

1 Measurement report: Oxidation potential of water-soluble 2 aerosol components in the southern and northern of Beijing

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14 15 Abstract

16 Water-soluble components have significant contribution to the oxidative
17 potential (OP) of atmospheric fine particles (PM_{2.5}), while our understanding of
18 water-soluble PM_{2.5} OP and its sources, as well as its relationship with water-soluble
19 components, is still limited. In this study, the water-soluble OP levels in wintertime
20 PM_{2.5} in the south and north of Beijing, representing the difference in sources, were
21 measured with dithiothreitol (DTT) assay. The volume normalized DTT (DTT_v) in the
22 north ($3.5 \pm 1.2 \text{ nmol min}^{-1} \text{ m}^{-3}$) was comparable to that in the south ($3.9 \pm 0.9 \text{ nmol}$
23 $\text{min}^{-1} \text{ m}^{-3}$), while the mass normalized DTT (DTT_m) in the north ($65 \pm 28 \text{ pmol min}^{-1}$
24 μg^{-3}) was almost twice that in the south ($36 \pm 14 \text{ pmol min}^{-1} \mu\text{g}^{-3}$). In both the south
25 and north of Beijing, DTT_v was better correlated with soluble elements instead of total
26 elements. In the north, soluble elements (mainly Mn, Co, Ni, Zn, As, Cd and Pb) and
27 water-soluble organic compounds, especially light-absorbing compounds (also known
28 as brown carbon), had positive correlations with DTT_v. However, in the south, the

29 DTT_v was mainly related to soluble As, Fe and Pb. The sources of DTT_v were further
30 resolved using the positive matrix factorization (PMF) model. Traffic-related
31 emissions (39%) and biomass burning (25%) were the main sources of DTT_v in the
32 south, and traffic-related emissions (> 50%) contributed the most of DTT_v in the north.
33 Our results indicate that vehicle emission was the important contributor to OP in
34 Beijing ambient PM_{2.5} and suggest that more study is needed to understand the
35 intrinsic relationship between OP and light absorbing organic compounds.

36

37 **1 Introduction**

38 Atmospheric fine particulate matter (PM_{2.5}) pollution is one of the major global
39 environmental issues, affecting air quality, climate and human health (Huang et al.,
40 2014; Burnett et al., 2018; An et al., 2019; Zheng et al., 2020). The exposure to PM_{2.5}
41 was estimated to be responsible for 8.9 million deaths worldwide in 2015, of which
42 28% occurred in China (Burnett et al., 2018). Numerous studies have shown that
43 oxidative stress is one possible mechanisms underlying the adverse effects of PM_{2.5}
44 on human health (Chowdhury et al., 2019; Lelieveld et al., 2021; Yu et al., 2022b;
45 Guascito et al., 2023). When entering the human body, PM_{2.5} can induce the
46 production of excessive reactive oxygen species (ROS) (e.g., H₂O₂, ·OH and ·O₂⁻),
47 leading to cellular redox imbalance and generating oxidative stress effects. The ability
48 of PM_{2.5} to cause oxidative stress is defined as oxidative potential (OP).

49 The methods to determine the OP of PM_{2.5} include cellular and acellular assays,
50 and acellular methods are more widely used than cellular methods (Charrier and
51 Anastasio, 2012; Xiong et al., 2017; Calas et al., 2018; Bates et al., 2019; Wang et al.,
52 2020b; Campbell et al., 2021; Oh et al., 2023). Among acellular methods, the
53 dithiothreitol (DTT) assay is extensively applied to determine the OP of ambient
54 particles (Charrier and Anastasio, 2012; Xiong et al., 2017; Liu et al., 2018; Wang et
55 al., 2020b; Puthussery et al., 2022; Wu et al., 2022a). DTT is a surrogate of cellular
56 reductants, and the consumption rate of DTT was used to assess the OP of PM_{2.5}.
57 Previous studies have shown that organic matters (e.g., water-soluble organic species

58 and PAHs) and some transition metals (e.g., Mn and Cu) are the important
59 contributors to DTT consumption of PM_{2.5} (Charrier and Anastasio, 2012; Verma et al.,
60 2015; Bates et al., 2019; Wu et al., 2022a; Wu et al., 2022b). For example, Charrier
61 and Anastasio (2012) measured the OP of PM_{2.5} in San Joaquin Valley, California and
62 reported that about 80% of DTT consumption was contributed by transition metals.
63 Verma et al. (2015) measured the OP of water-soluble PM_{2.5} in the southeastern
64 United States and reported that about 60% of DTT activity was contributed by water-
65 soluble organics. The mixtures of metals and organics may produce synergistic or
66 antagonistic effects, such as $\cdot\text{O}_2^-$ produced from oxidation of DTT by quinones is
67 more efficiently transformed to $\cdot\text{OH}$ in the presence of Fe, while the DTT
68 consumption and $\cdot\text{OH}$ generation of quinones are reduced in the presence of Cu
69 (Xiong et al., 2017; Yu et al., 2018; Bates et al., 2019).

70 A number of studies have investigated the OP of water-soluble components in
71 PM_{2.5}, which show that the average water-soluble OP values in urban areas ranged
72 from 0.1 to 10 nmol min⁻¹ m⁻³ (Fang et al., 2016; Liu et al., 2018; Chen et al., 2019;
73 Wu et al., 2022a; Yu et al., 2022a; Xing et al., 2023). Due to the complexity in
74 chemical composition and sources of PM_{2.5} that determine the OP levels, the sources
75 of OP are also diverse (Verma et al., 2015; Bates et al., 2019; Tuet et al., 2019; Yu et
76 al., 2019; Cao et al., 2021). Several studies have investigated the emission sources and
77 ambient samples to identify the sources of OP (Tuet et al., 2019; Yu et al., 2019; Wang
78 et al., 2020b; Cao et al., 2021), which include both primary and secondary sources.
79 For example, Cao et al. (2021) measured the water-soluble OP of PM_{2.5} samples from
80 six biomass and five coal burning emissions in China, with average values of 4.5-7.4
81 and 0.5-2.1 pmol min⁻¹ μg⁻¹, respectively. Tong et al. (2018) investigated the OP of
82 secondary organic aerosols (SOA) from oxidation of naphthalene, isoprene and β-
83 pinene with $\cdot\text{OH}$ or O₃, which were 104 ± 7.6, 48 ± 7.9 and 36 ± 3.1 pmol min⁻¹ μg⁻¹,
84 respectively. Verma et al. (2014) identified the sources of water-soluble OP of PM_{2.5}
85 in Atlanta, United States from June 2012 to September 2013 with positive matrix
86 factorization (PMF) and chemical mass balance (CMB) methods, of which biomass

