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Personal exposure to $PM_{2.5}$-bound organic species from domestic solid fuel combustion in rural Guanzhong Basin, China: Characteristics and health implication

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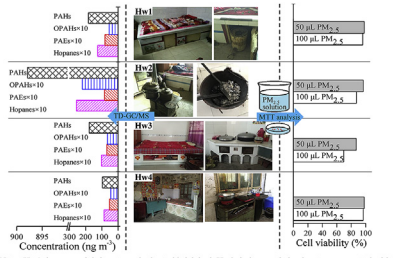
HIGHLIGHTS

- Domestic solid fuels emit toxic particulate-bound organics in rural northern China.
- Personal exposures to PAHs, OPAHs, PAEs were ~1.5 times of indoors and outdoors.
- $PM_{2.5}$ from coal chuck stove had the maximum decline in cell viability.
- Use of electricity reduced personal exposure levels to organics by 1.2–10 times.

GRAPHICAL ABSTRACT



Note: Hw1: honeycomb briquette under heated brick bed; Hw2: indoor coal chunks stove connected with a chimney; Hw3: wood burning driven brick bed connected with the hearth; Hw4: electrical heating equipment.

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ABSTRACT

Domestic solid fuels combustion produces a mass of fine particulate matter ($PM_{2.5}$). $PM_{2.5}$-bound organics, including polycyclic aromatic hydrocarbons (PAHs), oxygenated-PAHs (OPAHs), phthalate esters (PAEs) and hopanes, were quantified in indoor, outdoor and personal exposure samples collected in rural Guanzhong Basin, China. The average concentration of total quantified PAHs in personal exposure samples was 310 ± 443 ng m^{-3}, 1.5 times of those of indoor (211 ± 120 ng m^{-3}) and outdoor (189 ± 115 ng m^{-3}). Similar observations were found for the OPAHs and PAEs, i.e., much higher concentrations were seen in personal exposure samples. Hopanes average personal exposure concentration (13 ± 9.7 ng m^{-3}) was comparable to indoors (15 ± 9.7 ng m^{-3}) and outdoors (13 ± 9.6 ng m^{-3}). Among four common heating ways applied in Chinese dwelling, the highest exposure levels to PAHs, OPAHs and PAEs were found for indoor coal chunks stoves. Concentration under electric power was 1.2–4.5 folds lower than those with solid fuels in this study, proved to be the cleanest energy for the household heating. The exposures to $PM_{2.5}$ on cell viabilities were also investigated. The largest reduction of 70% on cell viabilities was seen for indoor coal chunks stove housewives, indicating that the emissions from coal combustion had the greatest cytotoxic effects. The results evidenced that the heating ways in rural area

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could greatly impact on the housewife health in northwestern China. Advanced heating technology and protection should be conducted to reduce the personal exposures to $PM_{2.5}$ from domestic solid fuel combustions.

1. Introduction

Solid fuels are the most traditional sources for household energy supply in rural areas of northwestern China (Du et al., 2018a). The fuels are burnt in simple stoves with poor combustion efficiencies, and without any proper filtration system nor emission controls, leading to produce large amounts of toxic $PM_{2.5}$ indoors (Shen et al., 2010a). Therefore, the air quality is greatly influenced by the combustions of biomass and other solid fuels through daily activities, especially in winter (Tian et al., 2017; Sun et al., 2018). Exposure to solid fuel combustion emissions is associated with the development of asthma, tuberculosis, cataracts, low birth weight and lung diseases (Rehfuess et al., 2011).

Organic carbon (OC) accounts for a significant fraction in atmospheric fine particulate matter ($PM_{2.5}$) which contains alkanes, alkenes, polycyclic aromatic hydrocarbons (PAHs), oxygenated-PAHs (OPAHs), phthalate esters (PAEs) and so on (Choi et al., 2012; Srogi, 2007; Wang et al., 2016b). In between, aromatics (i.e., PAHs and OPAHs) have been attracting widespread public concern due to their adverse health impacts (Yu et al., 2015). OPAHs consists of hydroxyl or carbonyl fractional groups in chemical structure which can be emitted from the incomplete combustions of fossil fuels and biomass burning or formed through atmospheric processes (Huang et al., 2014; Wei et al., 2015). These oxidized derivatives are frequently found at similar levels as their parent PAHs (pPAHs) in environments (Walgraeve et al., 2010).

PAEs are abundant species in atmosphere (Myridakis et al., 2015). They exist in widespread consumer products (i.e., plastics) and can be easily released in the air from the matrix through evaporation and combustion due to their weak chemical-bonding to the polymer (Czernych et al., 2017). PAEs total demand was about 1.36×10^6 tons in 2010 in China (Zhang et al., 2015). Their carcinogenic potentials and endocrine disrupting properties alert the publics (Swan et al., 2005). Exposures to high levels of di-n-butyl phthalate (DBP) and bis(2-ethylhexyl) phthalate (DEHP) have significant effects on fetus by decreasing testicular testosterone production, and harm to hepatic (Huang et al., 2010). These two PAEs have also been classified as probable human carcinogen (Group B2) by United States Environmental Protection Agency (U.S.EPA) and suspected carcinogen (Group 1B) by European Union (EU) (Pan et al., 2006). Although plastic products were not burned often in households, intentional or incidental burning of disposable tableware, plastic packing material or plastic bag can generate black smoke, decomposition and volatilization products, which strongly contributes to the level of PAEs in rural households and impacts on the health of housewives (Simoneit et al., 2005).

Hopanes, a group of cyclic hydrocarbons, are bio-markers for petroleum and coal combustion emissions (Choi et al., 2012; Han et al., 2015; Oros and Simoneit, 2000; Schauer et al., 1996). As we known, hopane ratios can be used to indicate the gasoline emission (Wang et al., 2009). Meanwhile, Oros and Simoneit (2000) and Zhang et al. (2008) found that the ratio of 17α(H)-21β(H)-(22S)-homohopane (αβ-S-HH)/[(17α(H)-21β(H)-(22S)-homohopane (αβ-S-HH) + 17α(H)-21β(H)-(22R)-homohopane (αβ-R-HH)] also can be used to investigate the coal combustions with the values between 0.05 and 0.35 (i.e., lignite: 0.05; brown coal: 0.09; sub-bituminous coal: 0.20; bituminous coal: 0.35). Huang et al. (2006) reported that hopanes are mainly from vehicle exhaust in southern cities (e.g., Guangzhou, Shenzhen and Hong Kong) in China due to increase in the number of automobiles (Wang et al., 2009), whereas coal burning contributed more to hopane levels in northern Chinese cities such as Beijing, especially in winter (Wang et al., 2006a).

