects (>80% cell viability) using the procedure detailed by Wilson et al. (2002).

2.3.3. Cell viability

Cell viability was assessed using a sulforhodamine B colorimetric assay according to the method used by Vichai and Kirtikara (2006). In brief, cells were fixed with 10% (wt/vol) trichloroacetic acid for 30 min of staining. The protein-bound dye was dissolved in a Tris base solution (10 mM) after excess dye had been removed. A plate reader (Bio-Rad Model 680, CA, USA) was used to measure the optical density at 510 nm. Cell viability is presented as a percentage (%) after adjusting for the control (0 µg/mL).

2.3.4. Cytotoxicity and inflammation

To investigate the effects of cytotoxicity and inflammation caused by $PM_{2.5}$, levels of cytotoxicity indicator lactic dehydrogenase (LDH) (Abcam, Cambridge, MA, USA) and inflammatory cytokine interleukin 6 (IL-6) (BD Biosciences, USA) were measured in cell supernatants after the cells' exposure to $PM_{2.5}$. The experiment was conducted in reference to manufacturer instructions.

2.4. Statistical analysis

The coefficient of divergence (CD) was used to quantify the composition profile of $PM_{2.5}$ and was calculated as follows:

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

where x_{ij} represents the average concentration of the ith chemical component at site j; j and k represent two sampling sites; and p is the number of measured chemical species (Han et al., 2010). A CD approaching 0 indicated that the two profiles were the same, whereas a CD of 1 indicated that the two profiles were different. A CD value of 0.2 has generally been regarded as the cutoff point for similarity in source-profile studies (Han et al., 2010; Niu et al., 2017). One-way analysis of variance with Tukey's post hoc test was conducted to compare multiple values in the analysis. Pearson's correlation coefficient analysis was performed to identify the correlation between (1) oxidative stress and inflammation as well as among (2) chemical species with oxidative-inflammation cytokines. The statistical analyses were conducted using GraphPad Prism software (Version 5 for Windows). The significance level was set at $p < 0.05$.

3. Results and discussion

3.1. Chemical components

3.1.1. Carbonaceous fraction

Table 1 presents the composition profiles of OC, EC, and total carbon (TC), together with the OC/EC ratios in the five types of samples. The results reveal that TC was the most abundant component in $PM_{2.5}$ (41.7%–54.9%). These findings are consistent with those of other research (Andreae and Merlet, 2001; Chen et al., 2006; Chow et al., 2011). Studies have reported that carbonaceous emissions account for approximately 0.5%–2.0% of TC emissions (Andreae and Merlet, 2001; Ni et al., 2015). Furthermore, the OC in

Table 1
Composition of OC, EC, TC and OC/EC ratios in biomass samples.

Type of sample	[a]TC/PM$_{2.5}$[d]	[b]OC/PM$_{2.5}$	[c]EC/PM$_{2.5}$	OC/EC
Rice straw	41.7%	39.1%	2.7%	14.6
Wheat straw	50.2%	48.6%	1.6%	31.2
Corn straw	54.9%	52.7%	2.2%	23.5
Sugarcane straw	47.7%	42.8%	4.9%	8.8
Sorghum straw	46.1%	42.8%	3.3%	13.0

[a] TC: total carbon.
[b] OC: organic carbon.
[c] EC: elemental carbon.
[d] PM$_{2.5}$: mass concentration of fine particles.

particles emitted from combustion originate from incomplete combustion reactions, whereas EC is primarily produced at higher temperatures under complete-combustion conditions (Han et al., 2010; Reece et al., 2017). This observation could possibly explain the differences between OC and EC emissions, because open biomass burning is typically conducted at low temperatures under smoldering conditions.

The OC/EC ratio ranged from 8.8 to 31.2, approximately 2–10 times higher than those in combustion in household stoves (Cao et al., 2008; Li et al., 2009) but similar to those produced from straw burning in Chinese-style heated bed-stoves (Sun et al., 2017). These high ratios could potentially be attributed to the smoldering condition dominant during combustion, although further investigation is required in future analysis.

