



Measurement report: Oxidation potential of water-soluble aerosol components in the south and north of Beijing

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Abstract. Water-soluble components significantly contribute to the oxidative potential (OP) of atmospheric fine particles (PM_{2.5}), but our understanding of the water-soluble PM_{2.5} OP and its sources, as well as its relationship with water-soluble components, is still limited. In this study, the water-soluble OP levels in wintertime PM_{2.5} in the south and north of Beijing, representing the difference in sources, were measured with the dithiothreitol (DTT) assay. The volume-normalized DTT (DTT_v) in the north ($3.5 \pm 1.2 \text{ nmol min}^{-1} \text{ m}^{-3}$) was comparable to that in the south ($3.9 \pm 0.9 \text{ nmol min}^{-1} \text{ m}^{-3}$), while the mass-normalized DTT (DTT_m) in the north ($65 \pm 28 \text{ pmol min}^{-1} \mu\text{g}^{-3}$) was almost twice that in the south ($36 \pm 14 \text{ pmol min}^{-1} \mu\text{g}^{-3}$). In both the south and north of Beijing, DTT_v was better correlated with soluble elements instead of total elements. In the north, soluble elements (mainly Mn, Co, Ni, Zn, As, Cd and Pb) and water-soluble organic compounds, especially light-absorbing compounds (also known as brown carbon), had positive correlations with DTT_v. However, in the south, DTT_v was mainly related to soluble As, Fe and Pb. The sources of DTT_v were further resolved using the positive matrix factorization (PMF) model. Traffic-related emissions (39 %) and biomass burning (25 %) were the main sources of DTT_v in the south, and traffic-related emissions (> 50 %) contributed the most to DTT_v in the north. Our results indicate that vehicle emission was an important contributor to the OP in Beijing ambient PM_{2.5} and suggest that more study is needed to understand the intrinsic relationship between the OP and light-absorbing organic compounds.

1 Introduction

Atmospheric fine particulate matter (PM_{2.5}) pollution is one of the major global environmental issues, affecting air quality, climate and human health (Huang et al., 2014; Burnett et al., 2018; An et al., 2019; Zheng et al., 2020). The exposure to PM_{2.5} was estimated to be responsible for 8.9 million deaths worldwide in 2015, of which 28 % occurred in China (Burnett et al., 2018). Numerous studies have shown that oxidative stress is one of the possible mechanisms underlying the adverse effects of PM_{2.5} on human health (Chowdhury et al., 2019; Lelieveld et al., 2021; Yu et al., 2022a; Guasc-

ito et al., 2023). When entering the human body, PM_{2.5} can induce the production of excessive reactive oxygen species (ROS) (e.g., H₂O₂, ·OH and ·O₂⁻), leading to cellular redox imbalance and generating oxidative stress effects. The ability of PM_{2.5} to cause oxidative stress is defined as oxidative potential (OP).

The methods to determine the OP of PM_{2.5} include cellular and acellular assays, and acellular methods are more widely used than cellular methods (Charrier and Anastasio, 2012; Xiong et al., 2017; Calas et al., 2018; Bates et al., 2019; Y. Wang et al., 2020; Campbell et al., 2021; Oh et al., 2023). Among acellular methods, the dithiothreitol (DTT) assay is

extensively applied to determine the OP of ambient particles (Charrier and Anastasio, 2012; Xiong et al., 2017; Liu et al., 2018; Y. Wang et al., 2020; Puthussery et al., 2022; Wu et al., 2022a). DTT is a surrogate of cellular reductants, and the consumption rate of DTT was used to assess the OP of PM_{2.5}. Previous studies have shown that organic matters (e.g., water-soluble organic species and polycyclic aromatic hydrocarbons (PAHs)) and some transition metals (e.g., Mn and Cu) are the important contributors to DTT consumption of PM_{2.5} (Charrier and Anastasio, 2012; Verma et al., 2015; Bates et al., 2019; Wu et al., 2022a, b). For example, Charrier and Anastasio (2012) measured the OP of PM_{2.5} in San Joaquin Valley, California, and reported that about 80 % of DTT consumption was contributed by transition metals. Verma et al. (2015) measured the OP of water-soluble PM_{2.5} in the southeastern United States and reported that about 60 % of DTT activity was contributed by water-soluble organics. The mixtures of metals and organics may produce synergistic or antagonistic effects; for example, $\cdot\text{O}_2^-$ produced from oxidation of DTT by quinones is more efficiently transformed to $\cdot\text{OH}$ in the presence of Fe, while the DTT consumption and $\cdot\text{OH}$ generation of quinones are reduced in the presence of Cu (Xiong et al., 2017; Yu et al., 2018; Bates et al., 2019).

