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

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Abstract

Water-soluble components have significant contribution to the oxidative potential (OP) of atmospheric fine particles (PM$_{2.5}$), while our understanding of water-soluble PM$_{2.5}$ OP and its sources, as well as its relationship with water-soluble components, ~~their relationship~~ 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 dithiothreitol (DTT) assay. The volume normalized DTT (DTT$_v$) in the north (3.5 ± 1.2 nmol min^{-1} m^{-3}) was comparable to that in the south (3.9 ± 0.9 nmol min^{-1} m^{-3}), while the mass normalized DTT (DTT$_m$) in the north (65.3 ± 27.6 pmol min^{-1} μg^{-3}) was almost twice that in the south (36.1 ± 14.5 pmol min^{-1} μg^{-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, the 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 (39.1%) and biomass burning (25.2%) were the main sources of DTT_v in the south, and traffic-related emissions (> 50%) contributed the most of DTT_v in the north. Our results indicate that vehicle emission was the important contributor to OP in Beijing ambient $PM_{2.5}$ and suggest that more study is needed to understand the intrinsic relationship between 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 main mechanisms underlying the adverse effects of $PM_{2.5}$ on human health (Chowdhury et al., 2019; Lelieveld et al., 2021; Yu et al., 2022b). When entering the human body, $PM_{2.5}$ can induce the production of excessive reactive oxygen species (ROS) (e.g., H_2O_2, ·OH and $\cdot O_2^-$), 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; Wang et al., 2020b; 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; Wang et al., 2020b; 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 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; Wu et al., 2022b). 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, such as $\cdot O_2^-$ produced from oxidation of DTT by quinones is more efficiently transformed to ·OH in the presence of Fe, while the DTT consumption and ·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; Yu et al., 2022a; 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 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 OP (Tuet et al., 2019; Yu et al., 2019; Wang et al., 2020b; 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 OP of secondary organic aerosols (SOA) from oxidation of naphthalene, isoprene and *β*-pinene with ·OH or O_3, which were 104.4 ± 7.6, 48.3 ± 7.9 and 36.4 ± 3.1 pmol min^{-1} μg^{-1}, respectively. Verma et al. (2014) identified the source of 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. Wang et al. (2020b) quantified the sources of 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. Despite these efforts, comparative studies on the differences in pollution levels and sources of $PM_{2.5}$ OP in different districts are still limited.

In this study, the DTT activity of water-soluble matter in $PM_{2.5}$ samples collected simultaneously in the southern and northern of Beijing in January 2018 were measured. The concentration and 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 PMF model. The results acquired in this study provide a ~~comprehensive~~ comparison of $PM_{2.5}$ 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 January 1 to 31, 2018 simultaneously in the south (the Dingfuzhuang village (DFZ), Daxing district; 39.61°N, 116.28°E) and north (the National Center for Nanoscience and Technology (NCNT), Haidian district; 39.99°N, 116.32°E) of Beijing (Figure S1). 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, 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. 31 samples were collected at each site. After collection, the samples were wrapped in baked aluminum foils 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 at a constant temperature (20-23 °C) and humidity (35-45%) chamber. Each filter was weighted 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 cm^2 for concentration analysis and 0.526 cm^2 for light absorption measurement) of filter was taken from each sample and extracted ultrasonically with ultrapure water (> 18.2 MΩ cm) for 30 min. After, the extracts were filtered with a 0.45 μm PVDF pore syring 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 an 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~~were~~ calculated according to formula S1 in the Supporting Information (SI).