Organic species in $PM_{2.5}$ are capable of cellular oxidative stresses by producing reactive oxygen species (ROS) (Li et al., 2010). ROS can induce inflammatory reactions in human cells, which are evidently related with several PAHs and other organic toxins (Benbrahim-Tallaa et al., 2012). Liu et al. (2018) reported that short-term elevations in $PM_{2.5}$ concentration may cause ST-elevation myocardial infarction (STEMI). Niu et al. (2017) proved that organics associated with $PM_{2.5}$ could lead to a concentration-dependent decline in cell viability. Even though the $PM_{2.5}$-bound organic compounds have been widely quantified in Chinese megacities, such as Xi'an, Nanjing, and Guangzhou (Li et al., 2005; Wang and Kawamura, 2005; Wang et al., 2016c; Xu et al., 2013; Yang et al., 2005), there is still no comprehensive assessment on their characteristics and cell viability effects in rural regions of China where air pollution is particularly high in the wintertime (Du et al., 2018b).

The Guanzhong Basin is located in Shaanxi Province with the population of 38 million in 2016, of which the rural population accounted for 45% (Shaanxi Statistical Yearbook, 2017). The atmospheric dispersion in Guanzhong Basin is usually weak due to the unique features of its topography (Sun et al., 2017), resulting in its heavily polluted from $PM_{2.5}$ (Cao et al., 2012; Wang et al., 2006a, 2006b). Guanzhong urban agglomeration is a key area of the “Three Districts and Ten Groups for Air Pollution Prevention” of the State Council, and is also part of “the Fenhe and Weihe Plain”, a key pollution control area for the “three-year plan on defending the blue sky” deployed in China in 2018. Coal and biomass are used as the main solid fuels for winter space heating in most of the rural households there (Sun et al., 2017). The stoves in the households are simple and rough, leading to the solid fuels inefficiently burning, which causes the large amount of $PM_{2.5}$ indoors, resulting in poor air quality and serious health damage. Therefore, Guanzhong rural area is a natural laboratory for scientific research on $PM_{2.5}$ emissions and its related health effects from household solid fuel combustion.

It has been estimated that biomass burning (288 million tons) accounted for 57% of the total rural household energy use in China in 2000, and other energy sources mainly relied on coal burning (P.R.C. China Agriculture Statistical Report, 2000;P.R.C. China Energy Statistical Yearbook, 2004). In Guanzhong Basin, heated brick beds driven by honeycomb briquette stoves or biomass/wood burning hearth with poor combustion efficiency are the traditional and the most popular heating ways in rural area. The rural residents usually spend over 90% of their time indoors, especially in cold climate (Castro et al., 2015; Klepeis et al., 2001). The rural women are more affected from the exposure to domestic solid fuels combustion emissions than men, due to the more time at home and more responsible for family affairs (Ruiz-Mercado et al., 2011). The effects on air quality and health from such abundant solid fuels combustion attract a growing attention from public and

researchers.

The objectives of current study are (i) to measure personal exposure levels to $PM_{2.5}$-bound organic species and interpret their relationships with indoor and outdoor from different solid fuels used in rural areas in Guanzhong Basin; and (ii) to assess the cytotoxicity of $PM_{2.5}$ by measuring cell viability and correlations with the target organic species. The results provide scientific data for the health and toxicity evaluations on $PM_{2.5}$, which are critical for protection of individuals against health hazards generated from solid fuel combustions in rural northwestern China.

2. Materials and methods

2.1. $PM_{2.5}$ sampling method

The sampling campaign was conducted at Nanliu village (N 34.35°, E 108.41°) of Xingping district, where is ~50 km west of Xi'an, center of Guanzhong Basin in northwestern China. Twenty-four-hour time integrated [i.e., from 10:00 a.m. to 10:00 a.m. on the next day, local time (L.T.)] personal exposure, indoor, and outdoor $PM_{2.5}$ samples were simultaneously collected from December 4th to 21st 2016. The sampling details (such as sampling instrument, method, and filter) and QA/QC information can be found in Xu et al. (2018).

Ten households and housewives (age range from 44 to 77 years old) in this village were selected for the personal $PM_{2.5}$ exposure assessment (Table 1). The selection criteria for the recruitment of the subjects were seen in Xu et al. (2018) and SI: Section S1. The selected ten households all owed yards, of which 6 were single-storey buildings and 4 were double-storey buildings. The specific housing structure was shown in Fig. S1 (Only the structure of the ground floor was drawn, shown the number of doors and windows of each room. If there are two stories in the house, the rooms on the higher floor are all bedrooms.). According to the results of the questionnaire, during the sampling period, doors and windows of 2 households (4B, 5B) were generally closed, 5 households (1A, 1B, 2A, 2B, 3A) kept doors and windows half open for more than 1 h in the daytime, 2 households (4A, 5A) maintained doors and windows wide open for more than 1 h and less than 3 h in the daytime, and doors and windows of 1 household (3B) were fully open every daytime.

It should be pointed out that variations on cooking fumes (i.e., emitted from foods and ingredients) was neglected in discussion since all of the participants had identical dietary habit and majority of cooking methods in winter of rural northwestern China are steaming and boiling, which generate minimal amounts of harmful gases and particles (Ju et al., 2018). Therefore, the interpretation would only focus on the heating ways (i.e., different fuels and equipment for household warming) in the participants' residential units.

Four heating ways (Hws) are commonly used in northwestern China, including (1) honeycomb briquette under heated brick bed (Hw1); (2) indoor coal chunks stove connected with a chimney (Hw2); (3) wood burning driven brick bed connected to the hearth (Hw3) and (4) electrical heating equipment (Hw4). The characteristics of four Hws were seen at Fig. S2. Among these, Hw1 and Hw3 are the two most popular ways, accounting for 43% and 36%, respectively, of total households applied in the studied village. The families selected in this study covered the four main heating types mentioned above. Total of 30 personal exposure samples, 30 indoor and 30 outdoor samples were collected in this study.

