



1     **VOCs emission profiles from rural cooking and heating**  
2     **in Guanzhong Plain, China and its potential effect on**  
3     **regional O<sub>3</sub> and SOA formation**

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20 **Abstract**

21 Solid fuels (i.e., biomass fuel and coal) burning for cooking and heating emit large amounts of  
22 pollutants into atmosphere including particulate matter (PM) and volatile organic compounds (VOCs).  
23 In this study, VOCs were directly collected in chimneys of residential cooking and heating stoves in  
24 Guanzhong Plain using adsorbent tube approach followed by thermal desorption-gas  
25 chromatography/mass spectrometry (TD-GC/MS) analysis. Emission factors (EFs) of targeted VOCs  
26 varied from  $47.2 \pm 19.4$  to  $3121.3 \pm 1592.4$  mg kg<sup>-1</sup> which had a descending order of biomass straw >  
27 woody fuel >> coal fuels. A remarkable finding is that semi-gasifier could not suppress the VOCs  
28 emission even though a high efficiency in reduction of PM was demonstrated. In addition, high values  
29 of coefficients of divergence (CD) (most >0.5) support that there were large variations on the VOC  
30 profiles with different fuels and stoves. Ozone formation potential (OFP) of VOCs from solid fuel  
31 burning ranged from 50.3 to 5914.8 mg kg<sup>-1</sup>, contributing ~20% of ozone formation in Guanzhong  
32 atmosphere. The values were much larger than the contribution from PM of 6.7%. However, much  
33 lower secondary organic aerosol formation potentials (SOAP) (0.5 – 45.6 mg kg<sup>-1</sup>) of VOCs emitted  
34 from solid fuel burning were estimated. The values were two orders of magnitude lower than OFP and  
35 only accounted for 0.23% of the SOA in Guanzhong in 2013. The results of this study demonstrated  
36 that the VOCs emission from solid fuel burning had a strong impact to the ozone pollution in  
37 Guanzhong Plain.

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## 39 1. Introduction

40 Solid fuels (mainly biomass and coal) are extensively used for daily cooking and heating in  
41 developing countries, particularly occurred in rural regions (Shen et al., 2013). Biomass burning is the  
42 largest contributor of fine carbonaceous particles and second largest source of trace gases in the global  
43 atmosphere (Akagi et al., 2011; Andreae et al., 2001). Over 60% of households adopt traditional  
44 biomass resources as major fuels (Hou et al., 2017). Additional contribution from coal burning should  
45 not be underestimated as well. However, because of relatively low efficiencies of burning with  
46 residential stoves, large quantities of incomplete combustion byproducts such as fine particulate matter  
47 (PM) and volatile organic compounds (VOCs) are emitted (Adkins et al., 2010; Zhang and Smith,  
48 2007).

49 Chemical profiles of PM emitted from residential burning of solid fuel have been widely studied  
50 (Bonjour et al., 2013; Lei et al., 2011; Winijkul and Bond, 2016). Studies on trace gases including  
51 VOCs are relatively rare even though their influences on atmospheric pollution can be comparable to  
52 PM (Lee et al., 2005). VOCs participate in formations of tropospheric ozone (O<sub>3</sub>) and other  
53 atmospheric oxidants, as well as secondary organic aerosols (SOA) in particulate phase (Duan et al.,  
54 2008; Liu et al., 2008). Primary-emitted VOCs towards with the resulting photochemical oxidants and  
55 fine particles can lead severe regional air pollutions and contribute to climate change (Langmann et al.,  
56 2009; Yuan et al., 2010). With discrepancies of burning conditions, fuels and apparatus (i.e., fuel and  
57 stove types), emission factors (EFs) of VOCs are highly valuable among different regions or even close  
58 areas (Inuma et al., 2010; Li et al., 2009; Reid et al., 2005).

59 Guanzhong Plain, with an area of ~ 36,000 km<sup>2</sup> and a population size of 23.92 million, is  
60 surrounded by Qinling Mountains to the south and the Loess Plateau to the north (Figure S1), where  
61 atmospheric dispersion is typically weak due to its unique features of topography (Niu et al., 2016).  
62 Hou et al. (2017) reported that solid fuel burning has a dependency level of >80% energy consumption  
63 for Guanzhong Plain (Hou et al., 2017), and plays a crucial role in haze and episode events in  
64 wintertime (Cao et al., 2005; Shen et al., 2009; Zhang et al., 2015). PM emitted from rural cooking and  
65 heating activities to the region has been well studied. In this paper, we particularly focus on the VOCs  
66 emissions from solid fuel burning in Guanzhong Plain. A comprehensive measurement campaign was  
67 conducted in its rural area. The objectives of this study are to determine the EFs of VOCs from rural  
68 solid fuel burning activities and their contributions to regional O<sub>3</sub> and SOA formations.

## 69 2. Methodology

### 70 2.1 Sample collection

71 VOCs samples were collected at three typical agricultural villages in rural Guanzhong Plain (Fig.  
72 S1). The village in Weinan city (V1) had the highest number of residents (~2000). Apple tree is the  
73 dominated crop breed and its wood branches and logs are often used as fuels in traditional stove, which  
74 is named as “Heated Kang” (Fig. S2a). At the village in Xianyang city (V2), residents mainly use coal  
75 and wood branches for household heating and cooking, respectively. The village in Baoji city (V3) is  
76 located at a core grain-producing area in Guanzhong Plain, where maize and wheat residues were used  
77 for both heating and cooking in Heated Kang. Detailed information on the solid fuels and stoves are  
78 summarized in Table S1. Three types of stoves were applied, including Heated Kang, traditional coal



79 heating stove (Fig S2b) and semi-gasifier stove (Fig. S2c). The characteristics of Heated Kang have  
80 been described in Sun et al. (2017). Traditional coal heating stove was a commonly used heating device  
81 with simple ion structure in Northern China. Fuels (e.g. anthracite) was combusted in the furnace  
82 chamber and heat was transferred with low efficiencies by heat conduction or thermal radiation.  
83 Semi-gasifier stove was based on a core technology called “secondary air supply” which could  
84 efficiently enhance the combustion efficiency and also reduce PM EFs (Sun et al., 2017). Totally 8  
85 types of solid fuels were selected in this study, namely firewood, branch, maize straw, wheat straw,  
86 corncob, anthracite, honey-comb and bitumite. These solid fuels were representative in rural  
87 Guanzhong.

