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1 **Source-specific health risk analysis on particulate trace elements: Coal combustion and**
2 **traffic emission as major contributors in wintertime Beijing**

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20 **ABSTRACT**

21 Source apportionment studies of particulate matter (PM) link chemical composition to emission
22 sources, while health risk analyses link health outcomes and chemical composition. There are limited
23 studies to link emission sources and health risks from ambient measurements. We show such an
24 attempt for particulate trace elements. Elements in PM_{2.5} were measured in wintertime Beijing and the
25 total concentrations of 14 trace elements were 1.3-7.3 times higher during severe pollution days than
26 during low pollution days. Fe, Zn, and Pb were the most abundant elements independent of the PM
27 pollution levels. Chemical fractionation shows that Pb, Mn, Cd, As, Sr, Co, V, Cu, and Ni were
28 present mainly in the bioavailable fraction. Positive matrix factorization (PMF) was used to resolve
29 the sources of particulate trace elements into dust, oil combustion, coal combustion and traffic-related
30 emissions. Traffic-related emission contributed 65% of total mass of the measured elements during
31 low pollution days. However, coal combustion dominated (58%) during severe pollution days. By
32 combining element-specific health risk analyses and source apportionment results, we conclude that
33 traffic-related emission dominates the health risks by particulate trace elements during low pollution
34 days, while coal combustion becomes equally or even more important during moderate and severe

35 pollution days.

36 INTRODUCTION

37 Atmospheric fine particulate matter (PM_{2.5} with an aerodynamic diameter less than 2.5 μm) in
38 urban areas has profound effects on human health. Particularly, trace elements such as Cd, Cr, Cu, Fe,
39 Mn, Ni, Pb, and Zn in PM_{2.5} can lead to an array of short-term or long-term adverse health effects,
40 including pulmonary and heart diseases, and potentially premature death.^{1,2} However, there are very
41 few studies that directly link metals associated with PM_{2.5} to human health outcomes. Toxicological
42 studies have revealed some mechanisms of the toxicity of those trace elements. For example,
43 particulate trace elements can catalyze the formation of reactive oxygen species (ROS), leading to
44 oxidative stress and consequently inflammation in respiratory tract epithelium.³⁻⁷ Therefore, the link
45 between particulate trace elements and health risk constitutes an important health issue. The adverse
46 health effects induced by trace elements were determined by their bioavailability and toxicity.⁸⁻¹⁰
47 Bioavailability of an element is a measure of the degree to which this element binds with active sites,
48 such as the pharyngeal and tracheal region and the alveolar region of lungs, indicating the extent and
49 rate of its absorption by a living system.^{11,12} Soluble metals are more readily bio-activated and
50 bioavailable than less soluble components in the alveoli of lung tissues.^{12,13} The solubility of an
51 element is dependent on the aerosol surface property, the aerosol-element bonds, the solvent media,
52 and the chemical form of the element.¹² Therefore, for risk assessment, it is important to investigate
53 the chemical fraction (e.g., those soluble fractions) of particulate trace elements instead of their total
54 contents.

55 A four-step Tessier's method modified by Espinosa et al. classifies the heavy metals into four
56 chemical fractions: soluble and exchangeable metals (F1: exchangeable fraction); carbonates, oxides
57 and reducible metals (F2: reducible fraction); metals bound to organic matter, oxidizable and
58 sulphidic (F3: oxidizable fraction); and residual metals (F4: residual fraction).^{8,14} The exchangeable
59 fraction and reducible fraction are highly soluble in the aqueous phase, often regarded as the
60 bioavailable fraction.^{15,16} Many recent studies have investigated the bioavailable fraction and its
61 associated health risk. For example, Balasubramanian et al. showed a significant influence of the size-
62 resolved particulate-bound heavy metals on the human health.¹⁷ Li et al. showed that Cd, Cr, Cu, Pb,
63 and Zn constitute a large proportion of the exchangeable fraction in ambient aerosol in a haze episode

64 in wintertime Nanjing, China.¹⁸

65 The haze pollution has become a severe environmental problem in China in recent winters,
66 characterized with poor air quality, high aerosol mass concentration and high health risk. A majority
67 of studies have been focused on the chemical nature and sources of the main components such as
68 sulfate, nitrate, ammonium and organic compounds.¹⁹⁻²¹ Studies on trace elements, however, are
69 limited. A few studies on trace elements mainly focused on the total concentration of individual
70 elements^{17,22}, or on the speciated/fractionated concentrations and associated health risk without
71 considering their sources.^{15,18,23} There are, however, limited studies on the relationships between the
72 emission sources and health risks of particulate trace elements.