A number of studies have investigated the OP of water-soluble components in PM_{2.5}, which show that the average water-soluble OP values in urban areas ranged from 0.1 to 10 nmol min⁻¹ m⁻³ (Fang et al., 2016; Liu et al., 2018; Chen et al., 2019; Wu et al., 2022a; Q. Yu et al., 2022; Xing et al., 2023). Due to the complexity in chemical composition and sources of PM_{2.5} that determine the OP levels, the sources of the OP are also diverse (Verma et al., 2015; Bates et al., 2019; Tuet et al., 2019; Yu et al., 2019; Cao et al., 2021). Several studies have investigated the emission sources and ambient samples to identify the sources of the OP (Tuet et al., 2019; Yu et al., 2019; Y. Wang et al., 2020; Cao et al., 2021), which include both primary and secondary sources. For example, Cao et al. (2021) measured the water-soluble OP of PM_{2.5} samples from six biomass and five coal burning emissions in China, with average values of 4.5–7.4 and 0.5–2.1 pmol min⁻¹ μg⁻¹, respectively. Tong et al. (2018) investigated the OPs of secondary organic aerosols (SOAs) from oxidation of naphthalene, isoprene and β-pinene with $\cdot\text{OH}$ or O₃, which were 104±7.6, 48±7.9 and 36±3.1 pmol min⁻¹ μg⁻¹, respectively. Verma et al. (2014) identified the sources of the water-soluble OP of PM_{2.5} in Atlanta, United States, from June 2012 to September 2013 with positive matrix factorization (PMF) and chemical mass balance (CMB) methods, of which biomass burning was the largest contributor. Y. Wang et al. (2020) quantified the sources of the water-soluble OP of PM_{2.5} in Xi'an, China, in 2017 using PMF and multiple linear regression (MLR) methods, with significant contributions from secondary sulfates, vehicle emissions and coal combustion. Some studies have also measured the OP of particles with different particle sizes

and reported that smaller size fractions typically have higher ROS activity compared to large PM size fractions (Saffari et al., 2014; Shafer et al., 2016; Besis et al., 2023). For example, Besis et al. (2023) measured the OP of the water-soluble fraction of size-segregated PM (< 0.49, 0.49–0.95, 0.95–1.5, 1.5–3.0, 3.0–7.2 and > 7.2 μm) collected during cold and warm periods at an urban site in Thessaloniki, northern Greece, and the results showed that the total DTT activity of the PM < 3 μm size fraction was higher (2–5 times) than that of the PM > 3 μm size fraction in both warm and cold periods. Despite these efforts, comparative studies on the differences in pollution levels and sources of the PM_{2.5} OP in different districts are still limited.

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

2 Materials and methods

2.1 Sampling

Ambient 24 h integrated PM_{2.5} filter samples were collected from 1 to 31 January 2018 simultaneously in the south (the village of Dingfuzhuang (DFZ), Daxing District; 39.61° N, 116.28° E) and north (National Center for Nanoscience and Technology (NCNT), Haidian District; 39.99° N, 116.32° E) of Beijing (Fig. S1 in the Supplement). The distance between the two sampling sites is about 42 km. The south site is surrounded by agricultural, industrial and transportation areas, and the north site is surrounded by residential, transportation and commercial areas. PM_{2.5} samples were collected on pre-baked (780°, 3 h) quartz-fiber filters (20.3 × 25.4 cm; Whatman, QM-A, Clifton, NJ, USA) using high-volume PM_{2.5} samplers (1.13 m⁻³ min⁻¹; Tisch Environmental, Cleveland, OH, USA) which were placed on the roof of buildings at heights of about 5 m (south) and 20 m (north) above the ground. A total of 31 samples were collected at each site. After collection, the samples were wrapped in baked aluminum foil and stored in a freezer (−20 °C) until further analysis.

2.2 Chemical analysis

The mass of PM_{2.5} on the filter was measured by a digital microbalance with a precision of 0.1 mg (LA130S-F, Sartorius, Germany) after 24 h equilibration in a chamber with constant

temperature (20–23 °C) and humidity (35%–45%). Each filter was weighed at least two times, and the deviations for blank and sampled filters among the repetitions were less than 5 and 10 µg, respectively. The PM_{2.5} mass concentration was calculated by dividing the weight difference before and after sampling by the volume of sampled air.