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 the details are shown in the SI. 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~~with same size~~ was used and ~~digestion after added of~~digested with 10 mL HNO_3 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% HNO_3. Afterwards, the diluents were filtered with a 0.22 μm PTFE pore syring 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 (Wang et al., 2020a), and more details about the analysis can be found in SI. 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 syring filter to remove insoluble substances. Several studies have shown that ultrasonic treatment of samples can lead to an increase in its OP values (Miljevic et al., 2014; Jiang et al., 2019), however, there was also a study showed that the difference in OP values of water-soluble $PM_{2.5}$ measured by DTT assay was little for samples extracted by ultrasonic and shaking (Gao et al., 2017). Consistent with the extraction methods of organic markers and trace elements analysis, 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-thiobenzonic acid (TNB) which has light absorption at 412 nm. Finally, the absorption of TNB was measured by a LWCC-UV-Vis. 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. Ambient samples were corrected for filter blank. 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 with significant contributions from species whose DTT response is non-linear related to $PM_{2.5}$ mass (e.g., Cu, Mn), the DTT_m value depends on the concentration of $PM_{2.5}$ in the extraction solution (Charrier et al., 2016). The response of DTT_m to $PM_{2.5}$ concentration in the extraction solution was analyzed using sample with high concentrations of soluble Cu and Mn (Figure S2). In the range of $PM_{2.5}$ concentrations less than 150 μg mL^{-1}, the DTT_m response was greatly affected by $PM_{2.5}$ concentrations, however, when the concentrations of $PM_{2.5}$ in the extract were greater than 150 μg mL^{-1}, the DTT_m response changed little (< 12%) with the increase of $PM_{2.5}$ concentrations. In this study, the concentrations of $PM_{2.5}$ in the extraction solution of most samples from the two sites were greater than 150 μg mL^{-1} (ranged from 78.7 to 748.7 μg mL^{-1}, with average values of 408.9 ± 164.1 and 206.6 ± 95.0 μg mL^{-1} in the south and north, respectively), therefore, the difference in $PM_{2.5}$ concentrations in different sample extracts should had a relatively small impact on the difference in DTT_m values of the samples. This study did not consider the impact of metal precipitation in phosphate matrix on the measured DTT values, as there is no a straightforward method to correct the artifacts caused by this phenomenon (Yalamanchili et al., 2023).

2.4 Source apportionment

The sources of DTT activities were identified and quantified using 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). A total of 62 samples and 23 species were input into PMF model. The number of samples is higher than the number of species, and approaching the ratio of at least 3:1 proposed by Belis et al. (2019). 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). More details are described in SI (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 S1. 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 (122.3 ± 48.9 μg m^{-3} and 8.1 ± 5.0 μgC m^{-3}, respectively) were both about two times higher than that in the north (62.3 ± 27.9 μg m^{-3} and 4.0 ± 2.0 μgC 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 three 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., 2020). 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 (108.5 ± 72.9 ng m^{-3}, 118.5 ± 91.5 ng m^{-3} and 12.4 ± 8.2 ng m^{-3}, respectively)

was about three, five and four times, respectively, those in the north (35.5 ± 21.7 ng m^{-3}, 24.1 ± 30.4 ng m^{-3} and 3.1 ± 3.0 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 trend of elements was also different between the south and north of Beijing, with Fe > Zn > Ti > Mn > Cu > Ba > Pb > Sr > Cr > As > V > Ni > Cd > Co in the south, and Fe > Ti > Zn > Ba > Mn > Pb > Cu > Cr > Sr > As > Ni > V > Cd > Co in the north. It should be noted that although the content 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 ± 0.9 nmol min^{-1} m^{-3}) was comparable to that in the north (3.5 ± 1.2 nmol min^{-1} m^{-3}), meanwhile, the average DTT_m value was much higher (1.8 times) in the north (65.3 ± 27.6 pmol min^{-1} μg^{-1}) than in the south (36.1 ± 14.5 pmol min^{-1} μg^{-1}). The lower DTT_m in the south than in the north may be due to ~~that~~ the increased $PM_{2.5}$ in the south containing~~s~~ 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~~toxicity~~ of water-soluble components of $PM_{2.5}$ was comparable in the two sites, and the water-soluble DTT_v was not consistent with the content of water-soluble substances.

