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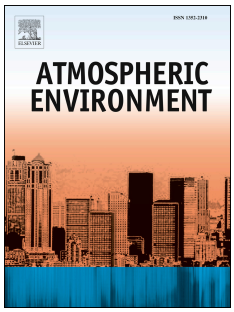

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Heating way 1: honeycomb briquette under heated brick bed


Heating way 2: indoor coal chunks stove connected with a chimney


Heating way 3: wood burning driven brick bed connected with the hearth

Personal exposure of $PM_{2.5}$ emitted from solid fuels combustion for household heating and cooking in rural Guanzhong Plain, northwestern China

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Abstract

Household solid fuel combustion for heating and cooking in rural areas is an important source of fine particulate matter ($PM_{2.5}$) in northwestern China, which largely contributes to $PM_{2.5}$ personal exposure concentrations during the cold winter. There is a general lack of understanding about the personal exposure to $PM_{2.5}$ and to its chemical components emitted from domestic solid fuel combustion in northwestern Chinese rural populations. In this work, personal exposure to $PM_{2.5}$ was sampled using a portative device together with fixed indoor and outdoor fixed samplings in Guanzhong Plain in December 2016 for the purpose of characterizing personal exposure to $PM_{2.5}$ as a function of different solid fuels used in rural households. The average housewife's personal exposure to $PM_{2.5}$ concentration was 263.4±105.8 μg m^{-3} (1σ, n=30), which was about 40% higher than the values found indoors (186.5±79.5 μg m^{-3}, 1σ, n=30) and outdoors (191.0±85.3 μg m^{-3}, 1σ, n=30). High personal exposure $PM_{2.5}$ levels were mainly related to the ignition of solid fuels for heating and cooking. Correlations among personal exposure, indoor and outdoor $PM_{2.5}$ levels and their mutual ratios were computed to investigate how personal exposure to fine aerosols can be related to microenvironmental $PM_{2.5}$ levels and to individual activities. The results showed that households using electric power for heating and cooking were characterized by an average personal exposure $PM_{2.5}$ value of 156.8±36.6 μg m^{-3} (1σ, n=6) while personal exposure to $PM_{2.5}$ in households using solid fuels was twice higher (310.8±90.4 μg m^{-3}, 1σ, n=24). Solid fuel combustion products and related secondary formed species dominated $PM_{2.5}$ mass in personal exposure, indoor and outdoor samples. Motor vehicle emission and various dust sources were two other main contributors identified. Our results demonstrated that the use of clean energy could be an effective measure to reduce personal exposure levels of $PM_{2.5}$ emitted from domestic solid fuels combustion in winter in rural areas, which implied that the government should speed up the upgrade of the heating and cooking equipment fleet to protect the health of rural residents in northwestern China.

Keywords: personal exposure; $PM_{2.5}$; solid fuel combustion; household air pollution; ambient air pollution

1. Introduction

Humans usually spend the majority of their time indoors, especially in their residence in cold winter (Klepeis et al., 2001). Domestic solid fuel combustion in rural areas can cause severe indoor air pollution (Mishra et al., 2004). It is associated with a significant health burden worldwide and is estimated to be responsible for more than 800,000 premature deaths in China in 2013 (GBD 2013 Mortality and Causes of Death Collaborators, 2015; Mestl et al., 2006).

In China, about 50% of the population lives in rural areas in 2010 (674,149,546) (2010 Sixth National Population Census Data Gazette, 2011), where more than half people rely on solid fuels as energy source. Common domestic solid fuels include wood, coal, charcoal, maize straw, wheat straw and other crop residues. It has been estimated that 288 million tons of agricultural biomass were burned in 2000 by rural households for cooking and heating, accounting for 57% of the total rural household energy use in China (PRCMA, 2001; Sun et al., 2017). In rural China, households usually burn solid fuels in simple stoves characterized by poor combustion efficiency without any filtration system nor any emissions management (only chimney), which produce a large amount of particulate matter (PM) emissions (Lei et al., 2011; Shen et al., 2010; Sun et al., 2017). Previous studies have shown that PM emitted from the combustion of household solid fuels can be, per unit of mass, 3-4 orders of magnitude higher than industrial solid fuels emissions (Zhang et al., 2008). The average primary $PM_{2.5}$ (PM with an aerodynamic equivalent diameter less than or equal to 2.5 μm) emission per hour from village household space heating was 0.736±0.138 kg $hour^{-1}$ (Liao et al., 2017). The emissions factors for $PM_{2.5}$ were 38.3±13.9 g kg^{-1} and 17.5±8.3 g kg^{-1}, respectively, from Chinese heated brick bed drove by biomass fuels and stove fired with maize straw in Guanzhong area, northern China (Sun et al., 2017). Rural household solid fuels combustion was recently found to be a larger source of overall emissions in northern China than previously expected (Liao et al., 2017; Zhi et al., 2015). Source apportionment of $PM_{2.5}$ in Beijing (northern China) indicated that coal and biomass combustion contributed 30% of $PM_{2.5}$ annually (Zhang et al., 2013).

Women and children in rural northern China are primarily affected through personal

exposure to combustion products in households. Solid fuels combustion emissions exposure has been implicated in the development of tuberculosis, asthma, cataracts and low birth weight (Fullerton et al., 2008). The latest research of Yu et al. (2018) found that based on the prospective cohort study of 271,217 adults, self-reported solid fuel use was associated with significantly higher risks of cardiovascular mortality (hazard ratio, 1.20 for cooking; 1.29 for heating) and all-cause mortality (hazard ratio, 1.11 for cooking; 1.14 for heating). Lower risks were observed among solid fuel users who reported having switched to clean fuels or using ventilation.

Most studies attempting to relate $PM_{2.5}$ to human health have long used ambient (outdoor) stationary sampling as a proxy of personal exposure (Franklin et al., 2006; Mejía et al., 2011). Because humans are exposed to particles not only outdoors but also indoors in microenvironments, as well as through their personal activities, direct measurement of exposure to $PM_{2.5}$ via personal samplers is to-date recognized as the most accurate assessment method. Hence, the growing attention to the health effects induced by inhaled $PM_{2.5}$ has led to a growing number of personal exposure studies performed worldwide (Allen et al., 2004; Chen et al., 2016, 2017; Jahn et al., 2013; Janssen et al., 2000; Johannesson et al., 2007; Meng et al., 2005, 2009; Xu et al., 2014; Yu et al., 2018). Some of them have tracked out several factors that may influence the relationship between personal exposure, indoor and outdoor $PM_{2.5}$ mass concentrations, including home ventilation, indoor sources and time activity patterns (Jahn et al., 2013; Buonanno et al., 2014). Some previous personal exposure studies (Chen et al., 2017; Hopke et al., 2003; Johannesson et al., 2007; Zhang et al., 2015) concluded that indoor sources (e.g., solid fuel combustion and cooking), outdoor sources (e.g., vehicle emissions and mineral dust) and personal activities (e.g., heating, smoking and cleaning) are significant contributors to $PM_{2.5}$ personal exposure. However, only a few studies have paid attention over the past decades to $PM_{2.5}$ chemical composition and sources in rural regions of developing countries (Chen et al., 2017; Johannesson et al., 2007; Wang et al., 2014; Yu et al., 2018). To our knowledge, the impact ways on personal exposure to $PM_{2.5}$ from solid fuels combustion have not been studied neither. Therefore, there is an urgent need to investigate this topic in order to improve the space heating and cooking conditions, indoor

air quality and respiratory health of rural people in northwestern China.