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

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

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

2.3 Oxidative potential

The DTT assay was applied to determine the oxidative potential of water-soluble components in PM_{2.5} according to the method by Gao et al. (2017). In brief, a quarter of a 47 mm filter was ultrasonically extracted with 5 mL ultrapure water for 30 min and then filtered with a 0.45 µm PVDF pore syringe filter to remove insoluble substances. Several studies have shown that ultrasonic treatment of samples can lead to an increase in their OP values (Miljevic et al., 2014; Jiang et al., 2019); however, there was also a study that showed that the difference in OP values of water-soluble PM_{2.5} measured by the DTT assay was small for samples extracted by ultrasonic and shaking (Gao et al., 2017). Consistent with the extraction methods for organic markers and trace elements, an ultrasonic method was used to extract samples for DTT analysis. Afterwards, 0.5 mL of the extract was mixed with 1 mL of potassium phosphate buffer (pH = 7.4) and 0.5 mL of 2 mM DTT in a brown vial and then placed in a water bath at 37 °C. Then, 20 µL of this mixture was taken at designated time intervals (2, 7, 13, 20 and 28 min) and mixed with 1 mL trichloroacetic acid (TCA; 1% w/v) in another brown vial to terminate the reaction. Then, 0.5 mL of 5,5'-dithiobis-(2-nitrobenzoic acid) (DTNB; 2.5 µM) and 2 mL of tris buffer (pH = 8.9) were added to form 2-nitro-5-thiobenzoic acid (TNB), which has a maximum light absorption at 412 nm. Finally, the absorption of TNB was measured by a UV–Vis spectrometer equipped with a LWCC. The DTT consumption rate was quantified by the remaining DTT concentration at different reaction times. Daily solution blanks and filter blanks were analyzed in parallel with samples to evaluate the consistency of the system performance. In addition, for every 10 samples, one sample was chosen to be measured three times to check the reproducibility, and the relative standard deviation was lower than 5%. Ambient samples were corrected for filter blanks. The DTT activities were normalized by the volume of sampled air (DTT_v; nmol min⁻¹ m⁻³) and the mass concentration of PM_{2.5} (DTT_m; pmol min⁻¹ µg⁻¹).

Considering that for samples containing a significant amount of substances whose DTT response is non-linear with PM_{2.5} concentration (e.g., Cu, Mn), the DTT_m value depends on the concentration of PM_{2.5} added to the reaction solution (Charrier et al., 2016). The response of DTT_m to PM_{2.5} concentration added to the reaction solution was analyzed using a sample containing high concentrations of soluble Cu and Mn (Fig. S2). When the PM_{2.5} concentration added to the reaction solution is less than 150 µg mL⁻¹, the DTT_m response is greatly affected by the difference in added PM_{2.5} concentration; however, when it is greater than 150 µg mL⁻¹, the DTT_m response is less affected by the difference in PM_{2.5} concentration (< 12%). In this study, the concentration of PM_{2.5} added to the reaction solution of most samples from the two sites was greater than 150 µg mL⁻¹ (ranged from 79 to 749 µg mL⁻¹, with an average of 409 ± 164 and 207 ± 95 µg mL⁻¹ in the south and north, respectively); therefore, the dif-

ference in $PM_{2.5}$ concentration added to the reaction solution of different samples should have had a relatively small impact on the difference in DTT_m values of different samples. This study did not consider the impact of metal precipitation in the phosphate matrix on the measured DTT values, as there is not a straightforward method to correct the artifact caused by this phenomenon (Yalamanchili et al., 2023).

2.4 Source apportionment

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

3 Results and discussion

3.1 DTT activity and concentrations of water-soluble $PM_{2.5}$ components

Figure 1 shows the daily variation of DTT activity, light absorption of WSOC at wavelength 365 nm (Abs_{365}), together with the concentrations of $PM_{2.5}$, WSOC, NACs and total elements in the south and north of Beijing. Their average values are shown in Table S2. Generally, the average values of $PM_{2.5}$, WSOC, Abs_{365} , NACs and total elements were higher in the south than in the north. Specifically, the concentrations of $PM_{2.5}$ and WSOC in the south ($122 \pm 49 \mu\text{g m}^{-3}$ and $8.1 \pm 5.0 \mu\text{gC m}^{-3}$, respectively) were both about 2 times higher than those in the north ($62 \pm 28 \mu\text{g m}^{-3}$ and $4.0 \pm 2.0 \mu\text{gC m}^{-3}$, respectively), indicating that the proportion of WSOC in $PM_{2.5}$ was similar in the south and north. However, the Abs_{365} in the south was about 3 times that in the north, indicating that the chemical composition of WSOC was different between the south and north. Previous studies have reported that NACs are the main water-soluble light-absorbing organic compounds (also known as brown carbon, BrC) of $PM_{2.5}$ (Lin et al., 2017; Huang et al., 2020; Li et al., 2021). For the 7 NACs quantified in this study, the total concentration of nitrophenols (4NP, 2M4NP and 3M4NP), nitrocatechols (4NC, 3M5NC and 4M5NC) and 4N1N in the south (108 ± 73 , 118 ± 91 and $12 \pm 8.2 \text{ ng m}^{-3}$, respectively) was about 3, 5 and 4 times, respectively, that in the north (35 ± 22 , 24 ± 30 and $3.1 \pm 3.0 \text{ ng m}^{-3}$, respectively).

