

1 **Cancer Risk from Gaseous Carbonyl Compounds in Indoor Environment Generated from**
2 **Household Coal Combustion in Xuanwei, China**

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Abstract

Airborne carbonyls were characterized from emitted indoor coal combustion. Samples were collected in Xuanwei (Yunnan Province), a region in China with a high rate of lung cancer. Eleven of 19 samples (58%) demonstrated formaldehyde concentrations higher than the World Health Organization exposure limit. Different positive significant correlations between glyoxal/methylglyoxal and formaldehyde/acetaldehyde concentrations were observed, suggesting possible different sources characteristics. A sample in highest inhalation risk shows 29.2 times higher risk than the lowest sample, suggesting different coal types could contribute to the variation of inhalation risk. Inhabitants in Xuanwei also tend to spend more time cooking, and more days per year indoors than the national average. The calculated cancer risk ranged from $2.2-63 \times 10^{-5}$, which is within acceptable risk levels. However, cumulative effect in combination with different carbonyls could have contributed to the additive actual inhalation cancer risk. There is a need to explicitly address the health effects of low and environmentally relevant doses, considering life-long exposure in indoor dwellings.

Keywords:

Carbonyl, Indoor Air, Coal, Cancer Risk

49 **1. Introduction**

50 Coal is a major energy source. Coal combustion accounts for ~25% energy consumption
51 worldwide (Zhang et al. 2008) and the trend for coal utilization is continuing to increase (i.e.
52 annual growth of 2-3%) (Energy Information Administration 2006). China is a large energy
53 consumer and over 75% electricity supply comes from coal combustion (Liu et al. 2008). The
54 country is facing severe carbonaceous aerosol pollution (~ 70% due to coal combustion) (Cooke
55 et al. 1999) and suffering from deteriorated environmental quality.

56 Xuan Wei County is located in the Yunnan Province of China with population approximately 1.2
57 million living in an area of 6,257 km². The county is one of the major coal producing region in
58 Yunnan and renowned for exceptionally high lung cancer rate (i.e. 2004-05 lung cancer mortality
59 rate: Xuan Wei; 91 per 100,000, national average; 31 per 100,000) (Lin et al. 2015). Past studies
60 linked lung cancer mortality with coal combustion emissions in the area (Barone-Adesi et al.
61 2012; Kim et al. 2014; Mumford et al. 1993). The relevant coal burning studies usually
62 concentrated on characterizing polycyclic aromatic hydrocarbons (PAHs), mineralogical
63 compositions, household fire pit for the emissions and etc. (Chuang et al. 1992; Dai et al. 2008;
64 Mumford et al. 1995; Tian et al. 2008). However, the role of carbonyl compounds in the coal
65 smoke has been largely overlooked.

66 Airborne carbonyls (aldehydes and ketones) have been the attention of atmospheric scientists
67 over the past few decades. Carbonyl compounds are identified with natural and anthropogenic
68 sources. The compounds can further be produced via primary and secondary source formation
69 such as incomplete combustion of fossil fuels and biomass, industrial emission, vehicular
70 exhaust and photochemical oxidation of atmospheric hydrocarbons (Atkinson 2000; Carlier et al.

71 1986; Grosjean et al. 2002; Kean et al. 2001; Lee et al. 1997; Perry and Gee 1995; Yokelson et
72 al. 1999). The lifetimes of airborne carbonyls are short in troposphere (De Smedt et al. 2008;
73 Wert et al. 2003) but nevertheless are able to undergo rapid photolysis and generate significant
74 amount of free radicals and precursors responsible for air pollution (e.g. Secondary organic
75 aerosol (SOA) and ozone (O₃) formation) (Carter 1994). Several carbonyl compounds are widely
76 accepted as toxic air contaminants and contain potential carcinogenic and mutagenic properties
77 (CEPA 1993; McLaughlin 1994; NCR 1981; Pal et al. 2008; Seco et al. 2007; WHO 2000).

78 Formaldehyde is a human carcinogen (Group 1) (IARC, 2006) and poses nasopharyngeal cancer
79 (IARC 2004). Repeated occupational exposure to formaldehyde in chemical factory could
80 increase opportunities of having health implication such as congestion in cornea, nasal
81 membrane and pharynx (Zhang 1999). Acetaldehyde is a suspected human carcinogen (Báez et
82 al. 2003; Zhang et al. 1994).

83 Indoor carbonyls concentrations is of a concern as people spend over 80% lifetime at indoor
84 environment (Klepeis et al. 2001). Cooking and heating often involve with impure solid fuels
85 usage in underprivileged areas (e.g. Xuan Wei) in China. The combustion processes in household
86 coal stoves usually generate gaseous pollutants (e.g. formaldehyde, CO, CO₂, NO_x and volatile
87 organic compounds (VOCs)) that are subject to indoor air pollution (Zhang and Smith 1999).
88 The present study deduces possible associations between exposure to indoor coal carbonyls
89 emissions and excess lung cancer risks at Xuan Wei, where in agony of abnormal lung cancer
90 mortality rate in many years.

91 The aim of this study is to: 1) characterize gaseous phase carbonyl compounds from nineteen
92 types of coal used in Xuanwei; 2) determine and characterize relationships between carbonyl

93 compounds; 3) estimate the potential health implications of interior coal emissions for local
94 inhabitants.

95

96 **2. Materials and Methods**

97 2.1 Experimental Procedures

98 2.1.1 Indoor Environmental Conditions Mimic “Pre-1990” Kitchen Design

99 Nineteen types of coal were tested for emissions. The samples were labeled 1-19 and were
100 collected from different locations as noticed in Table 1. The samples collected from different
101 coal seams were denoted in brackets (Table 1). Sample 7 and 8 were classified without coal
102 seams as the samples were re-processed from coal lumps collected from the surface in the
103 communities. Sample 10 and 12 were collected from different coal mines. The coal combustion
104 experiment was conducted between November 2012 and January 2013, in a separate kitchen area
105 opposite a one story building in a village called Shangzuosuo (Xuanwei). All doors and windows
106 in the living room were closed during the experiment. The volume of the kitchen was $\sim 42.6 \text{ m}^3$
107 (5.9 m long \times 3.8 m wide \times 1.9 m high). The air exchange rate in the kitchen was continuously
108 monitored by measuring the first-order decay of carbon dioxide using a Q-Trak™ indoor air
109 quality monitor (model 8550; TSI, Inc., Shoreview, MN, USA). The air change rate was set as
110 6.9 h^{-1} .