88 VOCs samples in this study were all collected in field experiments. The sampling platform was  
89 set at rooftop and beside the chimney of each stove. A self-made dilution system with dilution rate from  
90 5- to 50-fold was employed to collect the smoke emitted from solid fuel burning. More information  
91 about the dilution system could refer our previous studies (Sun et al., 2017). Experiments were  
92 conducted during real scenarios that residents used the stoves and solid fuels as their daily life. For  
93 cooking use, fuels were weighted before and after burning to clear the net fuel consumption, and the  
94 sampling period covered the whole cooking process. For heating activities, we weighted the fuels every  
95 time they added into the stove and sampling period covered several circles due to different duration of  
96 fuels and stoves. Certain number of parallel diluted smoke channels were set for not only VOCs but  
97 also other monitors such as PM<sub>2.5</sub>. For VOCs sampling, air-stream of diluted smoke was drawn into a ¼”  
98 o.d. stainless steel multi-bed adsorbent tube filled with Tenax-TA, Carbograph I TD and Carboxen 1003  
99 (Markes International Ltd., Llantrisant, U.K.) using a low-flow module pump (ACTI-VOC, Markes  
100 International Ltd.) at a flow rate of 50 mL min<sup>-1</sup> for 30-60 min due to different VOCs concentrations. A  
101 Teflon filter assembly (47mm, Whatman, Clifton, NJ, USA) and a home-made ozone scrubber,  
102 manufactured by a 1 m long and ¼” o.d. saturated potassium iodide (KI) coated copper tube, were  
103 installed in the air upstream to remove any influences from PM and O<sub>3</sub>, respectively. The sorbent tubes  
104 were pre-cleaned in a thermal conditioner (TC-20, Markes International Ltd.) at 330 °C for 20 min. All  
105 pre-conditioned and sampled tubes were capped and shipped at 0 °C. Insignificant breakthrough (<5%)  
106 was observed either in field or laboratory demonstration under this sampling flow and volume (Ho et  
107 al., 2017). Two sorbent tube samples were thus collected in each test and one field blank was collected  
108 on each sampling campaign.

## 109 2.2 Chemical analysis

110 A total 27 valid sorbent tube samples were collected. The samples were analyzed using a thermal  
111 desorption (TD) unit (Series 2 UNITY-xr system, Markes International Ltd.) coupled with a gas  
112 chromatograph/mass spectrometric detector (GC/MSD, Models 7890A/5977B, Agilent, Santa Clara,  
113 CA, USA). A tube was connected into the TD unit at room temperature (~25°C) and purged with  
114 ultra-high purity (UHP) helium (He) gas at a flow rate of 40 mL min<sup>-1</sup> for 10 s to eliminate air and  
115 oxygen intrusion. For the primary desorption stage, the analytes were desorbed at 330 °C for 5 min and  
116 refocused onto a cryogenic-trap (U-T1703P-2S, Markes International Ltd.) to capture high volatility  
117 target compounds at -15 °C. For the secondary desorption stage, the trap was dry-purged for 10 s and  
118 rapidly heated from -15 °C to 320 °C and maintained for 5 min. The analytes were passed via a heated



119 transfer line at 160 °C, and re-focused onto a cold GC capillary column head (Rtx®-1,  
120 105m×0.25mm×1µm film thickness, Restek Corporation, Bellefonte, PA, USA) at -45 °C with an aid  
121 of liquid nitrogen (N<sub>2</sub>) in GC oven. Once the second desorption is completed, the oven temperature  
122 program started at an initial temperature of -45 °C for 4 min, ramped to 230 °C at a rate of 6 °C min<sup>-1</sup>,  
123 and maintained at 230 °C for 5 min. The constant flow rate of He carrier gas was 1.0 mL min<sup>-1</sup>  
124 throughout the GC analysis. The MSD was operated in selective ion monitoring (SIM) mode at 230 °C  
125 and 70 eV for electron ionization. Identification was achieved by comparing the mass spectra and  
126 retention times of the chromatographic peaks with those authentic standards. Certified PAMS standard  
127 mixtures (Restek Corporation) were used in calibrations. A multi-point calibration curve was  
128 established to quantify each of the target compounds with linearity>0.999. The minimum detection  
129 limits (MDL) for 57 target analytes were in the range of 0.003-0.808 ppbv with a sampling volume of 3  
130 L. The measurement precisions for the analysis of eight replicates of standard samples at 2 ppbv were  
131 ≤5%. Duplicate samples were collected and the reproducibility was better than 95%. Detailed sampling  
132 and analytical method was shown in Ho et al. (2017).

### 133 2.3 Emission factors calculation

134 EFs were calculated based on fuel weight consumption (mg kg<sup>-1</sup>) as equation of

$$135 \quad EF = \frac{m_{tube} \times DR \times t_{sample} \times V_{stk} \times D}{Q_{tube} \times m_{fuel}} \quad (1)$$

136 where  $m_{tube}$  is the mass of VOC in the adsorbent tube (in mg),  $DR$  is the dilution ratio,  $t_{sample}$  is sampling  
137 duration (s),  $V_{stk}$  is stack flow velocity (m s<sup>-1</sup>), and  $D$  is stack cross section area of chimney (m<sup>2</sup>),  $Q_{tube}$   
138 is sampling volume through the adsorbent tube (m<sup>3</sup>), and  $m_{fuel}$  is fuel consumption (kg).

