

The oxidative potential of PM₁₀ from coal, briquettes and wood charcoal burnt in an experimental domestic stove

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Highlights:

1. Burning raw powdered coal emits more PM than burning honeycomb briquette.
2. The PM₁₀ emitted by burning honeycomb briquettes had a higher oxidative potential.
3. The water-soluble heavy metals in PM₁₀ were associated with high oxidative potential.
4. Burning raw powdered coal had a higher health risk than burning honeycomb briquette.

Abstract: Coal contains many potentially harmful trace elements. Coal combustion in unvented stoves, which is common in most parts of rural China, can release harmful emissions into the air that when inhaled cause health issues. However, few studies have dealt specifically with the toxicological mechanisms of the particulate matter (PM) released by coal and other solid fuel combustion. In this paper, PM₁₀ particles that were generated during laboratory stove combustion of raw powdered coal, clay-mixed honeycomb briquettes, and wood charcoal were analysed for morphology, trace element compositions, and toxicity as represented by oxidative DNA damage. The analyses included Field Emission Scanning Electron Microscopy (FESEM),

30 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Plasmid Scission Assay (PSA).
31 Gravimetric analysis indicated that the equivalent mass concentration of PM₁₀ emitted by
32 burning raw powdered coal was higher than that derived by burning honeycomb coal. FESEM
33 observation revealed that the coal burning-derived PM₁₀ particles were mainly soot aggregates.
34 The PSA results showed that the PM₁₀ emitted by burning honeycomb briquettes had a higher
35 oxidative capacity than that from burning raw powdered coal and wood charcoal. It is also
36 demonstrated that the oxidative capacity of the whole particle suspensions were similar to those
37 of the water soluble fractions; indicating that the DNA damage induced by coal burning-derived
38 PM₁₀ were mainly a result of the water-soluble fraction. An ICP-MS analysis revealed that the
39 amount of total analysed water-soluble elements in the PM₁₀ emitted by burning honeycomb
40 briquettes was higher than that in PM produced by burning raw powdered coal, and both were
41 higher than PM from burning wood charcoal. The total analysed water-soluble elements in
42 these coal burning-derived PM₁₀ samples had a significantly positive correlation with the level
43 of DNA damage; indicating that the oxidative capacity of the coal burning-derived PM₁₀ was
44 mainly sourced from the water soluble elements. The water-soluble As, Cd, Ge, Mn, Ni, Pb,
45 Sb, Se, Tl, and Zn showed the highest correlation with the oxidative potential, implying that
46 these elements in their water soluble states were the primary responsible factor for the plasmid
47 DNA damage. The exposure risk was further assessed using the particle mass concentrations
48 multiplied by the percent of DNA damage under the dose of 500 µg ml⁻¹. The results revealed
49 that the exposure risk of burning raw powdered coal was much higher than that of burning
50 honeycomb coal.

51 **Key words:** plasmid scission assay; inductively coupled plasma mass spectrometry (ICP-MS);
52 coal burning-derived PM₁₀; oxidative potential; water-soluble elements; exposure risk

53

54 **1. Introduction**

55 Emissions from coal combustion represent an important source of gaseous and particulate
56 pollutants in the atmosphere, and these pollutants can have a significant impact on atmospheric
57 chemistry, climate change, and human health (Dockery et al., 1993; Levine et al., 1995; Samet

58 et al., 2000; Andreae and Merlet, 2001; Kan et al., 2007, 2012; Jones et al., 2009).
59 Epidemiological investigations have demonstrated the association between exposure to
60 particulate matter (PM) and an increased incidence of mortality and morbidity from lung cancer
61 and cardiovascular diseases (Crabbe, et al., 2012; Xu et al., 2003; Hoek et al., 2013; Kheirbek,
62 et al., 2013; Shao et al., 2013). Recently, a literature review by Pui et al. (2013) demonstrated
63 that the components in PM_{2.5} from coal combustion and from vehicle emissions are the
64 dominant contributors to regional haze in China; they also demonstrated that short-term
65 exposure to PM_{2.5} is strongly associated with an increased risk of morbidity and mortality from
66 cardiovascular and respiratory diseases in China. Smoky coal used domestically indoors in
67 China is a known human carcinogen, and outdoor air containing coal-burning emissions is also
68 considered as a potential human lung carcinogen, (Loomis et al., 2013).

69 China is the largest coal producer and consumer in the world. In 2013, China produced
70 3.7 billion tons of coal and consumed approximately 3.61 billion tons of coal (China Statistical
71 Yearbook, 2013), which was equal to approximately 68% of the primary energy consumed in
72 China. Residential coal stoves are commonly used for cooking and heating, especially in the
73 winter. Approximately 25% of the coal production in China is high-sulphur coal, with a sulphur
74 content exceeding 2%, and the burning of these high-sulphur coals releases SO₂, together with
75 NO₂ and PM₁₀ into the atmosphere, resulting in atmospheric pollution (Luo, 2008; Chen et al.,
76 2009). Furthermore, coal contains many potentially harmful trace elements that may be
77 minimal on average, but can be enriched as a result of special geologic conditions (Bogdanovic
78 et al., 1995; Xu et al., 2003; Dai et al., 2003; Shao et al., 2003; Tang et al., 2004; Ren et al.,
79 2006; Li et al., 2006). During the combustion, processing, and utilization of coal, these trace
80 elements can be released into the air, causing harm to the environment and human health (Neas,
81 2000). Although we know that coal combustion can release harmful substances into the air, the
82 toxicological mechanisms of the inhaled PM released by coal-combustion is still not clear.
83 Although toxic metals are found to be associated with some types of coals (Tang et al., 2004;
84 Ren et al., 2006), it is still unclear which elements emitted during coal combustion are of most
85 concern in terms of their toxicity.

86 A number of studies have shown that atmospheric PM₁₀, in which coal-burning particles

87 dominate, is implicated in increased morbidity and mortality and can cause asthma, respiratory
88 disease, and respiratory inflammation; it can even involve the cardiovascular system, nervous
89 system, immune system and may eventually cause cancer (Zhang et al., 2003; Ostro et al. 2006;
90 Lin et al. 2007; Loomis et al., 2013). Although the biological mechanisms underlying the
91 induction of lung cancer by PM₁₀ have been examined extensively (Straif et al., 2006;
92 Benbrahim-Tallaa et al., 2012; Loomis et al., 2013), the role played in these adverse health
93 effects by coal burning-derived PM₁₀ remain unclear. A widely accepted hypothesis is that
94 oxidative damage originates from the bioreactive surface of airborne particles (Donaldson et
95 al., 1996; Li et al., 1997; Shao et al., 2007); the bioavailable transition metals on the surface of
96 airborne particles could activate oxidants that could damage DNA (Costa et al., 1997;
97 Greenwell et al., 2003; DiStefano et al., 2009; Sánchez-Pérez et al., 2009; Vidrio et al., 2009;
98 Zhong et al., 2010). Many other studies have also shown that soluble metal components
99 produce Reactive Oxygen Species (ROS), which can induce oxidative stress and inflammation
100 in the lungs and respiratory tract (See et al., 2007; Distefano et al., 2009; Vidrio et al., 2009;
101 Zhong et al., 2010). The USA Environmental Protection Agency (USEPA) defines Zn and Pb
102 as toxic elements, and Zn is regarded as a bioreactive element (Adamson et al., 2000). Other
103 studies have also indicated that Zn is likely to be a major element responsible for particle-
104 induced plasmid DNA damage (Greenwell et al., 2003; Shao et al., 2006, 2007; Lu et al., 2006).
105 Lan and co-workers (2004) demonstrated oxidative damage-related genes (e.g. *AKR1C3* and
106 *OGG1*) modulated risks for lung cancer due to exposure to PAH-rich coal combustion
107 emissions. Their human molecular epidemiology study took place in Xuan Wei County, China,
108 which had the highest lung cancer rates in China. It was demonstrated that PAHs were activated
109 to genotoxic intermediates to produce PAH metabolites that form DNA adducts or reactive
110 oxygen species (ROS) leading to oxidative DNA damage, such as 8-hydroxy-2'-
111 deoxyguanosine (8-oxo-dG).