87 burning was the largest contributor. Wang et al. (2020b) quantified the sources of
88 water-soluble OP of PM_{2.5} in Xi'an, China in 2017 using PMF and multiple linear
89 regression (MLR) methods, with significant contributions from secondary sulfates,
90 vehicle emissions and coal combustion. Some studies have also measured the OP of
91 particles with different particle sizes, and reported that smaller size fractions typically
92 have higher ROS activity compared to large PM size fractions (Saffari et al., 2014;
93 Shafer et al., 2016; Basis et al., 2023). For example, Basis et al. (2023) measured the
94 OP of water-soluble fraction of size segregated PM (< 0.49, 0.49-0.95, 0.95-1.5, 1.5-
95 3.0, 3.0-7.2 and > 7.2 μm) collected during the cold and warm periods at an urban site
96 in Thessaloniki, northern Greece, and the results showed that the total DTT activity of
97 the PM < 3 μm size fraction were higher (2-5 times) than that of PM > 3 μm size
98 fraction in both warm and cold periods. Despite these efforts, comparative studies on
99 the differences in pollution levels and sources of PM_{2.5} OP in different districts are
100 still limited.

101 In this study, the DTT activity of water-soluble matter in PM_{2.5} samples collected
102 simultaneously in the southern and northern of Beijing in January 2018 were
103 measured. The concentration and light absorption of water-soluble organic carbon
104 (WSOC), as well as the concentrations of 14 trace elements and 7 light-absorbing
105 nitroaromatic compounds (NACs) were quantified. The sources of DTT activity were
106 then identified with PMF model. The results acquired in this study provide a
107 comparison of PM_{2.5} OP in different districts of Beijing and its connection with
108 organic compounds, trace elements and sources, which could be helpful for further
109 study of the regional differences in the effects of PM_{2.5} on human health.

110

111 **2 Materials and methods**

112 **2.1 Sampling**

113 Ambient 24 h integrated PM_{2.5} filter samples were collected from January 1 to 31,
114 2018 simultaneously in the south (the Dingfuzhuang village (DFZ), Daxing district;
115 39.61°N, 116.28°E) and north (the National Center for Nanoscience and Technology

116 (NCNT), Haidian district; 39.99°N, 116.32°E) of Beijing (Figure S1). The distance
117 between the two sampling sites is about 42 km. The south site is surrounded by
118 agricultural, industrial, and transportation areas, and the north site is surrounded by
119 residential, transportation and commercial areas. PM_{2.5} samples were collected on pre-
120 baked (780 °C, 3 h) quartz-fiber filters (20.3 × 25.4 cm; Whatman, QM-A, Clifton, NJ,
121 USA) using high-volume PM_{2.5} samplers (1.13 m³ min⁻¹; Tisch, Cleveland, OH, USA)
122 which were placed on the roof of buildings at heights of about 5 m (south) and 20 m
123 (north) above the ground. 31 samples were collected at each site. After collection, the
124 samples were wrapped in baked aluminum foils and stored in a freezer (-20 °C) until
125 further analysis.

126 **2.2 Chemical analysis**

127 The mass of PM_{2.5} on the filter was measured by a digital microbalance with a
128 precision of 0.1 mg (LA130S-F, Sartorius, Germany) after 24-h equilibration at a
129 constant temperature (20-23 °C) and humidity (35-45%) chamber. Each filter was
130 weighted at least two times, and the deviations for blank and sampled filters among
131 the repetitions were less than 5 and 10 µg, respectively. The PM_{2.5} mass concentration
132 was calculated by dividing the weight difference before and after sampling by the
133 volume of sampled air.

134 For WSOC analysis, one punch (1.5 cm² for concentration analysis and 0.526
135 cm² for light absorption measurement) of filter was taken from each sample and
136 extracted ultrasonically with ultrapure water (> 18.2 MΩ cm) for 30 min. After, the
137 extracts were filtered with a 0.45 µm PVDF pore syring filter to remove insoluble
138 substances. Finally, the concentration of WSOC was measured with a total organic
139 carbon-total nitrogen analyzer (TOC-L, Shimadzu, Japan; (Ho et al., 2015)) and the
140 light absorption of WSOC was measured by an UV-Vis spectrophotometer (300-700
141 nm; Ocean Optics, USA) equipped with a liquid waveguide capillary cell (LWCC-
142 3100, World Precision Instruments, Sarasota, FL, USA; (Yuan et al., 2020)). The
143 absorption coefficient (Abs) of WSOC was calculated according to formula S1 in the
144 Supporting Information (SI).

145 The total concentration and soluble fraction concentration of 14 trace elements
146 (i.e., Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Cd, Ba, and Pb) were quantified by an
147 inductively coupled plasma mass spectrometer (ICP-MS, 7700x, Agilent Technologies,
148 USA), and the details are shown in the SI. For soluble fraction concentration analysis,
149 a punch of filter (47 mm diameter) was extracted with ultrapure water and then
150 centrifuged from residues. For total concentration analysis, another 47 mm diameter
151 filter of the same sample was used and digested with 10 mL HNO₃ and 1 mL HF at
152 180 °C for 12 h. The extracts were then heated and concentrated to ~ 0.1 mL, and
153 diluted to 5 mL with 2% HNO₃. Afterwards, the diluents were filtered with a 0.22 μm
154 PTFE pore syring filter and stored in a freezer (-4 °C) until further ICP-MS analysis.