2.2. Chemical analysis for $PM_{2.5}$ samples

A total number of 36 organic compounds, including 19 PAHs, 3 OPAHs, 6 PAEs and 8 hopanes (named in Table 2), were quantified by the in-injection port thermal desorption (TD) coupled with gas chromatography/mass spectrometry (GC/MS) method (Ho et al., 2008; Wang et al., 2015, 2016b, 2016c). The detail analytical procedures have been reported in previous publications (Chow et al., 2007; Ho and Yu, 2004; Ho et al., 2008, 2011; Xu et al., 2013; Wang et al., 2016b). In brief, part of the sample filter (0.126–1.578 cm^2) was cut into small pieces and transferred into a TD tube. As the temperature of the injector port increases from 50 °C to 275 °C while the GC oven temperature was kept at 30 °C, the organic species are separated, which is detected by a mass selective detector connected to the chromatography column. QA/QC of TD-GC/MS method can be found in SI: Section S2.

Elemental carbon (EC) was quantified on a 0.526 cm^2 punch of each filter sample using DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). The experimental details were shown in Cao et al. (2007) and Xu et al. (2018). EC used here aims at source apportionment accompanying with organic compounds.

2.3. MTT analysis (cell viability analysis)

The $PM_{2.5}$ samples extracted in 10 mL of distilled water were used for cell viability assay. The samples were analyzed on volume basis with two dose levels (i.e., 50 and 100 μL), and a 96-well plate was employed to measure cell viability by using MTT (3-[4,5-dimethylthiazol-2-yl]-2,5 diphenyl tetrazolium bromide) probes (Sigma Aldrich, St. Louis, MO, USA) (Gali et al., 2017; Niu et al., 2017). Details of cell viability analysis were seen at SI: Section S3. Correlation analyses of organic component concentrations and cell activities were done with the software of SPSS 21.

Table 1
Basic information of selected personal exposure sampling subjects and their households.

Site	Household information			Subject information	
	Heating ways (Hw)	Cooking ways	House area (m^2)	Age (years old)	Height/weight (cm/kg)
1A	honeycomb briquette under heated brick bed (Hw1)	biomass, methane[a]	200	72	3.2
1B		biomass, electricity[a]	210	77	3.0
4B	coal chunks stove (Hw2)	biomass	140	59	2.7
5B			160	54	2.6
2A	wood burning driven brick bed connected with the hearth (Hw3)	biomass	120	60	2.2
2B			200	71	3.2
3A			200	44	3.2
3B	electrical heating equipment (Hw4)	biomass[a], electricity	150	57	2.7
4A			300	56	2.9
5A			200	49	2.7

[a] Very low frequency of utilization.

Table 2
Concentrations of PAHs, OPAHs, PAEs and hopanes (ng m^{-3}) in personal exposure, indoor and outdoor $PM_{2.5}$ samples collected in rural area of Guanzhong Basin, China in winter.

Organic species (abbreviation)	Personal exposure		Indoor		Outdoor	
	Average	SD[a]	Average	SD[a]	Average	SD[a]
PAHs						
acenaphthene (ACE)	0.40	0.46	0.29	0.21	0.30	0.20
fluorene (FLO)	0.60	0.41	0.56	0.42	0.54	0.41
phenanthrene (PHE)	8.4	16	5.7	4.3	5.5	4.2
anthracene (ANT)	1.6	3.6	0.85	0.52	0.87	0.52
fluoranthene (FLU)	37	79	15	11	15	10
pyrene (PYR)	43	96	15	12	16	9.8
benzo [*a*]anthracene (BaA)	25	42	14	9.5	13	8.2
chrysene (CHR)	39	49	29	19	26	17
benzo [*b*]fluoranthene (BbF)	36	33	34	21	29	19
benzo [*k*]fluoranthene (BkF)	23	28	20	11	18	10
benzo [*a*]fluoranthene (BaF)	5.0	7.6	3.5	2.1	2.8	1.8
benzo [*e*]pyrene (BeP)	5.2	4.7	5.3	3.4	4.3	2.6
benzo [*a*]pyrene (BaP)	30	40	23	13	19	12
perylene (PER)	1.4	1.7	1.2	0.7	1.0	0.57
indeno [1,2,3-*cd*]pyrene (IcdP)	24	26	19	8.8	17	9.8
benzo [*ghi*]perylene (BghiP)	22	23	18	8.6	15	8.4
dibenzo [*a,h*]anthracene (DahA)	4.4	4.7	4.2	2.5	3.5	2.1
coronene (COR)	1.6	2.0	0.96	0.42	0.88	0.50
dibenzo (*a,e*)pyrene (DaeP)	1.7	1.8	1.1	0.62	0.94	0.55
∑PAHs	310	443	211	120	189	115
OPAHs						
9-fluorenone (9FLO)	0.90	1.8	0.53	0.32	0.53	0.31
anthraquinone (ANTQ)	4.5	5.1	3.1	2.0	3.2	2.0
benz(a)antnracene-7,12-dione (BaAQ)	3.7	2.9	3.8	2.5	3.8	2.4
∑OPAHs	9.0	9.0	7.5	4.6	7.5	4.6
PAEs						
dimethyl phthalate (DNP)	bd[b]	bd[b]	bd[b]	bd[b]	bd[b]	bd[b]
diethyl phthalate (DEP)	bd[b]	bd[b]	bd[b]	bd[b]	bd[b]	bd[b]
di-n-butyl phthalate (DBP)	2.8	2.2	2.4	1.5	2.0	1.3
bis (2-ethylhexyl) phthalate (DEHP)	3.3	2.3	2.1	1.1	1.8	1.2
di-n-octyl phthalate (DNOP)	0.12	0.12	bd[b]	bd[b]	bd[b]	bd[b]
bis (2-ethylhexyl) adipate (DEHA)	bd[b]	bd[b]	bd[b]	bd[b]	bd[b]	bd[b]
∑PAEs	6.4	4.5	4.6	2.4	4.0	2.2
hopanes						
17α(H)-22,29,30-trisnorhopane (Tm)	0.74	0.37	0.79	0.49	0.79	0.79
17α(H)-21β(H)-30-norhopane (αβ-NH)	4.4	4.5	4.8	3.2	4.1	3.4
17β(H)-21α(H)-30-norhopane (βα-NH)	1.5	0.79	2.4	1.6	1.9	1.5
17α(H)-21β(H)-hopane (αβ-HH)	1.6	0.77	1.8	1.1	1.5	1.0
17α(H)-21α(H)-hopane (αα-HH)	0.77	0.83	1.6	2.6	1.8	3.2
17β(H)-21α(H)-hopane (βα-HH)	0.77	0.39	1.3	0.91	1.0	0.84
17α(H)-21β(H)-(22S)-homohopane (αβ-S–HH)	0.73	0.43	0.75	0.47	0.62	0.40
17α(H)-21β(H)-(22R)-homohopane (αβ-R-HH)	2.5	3.5	1.9	1.4	1.6	0.85
∑hopanes	13	9.7	15	9.7	13	9.6