111

112 2.1.2 Preparation of Fuels

113 A laboratory stove (internal diameter of 15 cm; shown in Figure S1 of Supplementary Material)
114 was used to simulate a fire pit for routine daily burning of coal. Larger coal pieces were sieved to

115 retain only samples <5 cm in diameter, to facilitate combustion performance. The stove mass
116 (~7 kg) and coal masses sampled (0.8 ± 0.7 to 1.6 ± 0.1 kg) were monitored throughout the
117 experiment. The coal masses were a random factor and epitomized the usual mass range used for
118 domestic cooking activities.

119

120 2.1.3 Burning Cycle

121 Nineteen types of coal samples were used in the combustion tests to collect air particulate
122 samples. Analysis of samples of each type of coal was done in triplicate. The fire was set and
123 kindling was ensured. The air was then purged through a stove inlet to provide oxygen for
124 combustion and a chimney was installed over the stove to optimize the chimney effect. When
125 full kindling had occurred (~5 min after initial ignition), ~2 kg of the coal sample was
126 immediately added to the stove. After 10 min from initial ignition, the remainder of the coal
127 sample was used to fill up the stove. The stove was immediately positioned above the burning
128 coal and remained in place until completion of the experiment. The weight of the stove and coal
129 samples were recorded. All biomass materials were completely removed outdoors, prior to
130 setting the fire. A water pot containing 2 kg of water at room temperature was placed above the
131 stove. Coal lumps could melt and coagulate during combustion, which could extinguish the fire.
132 To simulate cooking in the best possible manner, the fire was stoked and poked at the beginning
133 and at 20 min intervals during the combustion cycle to assure favorable air ventilation through
134 the coal lumps. Additional coal was added to the stove at 20 min intervals, and the weights were
135 recorded throughout the cycle. The water was heated to a boil during the heating process. The
136 complete heating process required 30–60 min depending on the different types of coal
137 (Supplementary Materials: Table S1). The remaining ashes were weighed after each combustion

138 cycle. The combustion cycle was on par with household coal burning activity in Xuanwei (~1 h).
139 The fire was either re-used (for another burning cycle with the same type of coal) or extinguished
140 using a water sprayer. The weight of the coal and water was recorded at 10 min intervals during
141 the experiment.

142

143 2.2 Samples Collection

144 The air samples were collected in silica cartridges impregnated with acidified 2,4-
145 dinitrophenylhydrazine (DNPH) (Sep-Pak DNPH-silica, 55–105 μm particle size, 125 \AA pore
146 size; Waters Corporation, Milford, MA) at a flow rate of 0.7 L min^{-1} using an ATEC 8000
147 cartridge sampler. Collection efficiencies were confirmed in the field by sampling carbonyls in
148 two identical cartridges connected in series. Efficiencies were calculated as 100% $(1 - A_b/A_f)$, in
149 which A_f and A_b denote the amount of carbonyls collected in the front and back sampling tubes,
150 respectively. No breakthrough was observed in the sampling flow rate and time used. The
151 sampling flow rates were checked in the field at the start and end of each sampling period using a
152 calibrated flow meter (Gilibrator Calibrator; Gilian Instruments, W. Caldwell, NJ). A Teflon filter
153 assembly (Whatman, Clifton, NJ) and ozone scrubber were connected to the front of the DNPH-
154 silica cartridge to remove any particulate matter and prevent possible contamination by ozone
155 (Spaulding et al. 1999). Collocated samples were collected to testify sample collection
156 reproducibility (>95%) in the field. A cartridge was reserved for field blank analysis during each
157 sampling campaign and was handled in the same manner as the other sampling cartridges. The
158 amount of carbonyls detected in the cartridges was corrected for the field blank before
159 conversion to air concentration of carbonyl units. The DNPH-coated cartridges were stored in a
160 refrigerator ($<4^\circ\text{C}$) prior to analysis.

161

162 2.3 Carbonyls Analysis

163 A total of 19 carbonyls were quantified, including formaldehyde (C1), acetaldehyde (C2),
164 acetone (acetone), propionaldehyde (nC3), methyl ethyl ketone (MEK),
165 butyraldehyde/isobutyraldehyde (iso+nC4), benzaldehyde (benz), isovaleraldehyde (iso-C5),
166 valeraldehyde (nC5), *o*-tolualdehyde (*o*-tol), *m*-tolualdehyde (*m*-tol), *p*-tolualdehyde (*p*-tol),
167 hexaldehyde (C6), and 2,5-dimethylbenzaldehyde (2,5-DB), heptaldehyde (C7), octaldehyde
168 (C8), nonaldehyde (C9), glyoxal (gly) and methylglyoxal (mgly). Unsaturated carbonyls such as
169 acrolein and crotonaldehyde were detected but not reported because of their low abundances.
170 Unsaturated carbonyl DNP-hydrazones can react with excess reagent to form adducts, leading to
171 ambiguities in quantification due to chromatographic interferences (e.g., double peaks) and
172 response factor issues (Ho et al. 2011; Schulte-Ladbeck et al. 2001). In-house laboratory
173 experiments demonstrated that collection efficiencies were $>93\pm 5\%$ for all target carbonyls
174 under the same flow rate, relative humidity, and temperature. Collection efficiencies for heavy
175 carbonyl compounds (e.g., C6) were recorded to be $>96\pm 3\%$. Each DNPH-coated cartridge was
176 eluted with 2.0 mL acetone-free acetonitrile solution (HPLC/GCMS grade, J&K Scientific Ltd.,
177 Ontario, Canada) and transferred to a volumetric flask. Previous studies demonstrated that
178 neither DNPH nor DNPH derivatives remained in the cartridge after elution with 2.0 mL
179 acetone-free acetonitrile solution (Ho et al. 2007). Certified calibration standards for
180 monocarbonyl DNP-hydrazones were purchased from Supelco (Bellefonte, PA) and diluted to a
181 concentration range of 15–3000 $\mu\text{g mL}^{-1}$. The calibration solutions were allowed to rest at room
182 temperature for six hours for complete derivatization. The final volume of each calibration
183 solution was filled up to 2.0 mL with acetonitrile/pyridine (HPLC/GCMS grade, Sigma) at a