139

## 140 3. Results & Discussion

### 141 3.1 Emission factors

142 EFs of eight organic classes of VOCs for the examined solid fuels were summarized in Table 1.  
143 On average, the EFs for biomass fuels (1122.2±178.9 -3121.3±1592.4 mg kg<sup>-1</sup>) were higher than those  
144 for coal fuels (47.2±19.4 – 996.8±476.9 mg kg<sup>-1</sup>) (p<0.05). Among the biomass fuels, the values of EFs  
145 had a descending order of corncob > branch > firewood > maize straw > wheat straw. Our measured  
146 EFs are within the ranges reported for the biomass fuels shown in other relevant studies (Li et al., 2009;  
147 Wang et al., 2014). Our observations support that stoves and burning modes are dominating factors  
148 affected the EFs (Li et al., 2009). First, straws emitted more halogen-containing VOCs (93.2±23.2 and  
149 311.2±125.3 mg kg<sup>-1</sup>) than woody fuels (i.e., firewood and branch) (45.3±5.3 and 40.4±12.1 mg kg<sup>-1</sup>)  
150 with Heated Kang (p<0.05). It can be ascribed with the features of biomass straws, which had higher  
151 chloride contents than woody plants (Lindberg et al., 2016). Second, markedly differences in EFs were  
152 seen between the types of stoves used. The EFs of total quantified VOCs for the branches with Heated  
153 Kang and semi-gasifier stoves are 1830.0±330.1 and 2365.9±824.7 mg kg<sup>-1</sup>, respectively. The higher  
154 value from semi-gasifier was contributed by more aromatic hydrocarbons generations at relatively  
155 higher combustion temperatures (Chen et al., 2016; Lemieux et al., 2004). Even though some studies  
156 demonstrated that semi-gasifiers could effectively reduce particulate emission (Martin et al., 2011;  
157 Shen et al., 2015; Sun et al., 2017), the raise of VOCs emission is still a concern. Lastly, burning mode



158 (i.e. uses for either heating or cooking) also has strong impacts on EFs. For the heating activities with  
159 Heated Kang, users often extend the burning process by shutting down the air supply that leads to an  
160 oxygen-deficient environment (Zhuang et al., 2009). The extremely oxygen-deficient condition in  
161 Heated Kang favors larger productions of unsaturated alkenes but less alcohol, in comparison with the  
162 use of traditional cooking stoves. However, a sufficient air supply may not be a sole solution to reduce  
163 VOCs emission. The EFs of non-methane hydrocarbons from wheat straws at open burning are even  
164 over 100% greater than those reported in this study (Lemieux et al., 2004; Li et al., 2009).

165

166

*Insert Table 1 & Table S2*

167

168 Table 2 shows the top ten individual compounds with the highest contributions to the EFs of total  
169 quantified VOCs in each test. Acetone, accounted for 10% of the EFs for the biomass fuels, is one of  
170 the dominant VOCs regardless of any stove types and combustion modes. For the emissions from  
171 Heated Kang, the fractions of oxygenated-VOCs (O-VOCs) (27.2 – 31.2%) are also much higher than  
172 those of other stoves (6.6 – 23.1%). This could be explained by the severe oxygen-deficient condition  
173 during straw burning, while the volatile components could not be completely oxidized (Wang et al.,  
174 2014). Benzene and toluene are two most abundant aromatic compounds. The sum of their  
175 contributions had a descending order of semi-gasifier > cooking stove > Heated Kang. Aromatic  
176 hydrocarbons generations are associated with combustion temperatures (Shen et al., 2015). Since the  
177 semi-gasifier and traditional cooking stoves had a sufficient air supply, more aromatic hydrocarbons  
178 could be favorably formed. Methyl chloride was a sole halogen-containing compound in the top 10  
179 series among the tests. It acts as a typical tracer for straw burning (Liu et al., 2008), and is markedly  
180 important in source identification (Wang et al., 2014).

181

182

*Insert Table 2*

183

184 Alkane is the most abundant class for burning of anthracite and honeycomb coals. Dodecane and  
185 *n*-butane are the two most dominated alkanes for anthracite (26.6%) and honeycomb (29.2%) with  
186 cooking stoves. With the semi-gasifier, dodecane also accounted for 21.2% of the total quantified  
187 alkanes from the burning of anthracite. Bitumite had a different VOCs emission profile, which is as like  
188 as a mix between woody fuels and anthracite coals. Aromatic hydrocarbons (i.e., benzene, toluene and  
189 naphthalene) are the top ten species for bitumite with an average contribution of 25.2%, which is  
190 similar with loadings of woody fuels with semi-gasifier (Andreae and Merlet, 2001). However, alkanes,  
191 including dodecane, *n*-butane, undecane, iso-butane, propane, iso-pentane and *n*-pentane, for bitumite  
192 burning still had a high contribution of 37.6% to total quantified VOCs, which is consistent as that for  
193 anthracite (Liu et al., 2008). The small variations between the two fuels could be ascribed to their  
194 similarities of fuel properties such as ash content and fixed carbon fractions.

### 195 3.2 Source Profiles

196 Figure S3 illustrates the source profile for each test in this study. The identity numbers of each  
197 VOC are given in Table S1. Among those woody fuels (Fig. S3a), four characteristic fractions are



198 shown, including C<sub>3</sub>-C<sub>5</sub> alkanes, C<sub>3</sub> alkene, benzene and toluene, and C<sub>3</sub>-C<sub>4</sub> carbonyls (i.e., acrolein,  
199 acetone and methyl ethyl ketone). Coefficient of divergence (CD) was calculated to measure the  
200 similarity of profiles between the tests (Table S3). Similar profiles were obtained with the same stoves  
201 (CD = 0.23 for Heated Kang, and CD = 0.35 for semi-gasifier stove), in comparison of much higher  
202 CD values (> 0.5) between different stoves. The main difference between the profiles for Heated Kang  
203 and semi-gasifier were aromatic hydrocarbons especially benzene and toluene.