Figure 2 shows the comparison of water-soluble $PM_{2.5}$ DTT activity~~DTT_v and DTT_m values~~ measured in this study with those measured in other regions of Asia during similar periods. It can be seen that the DTT_v values measured in Beijing in this study ~~(Campbell et al., 2021; Oh et al., 2023; this study)~~ were lower than that 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), higher than that in Xi'an, Nanjing, Hangzhou, Guangzhou, and Shenzhen in China~~, and Gwangju in Korea~~ (Wang et al., 2019; Wang et al., 2020b; Ma et al., 2021; Yu et al., 2022c; ~~Oh et al., 2023;~~ Xing et al., 2023), and comparable with that in

Ningbo, China (Chen et al., 2022). Different from DTT_v, the DTT_m value measured in NCNT in Beijing was similar with 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 $PM_{2.5}$ ~~DTT_v and DTT_m values~~ in different regions ~~reflect the regional differences in $PM_{2.5}$ exposure risk and intrinsic toxicity, which~~ 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; Wang et al., 2020b; 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 RO_2 + NO-dominant dry reaction conditions had the highest DTT activity.

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 toxicity of particles can not be evaluated solely by the total $PM_{2.5}$ concentration. The correlations between DTT_v with WSOC and Abs_{365} were strong in the north (r of 0.69 and 0.70, respectively), while relatively weak in the south (r of 0.41 and 0.40, respectively). The high correlations between DTT_v with WSOC and Abs_{365} in the north of Beijing qualitatively agree~~are coincide~~ 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, the DTT_v was closely related to the concentrations of NACs (r of 0.57 to 0.79) (Figure S3~~2~~), suggesting that NACs may~~could~~ be important contributors to DTT consumption. Feng et al. (2022) reported the 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, 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 Figure 4. Generally, the correlations between DTT_v and soluble elements were higher than that between DTT_v and total elements in both the south and north of Beijing~~, suggesting that the consumption of DTT from elements depend primarily on its soluble fraction instead of their total content~~. For soluble elements, in the south, the 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 (Figure S4~~3~~), while the correlation between DTT_v and most soluble elements was lower in the south than in the north (Figure 4). The high correlations between DTT_v and soluble elements in the north of Beijing suggests that soluble elements also had significant contribution to DTT consumption. The low correlations between DTT_v and soluble elements in the south of Beijing may be due to the nonlinear relationship between DTT consumption and elements concentrations (Charrier and Anastasio, 2012; Wu et al., 2022a).

In addition to being associated with individual water-soluble species, the

interaction between metal and organic compounds also affects 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, the knowledge about the effects of organics and metal-organic interactions on DTT activity are still limited, especially the effects of BrC chromophores and their interactions with metals.

3.3 Sources of DTT activity

~~The PMF model was applied to quantify the sources of DTT_v in the south and the north of Beijing, which was widely used for the source apportionment of $PM_{2.5}$ OP (Liu et al., 2018; Shen et al., 2022; Cui et al., 2023). The input species include DTT_v, soluble elements, and~~This study analyzed eight organic markers (including levoglucosan, mannosan, and galactosan for biomass burning, hopanes for vehicle emissions, picene for coal combustion, and phthalic acid, isophthalic acid and terephthalic acid for secondary formation) to help identify the sources of DTT activity. The correlation coefficients between DTT_v and organic markers are shown in Figure S54. 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); 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 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 secondary formation may also have certain contribution to 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 was widely used for the source apportionment of $PM_{2.5}$ 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 mixed with vehicle emissions factor in the five-factor solution, and there was no new reasonable factor when increasing the factor number to seven in the PMF analysis (Figure S6). Finally, ~~Six~~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 Figure S7~~5~~. Factor 1 is characterized by 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 ± 6 pmol min^{-1} μg^{-1} of WSOC. Liu et al. (2018) quantified the sources of DTT_v in coastal cities (Jinzhou, Tianjin, and Yantai) in China with PMF model and multiple linear regression method, and the results showed that biomass burning contributed 27.8% on average in winter~~wither~~. Factor 2 exhibits a large fraction of picene, Zn, Mn, Cd, As, and Pb, which is considered to be coal burning (Huang et al., 2014; Huang et al., 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 26.2 ± 20.5 pmol min^{-1} μg^{-1} and 0.10 ± 0.06 nmol min^{-1} m^{-3} occurring at 550 °C. 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 nmol min^{-1} m^{-3} and 1.08 ± 0.60 nmol min^{-1} m^{-3}, respectively. Ting et al. (2023) reported that the DTT activity of $PM_{2.5}$ from vehicle emissions in Ziqing tunnel in Taiwan, China, was 0.15-0.46 nmol min^{-1} m^{-3}. Factor 4,