73 In this study, we investigate the trace elements in PM_{2.5} samples collected in Beijing during
74 winter. The concentration and fractionation of 14 elements on low pollution days, moderate pollution
75 days and severe pollution days are characterized. The sources of these particulate trace elements are
76 then quantified using a positive matrix factorization (PMF) receptor model. The bioavailability and
77 the carcinogenic and non-carcinogenic health risks of these elements are evaluated and contributions
78 from each source are quantified.

79 MATERIALS AND METHODS

80 **Aerosol samples collection.** Daily (from 1st to 25th January 2014) 24-h integrated PM_{2.5} samples
81 were collected on pre-baked (780 °C, 3 h) quartz-fiber filters (8×10 inch). Samples were collected
82 using a high-volume sampler (Model TE-6070VFC, Tisch Environmental Inc., Ohio, USA) at a flow
83 rate of 1.13 m³ min⁻¹. The sampling site was at the campus of the Institute of Atmospheric Physics,
84 Chinese Academy of Sciences in Beijing (116°20' E, 39°59' N), which is typical of urban site
85 surrounded by residential, commercial and education areas. Samples were taken on the roof of a
86 building, about 10 m above the ground. An overview of the sampling site is shown in Figure S1 in the
87 Supporting Information. The samples were stored at -20 °C until analysis.

88 **Sequential extraction and analysis.** A four-step sequential extraction procedure was used for
89 chemical fractionation of trace elements in PM_{2.5}.⁸ This approach can separate the elements into four
90 fractions: exchangeable fraction; reducible fraction; oxidizable fraction; and residual fraction. After

91 extraction, fourteen elements (i.e., Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Cd, Ba, and Pb) in the
92 extracts were quantified using an inductively coupled plasma mass spectrometer (ICP-MS, iCAP Q,
93 ThermoFisher Scientific, Waltham, MA, USA). More details about the sequential extraction and
94 quality control of analysis are shown in the Supporting Information (also see Table S1-S3).

95 **Source apportionment.** A positive matrix factorization (PMF) receptor model was used to
96 identify and quantify the main sources of these elements. The receptor model requires two inputs to
97 run PMF, namely concentration and its uncertainty. Different source numbers were tested by applying
98 a trial to determine the optimal solutions. The identification of sources was conducted based on major
99 marker species. More details are described in Supporting Information (PMF analysis).

100 **Health risk assessment.** The carcinogenic and non-carcinogenic risks posed by airborne metals
101 via direct inhalation of PM_{2.5} were calculated using US Environmental Protection Agency human
102 health risk assessment models, which mainly involve exposure assessment and risk
103 characterization.^{24,25} The bioavailable concentrations (exchangeable fraction and reducible fraction) of
104 particulate trace elements, instead of total concentrations, were used for the carcinogenic and non-
105 carcinogenic risks characterization. Details of health risk assessment of trace elements and emission
106 sources were described in Supporting Information (Health risk assessment).