112 Currently, many methods are employed in the toxicological study of atmospheric particles;
113 such as irrigation, the Ames test method, micronucleus experiments, chromosome aberration
114 tests, and the comet assay. However, most of these are only qualitative techniques. In recent
115 years, a plasmid DNA scission assay has been developed to study the toxicity of atmospheric

116 particulates (Li et al., 1997; Whittaker, 2003; Shao et al., 2007; Chuang et al., 2011, 2013); it
117 is a simple, rapid, high-sensitivity technique to detect DNA damage and allows for the toxicity
118 of particles to be quantified. This method has been proved to be effective in characterizing the
119 oxidative capacity of coal burning-derived particles (Wang et al., 2014). Inductively Coupled
120 Plasma Mass Spectrometry (ICP-MS) can be used to measure the levels of the water-soluble
121 trace elements responsible for the particle-induced DNA damages (Shao et al., 2006).

122 This paper evaluates the oxidative damage to plasmid DNA by PM₁₀ generated by
123 laboratory-stove combustion of different types of Chinese coal. The water-soluble trace
124 elements of PM₁₀ were examined using ICP-MS. The aim of this paper was to assess the
125 toxicity of coal burning-derived PM₁₀ and the relationship between the particle-induced
126 oxidative potential and the metal compositions of these coal burning-derived PM₁₀.

127 **2. Sampling and experiments**

128 **2.1 Combustion system and sample collection**

129 The coals that were used in these experiments were collected from a number of coal
130 mining areas, including Zhijin in Guizhou Province (ZJ), Datong in Shanxi Province (DT),
131 Dongsheng in the Inner Mongolia Autonomous Region (DS), Yinchuan in the Ningxia Hui
132 Autonomous Region (YC), and Jingxi (western Beijing mountain) in Beijing (JX). Raw, loose,
133 powdered coals were prepared from ZJ, DT, DS, YC, and JX, and the clay-mixed honeycomb
134 briquettes were prepared from ZJ and DT by a combination of 80% raw powdered coals and
135 20% clay. Wood charcoal was used as a comparison in the experiments. Information about the
136 proximate and ultimate analyses of raw powdered coals used in this study is given in Table 1.

137 We used a laboratory-made combustion system to conduct the burning experiments, which
138 were carried out at the Laboratory of the Chinese Research Academy of Environmental
139 Sciences (Geng et al., 2012). The system was composed of a combustion stove with smoke
140 dilution tunnels and smoke chambers. The coal-stove, which is used widely for domestic
141 cooking and heating in China, was purchased from the grocery market. It has a metallic outer
142 cover and thermal-insulated ceramic liner. The cylindrical inner volume is 0.01 m³. The
143 dilution tunnel consisted of two main parts made of stainless steel, including an orthogonal

144 pipe and a cylindrical tunnel, and an attached suction fan. The orthogonal pipe with a length of
145 1 m and a radius of 20 cm was connected to the stove for flue gas introduction and first-step
146 dilution with filtered air. At the end of the orthogonal pipe, a horizontal cylindrical tunnel with
147 a length of 4 m and a radius of 40 cm was connected for second-step dilution. At the end of the
148 tunnel, there were several outlets for suction fans and sampling. The flow rate of the suction
149 fan was controlled by a Venturic tube and was fixed at 5800 L/min. The residence time of flue
150 gas in the dilution tunnel was 5.5 second. After second-step dilution, the temperature of diluted
151 flue gas decreased to 30°C. The smoke chamber connected to the horizontal cylindrical tunnel
152 was used for real-time measurement of gaseous and particulate pollutant during the combustion
153 experiments. Our PM₁₀ sampler was connected to this smoke chamber. During the experiments,
154 the flow rate of the diluted flue gas into smoke chamber was fixed at 100 L/min.

155 Coal samples were ignited in the stove using pre-weighed wood charcoal (0.5 kg). To
156 minimise the influence of charcoal burning emissions, the coal samples (1.0 kg for each
157 experiment) were put into the stove until smoking from charcoal combustion stopped.
158 Sampling started when the raw coal samples were put into the stove and ended when the
159 combustion was complete, and the whole process lasted for approximately one hour. The
160 schematic diagram showing this combustion system is shown in Figure 1.

161 A medium-volume particle sampler (Dickel-80, Beijing Geological Instrument Dickel
162 Cooperation limited, China) and a MinivolTM particle sampler (Air Metric, U.S.A), which were
163 connected to the dynamic smoke chamber, were used to collect the particulate matter. Particles
164 with an aerodynamic diameter of 10 µm or less were collected. Quartz fibre filters (diameter
165 90 mm) were used in the Dickel-80 sampler (flow rate 78 L/min), and were used for the plasmid
166 scission assay and ICP-MS experiments. Polycarbonate filters (diameter 47 mm) were used in
167 the Minivol sampler (the flow rate was 5 L/min), and were used for the Field Emission
168 Scanning Electron Microscopy (FESEM).

169 **2.2 FESEM analysis**

170 A Field Emission Scanning Electron Microscope (FESEM) (JSM-6700F) was used to
171 investigate the morphology of the particles. Approximately one eighth of each polycarbonate

172 filter was cut and then mounted onto a copper washer using epoxy resin. The specimen was
173 gold-coated to a thickness of 20 nm. Secondary electron images were obtained to analyse the
174 morphology of the burning-derived PM₁₀ particles.

175 **2.3 Plasmid Scission Assay**

176 The plasmid scission assay is an *in-vitro* method for assessing and comparing the
177 oxidative potential of inhalable particles (Greenwell et al., 2003; Reche et al., 2012; Xiao et al.,
178 2013; Chuang et al., 2013; Sun et al., 2014). The assay is based on the principle that any free
179 radicals associated with particle surfaces can damage the supercoiled DNA by “nicking” the
180 strands. This damage initially causes the DNA to unwind from being supercoiled into a relaxed
181 coil. Further damage results in linearization followed by complete fragmentation. This change
182 in structure alters the electrophoretic mobility of the DNA, thereby allowing for separation and
183 quantification on an agarose gel.

184 A detailed experimental procedure has been described in Merolla and Richards (2005),
185 Shao *et al.* (2006), Reche *et al.* (2012) and Chuang et al. (2013). The PM₁₀ samples, together
186 with a procedural blank filter, were incubated in HPLC-grade water. The incubations were
187 gently agitated in a vortex mixer (Scientific Industries, Vortex Genie 2) for 20 h at room
188 temperature to ensure the maximum mixing of the PM₁₀ sample in water and to avoid
189 sedimentation. At this stage after incubation each sample was separated into two parts; one part
190 was taken to directly represent the intact whole-particle suspension, and another part was used
191 to prepare the water-soluble fraction. The water-soluble fraction of PM₁₀ sample was obtained
192 by spinning the intact whole-particle suspension in a centrifuge (D37520, Germany) at
193 13000r/min for 80 minutes. At the end of this centrifuging, the supernatant was collected using
194 a pipette; this supernatant represented the soluble fraction of the PM₁₀ samples. The plasmid
195 scission assay was used for both the intact whole-particle suspension and the centrifuged water-
196 soluble fraction of the PM₁₀ sample. Each of them was sequentially diluted into five particle
197 dosages; 25, 50, 100, 300, and 500 µg ml⁻¹ respectively. All of the dose-scaled incubations were
198 calibrated into a final volume of 20 µl, each containing 200 ng of φX174-RF DNA (Promega
199 Corporation, USA). The prepared dose-scaled incubations were gently agitated in a vortex
200 mixer for another 6 h to ensure the maximum mixing of the PM₁₀ sample with DNA. At this

201 stage, bromophenol blue dye (3.5 μ l) was added to each dose-scaled sample before injecting
202 the sample into the gel which is composed of 0.6% agarose and 0.25% ethidium bromide. Then
203 the gel carrying the injected samples was placed in a 30 V electrophoretic voltage for 16 h at
204 room temperature in a 1% tris-borate-EDTA (TBE) buffer. The electrophoresis gels were
205 photographed and a densitometric analysis was performed using the Genetools program
206 (TRANSILLUMINATOR 2020D). A semi-quantitative protocol was established that measured
207 the relative proportion of damaged DNA (relaxed and linearized) in each lane of the gel, and
208 was expressed as a percentage of the total DNA in each lane. Two replicates of each lane were
209 quantified in this way, and the means were recorded for each particle dosages. Subtracting the
210 damage caused by the negative control (HPLC-grade water), the DNA damage that was
211 induced by the airborne particles at different dosages was calculated.

212 To guarantee the accuracy of the experiment result, we analysed one procedural blank
213 quartz fibre filter. The oxidative damage to plasmid DNA induced by the blank quartz fibre
214 filter was below 10%, so it was considered that the quartz filter does not have a significant
215 influence on the experimental results. In addition, the water-soluble fraction obtained after
216 centrifuging will have had any broken quartz filter shards removed, thus avoiding any extra
217 oxidative damage.