184 concentration ratio of 8:2 (v/v). The calibration curve was linearized, and the correlation of
185 determination (r^2) was >0.999. The calibration standards and cartridge extracts were analyzed by
186 injecting 20 μL of the solution into a high-pressure liquid chromatography (HPLC) system
187 (Series 1200; Agilent Technology, Santa Clara, CA) coupled with a photodiode array detector
188 (DAD). A reversed-phase separation column (4.6×250 mm Spheri-5 ODS $5 \mu\text{m}$ C-18,
189 PerkinElmer, Norwalk, CT) was installed in the HPLC system and operated at room temperature
190 (25°C). The mobile phase consisted of three solvent mixtures: mixture A, 6:3:1 (v/v) of
191 water/acetonitrile/tetrahydrofuran; mixture B, 4:6 (v/v) of water/acetonitrile; and mixture C,
192 acetonitrile. The gradient program was operated first at (80% A)/(20% B) for one minute, second
193 at a linear gradient of (50% A)/(50% B) for eight minutes, third at (100% B) for ten minutes,
194 fourth (100% C) for six minutes, and finally at (100% C) for five minutes. The elution rate was
195 2.0 mL min^{-1} . The absorbance of the 360 and 390 nm wavelengths was applied to identify
196 aliphatic and aromatic carbonyls (e.g., benzaldehyde and tolualdehyde), respectively.
197 Identification and quantification of carbonyl compounds were based on retention time and peak
198 area integration of different carbonyl compounds. The minimum detection limit (MDL) was
199 estimated by analyzing a minimum of seven replicates of standard solution containing analyte at
200 a concentration of $0.015 \mu\text{g mL}^{-1}$. The following equation was used to estimate the MDL:

$$201 \quad \text{MDL} = t_{(n-1, 1-\infty=99\%)} \times S \quad (1)$$

202 where $t_{(n-1, 1-\infty=99\%)}$ is the student's t-distribution value at $n-1$ degrees of freedom and S is the
203 standard deviation of the replicates. The MDLs of the target carbonyls range from 0.002 to 0.010
204 $\text{ng } \mu\text{L}^{-1}$, which can be translated to 0.016–0.12 ppbv at a sampling volume of 2.02 m^3 . Measured
205 values, precision, accuracy, and validity were optimized throughout the measurements. Quality
206 assurance was performed to ensure the above attributes were within acceptable limits. A quality

207 control procedure was included to assure a measurement precision of 0.5–3.2% for the measured
208 carbonyls.

209

210 2.4 Exposure Assessment and Risk Characterization

211 Residents living in the area are potential receptors of airborne carbonyls. Cancer risk due to
212 exposure to gaseous phase carbonyls was estimated by considering direct inhalation exposure of
213 inhabitants in indoor environment according to the human health evaluation manual
214 supplemental guidance for inhalation risk assessment (Part F) (U.S.EPA 2011). The cancer risk
215 (CR) of carbonyl compounds can be calculated by the following equations:

$$216 \quad \text{CR} = \text{slope factor} \times \text{LADD} \quad (2)$$

$$217 \quad \text{LADD} = \frac{\text{C} \times \text{IR} \times \text{AF} \times \text{EF}}{\text{BW} \times \text{AT} \times \text{CV}} \quad (3)$$

218 where, LADD ($\text{mg kg}^{-1}\text{day}^{-1}$) is the lifetime average daily dose, C (mg m^{-3}) is the pollutant
219 concentration, IR is the average inhalation rate ($\text{m}^3 \text{hr}^{-1}$). AF (%) is the absorption fraction
220 (assume 100% absorption) (Cheng et al. 2015). EF is the exposure factor and determined by
221 average duration in indoor (hours day^{-1}), average indoor exposure frequency (days) and average
222 life expectancy (years). BW is the average body weight (kg). AT (days) is the average exposure
223 duration for carcinogenic/non-carcinogenic effects. An estimated average exposure duration of
224 25,550 days (70 years) for carcinogenic effect is applied for the calculation, respectively
225 (Hoddinott and Lee 2000). CV is a conversion factor (from μg to mg). The IR, EF and BW were
226 calculated based on the information given in the Chinese exposure factors handbook and the
227 average duration in indoor was assumed based on time-activity patterns of cooking status at
228 kitchens in a relevant study at China (Duan 2015; Jiang and Bell 2008) . In China, population in
229 various locations (e.g., inland versus coastal) have different economic conditions, dietary habits

230 and living styles, thus location and region is an exposure condition that cannot be ignored.
231 Further information can be referred to Table 2. The slope factor in equation (2) is determined by
232 reference dose (RFD, ((mg kg⁻¹day⁻¹)⁻¹)) for all carbonyl compounds according to the Integrated
233 Risk Information System (U.S.EPA 2015). Only formaldehyde (slope factor = 0.021 (mg
234 kg⁻¹day⁻¹)⁻¹) and acetaldehyde (slope factor = 0.01 (mg kg⁻¹day⁻¹)⁻¹) are considered as
235 carcinogenic substances and therefore provided with slope factors in all measured carbonyl
236 compounds. The CR value in a range of 1–100×10⁻⁶ is deemed in either acceptable (10⁻⁶) or
237 tolerable (10⁻⁴) level for regulatory purposes (Hu et al. 2012).

238

239 2.5 Statistical Analysis

240 All the data were analyzed using SPSS statistic 21.0 (IBM ®, New York, NY) or GraphPad
241 Prism software (Version 5 for Windows).