107 RESULTS AND DISCUSSION

108 **Total concentrations of particulate trace elements.** The daily mean concentrations of PM_{2.5}
109 ranged from 27.6 to 319.0 $\mu\text{g m}^{-3}$ with an average of 112.3 $\mu\text{g m}^{-3}$ during the entire measurement
110 campaign, which is much higher than the WHO standard for daily mean PM_{2.5} concentration (25 $\mu\text{g m}^{-3}$).
111 We categorized the 25 measurement days into low, moderate and severe pollution days
112 according to the Chinese national ambient air quality standard (NAAQS) of 75 $\mu\text{g m}^{-3}$ (daily
113 concentration) and the mean + σ (170 $\mu\text{g m}^{-3}$), that is, low pollution days ($\text{PM}_{2.5} \leq 75 \mu\text{g m}^{-3}$, 8 days),
114 moderate pollution days ($75 \leq \text{PM}_{2.5} \leq 170 \mu\text{g m}^{-3}$, 13 days), and severe pollution days ($\text{PM}_{2.5} \geq 170$
115 $\mu\text{g m}^{-3}$, 4 days) (see Figure S2a). The average concentrations of PM_{2.5} are approximately 2 and 5
116 times higher during moderate pollution days (112.1 $\mu\text{g m}^{-3}$) and severe pollution days (241.4 $\mu\text{g m}^{-3}$)
117 than during low pollution days (51.2 $\mu\text{g m}^{-3}$), respectively. Figure S2b shows the meteorological data

118 during the measurement period. The temperature was rather stable (around 0 °C) during the entire
119 measurement period. The wind speed was generally lower during moderate and severe pollution days
120 compared to low pollution days as low wind speed favors the development of stagnant weather
121 conditions. The relative humidity (RH) was also generally higher during moderate and severe
122 pollution days than during low pollution days. The high RH favors the decrease of planetary boundary
123 layer (PBL) height and therefore the accumulation of aerosol.²⁶

124 There are two main considerations for the selection of those 14 elements. On the one hand, these
125 elements are frequently used to determine health risks in previous studies.^{18,23} On the other hand, they
126 are commonly used in source apportionment studies because of their source specificity and significant
127 relative abundance allowing their precious quantification.^{20,27} The average concentrations of these
128 elements are shown in Table S4 for different pollution conditions. The total concentrations of all
129 measured elements constituted 0.9%, 2.2%, 3.3%, and 2.1% of PM_{2.5} mass during severe pollution
130 days, moderate pollution days, low pollution days and the entire measurement period, respectively.
131 The percentages are consistent with previous studies. For example, measurements in Beijing in winter
132 2006 showed that these fourteen elements constituted about 1.9% of the PM_{2.5} mass.²⁰ Another study
133 showed the total concentration of Fe, Zn, Pb, Ti, Mn, Ni, Cu, As, Ba, V, Cr constituted approximate
134 3.1% of PM_{2.5} mass in Beijing in December 2010.¹⁹ In Lanzhou, the capital of the Gansu Province in
135 China, the total concentration of these elements (except Fe) constituted 1.6% (haze days) and 2.0%
136 (non-haze days) of the PM_{2.5} mass in winter 2012.²¹ The percentage of particulate trace elements is
137 dependent on the mass of other chemical composition, particularly sulfate, nitrate, ammonium and
138 carbonaceous matter. The decrease of the elemental fraction with the increase of pollution levels could
139 be attributed to the enhanced formation of secondary inorganic aerosol and secondary organic aerosol
140 during pollution days.²⁷

141 Figure 1 shows the total concentrations of individual particulate trace elements during low
142 pollution, moderate pollution and severe pollution days. Fe, Zn, and Pb are the most abundant
143 elements (major elements), followed by a sub-major group (including Ba, Mn, Cu, Ni, Ti, and As) and
144 a minor group (including Co, Cr, V, Cd, and Sr). The concentrations of each measured element
145 increased as pollution levels increased. Statistically significant difference between the concentrations

146 of the elements during severe pollution days and low pollution days can be observed for all elements,
147 except for Ti and Sr (*t*-test, $p < 0.05$). The concentrations of trace elements are 1.1-2.5 times higher
148 during moderate pollution days and 1.3-7.3 times higher during severe pollution days than those
149 during low pollution days (see Table S4), indicating a significant accumulation of the particulate trace
150 elements during pollution days. Among all elements, the concentrations of carcinogenic elements
151 including As, Cd, and Pb increased most significantly by a factor of 4.4-7.3 from low pollution days
152 to severe pollution days. Therefore, it is crucial to understand the sources of these elements and
153 whether the sources and their contribution change with the pollution levels.