[a] Standard deviation.
[b] below detection limit.

2.4. Questionnaire and time-activity diary

Questionnaires were collected from each participant during the sampling period. The questions included basic information, living habits and environment, and travelling habits. Participants also completed daily time-activity diaries to assess the time subjects spent in each microenvironment and the personal activities during the sampling. Details of questionnaire and time-activity diary can also be referenced in Xu et al. (2018).

3. Results and discussion

3.1. $PM_{2.5}$-bound organic species in rural Guanzhong Basin

3.1.1. PAHs

Table 2 summarizes the concentrations of measured organic species in personal exposure, indoor and outdoor $PM_{2.5}$ samples. The average concentration of total quantified PAHs (∑PAHs) in personal exposure was 310 ± 443 ng m^{-3}, at least 1.5 times of those averages of the indoors (211 ± 120 ng m^{-3}) and outdoors (189 ± 115 ng m^{-3}). Our values were 1–2 orders of magnitude higher than those reported in a personal exposure study at Los Angeles, CA, USA (i.e., 2.5 ng m^{-3} on average) (Fraser et al., 1997). Pyrene (PYR) and chrysene (CHR) were the two most abundant PAHs in personal exposure samples, totally accounting for $27\% \pm 46\%$ of ∑PAHs. For the indoors and outdoors, CHR and benzo [*b*]fluoranthene (BbF) were the most abundant species, which accounted for $30\% \pm 19\%$ and $36\% \pm 20\%$ of ∑PAHs, respectively. PAH toxicity indicator-benzo [*a*]pyrene (BaP) average concentration (30 ± 40 ng m^{-3}) of personal exposure samples was much higher than the air-quality guidelines of 1.0 ng m^{-3} for $PM_{2.5}$ established by the World Health Organization (WHO) (WHO, 2010) and of 2.5 ng m^{-3} for PM_{10} recommended by the China National Ambient Air Quality Standards (Bi et al., 2015; GB 3095-2012, 2012).

The 4- and 5-ring PAHs were the two most abundant fractions, accounting for a total of approximately 80% of ∑PAHs in the personal exposure, indoor and outdoor samples. The personal exposure samples were dominated by the 4-ring PAHs ($47\% \pm 85\%$),

while the 5-ring PAHs had higher compositions in the indoors (43% ± 24%) and outdoors (41% ± 25%). Personal exposure samples were collected with housewives who were often close to the ignition of solid fuels combustion. PAHs emitted from the household solid fuels combustion initially in gaseous phase, resulted in housewives' exposure to more volatile PAHs, like 4-ring PAHs compared with the higher ring PAHs. Afterwards PAHs associated with PM as particle state through condensation and adsorption processes as the indoor and outdoor temperature decrease, which increased the occupation of 5-ring PAHs in the ambient samples. The higher abundances of the 5-ring PAHs were also reported in other indoor and outdoor studies (Chen et al., 2004; Hu et al., 2018; Ravindra et al., 2008; Shen et al., 2010b).

The average concentration of low molecular weight (LMW) PAHs ($\sum PAH_{LMW}$, 3 + 4 rings) (156 ± 277 ng m^{-3}) was comparable with high MW (HMW) PAHs ($\sum PAH_{HMW}$, 5 + 6 + 7 rings) (154 ± 171 ng m^{-3}) in personal exposure samples. $\sum PAH_{LMW}$ concentrations of indoor and outdoor samples were 81 ± 54 and 77 ± 49 ng m^{-3}, respectively, much lower than those of $\sum PAH_{HMW}$ (130 ± 69 and 112 ± 67 ng m^{-3}, respectively). In addition, our outdoor values of $\sum PAH_{LMW}$ and $\sum PAH_{HMW}$ in rural area were close to those measured outdoors in urban Xi'an (61 ng m^{-3} and 118 ng m^{-3}, respectively, on average) (Wang et al., 2016b). The ratios of $\sum PAH_{HMW}/\sum PAH_{LMW}$ were 1.0, 1.6 and 1.5 for the personal exposure, indoor and outdoor samples, respectively. The lower ratios for the personal exposure samples further evidenced that the participants were closer to the emission sources mentioned above. Besides, the indoor ratios are slightly higher than those of the outdoors, resulting from the more dominance of combustion products emitted by the in-house solid fuel combustion and the greater influences from the discharges to outside environment through chimney. Combustion processes (e.g., pyrolytic origins) in rural households can elevate both levels and compositions of HMW PAHs [e.g., BbF, BaP and indeno [1,2,3-*cd*]pyrene (IcdP)], which are common indicators of solid fuels combustion (Yan et al., 2006). Epidemiological study demonstrated that HMW PAHs can infiltrate deeply into lungs, causing severer bio-accessibilities than LMW PAHs (Yu et al., 2015).