155 The concentrations of organic markers (including levoglucosan, mannosan,
156 galactosan, hopanes (including 17α(H)-22,29,30-trisnorhopane, 17α(H),21β(H)-30-
157 norhopane, 17β(H),21α(H)-30-norhopane, 17β(H),21α(H)-hopane, 17β(H),21α(H)-
158 hopane and 17β(H),21α(H)-hopane), picene, phthalic acid, isophthalic acid and
159 terephthalic acid) and light-absorbing NACs (including 4-nitrophenol (4NP), 2-
160 methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 4-nitrocatechol
161 (4NC), 3-methyl-5-nitrocatechol (3M5NC), 4-methyl-5-nitrocatechol (4M5NC) and
162 4-nitro-1-naphthol (4N1N)) were determined by a gas chromatograph–mass
163 spectrometer (GC-MS; Agilent Technologies, Santa Clara, CA, USA) following the
164 method described elsewhere (Wang et al., 2020a), and more details about the analysis
165 can be found in SI. All of the results reported in this study were corrected for blanks.

166 **2.3 Oxidative potential**

167 The DTT assay was applied to determine the oxidative potential of water-soluble
168 components in PM_{2.5} according to the method by Gao et al. (2017). In brief, a quarter
169 of a 47 mm filter was ultrasonically extracted with 5 mL ultrapure water for 30 min
170 and then filtered with a 0.45 μm PVDF pore syring filter to remove insoluble
171 substances. Several studies have shown that ultrasonic treatment of samples can lead
172 to an increase in their OP values (Miljevic et al., 2014; Jiang et al., 2019), however,
173 there was also a study showed that the difference in OP values of water-soluble PM_{2.5}

174 measured by DTT assay was small for samples extracted by ultrasonic and shaking
175 (Gao et al., 2017). Consistent with the extraction methods for organic markers and
176 trace elements, ultrasonic method was used to extract samples for DTT analysis.
177 Afterwards, 0.5 mL of the extract was mixed with 1 mL of potassium phosphate
178 buffer (pH = 7.4) and 0.5 mL of 2 mM DTT in a brown vial, and then placed in a
179 water bath at 37 °C. Then, 20 μ L of this mixture was taken at designated time
180 intervals (2, 7, 13, 20, and 28 min) and mixed with 1 mL trichloroacetic acid (TCA;
181 1% w/v) in another brown vial to terminate the reaction. Then, 0.5 mL of 5,5'-
182 dithiobis-(2-nitrobenzoic acid) (DTNB; 2.5 μ M) and 2 mL of tris buffer (pH = 8.9)
183 were added to form 2-nitro-5-thiobenzonic acid (TNB) which has light absorption at
184 412 nm. Finally, the absorption of TNB was measured by a LWCC-UV-Vis. The DTT
185 consumption rate was quantified by the remaining DTT concentration at different
186 reaction times. Daily solution blanks and filter blanks were analyzed in parallel with
187 samples to evaluate the consistency of the system performance. Besides, for every 10
188 samples, one sample was chosen to be measured three times to check the
189 reproducibility, and the relative standard deviation was lower than 5%. Ambient
190 samples were corrected for filter blank. The DTT activities were normalized by the
191 volume of sampled air (DTT_v , $\text{nmol min}^{-1} \text{m}^{-3}$) and the mass concentration of $\text{PM}_{2.5}$
192 (DTT_m , $\text{pmol min}^{-1} \mu\text{g}^{-1}$).

193 Considering that for samples containing a significant amount of substances
194 whose DTT response is non-linear with $\text{PM}_{2.5}$ concentration (e.g., Cu, Mn), the DTT_m
195 value depends on the concentration of $\text{PM}_{2.5}$ added to the reaction solution (Charrier
196 et al., 2016). The response of DTT_m to $\text{PM}_{2.5}$ concentration added to the reaction
197 solution was analyzed using sample containing high concentrations of soluble Cu and
198 Mn (Figure S2). When the $\text{PM}_{2.5}$ concentration added to the reaction solution is less
199 than $150 \mu\text{g mL}^{-1}$, the DTT_m response is greatly affected by the difference in added
200 $\text{PM}_{2.5}$ concentration; however, when the $\text{PM}_{2.5}$ concentration added to the reaction
201 solution is greater than $150 \mu\text{g mL}^{-1}$, the DTT_m response is less affected by the
202 difference in $\text{PM}_{2.5}$ concentration ($< 12\%$). In this study, the concentration of $\text{PM}_{2.5}$

203 added to the reaction solution of most samples from the two sites was greater than 150
204 $\mu\text{g mL}^{-1}$ (ranged from 79 to 749 $\mu\text{g mL}^{-1}$, with an average of 409 ± 164 and 207 ± 95
205 $\mu\text{g mL}^{-1}$ in the south and north, respectively), therefore, the difference in $\text{PM}_{2.5}$
206 concentration added to the reaction solution of different samples should had a
207 relatively small impact on the difference in DTT_m values of different samples. This
208 study did not consider the impact of metal precipitation in phosphate matrix on the
209 measured DTT values, as there is not a straightforward method to correct the artifact
210 caused by this phenomenon (Yalamanchili et al., 2023).

211 **2.4 Source apportionment**

212 The sources of DTT activities were identified and quantified using PMF model
213 implemented by the multilinear engine (ME-2; (Paatero, 1997)) following the method
214 described in our previous studies (Huang et al., 2014; Yuan et al., 2020). For each site,
215 31 samples (a total of 62 samples) and 23 species were input into PMF model. The
216 number of samples is higher than the number of species. The input data include
217 species concentration (including DTT_v , 14 trace elements and 8 organic markers) and
218 uncertainties. The species-specific uncertainties were calculated following Liu et al.
219 (2017). For a clear separation of sources profiles, the contribution of corresponding
220 markers was set to 0 in the sources unrelated to the markers (see Table S1). More
221 details are described in SI (PMF analysis).