154 **Chemical fractionation and bioavailability index of trace elements in PM_{2.5}.** Figure 2 shows
155 the fractionation distribution of individual elements under different pollution conditions. Fe, Zn, Cr,
156 Ti and Ba were present mainly in residual fraction (>50%). The percentage of this fraction was rather
157 constant from low pollution days to moderate and severe pollution days (4-8% difference) except for
158 Zn and Ba which show larger decrease from low pollution days to severe pollution days (from 49% to
159 27% for Zn and 81% to 64% for Ba). The constitution of Ni was rather constant under different
160 pollution conditions, i.e., about 24% of exchangeable fraction, 23% of reducible fraction, 27% of
161 oxidizable fraction and 26% of residual fraction. The characteristics of Ni, Fe and Zn are consistent
162 with previous studies in Guangzhou and Nanjing.¹⁵ Pb existed predominantly in the reducible fraction
163 (64%) at different pollution levels, indicating a large potential in transformation to exchangeable
164 fraction. Mn and V present mainly in exchangeable fraction (49% for Mn, 41% for V) and reducible
165 fraction (27% for both Mn and V). Cd, As, Sr and Co were presented mainly in exchangeable fraction,
166 which were consistent with results reported by Schleicher et al.¹⁰ Cu was found mainly in
167 exchangeable fraction (29%), reducible fraction (28%) and oxidizable fraction (38%), but little in
168 residual fraction (5%). This observation could be attributed to its strong ability in combining with
169 organic matter.²⁸

170 As discussed above, the distribution pattern of these four fractions determines the bioavailability
171 of an element and therefore the health risk. The exchangeable fraction is readily dissolved and
172 penetrates to the bloodstream through lung fluids, and thus represents a high bioavailability.¹⁵ The
173 reducible fraction is thermodynamically unstable and susceptible to pH changes and redox conditions.

174 This fraction can become bioavailable and causes a potential risk to human health under anoxic
175 conditions.²⁹ The exchangeable and reducible fraction together can lead to ‘direct effect’ on human
176 health through biochemical reactions within cells and the formation of reactive oxygen species that
177 can cause cellular imbalance and oxidative stress.^{15,16,18} The exchangeable and reducible fraction of an
178 element is represented as a bioavailability index (BI) to estimate its potential bioavailability.^{15,16} The
179 values of BI <30%, 30%< BI <50% and BI >50% represent low, medium, and high bioavailability,
180 respectively.³⁰ As shown in Figure 2, the BI values of Cr, Ti and Ba were lower than 30% representing
181 low health risk. The BI values of Ni, Fe and Zn were between 30% and 50%, while the BI values of
182 Pb, Cd, Mn, Sr, As, V, Co and Cu were larger than 50% indicating high bioavailability and toxicity. It
183 should be noted that the BI values of Fe, Mn, Ti, Pb, As, Cu, Co, Cr, and Ni were rather constant at
184 different pollution levels. However, the BI values of Cd, Sr, V, Zn and Ba enhanced significantly in
185 the severe pollution days, compared to those in low pollution days ($p < 0.05$). In particular, the largest
186 transformation of Zn was observed from low pollution days (BI=31%) to severe pollution days
187 (BI=66%), suggesting a higher risk of some particulate heavy metals to human health in pollution
188 days than in low pollution days.

189 **Sources of trace elements.** A receptor model (PMF) has been widely used for source
190 apportionment of particulate matter and it was used to identify and quantify the main sources of
191 elements measured in this study. Figure S3 and S5 provide details regarding the estimated source
192 profiles, indicating the relative intensity of element to each factor and the fraction of the total
193 predicted concentration for a given element, which can be useful for qualitative identification of the
194 sources. In Figure S4 we show the correlation (R^2) of each element with each source identified by
195 PMF. Four factors were identified, including oil combustion, dust, traffic-related and coal combustion
196 emissions. The first factor is characterized by a high contribution of vanadium (~50%), often used as
197 a tracer for oil combustion in many previous studies in China.³¹⁻³⁵ It should be noted that the
198 composition of the emissions might be different depending on the country of origin. For example,
199 vanadium may not be a good tracer of oil combustion in some countries depending on quality and
200 country of origin of the oil. Selenium is a good tracer for coal combustion emission in the US, but not
201 the case in China.³⁶ Therefore, attention should be paid to the difference in emission signature for