The results for TC were higher (by ~38.0%) compared with biomass burning in household stoves, which confirmed that open burning promotes carbonaceous production (Shen et al., 2012). The TC fractions were similar to that of residential bitumite combustion (~45%) but higher than that of residential anthracite combustion (~17%) (Li et al., 2009). The fractions of OC in PM$_{2.5}$ were higher than those in samples collected from the atmosphere in urban areas in China (~17%–20%), whereas the EC fractions were similar to those of samples of urban PM$_{2.5}$ (Ho et al., 2016). These observations suggested that the OC/EC ratios in open burning of biomass aerosols are higher than those for atmospheric aerosols. Furthermore, fuel type may also contribute to the variation of carbonaceous fractions in PM$_{2.5}$.

Correlation and proximate analyses were performed for PM$_{2.5}$, OC, and EC emissions, and the results are presented in Table S5 (Supplementary Material). Strong positive correlations ($r \geq 0.8$) were observed between volatile matters in the samples and PM$_{2.5}$/OC emissions, which is consistent with the findings of other studies (Cao et al., 2008; Ni et al., 2015; Shen et al., 2010). This observation could be used to explain the low OC fractions in PM$_{2.5}$ emitted from the burning of sugarcane and sorghum straw in relation to the low volatile matter content of these two fuels. Moderate negative correlations ($r \geq -0.6$) were observed between OC emissions and both moisture and ash content. Studies have demonstrated that high moisture or ash content in fuel can lead to incomplete combustion (Chen et al., 2006; Ni et al., 2015). No correlations were determined between EC production and any of the chemical components of fuel (moisture, ash, volatile matter, and fixed carbon). This could be because EC production is primarily affected by combustion conditions.

3.1.2. Water-soluble inorganic ions and elements
Descriptive analysis and the relative abundances of water-soluble ions in PM$_{2.5}$ are presented in Table 2. The total contribution of water-soluble inorganic ions (sum of Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ ions) was in the range 12.3%–38.1%, which is consistent with the findings of related studies (Hays et al., 2005;

Li et al., 2007; Tang et al., 2014). Cl$^-$ and K$^+$ were the most abundant anion and cation in the PM$_{2.5}$, respectively. This could be attributed to the use of fertilizers and herbicides in the soil sampling locations. These two ions could potentially be used as markers indicating biomass burning in aerosol-source identification (Han et al., 2010; Okuda et al., 2010). The lower contribution of SO$_4^{2-}$ in PM$_{2.5}$ (~3%) compared with coal combustion could be a result of the relatively small amount of sulfur in biomass (Li et al., 2007). Rice straw contained the highest total ion composition (~38.1%), whereas corn straw had the lowest (~12.0%). The difference among emissions regarding the number of particles containing nitrogen and sulfate (NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$) could be attributed to the amount of sulfur and nitrogen present in the soil (Turn et al., 1997).

The concentrations of various elements are listed in Table 3. The total element composition accounted for 13.3%–45.5% of the total composition, which was higher than that of the total ion composition. The dominant components were, in the following descending order of prevalence, Cl > K > Na > S. These elements comprised >99% of the total elements in the analysis. Heavy metals accounted for <0.01% (except for Mn, Fe, and Pb), which could be attributable to low concentrations of heavy metals in soil from the collected straw. The abundance of heavy metals was less than 0.01% (except for Mn, Fe, and Pb) because the types of straw investigated were collected from grains grown by humans in areas where heavy metal concentrations in the soil are generally low (Nzihou and Stanmore, 2013).

Fig. 1 represents the relative concentration contributions of the three main components, excluding certain elements and ions (K$^+$ and K, Na$^+$ and Na, Cl$^-$ and Cl, and SO$_4^{2-}$ and S). Similar component distributions were identified for wheat and corn straw, together with the observation of high OC (~50%) and low EC (~3%) content. Furthermore, these two types of straw contained lower water-soluble ion concentrations than the other sample types (rice, sugarcane, and sorghum straw). More than 25.0% of the components were classified as undetected compared with 9.0%–19.4% in the other three sample types. Sugarcane and sorghum straw exhibited highly similar composition profiles. The water-soluble inorganic ion and EC content were approximately 2.0-times higher than those in wheat (corn) straw. This could be because complete-combustion conditions and a high-combustion temperature enabled the release of more EC and water-soluble ions (McMeeking et al., 2009). The water-insoluble element composition of rice straw was approximately 20% higher than that of sugarcane, and the quantity of undetected components was lowest for rice straw of the five types of samples.