242

243 3. Results and Discussion

244 3.1.1 Concentrations of Carbonyl Compounds

245 Table 1 shows the total and individual concentrations of carbonyls compounds in different coal
246 samples. The formaldehyde concentrations are in a range of 10.4±5.9–502.6±148.8 µg m⁻³.
247 Concentrations for the acetaldehyde range from 17.0±5.9 to 195.4±40.0 µg m⁻³. According to the
248 World Health Organization (WHO) guideline for indoor formaldehyde is a 30-min average of
249 100 µg m⁻³ (WHO 2010). A total of 19 samples were analyzed: 11 (58%) demonstrated
250 formaldehyde concentrations higher than the exposure limit. A previous study showed

251 formaldehyde concentrations ranged from 240 to 600 $\mu\text{g m}^{-3}$ in an indoor cigarettes combustion
252 experiment (Grimaldi et al. 1996). Typical indoor formaldehyde and acetaldehyde concentrations
253 could be in a range of 10-50 and 5-20 $\mu\text{g m}^{-3}$, respectively (Sarigiannis et al. 2011). The
254 concentration levels in present study are akin to the combustion experiment. Formaldehyde is the
255 most abundant compound in sample 1-7, 9-12 and 16 accounting for 21–45% of the total
256 measured carbonyls. Acetaldehyde is nevertheless the most abundant compound in sample 8, 13-
257 15 and 17-19 accounting for 16–33% of the total measured carbonyls. The results are consistent
258 with formaldehyde and acetaldehyde as the dominant components in a barbecue charcoal
259 combustion study, and also indicates concentration patterns of these carbonyls could be
260 associated with inhomogeneous nature of the combustion raw materials (observed high standard
261 deviation of concentrations in some of the sub-samples) (Kabir et al. 2010). A residential coal
262 combustion study in China also demonstrated formaldehyde and acetaldehyde were the most
263 abundant carbonyls in 5 types of coal (Feng et al. 2010). A study compared carbonyls emissions
264 using different fuels in diesel engine showed aldehyde emissions were formed by incomplete
265 oxidation of hydrocarbons. The formaldehyde was most abundant compound and accounted for
266 over 40%, and the next abundant acetaldehyde ranged from 10 to 30% in composition, which
267 have similar composition characteristics with present study (He et al. 2009). According to the
268 U.S. Environmental Protection Agency (EPA), both formaldehyde and acetaldehyde are
269 classified as Group B1 and B2 probable human carcinogens, respectively. The results in this
270 study show a large proportion of potentially carcinogenic carbonyls in emissions, indicating that
271 control is required.

272 Figure 1 shows correlations between the log-transformed concentrations of formaldehyde and
273 acetaldehyde, glyoxal and methylglyoxal. Both shows positive significant correlations ($p < 0.05$),

274 however, only glyoxal and methylglyoxal demonstrates correlation coefficient > 0.80 ($n = 60$).
275 The linear relationship between log-transformed concentrations of individual glyoxal and
276 methylglyoxal suggests quantitative dependence of the glyoxal on methylglyoxal, which also
277 implies the two compounds are from the same source regardless of sample locations and types.
278 The regression analysis shows variation of glyoxal and methylglyoxal concentrations depend on
279 the same combustion conditions (e.g. moisture content, amount of oxygen supply, temperature
280 and etc.). A lower correlation coefficient >0.40 ($n = 60$) is found between log-transformed
281 concentrations of individual formaldehyde and acetaldehyde. Carbonyl compounds could exist as
282 reaction products from reactions of primary emitted pollutants with ozone. Secondary production
283 of formaldehyde could be sufficient to affect indoor air concentrations. (Knudsen et al. 2003;
284 Nazaroff and Weschler 2004; Uhde and Salthammer 2007). A past study showed relative
285 humidity could affect the formaldehyde emissions (Parthasarathy et al. 2011). These could be
286 possibly altering the formaldehyde concentrations and hence the concentration ratios.
287 Nonetheless, the limitation in the correlations is that how individual combustion parameters (e.g.
288 temperature) correlate to the concentrations cannot be determined due to insufficient combustion
289 condition information.

290 The concentration ratios ($C1/C2$) further shows 60% samples are formaldehyde emissions
291 dominant over acetaldehyde emissions (>1). The average concentration ratios are in a range of
292 0.1-3.7. The $C1/C2$ ratio is a common tool for characterizing pollution sources (Hedberg et al.
293 2002), the present trend may reflect a variety of contributing factors (e.g. temperature, relative
294 humidity, different coal types, combustion conditions and sampling procedures), rather than
295 taking account into individual factors alone, could all play different roles altogether in the overall
296 variable outcome.

297 Strong contribution of original biogenic compounds in the lignite within early stage of coal
298 formation could ultimately increase the coal rank (Meyer et al. 2014; Püttmann and Schaefer
299 1990). A previous study suggested coal combustion process could be divided into three stages:
300 initial stage (moisture evaporation and chemical absorption), combustion stage and burnout
301 stage-which were classified based on weight and heat changes. Thermogravimetric and
302 differential thermal analysis showed low-rank coals could influence ignition temperatures,
303 whereas high-rank coals influenced the burnout temperature (Moon et al. 2013).

304 Future studies should be concentrating on characterizing the coal materials (maturity) and
305 different stages of carbonyls emissions such as using Proton-Transfer-Reaction Mass-
306 Spectrometry (PTR-MS). This technique enables real-time monitoring and is able to
307 instantaneously detect and quantify the emissions, leading to a more thorough understanding
308 about the combustion processes.

309

310 3.1.2 Carbonyls Emissions from Various Emission Sources

311 Many studies targeted characterizing carbonyls emissions under different emission
312 circumstances. A residential fireplace wood combustion study showed aliphatic aldehydes were
313 major contributors to the gas-phase emissions from wood combustion. Acetaldehyde was emitted
314 at highest rate among all carbonyls and the formaldehyde was at the second highest (Schauer et
315 al. 2001). Another residential wood (softwood and hardwood) combustion emissions study
316 suggested formaldehyde and acetaldehyde were the most abundant lower molecular weight
317 carbonyl compounds arising primarily from the combustion of cellulose (McDonald et al. 2000).