204 *Insert Figure S3*

205 *Insert Table S1 & S3*

206

207 For burning of coal fuels, two more characteristic fractions were ethanol and dichlorobenzene  
208 (including three isomers) were seen in their VOC profiles. Moreover, their proportions of halogen  
209 containing compounds were obviously higher than those for woody fuels. This phenomenon was also  
210 observed in previous studies (Chagger et al., 1999; Liu et al., 2017), attributed to the rich chlorine  
211 content in coals (Vassilev et al., 2000; Yudovich and Ketris, 2006). In addition, the woody fuels burning  
212 emitted large proportion of alkenes (mainly propylene) while coals combustion emitted more C<sub>11</sub>-C<sub>12</sub>  
213 alkanes (i.e., dodecane and undecane). And dodecane is even the most abundant VOC from the four  
214 coals combustion (shown in Table 2). It must be noted that CD values of bitumite-SG (abbreviated for  
215 semi-gasifier) vs. branch-SG/firewood-SG (0.46/0.47) are lower than anthracite-SG vs.  
216 branch-SG/firewood-SG (0.58/0.61), indicating VOCs emissions from bitumite are more similar to  
217 those of woody fuels than anthracite. The same result was also reported in Wang et al. (2014) in which  
218 EFs of VOCs had good correlations with calorific value and volatile matters (VM) of fuels. And in our  
219 study, the VM of anthracite, bitumite and firewood were 6.12%, 33.20% and 82.96% (shown in Table  
220 S4), and the calorific values of bitumite and firewood were close as well.

221

222 *Insert Table S4*

223

224 Among the coal fuels, anthracite in coal stove and honeycomb in cook stove showed the highest  
225 similarity (CD=0.32) because the honeycomb briquette used in this study is made of anthracite mixed  
226 with some additive. Similar to the woody fuels, coal combustions with semi-gasifier stove favored  
227 aromatic hydrocarbon productions. However, semi-gasifier stove emitted less halogen-containing  
228 compounds than traditional coal stoves. The differences between combustion styles could affect the  
229 distribution of chlorine in solid and vapor phases (Westberg et al., 2003).

230 For the residue group (Fig.S3c), high CD values for the four characteristic fractions were shown  
231 between the woody fuels emission. However, their emissions of halogen-containing compounds were  
232 much similar with those for coal fuels because both of biomass residue and coal fuels are rich in  
233 chlorine (Baxter, 2005). Table S3 also indicated that more similar VOCs profiles could be obtained  
234 with the same types of stove (CD=0.52 & 0.45) than the cross-stoves (CD=0.71~0.84) even though  
235 different solid fuels were used. The VOCs profiles for the traditional cooking stove and semi-gasifier  
236 had low CD values (0.44 & 0.49) as they were both operated at oxygen-rich burning mode. This can be  
237 further supported the fact that the VOCs profiles could be affected by both fuel types, stoves and



238 burning modes. High variations can be observed for the same fuels and stoves if different burning  
239 modes (heating or cooking) were applied.

### 240 3.3 Ozone Formation Potentials

241 Many VOCs are well known O<sub>3</sub> precursors in the atmosphere (Ho et al., 2013; Wang et al., 2017).  
242 To assess the photochemical reactivity of VOCs from the solid fuels burning, two methods were  
243 applied to evaluate the contributions of individual VOCs to O<sub>3</sub> production. The first one is maximum  
244 incremental reactivity (MIR) method (Carter, 2009), which is expressed as:

$$245 \text{OFP} = [\text{VOC}_i] \times \text{MIR}_i \quad (2)$$

246 where OFP is the ozone formation potential, and VOC<sub>i</sub> and MIR<sub>i</sub> is the concentration and its maximum  
247 incremental reactivity of individual VOC<sub>i</sub>. Another method is propene-equivalent (Prop-Equiv)  
248 concentrations (Atkinson and Arey, 2003), which is calculated as:

$$249 \text{Prop-Equiv}_i = [\text{VOC}]_i \times K_{\text{OH},i} / K_{\text{OH,propene}} \quad (3)$$

250 where K<sub>OH,i</sub> and K<sub>OH,propene</sub> are the rate constant of NMHCs react with OH at 298 K (cm<sup>3</sup> molecule<sup>-1</sup>  
251 s<sup>-1</sup>).

252 The average and standard error values of OFPs and Prop-Equivalents are given in Figure 1a and 1b.,  
253 respectively. The total OFP for solid biomass fuels are higher than those for coal fuels. The highest of  
254 total OFP of 5914.8 mg kg<sup>-1</sup> was seen for firewood with Heated Kang. Among those burning activities  
255 with Heated Kang, alkenes are the major contributors which formed at an oxygen-deficient combustion  
256 condition. Higher OFP contributions from aromatic hydrocarbons were seen for the semi-gasifier due  
257 to their higher abundances. Alkanes contributed less to the total OFP for most fuels except anthracite  
258 due to their relatively low MIR values even though the concentrations of propene and 1,3-butadiene  
259 were high (Duan et al., 2008). For the calculated Prop-Equiv (Figure 1b), the contributions from each  
260 organic group were similar with the results of OFP. An obvious difference is that alkanes weighted in  
261 higher fractions of Prop-Equiv, especially for the cooking and coal fuels emissions. Even though  
262 alkanes have relatively high K<sub>OH</sub> values (William P. L. Carter, 2012), their reactivity towards the  
263 formation of O<sub>3</sub> through photochemical reactions are comparatively less significant. As a result, there  
264 might be reasonably over-estimated contributions of alkanes to the O<sub>3</sub> formation by Prop-Equiv  
265 method.