3.1.3. Coefficient of divergence analysis
The CD results are presented in Table 4. The average CD for all of the profiles was 0.42 ± 0.08, which suggested that other sources may have interfered with the source identification and bioreactivity analysis. The CD values from burning sugarcane and sorghum straw were similar (0.27), whereas the average CD values in other samples were all >0.45. This indicates that the PM$_{2.5}$ emitted from the burning of sugarcane and sorghum straw had different chemical profiles than those from other types of samples. The chemical profiles of wheat and corn straw revealed low CD values (0.32), but these values still exceeded the threshold for similarity. These findings suggest that other sources were dominant in the composition profiles. Moreover, the high overall CD values indicate the necessity of further bioreactivity analysis (Ho et al., 2016; Niu et al., 2017).

3.1.4. Bioreactivity
Fig. 2 displays the viability of human A549 cells after 6 h of exposure to the PM$_{2.5}$ samples. The overall results revealed a

Table 2
Composition of water-soluble ions in PM$_{2.5}$ samples.

Type of sample	[a]Na$^+$	[b]NH$_4^+$	[c]K$^+$	[d]Mg^{2+}	[e]Ca^{2+}	[f]Cl$^-$	[g]NO$_3^-$	[h]SO$_4^{2-}$	[i]$\sum$WSI
Rice straw	2.1%	1.6%	10.6%	0.0%	0.9%	19.5%	0.3%	2.8%	38.1%
Wheat straw	1.3%	01.0%	4.3%	0.1%	0.8%	10.1%	0.2%	1.1%	18.7%
Corn straw	1.4%	0.5%	2.1%	0.1%	0.7%	5.3%	0.2%	1.7%	12.0%
Sugarcane straw	7.7%	0.0%	3.6%	0.7%	2.0%	9.7%	0.1%	6.9%	30.8%
Sorghum straw	5.5%	0.9%	2.7%	0.6%	1.7%	13.5%	0.7%	3.1%	28.6%

[a] Na$^+$: sodium ion.
[b] NH$_4^+$: ammonium ion.
[c] K$^+$: potassium ion.
[d] Mg^{2+}: magnesium ion.
[e] Ca^{2+}: calcium ion.
[f] Cl$^-$: chloride ion.
[g] NO$_3^-$: nitrate ion.
[h] SO$_4^{2-}$: sulphate ion.
[i] $\sum$WSI: sum of total water soluble ions.

Table 3
Composition of elements in PM$_{2.5}$ samples.

Type of sample	Na[a]	Mg[a]	S[a]	Cl[a]	K[a]	Ca[b]	Ti[b]	V[b]	Cr[b]	Mn[b]	Fe[b]	Co[b]	Ni[b]	Cu[b]
Rice straw	4.4%	0.5%	0.3%	24.1%	15.9%	0.000%	0.000%	0.00%	0.005%	0.019%	0.048%	0.002%	0.004%	0.013%
Wheat straw	2.8%	0.4%	0.0%	12.2%	6.6%	0.021%	0.000%	0.00%	0.004%	0.010%	0.032%	0.001%	0.001%	0.008%
Corn straw	2.6%	0.4%	0.4%	6.1%	3.4%	0.021%	0.000%	0.00%	0.005%	0.021%	0.047%	0.001%	0.001%	0.011%
Sugarcane straw	7.7%	1.9%	0.3%	11.8%	6.5%	0.000%	0.000%	0.00%	0.009%	0.061%	0.137%	0.005%	0.014%	0.042%
Sorghum straw	6.8%	0.8%	0.0%	15.6%	4.4%	0.111%	0.010%	0.00%	0.010%	0.033%	0.135%	0.003%	0.010%	0.020%
	Zn[b]	As[b]	Se[b]	Br[b]	Rb[b]	Sr[b]	Mo[b]	Sn[b]	Sb[b]	Ba[b]	Hg[b]	Pb[b]	[aa]$\sum$Elements	
Rice straw	0.021%	0.001%	0.005%	0.039%	0.028%	0.002%	0.010%	0.035%	0.020%	0.066%	0.003%	0.019%	45.2%	
Wheat straw	0.009%	0.001%	0.001%	0.009%	0.005%	0.003%	0.008%	0.020%	0.009%	0.046%	0.001%	0.012%	21.9%	
Corn straw	0.018%	0.041%	0.001%	0.020%	0.000%	0.004%	0.012%	0.027%	0.014%	0.089%	0.001%	0.088%	12.9%	
Sugarcane straw	0.052%	0.000%	0.000%	0.024%	0.014%	0.014%	0.014%	0.104%	0.042%	0.146%	0.033%	0.099%	27.7%	
Sorghum straw	0.036%	0.000%	0.007%	0.030%	0.007%	0.000%	0.013%	0.056%	0.023%	0.191%	0.026%	0.063%	28.0%	