218 **2.4 ICP-MS analysis**

219 This study used a high-resolution Inductively Coupled Plasma Mass Spectrometer (model
220 number: ELEMENT; Manufacturer: Finnigan-MAT company) for the analysis of trace
221 elements from coal burning-derived PM₁₀ with a detection limit of 1ppt~1ppb (10^{-12} ~ 10^{-9}). The
222 experiments were carried out at a laboratory in the Beijing Research Institute of Uranium
223 Geology. The procedure used was based on Shao et al. (2013). Water-soluble trace elements
224 were obtained by directly analysing the water-soluble fractions of the PM₁₀ samples that were
225 previously processed by centrifugation before the plasmid scission assay. The results were
226 reported as a concentration of the element in its soluble form in the intact PM₁₀ sample, which
227 were expressed in ppm by weight.

228 **3 Results**

229 **3.1 Mass concentration and particle morphology of the coal burning-derived PM₁₀**

230 In order to investigate the relative amounts of PM₁₀ emitted by burning different fuels, the
231 equivalent (equal amount of fuel, equal time of combustion, and equal combustion conditions)
232 mass concentration of the coal burning-derived PM₁₀ were estimated by combining the
233 sampling air volume and the loaded PM₁₀ mass in filters. The equivalent mass concentration
234 can be calculated by following formula:

$$235 \quad MC(\mu\text{g} / \text{m}^3) = \frac{M_2 - M_1}{V}$$

236 In this formula, MC represented equivalent mass concentration of the coal burning-derived
237 PM₁₀ (μg/m³), M₁ represented the mass of the quartz fibre filters before sampling (μg), M₂
238 represented the mass of the quartz fibre filters loaded with particles after sampling (μg), V
239 represented the sampling volume (m³), which was the value of sampling time multiplied by the
240 flow rate of the sampler.

241 Table 2 showed the mass concentrations of the PM₁₀ emitted by burning different coals.
242 The mass concentration of the coal burning-derived PM₁₀ varied greatly, ranging from 689
243 μg/m³ for the DT honeycomb briquette to 10694 μg/m³ for the DS raw powdered coal. The
244 mass concentrations of the PM₁₀ emitted by burning honeycomb briquette were from 689
245 μg/m³ to 1282 μg/m³, and averaged 986 μg/m³. The mass concentrations of the PM₁₀ emitted
246 by raw powdered coal were from 1436 μg/m³ to 10694 μg/m³, and averaged 5251 μg/m³. This
247 result demonstrated that the mass concentration of PM₁₀ emitted by burning raw powdered coal
248 was higher than that by burning honeycomb briquette.

249 FESEM observation revealed that the morphology types of coal burning-derived particles
250 were almost all soot aggregates, which consisted of many carbon spheres. Figure 2
251 demonstrates that the number density per unit area in the images of the PM₁₀ emitted by burning
252 honeycomb briquette was relatively small, while number density per unit area in the images of
253 the PM₁₀ emitted by burning raw powdered coal was much denser. This reconfirmed that
254 burning raw powdered coal would generate more particles than burning honeycomb briquettes.

255 **3.2 Oxidative potential of PM₁₀ generated from burning different types of coal**

256 The oxidative potential of the PM₁₀ generated by burning honeycomb briquettes, the raw
257 powdered coals, and the wood charcoal were examined with a plasmid scission assay. A total
258 of 8 types of PM₁₀ samples were used in this study and represented emissions from burning
259 raw powdered coals from ZJ, DT, DS, YC, and JX, the clay-mixed honeycomb briquettes from
260 ZJ and DT, and wood charcoal. The gel images and histograms shown in Figure 3 and Table 3
261 provide a quantitative analysis of the oxidative DNA damage induced by a whole-particle
262 suspension and a water-soluble fraction in five particle doses (25, 50, 100, 300, 500 µg ml⁻¹).
263 It can be seen that with increasing doses, the particle-induced DNA damage for all of the coal
264 burning-derived PM₁₀ types showed a general increasing trend. A positive dose-response
265 relationship exists between the amounts of DNA damages and the sample doses, which implies
266 that higher mass concentrations of PM in the ambient air could cause a higher oxidative
267 potential, and thus a higher toxicity per cubic metre of air.

268 The amount of damage to the plasmid DNA that was induced by coal burning-derived
269 PM₁₀ varied from 5% to 55%. Table 3 and Figure 3 also demonstrated that, under the same
270 dose (Table 3), the oxidative potential of both the whole-particle suspension and the water-
271 soluble fraction of the PM₁₀ followed a clear pattern. High from the ZJ and DT honeycomb
272 briquettes emissions, moderately high from the YC and ZJ powdered coals emissions, and
273 relatively low from the DT, DS, and JX powdered coals and wood charcoal emissions.

274 It was found that the oxidative potential of the PM₁₀ generated from burning honeycomb
275 briquettes was significantly higher than that generated by burning the corresponding raw
276 powdered coals. At a particle dose of 500 µg ml⁻¹, the PM₁₀ generated from burning ZJ and DT
277 honeycomb briquettes induced DNA damage of 55% and 46% by their whole-particle
278 suspension respectively, which was higher than the damage percentages of 34% and 19% from
279 their corresponding raw powdered coals.

280 Furthermore, the differences between the amount of DNA damage induced by the whole-
281 particle suspension and the corresponding water-soluble fraction of the PM₁₀ samples at all
282 dose levels were relatively small. Figure 4 shows a comparison between the amount of DNA

283 damage resulting from the whole-particle suspension and from the soluble fraction of the coal
284 burning-derived PM₁₀ at a dose of 500 µg ml⁻¹; it is clear that the differences between the
285 amount of DNA damage induced by the whole-particle suspension and by the corresponding
286 water-soluble fraction of these PM₁₀ were mostly insignificant, ranging from 4% to 30%, but
287 mostly less than 20%. The amount of damage induced by the soluble fraction can contribute
288 more than 70% to the amount of damage induced by the whole-particle suspension. This result
289 indicates that the oxidative potential of the PM₁₀ generated by coal burning-derived is mainly
290 sourced from their water-soluble components.

291 **3.3 Trace elements in the PM₁₀ emitted by burning different coals**

292 An ICP-MS was used to detect the concentration of elements in the coal burning-derived
293 PM₁₀. The elements analysed included As, Cd, Co, Cr, Cs, Cu, Ge, Mo, Mn, Ni, Pb, Sb, Se, Sr,
294 Ti, Tl, V, and Zn. The concentrations of these elements in their water-soluble fractions were
295 analysed and the results were reported in weight ppm of each element in its soluble state in the
296 original intact PM₁₀ samples (Table 4).

297 For the total analysed water-soluble elements, the PM₁₀ emitted by burning the ZJ
298 honeycomb briquette had the highest level (21480.63 ppm), followed by those emitted by
299 burning the DT honeycomb briquette (5658.73 ppm). For coal samples the values were YC
300 powdered coal (3960.71 ppm), the ZJ powdered coal (3196.05 ppm), the DT powdered coal
301 (219.28 ppm), the DS powdered coal (212.65 ppm), the JX powdered coal (201.52 ppm), and
302 the wood charcoal (140.11 ppm) in descending order. It is clear that the PM₁₀ particles emitted
303 by burning honeycomb briquettes produced a higher content of total analysed water-soluble
304 trace elements than those emitted by burning raw powdered coals, with the lowest values being
305 the PM₁₀ emitted by burning wood charcoal.

306 Table 4 also showed that the PM₁₀ emitted by burning honeycomb briquettes was enriched
307 with water-soluble elements such as As, Cd, Cu, Ge, Mn, Ni, Pb, Se, Sb, Ti, Tl, V, and Zn. All
308 of these elements were present at concentrations greater than 10 ppm, and the water-soluble
309 As, Ge, Pb, Tl, and Zn were present at levels greater than 100 ppm. For the raw powdered coals,
310 the coal burning-derived PM₁₀ was enriched with water-soluble As, Cu, Ni, Pb, Ti, and Zn;
311 these individual elements reached levels that were greater than 10 ppm.