222

223 **3 Results and discussion**

224 **3.1 DTT activity and concentrations of water-soluble $\text{PM}_{2.5}$ components**

225 Figure 1 shows the daily variation of DTT activity, light absorption of WSOC at
226 wavelength 365 nm (Abs_{365}), together with the concentrations of $\text{PM}_{2.5}$, WSOC,
227 NACs and total elements in the south and north of Beijing. Their average values are
228 shown in Table S2. Generally, the average values of $\text{PM}_{2.5}$, WSOC, Abs_{365} , NACs and
229 total elements were higher in the south than in the north. Specifically, the
230 concentrations of $\text{PM}_{2.5}$ and WSOC in the south ($122 \pm 49 \mu\text{g m}^{-3}$ and $8.1 \pm 5.0 \mu\text{gC}$
231 m^{-3} , respectively) were both about two times higher than that in the north ($62 \pm 28 \mu\text{g}$

232 m^{-3} and $4.0 \pm 2.0 \mu\text{gC m}^{-3}$, respectively), indicating that the proportion of WSOC in
233 $\text{PM}_{2.5}$ was similar in the south and north. However, the Abs_{365} in the south was about
234 three times that in the north, indicating that the chemical composition of WSOC was
235 different between the south and north. Previous studies have reported that NACs are
236 the main water-soluble light-absorbing organic compounds (also known as brown
237 carbon, BrC) of $\text{PM}_{2.5}$ (Lin et al., 2017; Huang et al., 2020; Li et al., 2020). For the 7
238 NACs quantified in this study, the total concentration of nitrophenols (4NP, 2M4NP
239 and 3M4NP), nitrocatechols (4NC, 3M5NC and 4M5NC), and 4N1N in the south
240 ($108 \pm 73 \text{ ng m}^{-3}$, $118 \pm 91 \text{ ng m}^{-3}$ and $12 \pm 8.2 \text{ ng m}^{-3}$, respectively) was about three,
241 five and four times, respectively, those in the north ($35 \pm 22 \text{ ng m}^{-3}$, $24 \pm 30 \text{ ng m}^{-3}$
242 and $3.1 \pm 3.0 \text{ ng m}^{-3}$, respectively). These results indicate that the sources and
243 emission strength of water-soluble organic compounds were different in the south and
244 north of Beijing, suggesting the different contribution of water-soluble organic
245 compounds to DTT activity. The concentration trends of total trace elements were also
246 different between the south and north of Beijing, with $\text{Fe} > \text{Zn} > \text{Ti} > \text{Mn} > \text{Cu} > \text{Ba} >$
247 $\text{Pb} > \text{Sr} > \text{Cr} > \text{As} > \text{V} > \text{Ni} > \text{Cd} > \text{Co}$ in the south, and $\text{Fe} > \text{Ti} > \text{Zn} > \text{Ba} > \text{Mn} >$
248 $\text{Pb} > \text{Cu} > \text{Cr} > \text{Sr} > \text{As} > \text{Ni} > \text{V} > \text{Cd} > \text{Co}$ in the north. It should be noted that
249 although the contents of $\text{PM}_{2.5}$, WSOC and total elements measured in this study were
250 higher in the south than in the north, the average DTT_v value in the south (3.9 ± 0.9
251 $\text{nmol min}^{-1} \text{ m}^{-3}$) was comparable to that in the north ($3.5 \pm 1.2 \text{ nmol min}^{-1} \text{ m}^{-3}$),
252 meanwhile, the average DTT_m value was much higher (1.8 times) in the north ($65 \pm$
253 $28 \text{ pmol min}^{-1} \mu\text{g}^{-1}$) than in the south ($36 \pm 14 \text{ pmol min}^{-1} \mu\text{g}^{-1}$). Ahmad et al. (2021)
254 also reported that the concentrations of $\text{PM}_{2.5}$, WSOC, and most elements in Lahore,
255 Pakistan, were higher than those in Peshawar, Pakistan, while the DTT_v values of the
256 two sites were similar, and the DTT_m value in Peshawar was higher than that in
257 Lahore. The lower DTT_m in the south than in the north may be due to the increased
258 $\text{PM}_{2.5}$ in the south containing more substances with no or little contribution to DTT
259 activity, and indicates that the intrinsic OP of water-soluble components of $\text{PM}_{2.5}$ was
260 higher in the north than in the south. The similar DTT_v values in the south and north

261 indicate that the exposure-relevant OP of water-soluble components of PM_{2.5} was
262 comparable in the two sites, and the water-soluble DTT_v was not consistent with the
263 content of water-soluble substances. Due to the complex chemical composition of
264 PM_{2.5}, there may also be antagonistic and synergistic effects, contributing to the
265 inconsistent relationship between DTT activity and compounds content (Xiong et al.,
266 2017; Lionette et al., 2021).

267 Figure 2 shows the comparison of water-soluble PM_{2.5} DTT activity measured in
268 this study with those measured in other regions of Asia during similar periods. It can
269 be seen that the DTT_v values measured in Beijing in this study were lower than that in
270 Jinzhou, Tianjin, Yantai, and Shanghai in China, Lahore and Peshawar in Pakistan,
271 and Delhi in India (Liu et al., 2018; Ahmad et al., 2021; Puthussery et al., 2022; Wu et
272 al., 2022a), higher than that in Xi'an, Nanjing, Hangzhou, Guangzhou, and Shenzhen
273 in China (Wang et al., 2019; Wang et al., 2020b; Ma et al., 2021; Yu et al., 2022c;
274 Xing et al., 2023), and comparable with that in Ningbo, China (Chen et al., 2022).
275 Different from DTT_v, the DTT_m value measured in NCNT in Beijing was similar with
276 that in Jinzhou, Tianjin, Yantai, Shanghai and Ningbo in China (Liu et al., 2018; Chen
277 et al., 2022; Wu et al., 2022a), and higher than that in other regions. The differences in
278 water-soluble DTT activity of PM_{2.5} in different regions can be explained by the
279 differences in chemical composition, sources and atmospheric formation processes
280 (Tong et al., 2017; Wong et al., 2019; Daellenbach et al., 2020; Wang et al., 2020b;
281 Cao et al., 2021). For example, Cao et al. (2021) reported the water-soluble DTT
282 activity of PM_{2.5} from biomass and coal burning emissions in China, and the average
283 value of biomass burning (4.5-7.4 pmol min⁻¹ μg⁻¹) was much higher than that of coal
284 burning (0.5-2.1 pmol min⁻¹ μg⁻¹). Tuet et al. (2017) measured the water-soluble DTT
285 activity of SOA generated under different precursors and reaction conditions, with
286 SOA from naphthalene photooxidation under RO₂ + NO-dominant dry reaction
287 conditions had the highest DTT activity.