318 A previous study collected samples in two residential kitchens during cooking period (used
319 towngas and liquefied petroleum gas). The formaldehyde concentrations were 60.4 and 151.0 $\mu\text{g m}^{-3}$.
320 Concentrations for the acetaldehyde were 65.9 and 4.5 $\mu\text{g m}^{-3}$, respectively (Huang et al.
321 2011). A study measured formaldehyde and acetaldehyde levels in Paris dwellings from
322 potentially different sources in 61 flats with no previous history of complaint for olfactory
323 nuisance or specific symptoms. The result showed average formaldehyde and acetaldehyde
324 concentrations (n = 61) in the kitchen were 21.7 ± 1.9 and $10.1 \pm 1.8 \mu\text{g m}^{-3}$ (Clarisse et al. 2003).
325 A past study targeted domestic levels of formaldehyde in kitchens in 185 homes at Perth,
326 Australia with mean concentration of $25.9 \mu\text{g m}^{-3}$. The result did not exceed the recommended
327 Australian guideline due to good inter-room mixing of formaldehyde within homes (Dingle and
328 Franklin 2002). A similar study measured formaldehyde concentrations in 399 home's kitchen at
329 Ankara in Turkey showed average formaldehyde concentration was $74.9 \pm 3.7 \mu\text{g m}^{-3}$ (Vaizoğlu
330 et al. 2003).

331 A study targeted different indoor areas at France (e.g. Railway station, airport, shopping center,
332 libraries and underground parking garage). The formaldehyde and acetaldehyde concentrations
333 ranged from 7.0-63.9 and 1.6-28.6 $\mu\text{g m}^{-3}$, respectively. Mean indoor concentrations (living
334 room and bedroom) of formaldehyde and acetaldehyde in 16 homes were in a range of
335 18.1 ± 17.5 - $46.1 \pm 27.3 \mu\text{g m}^{-3}$ (Marchand et al. 2006). A study measured residences (71 homes)
336 indoor concentrations of formaldehyde and acetaldehyde in Saskatchewan, Canada. The result
337 suggested in both summer and winter the formaldehyde and acetaldehyde concentrations was in
338 a range of 10.7 ± 6.4 - $36.9 \pm 18.6 \mu\text{g m}^{-3}$ (Héroux et al. 2010) All of the above findings suggest the
339 usual indoor concentrations of formaldehyde and acetaldehyde were below $100 \mu\text{g m}^{-3}$, whereas
340 a sample in present study showed formaldehyde concentrations from the coal emissions could be

341 up to ~5 times, and several samples are at least ~2-3 times higher than the $100 \mu\text{g m}^{-3}$ level.
342 The present study suggests residential coal combustion at Xuanwei could emit higher
343 formaldehyde concentrations than ordinary indoor levels as mentioned.

344

345 3.2 Health Risk of Carbonyl Compounds via Inhalation Exposure

346 3.2.1 Lifetime Excess Inhalation Cancer Risk

347 Inhalation exposure is typically the primary route of direct exposure to airborne carbonyls.
348 Figure 2 shows the estimated lifetime excess inhalation cancer risk (CR) per million people due
349 to carbonyls exposure in the kitchen at Xuanwei, Yunnan Province. The non-dietary exposure in
350 this study is defined as human exposure to gaseous carbonyls via household air. Total cancer risk
351 value $>10^{-4}$ is considered to be at high risk in common regulatory programs (Chen and Liao
352 2006). Under the same carbonyls exposure condition (as in Table 1), the mean estimated excess
353 inhalation cancer risk associated with the exposure is in a range of 22-629 cancer cases per
354 million people ($\sim 2.2\text{-}63 \times 10^{-5}$) in the kitchen area at Yunnan. Formaldehyde dominated over
355 acetaldehyde and contributed an average of ~67% of the total risk in all samples. Sample in
356 highest inhalation risk shows ~29.2 times higher risk than the lowest sample, suggesting
357 different coal types could contribute to the variation of inhalation risk. Under the same set of
358 PAC emissions, the inhabitants of Yunnan show ~3.61 times higher risk compared to the
359 national average due to different exposure conditions (Table 2) (Duan 2015; Jiang and Bell
360 2008) . All of the above results show the inhalation cancer risk is within acceptable (10^{-6}) or
361 tolerable (10^{-4}) level. The carbonyls levels in the kitchen could be an important reference to other
362 living areas in the house especially during winter as all the house windows are usually fastened

363 with limited ventilation, in addition, inhabitants at Xuanwei spend an average of >75% of their
364 time per day at indoors (Duan 2015). Although individual carbonyls do not demonstrate any risk
365 under the current exposure levels, cumulative effect in combination with different carbonyls
366 might have contributed to the actual inhalation cancer risk outcome in additive manner. The
367 above findings suggest there is a need to revise the current risk assessment in order to explicitly
368 address the health effects of low and environmentally relevant doses (e.g. absent of carcinogenic
369 risk information except for formaldehyde and acetaldehyde, cancer potency factors in more than
370 binary mixtures), considering the case of life-long exposure in indoor dwellings.

371

372 3.2.2 Limitation and Uncertainty Discussion

373 Many of the studies on household indoor air pollution have concentrated only on indoor air
374 concentrations without considering personal exposure factors (Clark et al. 2013). The present
375 cancer risk calculation is an attempt to use relevant and accessible information, as the exposure
376 factor is specifically catered for Yunnan province and only recently launched (Duan 2015).
377 However, the present CR calculation is not without uncertainties. A closer approximation of the
378 actual risks could be produced if a range of weights, inhalation rates, ages and sex specific for
379 Xuanwei inhabitants were available for the calculations. Moreover, insufficient characterization
380 of the sampling households, for example, the number of windows and number of stoves in each
381 household, as well as seasonal variation, could have affected the final cancer risk outcome.
382 Furthermore, the limitation of slope factors and reference doses of several targeted carbonyls
383 could have caused a significant under representation of the actual total risk for the analysis.
384 Additional studies should focus on quantifying and harmonizing these uncertainties (e.g., using

385 personal air monitoring devices to collect personal exposure data in Xuanwei households) to
386 improve future cancer risk analyses.