312 **4 Discussion**

313 **4.1 Relationship between the oxidative potential and the content of water-soluble trace** 314 **elements**

315 To examine the most probable source of the oxidative potential of the coal burning PM₁₀,
316 the amounts of DNA damage were correlated with corresponding concentrations of the water-
317 soluble elements in the intact PM₁₀ samples. As the DNA damage values from all particle doses
318 showed the same trend, we only choose one dose level (500 µg ml⁻¹) for the correlation analysis.
319 The Pearson correlation coefficients are provided in Table 5, with a sample number n=8 and a
320 threshold correlation coefficient of 0.71 at 95% confidence level.

321 The particle-induced oxidative potential displayed a significant positive correlation with
322 the total analysed water-soluble metal concentrations with a Pearson correlation coefficient of
323 0.87, implying that the oxidative potential of coal burning-derived PM₁₀s was derived mainly
324 from its water-soluble elements. This finding was also supported by the fact that the whole-
325 particle suspension of these coal burning-derived PM₁₀ induced similar amounts of DNA
326 damages relative to their corresponding water-soluble fractions.

327 The correlation coefficients between the particle-induced oxidative potentials from a
328 dosage of 500 µg ml⁻¹ and the concentrations of individual water-soluble heavy metals in PM
329 (Table 5) can be used to determine which individual elements were most responsible for the
330 particle-induced oxidative potential of these coal burning-derived PM₁₀. The water-soluble As,
331 Cd, Ge, Mn, Ni, Pb, Sb, Se, Tl, and Zn exhibited relatively significant positive correlations
332 with the oxidative potential (correlation coefficients higher than 0.71), indicating that these
333 elements in their water-soluble states were likely responsible for the plasmid DNA damage.
334 Similar conclusions have been reached by other reports for PM₁₀, from Beijing (Shao et al.,
335 2006, Sun et al., 2014) and in the UK (Moreno et al., 2004; Merolla and Richards, 2005; Reche
336 et al., 2012).

337 Some previous studies (Querol et al., 2006; Liu et al., 2010) have shown that heavy metal
338 pollutants, such as Cr, Zn, Pb, and Mn, can be produced from combustion-related industry.
339 Tang and Huang (2004) and Ren et al.(2006) found that high levels of As, Se, Zn and Pb might

340 be sourced from the combustion of different types of coal, and all of these elements are
341 considered to be potentially harmful to human health. The results of this study demonstrated
342 the occurrence of Cr and Zn, and to a lesser extent Pb and Mn in coal burning-derived PM₁₀;
343 although this does depend on the geochemistry of the original coal.

344 **4.2 Possible causes of the variation in the oxidative potential of coal burning-derived PM₁₀.**

345 The PM₁₀ emitted by burning honeycomb briquettes had a higher content of total analysed
346 water-soluble trace elements and a higher oxidative potential than those emitted by burning
347 raw powdered coals. This can be attributed to the clay mixed into the briquettes, which would
348 enrich the inorganic elements in the PM₁₀, effectively being released as fly ash.

349 For the intact powdered coals, the variations in the oxidative potential could be explained
350 by the raw coal quality; especially in terms of the difference in the sulphur and ash content.
351 The higher percentages of total water-soluble trace elements and the higher oxidative potential
352 of the PM₁₀ emitted by burning ZJ powdered coal can be attributed to the higher sulphur content
353 of the raw ZJ coal (Table 1). The sulphur-rich coals of the Late Permian age from the Zhijin
354 coal mining area of southwestern China normally contain higher levels of pyritic sulphur that
355 tends to be associated with some toxic heavy metals (Ren et al., 2006). Therefore, the PM₁₀
356 emitted by burning high-sulphur coal would have higher percentages of trace elements and a
357 higher oxidative potential.

358 The PM₁₀ that was emitted by burning YC powdered coal also had higher percentages of
359 total water-soluble trace elements and a higher oxidative potential. This could have been
360 because the YC powdered coal had a higher ash content (Table 1). The high coal ash content
361 tends to be accompanied by higher levels of certain trace elements (Ren et al., 2006). This
362 finding allows us to infer that the PM₁₀ emitted by burning high-ash coals can be associated
363 with a relatively high percentage of water-soluble trace elements, thereby inducing a high
364 oxidative potential. The JX coal had high ash content but was associated with a lower PM₁₀-
365 induced oxidative potential. This is due to the lower sulphur content in the raw coal.

366 **4.3 Exposure risk of the PM₁₀ emitted by burning different coal types**

367 In order to elucidate the exposure risk to humans we devised a toxicity index to represent

368 the relative risk for people exposed to the ambient air with different types of coal burning-
369 derived PM₁₀:

$$370 \quad TI = MC \times P_{DNA}$$

371 In this formula, *TI* represents toxicity index, *MC* represents the mass concentration of the coal
372 burning-derived PM₁₀, *P_{DNA}* represented the percentage of DNA damage at the 500 µg/ml PM₁₀
373 dose. Table 6 showed that the *TI* of the PM₁₀ emitted by burning YC raw powdered coal and
374 DS raw powdered coal were much higher than that by burning other types of coals. It can also
375 been seen that the *TI* values of the PM₁₀ emitted by burning ZJ and DT honeycomb briquettes,
376 (70987 and 31754 respectively) were clearly lower than those by burning their corresponding
377 raw powdered coals (96577 and 80265 respectively). This result indicated that exposure to the
378 PM₁₀ emitted by burning raw powdered coals is associated with higher risks to human health
379 than exposure to the PM₁₀ emitted by burning honeycomb briquettes.

380 **5. Conclusion**

381 1) Burning raw powdered coal emits more PM₁₀ than burning honeycomb briquette. The
382 oxidative potential of the PM₁₀ emitted by burning honeycomb briquettes was significantly
383 higher than that by burning raw powdered coals and wood charcoal.

384 2) The PM₁₀ emitted by burning honeycomb briquettes had a higher content of total water-
385 soluble trace elements than that emitted by burning raw powdered coals and wood charcoal.
386 The PM₁₀ particles emitted by burning honeycomb briquettes were enriched with water-soluble
387 As, Ge, Pb, Tl, and Zn, and the PM₁₀ particles emitted by burning raw powdered coals was
388 enriched with water-soluble As, Cu, Ni, Pb, Ti, and Zn.

389 3) The oxidative potential of the coal burning-derived PM₁₀ was mainly sourced from
390 their water-soluble fractions. The water-soluble As, Cd, Ge, Mn, Ni, Pb, Sb, Se, Tl, and Zn
391 showed the most significant correlation with the oxidative potential, implying that these
392 elements in their water-soluble states were responsible for the particle-induced DNA damage.

393 4) The PM₁₀ emitted by burning coals with high levels of mixed clay, sulphur, and ash is
394 associated with a correspondingly high percentage of water-soluble trace elements, thereby

395 inducing a high oxidative potential.

396 5) The exposure risk to humans from the PM₁₀ emitted by burning raw powdered coal was
397 significantly higher than that from burning honeycomb briquette emissions.

398

399 **Acknowledgements**

400 This work was supported by the National Basic Research Program of China (Grant No.
401 2013CB228503) and the National Natural Science Foundation of China (Grant No. 41175109).

