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Characterization and cytotoxicity of PAHs in $PM_{2.5}$ emitted from residential solid fuel burning in the Guanzhong Plain, China☆

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ABSTRACT

The emission factors (EFs) of polycyclic aromatic hydrocarbons (PAHs) in $PM_{2.5}$ were measured from commonly used stoves and fuels in the rural Guanzhong Plain, China. The toxicity of the $PM_{2.5}$ also was measured using *in vitro* cellular tests. EFs of PAHs varied from 0.18 mg kg^{-1} (maize straw charcoal burning in a clean stove) to 83.3 mg kg^{-1} (maize straw burning in Heated Kang). The two largest influencing factors on PAH EFs were air supply and volatile matter proportion in fuel. Improvements in these two factors could decrease not only EFs of PAHs but also the proportion of 3-ring to 5-ring PAHs. Exposure to $PM_{2.5}$ extracts caused a concentration-dependent decline in cell viability but an increase in reactive oxygen species (ROS), tumor necrosis factor *a* (TNF-α) and interleukin 6 (IL-6). $PM_{2.5}$ emitted from maize burning in Heated Kang showed the highest cytotoxicity, and EFs of ROS and inflammatory factors were the highest as well. In comparison, maize straw charcoal burning in a clean stove showed the lowest cytotoxicity, which indicated a clean stove and fuel treatment were both efficient methods for reducing cytotoxicity of primary $PM_{2.5}$. The production of these bioreactive factors were highly correlated with 3-ring and 4-ring PAHs. Specifically, pyrene, anthracene and benzo(a)anthracene had the highest correlations with ROS production ($R = 0.85$, 0.81 and 0.80, respectively). This study shows that all tested stoves emitted $PM_{2.5}$ that was cytotoxic to human cells; thus, there may be no safe levels of exposure to $PM_{2.5}$ emissions from cooking and heating stoves using solid fuels. The study may also provide a new approach for evaluating the cytotoxicity of primary emitted $PM_{2.5}$ from solid fuel burning as well as other $PM_{2.5}$ sources.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), which are the principal organic pollutants from incomplete combustion of fuel, are of special interest due to their toxicity, carcinogenicity and ubiquitous presence in the environment (Niu et al., 2017; Shen et al., 2011b). Generally, compared to industrial combustion processes equipped with pollution control systems, the domestic cooking/heating process in rural areas without pollution control has much higher emission factors (EFs) of PAHs (Oanh et al., 1999). An estimated 504 Gg PAHs were emitted in 2007 globally and nearly half originated from residential solid fuel burning (RSFB) (Shen et al., 2013b).

High emission of PAHs from combustion sources is related to several factors. The first of these is the type of residential solid fuels (such as branches, crop residues, charcoal and bituminous coal). Approximately 41% of total households globally in 2010 relied on solid fuels for cooking and space heating, and crop residue was the most popular fuel used (Bonjour et al., 2013; Xu et al., 2016b). In developing countries, this proportion reached 80% (Zhang and Tao, 2009). Solid fuels with high volatile matter (VM) contents (i.e., straw, branch and bitumite) lead to a higher possibility of incomplete combustion than those having low VM content (Shen, 2017; Shen et al., 2014a). The second reason for high PAH emission from RSFB is low energy efficiency for the traditional combustion stove. Worldwide, three-stone stoves with an energy efficiency of 8–12% and traditional domestic cookstoves with an energy efficiency of

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10–15% are still widely used in rural areas (MacCarty and Bryden, 2015). Moreover, a wide range of traditional space-heating cookstoves with energy efficiencies in the range of 25–30% are used as main heating measures in the rural areas where individual residential heating is popular (Zeng et al., 2007). The extremely low combustion efficiencies lead to high energy wastage and high emissions of contaminants such as particulate matter (PM), carbon monoxide and PAHs (Shen et al., 2011a; Shen et al., 2010; Sun et al., 2017).

After two "energy conservation and emission reduction" campaigns implemented by the Chinese government (National Improved Stove Program, 1982–1992; 11th to 12th Five-year Plan, 2011–2015) (Chowdhury et al., 2013; Mehetre et al., 2017), the residential stove market in China is currently (2017) selling an unprecedented number of units. Consequently, various types of stoves coexist in rural areas of China. This situation suggests the effectiveness of the emission reduction policy, but causes difficulties for documenting environmental impacts because the EFs statistics for different stoves vary enormously (Shen et al., 2014a; Zhi et al., 2008). For instance, EF of PM and PAHs from traditional stoves could be 1–2 orders of magnitudes higher than those of modern stoves that have a secondary air supply (Shen et al., 2010; Sun et al., 2017). Accurate measurements of EFs from different solid fuels and stoves could reduce the high uncertainty in emission inventories (Gullett et al., 2004; Johnson et al., 2010; Lu et al., 2009).

The majority of previous studies on emissions from cookstoves and heating stoves focused on the exposure assessment of PM or equivalent PAHs; however, these metrics are only indicative of carcinogenic and noncarcinogenic risks (Bostrom et al., 2002; Dorne et al., 2011; Zhang et al., 2009). Organic matter in PM is capable of causing cellular oxidative stress (Li et al., 2010) and some PAHs can cause pro-inflammatory effects (Lin et al., 2013). Furthermore, production of reactive oxygen species (ROS), which can induce inflammatory reactions in human cells, is closely related with some PAHs (Benbrahim-Tallaa et al., 2012). The research on estimating ROS production triggered by primary PM from RSFB is rare, but it could be useful for visualizing and evaluating the cytotoxicity of PM from RSFB.

The Guanzhong Plain area in China covers approximately 36,000 km^2 and has a population of almost 24 million. The traditional type of wintertime residential heating in rural areas is burning maize straw in a "Heated Kang", which causes serious rural and urban air pollution problems (Shen et al., 2009, 2014a; 2014b; Sun et al., 2017). The dependency on solid fuels exceeds 80% in the rural Guanzhong Plain (Hou et al., 2017). Sun et al. (2017) described the field and laboratory measurements of $PM_{2.5}$ EFs from RSFB in detail.

The objectives of this study were 1) to measure and characterize the EFs of PAHs from RSFB in different conditions in the Guanzhong Plain, China, and 2) to investigate the cytotoxicity of the $PM_{2.5}$ emitted from RSFB and the correlation between cytokines and particle-bound PAHs.