202 source identification. The second factor is dominated by crustal elements, e.g., Ti and Fe.¹⁸ This factor
203 represents crustal materials, mainly from unpaved road and/or construction activities, and constitutes
204 13.5-30.1% of the total mass of measured elements (Figure 3a). The third factor is characterized by
205 high contributions of Ni, Ba, Cr and Cu, which have been considered to be from tire abrasion, brake
206 linings, lubricants, and corrosion of vehicular parts.^{19,37,38} The relative contributions of this factor to
207 Cr and Ni are >70%, most likely from brake wear as reported in Visser et al.³⁸ Also for this factor, Fe
208 constitutes ~45% of the total mass of measured elements, consistent with previous results that traffic-
209 related emissions are dominated by Fe.³⁸ The fourth factor contributes more than 80% to As, Cd, and
210 Pb, and ~50% to Mn, Co, and Zn. As, Pb, and Cd are found in the exhaust from the activities
211 associated with coal burning processes and smelting furnace and have been used as tracers for coal
212 combustion emissions.³⁵

213 The relative contribution of each factor to the total mass concentration of measured elements is
214 shown in Figure 3a. Oil combustion was a negligible source, contributing <1% of total mass of
215 elements measured in Beijing, irrespective of the pollution level. Traffic-related emission was the
216 dominant source during low pollution days, contributing 65% of total mass of the measured elements,
217 followed by dust emission (21%) and coal combustion (14%). During moderate pollution days, the
218 contribution of traffic-related emission decreased significantly to 35%, and the contribution of dust
219 (30%) and coal combustion (34%) increased to around one third, respectively. During severe pollution
220 days, the coal combustion emission increased to be the dominant contribution (58%), followed by
221 traffic-related (28%) and dust emission (14%). Figure 3b shows the absolute contribution of each
222 factor to the mass concentrations of trace elements in PM_{2.5} at different pollution levels. With
223 increasing pollution level, the absolute contribution of coal combustion increased dramatically (from
224 0.15 to 1.24 $\mu\text{g m}^{-3}$). However, traffic emissions remained rather stable ($\sim 0.6 \mu\text{g m}^{-3}$). The observed
225 differences in both relative and absolute source contributions highlight the changes in emissions
226 and/or accumulation at different pollution levels.

227 **Health risk assessment.** The health risk from inhalation of particulate trace elements in
228 wintertime 2014 in Beijing is assessed. The calculated values of exposure concentration (EC),
229 inhalation reference concentration (RfC) and inhalation unit risk (IUR) are shown in Table S5. Mn

230 (10.8 ng m⁻³ for both children and adults) and Pb (3.16 ng m⁻³ for children and 12.6 ng m⁻³ for adults)
231 are found to have the highest exposure concentrations among the non-carcinogenic and carcinogenic
232 elements, respectively. The carcinogenic risks of inhaling particulate Cd, Co, and Ni are lower than
233 the precautionary criterion (10⁻⁶) both for children and adults. The carcinogenic risks of Pb and As are
234 higher than 10⁻⁶ for adults only, but the carcinogenic risks of Cr for children and adults both exceed
235 the precautionary criterion (Table S6). Furthermore, the combined carcinogenic risks from these trace
236 elements are 2.85×10⁻⁶ for children and 1.14×10⁻⁵ for adults, both higher than the precautionary
237 criterion, indicating that for every million children and million adults living in local environment,
238 approximately three children and twelve adults may develop cancer from inhaling these particulate
239 trace elements during their lifetime. The non-carcinogenic health risks via inhalation of particulate As,
240 Cd, Co, Cr, Mn, Ni and V are all lower than the safe limit (i.e., hazard quotient (HQ) <1) for both
241 children and adults (Table S6). However, the sum of HQ values from these trace elements is 1.14,
242 indicating accumulative non-carcinogenic risks.