387

388 **4. Conclusions**

389 The characteristics of airborne carbonyls emitted during indoor coal combustion in Xuanwei
390 were investigated. This was 58% samples contained higher formaldehyde concentrations higher
391 than the World Health Organization exposure limit. Positive correlations were identified in a
392 statistical regression analysis, showing possible different sources characteristics. The lifetime
393 excess cancer risk from inhalation of gaseous carbonyls suggests that the risk in each sample was
394 within tolerable level. Acceptability of the risk depends on scientific data, social, economic and
395 political factors on the perceived benefits arising from exposure to an agent.

396 These findings support claims that household coal combustion is associated with human health
397 conditions. The results suggest there is a need to revise the current risk assessment in order to
398 explicitly address the health effects of low and environmentally relevant doses.

399

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405

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598 Figure 2 Excess cancer risk associated with inhalation of selected carbonyls in coal
599 emissions.

600 Table 1 Descriptive Analysis and Relative Abundances of Carbonyls Concentrations*

| Sampling Location | C1 | C2 | acetone | nC3 | MEK | iso+nC4 | benz | iso-C5 | nC5 | o-tol | m-tol | p-tol | C6 | 2,5-DB | C7 | C8 | C9 | gly | mgly | Total Carbonyls |
|-------------------|-------------------|-------------|------------|-----------|-----------|----------|-----------|-----------|-------------------|-----------|-----------|-----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|-----------------|
| | µg/m ³ | | | | | | | | | | | | | | | | | | | |
| 1 (Huchang) | 305.1±311.3 | 162.0±115.9 | 71.1±43.2 | 27.5±19.5 | 43.1±26.8 | 15.0±7.1 | 88.6±62.5 | 20.2±11.2 | 20.2±12.7 | 16.9±11.4 | 46.5±32.5 | 19.4±13.6 | 23.5±19.1 | 15.4±14.1 | 15.0±9.2 | 11.6±7.5 | 15.0±8.4 | 18.3±17.1 | 12.3±11.3 | 946.7±636.3 |
| 2 (Wenxing) | 286.3±210.6 | 93.7±53.9 | 41.6±8.3 | 13.0±5.2 | 20.8±8.0 | 6.7±2.4 | 64.0±48.9 | 9.3±0.8 | 9.7±2.7 | 10.6±5.1 | 39.4±27.7 | 12.9±7.1 | 12.4±6.3 | 7.9±1.3 | 10.5±6.1 | 10.0±4.3 | 16.3±3.1 | 18.6±6.3 | 13.2±5.4 | 697.1±410.0 |
| 3 (Dongshan) | 201.9±161.5 | 130.4±59.5 | 60.4±23.5 | 25.4±5.6 | 43.1±13.0 | 14.7±3.8 | 70.9±40.9 | 27.8±3.8 | 32.8±8.5 | 18.1±4.4 | 40.2±13.1 | 18.1±5.5 | 19.4±5.0 | 12.8±3.3 | 17.2±8.0 | 16.0±3.7 | 20.6±7.1 | 7.9±4.5 | 8.0±5.2 | 785.7±360.2 |
| 4 (Tianba) | 124.8±67.1 | 114.6±12.6 | 81.8±4.0 | 21.8±2.1 | 40.3±1.9 | 12.2±0.7 | 48.7±4.1 | 18.2±1.8 | 17.0±2.0 | 10.5±3.2 | 26.7±4.8 | 10.6±2.2 | 13.8±3.5 | 8.4±1.7 | 12.6±4.9 | 16.3±4.1 | 19.1±6.7 | 5.8±1.4 | 4.7±1.7 | 607.9±98.5 |
| 5 (Dongshan) | 69.9±54.8 | 50.8±41.8 | 32.8±17.2 | 9.0±6.4 | 18.9±12.5 | 6.3±3.0 | 27.7±19.9 | 8.0±3.2 | 6.1±1.9 | 2.9±3.0 | 10.8±8.3 | 4.0±3.5 | 7.3±3.4 | 5.1±1.7 | B.D. | 7.8±0.7 | 10.3±1.8 | 3.0±1.3 | 2.3±1.2 | 283.3±184.1 |
| 6 (Jiubao) | 423.0±208.5 | 167.1±62.5 | 54.7±20.5 | 25.5±12.2 | 34.8±16.1 | 14.8±5.8 | 72.4±21.2 | 14.5±6.4 | 14.7±6.7 | 12.4±6.9 | 37.8±22.4 | 10.3±4.2 | 18.1±5.8 | 6.8±3.8 | B.D. | 14.1±2.9 | 15.3±2.8 | 9.3±5.3 | 8.6±4.4 | 954.1±405.9 |