These results indicate that the sources and emission strength of water-soluble organic compounds were different in the south and north of Beijing, suggesting the different contribution of water-soluble organic compounds to DTT activity. The concentration trends of total trace elements were also different between the south and north of Beijing, with $\text{Fe} > \text{Zn} > \text{Ti} > \text{Mn} > \text{Cu} > \text{Ba} > \text{Pb} > \text{Sr} > \text{Cr} > \text{As} > \text{V} > \text{Ni} > \text{Cd} > \text{Co}$ in the south and $\text{Fe} > \text{Ti} > \text{Zn} > \text{Ba} > \text{Mn} > \text{Pb} > \text{Cu} > \text{Cr} > \text{Sr} > \text{As} > \text{Ni} > \text{V} > \text{Cd} > \text{Co}$ in the north. It should be noted that although the contents of $PM_{2.5}$, WSOC and total elements measured in this study were higher in the south than in the north, the average DTT_v value in the south ($3.9 \pm 0.9 \text{ nmol min}^{-1} \text{ m}^{-3}$) was comparable to that in the north ($3.5 \pm 1.2 \text{ nmol min}^{-1} \text{ m}^{-3}$); meanwhile, the average DTT_m value was much higher (1.8 times) in the north ($65 \pm 28 \text{ pmol min}^{-1} \mu\text{g}^{-1}$) than in the south ($36 \pm 14 \text{ pmol min}^{-1} \mu\text{g}^{-1}$). Ahmad et al. (2021) also reported that the concentrations of $PM_{2.5}$, WSOC and most elements in Lahore, Pakistan, were higher than those in Peshawar, Pakistan, while the DTT_v values of the two sites were similar, and the DTT_m value in Peshawar was higher than that in Lahore. The lower DTT_m in the south than in the north may be due to the increased $PM_{2.5}$ in the south containing more substances with no or little contribution to DTT activity and indicates that the intrinsic OP of water-soluble components of $PM_{2.5}$ was higher in the north than in the south. The similar DTT_v values in the south and north indicate that the exposure-relevant OP of water-soluble components of $PM_{2.5}$ was comparable at the two sites, and water-soluble DTT_v was not consistent with the content of water-soluble substances. Due to the complex chemical composition of $PM_{2.5}$, there may also be antagonistic and synergistic effects contributing to the inconsistent relationship between DTT activity and compounds' content (Xiong et al., 2017; Lionetto et al., 2021).

Figure 2 shows the comparison of water-soluble $PM_{2.5}$ DTT activity measured in this study with that measured in other regions of Asia during similar periods. It can be seen that the DTT_v values measured in Beijing in this study were lower than those in Jinzhou, Tianjin, Yantai, and Shanghai in China; Lahore and Peshawar in Pakistan; and Delhi in India (Liu et al., 2018; Ahmad et al., 2021; Puthussery et al., 2022; Wu et al., 2022a). They were higher than those in Xi'an, Nanjing, Hangzhou, Guangzhou and Shenzhen in China (Y. Wang et al., 2019, 2020; Ma et al., 2021; Yu et al., 2022b; Xing et al., 2023) and comparable with those in Ningbo, China (Chen et al., 2022). Different from DTT_v , the DTT_m value measured in NCNT in Beijing was similar to that in Jinzhou, Tianjin, Yantai, Shanghai and Ningbo in China (Liu et al., 2018; Chen et al., 2022; Wu et al., 2022a) and higher than that in other regions. The differences in water-soluble DTT activity of $PM_{2.5}$ in different regions can be explained by the differences in chemical composition, sources and atmospheric formation processes (Tong et al., 2017; Wong et al., 2019; Daellenbach et al., 2020; Y. Wang et