Guanzhong Plain, located in the center of Shaanxi province in northwestern China, is about 36,000 km^2 for a population of approximately 23.4 million, including >70% of rural people (2010 Sixth National Population Census Data Gazette, 2011). Guanzhong Plain air quality is heavily affected by the high concentrations of $PM_{2.5}$ due to the unique features of its topography and a large amount of local emissions (Niu et al., 2016). Coal and biomass burning are used as the main solid fuels for winter space heating and cooking in most of the rural households there (Sun et al., 2017). 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 resulting effects on air quality and health from such a dramatic combination of solid fuels and combustion means attract a growing attention from public and researchers.

This study *(i)* investigates personal exposure to $PM_{2.5}$ mass and chemical concentrations and their relationships with indoor and outdoor samples, according to different solid fuel burning types and processes commonly used in rural areas, and *(ii)* identify the potential sources of $PM_{2.5}$ affecting personal exposure. This information aims at providing scientific information for individual protection against health hazard resulting from solid fuel combustion for household space heating and cooking in winter, and improving of the heating and cooking equipment fleet in the northwestern rural areas of China.

2. Materials and methods

2.1. Site description

24-hour integrated (from 10:00 am to 10:00 am on the next day, local time) samples of personal exposure to $PM_{2.5}$, together with indoor and outdoor $PM_{2.5}$ samples, were collected during the winter heating season (November 15th to March 15th next year), from December 4th to 21st, 2016, in Nanliu village (N 34.35°, E 108.41°) of Xingping, located about 50 km west of Xi'an, Shaanxi province, northwestern China (Fig.1). The mean outdoor air temperature over the sampling period was 2.1 °C. There were approximately 800 households in this village. Ten participants (permanent inhabitants) in this village were selected for the personal

$PM_{2.5}$ exposure measurement (Appendix A). All participants were non-smoking housewives who are usually responsible for heating and cooking at home, with an average age of 60.

The selected ten targeted participants and households were separated into four groups based on the heating ways (Hw), including honeycomb briquette under heated brick bed (Hw1), indoor coal chunks stove connected with a chimney (Hw2), wood burning driven brick bed connected to the hearth (Hw3) and electrical heating equipment (Hw4). Hw1 and Hw3 were the most two popular ways in the village, accounted for 43% and 36% of all the heated households, respectively, while 14% and 7% heated households used Hw2 and Hw4, respectively. The cooking emission (cooking fume) in this study was neglected owing to the similar dietary habits of the rural residents in this village and their cooking methods, mainly relying on steaming and boiling (few particles emitted). Hw1-3 households all used biomass and wood for cooking by kitchen hearth (typical cooking stove in rural China, shown as the lower right portion of Fig.S1), while the households with Hw4 used induction cooker for cooking during the sampling period and most of the time over the year.

2.2. $PM_{2.5}$ samples collection and QA/QC

Sampling of personal exposure to $PM_{2.5}$ (hereafter defined as personal exposure $PM_{2.5}$ or PE $PM_{2.5}$) was conducted during three consecutive days, in parallel with the corresponding fixed $PM_{2.5}$ samplings conducted inside and outside the individuals' houses. Personal exposure and indoor/outdoor $PM_{2.5}$ samples were collected using the PEM (Personal Environmental Monitor) $PM_{2.5}$ sampling device (SKC Inc., USA) and the Mini-Vol $PM_{2.5}$ portable air samplers (Airmetrics Inc., USA), respectively. The PEM sampler consists of three major parts: cap, impaction ring assembly, and base with after-filter: 1) The cap contains the round nozzles by which the air enters the sampler; 2) The impaction ring assembly serves as an impaction surface, as well as a clamping ring for the after-filter; 3) The base supports the after-filter (one 37-mm pre-baked (780 °C, 3 hours) quartz filter (QM/A®, Whatman Inc., U.K.)). The PEM $PM_{2.5}$ sampling device was operated with a SKC pump (SKC Inc., USA) at a flow rate of 10 liter per minute (lpm). The PEM $PM_{2.5}$ sampling head worn in the breathing zone of participants in this study. The indoor and outdoor Mini-Vol $PM_{2.5}$ portable air samplers were respectively located in the bedrooms of participants (heating

171 room) and in the yard of participants' houses, hence accounting for the $PM_{2.5}$ concentration
172 levels in the microenvironments where the participants mostly lived. Samples were collected
173 on 47-mm pre-baked quartz filters (780 °C, 3 hours, QM/A®, Whatman Inc., U.K.) at a flow
174 rate of 5 lpm. The two sets of instruments were located around 1.2 m above the ground, a
175 height consistent with the level of participants breathing.

176 According to the proportions of each heating way mentioned above, three households
177 (one participant in each) were selected for Hw1 and Hw3, respectively, while Hw2 and Hw4
178 were each investigated in two households. A set of nine personal exposure, indoor and
179 outdoor samples were collected to characterize Hw1, six for Hw2, nine for Hw3 and six for
180 Hw4; hence a total of 30 personal exposure, 30 indoor and 30 outdoor samples were collected
181 in this study. Moreover, ten personal exposure $PM_{2.5}$ field blanks (one field blank by
182 participant, collected on the second day of the three consecutive sampling days), one indoor
183 and one outdoor field blanks (both collected on December 10th, 2016) were sampled in this
184 study, respectively. Blank values were used to account for any artifacts caused by gas
185 absorption and subtract the background $PM_{2.5}$ concentrations in this area. One laboratory
186 blank filter was assigned to each batch to account for any contamination in transfer and
187 weighing.

188 In order to verify the comparability of individual and household data caused by not
189 identical sampling devices, 14 pairs of $PM_{2.5}$ samples were synchronously collected by PEM
190 with SKC pump (used as a fixed sampler in this comparison test) and by a Mini-Vol sampler.
191 The comparison results led to a significant correlation between the $PM_{2.5}$ mass concentrations
192 obtained from different sampling devices (Y=1.070X-0.038, R^2=0.935, P<0.0001). Identical
193 aerosol size fraction ($PM_{2.5}$), membrane (quartz fiber) and analytical treatments were used
194 and a strict QA/QC protocol was established. The pumps were calibrated with a flow
195 calibrator before and after sampling. After sampling, the filter samples were placed in Petri
196 dishes, sealed with parafilm and stored in a -4°C freezer to prevent loss of mass through
197 volatilization prior to analysis.

198 *2.3. $PM_{2.5}$ gravimetric, chemical analysis and online monitoring*

199 The analyses for particle mass, organic carbon (OC), elemental carbon (EC), and

water-soluble inorganic ions concentrations were performed for all $PM_{2.5}$ samples collected in this study. $PM_{2.5}$ mass concentrations were obtained by weighing the filters with a Sartorius ME 5-F electronic microbalance (sensitivity ±1 μg, Sartorius, Germany) after equilibration at a temperature of 20-23 °C and a relative humidity of 35%-45% for at least 24 hours. The absolute errors between duplicate weights were ≤0.015 mg.

OC and EC were measured on a 0.526 cm^2 filter punch using DRI Model 2001 Thermal/Optical Carbon Analyzer, following the IMPROVE_A protocol (Cao et al., 2007). The method decomposed four OC thermal fractions (OC1, OC2, OC3 and OC4 in a non-oxidizing helium (He) atmosphere at 140 °C, 280 °C, 480 °C and 580 °C, respectively), one OP (a pyrolyzed carbon fraction obtained in an oxidizing atmosphere and analytically determined when the reflected laser light reaches its original intensity) and three EC fractions (EC1, EC2 and EC3 in an oxidizing atmosphere of 2% oxygen (O_2) in a balance of 98% helium at 580 °C, 780 °C and 840 °C, respectively). The IMPROVE_A protocol defines total carbon (TC) as OC+EC, OC as OC1+OC2+OC3+OC4+OP, and EC as EC1+EC2+EC3–OP.