2. Methodology

2.1. Stoves and fuels

Three types of stoves were evaluated: a Heated Kang (HK), an "old-fashioned" stove (OS) and a clean stove (CS). A brief description and nomenclature for each experiment are given in Table 1. Sampling was conducted both in a laboratory and on site in a typical village in the Guanzhong Plain, China. $PM_{2.5}$ samples were collected on site both HK (Fig. S1a) and OS (Fig. S1b). Maize straw was the typical fuel used in HK. Two scenarios were examined according to usual domestic practices: long smoldering for almost the whole night (MS-HK1) and short smoldering before bedtime (MS-HK2). The smoldering time control was realized by regulating the air supply rate. For OS, bitumite (BI-OS) and anthracite (AN-OS) were the main fuels used for heating, and maize straw (MS-OS) was usually used for ignition.

For CS (Fig. S1c), the experiments were conducted in a laboratory combustion chamber (described by Sun et al., 2017). The CS tested in this study was fitted with a secondary air supply, and was a type that was widely used for cooking and heating in the selected village. The stove could use several types of fuels, including straw, briquettes and charcoal. Three of the main fuels used in the area (maize straw, rice straw and wood branches) were selected for the laboratory tests to simulate the real scenarios. The fuels collected were air-dried under storage, which means they were stored in ambient temperature (~20 °C) and controlled relative humidity (~35–40%) before analyzed and used. Proximate analysis was conducted for the air-dry fuels and the results are shown in Table S1. On an air-dry fuel basis, the sum of moisture, ash, volatile matter and fixed carbon (all in %) were 100%.

A specially fabricated dilution system having a dilution rate from 5- to 50-fold was used to collect the smoke emitted from solid fuel burning stoves in the on-site experiments. A certain number of parallel diluted smoke channels were fitted for online and offline samplers. The air-stream of diluted smoke was drawn into three channels fitted with mini-volume samplers (Airmetrics, Springfield, OR, USA). Each sampler operated at a flow rate of 5.0 L min^{-1} and collected the $PM_{2.5}$ on Quartz-fiber (QM/A, Whatman, Maidstone, UK) and Teflon® filters, which were both pre-treated before being used. For each stove -fuel experiment, replication was conducted at least 3 times to get the average and standard deviation data. The number of replicate experiments is shown in Table 1. The field dilution sampling equipment and procedures are described in detail in Sun et al. (2017).

2.2. PAHs measurements

Collection methods of $PM_{2.5}$ samples, both in laboratory and on site, were the same as described in Sun et al. (2017). One-half of each quartz-fiber filter was extracted with high-purity dichloromethane and methanol (2:1, v/v) under ultrasonication for 15 min. The extraction procedure was repeated three times to ensure the completeness of extraction. Water and debris in the combined extracts were then removed by passing the liquid through Pasteur pipettes filled with sodium sulfate (Na_2SO_4) and glass wool. The extracts were finally concentrated to 1 mL by a rotary evaporator under vacuum. Then the samples were analyzed using a gas chromatography/mass spectrometer (GC/MS) (Model 7890A/5975C, Agilent Technologies, Santa Clara, CA, USA). The settings of GC/MS programs are shown in Niu et al. (2017). In all, 16 preferential controlled PAH species were measured: naphthalene (NAP), acenaphthene (ACE), acenaphthyleme (ACY), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo- (a)pyrene (BaP), dibenz(a,h)anthracene (DahA), indeno(l,2,3- cd)pyrene (IcdP), and benzo(g,h,i)perylene (BghiP).

2.3. Filter extraction for cell toxicity studies

One-half of each particle-laden Teflon® filter was immersed in 2 mL of high-purity methanol, and then subjected to ultrasonication in an ice-cooled water bath for 30 min. The extraction procedure was repeated twice, and the combined extracts of each filter were purged under a gentle stream of nitrogen (N_2 > 99.995%) for 2 h to completely remove the solvent. The extracts after

Table 1
EFs of $PM_{2.5}$ emitted from solid fuels burned in different stoves.

Source	Stove	EF-$PM_{2.5}$	SD	Explaination	Abbreviation	No. of repetitive experiments
Maize straw	Heated Kang	46.1	1.4	Long time Smoldering	MS-HK1	3
Maize straw	Heated Kang	17.4	5.5	Short time smoldering	MS-HK2	4
Maize straw	Old-fashioned stove	20.7	12.1	Nomal	MS-OS	3
Bitumite	Old-fashioned stove	26.8	1.1	Nomal	BI-OS	4
Anthracite	Old-fashioned stove	2.8	0.5	Nomal	AN-OS	4
Maize straw	Clean stove	9.5	2.6	Nomal	MS-CS	3
Maize straw briquette	Clean stove	2.5	1.1	Smoldering & flaming	MB-CS1	3
Maize straw briquette	Clean stove	2.3	0.3	Flaming	MB-CS2	3
Maize straw briquette charcoal	Clean stove	1.6	0.1	Nomal	MC-CS	3
Rice straw	Clean stove	9.9	0.3	Nomal	RS-CS	3
Rice straw briquette	Clean stove	6.4	0.5	Nomal	RB-CS	3
Rice straw briquette charcoal	Clean stove	4.8	0.3	Nomal	RC-CS	3
Branch	Clean stove	7.2	1.1	Smoldering	BR-CS1	3
Branch	Clean stove	1.1	0.1	Optimal	BR-CS2	3
Branch	Clean stove	2.1	0.1	Over aired	BR-CS3	3
Branch briquette	Clean stove	1.9	0.1	Nomal	BB-CS	3
Branch charcoal	Clean stove	1.3	0.1	Nomal	BC-CS	3

weighing were dissolved in phosphate buffered saline (PBS) solution and diluted to concentrations of 100 and 200 μg mL^{-1}; and the PBS diluent alone was used as a control. A small amount of dimethyl sulfoxide (<0.05% v/v) was added to the samples and controls to dissolve any water-insoluble matter.

Human alveolar epithelial cells (A549) were obtained from the American Type Culture Collection (ATCC, Rockville, MD, USA). A549 cells were cultured using F-12 cell culture medium (Thermo Fisher Scientific Inc., Waltham, MA, USA) supplemented with 10% heat-inactivated fetal bovine serum (Biowest, Riverside, MO, USA) and 1% antibiotics penicillin/streptomycin (100 units mL^{-1}) in a humidified incubator supplied with 5% carbon dioxide at 37 °C. The A549 cells were seeded into inserts for 24-well trans wells (Thermo Fisher Scientific Inc., Waltham, MA, USA) at a density of 1×10^5 cells mL^{-1} and incubated for 24 h. The cultured cells were exposed to $PM_{2.5}$ extracts for 24 h. Cell viability was measured using the MTT (3-[4, 5-dimethylthiazol-2-yl]-2, 5 diphenyl tetrazolium bromide) assay.