| 7 (Yefei) | 502.6±148.8 | 195.4±40.0 | 72.5±26.6 | 30.9±5.5 | 39.9±9.7 | 18.4±5.3 | 87.1±26.7 | 20.2±9.2 | 22.2±12.3 | 18.5±3.1 | 46.2±9.1 | 17.9±2.9 | 20.4±6.8 | 11.6±6.6 | 10.6±3.7 | 12.7±3.8 | 13.5±3.1 | 10.4±6.3 | 12.5±6.4 | 1,163.6±296.4 |
| 8 (Reshui) | 36.4±18.8 | 58.2±9.4 | 23.9±7.5 | 3.2±0.4 | 4.7±1.3 | 2.0±0.5 | 13.7±5.7 | 1.8±0.4 | ^a B.D. | 0.9±0.2 | 5.2±0.8 | 2.3±0.3 | 3.3±0.6 | 2.2±0.4 | B.D. | 9.4±2.0 | 5.5±0.8 | 0.8±0.4 | 1.2±0.4 | 174.8±16.5 |
| 9 (Laibin) | 269.3±128.6 | 73.1±35.0 | 38.9±17.3 | 11.9±4.7 | 21.3±11.6 | 7.3±2.9 | 39.6±15.0 | 10.7±3.4 | 9.3±2.7 | 7.7±1.2 | 23.5±8.9 | 9.2±1.5 | 13.0±5.6 | 11.5±12.1 | 8.1±2.9 | 9.7±0.9 | 16.2±1.7 | 8.3±2.9 | 8.1±3.7 | 596.6±259.4 |
| 10 (Laibin) | 250.1±399.8 | 154.7±134.9 | 82.3±37.1 | 24.8±19.8 | 47.9±32.7 | 12.1±8.2 | 79.4±87.4 | 21.1±9.0 | 15.5±8.8 | 14.3±12.9 | 40.1±40.5 | 16.4±15.7 | 21.1±18.8 | 9.1±5.2 | 13.9±6.7 | 11.0±4.8 | 18.6±5.9 | 10.2±11.0 | 9.9±11.0 | 852.7±867.8 |
| 11 (Laibin) | 155.4±117.3 | 80.2±47.6 | 59.5±29.8 | 12.5±7.1 | 32.5±17.3 | 8.3±4.5 | 52.2±39.4 | 13.2±3.6 | 10.1±4.8 | 7.1±3.6 | 23.6±14.2 | 10.2±6.3 | 13.7±6.2 | 6.7±2.1 | 14.6±4.5 | 12.0±4.2 | 15.9±2.2 | 5.2±1.0 | 4.7±2.5 | 537.5±312.1 |
| 12 (Laibin) | 122.3±20.8 | 96.5±31.8 | 74.2±25.1 | 17.7±4.6 | 38.2±8.9 | 8.9±1.9 | 41.6±6.8 | 19.0±5.6 | 13.7±2.3 | 7.8±1.4 | 22.2±4.5 | 9.2±2.2 | 13.6±3.9 | 7.3±2.1 | 16.0±9.6 | 11.8±4.3 | 19.3±3.4 | 8.2±2.3 | 6.8±2.5 | 554.3±130.0 |
| 13 (Zhaojiachong) | 39.6±55.2 | 83.8±26.4 | 92.6±39.8 | 17.0±6.9 | 46.4±21.2 | 12.1±6.5 | 42.3±17.2 | 27.2±16.2 | 17.7±11.0 | 9.7±2.9 | 23.9±10.4 | 10.1±3.5 | 11.5±7.1 | 6.9±4.2 | 13.3±8.8 | 9.8±5.7 | 16.2±8.5 | 7.1±2.7 | 5.8±3.2 | 493.0±201.5 |
| 14 (Laibin) | 12.3±4.8 | 17.0±5.9 | 17.6±4.1 | 2.4±0.7 | 4.3±0.3 | 1.6±0.3 | 5.6±0.3 | 2.3±0.6 | B.D. | B.D. | 2.1±0.3 | 1.1±0.2 | 2.7±0.1 | 1.6±0.5 | B.D. | 7.3±3.2 | 8.9±1.0 | 1.2±0.0 | 1.2±0.6 | 89.2±17.5 |
| 15 (Laibin) | 51.0±39.8 | 122.4±11.5 | 95.0±15.3 | 24.4±2.6 | 54.5±3.0 | 14.3±2.5 | 61.9±2.9 | 31.1±6.0 | 27.5±7.5 | 12.5±6.0 | 33.1±7.7 | 14.6±5.5 | 17.0±0.8 | 10.8±2.7 | 15.0±6.6 | 12.8±1.5 | 13.3±3.0 | 5.0±1.5 | 5.0±3.1 | 566.3±28.8 |
| 16 (Laibin) | 158.3±87.9 | 82.1±73.8 | 67.5±18.3 | 12.6±11.6 | 23.9±18.6 | 7.4±5.8 | 48.7±40.8 | 10.6±9.1 | 9.9±10.9 | 6.6±7.5 | 21.0±18.9 | 8.9±9.3 | 12.9±9.4 | 7.1±5.7 | 11.6±10.3 | 11.0±3.1 | 16.0±0.4 | 5.8±1.8 | 6.2±3.2 | 528.1±327.2 |
| 17 (Longchang) | 57.1±48.9 | 90.1±34.3 | 75.8±24.8 | 12.5±4.5 | 27.3±10.8 | 7.5±2.6 | 38.3±15.4 | 9.8±2.1 | 7.1±1.0 | 3.2±1.8 | 15.3±6.2 | 5.5±2.5 | 8.4±1.5 | 4.4±2.2 | 7.7±1.6 | 10.9±0.6 | 13.4±0.4 | 4.3±0.8 | 3.7±1.9 | 402.2±152.4 |
| 18 (Laibin) | 10.4±5.9 | 79.5±38.8 | 111.3±38.9 | 16.5±8.2 | 39.8±12.1 | 9.5±4.0 | 39.5±12.9 | 24.6±6.5 | 17.6±4.2 | 12.6±2.0 | 26.2±7.2 | 13.9±3.1 | 14.1±2.8 | 13.4±2.7 | 16.0±7.3 | 15.3±4.8 | 22.4±12.1 | 5.3±2.4 | 3.9±2.0 | 491.9±125.1 |
| 19 (Zhaojiachong) | 19.2±12.2 | 73.6±31.4 | 86.2±47.4 | 14.5±4.2 | 30.9±10.1 | 8.5±2.5 | 38.8±19.3 | 13.7±4.6 | 12.8±6.7 | 7.9±5.9 | 20.2±9.5 | 9.5±5.4 | 8.7±1.6 | 8.5±5.4 | 12.1±4.0 | 11.0±3.1 | 15.4±8.4 | 4.9±1.9 | 4.0±2.0 | 400.4±140.7 |

601 ^aB.D. indicates below detection limit.

602 *n = 3 for each type of coal.