288 **3.2 Correlation between DTT activity and water-soluble PM_{2.5} components**

289 Figure 3 shows the correlations of DTT_v with PM_{2.5}, WSOC and Abs₃₆₅ in the

290 south and north of Beijing. It can be seen that the correlation coefficient between
291 DTT_v and $PM_{2.5}$ was moderate in both the south ($r = 0.42$) and north ($r = 0.45$),
292 indicating that the OP of particles cannot be evaluated solely by the total $PM_{2.5}$
293 concentration. The correlations between DTT_v with WSOC and Abs_{365} were strong in
294 the north (r of 0.69 and 0.70, respectively), while relatively weak in the south (r of
295 0.41 and 0.40, respectively). The high correlations between DTT_v with WSOC and
296 Abs_{365} in the north of Beijing qualitatively agree with previous studies in Xi'an, China
297 and Atlanta, United States (Verma et al., 2012; Chen et al., 2019), and suggest that
298 water-soluble organic matter, especially BrC, has a significant contribution to DTT
299 consumption in the north. Light-absorbing BrC typically has conjugated electrons,
300 making it more likely to transport electrons for catalytic reactions, thereby
301 contributing to DTT activity (Chen et al., 2019; Wu et al., 2022). Further, in the north,
302 the DTT_v was closely related to the concentrations of NACs (r of 0.57 to 0.79) (Figure
303 S3), suggesting that NACs may be important contributors to DTT consumption. Feng
304 et al. (2022) reported the positive correlations between NACs and biomarkers in
305 saliva and urine (interleukin-6 and 8-hydrox-2'-deoxyguanosine). Zhang et al. (2023)
306 also reported that NACs are major proinflammatory components in organic aerosols,
307 contributing about 24% of the interleukin-8 response of all compounds detected by
308 Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) in
309 electrospray ionization negative mode (ESI-). Certainly, it may also be other
310 substances related to NACs that contribute to the DTT activity, including those not
311 detected in this study, driving the good correlation between NACs and DTT_v in the
312 north of Beijing, which is worth studying in the future.

313 The correlation coefficients between DTT_v and 14 trace elements are shown in
314 Figure 4. Generally, the correlations between DTT_v and soluble elements were higher
315 than that between DTT_v and total elements in both the south and north of Beijing. For
316 soluble elements, in the south, the DTT_v showed positive correlations with Mn, Fe, Cr,
317 Co, As and Pb ($r > 0.5$), while in the north, it exhibited strong positive correlations
318 with Mn, Co, Ni, Zn, As, Cd and Pb ($r > 0.7$), indicating the different sources of DTT_v

319 in the south and north of Beijing. It is worth noting that the concentrations of all
320 soluble elements were higher in the south than in the north (Figure S4), while the
321 correlation between DTT_v and most soluble elements was lower in the south than in
322 the north (Figure 4). The high correlations between DTT_v and soluble elements in the
323 north of Beijing suggests that soluble elements also had a significant contribution to
324 DTT consumption. The low correlations between DTT_v and soluble elements in the
325 south of Beijing may be due to the nonlinear relationship between DTT consumption
326 and element concentration (Charrier and Anastasio, 2012; Wu et al., 2022a). As shown
327 in Figure S5, the relationship between most soluble trace elements and DTT_v was
328 more non-linear than linear. As the concentration of soluble elements increases, the
329 growth rate of DTT_v obviously decreases.

330 In addition to being associated with individual water-soluble species, the
331 interactions between metals and organic compounds also affect the consumption of
332 DTT (Xiong et al., 2017; Wu et al., 2022b), with both synergistic and antagonistic
333 effects. For example, Wu et al. (2022b) measured the DTT consumption of Fe(III) and
334 Cu(II) interacting with 1,4-naphthoquinone, 9,10-phenanthraquinone, citric acid, and
335 4-nitrocatechol, respectively. Their results showed that Cu(II) had antagonistic effects
336 in interacting with most organics except for citric acid, and Fe(III) had an additive
337 effect on DTT consumption of 1,4-naphthoquinone and citric acid, while it had an
338 antagonistic effect on 1,4-naphthoquinone and 9,10-phenanthraquinone. Due to the
339 complex composition of water-soluble organic aerosols, the knowledge about the
340 effects of organics and metal-organic interactions on DTT activity are still limited,
341 especially the effects of BrC chromophores and their interactions with metals.

342 **3.3 Sources of DTT activity**

343 This study analyzed eight organic markers (including levoglucosan, mannosan,
344 and galactosan for biomass burning, hopanes for vehicle emissions, picene for coal
345 combustion, and phthalic acid, isophthalic acid and terephthalic acid for secondary
346 formation) to help identify the sources of DTT activity. The average concentrations of
347 these organic markers are shown in Table S2. The correlation coefficients between

348 DTT_v and organic markers are shown in Figure S6. In the south, levoglucosan,
349 mannosan, galactosan, and hopanes had moderate correlation with DTT_v (r of 0.41 to
350 0.48); phthalic acid, isophthalic acid and terephthalic acid had low to moderate
351 correlation with DTT_v (r of 0.28 to 0.54); picene had low correlation with DTT_v (r of
352 0.21). These results suggest that biomass burning and vehicle emissions could have
353 significant contribution to water-soluble PM_{2.5} OP in the south. In the north, hopanes
354 had the highest correlation with DTT_v (r = 0.70), indicating that vehicle emissions
355 could have an important contribution. Levoglucosan, mannosan, galactosan, phthalic
356 acid, isophthalic acid, terephthalic acid, and picene had moderate to high correlations
357 with DTT_v in the north, suggesting that biomass and coal burning, and secondary
358 formation may also have certain contribution to water-soluble PM_{2.5} OP.