secondary formation, which is identified by high levels of phthalic acid, isophthalic acid, and terephthalic acid (Al-Naiema and Stone, 2017; Wang et al., 2020a). 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 were 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 Figure 5, exhibiting obvious district~~regional~~ differences. In the south, traffic-related emissions (39.1%) and biomass burning (25.2%) had the most contribution to DTT_v, followed by secondary formation (17.2%), coal burning (15%), dust (2%), and oil combustion (1.5%). In the north, traffic-related emissions (51.6%) had the highest contribution to DTT_v, followed by coal burning (19.9%), secondary formation (13%), biomass burning (8.4%), oil combustion (4.1%), and dust (3%). The large district~~regional~~ 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 OP of $PM_{2.5}$.

4 Conclusions

In this study, the water-soluble OP 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 ± 0.9 nmol min^{-1} m^{-3}) and north (3.5 ± 1.2 nmol min^{-1} m^{-3}), while the DTT_m was higher in the north

(65.3 ± 27.6 pmol min^{-1} μg^{-1}) than in the south (36.1 ± 14.5 pmol min^{-1} μg^{-1}), indicating that the ~~$PM_{2.5}$~~ exposure-relevant ~~toxicity~~OP of water-soluble components of $PM_{2.5}$ was similar in the two sites and that the ~~$PM_{2.5}$~~ intrinsic ~~toxicity~~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, the DTT_v was strongly correlated with soluble Mn, Co, Ni, Zn, As, Cd and Pb ($r > 0.7$), and in the south it positively correlated with Mn, Fe, Cr, Co, As and Pb ($r > 0.5$). In addition, in the north the DTT_v was also positively correlated with WSOC, Abs_{365} 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 be mainly 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 (39.1%) and biomass burning (25.2%) were the major contributors of DTT_v in the south, and traffic-related emissions (51.6%) was the predominated 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 processes and $PM_{2.5}$ OP deserve further exploration in order to better understand the regional differences of health impacts of $PM_{2.5}$.