603

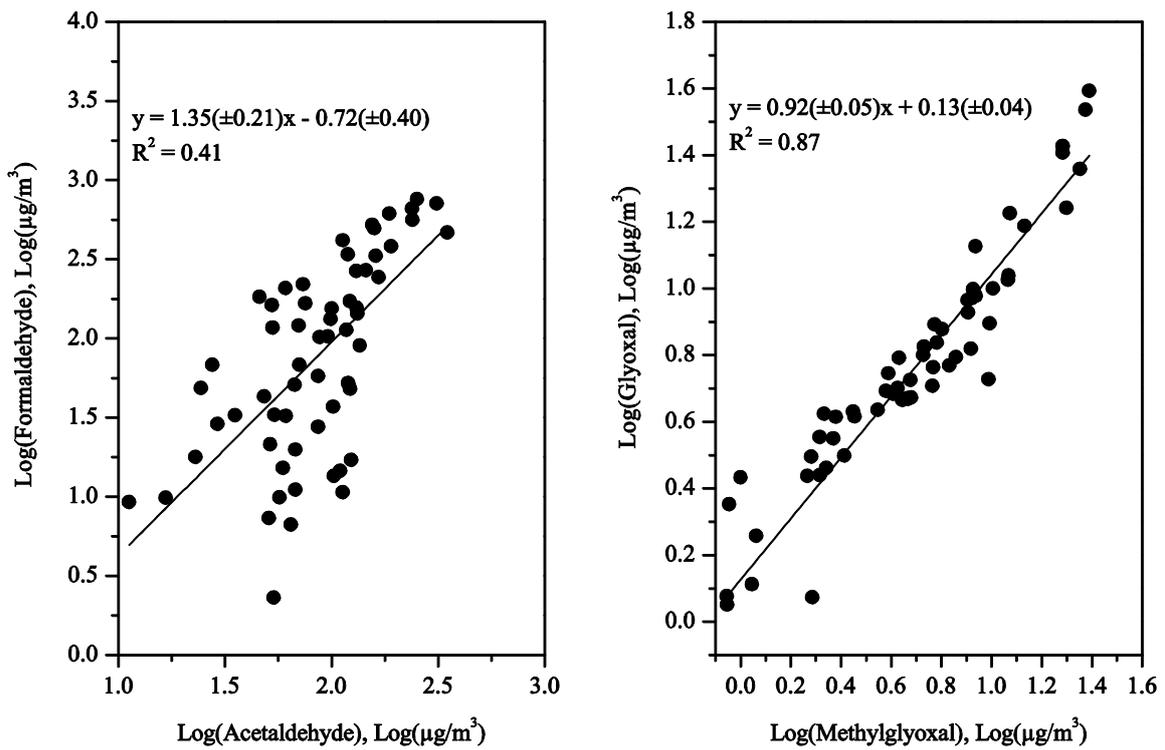
604 Table 2 Information about the Chinese Exposure Conditions

| Exposure Factors | Yunnan | National Average by Provinces |
|---|--------|-------------------------------|
| Average inhalation rate (IR) (m ³ hr ⁻¹) | 0.645 | 0.654 |
| Average duration in indoor (hrs day ⁻¹) | 5.0 | 2.0 |
| Average indoor exposure frequency (days) | 320 | 221 |
| Average life expectancy (years) | 69.54 | 74.83 |

| | | |
|---------------------------------------|-------|-------|
| Average body weight (BW) (kg) | 55.9 | 60.6 |
| Average exposure duration (AT) (days) | 25550 | 25550 |

605

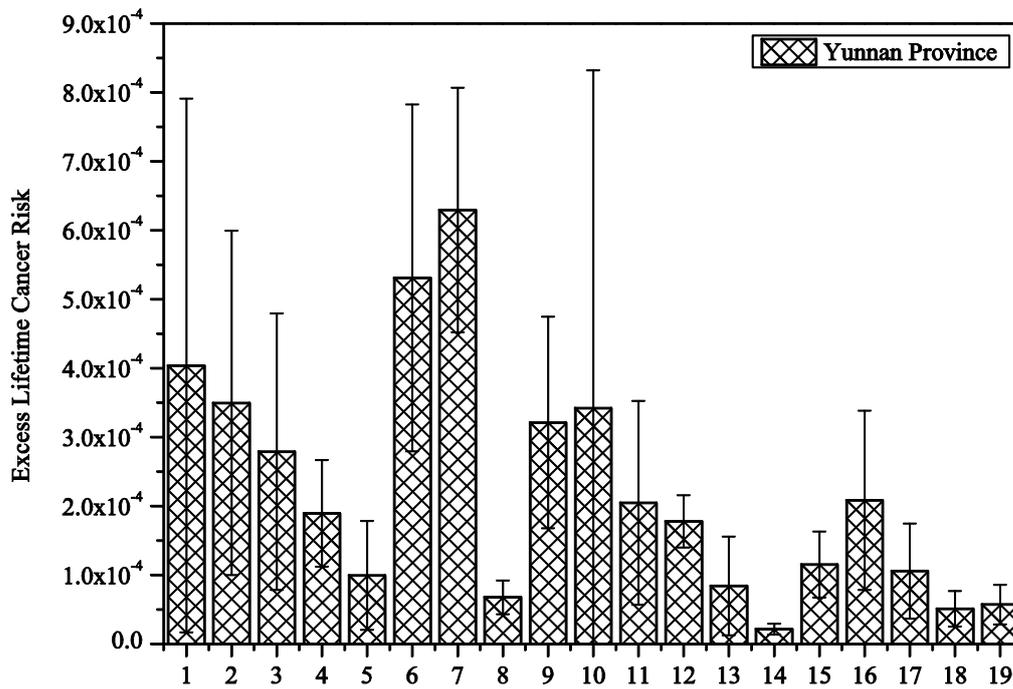
606



607

608 Figure 1 Relationships between log-transformed concentrations of Formaldehyde/
 609 Acetaldehyde and Glyoxal/Methylglyoxal. There were nineteen types of coal
 610 with 3 replicates each except one type of coal with 6 replicates ($n = 60$).
 611 Coefficients and standard errors were included in the regression equations.

612



613

614 Figure 2 Excess cancer risk associated with inhalation of selected carbonyls in coal
 615 emissions. Risk error bars represent minimum and maximum values.

616