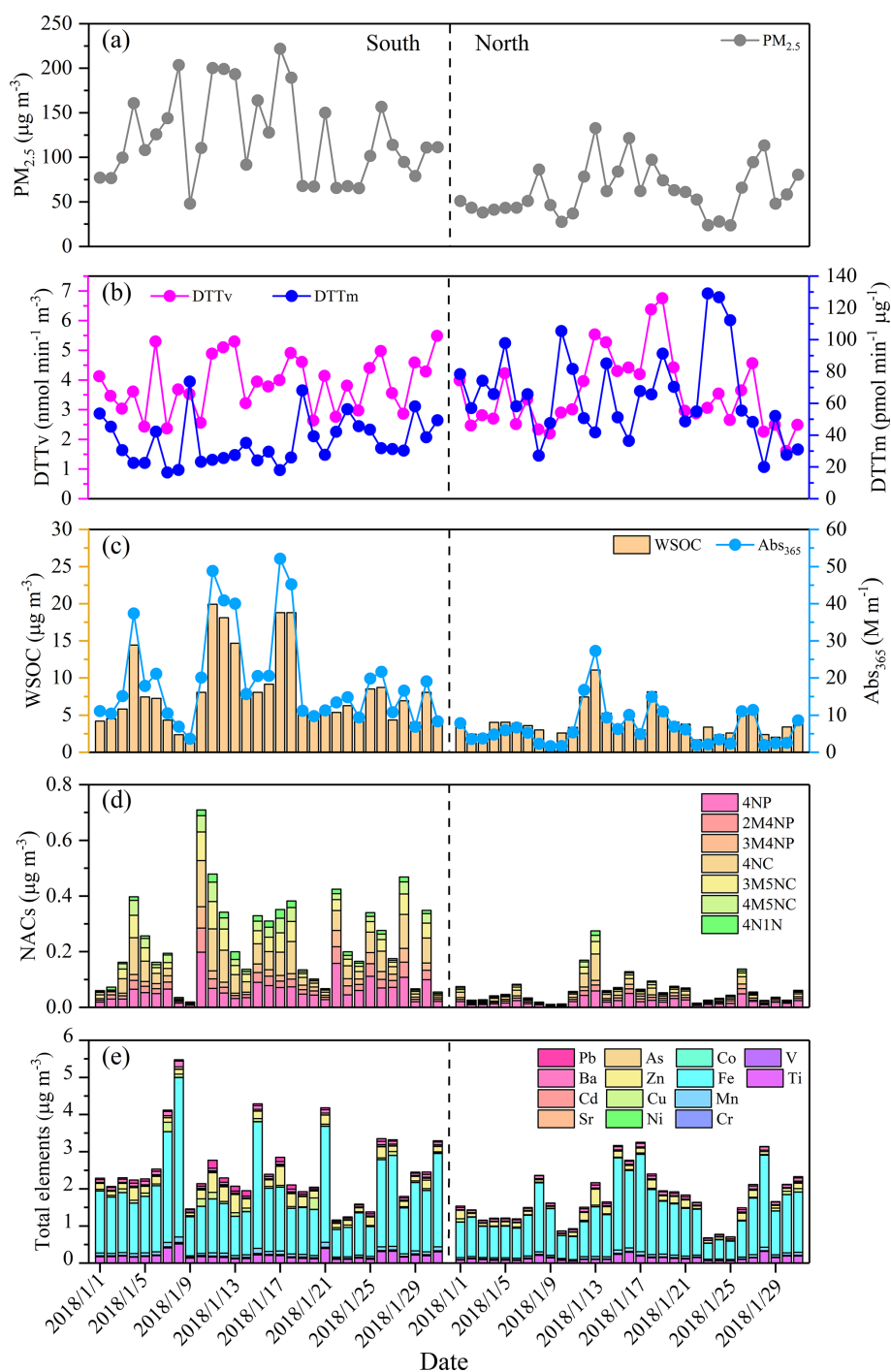


Figure 1. Time series of (a) PM_{2.5} concentration and (b) DTT_v and DTT_m. (c) Concentration and light absorption at wavelength 365 nm (Abs₃₆₅) of WSOC and concentrations of (d) NACs and (e) total elements.

al., 2020; Cao et al., 2021). For example, Cao et al. (2021) reported the water-soluble DTT activity of PM_{2.5} from biomass and coal burning emissions in China, and the average value of biomass burning (4.5–7.4 pmol min⁻¹ μg⁻¹) was much higher than that of coal burning (0.5–2.1 pmol min⁻¹ μg⁻¹). Tuet et al. (2017) measured the water-soluble DTT activity

of SOA generated under different precursors and reaction conditions, with SOA from naphthalene photooxidation under RO₂+NO-dominant dry reaction conditions having the highest DTT activity.