3.1.2. OPAHs

The average total concentration of quantified OPAHs ($\sum$OPAHs) was 9.0 ± 9.0, 7.5 ± 4.6 and 7.5 ± 4.6 ng m^{-3} for the personal exposure, indoor and outdoor samples (Table 2). The indoor and outdoor $\sum$OPAHs in rural area in this study were much lower than those reported in the middle-school in urban Xi'an (16 ± 4.2 and 19 ± 3.9 ng m^{-3}, respectively) (Wang et al., 2017). Higher air permeability and mobility are often observed in rural than urban area, resulting in a shorter suspending time of fine particles and thus less oxidation of pPAHs.

In this study, correlations between OPAHs and the corresponding pPAHs were determined for three pair PAHs: 9-fluorenone (9FLO)/fluorene (FLO), anthraquinone (ANTQ)/anthracene (ANT) and benz(*a*)antnracene-7,12-dione (BaAQ)/benzo [*a*] anthracene (BaA), investigating oxidation rates in secondary formation or degradation of PAHs, and gas-particle conversion (Li et al., 2015; Walgraeve et al., 2010). The average ratios (R_o) of 9FLO/FLO, ANTQ/ANT and BaAQ/BaA were 1.5, 2.8 and 0.1 in the personal exposures, 1.0, 3.7 and 0.3 in indoors, and 1.0, 3.6 and 0.3 in outdoors, respectively (Fig. 1). The R_o values were constant between indoors and outdoors, while those ratios were variable in the personal exposure samples. The potential explanations are that the influences from the frequent human activities for personal exposures, but the more stable atmospheric oxidation state for indoor and outdoor PAHs. In comparison with pPAHs, OPAHs mostly exist in the particulate phase due to their lower vapor pressure (Shen et al., 2012). In addition, our indoor and outdoor R_o values for the three OPAH/pPAH pairs were slightly lower than those in Beijing-Tianjin region (2.9, 7.9 and 0.5, respectively, for 9FLO/FLO, ANTQ/ANT and BaAQ/BaA) (Wang, 2010). This might be ascribed with more oxidizing agents presented in the developed area (Beijing-Tianjin region) of China.

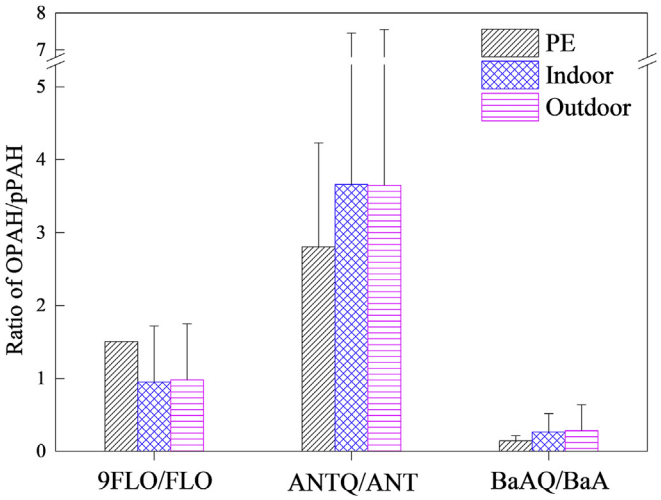

Fig. 1. The ratios of OPAHs to corresponding parent PAHs (pPAHs) in personal exposure (PE), indoor and outdoor $PM_{2.5}$ samples.

3.1.3. PAEs

The concentrations of total PAEs ($\sum$PAEs) in the personal exposure samples (6.4 ± 4.5 ng m^{-3}) were 40%–60% higher than the indoors (4.6 ± 2.4 ng m^{-3}) and outdoors (4.0 ± 2.2 ng m^{-3}). The results reflect that the participants frequently exposed to plastic products in daily life, such as tableware, bags, and other materials burnt in stoves. In this study, DBP and DEHP were the two most dominant PAEs with the total concentrations of 6.1 ± 4.3, 4.4 ± 2.3 and 3.8 ± 2.1 ng m^{-3} for personal exposure, indoor and outdoor samples, respectively, accounting for approximately 48% of $\sum$PAEs. The concentration range of DBP (2.0–2.8 ng m^{-3}) and DEHP (1.8–3.3 ng m^{-3}) in this study were much lower than suburban in Nanjing, China (DBP: 15.6 ng m^{-3}; DEHP: 7.4 ng m^{-3}) (Wang et al., 2008), which may be explained by the highly development (e.g., plastics industry) in Nanjing. Similar distributions were observed in the studies conducted in Guangzhou and Tianjin, China (Wang et al., 2016c; Zhang et al., 2014). Our DEHP levels were comparable with or higher than those in the developed countries, e.g., United States (Kansas and Texas: 2.0 ng m^{-3}) (Weschler, 1984), Sweden (averages of 14 stations: 2.0 ng m^{-3}) (Thuren and Larsson, 1990) and France (Paris: 5.4 ng m^{-3}) (Teil et al., 2006).

Fig. 2 shows the correlations between the personal exposure and indoor/outdoor concentrations for the total quantified organic classes. The highest correlation coefficients (R^2) were found for $\sum$PAEs, with the values of 0.96 for personal exposure *vs.* indoors and 0.97 for personal exposure *vs.* outdoors (Fig. 2b), owing to the peculiarity of PAE sources (e.g., plastic evaporation and burning). Other three organic classes (i.e., PAHs, OPAHs and hopanes) could be influenced by multiple emission sources.

3.1.4. Hopanes

The average total concentration of personal exposure to hopanes ($\sum$hopanes) was 13 ± 9.7 ng m^{-3}, comparable with that in indoors (15 ± 9.7 ng m^{-3}) and outdoors (13 ± 9.6 ng m^{-3}). 17α(H)-21β(H)-30-norhopane (αβ-NH) and 17α(H)-21β(H)-(22R)-