(Na: sodium; Mg: magnesium; S: sulfur; Cl: chloride; K: potassium: Ca: calcium; Ti: titanium; V: vanadium; Cr: chromium; Mn: manganese; Fe: iron; Co: cobalt; Ni: nickel; Cu: copper; Zn: zinc; As: arsenic; Se: selenium; Br: bromide; Rb: rubidium; Sr: strontium; Mo: molybdenum; Sn: tin; Sb: antimony; Ba: barium; Hg: mercury; Pb: lead; $\sum$Elements: sum of total elements).
[a] One decimal places for elements with abundance over 0.1%.
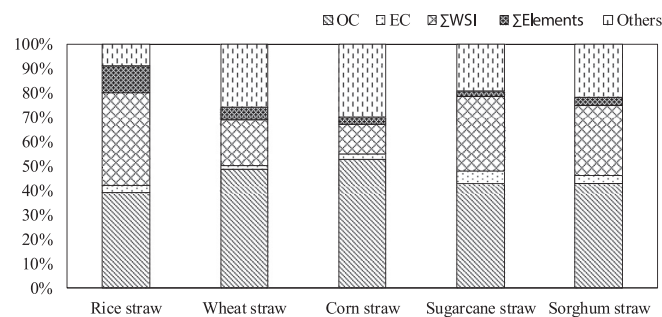[b] 3 decimal places for elements with abundance below 0.1%.

Fig. 1. Relative percentage contributions of components in biomass samples. OC stands for organic carbon fraction, EC stands for elemental carbon fraction, $\sum$WSI stands for sum of total water-soluble ions fraction, $\sum$Elements stands for sum of total elements fraction and Others stands for the unmeasured components.

descending pattern, which was particularly noticeable for the rice and corn straw samples ($p < 0.05$). Cell viability (exposure in 20 μg/mL) was approximately 95% without a clear pattern compared with the control group. Under the 150 μg/mL dosage, an approximate decrease of 20% was observed in the cell viability for the rice, wheat, and corn straw samples. By contrast, the sugarcane and sorghum samples retained high cell viability under the same dosage: 94% and 86%, respectively. These findings suggest that the open burning of biomass can lead to decreased cell viability. The effects of cell viability can be used to explain both cell death and the variation in toxic components under the same PM$_{2.5}$ concentration (Michael et al., 2013). Reactive oxygen species are able to attack cellular DNA and cause DNA damage. Cell-cycle checkpoints can further provoke the cell death mechanism to prevent DNA aberration (Chuang et al., 2011). Therefore, the results reveal that
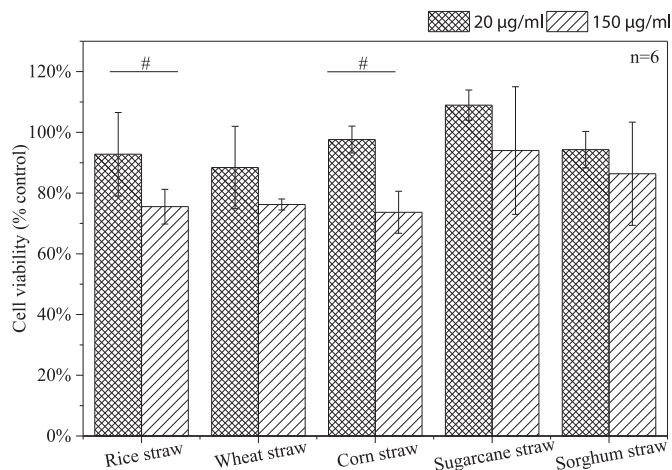
Table 4
The coefficient of divergence (CD) values between biomass samples.