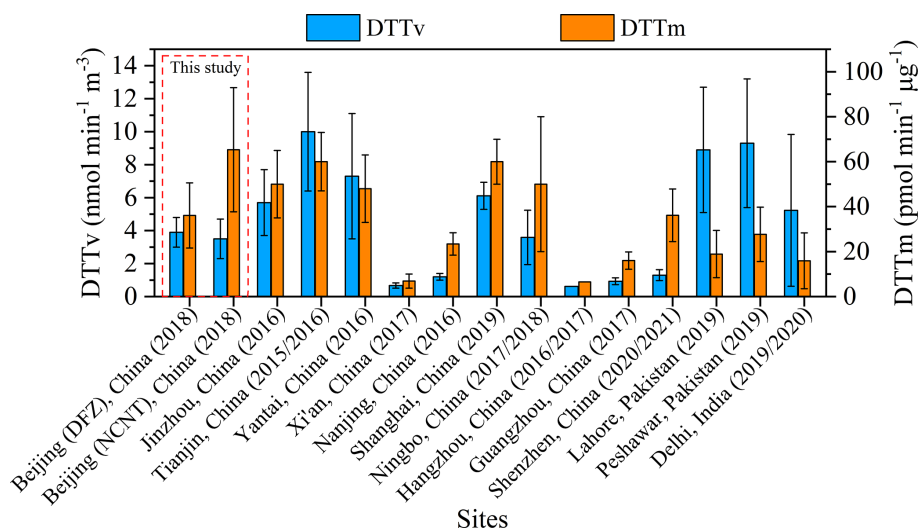


Figure 2. Comparison of DTT_v and DTT_m values of water-soluble $PM_{2.5}$ measured in this study with those measured in other areas of Asia during a similar period.

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

Figure 3 shows the correlations of DTT_v with $PM_{2.5}$, WSOC and Abs_{365} in the south and north of Beijing. It can be seen that the correlation coefficient between DTT_v and $PM_{2.5}$ was moderate in both the south ($r = 0.42$) and north ($r = 0.45$), indicating that the OP of particles cannot be evaluated solely by the total $PM_{2.5}$ concentration. The correlations between DTT_v and WSOC and Abs_{365} were strong in the north (r of 0.69 and 0.70, respectively), while they were relatively weak in the south (r of 0.41 and 0.40, respectively). The high correlations between DTT_v and WSOC and Abs_{365} in the north of Beijing qualitatively agree with previous studies in Xi'an, China, and Atlanta, United States (Verma et al., 2012; Chen et al., 2019), and suggest that water-soluble organic matter, especially BrC, has a significant contribution to DTT consumption in the north. Light-absorbing BrC typically has conjugated electrons, making it more likely to transport electrons for catalytic reactions, thereby contributing to DTT activity (Chen et al., 2019; Wu et al., 2022). Further, in the north, DTT_v was closely related to the concentrations of NACs (r of 0.57 to 0.79) (Fig. S3), suggesting that NACs may be important contributors to DTT consumption. Feng et al. (2022) reported positive correlations between NACs and biomarkers in saliva and urine (interleukin-6 and 8-hydrox-2'-deoxyguanosine). Zhang et al. (2023) also reported that NACs are major proinflammatory components in organic aerosols, contributing about 24 % of the interleukin-8 response of all compounds detected by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) in electrospray ionization negative mode (ESI⁻). Certainly, it may also be other substances related to NACs that contribute to the DTT activity, including those not detected in this study,

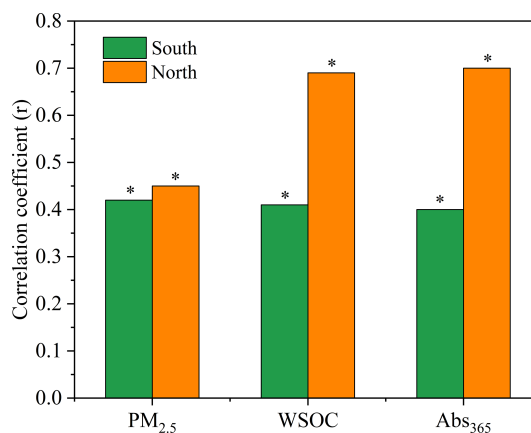


Figure 3. Correlation coefficients between DTT_v and $PM_{2.5}$, WSOC and Abs_{365} in the south and north of Beijing (* indicates correlation is significant at the 0.05 level).

driving the good correlation between NACs and DTT_v in the north of Beijing, which is worth studying in the future.

The correlation coefficients between DTT_v and 14 trace elements are shown in Fig. 4. Generally, the correlations between DTT_v and soluble elements were higher than those between DTT_v and total elements in both the south and north of Beijing. For soluble elements, in the south, DTT_v showed positive correlations with Mn, Fe, Cr, Co, As and Pb ($r > 0.5$), while in the north, it exhibited strong positive correlations with Mn, Co, Ni, Zn, As, Cd and Pb ($r > 0.7$), indicating the different sources of DTT_v in the south and north of Beijing. It is worth noting that the concentrations of all soluble elements were higher in the south than in the north (Fig. S4), while the correlation between DTT_v and most soluble elements was lower in the south than in the north (Fig. 4).