2.4. Enzyme-linked immunosorbent assays and intracellular ROS measurement

The supernate from exposed A549 cells was analyzed to determine concentrations of tumor necrosis factor *a* (TNF-α) and interleukin 6 (IL-6). Enzyme-linked immunosorbent assays (ELISA) kits (R&D Systems, Inc., Minneapolis, MN, USA) were used to determine the TNF-α and IL-6 concentrations. All ELISA experiments were performed using the manufacturer's instructions.

ROS production was determined using a fluorogenic cell-based method with 2′,7′-dichlorofluorescin diacetate (DCFH-DA) as the probe. The highly fluorescent compound 2′,7′-dichlorofluorescin (DCF) was produced by oxidation reactions of DCFH with ROS. The probe was responsive to the dominant cellular ROS (Daher et al., 2014). After exposure, the fluorescence intensity was determined at an excitation wavelength of 485 nm and an emission wavelength of 530 nm using a VICTOR™ X Light Luminescence Plate Reader (PerkinElmer, Inc., Waltham, MA, USA). The cellular oxidative stress was presented as fluorescence units to clearly show the level of ROS production in cells and from primary emission, and the unit of ROS was changed to μg Zymosan equivalents mL^{-1} and μg Zymosan equivalents kg^{-1} (Landreman et al., 2008). To get enough data for statistical analysis, three parallel biological assays were set for each experiment.

2.5. Statistical analysis

All averages in this paper are expressed as arithmetic mean values with standard deviations. One-way analyses of variance were used to test the statistical significance of between-group differences. Pearson's correlation coefficients were calculated to assess the associations between PAHs and ROS and pro-inflammatory cytokines (i.e., TNF-α and IL-6). The level of significance for all statistical tests was set as $P < 0.05$. The statistical analyses were completed using SPSS software (version 12.0, SPSS Inc., Chicago, IL, USA).

3. Results and discussion

3.1. EFs of PAHs

As shown in Fig. 1, total PAHs (∑PAHs) EFs (air-dry fuel basis) ranged from 0.18 mg kg^{-1} (kg means air-dry fuel burned) (MC-CS) to 83.3 mg kg^{-1} (MS-HK1), a difference greater than 400-fold. Some of these results were lower than the range reported in the literature (4–76 mg kg^{-1}) primarily because the literature-reported data were based on raw solid fuels such as straws and coals. (Dhammapala et al., 2007; Hays et al., 2005; Lu et al., 2009). The EFs followed a decreasing order of straw > straw briquettes > straw briquette charcoal. Similar results were obtained in coal burning tests such that bitumite (68.7 ± 21.8 mg kg^{-1}) had over 40-times higher EF of ∑PAHs than anthracite (1.7 ± 0.9 mg kg^{-1}). Another crucial influencing factor on PAH EFs was stove type; the traditional stoves (Heated Kang and old-fashioned coal stove) had much higher ∑PAHs EFs than clean stoves even using the same fuel. The poor air supply conditions in traditional stoves should be blamed for the high EFs of PAHs from these devices (Jetter et al., 2012; Shen et al., 2013a). Thus, the EFs of PAHs from clean stoves with secondary air supply system were markedly lower than those from traditional stoves.

To further investigate the effects of air supply on PAH EFs, controlled laboratory experiments also were conducted. The results showed that air supply could have a non-linear effect on PAH emission in solid fuel burning. First, EFs of PAHs decreased with increasing air supply, such as MS-HK1 compared to MS-HK2, and MB-CS1 compared to MB-CS2. These results can be partly explained by the fact that oxygen-deficient burning promotes formation of PAHs by the pathway of hydrogen abstraction/carbon addition reactions (Wang et al., 2017). While the increasing enhances of air supply (BR-CS3) could lead to even higher EFs than a moderate air supply (BR-CS2). It is probably because an excessive air supply might reduce the combustion temperature, leading to an increased amount of incomplete combustion products, e.g. PAHs (Shen et al.,

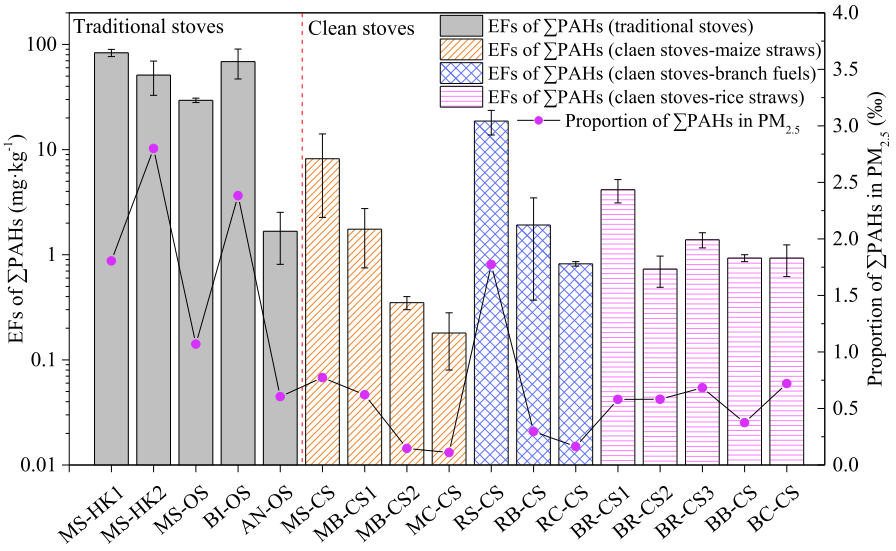

Fig. 1. EFs of ∑PAHs and their proportions in $PM_{2.5}$.

2013a; Sun et al., 2017).

The proportion of PAHs to $PM_{2.5}$ mass ranged from 0.11‰ to 2.80‰ in this study. There were various reasons for the large range, including fuel property, combustion temperature, air supply, and fire management (Dhammapala et al., 2007; Gullett et al., 2004). Generally, these parameters were inter-related. To further study the reasons, the correlation between EFs of ∑PAHs and their proportion in $PM_{2.5}$ were calculated (Fig. S2). Because the air supply conditions were similar, the most probable influencing factor should have been the fuel properties. Previously, fuel moisture and VM were reported as the most crucial factors influencing the EFs of $PM_{2.5}$ and PAHs (Lu et al., 2009). It is because the VM combustion phase is more likely to produce black carbon particles, which are often co-emitted with PAHs (Richter and Howard, 2000). For traditional stoves (except those burning coal), the correlation between EFs of ∑PAHs and their proportion in $PM_{2.5}$ was negative ($R^2 = 0.96$, $P < 0.01$). This is possibly caused by the long smoldering phase in traditional stoves. In large scale, the ratios of PAHs proportions in $PM_{2.5}$/EFs of PAHs are still higher than those from clean stoves. Therefore, the overall correlation between PAH proportions in $PM_{2.5}$ and EFs of PAHs could be positive.