359 To further quantify the sources of DTT activity in the south and the north of
360 Beijing, the PMF model, which was widely used for the source apportionment of
361 PM_{2.5} OP (Liu et al., 2018; Shen et al., 2022; Cui et al., 2023), was applied. The input
362 species include DTT_v, soluble elements and organic markers, and five to seven factors
363 were examined. Due to the oil factor mixed with vehicle emissions factor in the five-
364 factor solution, and there was no new reasonable factor when increasing the factor
365 number to seven in the PMF analysis (Figure S7). Finally, six factors were resolved
366 and quantified using PMF model in the south and north of Beijing, including biomass
367 burning, coal burning, traffic-related, dust, oil combustion, and secondary formation,
368 and the profiles of these sources are shown in Figure S8. The uncertainties of PMF
369 analysis for these sources were 2-14%. Factor 1 is characterized by high contribution
370 of levoglucosan, mannosan, and galactosan, mainly from biomass burning (Huang et
371 al., 2014; Chow et al., 2022). The DTT activity of biomass burning organic aerosol
372 was measured by Wong et al. (2019), which was 48 ± 6 pmol min⁻¹ μg⁻¹ of WSOC.
373 Liu et al. (2018) quantified the sources of DTT_v in coastal cities (Jinzhou, Tianjin, and
374 Yantai) in China with PMF model and multiple linear regression method, and the
375 results showed that biomass burning contributed 28% on average in winter. Factor 2
376 exhibits a large fraction of picene, Zn, Mn, Cd, As, and Pb, which is considered to be

377 coal burning (Huang et al., 2014; Huang et al., 2018). Joo et al. (2018) measured the
378 DTT activity of PM_{2.5} emitted from coal combustion at different temperatures, with
379 the highest values of $26 \pm 21 \text{ pmol min}^{-1} \mu\text{g}^{-1}$ and $0.10 \pm 0.06 \text{ nmol min}^{-1} \text{ m}^{-3}$
380 occurring at 550 °C. Factor 3 is identified as traffic-related emissions, which is
381 characterized by the higher loading of hopanes, Ba, Sr, Cu and Ni (Huang et al., 2018;
382 Chow et al., 2022). Vreeland et al. (2017) measured the DTT activity of PM_{2.5} emitted
383 by side street and highway vehicles in Atlanta, with values of $0.78 \pm 0.60 \text{ nmol min}^{-1}$
384 m^{-3} and $1.1 \pm 0.60 \text{ nmol min}^{-1} \text{ m}^{-3}$, respectively. Ting et al. (2023) reported that the
385 DTT activity of PM_{2.5} from vehicle emissions in Ziqing tunnel in Taiwan, China, was
386 0.15-0.46 $\text{nmol min}^{-1} \text{ m}^{-3}$. Factor 4, secondary formation, which is identified by high
387 levels of phthalic acid, isophthalic acid, and terephthalic acid (Al-Naiema and Stone,
388 2017; Wang et al., 2020a). Verma et al. (2014) reported that secondary formation
389 contributed about 30% to the water-soluble DTT activity of PM_{2.5} in urban Atlanta. It
390 is worth noting that the DTT activity of SOA generated from different precursors is
391 different (Tuet et al., 2017; Tong et al., 2018). For example, the DTT activity of SOA
392 from naphthalene was higher than that from isoprene (Tuet et al., 2017; Tong et al.,
393 2018). Factor 5 is dominated by crustal elements Fe and Ti, mainly from dust (Huang
394 et al., 2018). The DTT activity of atmospheric particulate matter during dust periods
395 were reported in previous studies (Chirizzi et al., 2017; Khoshnamvand et al., 2023)
396 and it has a low contribution in this study. Factor 6 is identified as oil combustion
397 because of the high levels of V and Ni (Moreno et al., 2011; Minguillón et al., 2014;
398 Huang et al., 2018).

399 The source contributions of DTT_v in the south and north of Beijing are shown in
400 Figure 5, exhibiting obvious district differences. In the south, traffic-related emissions
401 (39%) and biomass burning (25%) had the most contribution to DTT_v, followed by
402 secondary formation (17%), coal burning (15%), dust (2%), and oil combustion (2%).
403 In the north, traffic-related emissions (52%) had the highest contribution to DTT_v,
404 followed by coal burning (20%), secondary formation (13%), biomass burning (8%),
405 oil combustion (4%), and dust (3%). The absolute contribution of each source to

406 DTT_v varies by 1.2-3.4 times between the south and north of Beijing (Table S3). The
407 large district differences in sources of DTT_v of water-soluble PM_{2.5} call for more
408 research on the relationship between sources, chemical composition, formation
409 processes and OP of PM_{2.5}.

410

411 **4 Conclusions**

412 In this study, the water-soluble OP of ambient PM_{2.5} collected in winter in the
413 south and north of Beijing were quantified, together with the concentration and light
414 absorption of WSOC, and concentrations of 7 light-absorbing NACs and 14 trace
415 elements. The average DTT_v value was comparable in the south ($3.9 \pm 0.9 \text{ nmol min}^{-1}$
416 m^{-3}) and north ($3.5 \pm 1.2 \text{ nmol min}^{-1} \text{ m}^{-3}$), while the DTT_m was higher in the north (65
417 $\pm 28 \text{ pmol min}^{-1} \mu\text{g}^{-1}$) than in the south ($36 \pm 14 \text{ pmol min}^{-1} \mu\text{g}^{-1}$), indicating that the
418 exposure-relevant OP of water-soluble components of PM_{2.5} was similar in the two
419 sites and that the intrinsic OP of water-soluble components of PM_{2.5} was higher in the
420 north than in the south. The correlation between DTT_v and soluble elements was
421 higher than that between DTT_v and total elements in both the south and north. In the
422 north, the DTT_v was strongly correlated with soluble Mn, Co, Ni, Zn, As, Cd and Pb
423 ($r > 0.7$), and in the south it positively correlated with Mn, Fe, Cr, Co, As and Pb ($r >$
424 0.5). In addition, in the north the DTT_v was also positively correlated with WSOC,
425 Abs₃₆₅ and NACs (r of 0.56 to 0.79), while in the south it was weakly correlated ($r \leq$
426 0.4). These results indicate that in the north trace elements and water-soluble organic
427 compounds, especially BrC chromophores, both had significant contributions to DTT
428 consumption, and in the south the consumption of DTT may be mainly from trace
429 elements. Six sources of DTT_v were resolved with the PMF model, including biomass
430 burning, coal burning, traffic-related, dust, oil combustion, and secondary formation.
431 On average, traffic-related emissions (39%) and biomass burning (25%) were the
432 major contributors of DTT_v in the south, and traffic-related emissions (52%) was the
433 predominated source in the north. The differences in DTT_v sources in the south and
434 north of Beijing suggest that the relationship between source emissions and

435 atmospheric processes and PM_{2.5} OP deserve further exploration in order to better
436 understand the regional differences of health impacts of PM_{2.5}. Besides, in order to
437 gain a more comprehensive understanding of the regional differences in PM_{2.5} OP,
438 sources and its relationship with chemical composition, longer periods and different
439 seasonal datasets are also need to be studied in the future.