One quarter filter was extracted using Milli-Q water and aliquots were analyzed by ion chromatography (IC) to determine the water-soluble inorganic ions concentrations (five cations: Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} and four anions: F^-, Cl^-, $NO_3^-$and SO_4^{2-}) (Zhang et al., 2011) in this study. The IC analyzer (Dionex-600, Dionex, Sunnyvale, USA) was equipped with an AS11-HC anion column and a CS12A cation column for separation. Details of the IC method are described in Zhang et al. (2011).

Q-TRAK indoor air quality monitor (model 7575-X, TSI Inc., USA) was operated in the heating room of each participant for real-time monitoring of temperature (T) and CO_2; measurements for these variables were made simultaneously every 5 min. Monitor was calibrated before and after the sampling period. Resolutions, precisions, and measurement ranges of the analyses were as follows: 0.1, ±0.6, 0-60 □ for T, and 1, ±50, 0-5,000 ppm for CO_2.

2.4. Questionnaire and time-activity diary

The basic information, including number of villagers and households, types of heating and cooking ways and their proportions, as well as the age composition of the villagers, were

obtained from the village head and the village committee office. Questionnaire (Appendix B) and time-activity diary (Appendix C) were collected from each participant during the sampling period (Allen et al., 2004; McGrath et al., 2017). The questions were specifically designed for housewives who are living in a rural area of northwestern China, and included: (1) Basic information (personal information, family status, housing conditions, dermatological, asthma symptoms, medical history and current health status); (2) Living habits and environment (past and current living environments, general living habits, cooking and heating habits); and (3) Travel habits. Participants completed daily time-activity diaries to assess how much time subjects spent in each microenvironment and doing what. The time-activity diaries requested the participants to mark on half an hour basis (sleeping time excluded) their appropriate microenvironment-activity.

2.5. Principal component analysis (PCA)

PCA is the true eigenvector-based multivariate analysis. Often, its operation can be thought of as revealing the internal structure of the data in a way that best explains the variance in the data. In this study, it was applied to identify and quantify the main sources of $PM_{2.5}$ and their contributions to the levels observed in the personal exposure, indoor and outdoor samples. This was achieved through the sorting of initially correlated data into a hierarchy of statistically independent modes of variation, which successfully explain less and less of the total variance (Brinkman et al., 2009; Ho et al., 2006; Jolliffe, 2002). PCA was performed on original data by using SPSS 19.0 statistics software in this study.

3. Results and discussion

3.1. Personal exposure to $PM_{2.5}$

Table 1 summarizes the $PM_{2.5}$ chemical mass concentrations (arithmetic mean ± standard deviation) determined from the personal exposure, indoor and outdoor samples during the study period. On average, personal exposure to $PM_{2.5}$ (PE $PM_{2.5}$) concentration was 263.4±105.8 μg m^{-3}, which was much higher than the values found indoors and outdoors (186.5±79.5 and 191.0±85.3 μg m^{-3}, respectively) (Table 1). High PE $PM_{2.5}$ levels resulted from $PM_{2.5}$ exposures related to specific individual's activities, e.g., local sources when the

subjects were outdoors in the yard of the house, and indoor sources when the subjects were in the kitchen or in some other potentially contaminated microenvironments (Crist et al., 2008; Huang et al., 2015; Meng et al., 2009). Noticeably, only about 6% of outdoor concentrations (2 out of 30 outdoor samples) reported in our study met the requirement of $PM_{2.5}$ limitation (75 μg m^{-3}) in China's 24-hour Ambient Air Quality Standards (AAQS, GB3095-2012). No indoor or PE $PM_{2.5}$ limit was established in China yet. The average indoor and PE $PM_{2.5}$ concentrations were more than 1.2 and 2.5 times over the concentration limit set for PM_{10} (PM with an aerodynamic equivalent diameter less than or equal to 10 μm) in the China National Indoor Air Quality Standards (150 μg m^{-3} for 24-hour average) (GB/T18883-2002).

TC was the leading constituent in $PM_{2.5}$, accounting for 34.1%, 23.8% and 26.8% of $PM_{2.5}$ mass in personal exposure, indoor and outdoor samples, respectively. This high TC percentage in PE $PM_{2.5}$ indicated that combustion sources significantly contributed to the participants' exposure. OC and EC ratios (OC/EC) varied from 1.3 to 6.7 (average: 4.2±1.2) for personal exposure, 2.3 to 7.1 (average: 3.4±1.1) for indoors, and 2.6 to 5.8 (average: 3.5±0.7) for outdoors. In a previous study, the average OC/EC ratio for agricultural biomass (13.7±2.7) was higher than that for bituminous coal (1.4±1.3) or anthracite coal (6.3±1.3) (Cao et al., 2008; Li et al., 2009; Tian et al., 2017). According to the questionnaire, residents in this sampling site (Hw1-3) mainly used anthracite coal (coal chunks) and biomass (wheat straw and maize straw) for heating and cooking, which combustion generally leads to high OC/EC ratios. Personal exposure samples displayed higher and slightly more scattered OC/EC ratios than those collected indoors and outdoors. The main reason may be the particularly high exposure of the participants to solid fuels burning.

Water-soluble inorganic ions accounted for 25.6%, 32.3% and 32.5% of $PM_{2.5}$ mass in personal exposure, indoor and outdoor samples, respectively, which showed an opposite pattern to TC. In previous studies, SO_4^{2-} was the most abundant species in all measured ions (Chen et al., 2017; Niu et al., 2016; Xu et al., 2016), therefore it is surprising to note that NO_3^- dominated in our results, leading to NO_3^- to SO_4^{2-} ratios (NO_3^-/SO_4^{2-}) of 1.20±0.42 (range: 0.20-1.83) for personal exposure and 1.6 for both indoors (average: 1.62±0.47, range: 0.62-2.38) and outdoors (average: 1.57±0.43, range: 0.60-2.21). 77% of NO_3^-/SO_4^{2-} ratios in

personal exposure samples and 87% in both indoor and outdoor microenvironments were higher than 1.0, indicating the dominance of ammonium nitrate (Zhang et al., 2011). Our high NO_3^-/SO_4^{2-} values were consistent with the decrease of SO_4^{2-} concentrations (regional background) in Guanzhong area (Xu et al., 2016) due to the nationwide implementation of flue gas desulfurization using SO_2 scrubbers in coal-fired power plants (Wang et al., 2013) over the recent years. The quite low air temperature (indoor average: 9.3 °C; outdoor average: 2.1 °C) in winter during the sampling was the other reason for high nitrate concentrations (Wang et al., 2013).

Moreover, Ca^{2+} concentration was about 5 times higher in personal exposure samples than outdoors and indoors, accounting for 15% of total measured ions. Particle resuspension by personal activities may be the main factor to determine personal exposure to dust-related $PM_{2.5}$ component (Chen et al., 2017; Xu et al., 2015). K^+, a marker of biomass burning (Kang et al., 2004; Zhang et al., 2014b), also displayed high absolute concentrations and percentages in $PM_{2.5}$ of personal exposure samples, confirming the expected exposure of housewives to biomass burning during the sampling period.