243 In combination with the source profiles resolved by PMF, the element-specific risk is then
244 translated into source-specific risk. The results in Table S7 show that coal combustion has the highest
245 carcinogenic risk (5.31×10⁻⁶ for adults and 1.33×10⁻⁶ for children), followed by traffic-related
246 emissions (4.84×10⁻⁶ for adults and 1.21×10⁻⁶ for children). The carcinogenic risk of dust (1.05×10⁻⁶)
247 is slightly higher than the precautionary criterion (10⁻⁶) for adults only. As for the non-carcinogenic
248 health risk, the HQ value of individual emission sources identified in this study is lower than the safe
249 limit (HQ <1), but the accumulative HQ values from these emission sources are higher than 1 for both
250 children and adults.

251 The contribution of each source to health risk is finally calculated by combining the source-
252 specific risk and the PMF source apportionment results. For carcinogenic risk, traffic-related emission
253 was the dominant source (76.6%) during low pollution days. This percentage decreased to 44.4%
254 during moderate pollution days and contribution from coal combustion increased from 18.1% to
255 47.3%. The contribution from coal combustion increased further to 67% during severe pollution days
256 (Figure 4). These results suggest that significant carcinogenic risks can result from coal combustion
257 and traffic-related emission in wintertime Beijing. The contribution patterns for non-carcinogenic

258 risks are somewhat different from those for carcinogenic risks (Figure 4). Traffic-related emission was
259 the major contributor, but had a higher contribution (88.6%) during low pollution days. During
260 moderate pollution days, the traffic-related contribution decreased to 65.3% and coal combustion
261 increased to 30.2%. The contribution from coal combustion increased further to around 50%, showing
262 importance equal to traffic-related emission. The difference in health risks may be due to difference in
263 the source composition of PM_{2.5} at different pollution levels. Furthermore, the large contribution from
264 these two sources is associated with the high normalized health risk (i.e., carcinogenic or non-
265 carcinogenic risk normalized by element mass) of Cr, Co, Cd, As, and Ni from vehicular emission and
266 coal combustion (see Figure S6).

267 The results are in agreement with previous work on source apportionment that used actual
268 mortality data from six US cities.³⁹ Our work further extends to source-specific health risk assessment
269 from the concentration- and/or component-response risk assessment.^{40,41} In addition, other studies
270 relate specific particulate matter source apportionment with actual health data (e.g., hospital
271 admissions, or mortality).⁴²⁻⁴⁴ For example, Ozkaynak and Thurston showed that particles from
272 industrial sources (e.g., from iron/steel emissions) and coal combustion were more significant
273 contributors to human mortality than soil-derived particles.⁴² Ostro et al. found that several sources of
274 PM_{2.5}, including vehicle exhaust, fuel oil combustion, secondary nitrate/organics, minerals, secondary
275 sulfate/organics, and road dust, had statistically significant associations ($p < 0.05$) with cardiovascular
276 risks.⁴³ The results of Bell et al. suggested that some particle sources and constituents are more
277 harmful than others and that in this Connecticut/Massachusetts region the most harmful particles
278 include black carbon, calcium, and road dust PM_{2.5}.⁴⁴ In our work, traffic-related emission is the
279 dominant contributor for both carcinogenic and non-carcinogenic risks during low pollution days,
280 while coal combustion becomes equally or even more important contributor during moderate and
281 severe pollution days.