3.2. PAHs composition profile

Table 2 shows the EFs of individual PAH species from different experiments. NAP was barely measured because it generally occurred in the gas phase (Lu et al., 2009; Shen et al., 2011a). Among the remaining particulate-bound PAHs, FLA and PYR were the two most abundant species, while ACY, ACE and DahA appeared in the lowest concentrations. Overall, PAH ring-number profiles for maize (rice) straws were similar to maize (rice) straw briquettes (Fig. S3). That is, 4-ring species were dominant, and followed in proportion by 5-ring and 3-ring species. Notably, only 4-ring species were measured for the two cleanest experiments (AN-OS and MC-CS). The profiles for rice straw charcoal and branch charcoal were similar to that for bitumite, in which the proportion of 5- and 6-ring species were markedly enhanced and 5-ring PAH species replaced the 4-ring species as the most abundant ($P < 0.05$).

Previously, the parent PAH isomer ratios between sources and receptors often have been used in receptor modeling for source apportionment (Niu et al., 2017; Xu et al., 2016a). Several commonly used isomer ratios including ANT/(ANT + PHE), FLA/(FLA + PYR), BaA/(BaA + CHR), IPY/(IPY + BghiP), BbF/(BbF + BkF), and BaP/(BaP + BghiP) were calculated in this study to give insight into the PAH sources. Isomer ratios from this study are compared with some typical ratios from previous studies in Table 3. The six parent PAH isomer ratios from maize straw burning in traditional stoves in this study were generally similar to those from similar stove types burning crop residues (Oanh et al., 2005; Sheesley et al., 2003). Moreover, the PAH isomer ratios of clean stoves showed a larger variation than those of crop residue burning in traditional stoves or open fires (Hays et al., 2005). For example, ANT/(ANT + PHE) ratios showed a large variation (ranged from 0.06 to 0.46)for residue burning in a clean stove in this study compared to 0.13–0.16 for crop residue burning in traditional stoves and 0.17–0.25 for crop residue burning in an open fire (Hays et al., 2005). Probably these results could be explained by the difference in combustion conditions (Shen et al., 2013a). The large variations in ratios from parallel experiments (MB-CS1 and MB-CS2, and BR-CS1, BR-CS2 and BR-CS3) could support this explanation as well. Additionally, PAH ratios from branch burning in this study did not show significant differences ($P > 0.05$) compared to those of crop residues because they were in the same category of biomass (Oanh et al., 2005; Xu et al., 2016a; Zhang et al., 2008).

Lastly, PAH ratios (except BaP/(BaP + CHR)) for charcoal burning, including rice straw charcoal and branch charcoal, were very similar to that for bitumite. However, these PAH ratios cannot be used to distinguish coal (and charcoal) combustion sources from biomass sources due to the wide range in values for various diagnostic PAH ratios. For example, IPY/(IPY + BghiP) ratios in the range 0.50–0.63 have been reported for residential burning of coal chunks (Chen et al., 2005; Zhang et al., 2008), and residential biomass burning ratios in this study also fall into this range. Thus, these ratios should be used with caution in source apportionment because the ratios varied not only with fuel types but also with burning conditions.

3.3. Cell response of $PM_{2.5}$ from RSFB

The viabilities of A549 cells after 24-h exposure to the $PM_{2.5}$ sample extracts (Fig. 2) showed that majority of the treatments induced a concentration-dependent decrease in MTT-reduction activity. These results indicated that higher $PM_{2.5}$ concentration exposure emitted from RSFB could lead to a greater decline in cell

Table 2
EFs of 16 priority PAHs in different experiments ($mg \cdot kg^{-1}$).