3.2. Relationships of personal exposure-indoor-outdoor $PM_{2.5}$

To further investigate the influence of human activities on $PM_{2.5}$ concentrations and the relationships between personal exposure and the microenvironments, personal exposure/indoor (PE/in), personal exposure/outdoor (PE/out) and indoor/outdoor (in/out) ratios of $PM_{2.5}$ and its chemical compositions were evaluated (Fig.2). The in/out ratio can be used as a measure of the relative intensities of the indoor *vs*. outdoor emission sources modulo the infiltration effects between the two environments (Janssen et al., 2000; Zhu et al., 2010). As shown in Fig.2, in/out ratios for $PM_{2.5}$ mass and most chemical species were observed around 1.0 in our results, suggesting that some of the subjects' houses were naturally ventilated, which was also confirmed by questionnaire, or indicating that the distribution of indoor and outdoor $PM_{2.5}$ and its components in some of the households could be considered as homogeneous (Xu et al., 2018). Because $PM_{2.5}$ emitted from the solid fuels burning in the indoor combustion facility was basically discharged out of the house through the chimney, a comparable level of $PM_{2.5}$ and its chemical components can be found both

316 indoors and outdoors. Additionally, we should pay attention to the solid fuel combustion
317 markers, such as OC1, OP, F^- and Cl^- (Sun et al., 2017), which displayed the extremely high
318 indoor/outdoor ratios in some cases. On the contrary, PE/in and PE/out ratios were much
319 higher than 1.0 regarding most of the $PM_{2.5}$ chemical species (Fig.2); the average PE/in and
320 PE/out ratios were 2.6 and 2.5, respectively. Especially, the solid fuel combustion markers,
321 like OC1~OC3, OP, EC2 and F^- (Cao et al., 2005; Sun et al., 2017) and the crustal dust
322 markers, such as Mg^{2+} and Ca^{2+} (Shen et al., 2016; Xu et al., 2016), were elevated in those
323 two ratios.

324 Results from the regression analyses of personal exposure, indoor and outdoor $PM_{2.5}$
325 concentrations and their chemical compositions are presented in Fig.3. Statistically
326 significant correlations were found with linear regression (*R*) ranging from 0.40 to 0.96
327 between indoor and outdoor concentrations, except for EC2, Cl^-, Na^+, Mg^{2+} and Ca^{2+}. It may
328 be due to the fact that EC2 corresponds to vehicle emissions (Cao et al., 2005; Xu et al.,
329 2016), while the listed ions are generally associated with soil dust, and can thus widely vary
330 in both indoor and outdoor sources. The highest *R* was observed for the biomass burning
331 marker K^+, suggesting that $PM_{2.5}$ related to indoor and outdoor biomass burning were emitted
332 from the same sources. However, moderate to poor correlations were found for personal
333 exposure *vs*. indoor (PE *vs*. in) and personal exposure *vs*. outdoor (PE *vs*. out) $PM_{2.5}$. PE *vs*.
334 in correlations were however stronger than those found for PE *vs*. out, indicating a relatively
335 higher importance of indoor than outdoor pollution on $PM_{2.5}$ personal exposure samples
336 (Crist et al., 2008). We also noted that secondary formed ions (SO_4^{2-}, NO_3^- and NH_4^+)
337 exhibited high *R* in the range of 0.715 to 0.949 for PE *vs*. in and PE *vs*. out. It confirms the
338 importance of secondary formed ions in rural Guanzhong area, in consistency with previous
339 studies (Chen et al., 2017; Zhang et al., 2015), and suggests that secondary formed fine
340 aerosol pollution was serious and largely impregnated the living environments in the studied
341 rural area.

342 *3.3. $PM_{2.5}$ influenced by household heating ways*

343 In order to investigate the impact on $PM_{2.5}$ personal exposure to different solid fuels
344 under different combustion processes for heating and cooking in winter in rural Guanzhong

Plain, Fig.4 shows the different $PM_{2.5}$ mass concentrations and distributions based on the four types of household heating ways (Hw) mentioned above (The same cooking solid fuels (biomass and wood) and identical cooking stove make $PM_{2.5}$ personal exposure characteristics from Hw1-3 households comparable). In this figure, the different heating ways led to contrasted $PM_{2.5}$ mass concentrations. The average personal exposure to $PM_{2.5}$ concentration in Hw1 (297.3±104.6 μg m^{-3}) and Hw3 (293.1±79.2 μg m^{-3}) were similar, lower than in Hw2 (366.4±90.0 μg m^{-3}) and higher than in Hw4 (156.8±36.6 μg m^{-3}). The personal exposure results well matched with the potential PM emissions from each solid fuel combustion way (Chen et al., 2017; Sun et al., 2017). There were direct combustion sources in the houses with Hw1 and Hw2. The honeycomb briquettes were burned in a honeycomb stove, which was placed in a channel under the brick bed to warm bed, in the bedroom of the participant. The honeycomb stove was reachable from the bedroom by a tiny door on the side of the brick bed, and the smoke from the stove was exported through a chimney connected to the brick bed itself in Hw1. The Hw2 corresponded to coal chunks stove located in the bedroom of the participants. Smoke from the stove was evacuated outdoors through a chimney. The participants needed to ignite and change the coal or honeycomb briquette several times each day in winter.

In addition, indirect combustion source existed in Hw3 and Hw4. Biomass residues were burned in the bedroom-adjoining hearth during cooking in the kitchen and the heat flow was transmitted to a brick bed in the bedroom from kitchen for heating. Although there was no direct combustion source in the targeted bedroom in Hw3, the participants needed to ignite crop residues (maize leaves and/or wheat straws) and wood (mainly tree branches) for cooking and heating, which led to a lot of direct and close exposure to $PM_{2.5}$ despite a chimney connected to the hearth. It should be noted that surveyed households with Hw1-3 all used biomass and wood as cooking energy in the kitchen. As expected, Hw4 was the cleanest method in this study, which resulted in the lowest personal exposure $PM_{2.5}$ mass. It is worth mentioning that solid fuels were seldom used in the Hw4 households of this study. Nevertheless, the average personal exposure $PM_{2.5}$ concentrations associated to Hw1-3 (310.8±90.4 μg m^{-3}) were on average two times higher than those in Hw4. It shows that

households using clean energy (electrical power here) for heating and cooking can at least reduce by half of the personal exposure to $PM_{2.5}$ in winter in this area. The independent-sample test T was carried out for these two data groups, i.e., Hw1-3 and Hw4 $PM_{2.5}$ mass concentrations by using SPSS 19 software. The low significant values (p=0.028 and 0.000) indicates the obvious difference between $PM_{2.5}$ mass levels of Hw1-3 and Hw4 in this study. Personal exposure to $PM_{2.5}$ chemical compositions for different heating ways in this study can be found in Table S1 to further support the conclusions above.

Unlike the $PM_{2.5}$ concentrations change pattern of personal exposure samples (Hw2 > Hw1 > Hw3 > Hw4), $PM_{2.5}$ mass concentrations indoors showed the descending following order: Hw2 (229.4±118.0 μg m^{-3}) > Hw4 (214.2±88.1 μg m^{-3}) > Hw3 (167.1±18.5 μg m^{-3}) > Hw1 (131.2±42.6 μg m^{-3}) and the same order outdoors: Hw2 (245±137.8 μg m^{-3}) > Hw4 (203.1±83.9 μg m^{-3}) > Hw3 (178.2±23.7 μg m^{-3}) > Hw1 (137.4±59.2 μg m^{-3}). $PM_{2.5}$ related to Hw2 exhibited the highest concentrations for indoor and outdoor microenvironments (Liao et al., 2017), owing to the obvious solid fuel combustion source at home. But it is surprising that $PM_{2.5}$ mass of Hw4 ranked at the second place and showed much higher values than the corresponding personal exposure levels. The electric blankets and/or electric heaters were used only for a short time at night before sleeping in Hw4 households for space heating. Family members in such houses spent most of their time away from home except for cooking, eating and sleeping. The participants visited relatives/friends in the village and spent time outside to bask in the sunshine in the rest of the time. This description can be supported by the outcomes from the questionnaire and time-activity diary (Appendix B and C), as well as the online data from the Q-TRAK indoor air quality monitor, which showed the much lower room temperatures (Fig.S2) and lower CO_2 concentrations (Fig.S3) in Hw4 households. In addition, the outdoor air temperature of daytime (8:00 to 20:00) to nighttime (20:00 to 8:00 of the following day) ratio was 11.6 on average, which provides the basic condition for the participants to bask in the sun during the relatively high temperature at daytime. Hence, the potential reason explaining relatively high $PM_{2.5}$ indoor and outdoor mass concentrations in Hw4 households could be related to a high ventilation rate in their houses (answers to Question B12 of Appendix B were Options 7 or 8, i.e., 3h < window and door half open time