266

267 *Insert Figure 1a and 1b*

268

269 The total OFP were generally lower for coal burning than biomass burning. The lowest OFP of  
270 50.3±19.6 mg kg<sup>-1</sup> was seen for honeycomb-CS (abbreviated for coal stove). Traditional coal stove, due  
271 to its low operation temperature and moderate combustion conditions, has the lowest OFP among the  
272 tests, which were two orders of magnitude lower than those for the woody fuels. Aromatic  
273 hydrocarbons contributed the majority of total OFP (~50%) with the coal stoves. Compared with the  
274 biomass fuels, OFP of the non-classified organic group, namely as “others”, were much lower for the  
275 coal burning, that is consistent with the results obtained in Liu et al. (2008). Bitumite is a mix of high  
276 VM fuels, while its burning can lead the formation of VOCs with the highest OFP among the four types  
277 of coal fuels. Besides of fuel features, the semi-gasifier also contributed in the high OFP for





278 bitumite-SG. The OFP of anthracite-SG ( $616.1 \pm 139.7 \text{ mg kg}^{-1}$ ) was eight times higher than that of  
279 anthracite-CS ( $87.5 \pm 3.3 \text{ mg kg}^{-1}$ ) when anthracite was applied for both fuel tests ( $p < 0.05$ ). No  
280 statistical difference ( $p > 0.1$ ) between OFP for firewood-SG ( $5743.3 \pm 208.9 \text{ mg kg}^{-1}$ ) and  
281 firewood-HK ( $5914.8 \pm 1340.5 \text{ mg kg}^{-1}$ ) was seen, demonstrating that semi-gasifier could not suppress  
282 the potential  $\text{O}_3$  formations in comparison of Heated Kang. Our results could be further concluded that  
283 the semi-gasifier stove is not efficient in decreases of both VOCs emissions and OFP even though it  
284 showed the feasibility in PM reduction (Shen et al., 2013; Sun et al., 2017).

285 An evaluation of  $\text{O}_3$  contribution from solid fuel burning in Guanzhong Basin was conducted  
286 and all parameters and results were shown in Table S5. The calculation method was shown in Tie et al.  
287 (2015) and Niu et al. (2016). We complicated the box model and atmospheric capacity methods, and  
288 applied the hypothesis that the atmosphere would update every 24 h due to wind speed (Sun et al., 2017;  
289 Tie et al., 2015). From Table S5, the emission rate of OFP from biomass fuels ( $7.17 \times 10^4 \text{ kg day}^{-1}$ ) was  
290  $\sim 5$  times higher than that of coal fuels ( $1.55 \times 10^4 \text{ kg day}^{-1}$ ), provided that the annual consumptions of  
291 two types of fuels were in the same level. In addition, based on the calculations, we estimated that the  
292 contribution of solid fuel burning to the  $\text{O}_3$  production in Guanzhong Basin in winter of 2013 was  $\sim 20\%$   
293 (OFP emission rate /  $\text{O}_3$  atmospheric capacity). The value was much higher than that estimated with  
294 source apportionment approach with  $\text{PM}_{2.5}$  of 7.6% (Huang et al., 2014). Similar phenomenon was seen  
295 in other regions of China. For instance, biomass burning contributed 6.7% to  $\text{PM}_{2.5}$  (Huang et al., 2014)  
296 but 17.7% to VOCs (Yuan et al., 2010) in Guangzhou, and for Shanghai, these two fractions were 4.8%  
297 (Huang et al., 2014) and 9.0% (Cai et al., 2010), respectively. The above discussion could conclude that  
298 solid fuel burning contributed more in VOCs emissions than PM productions in atmospheric  
299 environment.

300 As the sample number in this study was limited, using the EFs of VOCs in study to evaluate the  
301 regional contribution of  $\text{O}_3$  from solid fuel burning could lead to very high uncertainties. However, in  
302 our previous study, the box model could output a comparable result when simulating the primary  $\text{PM}_{2.5}$   
303 contributions in Guanzhong Plain from solid fuel burning (Sun et al., 2017). Besides, the biggest source  
304 of uncertainties in box model was from the fuel consumption. Total solid fuel consumption in this  
305 model was evaluated according to relative studies and statistical data from local government. There  
306 might be huge gap between our evaluated fuel consumption and the real fuel used. However, the  
307 simulated data also had referential meanings to local  $\text{O}_3$  source identification. Moreover, a detailed  
308 activities investigation about solid fuel use in Guanzhong Plain was necessary in future study.

309

310

*Insert Table S5*

311

### 312 3.4 Secondary Organic Aerosol Formation Potential

313 It has been widely known that VOCs are crucial precursors for secondary organic aerosols (SOA)  
314 formation (Ho et al., 2017; Iinuma et al., 2010). The contributions of photochemical reactivity of VOCs  
315 from solid fuel burning to SOA formation was thus estimated as well. Firstly, we adopted a  
316 Toluene-Equivalent method to calculate the SOA formation potential (SOAP) of VOCs as (Derwent et  
317 al., 2010):



$$SOAP_i = \frac{\text{Increment in SOA mass concentration with species}_i}{\text{Increment in SOA with toluene}} \times 100 \quad (4)$$

318  
319 where SOAPs are expressed as an index relative to toluene equal to 100. Toluene was chosen as the  
320 base compound for the SOAP scale because its emissions are well characterized and it is widely  
321 recognized as an important human-made precursor to SOA formation (Hu et al., 2008; Kleindienst et al.,  
322 2007). Secondly, to have a direct evaluation of VOCs to SOA, we converted the Toluene-Equivalent  
323 SOAP into mass-based values according to a toluene gas-to-particle chamber test results under a high  
324 nitrogen oxide (NO<sub>x</sub>) condition and low temperature (Johnson et al., 2004). The case was chosen  
325 because the simulation conditions were similar with those in Guanzhong Basin in wintertime. Under  
326 such conditions, the final gas-to-particle ratio was calculated as 0.045 for toluene (Johnson et al., 2004).  
327 The Toluene-Equivalent SOAPs and the gas-to-particle converted SOAP were shown in Figure 2.

328

329

*Insert Figure 2a and 2b*

330

331 Overall, aromatic hydrocarbons is the dominated group for the estimated Toluene-Equivalent  
332 SOAP due to higher photo-oxidation reactivity than those of alkane and alkenes, especially for the  
333 more volatile ones participated in gas-to-particle reactions (Johnson et al., 2004). Followed by aromatic  
334 hydrocarbons, alkane was the second largest contributor in Toluene-Equivalent SOAP that could be  
335 explained by the relatively high photo-oxidation reactivity for long chain alkanes (Derwent et al., 2010).  
336 Since alkenes and oxygenated VOCs (grouped as "Others") are generally inactive in photo-oxidation  
337 reactions, their contributions to SOAP were low. Similar observation was seen on the gas-to-particle  
338 transferred SOAP (Figure 2b) with lower conversion values.