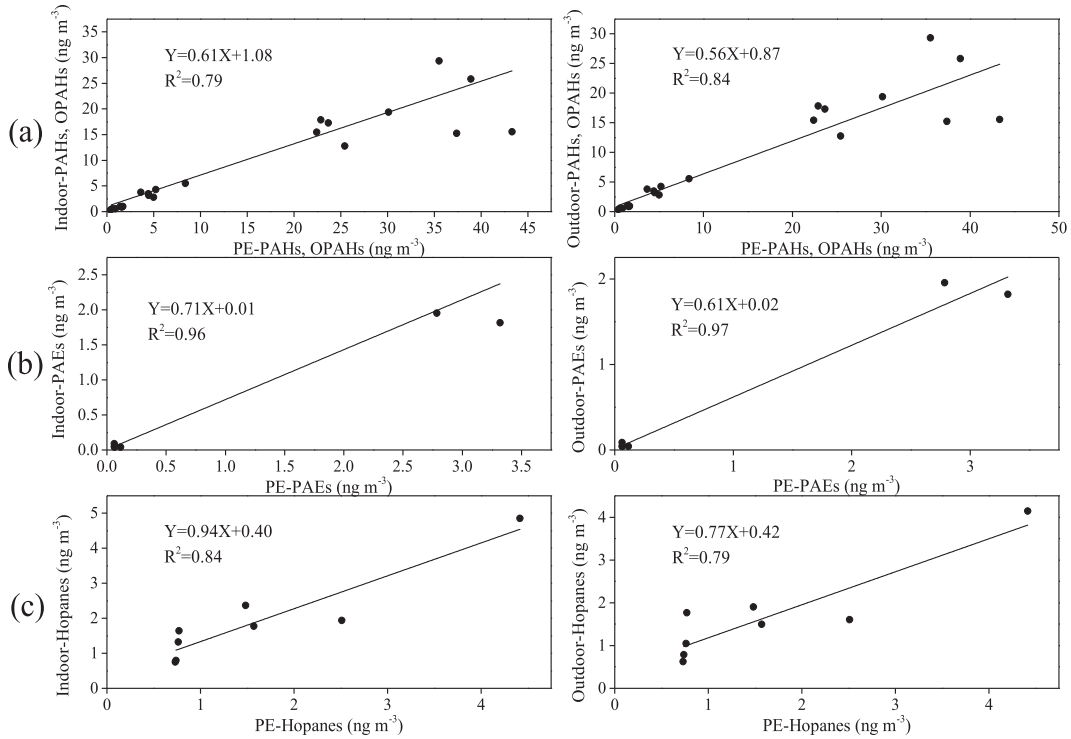

Fig. 2. Correlations of total quantified $PM_{2.5}$-bound PAHs and OPAHs (a), PAEs (b) and hopanes (c) between personal exposure (PE), indoor and outdoor samples.

homohopane (αβ-R-HH) were the two dominant hopanes in the personal exposure (53%), indoor (44%) and outdoor (43%) samples. The homohopane ratios of 17α(H)-21β(H)-(22S)-homohopane (αβ-S-HH)/[(17α(H)-21β(H)-(22S)-homohopane (αβ-S-HH) + 17α(H)-21β(H)-(22R)-homohopane (αβ-R-HH)] ranged from 0.23 to 0.28, which were much lower than those in the urban area of Xi'an (0.41) (Wang et al., 2016b) and Shanghai (0.59) (Wang et al., 2016a), China. Wang et al. (2009) found that the mentioned homohopane ratio of 0.60 can be used to indicate gasoline emission. Oros and Simoneit (2000) reported the coal combustions with the ratio values between 0.05 and 0.35 (i.e., lignite: 0.05; brown coal: 0.09; sub-bituminous coal: 0.20; bituminous coal: 0.35). The low value of αβ-S-HH/(αβ-S-HH + αβ-R-HH) (0.23–0.28) in this study can be explained by the fact that the amounts of motor vehicles were fewer in rural than urban area, and the hopanes are mainly influenced by coal combustion. This can be also supported by the questionnaire and time-activity diary in our study (Xu et al., 2018). All participants in this study had not been travelled by motor vehicles during entire sampling period. The time for spent indoors for all the housewives ranged from 67% to 100%, so minimal impact from the motor vehicle emissions in this village. Besides, our homohopane ratio was considerable with those of the bituminous coal, indicating that honeycomb briquettes had a certain impact on hopanes in this study (Oros and Simoneit, 2000).

3.2. Personal exposure to $PM_{2.5}$-bound organic species from different heating ways

3.2.1. Concentration of organic species

The personal exposures to $PM_{2.5}$ not only depended on the pollutant levels in microenvironments, but also related to their personal activities. Heating is the most dominant indoor activity for housewives and its emission is the most important source to $PM_{2.5}$ as well during wintertime in this study (Xu et al., 2018). Therefore, the discussion in this section would only focus on the personal exposure data with different household heating ways (Hws).

The average personal exposure concentrations of $PM_{2.5}$-bound organic species based on Hws are shown in Table 3. The lowest ∑PAHs level of 97 ± 30 ng m^{-3} was seen on Hw4 (using electric power) households which was ~50% lower than that of Hw1 (driven by honeycomb briquette, 183 ± 72 ng m^{-3}) and Hw3 (driven by biomass fuels, 178 ± 42 ng m^{-3}) households. The highest value of 898 ± 719 ng m^{-3} was found in Hw2 households where indoor coal chunks stoves were applied for heating, more than 9 times of ∑PAHs level in Hw4. BbF was the most dominant PAH in personal exposure samples, particularly in Hw1 of 31 ± 14 ng m^{-3}, accounting for 18% of ∑PAHs (Fig. S3). As we know, BbF is mainly derived from the combustion emissions of any fuels, such as treated fossil fuel, wood and biomass (Aubin and Farant, 2000). The highest average concentration (162 ± 169 ng m^{-3}) and composition (18% of ∑PAHs) of PYR were seen in Hw2. PYR is a marker of low temperature combustion of raw coal or coal tar pitch (Dai et al., 2015). As the same trend of ∑PAHs, the personal exposure level of BaP in Hw2 (83 ± 65 ng m^{-3}) was significantly higher than other three heating methods (9.0 ± 3.4 to 20 ± 10 ng m^{-3}). BaP average value in Hw2 was >82 times above the guideline of WHO (WHO, 2010), indicating that inhalation of BaP could cause severe harmful effect to human health in this area.

Table 3
Concentrations of PAHs, OPAHs, PAEs and hopanes (ng m^{-3}) in personal exposure samples with four heating ways.