per day < 8h) allowing regional air pollution (caused by the solid fuels combustions mainly) to enter the indoor environments. Another potential reason of higher indoor and outdoor $PM_{2.5}$ than personal exposure in Hw4 households could be that the housewives in this case were seldom exposed to direct or indirect combustion sources in their houses, especially they were barely involved in the ignition of biomass, wood, coal or honeycomb briquette for heating or cooking. This interpretation can also be used to explain the poor correlations between personal exposure against indoor levels, as well as against outdoor $PM_{2.5}$. Besides, due to inadequate samples, it was hard to find out the exact cause of high $PM_{2.5}$ observed in Hw4 households in this study, which requires further study to uncover unknown sources or related mechanisms in the future.

$PM_{2.5}$ average concentrations for Hw1 to Hw3 were observed at a slightly lower level in bedrooms compared to outdoors, which may result from the direct discharge outdoors through the chimney of $PM_{2.5}$ emitted indoors. Even though indoor $PM_{2.5}$ concentrations were a little bit lower than outdoors in Guanzhong rural area, the high indoor $PM_{2.5}$ levels are still a cause for concern. Lastly, in the comparison of the results from the Hw1 to Hw3 households, the variability of $PM_{2.5}$ levels in Hw3 were the smallest one, both regarding the indoor and outdoor samples, due to the indirect combustion activity in the bedroom, which was less affected by the solid fuel types and combustion conditions. The uncertainties of $PM_{2.5}$ mass concentrations indoors and outdoors were enhanced when the direct combustion sources were present in the households (Hw1 and Hw2) or when the households were better ventilated (Hw4). Moreover, Table S2 and S3 showed the indoor and outdoor $PM_{2.5}$ chemical species concentrations in different heating ways in this study, which provided more detailed information for this study.

3.4. Estimated $PM_{2.5}$ personal exposure levels

In order to estimate personal exposure to $PM_{2.5}$ based on the short-term measurement, a survey was conducted to investigate the daily time activity patterns of the housewives as mentioned above (Appendix C). Based on the use rate of solid fuels in household heating, we divided participants into Hw1-3 (solid fuels used at home) and Hw4 (no solid fuels used at home). Personal exposure $PM_{2.5}$ concentration (PE) can be estimated using the following

equation (time-weighted method) (Burke et al., 2001; McGrath et al., 2017; Meng et al., 2009):

$$PE = (t_{outdoor} \times C_{outdoor}) / T + (t_{indoor} \times C_{indoor}) / T \quad (1)$$

where: $C_{outdoor}$=outdoor $PM_{2.5}$ concentration, μg m^{-3}; C_{indoor}=indoor $PM_{2.5}$ concentration, μg m^{-3}; t=daily average time spent by an individual at microenvironments, including $t_{outdoor}$=time spent outdoors, h, and t_{indoor}=time spent indoors, h; Participants' exposure time were contributed by indoor environment by 69%±6% and 58%±3%, respectively in Hw1-3 and Hw4; T=total time per day, 24 h.

The time-weighted (estimated) and measured personal exposure concentrations to $PM_{2.5}$ were compared in Fig.5. Fig.5A displays the $PM_{2.5}$ mass differences between estimated and measured values ranging from 4% to 135% in Hw1-3 household (using solid fuels for household heating and cooking). The poor correlation was associated to participants exposed to direct combustion sources and ignition process, while no obvious ignition process was present in the measured indoor and outdoor environments. However, the estimated $PM_{2.5}$ personal exposure concentrations were more consistent with the measured values in Fig.5B for Hw4 since no domestic solid fuels burning was involved. Therefore, the time-weighted method leads to underestimate PE $PM_{2.5}$ mass concentrations for Hw1-3, while results were predictable for Hw4. The stability of the latter case and its correlation with the measured values exhibited the better performance of the time-weighted personal exposure to air pollutant concentrations estimated method.

There are similar discoveries from previous researches. McGrath et al. (2017) found outdoor $PM_{2.5}$ contributed in the range of 20%-90% to indoor and personal exposures $PM_{2.5}$ levels. Several personal activities had a dramatic impact on personal $PM_{2.5}$ exposures, including smoking and woodworking. The results from Meng et al. (2009) showed that personal exposures were usually under-predicted using the time-weighted approach, in some cases by up to 135%, especially for people not exposed neither to environmental tobacco smoke nor obvious combustion source in the residence. Burke et al. (2001) demonstrated that among the different daily microenvironmental $PM_{2.5}$ exposures (exposures due to time spent in various microenvironments), indoor residential $PM_{2.5}$ had the greatest influence. Such

studies support that time-weighted method can be used to predict human exposure to $PM_{2.5}$ concentration in the absence of distinct indoor emission sources. And prove that there is a big uncertainty with the fixed sampling as a proxy of personal exposure in some cases and the direct measurement of exposure to $PM_{2.5}$ via personal exposure monitoring is the most accurate assessment method.

3.5. Source apportionments of $PM_{2.5}$

A total of 13 chemical species determined in personal exposure, indoor and outdoor $PM_{2.5}$ samples, i.e., OC1, OC2, OC3, OP, EC1, EC2, NO_3^-, SO_4^{2-}, NH_4^+, K^+, Na^+, Mg^{2+} and Ca^{2+} fed the Principal Component Analysis (PCA) model to investigate the sources of $PM_{2.5}$ and their rough contributions (Ho et al., 2006; Jolliffe, 2002; Kumar et al., 2001). We identified four main sources including solid fuel combustion, secondary formed aerosols, vehicle emission and various dust sources (including fugitive dust marked by Mg^{2+} and Ca^{2+}, road dust marked by EC1, Mg^{2+} and Ca^{2+}, construction dust marked by Ca^{2+}, and combustion dust marked by OC1, OC2, EC2, Mg^{2+} and Ca^{2+}) (Chow et al., 2004; Shen et al., 2016; Zhang et al., 2014a). The source factor analysis and variance explained are shown in Table 2. Those main source factors showed in Table 2 explained 82.7%-88.7% of contributions for personal exposure, indoor and outdoor to the total variance in $PM_{2.5}$ data set in this study.

PCA indicated that solid fuel combustion was the largest contributor (44.2% of the total variance) to PE $PM_{2.5}$ mass concentrations during winter in Guanzhong rural area, and this factor was dominated by OC fractions, OP, EC1, EC2 and K^+. This factor also showed the contribution from NO_3^-, SO_4^{2-} and NH_4^+, which indicated the importance of secondary inorganic aerosol formed from gases emitted by solid fuel combustion processes. The second factor was characterized by high load of EC1, Mg^{2+} and Ca^{2+}, moderate load of OC3 and EC2, which are all associated with motor vehicle emission and related road dust. Contributions of this factor reached 26.8% of the total variance in PE $PM_{2.5}$. The last factor was driven by Ca^{2+}, associated with construction dust (Zhang et al., 2014a), which constituted 11.7% of the total variance for PE $PM_{2.5}$ in this study.