402 Two anonymous reviewers are thanked for their helpful comments.

403

404 **References**

- 405 Adamson I Y R, Prieditis H, Hedgecock C, Vincent R. Zinc is the toxic factor in the lung response to an
406 atmospheric particulate sample. *Toxicology and Applied Pharmacology* 2000; 166: 111–119.
- 407 Andrae M O, Merlet P. Emission of trace gases and aerosols from biomass burning. *Global Biogeochemical*
408 *Cycles* 2001; 15: 955-966.
- 409 Benbrahim-Tallaa, L., Baan, R.A., Grosse, Y., Lauby-Secretan, B., Ghissassi, F.E., Bouvard, V., Guha, N.,
410 Loomis, D., Straifa, K.. Carcinogenicity of diesel-engine and gasoline-engine exhausts and some
411 nitroarenes. *The Lancet Oncology* 2012; 13: 663-664.
- 412 Bogdanovic I, Fazinic S, Itkos S, et al.. Trace element characterization of coal fly ash particle. *Nuclear*
413 *Instrument and Methods in Physics Research B* 1995; 99: 402-405.
- 414 Geng, C., Wang, K., Wang, W., Chen, J., Liu, X., Liu, H.. Smog chamber study on the evolution of fume
415 from residential coal combustion. *Journal of Environmental Sciences* 2012; 24: 169-176.
- 416 Chen Y Q, Liu H. The analysis of toxic trace elements in coal and fly ash in the region of Beijing.
417 *Comprehensive Utilization Of Fly Ash* 2009; 3: 20-22.
- 418 China Statistic Department. *China Statistics Yearbook* 2013.
- 419 Chuang H C, Jones T, Lung S C, BéruBé K A. Soot-driven reactive oxygen species formation from incense
420 burning. *Science of Total Environment* 2011; 409: 4781-4787.
- 421 Chuang H C, BéruBé K A, Lung S C, Bai K J, Jones T. Investigation into the oxidative potential generated
422 by the formation of particulate matter from incense combustion. *Journal of Hazardous Materials* 2013;
423 244-245: 142-150.
- 424 Costa D L, Dreher K L. Bioavailable transition metals in particulate matter mediate cardiopulmonary injury
425 in healthy and compromised animal models. *Environmental Health Perspectives* 1997; 105: 1053–1060.
- 426 Crabbe H. Risk of respiratory and cardiovascular hospitalization with exposure to bushfire particulates: new
427 evidence from Darwin, Australia. *Environmental Geochemistry and Health* 2012; 34: 697-709.
- 428 Dockery D W, Pope III A, Xu X, Spengler J D, Ware J H, Fay M E, Ferris B G, Jr., Speizer F E. An association
429 between air-pollution and mortality in 6 United-States cities. *The New England Journal of Medicine* 1993;
430 329: 1753-1759.
- 431 Dai S F, Ren D Y, Liu J R, Li S S. The occurrence and distribution of toxic trace elements in the coal of
432 Fengfeng mine of Hebei Province. *Journal of China University of mining and technology* 2003; 32(4):

433 358-361.

434 Distefano E, Eiguren-Fernandez A, Delfino R J, Sioutas C, Froines J R, Cho A K. Determination of metal-
435 based hydroxyl radical generating capacity of ambient and diesel exhaust particles. *Inhalation*
436 *Toxicology* 2009; 21: 731-738.

437 Donaldson K, Beswick P H, Gilmour P S. Free radical activity associated with the surface of the particles: a
438 unifying factor in determining biological activity. *Toxicology Letters* 1996; 88: 293-298.

439 Greenwell L L, Moreno T, Richard R J. Pulmonary antioxidants exert differential protective effects against
440 urban and industrial particulate matter. *Journal of Biosciences* 2003; 28: 101–107.

441 Hoek G, Krishnan RM, Beelen R, Peters A, Ostro B, Brunekreef B, Kaufman J D. Long-term air pollution
442 exposure and cardio-respiratory mortality: a review. *Environmental Health* 2013; 12: 43.

443 Jones T, Wlodarczyk A, Koshy L, Brown P, Shao L Y, BéruBé K. The geochemistry and bioreactivity of fly-
444 ash from coal-burning power stations. *Biomarkers* 2009; 14(S1): 45–48.

445 Kan H, London S, Chen G, Zhang Y, Song G, Zhao N, Jiang L, Chen B. Differentiating the effects of fine
446 and coarse particles on daily mortality in Shanghai, China. *Environment International* 2007; 33: 376–384.

447 Kan H, Chen R, Tong S. Ambient air pollution, climate change, and population health in China. *Environment*
448 *International* 2012; 42: 10–19.

449 Kheirbek I, Wheeler K, Walters S, Kass D, Matte T. PM_{2.5} and ozone health impacts and disparities in New
450 York City: sensitivity to spatial and temporal resolution. *Air Quality, Atmosphere and Health* 2013; 6:
451 473-486.

452 Lan Q, Mumford J L, Shen M, Demarini D M, Bonner M R, He X, Yeager M, Welch R, Chanock S, Tian L,
453 Chapman R S, Zheng T, Keohavong P, Caporaso N, Rothman N. Oxidative damage-related genes
454 AKR1C3 and OGG1 modulate risks for lung cancer due to exposure to PAH-rich coal combustion
455 emissions. *Carcinogenesis* 2004; 25(11): 2177-2181.

456 Levine J S, Cofer W R, Cahoon D R, Winstead E L. Biomass burning: a driver for global change.
457 *Environmental Science & Technology* 1995; 29: 120A-125A.

458 Luo W Q. Briefly on the atmospheric pollution and its control by burning coals. *Energy saving technology*
459 2008; 26: 267-268.

460 Li S S. Problems and countermeasures of the harmful trace elements in Chinese coal. *Coal science and*
461 *technology* 2006; 34(1): 28-31.

462 Li X Y, Gilmour P S, Donaldson K, MacNee W. In vivo and in vitro proin- flammatory effects of particulate
463 air pollution (PM₁₀). *Environmental Health Perspectives* 1997; 105: 1279–1283.

464 Lin Z Q, Xi Z G, Chao F H. Research progress in the toxicity effects of the nano particles. *Journal of*
465 *Preventive Medicine of Chinese People's Liberation Army* 2007; 25: 383–386.

466 Liu Y W, Mao X L, Sun L Y, Ni J R. Characteristics of heavy metals discharge from industrial pollution
467 sources in Shenzhen. *Acta Scientiarum Naturalium Universitatis Pekinensis* 2010; 46: 279-285.

468 Loomis D, Grosse Y, Lauby-Secretan B, Ghissassi F E, Bouvard V, Benbrahim-Tallaa L, Guha N, Baan R,
469 Mattock H, Straif K. The carcinogenicity of outdoor air pollution, *Lancet Oncology* 2013; 14:1262-
470 1263.

471 Lu S L, Shao L Y, Wu M H, Jones, T P, Merolla L, Richard, R J. The related research of the bioactivity and
472 trace elements of PM₁₀ in Beijing. *Science in China D: Geochemistry* 2006; 36(8): 777-784.

473 Merolla L, Richards R J. In vitro effects of water-soluble metals present in UK particulate matter.
474 *Experimental Lung Research* 2005; 31: 671–683.

475 Moreno T, Merolla L, Gibbons W, Greenwell L, Jones T, Richards R. Variations in the source, metal content
476 and bioreactivity of technogenic aerosols: a case study from Port Talbot, Wales, UK. *Science of Total*

477 Environment 2004; 333: 59–73.

478 Neas L M. Fine particulate matter and cardiovascular disease. *Fuel Processing Technology* 2000; 65-66: 55-
479 67.

480 Ostro B, Broadwin R, Green S, Feng W Y, Lipsett M. Fine particulate air pollution and mortality in nine
481 California counties: Result from CALFINE. *Environmental Health Perspectives* 2006; 114(1): 29-33.

482 Pui D Y H, Chen S C, Zuo Z. PM_{2.5} in China: Measurements, sources, visibility and health effects, and
483 mitigation. *Particuology* 2014; 13: 1-26.

484 Querol X, Zhuang X, Alastuey A, Viana M, Lv W, Wang Y, Lopez A , Zhu Z, Wei H, Xu S. Speciation and
485 sources of atmospheric aerosols in a highly industrialised emerging mega-city in Central China. *Journal*
486 *of Environmental Monitoring* 2006; 8: 1049-1059.

487 Ren D Y, Zhao F H, Dai S F, et al. *The Trace Element Geochemistry of Coal*, Beijing: Science Press; 2006.

488 Reche C, Moreno T, Amato F, Viana M, van Drooge B L, Chuang H C, et al.. A multidisciplinary approach
489 to characterise exposure risk and toxicological effects of PM₁₀ and PM_{2.5} samples in urban environments.
490 *Ecotoxicology and Environmental Safety* 2012; 78: 327-335.

491 Samet J M, Dominici F, Curreiro F C, Coursac I, Zeger S L. Fine particulate air pollution and mortality in
492 20 US cities, 1987-1994. *The New England Journal of Medicine* 2000; 343: 1742-1749.

493 Sánchez-Pérez Y, Chirino Y I, Osornio-Vargas A R, Morales-Bárceñas R, Gutiérrez-Ruíz C, Vázquez-López
494 I, et al.. DNA damage response of A549 cells treated with particulate matter (PM₁₀) of urban air
495 pollutants. *Cancer Letters* 2009; 278(2): 192-200.

496 See S W, Wang Y H, Balasubramanian R. Contrasting reactive oxygen species and transition metal
497 concentrations in combustion aerosols. *Environmental Research* 2007; 103: 317-324.

498 Shao L Y, Hu Y, Wang J, Hou C, Yang Y Y, Wu M Y. Particle-induced oxidative damage of indoor PM₁₀
499 from coal burning homes in the lung cancer area of Xuan Wei, China. *Atmospheric Environment* 2013;
500 77: 959-967.