Source	NAP	ACY	ACE	FLO	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IcdP	DahA	BghiP	∑EF
MS-HK1	1.3 ± 0.2	1.1 ± 0.1	0.2 ± 0	3.6 ± 0.2	10.3 ± 0.7	1.6 ± 0.1	17.0 ± 1.7	17.3 ± 1.7	4.5 ± 0.3	6.8 ± 0.6	4.5 ± 0.5	4.2 ± 0.3	3.6 ± 0.1	3.2 ± 0.3	0.5 ± 0	3.7 ± 0.3	83.3 ± 6.6
MS-HK2	0.1 ± 0	0.4 ± 0.1	0.1 ± 0.1	1.5 ± 0.6	0.8 ± 0.6	0.2 ± 0.1	10.2 ± 3.2	11.3 ± 4.6	5.6 ± 4.1	11.1 ± 4	2.9 ± 0.5	1.3 ± 0.8	0.8 ± 1.1	2.4 ± 2.1	0.3 ± 0	2.5 ± 2.4	51.2 ± 18.3
MS-OS	<DL	<DL	<DL	1.1 ± 0.1	6.2 ± 1.9	1.1 ± 0.8	4.8 ± 0.5	7.2 ± 0.8	1.2 ± 0	2.3 ± 0	0.9 ± 0	1.0 ± 0.3	1.7 ± 0	1.0 ± 0.1	<DL	1.1 ± 0.1	29.5 ± 1.4
BI-OS	<DL	<DL	<DL	5.2 ± 1.2	2.9 ± 0.2	2.0 ± 0	3.1 ± 0.3	8.3 ± 1.1	7.1 ± 4.4	7.4 ± 3.1	7.1 ± 2.6	7.0 ± 3.3	7.1 ± 2.4	5.8 ± 3.4	<DL	5.8 ± 2.2	68.7 ± 21.8
AN-OS	<DL	<DL	<DL	<DL	<DL	<DL	0.3 ± 0.2	1.4 ± 0.7	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	1.7 ± 0.9
MS-CS	<DL	<DL	<DL	0.5 ± 0.4	0.7 ± 0.2	0.2 ± 0.1	1.0 ± 0.7	1.5 ± 0.9	0.6 ± 0.6	0.9 ± 0.8	0.7 ± 0.5	0.7 ± 0.7	0.6 ± 0.5	0.4 ± 0.4	<DL	0.5 ± 0.4	8.2 ± 5.9
MB-CS1	<DL	0.1 ± 0.1	<DL	0.1 ± 0.1	0.4 ± 0.4	0.03 ± 0.02	0.3 ± 0.3	0.1 ± 0.2	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.2	<DL	0.02 ± 0.01	1.8 ± 1.0
MB-CS2	<DL	<DL	<DL	0.02 ± 0.02	0.01 ± 0.02	0.01 ± 0.02	0.05 ± 0.02	0.12 ± 0.01	0.03 ± 0.01	0.04 ± 0.02	0.03 ± 0.01	0.03 ± 0.02	0.03 ± 0.02	0.02 ± 0.01	<DL	0.02 ± 0.02	0.35 ± 0.05
MC-CS	<DL	<DL	<DL	<DL	<DL	<DL	0.03 ± 0.02	0.15 ± 0.08	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.18 ± 0.10
RS-CS	<DL	0.05 ± 0.06	3.7 ± 1.8	1.0 ± 0.1	0.02 ± 0.03	0.02 ± 0.01	1.1 ± 0.1	3.8 ± 1.7	1.2 ± 0.3	1.5 ± 0.3	1.4 ± 0.2	1.8 ± 0.3	1.2 ± 0.3	1.0 ± 0.1	<DL	1.0 ± 0.1	18.7 ± 4.9
RB-CS	<DL	<DL	<DL	0.1 ± 0.1	0.03 ± 0.01	0.02 ± 0.01	0.4 ± 0.3	0.6 ± 0.3	0.2 ± 0.2	0.2 ± 0.2	0.1 ± 0.1	0.1 ± 0.2	0.1 ± 0.1	0.06 ± 0.06	<DL	0.06 ± 0.07	1.9 ± 1.6
RC-CS	<DL	<DL	<DL	0.05 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.12 ± 0.01	0.25 ± 0.05	0.07 ± 0.02	0.10 ± 0.02	0.07 ± 0.02	0.06 ± 0.02	0.06 ± 0.01	0.03 ± 0.02	<DL	0.03 ± 0.01	0.8 ± 0.2
BR-CS1	<DL	0.07 ± 0.10	<DL	0.1 ± 0.1	0.1 ± 0	0.1 ± 0.1	1.0 ± 0.2	1.3 ± 0.4	0.3 ± 0.1	0.4 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.15 ± 0.04	0.09 ± 0.04	0.07 ± 0.09	0.04 ± 0.05	4.2 ± 1.0
BR-CS2	<DL	<DL	<DL	0.03 ± 0.02	0.07 ± 0.01	0.04 ± 0.01	0.09 ± 0.03	0.2 ± 0.1	0.08 ± 0.03	0.10 ± 0.04	0.04 ± 0.03	0.05 ± 0.03	0.05 ± 0.03	0.02 ± 0.01	<DL	0.02 ± 0.01	0.7 ± 0.2
BR-CS3	<DL	<DL	<DL	0.07 ± 0.01	0.09 ± 0.07	0.02 ± 0.02	0.22 ± 0.07	0.35 ± 0.07	0.12 ± 0.01	0.16 ± 0.03	0.09 ± 0.01	0.09 ± 0.01	0.08 ± 0.01	0.05 ± 0.01	0.07 ± 0.01	0.03 ± 0.01	1.4 ± 0.2
BB-CS	<DL	<DL	0.10 ± 0.02	0.05 ± 0.02	0.02 ± 0.01	0.02 ± 0.01	0.19 ± 0.05	0.26 ± 0.01	0.04 ± 0.02	0.06 ± 0.02	0.04 ± 0.03	0.06 ± 0.03	0.07 ± 0.01	0.05 ± 0.03	<DL	0.03 ± 0.03	0.9 ± 0.1
BC-CS	<DL	<DL	0.05 ± 0.03	0.09 ± 0.02	<DL	<DL	<DL	0.21 ± 0.16	0.05 ± 0.01	0.11 ± 0.01	0.10 ± 0.03	0.12 ± 0.02	0.09 ± 0.04	0.06 ± 0.02	<DL	0.08 ± 0.01	0.9 ± 0.3

<DL means the concentration was lower than detect limit.

viability than lower concentrations. In detail, 200 μg mL^{-1} $PM_{2.5}$ extracts decreased cell viability by 6.0–23.4% compared to the effect from 100 μg mL^{-1} extracts. Furthermore, cell viability also was linked to different $PM_{2.5}$ sources because of the variation in chemical compounds associated with the $PM_{2.5}$. Therefore, even when exposed to the same $PM_{2.5}$ concentrations, cell viability exhibited some differences. For example, the cell viability could be as high as 79.6 ± 9.6% in MB-CS2, but as low as 52.9 ± 8.6% in MS-HK1, both at a $PM_{2.5}$ concentration of 100 μg mL^{-1} ($P < 0.05$). Because the cell exposures were adjusted to the same $PM_{2.5}$ concentrations, the effects on cell viabilities can be explained by variations in particle toxicity (Niu et al., 2017). The results indicated that the $PM_{2.5}$ emitted from MS-HK1 had greater cytotoxic effects than $PM_{2.5}$ from MB-CS2. Therefore, the clean stove used in this study could efficiently reduce the cytotoxicity of emitted $PM_{2.5}$ compared to emissions from traditional stoves, including Heated Kang and old-fashioned stoves (except when anthracite was the fuel, $P < 0.05$).

An increase of ROS level in epithelial lung cells could result in oxidative stress when ROS exceeds the capacity of anti-oxidative defenses (Janssen et al., 2014). The ROS production differed as a function of fuels and stove types in this study because these variables caused great changes in PAH profiles of the emitted $PM_{2.5}$. The ROS production was determined from the cell culture supernatants after 24 h of incubation in $PM_{2.5}$ extracts (Fig. 3). Similar to cell viability, ROS levels were also concentration dependent; 200 μg mL^{-1} $PM_{2.5}$ extracts could, on average, stimulate ROS ~1.7 times higher than 100 μg mL^{-1} extracts. Among all 17 groups of experiments, MS-HK1 showed the highest level of ROS for exposure to 100 μg mL^{-1} $PM_{2.5}$ extracts (ROS = 1696.9 μg Zymosan·mL^{-1}) and 200 μg mL^{-1} $PM_{2.5}$ extracts (ROS = 2790.3 μg Zymosan·mL^{-1}). ROS from MS-HK2 at the two exposure concentrations was 23.8% and 29.3% lower, respectively, compared to MS-HK1, which indicated that an improvement in air supply could effectively reduce the oxidative stress associated with $PM_{2.5}$. Similar results were observed between MB-CS1 and MB-CS2 and in previous studies (Ho et al., 2016; Ziech et al., 2010). Likewise, fuel property played a crucial role in altering the chemical composition emitted $PM_{2.5}$ and affected ROS production (Shen et al., 2013a). AN-OS induced the lowest ROS level in traditional stove groups due to the extremely low VM proportion in the stove emissions. Similarly, all charcoal burning (of both straws and branches) in a clean stove induced lower ROS levels than traditional stoves (except AN-OS) ($P < 0.05$).