	∑PAHs		∑OPAHs		∑PAEs		∑hopanes	
	Average	SD[a]	Average	SD[a]	Average	SD[a]	Average	SD[a]
Hw1	183	72	5.5	1.5	8.1	5.8	13	3.5
Hw2	898	719	22	13	8.3	5.9	26	15
Hw3	178	42	6.6	1.2	7.0	2.9	10	2.4
Hw4	97	30	4.5	1.1	5.3	6.1	8.7	6.3

[a] Standard deviation.

The use of cleaner energy (i.e., electricity in Hw4) significantly reduced the personal exposure concentrations of OPAHs, PAEs and hopanes by 1.2–4.5 times compared with solid fuels combustions in this study (Table 3). The highest concentration of ∑OPAHs was found in Hw2 (22 ± 13 ng m^{-3}), while the lowest in Hw4 (4.5 ± 1.1 ng m^{-3}). The ∑PAEs in Hw1-3 were constant and ranged from 7.0 ± 2.9 to 8.3 ± 5.9 ng m^{-3}, ~1.5 times of Hw4 of 5.3 ± 6.1 ng m^{-3}. The most abundant PAEs in personal exposure $PM_{2.5}$ were also DBP and DEHP for all heating ways, consistent with a previous study conducted in Tianjin, China (Zhang et al., 2014). The lowest concentration of DBP was seen in Hw4 (2.2 ± 3.1 ng m^{-3}), only 61% of the highest value in Hw2 (3.6 ± 2.1 ng m^{-3}). Similarly, Hw2 had the highest ∑hopanes (26 ± 15 ng m^{-3}), followed by Hw1 (13 ± 3.5 ng m^{-3}), Hw3 (10 ± 2.4 ng m^{-3}) and Hw4 (8.7 ± 6.3 ng m^{-3}). Our results prove that the nature of fuels and heating equipment had a close relationship with the personal exposure $PM_{2.5}$ levels.

3.2.2. Sources of organic species

The PAHs isomer ratios between sources and receptors have been often used for source characterization (Tobiszewski and Namieśnik, 2012; Xu et al., 2016). As shown in Table S1, the ratios of IcdP/(IcdP + BghiP) were all >0.50 (i.e., 0.5 is the boundary of this ratio for coal, grass, firewood and for oil) (Yunker et al., 2002), which was higher than Nanjing, China (0.25–0.38) (Miettinen et al., 2019), indicating that the participants were influenced by coal, grass and firewood burning in their exposures. Besides, the average ratios of BaA/(BaA + CHR) in Hw1 and Hw2 were >0.35, suggesting large contributions from pyrolytic sources (Simcik et al., 1999). Fig. 3 compares the ratios of BghiP/EC to IcdP/EC in our personal exposure samples and the source samples from the previous studies (Sheesley et al., 2003; Wang et al., 2016c; Yu and Yu, 2011). The two ratios indicated that Hw1 was co-influenced by brown coal and rice straw. For Hw2, our values were well among the three ratios of coal combustion source samples, suggesting a definite contribution from coal burning. It is obvious that the ratios of BghiP/EC and IcdP/EC for Hw3 were close to the ratios of rice straw sources, representing the majority of biomass combustion contribution. However, the ratios for Hw4 with electricity as an energy supply were more dispersed in Fig. 3 due to a lack of dominant indoor combustion source. The personal exposures of Hw4 housewives should be more related to the pollution from surrounding environment.

Correlations and ratios of OPAHs and pPAHs can be used to distinguish their sources and determine the oxidation properties of carbon particles emitted from different domestic fuel burning sources (Shen et al., 2011). The maximum correlation coefficient ($R^2 = 0.90$) between different OPAHs and pPAHs exhibited in Hw2, followed by Hw1 ($R^2 = 0.42$), representing that the stoves driven by honeycomb or coal chunks indoors can enhance the oxidability of pPAHs and form more toxic OPAHs (Wang et al., 2016b; Wei et al., 2012). The R_o values of ANTQ/ANT and BaAQ/BaA ranged from 2.4 to 4.1 and 0.1–0.3, respectively, for the four Hws in this study. Previous studies demonstrated that R_o values of ANTQ/ANT and BaAQ/BaA were 0.89 ± 0.41 and 0.16 ± 0.05 for crop residue burning; 0.14 ± 0.08 and 0.03 ± 0.02 for coal combustion; and 0.79 ± 0.23 and $6.6 \pm 7.5 \times 10^{-2}$ for residential fuel wood and brushwood combustions, respectively (Shen et al., 2011, 2012). The results of our personal exposure samples confirm that the participants with Hw2 (ANTQ/ANT = 2.4 and BaAQ/BaA = 0.1) were strongly influenced by emissions from lump coal combustion, while the participants with other three Hws (ANTQ/ANT = 3.0, 3.5, 4.1 and BaAQ/BaA = 0.2, 0.2, 0.3) were mainly affected by biomass burning. Even though the honeycomb coal was used as solid fuel in Hw1, the treated briquette and the exhaust channel connected to the brick bed (i.e., a chimney directed the emissions to outside of the house) could vary the characteristics of raw coal combustion and reduce PAH levels. To some extent, the participants with Hw1 were mostly exposed to a mix of biomass and the honeycomb briquette burning.

3.3. Cell viability and its relationship with organic species

Exposure to $PM_{2.5}$ can damage human cells and reduce cell activity and viability (Li et al., 2010; Niu et al., 2017). Cells viabilities after 24 h exposure to the $PM_{2.5}$ extract solutions from the personal exposure filters were analyzed in this study. It is obvious that the $PM_{2.5}$ extract caused different degrees of declines in cell viabilities. For the inoculation with 50 μL $PM_{2.5}$ extract, the average cell viability was 94% ± 10% (range: 50%–98%). For the inoculation with 100 μL $PM_{2.5}$ extract, the average cell viability dropped to 86% ± 17%, with a minimum value of 25%. In summary, the cell viabilities in ~70% samples decreased for 0.30%–50% when the inoculation volume of $PM_{2.5}$ solutions was doubled.