339 For biomass fuels, the Toluene-Equivalent SOAPs ranged from 242.6±32.2 to 1013.6±66.6 mg  
340 kg<sup>-1</sup>, with the highest and lowest SOAP found for firewood-SG and branch-TS, respectively. Different  
341 from the results of OFP, the SOAP from semi-gasifier emissions were at least double (p<0.05) of those  
342 from Heated Kang when the same fuel was used. Alkane was the second largest contributor with  
343 semi-gasifier and cooking stoves but its contribution was lower than alkene with Heated Kang. The  
344 SOAPs of the group of "Others" were negligible as they were 1-2 orders of magnitude lower than the  
345 major groups (p<0.05). The average SOAPs were much lower for coal than biomass fuels. The lowest  
346 SOAP of 11.0±4.2 mg kg<sup>-1</sup> was observed for honeycomb-CS, and the highest was seen for bitumite-SG  
347 of 364.6±99.2 mg·kg<sup>-1</sup>, which was even lower than the average value for the biomass burning although  
348 the difference was not so significant (p>0.05). As discussed above, the long chain alkanes and aromatic  
349 hydrocarbons are dominated VOCs in the coal burning emissions which occupied the majority of  
350 SOAPs. The fractions of alkenes and other group were obviously lower than those of biomass burning  
351 (p<0.05). The mass-based SOAPs ranged from 0.5±0.2 to 45.6±3.0 mg kg<sup>-1</sup>. Compared with the data in  
352 previous studies, the SOAPs were about 1,000 times lower than the EFs of primary PM<sub>2.5</sub> (Shen et al.,  
353 2015; Sun et al., 2017).

354 To evaluate the SOA contribution from solid fuel burning in Guanzhong Basin, a rough  
355 calculation was done and all parameters and results were shown in Table S6. As shown in Figure S6,  
356 the emission rate of SOAP from biomass fuels burning (386.85 kg day<sup>-1</sup>) was at the same level as coal  
357 burning (410.00 kg day<sup>-1</sup>). The contribution of solid fuel burning to SOA in Guanzhong Basin was



358 estimated to be 0.23%, which was much lower than that obtained with PM<sub>2.5</sub> source apportionment  
359 method of 7.6% (Huang et al., 2014). Hence, the contribution of VOCs to SOA was not comparable to  
360 the primary PM<sub>2.5</sub>. Hence, the VOCs emission from solid fuel burning was more significantly impacted  
361 on the O<sub>3</sub> pollution in Guanzhong atmosphere. Uncertainties about SOA contribution evaluation was  
362 similar to that in O<sub>3</sub> evaluation.

363

364

*Insert Table S6*

365

#### 366 **4. Conclusion**

367 Residential solid fuel burning for cooking and space heating are common in rural Guanzhong Plain,  
368 China. Eight types of widely used solid fuels and three kinds of stoves were selected in this study to  
369 detect the VOCs emission profiles and their potentials influence on ozone and SOA formation. VOCs  
370 samples were collected on site using a custom-made dilution system set directly on the chimney of each  
371 stove. Results of VOCs EFs illustrated that biomass residues burning emitted the highest VOCs with  
372 EFs of 1811.4±833.5 - 3121.3±1592.4 mg·kg<sup>-1</sup>, followed by fuel woods (1122.2±178.9 - 2502.8±726.4  
373 mg·kg<sup>-1</sup>), and coals (47.2±19.4 - 996.8±476.9 mg·kg<sup>-1</sup>). Alkanes and aromatic hydrocarbons were the  
374 most abundant two categories in VOCs emitted from coal burning. While for residues and fuel woods  
375 burning, alkenes and carbonyls also contributed considerable proportions to the total VOCs other than  
376 alkanes and aromatic hydrocarbons. Semi-gasifier was proved to be ineffective in decreasing total  
377 VOCs emissions for residues and woods burning when compared to traditional stoves, and it even  
378 emitted 10 times higher VOCs when using coal as fuels. CD value between VOCs profiles from the  
379 same stove was lower than that from different stoves using the same fuel, and this indicated that  
380 collecting VOCs profiles by stove types were useful in sources inventory making. Simplified box  
381 model results indicated that solid fuel burning related VOCs in Guanzhong plain contributed ~20% to  
382 regional O<sub>3</sub> formation, which is much higher than its contribution to SOA formation (only 0.23%).  
383 Therefore, controlling of VOCs emission from residential solid fuel burning could provide an effective  
384 approach to decrease O<sub>3</sub> levels in Guanzhong Plain, China.

385

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- 532



533 **Figure Legends**

534 **Figure 1** EFs of MIR-OFP (a) and propane-equivalent (b) emitted from residential heating and cooking  
535 activities

536 **Figure 2** EFs of SOAP (Toluene-equivalent) (a) and SOAP (Gas to Particle transfer rate) (b) emitted  
537 from residential heating and cooking activities

538

539 **Supporting Information (SI)**

540 (1) SI1: Raw data of manuscript. (2) SI2: Detailed information on results and discussions: Table S1-S6

541 and Figure S1-S3.

542



543  
 544

Table 1 EFs of eight classes of VOCs emitted from residential heating and cooking activities