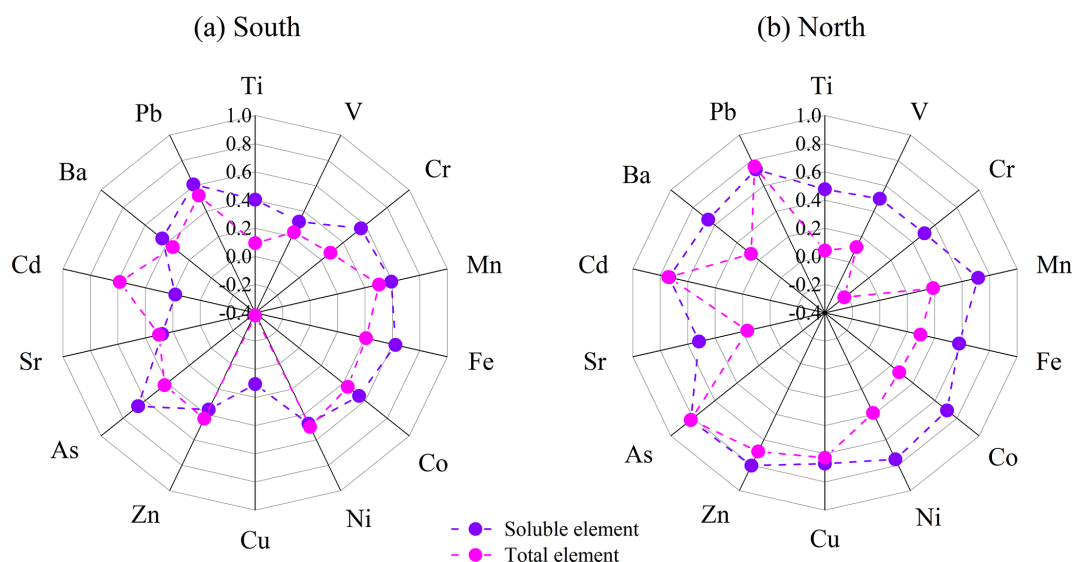


Figure 4. Correlation coefficients between DTT_v and elements in the (a) south and (b) north of Beijing.

The high correlations between DTT_v and soluble elements in the north of Beijing suggest that soluble elements also had a significant contribution to DTT consumption. The low correlations between DTT_v and soluble elements in the south of Beijing may be due to the non-linear relationship between DTT consumption and element concentration (Charrier and Anastasio, 2012; Wu et al., 2022a). As shown in Fig. S5, the relationship between most soluble trace elements and DTT_v was more non-linear than linear. As the concentration of soluble elements increases, the growth rate of DTT_v obviously decreases.

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

3.3 Sources of DTT activity

This study analyzed eight organic markers (including levoglucosan, mannosan and galactosan for biomass burning; hopanes for vehicle emissions; picene for coal combustion;

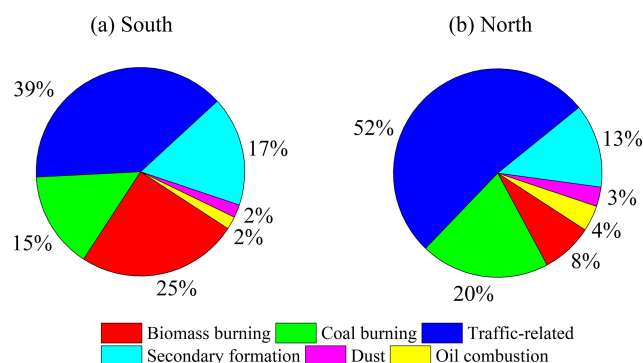


Figure 5. Contributions of resolved sources to DTT_v in the (a) south and (b) north of Beijing.

and phthalic acid, isophthalic acid and terephthalic acid for secondary formation) to help identify the sources of DTT activity. The average concentrations of these organic markers are shown in Table S2. The correlation coefficients between DTT_v and organic markers are shown in Fig. S6. In the south, levoglucosan, mannosan, galactosan and hopanes had moderate correlation with DTT_v (r of 0.41 to 0.48); phthalic acid, isophthalic acid and terephthalic acid had low to moderate correlation with DTT_v (r of 0.28 to 0.54); and picene had low correlation with DTT_v (r of 0.21). These results suggest that biomass burning and vehicle emissions could have significant contribution to the water-soluble $PM_{2.5}$ OP in the south. In the north, hopanes had the highest correlation with DTT_v ($r = 0.70$), indicating that vehicle emissions could have an important contribution. Levoglucosan, mannosan, galactosan, phthalic acid, isophthalic acid, terephthalic acid and picene had moderate to high correlations with DTT_v in the north, suggesting that biomass and coal burning and sec-

ondary formation may also have a certain contribution to the water-soluble PM_{2.5} OP.