EFs of ROS were calculated based on the ROS levels exposure to 100 μg mL^{-1} and refer to the method of EF-$PM_{2.5}$ calculations (Sun et al., 2017). The results are plotted in Fig. 3. EFs of ROS varied from 3.02 to 391.44 g Zymosan·kg^{-1}, a difference of more than 2 orders of magnitude. Overall, clean stoves showed much lower EFs of ROS than traditional stoves (except when anthracite was the fuel, $P < 0.05$) due to the lower EF-$PM_{2.5}$ and equivalent ROS levels. Charcoal had lower EF of ROS compared with their parent fuels and their briquettes. Furthermore, the ROS EFs of briquettes with optimal air supply were comparable with those of charcoal. The results indicated that clean stoves, fuel treatment, and controlled air supply could all reduce the EFs of ROS. In fact, the final EFs of ROS from BR-CS2 (3.02 ± 0.42 g Zymosan·kg^{-1}) was even lower than that of anthracite (5.18 ± 0.74 g Zymosan·kg^{-1} for AN-OS), which has been proved to be a clean energy source (Chen et al., 2005). Therefore, the EFs of ROS could intuitively reflect the oxidative stress potential of primary $PM_{2.5}$ from different fuels and stoves.

Moreover, oxidative stress can activate signaling pathways that cause inflammatory response, for which the inflammatory mediators such as IL-6 and TNF-α have been used as biomarkers (Gerlofs-Nijland et al., 2009). The IL-6 and TNF-α production in the A549

Table 3
Comparison of parent PAH isomer ratios from this study and previous studies.

	ANT/(ANT + PHE)	FLA/(FLA + PYR)	BaP/(BaP + CHR)	IPY/(IPY + BghiP)	BbF/(BbF + BkF)	BAP/(BaP + BghiP)
MS-HK1	0.13	0.50	0.40	0.46	0.51	0.50
MS-HK2	0.16	0.48	0.33	0.48	0.70	0.24
MS-OS	0.15	0.40	0.35	0.47	0.47	0.60
BI-OS	0.41	0.27	0.49	0.50	0.50	0.55
AN-OS	–	0.16	–	–	–	–
MS-CS	0.21	0.39	0.43	0.46	0.49	0.55
MB-CS1	0.06	0.69	0.43	0.95	0.51	0.91
MB-CS2	0.46	0.28	0.38	0.53	0.52	0.70
MC-CS	–	0.17	–	–	–	–
RS-CS	0.45	0.22	0.43	0.50	0.44	0.54
RB-CS	0.38	0.40	0.44	0.48	0.46	0.69
RC-CS	0.59	0.31	0.38	0.44	0.53	0.68
BR-CS1	0.49	0.43	0.43	0.70	0.51	0.81
BR-CS2	0.36	0.29	0.44	0.46	0.42	0.72
BR-CS3	0.17	0.38	0.43	0.71	0.51	0.79
BB-CS	0.51	0.42	0.39	0.63	0.37	0.69
BC-CS	0.44	0.21	0.30	0.45	0.45	0.56
crop residue/stove[a,b]	0.20	0.51–0.80	0.46	0.31–0.50	0.50–0.65	0.23–0.67
crop residue/open fire[c,d,e]	0.17–0.25	0.34–0.53	0.39–0.50	0.39–0.94	0.35–0.80	0.43–0.98
wood/stove[a,f,g,h]	0.10–0.30	0.43–0.74	0.39–0.56	0.16–0.69	0.35–0.51	0.38–0.78
coal/stove[a,i,j]	0.13–0.58	0.32–0.70	0.27–0.56	0.23–0.63	0.60–0.89	0.35–0.69

[a] Oanh et al. (2005).
[b] Sheesley et al. (2003).
[c] Hays et al. (2005).
[d] Jenkins et al. (1996a).
[e] Jenkins et al. (1996b).
[f] Conde et al. (2005).
[g] Khalfi et al. (2000).
[h] Hedberg et al. (2002).
[i] Chen et al. (2005).
[j] Zhang et al. (2008).

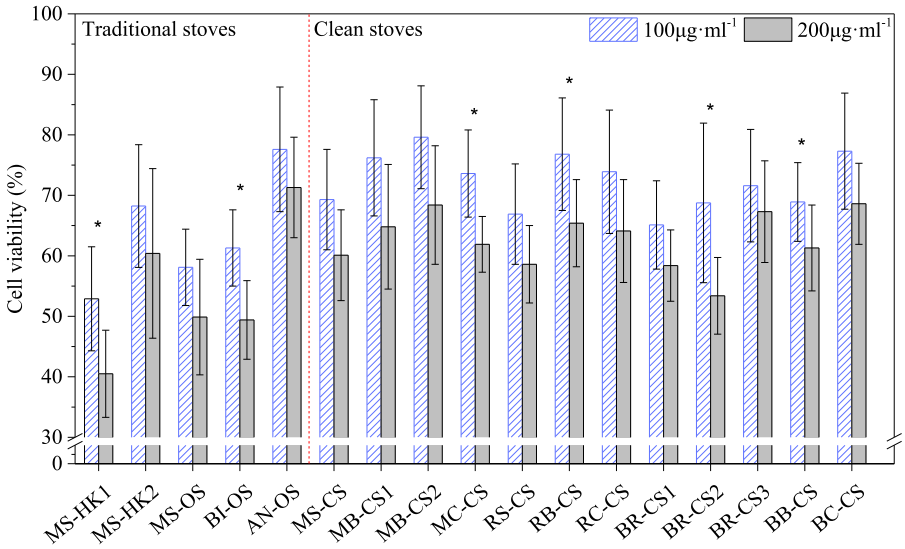

Fig. 2. Cell viability following exposure to different mass concentrations of $PM_{2.5}$ extracts from residential solid fuel burning emissions. *$p < 0.05$ compared between 100 and 200 μg ml^{-1} groups.

epithelial cells after 24 h of exposure to $PM_{2.5}$ extracts are shown in Fig. 4. Over half of the treatments in the two inflammatory cytokines showed a concentration-dependent increase ($P < 0.05$). IL-6 and TNF-α levels both increased by ~1.3 times when the exposure concentration of $PM_{2.5}$ extracts doubled from 100 to 200 μg mL^{-1}. This concentration-dependent increase was lower than that exhibited by ROS (~1.7) and indicated that the induced effects between $PM_{2.5}$ and ROS and between ROS and inflammatory cytokines were not linear, a phenomenon also observed in related studies (Ho et al., 2016). Variations in the levels of IL-6 and TNF-α induced in different experiments were similar to the variations in ROS levels. That is, $PM_{2.5}$ emitted from a clean stove had averagely lower cytotoxicity than $PM_{2.5}$ from traditional stoves (except AN-OS) ($P < 0.05$) (shown in Fig. S4); however, the differences between the highest and lowest levels of cytokines were not as large as the ROS variations. For instance, under 100 μg mL^{-1} exposure condition, IL-6 ranged from 22.9 to 39.6 pg mL^{-1} and TNF-α ranged from 13.5 to 21.6 pg mL^{-1} compared with the range from 377.0 to