R value	Rice straw	Wheat straw	Corn straw	Sugarcane straw	Sorghum straw
Rice straw	0				
Wheat straw	0.39	0			
Corn straw	0.44	0.32	0		
Sugarcane straw	0.43	0.52	0.48	0	
Sorghum straw	0.38	0.49	0.45	0.27	0

Fig. 2. Cell viability of A549 after 6 h exposure to PM$_{2.5}$ samples. ($*p < 0.05$ between different doses; n = 6 denotes each test was conducted in sextuplicate).

sugarcane and sorghum straw samples are less likely to induce cell death than other types of samples.

Fig. 3 displays cytotoxic LDH and inflammatory IL-6 levels after 6 h of exposure to the PM$_{2.5}$ samples. The LDH level in the 150 μg/
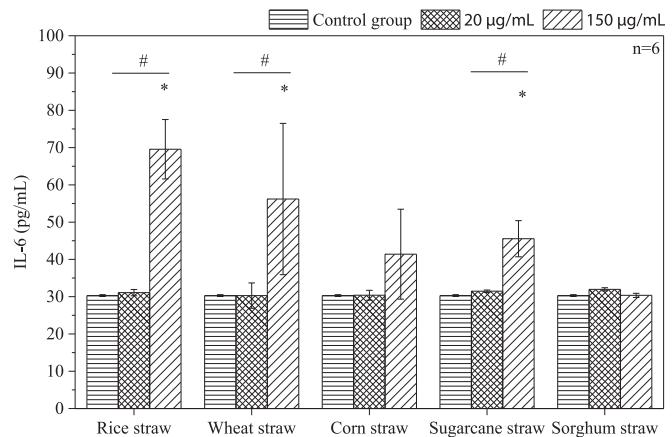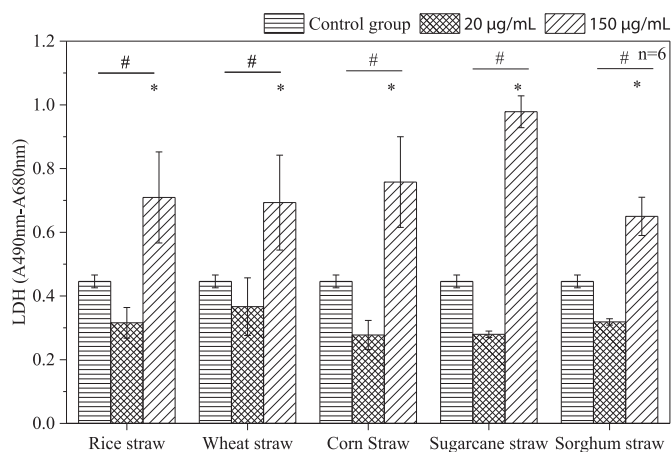

Fig. 3. LDH and IL-6 production in A549 cell after 6 h exposure to PM$_{2.5}$ samples. ($*p < 0.05$ compared to control group; #$p < 0.05$ between different doses; n = 6 denotes each test was conducted in sextuplicate).

mL group was significantly higher than that of the control group, which was not observed for the 20 μg/mL group. The fact that a dose of 20 μg/mL could not induce significant bioreactivity may suggest that a threshold exists for bioreactivity caused by PM$_{2.5}$ exposure in A549 cells. LDH level is considered an indicator of cell injury (Gavett et al., 2003) and is commonly used to determine the level of cytotoxicity induced by ambient PM$_{2.5}$ (Belcik et al., 2018; Chuang et al., 2018a; Chuang et al., 2018b). The loss of intracellular LDH and release to the culture medium is an indicator of irreversible cell death caused by damage to the cell membrane (Castell et al., 2005; Happo et al., 2010). The inflammatory response, indicated by IL-6 production after the PM$_{2.5}$ exposure is depicted in Fig. 3. An increase in IL-6 levels was observed for the rice, wheat, corn, and sugarcane straw samples. Significant increases in IL-6 levels ($p < 0.05$) between the 150 μg/mL group and control group were only observed for the rice, wheat, and sugarcane samples. IL-6 is a proinflammatory mediator, and its production is caused by the generation of reactive oxygen species (Gerlofs-Nijland et al., 2009). *In vivo* and *in vitro* studies have demonstrated that PM can induce pulmonary inflammation, such as IL-6 production (Capistrano et al., 2016). Patients with chronic obstructive pulmonary disease were shown to have a higher risk of pulmonary inflammation under exposure to biomass burning (Ramos et al., 2017). The IL-6 levels induced in this study can be presented in the following order: rice straw > wheat straw > sugarcane straw. The samples exhibited significant ($p < 0.05$) differences in bioreactivity in comparison with the control group. This finding suggests that the bioreactivity of the aforementioned sample types differed in comparison with the other types of samples (corn and sorghum straw).