Regarding indoor $PM_{2.5}$, the first factor had high loadings of OC fractions, OP, EC1, K^+ and secondary inorganic species (NO_3^-, SO_4^{2-} and NH_4^+), which was best explained by

emissions from solid fuel combustion and related secondary formed species, accounting for 56.4% of the total variance of $PM_{2.5}$ mass. Factor 2 was enriched in OC fractions, EC2 and crustal ions (Mg^{2+} and Ca^{2+}). Although their loadings were not so high, they can be considered to be more enriched than other species. This factor represented solid fuel combustion emission related dust (same as the combustion dust above mentioned). This source accounted for 21.2% of the total variance of indoor $PM_{2.5}$ mass. The third factor of $PM_{2.5}$ indoors was characterized with high concentrations of Mg^{2+} and Ca^{2+}, corresponding to fugitive dust, accounting for 11.0% of the total variance.

The most important PCA factor for outdoor $PM_{2.5}$ mass was virtually identical to the first factor of personal exposure and indoor samples; it was dominated by all the OC and EC fractions, K^+, NO_3^-, SO_4^{2-} and NH_4^+, and attributed to solid fuel combustion and related secondary formed species (65.7% of the total variance of outdoor $PM_{2.5}$). Fugitive dust has been shown to be a second important source of outdoor $PM_{2.5}$ mass, contributing by 10.5%. As already stated, Ca^{2+} is commonly used as a marker of construction dust, as shown in the third factor for $PM_{2.5}$ outdoors, which accounted for 9.3% of the total variance.

In summary, the primary species emitted from solid fuel combustion, together with the related secondary formed species, were the most important contributors to $PM_{2.5}$ mass concentrations. Their fingerprints were stronger outdoors (65.7% of the total variance in $PM_{2.5}$) than indoors (56.4%) and in personal exposure results (44.2%). It probably resulted from the fact that $PM_{2.5}$ was directly emitted out of the chimney to the ambient air. Interestingly, emissions from motor vehicles appeared to mainly affect personal exposure and only to a much lesser extent the indoor and outdoor $PM_{2.5}$, pointing out a relatively significant exposure of individuals to traffic out of their domestic environments, primarily from gasoline cars and motorcycles (agricultural vehicles were not in use over winter) in this village. The contribution of dust, mainly from unpaved road dust resuspension and uncovered construction activities, which are common in most rural areas of the Guanzhong Plain, was observed in the three types of $PM_{2.5}$ samples, with specific contribution indoors from dust associated to solid fuel combustion emissions, while construction dust contributed to $PM_{2.5}$ in personal exposure and outdoor samples.

519

520 **4. Conclusions**

521 Personal exposure to $PM_{2.5}$ coupled with indoor and outdoor $PM_{2.5}$ were collected
522 during the wintertime of 2016 in a rural area of Guanzhong Plain, China. Results were
523 analyzed to investigate the $PM_{2.5}$ chemical composition and potential sources, with a
524 particular focus on the different domestic heating and cooking solid fuels in rural
525 northwestern China. Personal exposure to $PM_{2.5}$ led to concentrations 40% higher than those
526 measured indoors and outdoors, indicating the determining role of individual's activities such
527 as the ignition of solid fuels for heating and/or cooking. The high concentration ratios and
528 poor correlations between personal exposure and the outdoor and indoor microenvironments
529 were observed for $PM_{2.5}$ and its primary chemical components. That probably resulted from
530 the fact that most housewives were usually exposed to the direct combustion sources (solid
531 fuel ignition), while no intense emission sources characterized the indoor and outdoor
532 microenvironments (except for Hw2 household). The results also confirmed that households
533 using electrical power for heating and cooking could at least reduce by half personal exposure
534 to $PM_{2.5}$ in the study area.

535 The major pollution sources distinguished in this study included solid fuels burning and
536 the related secondary formed species, and also vehicle emissions and various dust sources.
537 Solid fuel burning and the related secondary formed species dominated $PM_{2.5}$ mass in
538 personal exposure (44.2% of the total variance), indoor (56.4% of the total variance) and
539 outdoor (65.7% of the total variance) samples. Our results therefore support the use of clean
540 energy (such as electricity), instead of the domestic solid fuels for heating and cooking, as an
541 effective measure to reduce $PM_{2.5}$ personal exposure to housewives in the heating season,
542 particularly in rural areas of northwestern China, together with control measures regarding
543 dust emissions from unpaved roads and construction sites in the village.

544

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Author Contributions

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

Additional Information

Fig.S1-S3, Table S1-S3, Appendix A, B and C accompany this manuscript can be found in Supplementary information.

Competing financial interests

The authors declare no competing financial interests.

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752 **Figure Legends:**

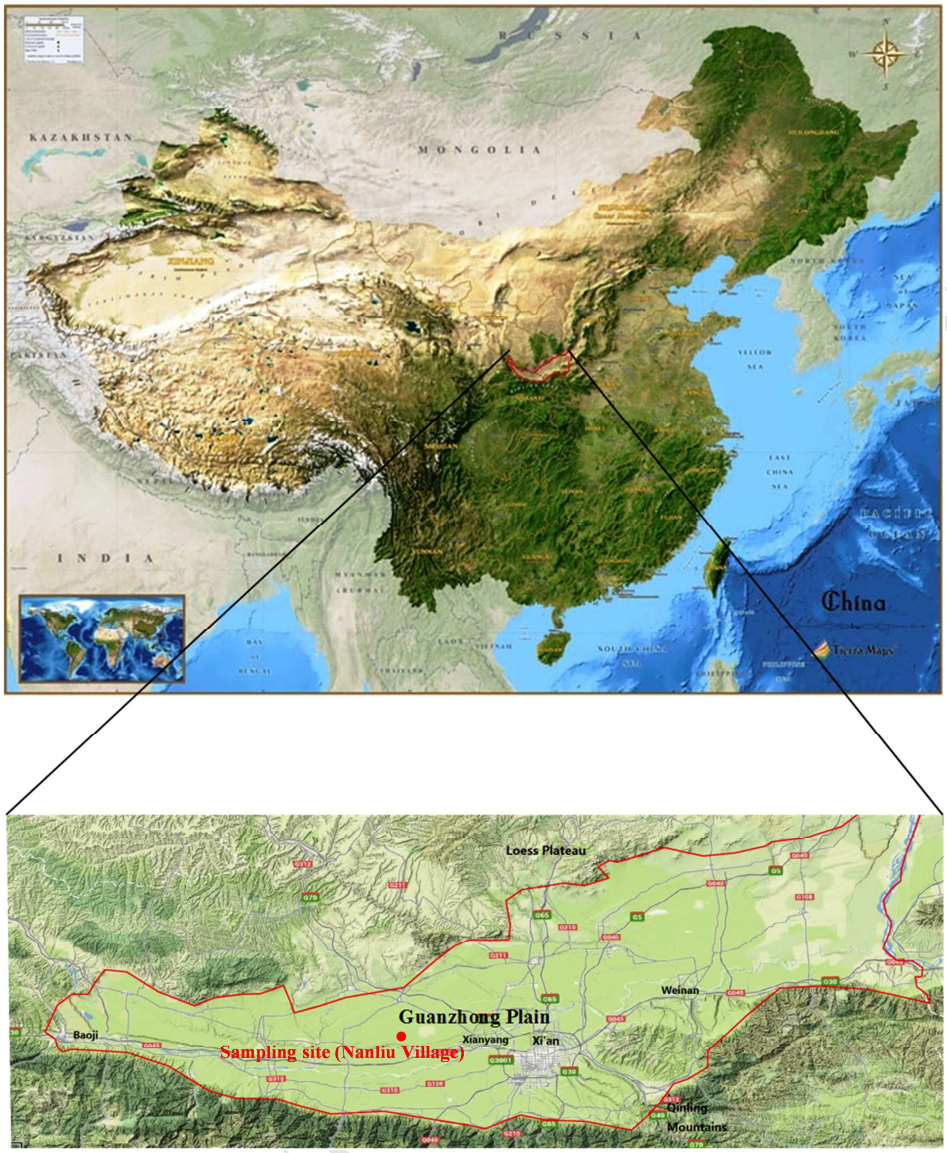
753 **Fig.1** Maps of the sampling site in Nanliu village, Guanzhong Plain, northwestern China.