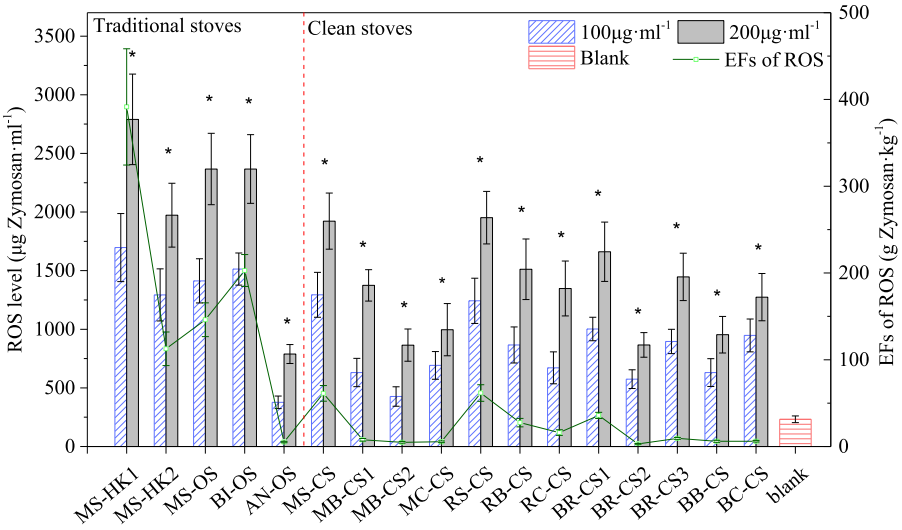

Fig. 3. ROS production of A549 exposed to different mass concentrations of $PM_{2.5}$ extracts from residential solid fuel burning emissions and primary ROS EFs estimated exposure to 100 μg ml^{-1} RBB $PM_{2.5}$. *$p < 0.05$ compared between 100 and 200 μg ml^{-1} groups; $p < 0.05$ for all bars compared to control group.

1696.9 μg Zymosan·mL^{-1} for ROS.

EFs of IL-6 and TNF-α were calculated and are shown in Fig. 4. Variation patterns of the two cytokines were very similar to each other and also to variations in EFs of ROS. The lowest EFs of IL-6 and TNF-α were generally associated with treated fuels (straw briquette and charcoal) burning in a clean stove. Comparing the results from MS-HK1 and MC-CS, the emission reduction efficiency could be as high as 97.6% for IL-6 and 97.4% for TNF-α. Furthermore, the results showed that anthracite is a good alternative fuel when clean-stove and fuel-treatment technologies are not available. The extremely low EFs of IL-6 (0.35 μg kg^{-1}) and TNF-α (0.22 μg kg^{-1}) from anthracite proved that the cytotoxicity of $PM_{2.5}$ emissions from anthracite burning in traditional stoves rivals that of emissions from a clean stove and from treated fuels. However, the extremely high price of it might beyond the economic capability of rural residents.

3.4. Relationships between specific chemicals and bioreactive responses

A few studies reported that ROS could be generated in response to PAHs (Klaunig and Kamendulis, 2004; Ushio-Fukai and Nakamura, 2008; Ziech et al., 2010). Pearson's correlation coefficients were calculated and used to determine whether the EFs of PAHs with different ring numbers or specific PAH species were related to the production of ROS, IL-6 or TNF-α. Selected correlations are plotted in Fig. 5. First, ROS had higher correlations with PAHs than IL-6 and TNF-α. It could be explained on the basis that ROS could be induced by PAHs and their hydroxyl derivatives (i.e., quinones) (Lin et al., 2013), whereas inflammatory factors were usually induced by more than PAHs in the extracts (Chuang et al., 2012). In comparison, cell variability was negatively correlated with PAHs, especially for 3-ring ($R = -0.86$) and 4-ring species ($R = -0.73$) (Table S2a), which was also observed in many previous studies (Ho et al., 2016; Niu et al., 2017; Ziech et al., 2010). It indicates that PAHs in $PM_{2.5}$ extracts are related to the cell apoptosis. PAHs with 3-ring and 4-ring structures had higher correlations with ROS and also inflammatory factors than did less complex PAHs; thus, 3-ring and 4-ring PAHs had a greater ability to induce oxidative stress and inflammatory response. Although correlations of 5-ring and 6-ring PAHs with ROS, IL-6 and TNF-α were quite high, they were weaker than correlations of 3-ring and 4-ring PAHs. Toxicological studies have indicated that 3- and 4-ring PAHs mainly induce acute reactions, e.g. stress reactions and pro-inflammatory reactions, while PAHs having a greater number of rings strengthen chronic reactions such as cell cancerization (Bostrom et al., 2002). Clean stove technology and fuel treatment could promote the formation of 5- and 6-ring PAHs (Fig. S2). Therefore, caution should be exercised over the chronic effects (i.e. carcinogenicity) of $PM_{2.5}$ emitted from clean stoves, although the ability of these emissions to cause acute reactions is weak compared to $PM_{2.5}$ from traditional stoves.

To clarify the bearing of selected PAH species with ROS and inflammatory factors production, correlation between the bioreactive factors and PAH species with 3- and 4-ring structures were plotted (Fig. 5b). For ROS, the R values of PYR, ANT and BaA exceeded 0.80, and IL-6 and TNF-α also exhibited better correlations with these three species than with other PAH species ($P < 0.05$ for ACY and ACE, $P > 0.05$ for the others), demonstrating that inflammatory response was induced by oxidative stress. The good intercorrelations between the three bioreactive factors (shown in Table S2b) could evidently indicate a cooperative production mechanism (Cachon et al., 2014; Gualtieri et al., 2012). The cytotoxicity of $PM_{2.5}$ extracts pointed out that there is no safe level of exposure to residential solid fuel burning emitted $PM_{2.5}$ although the toxicity of $PM_{2.5}$ emitted from clean stoves were relatively low. Meanwhile, the underlying mechanisms of $PM_{2.5}$ oxidative and inflammatory responses also deserve further study.

4. Conclusions

Sixteen priority PAHs were quantified in $PM_{2.5}$ emitted from residential solid fuel burning using different stoves. The toxicity of the $PM_{2.5}$ extracts was also investigated *in vitro*. The study results justify the following conclusions.