501 Shao L Y, Jones T P, Gayer R A, Dai S F, Li S S, Jiang Y F. Petrology and geochemistry of the high-sulphur
502 coals from the Upper Permian carbonate coal measures in the Heshan Coalfield, southern China.
503 *International Journal of Coal Geology* 2003; 55: 1-26.

504 Shao L Y, Li J J, Zhao H Y, Yang S S, Li H, Li W J, Jones T P, Sexton K, Bérubé K A. Associations between
505 particle physicochemical characteristics and oxidative capacity: an indoor PM₁₀ study in Beijing, China.
506 *Atmospheric Environment* 2007; 41: 5316–5326.

507 Shao L Y, Shi Z B, Jones T P, Li J J, Whittaker A G, Bérubé K A. Bioreactivity of particulate matter in
508 Beijing air: results from plasmid DNA assay. *Science of The Total Environment* 2006; 367: 261-272.

509 Straif K, Baan R, Grosse Y, Secretan B, El Ghissassi F, Coglianò V. Carcinogenicity of household solid fuel
510 combustion and of high-temperature frying. *The Lancet Oncology* 2006; 7: 977-978.

511 Sun Z Q, Shao L Y, Mu Y J, Hu Y. Oxidative capacities of size-segregated haze particles in a residential area
512 of Beijing. *Journal of Environmental Sciences* 2012; 26: 167–174.

513 Tang X Y, Huang W H. *Trace elements in coal in China*, Beijing: The commercial press; 2004.

514 Vidrio E, Phuah CH, Dillner A M, Anastasio C. Generation of hydroxyl radicals from ambient fine particles
515 in a surrogate lung fluid solution. *Environmental Science & Technology* 2009; 43: 922-927.

516 Wang J, Shao L Y, Geng C M, Wang J Y, Liu J X, Yang W, Hu Y. Oxidative capacity of PM₁₀ emitted by
517 burning coals. *Journal of Central South University (Science and Technology)* 2014; 45(6): 2137-2143
518 (in Chinese)

519 Whittaker A G. *Black smokes: Past and present*. The Thesis for the Degree of Ph.D. Cardiff University, 2003.

520 Xiao Z H, Shao L Y, Zhang N, Wang J, Wang J Y. Heavy metal compositions and bioreactivity of airborne

521 PM₁₀ in a valley-shaped city in northwestern China. *Aerosol and Air Quality Research* 2013; 13: 1116–
522 1125.

523 Xu M H, Yan R, Zheng C G, Qiao Y, Han J, Sheng C D. Status of trace element emission in a coal combustion
524 process: a review. *Fuel Processing Technology* 2003; 85: 215-237.

525 Zhang W L, Xu D Q, Cui J S. Air pollutant PM_{2.5} monitoring and study on its genotoxicity. *Journal of*
526 *Environment and Health* 2003; 1: 3–4.

527 Zhong C Y, Zhou Y M, Smith K R, Kennedy I M, Chen C Y, Aust A E, Pinkerton K E. Oxidative injury in
528 the lungs of neonatal rats following short-term exposure to ultrafine iron and soot particles. *Journal of*
529 *Toxicology and Environmental Health, Part A: Current Issues* 2010; 73: 837-847.

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531

532 **Tables:**

533

534 Table 1. Information of the proximate and ultimate analysis of the raw coals used in this study

535

536 Table 2. Mass concentration of the PM₁₀ emitted by burning different coals (µg/m³)

537

538 Table 3. Percentage of DNA damage induced by the PM₁₀ emitted from burning different fuels

539

540 Table 4. Contents of water-soluble trace elements in the intact whole PM₁₀ emitted from
541 burning different types of coal and wood charcoal (ppm)

542

543 Table 5. Correlation coefficients between the total and individual water-soluble heavy metal
544 concentrations and the percentages of DNA damage by coal-burning PM₁₀

545

546 Table 6. Toxic index of the PM₁₀ emitted by burning different coals

547

548 **Figures:**

549

550 Fig.1 Sketch diagram showing composition of the coal combustion stove system which
551 contains a stove, a dilution tunnel and the smoke chambers. "HC" represents honeycomb
552 briquette; "RC" represents raw powdered coal.

553

554 Fig.2 A comparison between the morphology and the quantity of PM₁₀ emitted by burning
555 honeycomb briquette and raw powdered coal. DT-H and ZJ-H represent Datong and Zhijin
556 honeycomb briquettes respectively, DT-R and ZJ-R represent Datong and Zhijin raw powdered
557 coals respectively.

558

559 Fig.3 Gel images and histograms of the oxidative damage on DNA that was induced by PM₁₀
560 emitted by burning different fuels. ("a" represents ZJ honeycomb briquette; "b" represents DT
561 honeycomb briquette; "c" represents ZJ powder coal; "d" represents DT powder coal; "e"
562 represents DS powder coal; "f" represents YC powder coal; "g" represents JX powder coal; "h"
563 represents wood charcoal; "W" represents the whole-particle suspension; and "S" represents
564 the water soluble fraction).

565

566 Fig. 4. Comparison between the DNA damage percentages of the whole particles and the water-
567 soluble fraction of the coal burning-derived PM₁₀ under a dose of 500mgml⁻¹ ("H" represents
568 honeycomb briquette, "R" represents raw powdered coal).

569

Table 1. Information of the proximate and ultimate analysis of the raw coals used in this study

	Proximate analysis						Ultimate analysis				
	moisture %	ash content %	Volatiles %	Fixed carbon %	Higher heating value MJ/kg	Lower heating value MJ/kg	S%	C%	H%	N%	O%
Coal of ZJ	0.94	9.08	5.76	84.22	31.82	31.23	2.24	81.86	2.76	1.04	2.08
Coal of DT	6.98	9.50	32.07	51.45	27.12	26.19	0.21	64.6	3.56	0.84	14.31
Coal of DS	7.46	6.68	30.82	55.04	28.45	27.51	0.20	68.72	3.76	0.90	12.28
Coal of YC	1.30	23.28	19.74	55.68	19.85	19.51	0.36	62.68	2.16	0.62	9.60
Coal of JX	3.02	26.34	4.44	66.20	22.96	22.73	0.25	68.26	0.79	0.26	1.08

571 Note: the above content is for the air dry basis of coal; “ZJ” represents Zhijin; “DT” represents Datong; “DS” represents

572 Dongsheng; “YC” represents Yinchuan; and “JX” represents Jingxi.

573

574

Table 2 Mass concentration of the PM₁₀ emitted by burning different coals (μg /m³)

Fuel types	Mass (μg)	flow rate (L/min)	sampling time (min.)	mass concentration (μg/m ³)
ZJ-H	7800	78	78	1282.05
DT-H	4300	78	80	689.10
ZJ-R	13400	78	60	2863.25
DT-R	18100	78	56	4143.77
DS-R	34200	78	41	10694.18
YC-R	16100	78	29	7117.60
JX-R	5600	78	50	1435.90

575

Note: H represents honeycomb briquettes; R represents raw powdered coal.

576

Table 3. Percentages of DNA damage induced by the PM₁₀ emitted from burning different fuels

Fuel Types	Samples status	Dosage of PM ₁₀ (μg/ml)				
		25	50	100	300	500
ZJ-H	Whole-particle suspension (%)	12.46(±0.69))	30.70(±1.67))	33.03(±1.48))	38.61(±2.49))	55.37(±1.91))
	Water-soluble fraction (%)	14.05(±0.02))	23.42(±1.05))	25.89(±0.75))	36.73(±0.89))	48.34(±1.40))
DT-H	Whole-particle suspension (%)	12.29(±1.14))	11.95(±1.75))	26.22(±0.22))	37.85(±1.18))	46.08(±1.34))
	Water-soluble fraction (%)	10.98(±0.94))	11.35(±2.09))	22.54(±0.38))	34.10(±1.58))	44.97(±1.70))
ZJ-R	Whole-particle suspension (%)	13.32(±0.36))	15.18(±0.39))	17.17(±1.11))	23.18(±1.43))	33.73(±1.22))
	Water-soluble fraction (%)	8.58(±0.37))	9.63(±0.71))	11.79(±1.39))	23.81(±0.30))	23.61(±0.98))
DT-R	Whole-particle suspension (%)	12.55(±0.24))	13.59(±0.18))	13.44(±0.60))	20.09(±0.64))	19.37(±0.15))
	Water-soluble fraction (%)	7.70(±0.46))	9.86(±0.04))	9.30(±0.16))	12.37(±0.37))	15.60(±0.92))
DS-R	Whole-particle suspension (%)	10.33(±0.65))	11.29(±0.25))	12.24(±0.06))	14.27(±0.18))	16.85(±0.45))
	Water-soluble fraction (%)	7.58(±0.06))	10.14(±0.86))	12.46(±0.91))	13.57(±0.04))	15.52(±0.13))
YC-R	Whole-particle suspension (%)	15.68(±1.85))	16.62(±0.27))	20.70(±0.45))	31.89(±0.74))	33.70(±1.14))
	Water-soluble fraction (%)	20.66(±1.26))	22.51(±0.79))	23.02(±0.28))	25.52(±0.43))	30.01(±1.49))
JX-R	Whole-particle suspension (%)	6.83(±0.81))	8.84(±0.79))	11.65(±0.67))	14.71(±0.83))	16.37(±0.50))
	Water-soluble fraction (%)	4.84(±0.74))	7.45(±0.26))	8.85(±1.38))	10.72(±0.83))	12.21(±1.11))
wood charcoal	Whole-particle suspension (%)	11.37(±0.93))	12.25(±0.07))	14.48(±0.69))	15.55(±0.13))	16.99(±1.05))
	Water-soluble fraction (%)	11.61(±1.01))	11.89(±0.75))	13.15(±0.20))	13.95(±1.42))	14.38(±0.25))