	Wood heating			Residue heating			Coal heating			Cooking	
	Heated Kang	Firewood	Semi-gasifier stove	Maize straw	Wheat straw	Traditional coal stove	Honey-comb	Anthracite	Bitumite	Old fashioned stove	Corn cob
Alkanes	711.8±204. <sub>2</sub>	518.5±61	715.6±265.1	637.8±29 9.6	409.1±22 0.5	35.3±11.1	20.6±11.6	227.9±131.5	449.8±293. <sub>6</sub>	331.8±91	811.7±744
Alkenes	515.5±140. <sub>9</sub>	321.4±71.9	259.4±108.8	405.4±14 6.4	30±14.2	2.9±1	1.1±0.5	14.9±7.1	65.9±33.6	59±12.2	145.9±161. <sub>3</sub>
Aromatic hydrocarbons	404.2±24.7	410.6±119. <sub>4</sub>	1141.9±261.5	317±224. <sub>1</sub>	355.3±14 7.5	12.5±1.8	11.3±3.4	181±39.5	382.6±126. <sub>2</sub>	264.4±36.8	1118.2±540. <sub>2</sub>
Carbonyls	712.1±121. <sub>3</sub>	516.5±59.8	258.8±39.6	679±150. <sub>4</sub>	525.1±25 2.6	5.9±1.5	2.9±1.4	47.8±22.2	19±3.4	196.1±9.3	640.3±61.4
Alcohols	0.7±0	0.5±0.2	8.8±8.9	104.9±36.6 4	20.4±3.6 7	6.2±2.1	1.7±0.1	30.8±11.7	19.7±2.4	61.3±14.1	32.7±3.5
Esters	6.7±0.7	5.7±1.3	9.2±5.7	13.5±5.7	6.5±3.5	2.7±0.3	1.5±0.5	9.5±3.6	6.7±0.9	25.1±2.5	31.4±7.6
Halogen-containing compounds	45.3±5.3	40.4±12.1	102.3±31.2	116.2±28.2 2	93.2±23. 5.3	11.7±1.6	7.9±1.9	65.7±23.4	50.3±14.7	173.1±12	321.1±73.3
Others	29.3±3.1	16.3±4.3	6.9±5.7	5.8±4.5	15.7±8.1	0.7±0.2	0.2±0.1	17.3±8.7	2.8±2.2	11.3±1	20±1.1
Total	2425.7±500. <sub>2</sub>	1830±330.1	2502.8±726.4	2175.1±8 58.9	1811.4±8 33.5	77.9±19.6	47.2±19.4	594.9±247.7	996.8±476. <sub>9</sub>	1122.2±178.9	3121.3±159. <sub>2,4</sub>

545





546 Table 2 Contributions of the top ten VOC to the EFs in each test

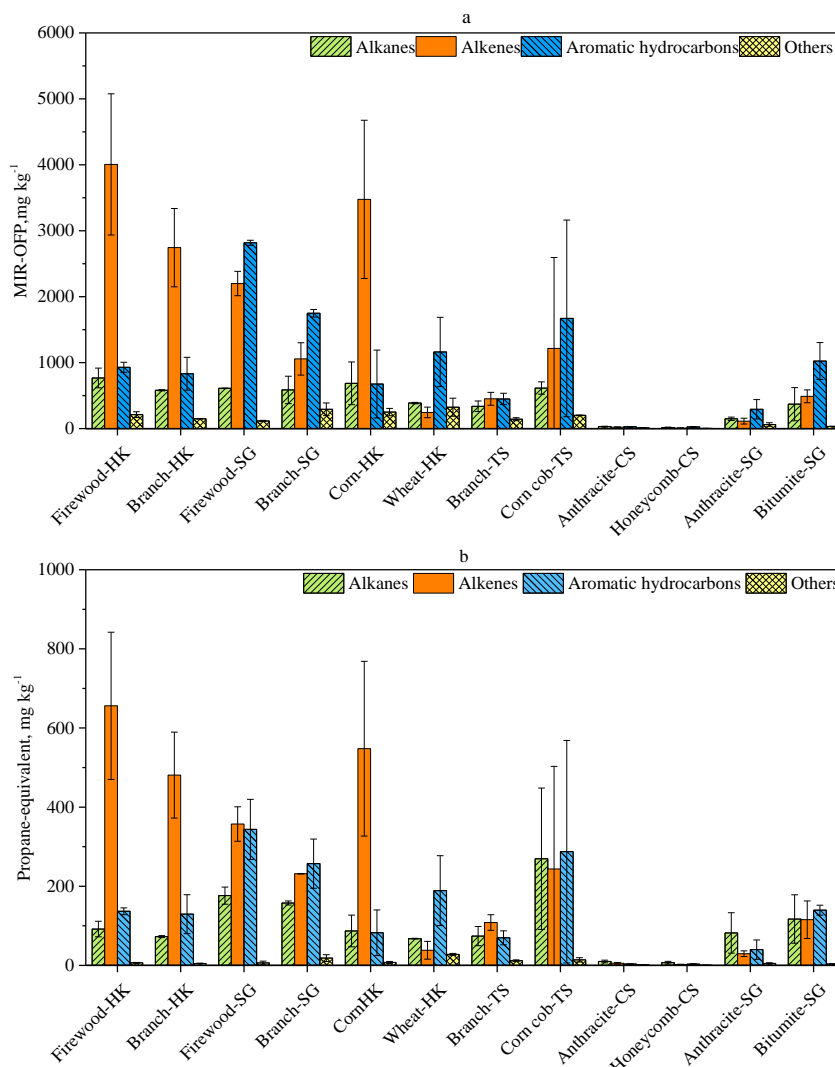
Firewood-HK	EFs	Branch-HK	EFs	Firewood-SG	EFs	Branch-SG	EFs
iso-Pentane	14.8%	iso-Pentane	13.5%	Benzene	16.5%	Benzene	17.1%
Acetone	14.5%	Acetone	13.2%	Toluene	11.0%	Acetone	10.6%
Propylene	12.1%	Benzene	10.3%	Acetone	6.6%	iso-Pentane	7.4%
Methyl ethyl ketone	7.4%	Propylene	10.2%	Propylene	6.5%	Naphthalene	6.1%
Acrolein	7.0%	Methyl ethyl ketone	8.1%	Dodecane	6.2%	Toluene	5.3%
Propane	6.9%	Acrolein	5.9%	iso-Pentane	4.4%	Dodecane	5.0%
Benzene	6.8%	Toluene	5.8%	Naphthalene	4.2%	Acrolein	4.9%
Toluene	4.3%	Propane	5.5%	Propane	4.2%	Ethanol	4.3%
1,3-Butadiene	2.4%	1,3-Butadiene	2.4%	p-Xylene	2.5%	Methyl ethyl ketone	3.3%
1-Butene	2.0%	2-Methylpentane	2.2%	m-Xylene	2.5%	Propane	2.7%
Maize-HK	EFs	Wheat-HK	EFs	Branch-TS	EFs	Comcob-TS	EFs
Acetone	17.5%	Acetone	13.2%	Benzene	10.6%	Benzene	14.4%
iso-Pentane	15.6%	Methyl ethyl ketone	8.1%	Acetone	8.4%	Dodecane	11.6%
Propylene	12.5%	iso-Pentane	7.3%	iso-Pentane	8.2%	Naphthalene	8.6%
Methyl ethyl ketone	8.8%	Chloromethane	5.3%	Dodecane	5.6%	Acetone	7.3%
Benzene	6.4%	Acrolein	5.0%	Ethanol	5.1%	Acrolein	7.1%
Propane	6.3%	Ethanol	4.9%	Acrolein	4.1%	iso-Pentane	5.7%
Toluene	4.7%	Toluene	4.6%	Toluene	4.0%	Methyl ethyl ketone	4.9%
Acrolein	4.4%	Benzene	3.8%	Methyl ethyl ketone	4.0%	Toluene	4.5%
1-Butene	2.0%	1,3-Butadiene	3.5%	n-Butane	3.7%	1,4-Dichlorobenzene	4.2%
Chloromethane	2.0%	Propane	3.4%	Naphthalene	3.4%	1,3-Butadiene	2.8%
Anthracite-CS	EFs	Honeycomb-CS	EFs	Anthracite-SG	EFs	Bitumate-SG	EFs
Dodecane	17.1%	Dodecane	21.3%	Dodecane	21.2%	Benzene	12.1%
n-Butane	9.5%	n-Butane	7.9%	Naphthalene	15.2%	Dodecane	10.5%
Ethanol	7.6%	Naphthalene	6.6%	Acetone	5.5%	Toluene	8.4%
iso-Pentane	6.5%	Benzene	5.9%	Ethanol	5.0%	n-Butane	7.8%