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443 **Date availability.** Raw data used in this study can be obtained from the following
444 open link: <https://doi.org/10.5281/zenodo.10791126> (Yuan et al., 2024). It is also
445 available on request by contacting the corresponding authors.

446

447 **Supplement.** The supplement related to this article is available online.

448

449 **Author contributions.** RJH designed the study. Data analysis was done by WY, CL,
450 LY, HY and RJH. WY, CL, LY, HY and RJH interpreted data, prepared the display
451 items and wrote the manuscript. All authors commented on and discussed the
452 manuscript.

453

454 **Competing interests.** The authors declare that they have no conflict of interest.

455

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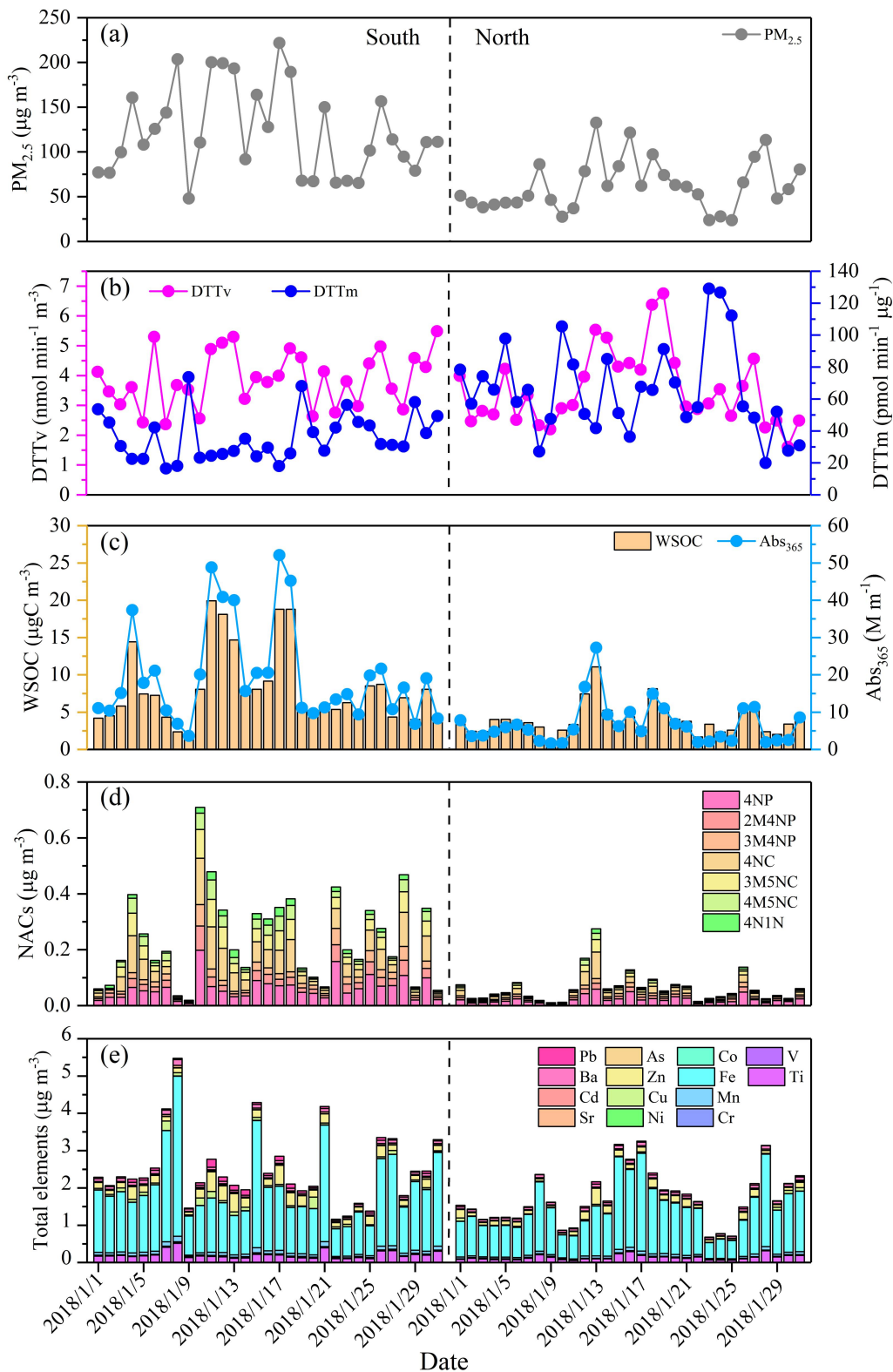
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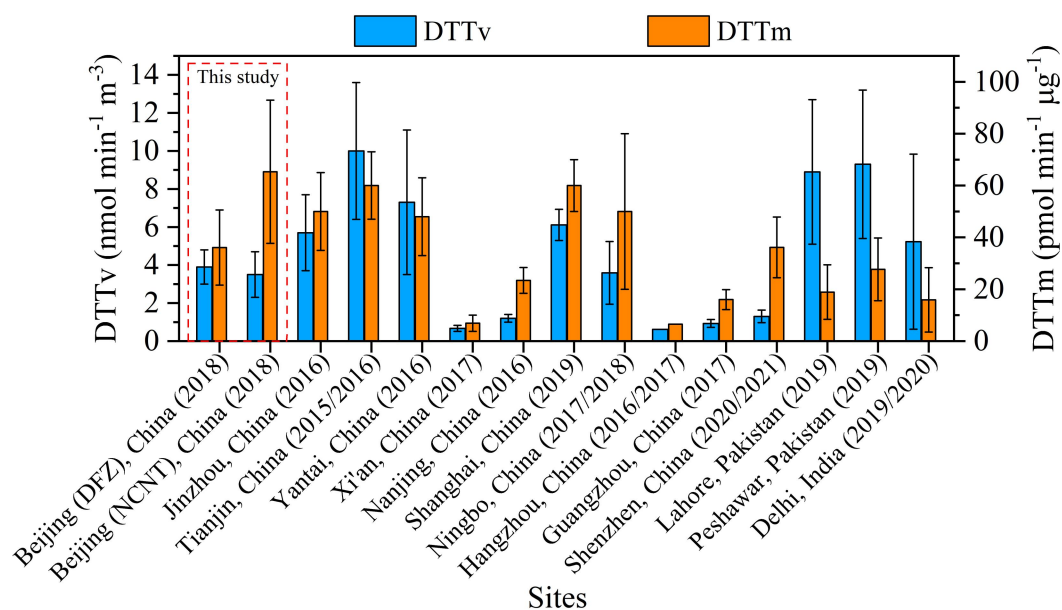
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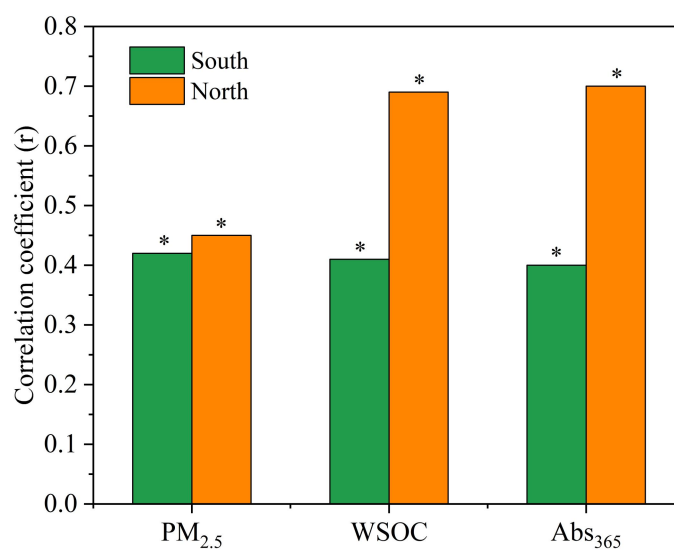
805 **Figure 1.** Time series of (a) $PM_{2.5}$ concentration, (b) DTT_v and DTT_m , (c)
 806 concentration and light absorption at wavelength 365 nm (Abs_{365}) of WSOC,
 807 concentrations of (d) NACs and (e) total elements.