To further quantify the sources of DTT activity in the south and the north of Beijing, the PMF model, which had widely been used for the source apportionment of the PM_{2.5} OP (Liu et al., 2018; Shen et al., 2022; Cui et al., 2023), was applied. The input species include DTT_v, soluble elements and organic markers, and five to seven factors were examined. Due to the oil factor being mixed with the vehicle emissions factor in the five-factor solution, there was no new reasonable factor when increasing the factor number to seven in the PMF analysis (Fig. S7). Finally, six factors were resolved and quantified using PMF model in the south and north of Beijing, including biomass burning, coal burning, traffic-related, dust, oil combustion and secondary formation, and the profiles of these sources are shown in Fig. S8. The uncertainties of PMF analysis for these sources were 2%–14%. Factor 1 is characterized by a high contribution of levoglucosan, mannosan and galactosan, mainly from biomass burning (Huang et al., 2014; Chow et al., 2022). The DTT activity of biomass burning organic aerosol was measured by Wong et al. (2019), which was $48 \pm 6 \text{ pmol min}^{-1} \mu\text{g}^{-1}$ of WSOC. Liu et al. (2018) quantified the sources of DTT_v in coastal cities (Jinzhou, Tianjin and Yantai) in China with the PMF model and multiple linear regression method, and the results showed that biomass burning contributed 28% on average in winter. Factor 2 exhibits a large fraction of picene, Zn, Mn, Cd, As and Pb and is considered to be coal burning (Huang et al., 2014, 2018). Joo et al. (2018) measured the DTT activity of PM_{2.5} emitted from coal combustion at different temperatures, with the highest values of $26 \pm 21 \text{ pmol min}^{-1} \mu\text{g}^{-1}$ and $0.10 \pm 0.06 \text{ nmol min}^{-1} \text{ m}^{-3}$ occurring at 550°. Factor 3 is identified as traffic-related emissions, which is characterized by the higher loading of hopanes, Ba, Sr, Cu and Ni (Huang et al., 2018; Chow et al., 2022). Vreeland et al. (2017) measured the DTT activity of PM_{2.5} emitted by side street and highway vehicles in Atlanta, with values of 0.78 ± 0.60 and $1.1 \pm 0.60 \text{ nmol min}^{-1} \text{ m}^{-3}$, respectively. Ting et al. (2023) reported that the DTT activity of PM_{2.5} from vehicle emissions in Ziqing tunnel in Taiwan was 0.15–0.46 $\text{nmol min}^{-1} \text{ m}^{-3}$. Factor 4, secondary formation, is identified by high levels of phthalic acid, isophthalic acid and terephthalic acid (Al-Naiema and Stone, 2017; T. Wang et al., 2020). Verma et al. (2014) reported that secondary formation contributed about 30% to the water-soluble DTT activity of PM_{2.5} in urban Atlanta. It is worth noting that the DTT activity of SOA generated from different precursors is different (Tuet et al., 2017; Tong et al., 2018). For example, the DTT activity of SOA from naphthalene was higher than that from isoprene (Tuet et al., 2017; Tong et al., 2018). Factor 5 is dominated by crustal elements Fe and Ti, mainly from dust (Huang et al., 2018). The DTT activity of atmospheric particulate matter during dust periods was reported in previous studies (Chirizzi et al., 2017; Khoshnamvand et al., 2023), and it has a low contribution in this study. Factor 6

is identified as oil combustion because of the high levels of V and Ni (Moreno et al., 2011; Minguillón et al., 2014; Huang et al., 2018).

The source contributions of DTT_v in the south and north of Beijing are shown in Fig. 5, exhibiting obvious district differences. In the south, traffic-related emissions (39%) and biomass burning (25%) had the most contribution to DTT_v, followed by secondary formation (17%), coal burning (15%), dust (2%) and oil combustion (2%). In the north, traffic-related emissions (52%) had the highest contribution to DTT_v, followed by coal burning (20%), secondary formation (13%), biomass burning (8%), oil combustion (4%) and dust (3%). The absolute contribution of each source to DTT_v varies by 1.2–3.4 times between the south and north of Beijing (Table S3). The large district differences in sources of DTT_v of water-soluble PM_{2.5} call for more research on the relationship between sources, chemical composition, formation processes and the OP of PM_{2.5}.

4 Conclusions

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

cesses and the PM_{2.5} OP deserves further exploration in order to better understand the regional differences of health impacts of PM_{2.5}. In addition, in order to gain a more comprehensive understanding of the regional differences in the PM_{2.5} OP, sources and its relationship with chemical composition, longer periods and different seasonal datasets are also need to be studied in the future.

Data availability. Raw data used in this study can be obtained from <https://doi.org/10.5281/zenodo.10791126> (Yuan et al., 2024). They are also available on request by contacting the corresponding authors.

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