3.1.5. Relationships between chemical components and bioreactivity

To determine the concentrations of chemical components and the association with bioreactivity during open burning for different types of biomass, Pearson's correlation coefficients (r) were evaluated between bioreactivity and selected PM components (Fig. 4). A strong negative correlation was discerned between OC and cell viability (r = −0.66, $p < 0.05$). An association was observed between the OC component and various organic materials in PM$_{2.5}$ that are considered cytotoxic to human cells (e.g. PAHs, dioxins, polychlorinated biphenyl, and furans) (Albinet et al., 2007; Ovrevik et al., 2010; Wang et al., 2011). The OC component was more strongly correlated with bioreactivity (determined by LDH) (r = 0.88, $p < 0.05$) than with IL-6 level (r = 0.65, $p < 0.05$). This could be because OC is a major determining factor for LDH production. The correlation coefficients between bioreactivity and TC/OC were similar, perhaps because of the high concentration of OC in the TC (>90%). Strong positive correlations were observed between EC component and bioreactivity (determined by LDH and IL-6). EC is composed of graphitic carbon and different nonvolatile organic compounds with high molecular weights that are considered to be biologically stable (Bond et al., 2004; Deng et al., 2013). Thus, the strong associations could be attributable to the relationship between OC and EC during the biomass burning process (Li et al., 2009; Ni et al., 2015), although further investigation is necessary. Pearson's correlation coefficients were determined between bioreactivity and selected elements (Fig. 4b). Neither of the highly abundant elements (Cl and K) exhibited moderate or strong positive correlations with oxidative-inflammatory responses. Similar results were obtained for elements such as Na and Mg, which could be attributable to the nontoxic interaction between human cells and the elements (e.g. Na, Mg, K, and Cl are crucial constituents in the human body) (Fraga, 2005). Strong positive correlations were discerned between the concentrations of heavy metals (Cr, Mn, Fe, Ni, Cu, Zn, Sn, and Ba) and the bioreactivity (determined by LDH)
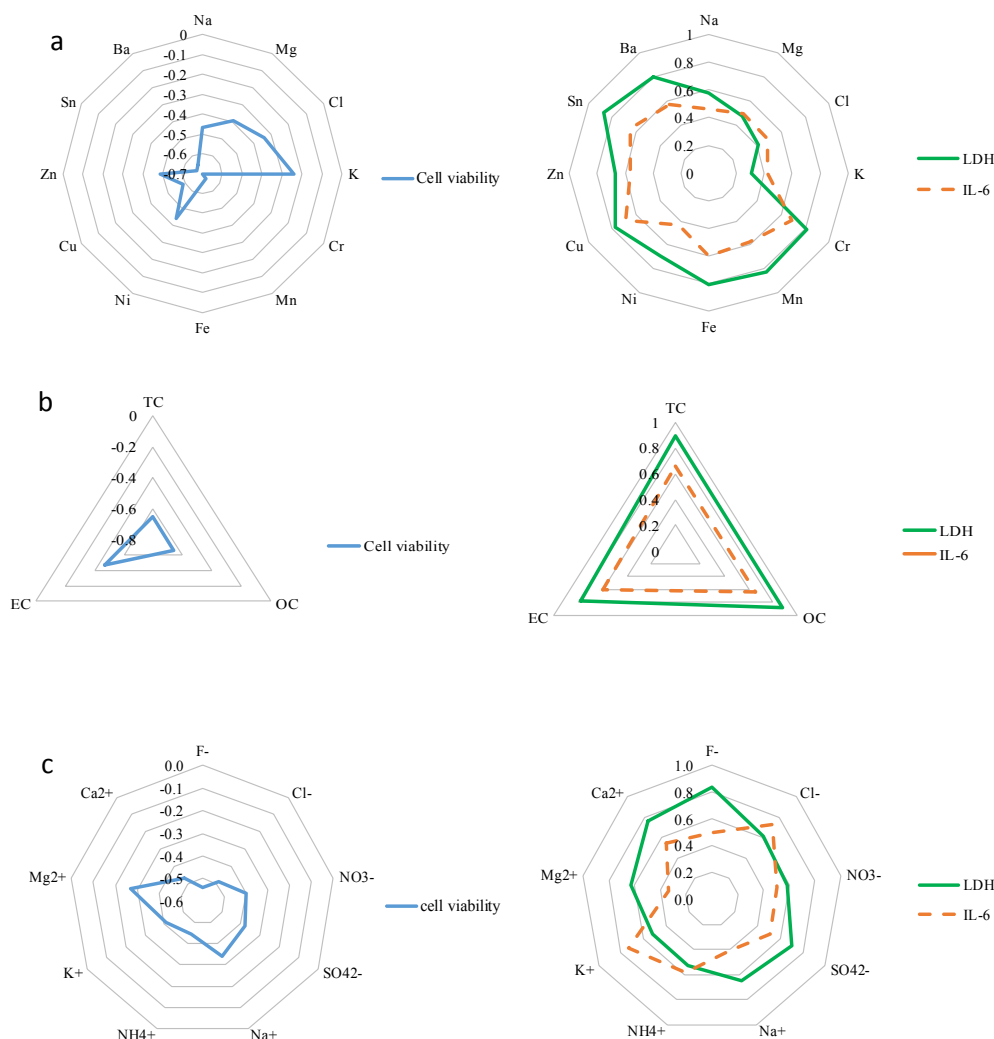
Fig. 4. Correlations analysis between cytotoxicity and (a) carbonaceous fractions, (b) elements, and (c) particulate-bound water-soluble inorganic ions. (The correlation were done with mass factions of PM$_{2.5}$ components with bioreactivities).