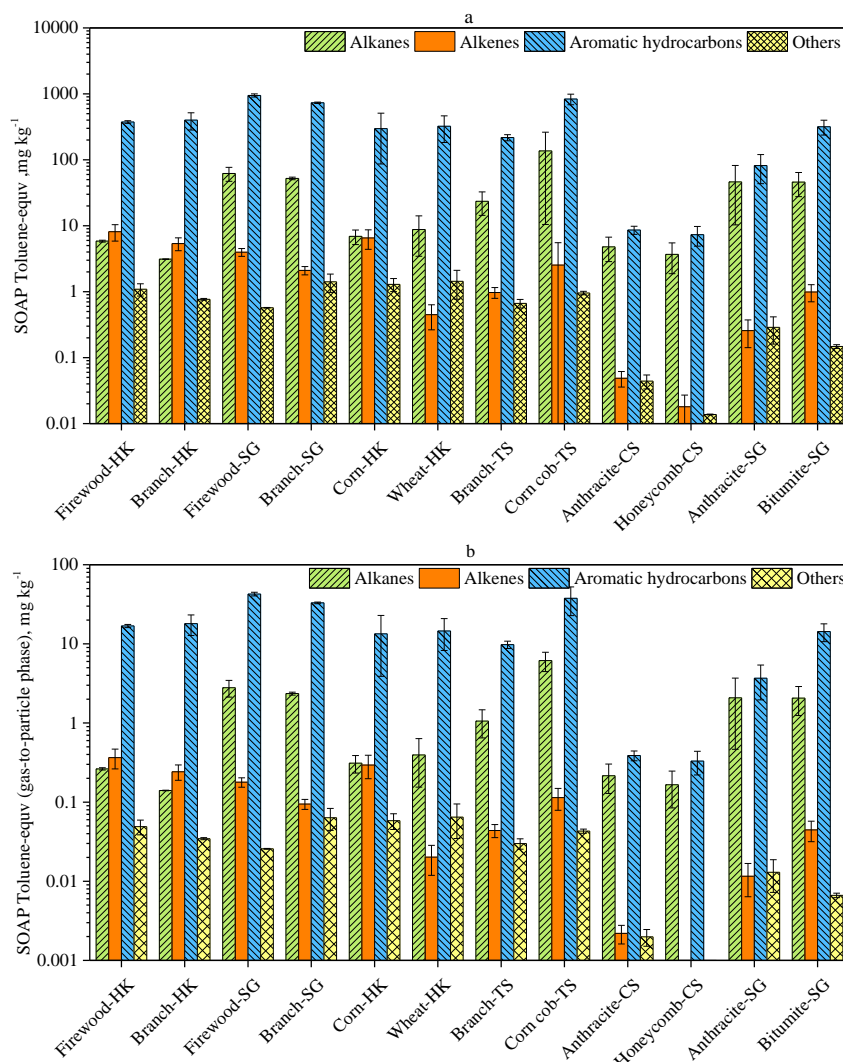
Benzene	4.3%	1,4-Dichlorobenzene	4.3%	Benzene	4.6%	Undecane	5.3%
Naphthalene	3.8%	Toluene	3.7%	n-Butane	3.7%	Isobutane	5.3%
Methyl ethyl ketone	3.5%	Ethanol	3.3%	Toluene	3.6%	Naphthalene	4.7%
1,4-Dichlorobenzene	3.1%	Methyl ethyl ketone	2.9%	1,4-Dichlorobenzene	2.7%	Propane	3.9%
Toluene	3.1%	1,3-Dichlorobenzene	2.8%	Isobutane	2.4%	iso-Pentane	2.6%
Acetone	2.6%	Ethyl Acetate	2.4%	Undecane	2.1%	n-Pentane	2.2%

\*Top ten species were selected according to majority of results. The cumulative frequency of top ten species was over 60%, which were sufficiently representative to each test.

547  
 548  
 549



**Figure 1.** EFs of MIR-OFP (a) and propane-equivalent (b) emitted from residential heating and cooking activities



**Figure 2** EFs of SOAP (Toluene-equivalent) (a) and SOAP (Gas to Particle transfer rate) (b) emitted from residential heating and cooking activities