There were distinct cytotoxic effects from $PM_{2.5}$ extracts collected from different household heating ways (Table 4). For the inoculation with 50 μL $PM_{2.5}$ extract, the cell viabilities of Hw1 and Hw4 maintained the highest values (both 98%), followed by Hw3 (97%) and Hw2 (87%). When the inoculation volume of $PM_{2.5}$

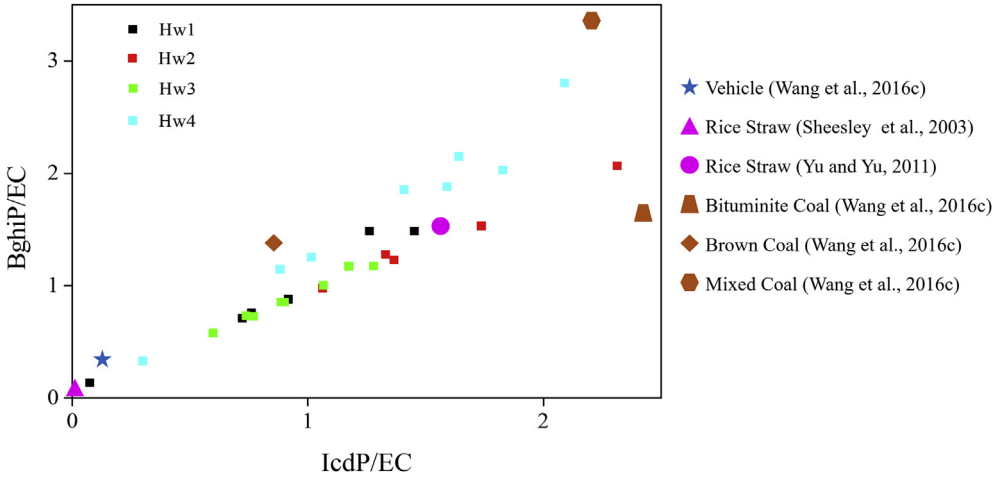

Fig. 3. Ratio-ratio diagram for BghiP/EC to IcdP/EC in personal exposure samples.

Table 4
Cell viability from 24 h exposure to $PM_{2.5}$ extracts from personal exposure samples using MTT dye for four heating ways (Hws).

24 h MTT assay (% Cells alive)	50 μL $PM_{2.5}$ extract		100 μL $PM_{2.5}$ extract	
	Average	Standard deviation	Average	Standard deviation
Hw1	98	0.14	97	2.0
Hw2	87	18	70	24
Hw3	97	1.7	87	7.5
Hw4	98	0.23	96	3.3

extract increased to 100 μL, the cell viabilities had a descending order of Hw1 (97%) ≈ Hw4 (96%) > Hw3 (87%) > Hw2 (70%), corresponding to a drop of 1.1%, 2.1%, 9.8% and 20%, respectively. The lowest cell viability found in Hw2 indicates that the indoor coal chunks stove could lead a greater cytotoxic effect to the participants than other three heating ways in rural areas.

Correlation analysis is used to determine the relationships between the concentrations of target $PM_{2.5}$ bounded organic species and the cell viabilities. The concentrations of most organic species in this study negatively correlated with cell viability (Tables S2 - S5). Eleven PAHs were significantly associated with cell viability ($R = 0.58–0.98$, $p < 0.01$) for the inoculation with 50 μL $PM_{2.5}$ extract. The highest R of 0.98 was observed between ANT and cell viability. With double volume of $PM_{2.5}$ extract for inoculation, there were 17 individual PAH significantly correlated to cell viabilities ($R = 0.44–0.84$, $p < 0.01$). Two OPAH (ANTQ and 9FLO) were well correlated with cell viabilities ($R = 0.71$ and 0.94 respectively, $p < 0.01$) with 50 μL $PM_{2.5}$ extract inoculation, and all of three OPAHs (ANTQ, 9FLO and BaAQ) showed significant relationships ($R > 0.63$, $p < 0.01$) while the volume of $PM_{2.5}$ extract used for inoculation increased to 100 μL. However, no significant correlation between individual PAE and cell viability was observed ($R = 0.11–0.36$, $p < 0.01$). It is probably because that PAEs are characterized as endocrine disruptor, instead of reducing the cell viability. Their impacts on cells are required further study in the future. Most hopanes showed weak to poor correlations with cell viabilities ($R < 0.29$, $p < 0.01$), besides αβ-NH ($R > 0.82$, $p < 0.01$) and αβ-R-HH ($R > 0.68$, $p < 0.01$). The results of our study support that the cell viabilities were mainly impacted by polyaromatics significantly (e.g., PAHs and OPAHs), while influences from PAEs and hopanes were limited.

4. Conclusion

The $PM_{2.5}$-bound PAHs, OPAHs, PAEs and hopanes were quantified in the personal exposure, indoor and outdoor samples in rural area of Guanzhong Basin, China in the wintertime, and the relationships between the personal exposures to organic species and cell viability were also studied. Most of the target organic compounds had higher concentrations in personal exposure samples than those of either indoors or outdoors. Among four heating ways in this study, electricity was the cleanest which reduced the concentrations of target organic pollutants in personal exposure samples by 1.2–10 folds, in comparison with solid fuel combustions heating ways in this study. The lowest cell viability was found in the households equipped with coal chunks stoves (Hw2), demonstrating that the most serious health impacts to rural residents in this study was from indoor coal chunks burning. Proper and efficient control measures such as improvement of heating methods and replacement for cleaner energy must be applied to reduce the $PM_{2.5}$ and its toxic pollutants in rural area of northwest China.

Because of the limitations of human and material resources, the number of participants below the original expectation. This potentially limited the generalities of the results and increased uncertainties of this study. However, this work can be regarded as the first attempt in an inland rural and severe polluted area of underdeveloped country at the current condition. More investigations and large crowds of personal exposure samples should be considered further and related health risks with effects by cohort study will be conducted in the future.

Author contributions

H.X. conceived and designed the study. Y.L., H.X., J.W. and S.S.H.H. contributed to the literature search, data analysis and interpretation, and manuscript writing. H.X., Y.L., J.S., L.L., Y.L. and L.Y. carried out the particulate samples collection and chemical experiments, analyzed the experimental data. Z.N., K.H. and J.W. contributed to the cell MTT analysis. Z.S., T.Z. and Q.Z. contributed to manuscript revision. All authors commented on the manuscript and reviewed the manuscript.

Competing financial interests

The authors declare no competing financial interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.04.010.

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