Note: "H" represents honeycomb briquettes, "R" represents raw powdered coal, "±" represent error range

581 Table 4. Contents of water-soluble trace elements in the intact whole PM₁₀ emitted from burning different types of coal and
 582 wood charcoal (ppm)

	ZJ-H	DT-H	ZJ-R	DT-R	DS-R	YC-R	JX-R	Wood charcoal
As	412	155	19.6	19.9	18.3	46.5	9.46	19.7
Cd	93.6	15.8	10.3	0.08	0.23	19.8	0.6	0.3
Cr	1.92	9.08	9.36	8.02	3.09	5.2	3.99	13.5
Co	0.6	1.92	0.15	0.63	1	0.23	0.02	—
Cs	2.57	6.42	2.97	4.48	2.3	5.9	3.88	5.34
Cu	86.4	16.2	278	12.4	8.69	18.8	15.3	16.5
Ge	890	37.5	7.88	2.86	2.71	1.08	0.471	0.74
Mn	16.6	30.5	12.2	0.42	1.44	8.76	3.79	—
Mo	13	5.02	3.73	7.36	7.57	7.5	2.56	2
Ni	47.4	22.7	22.9	13.6	19	8.37	18.8	13.1
Pb	2385	824	324	0.39	2.12	77.1	3.39	16
Se	61.3	43.2	10.5	12	2.57	4.16	1.5	8.88
Sr	8.28	7.86	12.3	3.15	2.23	10.1	5.42	14
Sb	46.5	14.8	0.93	1.92	9.38	4.21	1.16	0.75
Ti	84.1	19.5	61.5	29.2	65.2	20.5	56.6	3.16
Tl	179	98.1	9.86	2.76	1.73	16.5	2.19	4.83
V	2.36	1.13	1.87	1.9	1.59	4	1.39	2.5
Zn	17150	4350	2408	98.2	63.5	3702	71	18.8
Total	21480.63	5658.73	3196.05	219.28	212.65	3960.71	201.52	140.11

583 Note: “—” represents that the measured values of the corresponding element are below the detection limit. “Total” represents
 584 sum of the analysed elements. “H” represents honeycomb briquettes. “R” represents raw powdered coal.

585

586 Table 5. Correlation coefficients between the total and individual water-soluble heavy metal concentrations and the
 587 percentages of DNA damage by coal-burning PM₁₀

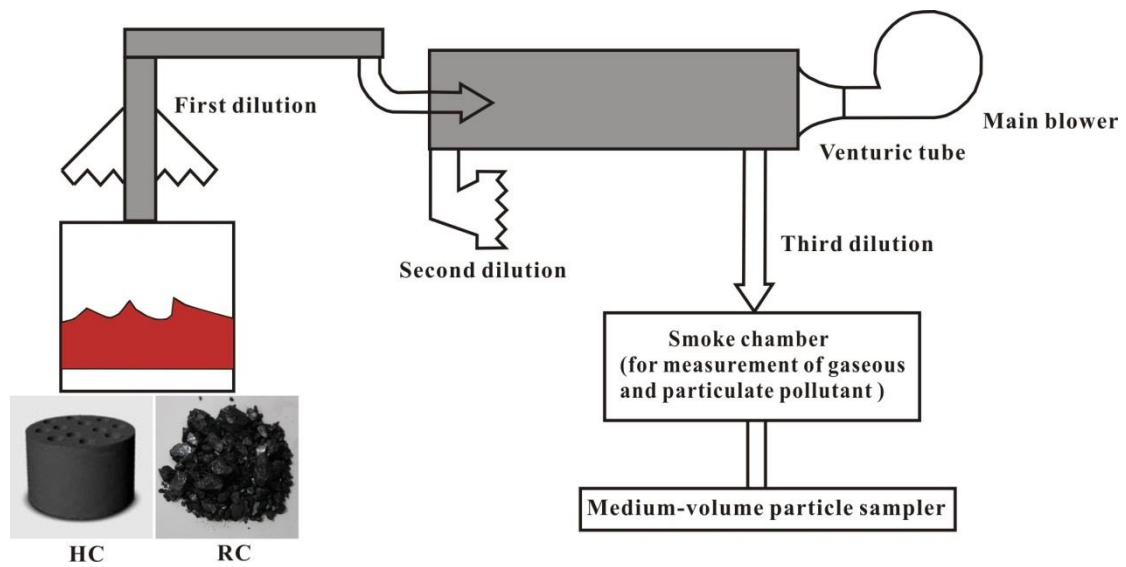
Elements	As	Cd	Cr	Co	Cs	Cu	Ge	Mn	Mo	Ni
DNA damage percentages at 500 µg/ml	0.854	0.828	-0.237	0.335	0.047	0.305	0.712	0.823	0.595	0.718
Elements	Pb	Se	Sb	Sr	Ti	Tl	V	Zn	total	
DNA damage percentages at 500 µg/ml	0.869	0.882	0.785	0.258	0.284	0.898	0.111	0.871	0.870	

588

Table 6. Toxic index of the PM₁₀ emitted by burning different coals

Fuel types	mass concentration ($\mu\text{g}/\text{m}^3$)	percentage of DNA damage at 500 $\mu\text{g}/\text{ml}$ dose	toxicity index
ZJ-H	1282.05	55.37	70987
DT-H	689.10	46.08	31754
ZJ-R	2863.25	33.73	96577
DT-R	4143.77	19.37	80265
DS-R	10694.18	16.85	180197
YC-R	7117.60	33.70	239863
JX-R	1435.90	16.37	23506

Note: "H" represents honeycomb briquette, "R" represents raw powdered coal.