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809 **Figure 2.** Comparison of DTT_v and DTT_m values of water-soluble PM_{2.5} measured in
 810 this study with those measured in other areas of Asia during similar period.

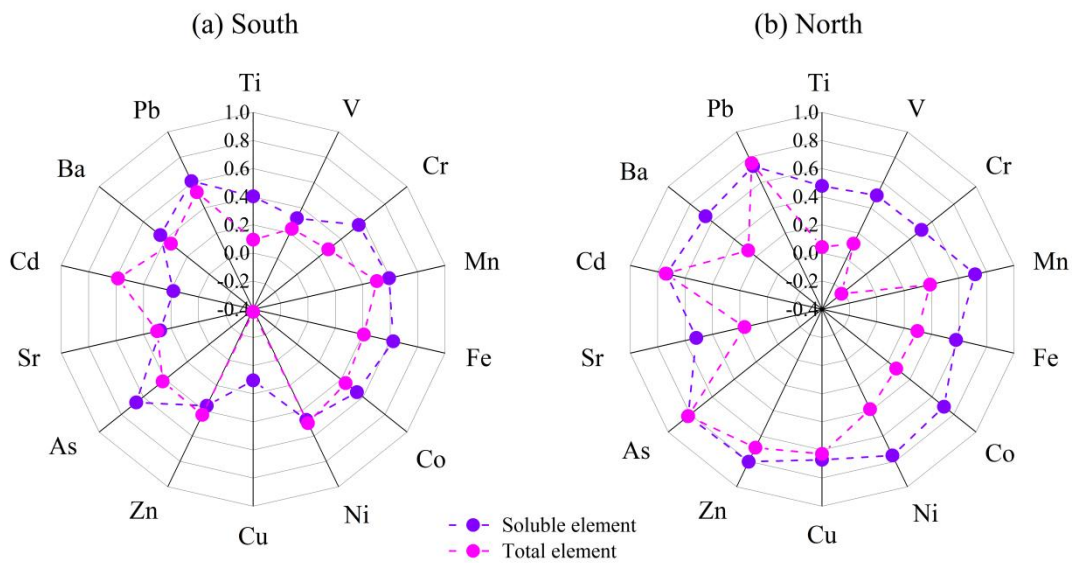
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813 **Figure 3.** Correlation coefficients between DTT_v and PM_{2.5}, WSOC, and Abs₃₆₅ in the
 814 south and north of Beijing (* indicates correlation is significant at the 0.05 level).

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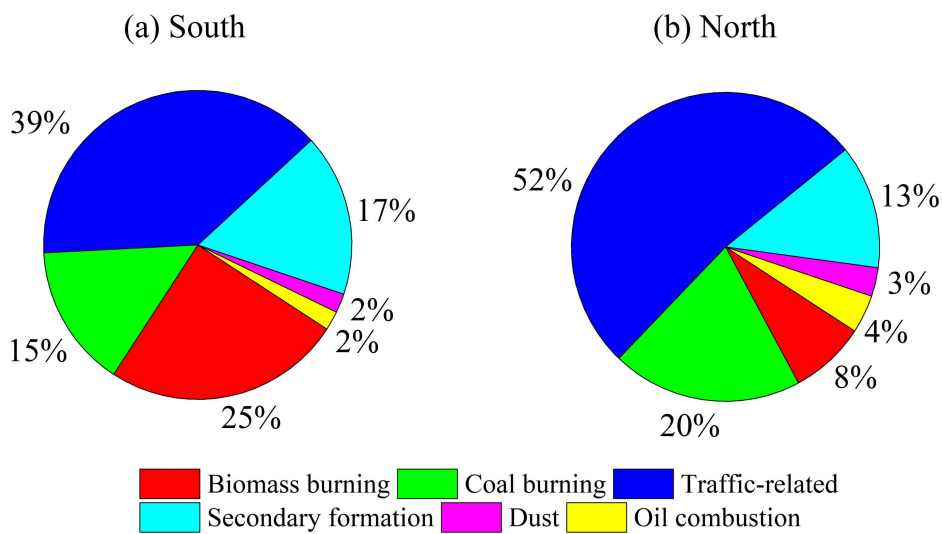


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817 **Figure 4.** Correlation coefficients between DTT_v and elements in the (a) south and (b)

818 north of Beijing.

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821 **Figure 5.** Contributions of resolved sources to DTT_v in the (a) south and (b) north of

822 Beijing.