282 **Limitations of the risk assessment.** The carcinogenic and non-carcinogenic risks through
283 direct inhalation of particulate trace elements were calculated using US Environmental Protection
284 Agency (US EPA) human health risk assessment models (US EPA 2009).²⁴ In this study, we extend
285 such chemical component-response health risk assessment to source-specific risk assessment by

286 combining with source apportionment analysis. This assessment was made by a number of
287 assumptions, including the assessment models used, reference toxic data, default exposure parameters
288 and population characteristic parameters. Other exposure routes, including ingestion of atmospheric
289 particulates after deposition, dermal absorption of particles adhered to exposed skin, and atmospheric
290 particle exposure indoors, were not considered. Notwithstanding, inhalation is regarded as the most
291 efficient administration route of particulate matter into the human blood. Other important toxic
292 constituents in $PM_{2.5}$, e.g., atmospheric mercury, elemental carbon, and polycyclic aromatic
293 hydrocarbons, were not considered. Therefore, health risk assessments presented here are only limited
294 to trace elements. Nevertheless, the four sources identified through trace elements in this study are
295 widespread in China and therefore estimates are relevant on a regional scale. It should also be noted
296 that the source-related risks derived may differ from the sum of the risks from each constituent as the
297 actual risks of the mixtures may be synergistic. Despite uncertainties related with the absolute risk
298 assessments provided in this study, they may serve as useful (although untested here) indices for
299 comparing our results with previous and future work aiming at the determination of health risks
300 associated with the chemical composition and sources of particulate matter.^{15,30,45,46} In particular, the
301 risk indices determined in this study should be validated in future studies against direct measurements
302 of health impact.

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307 **Supporting Information**

308 The Supporting Information is available free of charge on the ACS Publications website at DOI:

309 Tables S1-S7 and Figures S1-S6 with additional experimental procedures and results as described in the
310 text (PDF).

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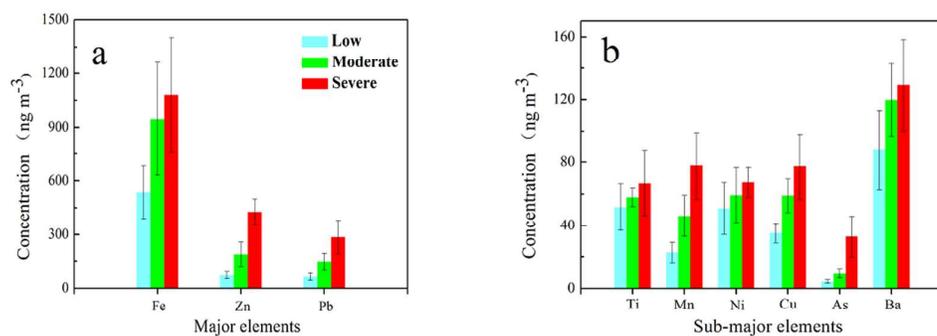
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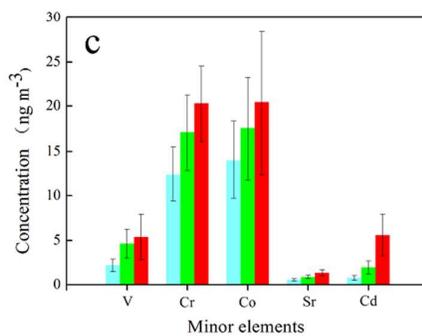
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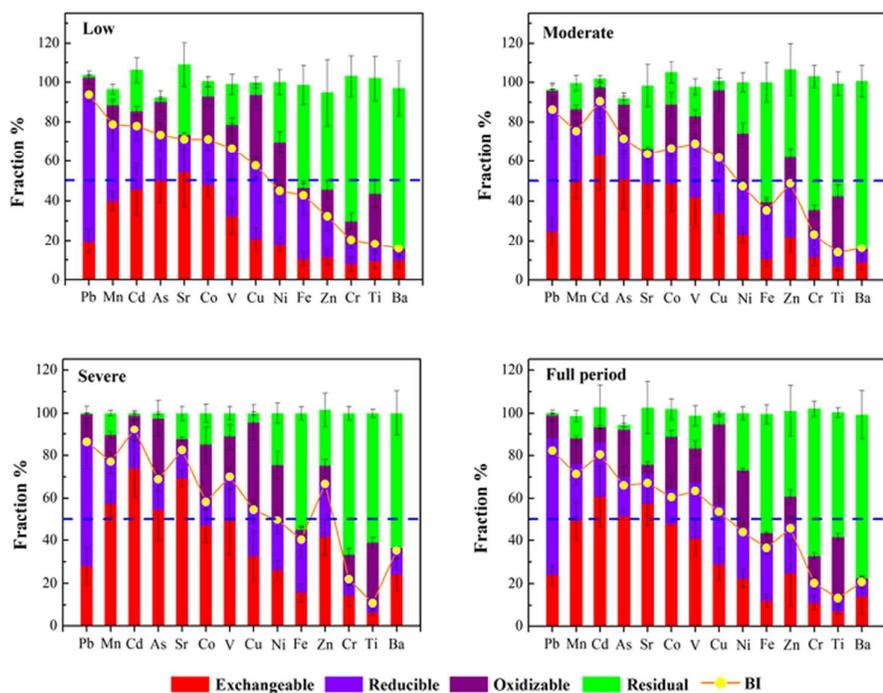