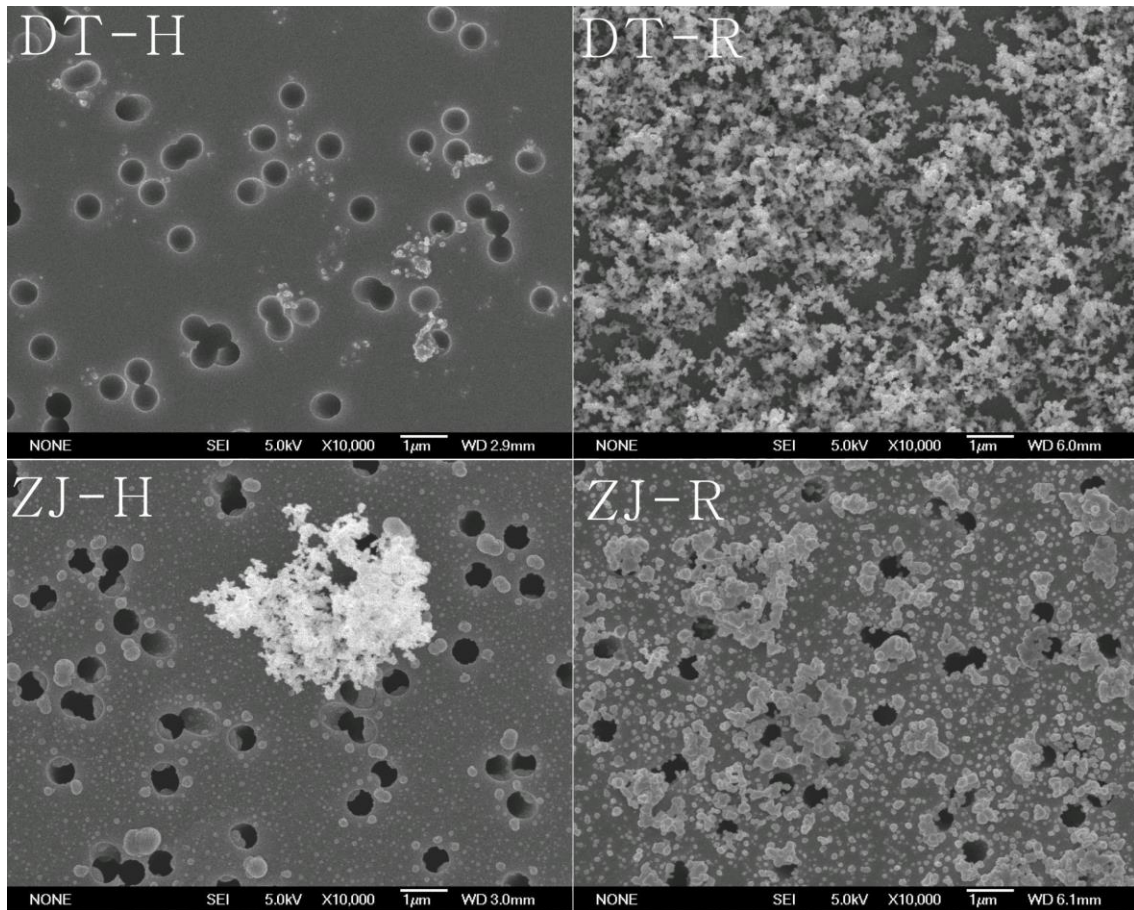


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593 Fig.1 Sketch diagram showing composition of the coal combustion stove systems which contains a stove, a dilution tunnel and

594 the smoke chambers. "HC" represents honeycomb briquette; "RC" represents raw powdered coal

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Fig.2 A comparison between the morphology and the quantity of PM₁₀ emitted by burning honeycomb briquette and raw powdered coal. DT-H and ZJ-H represent Datong and Zhijin honeycomb briquettes respectively, DT-R and ZJ-R represent Datong and Zhijin raw powdered coals respectively.

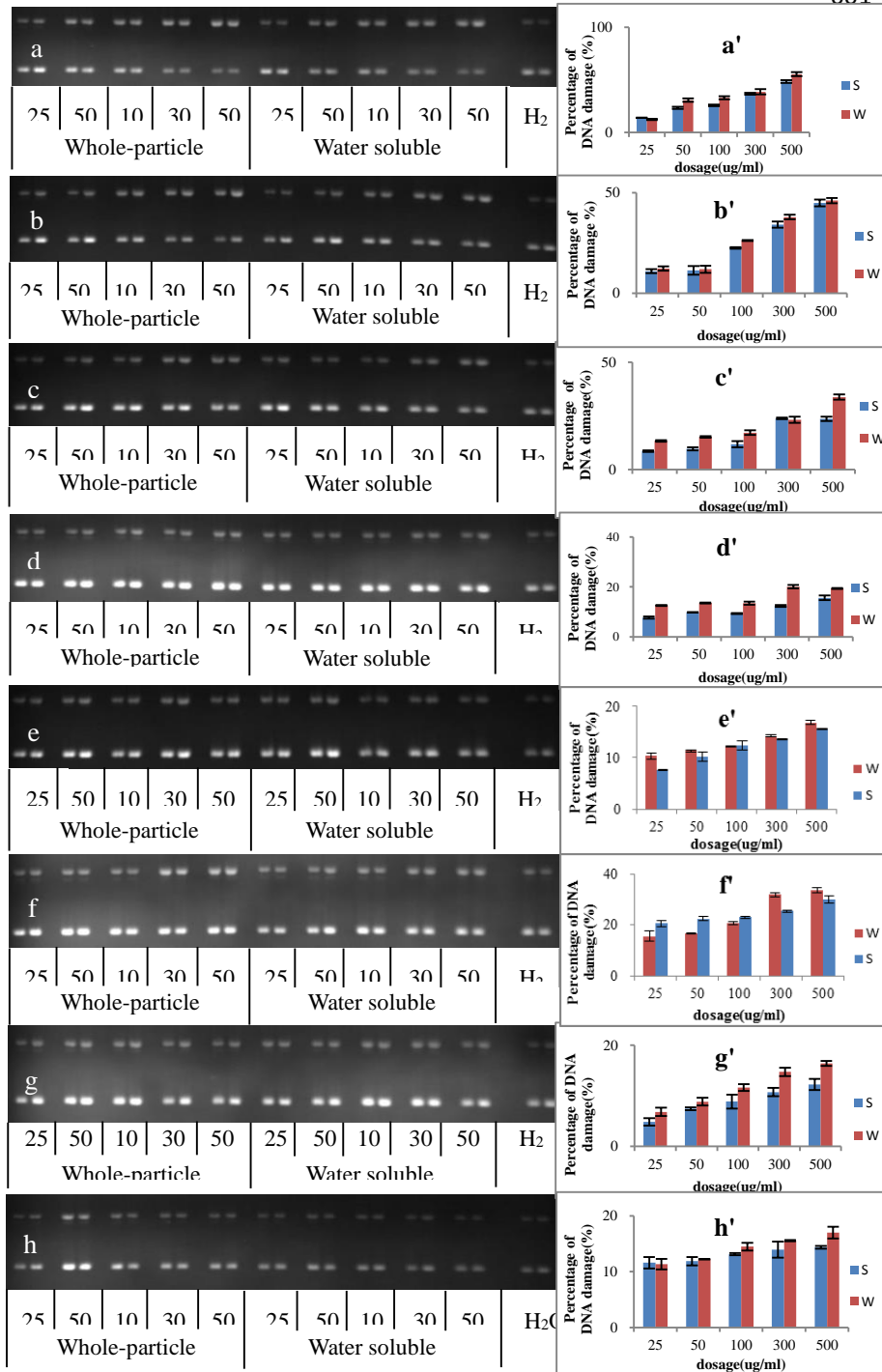
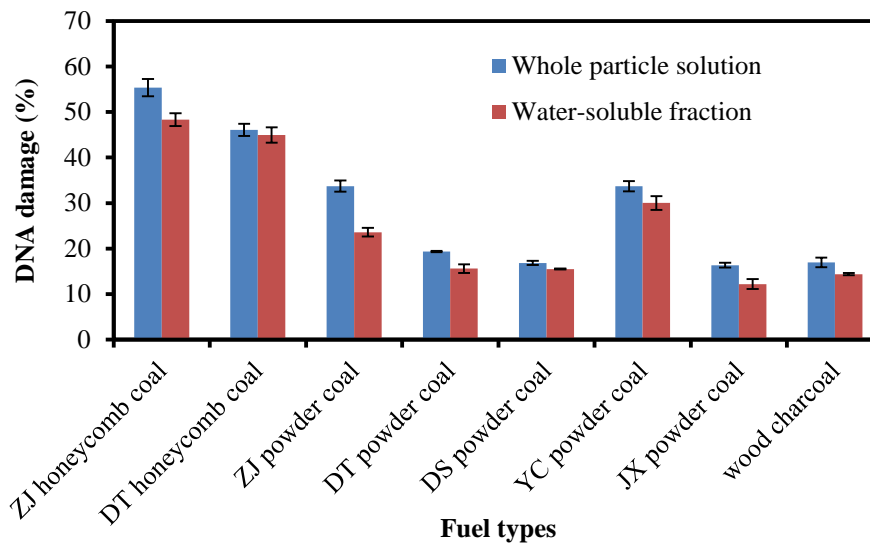


Fig.3 Gel images and histograms of the oxidative damage on DNA that was induced by PM₁₀ emitted by burning different fuels. (“a” represents ZJ honeycomb briquette; “b” represents DT honeycomb briquette; “c” represents ZJ powder coal; “d” represents DT powder coal; “e” represents DS powder coal; “f” represents YC powder coal; “g” represents JX powder coal; “h” represents wood charcoal; “W” represents the whole-particle suspension; and “S” represents the water soluble fraction).



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Fig. 4. Comparison between the DNA damage percentages of the whole particles and the water-soluble fraction of the coal burning-derived PM₁₀ under a dose of 500mgml⁻¹.