754 **Fig.2** Personal exposure (PE)/indoor, PE/outdoor and indoor/outdoor ratios of $PM_{2.5}$ mass
755 concentrations and chemical compositions in this study (The box plots indicate the average
756 value and the min, 1^{st}, 25^{th}, 50^{th}, 75^{th}, 99^{th} and max percentiles).

757 **Fig.3** Correlations of $PM_{2.5}$ mass concentrations and chemical compositions among personal
758 exposure (PE), indoor and outdoor samples.

759 **Fig.4** The box plots of $PM_{2.5}$ mass concentrations of personal exposure (PE), indoor and
760 outdoor according to different household heating ways (Hw) in the studied rural area (A
761 normal curve is fitted to the measurements).

762 **Fig.5** Estimated *vs*. measured personal exposure (PE) to $PM_{2.5}$ in winter of rural Guanzhong
763 Plain. A: Using solid fuels for household heating and cooking (Hw1-3); B: Using electrical
764 equipment for household heating and cooking (no solid fuels used at home, Hw4).



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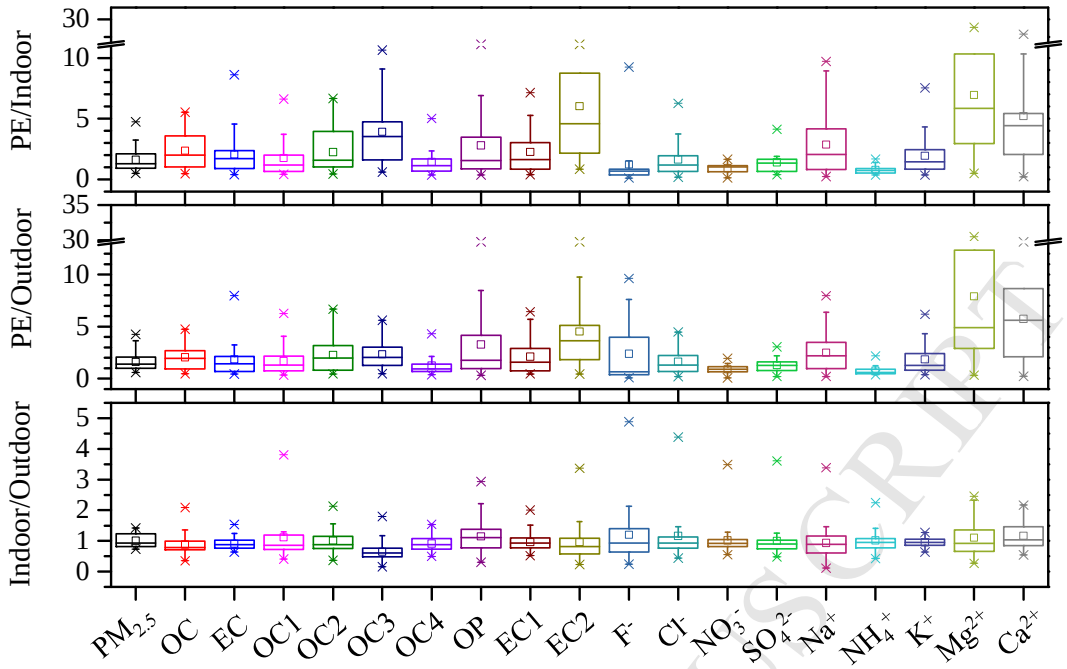

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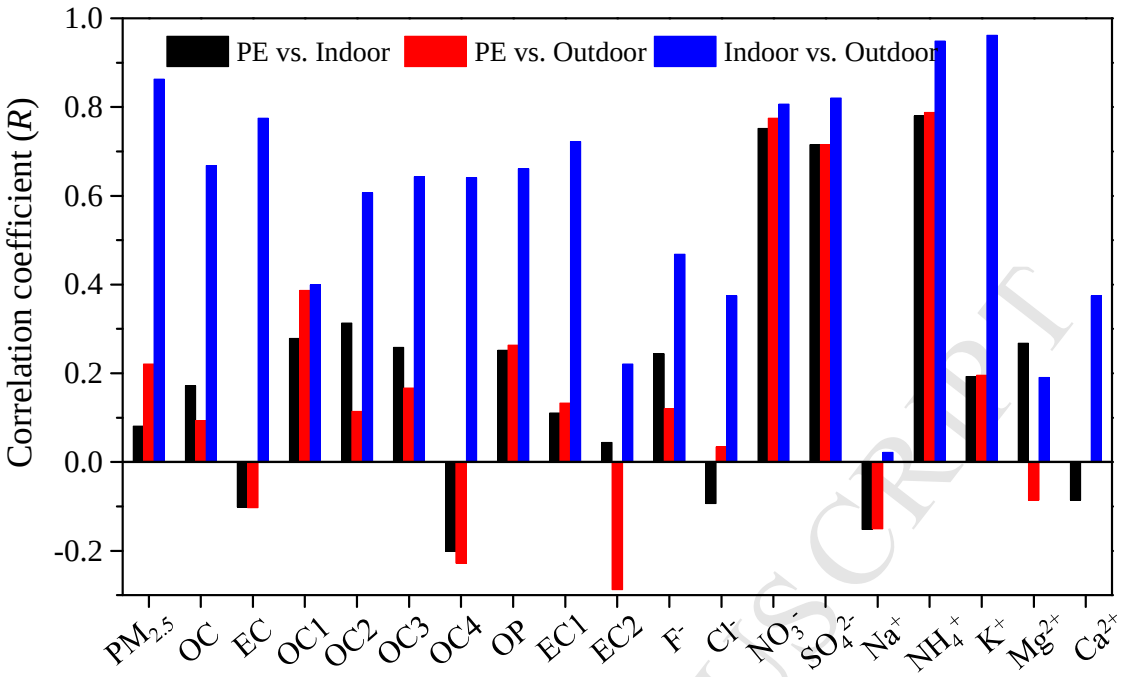

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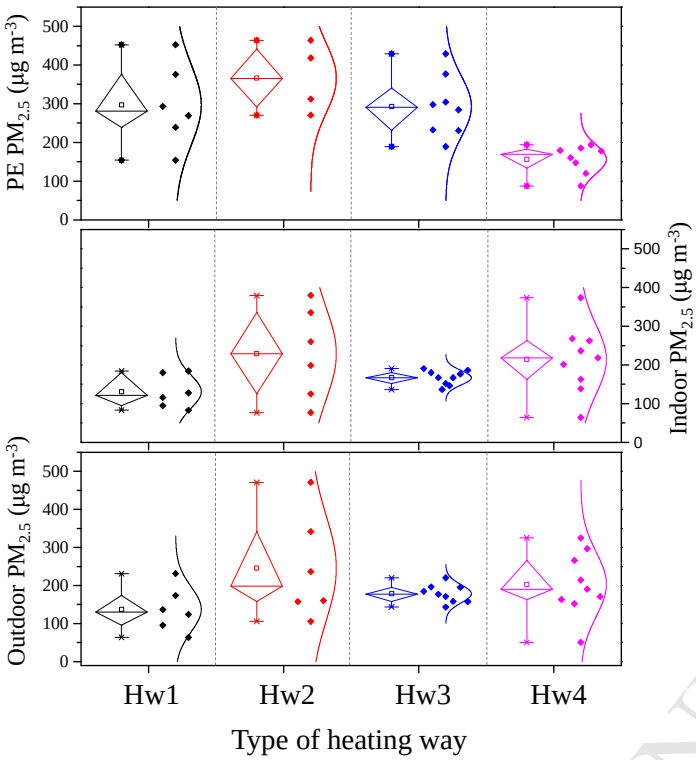