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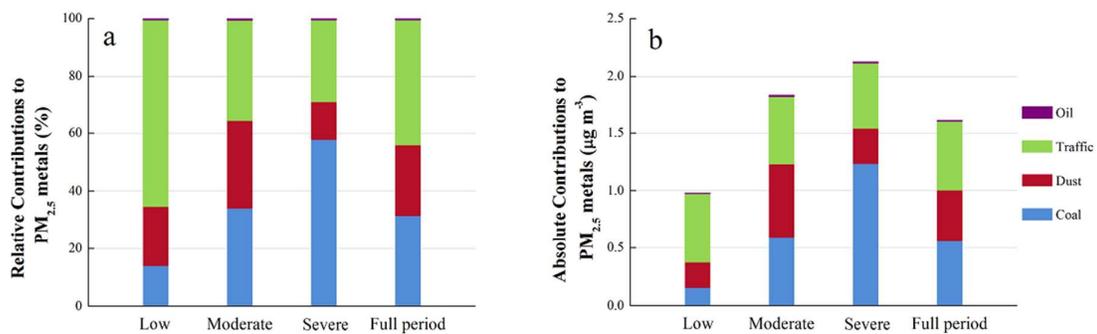
455 Figure 1. Concentration distribution of trace elements in PM_{2.5}: (a) major elements, (b) sub-major
456 elements and (c) minor elements during low pollution days, moderate pollution days and severe
457 pollution days.

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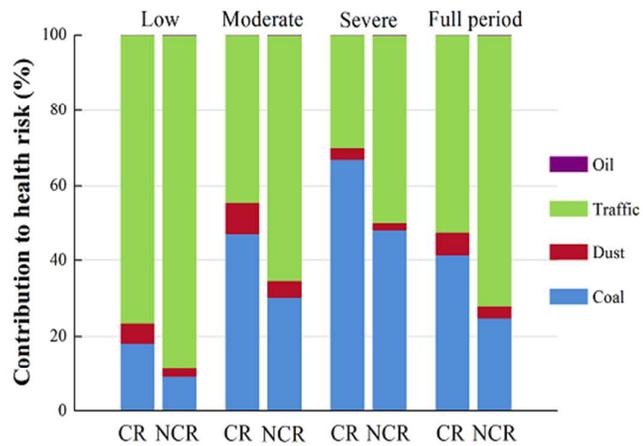
460 Figure 2. Exchangeable, reducible, oxidizable and residual fraction of trace elements in PM_{2.5} during
 461 low pollution days, moderate pollution days, severe pollution days and full period. Blue dashed line
 462 represents 50% bioavailability index (BI).



463

464 Figure 3. The relative (a) and absolute (b) source contributions to the measured trace elements in

465 $PM_{2.5}$ during low, moderate, and severe pollution days and entire measurement period, respectively.



466

467 Figure 4. The contribution of each source to carcinogenic risks (CR) and non-carcinogenic risks
 468 (NCR) via inhalation exposure to PM_{2.5}-bound trace elements on low, moderate, severe pollution days
 469 and full period in wintertime Beijing.