Compared to traditional stoves and untreated fuels, clean stove technology and fuel treatment can both reduce the EFs of PAHs (from 83.31 mg kg^{-1} [MS-HK1] to 0.18 mg kg^{-1} [MC-CS] in this study). Both clean stoves and fuel treatment increase the proportion of emitted PAHs that have higher ring numbers. The emission from MS-HK1 had the highest cytotoxicity among all experiments with EFs of ROS, IL-6 and TNF-α being 1–2 orders of magnitude

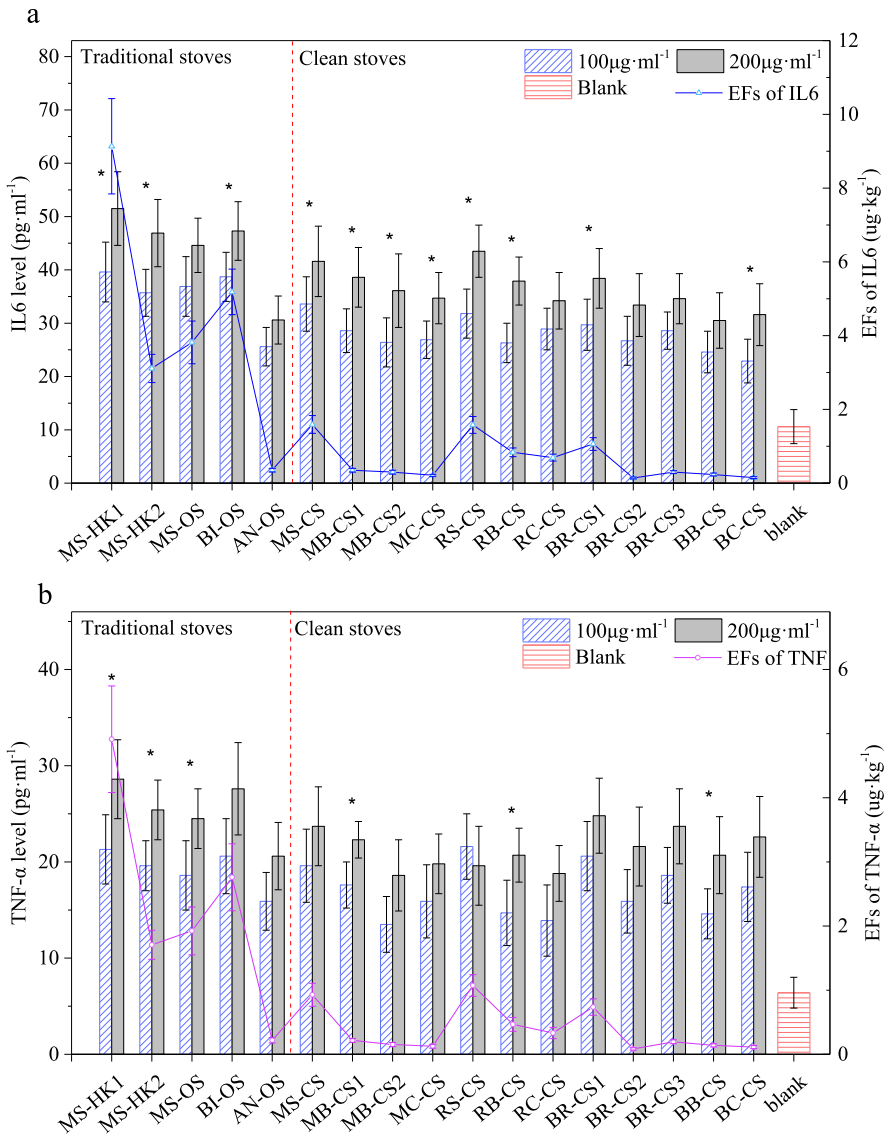

Fig. 4. Tumor necrosis factor α TNF-α (a) and interlukin-6 (IL-6) (b) production of A549 exposed to different mass concentrations of $PM_{2.5}$ extracts from residential solid fuel burning emissions and their EFs exposure to 100 μg ml^{-1} RBB $PM_{2.5}$. *p < 0.05 compared between 100 and 200 μg ml^{-1} groups; p < 0.05 for all bars compared to control group.

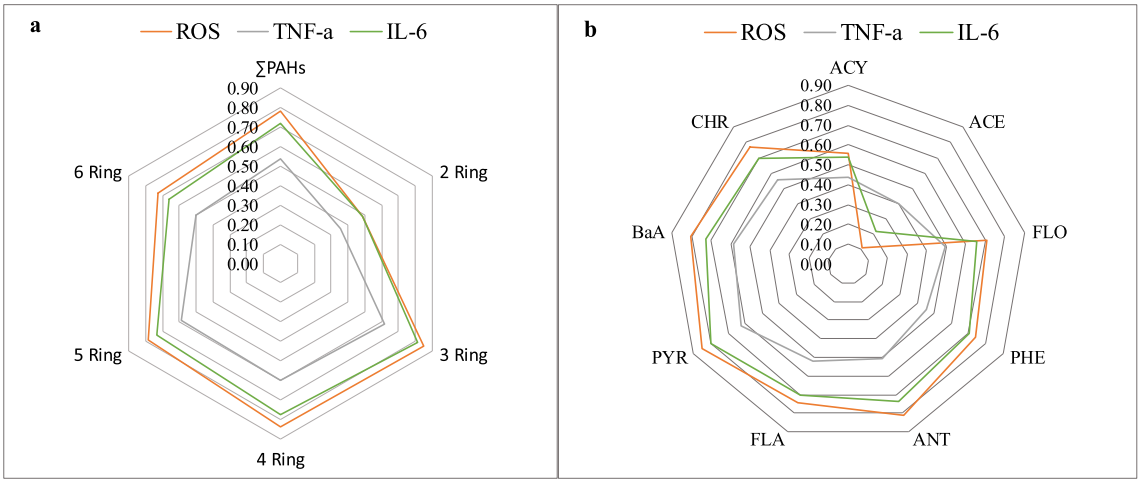

Fig. 5. Associations between bioreactive parameters and EFs of PAHs with different ring number (a) and specific PAHs species (b).

higher than those from a clean stove. Compared to PAHs with more rings, 3-ring and 4-ring PAHs are more highly correlated with production of ROS, IL-6 and TNF-α. Among the 16 PAHs examined in this study, PYR, ANT and BaA showed the highest R values (0.85, 0.81 and 0.80, respectively) with ROS. Notably, due to the high proportion of 5- and 6-ring PAHs, $PM_{2.5}$ emitted from clean stoves and treated fuels may cause more severe carcinogenic effects than those from traditional stoves and untreated fuels. However, the oxidative-inflammatory responses to $PM_{2.5}$ emitted from clean stoves and treated fuels are relatively weaker than those to $PM_{2.5}$ emitted from traditional stoves and untreated fuels. More research should be conducted to clarify the toxicity of individual PAH species and their underlying mechanism in oxidative and inflammatory responses.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.05.076.

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