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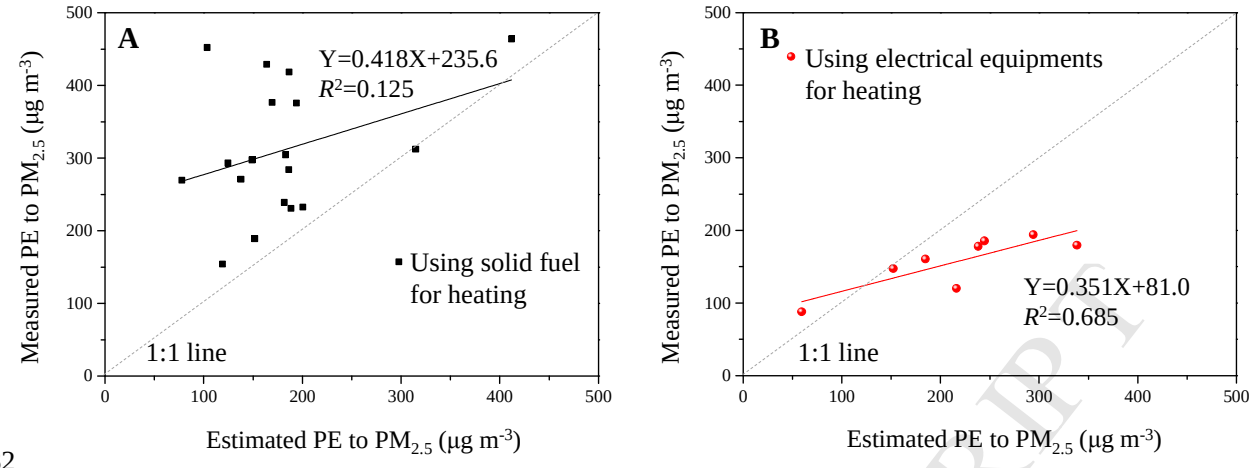

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783 **Fig.5** Estimated *vs*. measured personal exposure (PE) to $PM_{2.5}$ in winter of rural
784 Guanzhong Plain. A: Using solid fuels for household heating and cooking (Hw1-3); B:
785 Using electrical equipment for household heating and cooking (no solid fuels used at
786 home, Hw4).

787

788 **Table 1** Statistical analysis (arithmetic mean±standard deviation) of $PM_{2.5}$ mass
789 concentrations and chemical compositions (units: μg m^{-3}) of personal exposure,
790 indoor and outdoor $PM_{2.5}$ during the sampling period.

	Personal exposure	Indoor	Outdoor
Sample No.	30	30	30
$PM_{2.5}$ mass	**263.4±105.8**	**186.5±79.5**	**191.0±85.3**
OC	71.4±36.1	34.4±17.2	40.0±19.2
EC	18.4±12.0	10.0±3.7	11.2±3.7
OC1*	5.6±4.4	4.0±3.1	4.0±3.3
OC2*	13.6±9.1	6.7±3.6	6.8±3.4
OC3*	26.4±14.1	7.9±4.3	12.2±5.1
OC4*	11.8±5.6	9.3±3.0	10.4±2.9
OP*	13.9±12.4	6.5±6.2	6.7±7.4
EC1*	31.0±20.4	16.2±9.0	17.6±10.4
EC2*	1.1±1.2	0.2±0.1	0.2±0.1
EC3*	0.1±0.2	0.0±0.0	0.0±0.0
Total carbon	**89.8±45.0**	**44.4±20.1**	**51.2±22.5**
F^-	0.1±0.1	0.2±0.1	0.2±0.1
Cl^-	3.6±2.6	2.8±1.3	2.7±1.1
NO_3^-	20.9±15.6	25.4±17.6	25.7±17.1
SO_4^{2-}	16.7±11.1	15.5±11.3	16.2±11.4
Na^+	2.6±2.1	1.0±0.4	1.4±1.1
NH_4^+	8.0±5.7	10.5±6.9	10.8±6.8
K^+	4.6±3.6	2.8±2.1	2.9±2.0
Mg^{2+}	0.7±0.6	0.1±0.0	0.1±0.0
Ca^{2+}	10.4±8.6	1.9±0.4	1.8±0.6
Total ions	**67.4±35.4**	**60.2±38.2**	**62.0±37.3**

791 *OC, OP and EC represent organic carbon, organic pyrolyzed carbon and elemental carbon,
792 respectively.
793

794 **Table 2** Factor analysis of personal exposure, indoor and outdoor $PM_{2.5}$ during the
795 sampling period by principal component analysis (PCA).

	Personal exposure			Indoor			Outdoor		
	1	2	3	1	2	3	1	2	3
OC1*	**0.82**	-0.29	-0.16	0.67	0.58	-0.31	**0.92**	-0.20	0.19
OC2*	**0.78**	0.37	-0.40	**0.77**	0.56	-0.24	**0.94**	-0.21	0.19
OC3*	0.65	0.59	-0.24	**0.83**	0.47	-0.18	**0.90**	-0.25	0.30
OP*	**0.93**	-0.02	-0.04	**0.93**	-0.17	-0.14	**0.94**	-0.19	0.01
EC1*	**0.93**	**0.72**	-0.11	**0.96**	-0.11	-0.11	**0.97**	-0.13	0.01
EC2*	0.38	0.50	0.27	0.28	0.61	-0.24	**0.74**	-0.37	0.27
NO_3^-	0.65	-0.61	0.36	**0.83**	-0.44	0.21	**0.88**	0.15	-0.34
SO_4^{2-}	0.65	-0.53	0.46	**0.86**	-0.44	0.11	**0.82**	0.19	-0.49
NH_4^+	0.55	-0.77	0.23	**0.87**	-0.41	0.13	**0.83**	0.16	-0.47
K^+	**0.82**	-0.21	-0.34	**0.87**	-0.40	0.01	**0.81**	0.08	-0.27
Na^+	0.11	0.38	0.69	0.20	0.53	0.29	0.13	0.65	0.31
Mg^{2+}	0.49	**0.74**	0.10	0.42	0.67	**0.76**	0.58	0.62	0.25
Ca^{2+}	0.28	**0.81**	**0.75**	0.25	0.56	**0.72**	0.38	0.56	**0.81**
Variance explained (%)	**44.2**	**26.8**	**11.7**	**56.4**	**21.2**	**11.0**	**65.7**	**10.5**	**9.3**

796 *OC, OP and EC represent organic carbon, organic pyrolyzed carbon and elemental carbon,
797 respectively.

798

Research Highlights:

- Personal exposure (PE) $PM_{2.5}$ was 40% higher than indoor and outdoor values.
- High PE $PM_{2.5}$ was related to the ignition of domestic solid fuels in winter.
- Use of clean energy was an effective way to reduce PE $PM_{2.5}$ in rural northern China.
- Solid fuels combustion was a dominated source to PE $PM_{2.5}$ in Guanzhong rural area.