($r \geq 0.67$), suggesting the potential role of heavy metals in the induction of cell damage (in A549 cells).

The correlations between water-soluble inorganic ions and bioreactivity are displayed in Fig. 4c. None of the water-soluble ions demonstrated significant correlations with cell viability in any sample type. However, strong correlations were observed between major ions (F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, Mg^{2+}, and Ca^{2+}) and bioreactivity (determined by LDH) ($r \geq 0.60$). Studies have revealed that water-soluble ions are the main factors causing disruption of the cell membrane and can therefore be used as markers for cell membrane damage (Cachon et al., 2014; Zou et al., 2016). One study demonstrated that cell-membrane lysis could be induced by water-soluble inorganic ions (Zou et al., 2016). The high correlation coefficients (determined by LDH) that were observed for F$^-$, Ca^{2+}, and SO$_4^{2-}$ ions suggest possible strong associations between these ions and cell-membrane damage. Bioreactivity (determined by IL-6) was positively correlated with K$^+$ and Cl$^-$ ($r \geq 0.60$). This observation could be attributable to the abundance of K$^+$ and Cl$^-$ in the environment. All of these results suggest that the ionic components in PM$_{2.5}$ can induce bioreactivity in A549 cells but without reaching the lethal level.

4. Conclusions

The characteristics of PM$_{2.5}$ emitted during the open burning of biomass were investigated in this study. Carbonaceous fractions were determined to be the most abundant components of PM$_{2.5}$. The OC/EC ratios indicated that the open burning of biomass primarily produced organic matter. The amount of potassium and chlorine produced (in element and ion form) was higher than that produced through coal combustion or by atmospheric aerosols but nevertheless lower than the content of heavy metals (Cr, Mn, Fe, Ni, Cu, Zn, Sn, and Ba). The CD revealed different chemical profiles for the five sample types. All of the PM$_{2.5}$ samples significantly increased bioreactivity (determined by cell viability, LDH, and IL-6). Rice, wheat, and corn straw samples all resulted in higher LDH and IL-6 production, possibly indicating higher bioreactivity compared with other sample types. Correlation analysis revealed that OC, heavy metals (Cr, Mn, Fe, Ni, Cu, Zn, Sn, and Ba), and water-soluble ions (F$^-$, Ca^{2+}, and SO$_4^{2-}$) were the determinant components for inducing LDH release. These findings suggest that the open burning of biomass may affect human health conditions and therefore that the use of biomass products must be controlled.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2018.10.119.

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