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

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

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

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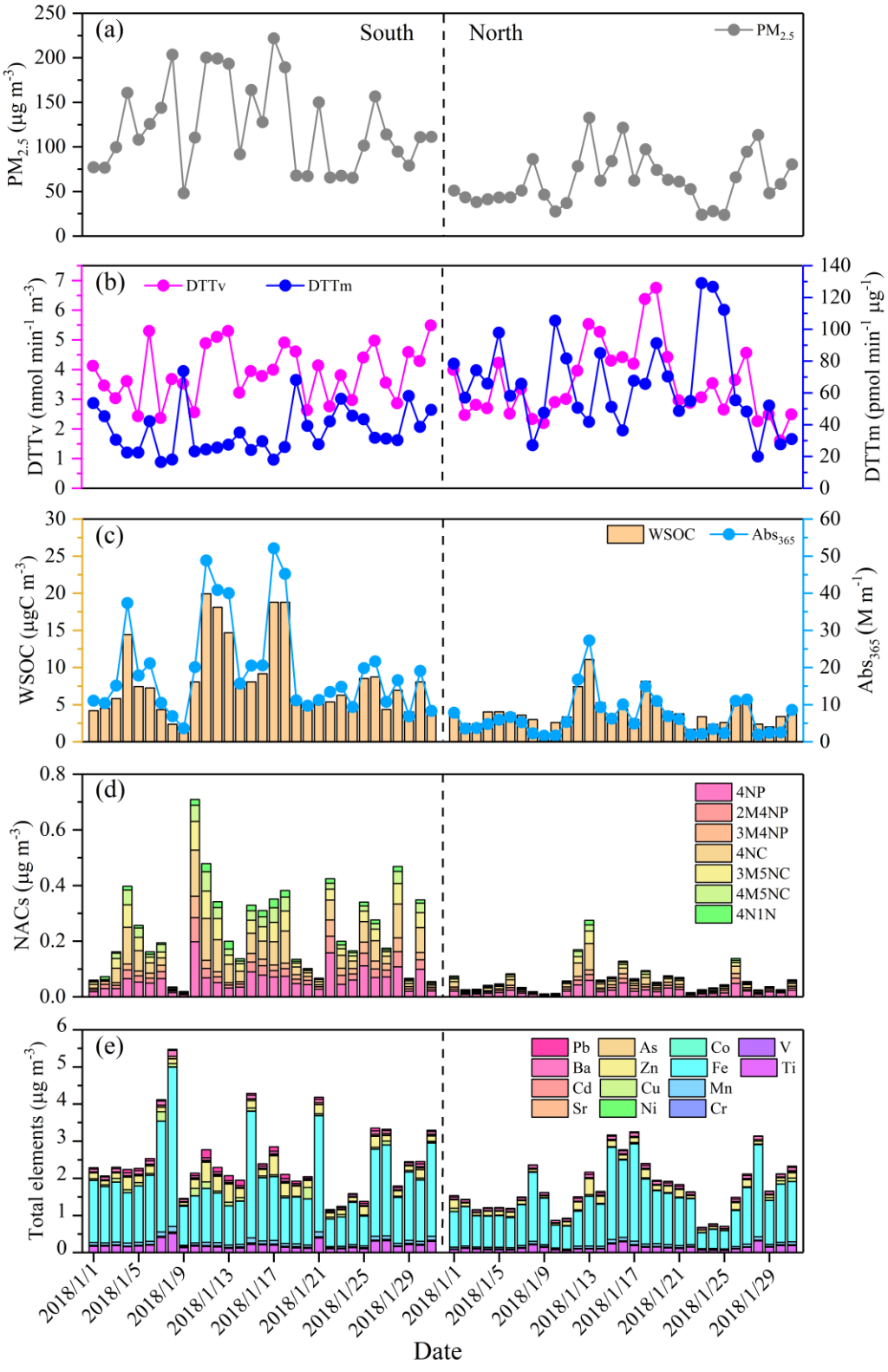
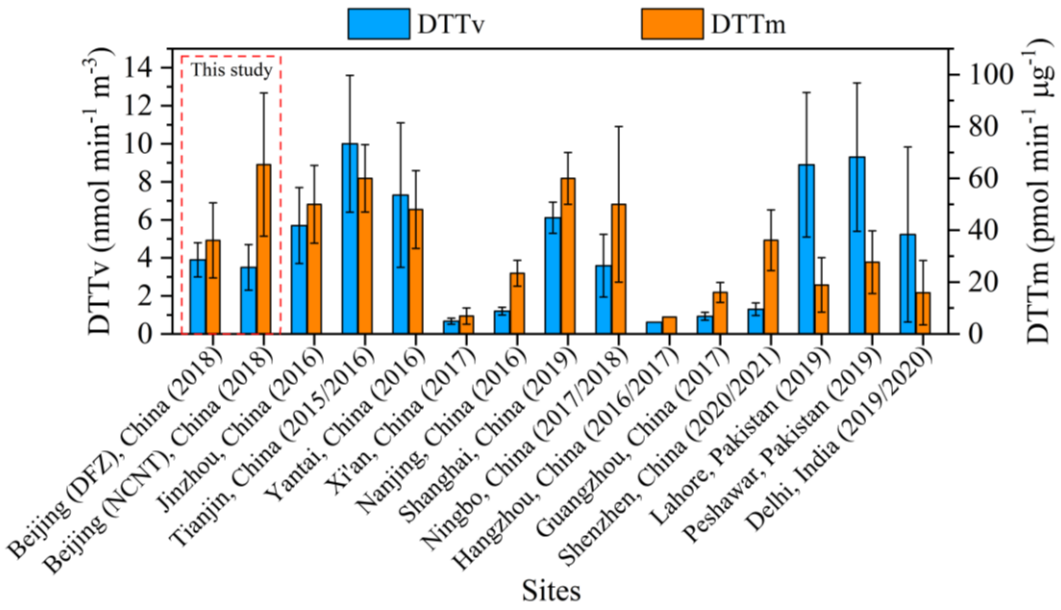


773

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



777

778 **Figure 2.** Comparison of DTT_v and DTT_m values of water-soluble $PM_{2.5}$ measured in

779 this study with those measured in other areas of Asia during similar period.

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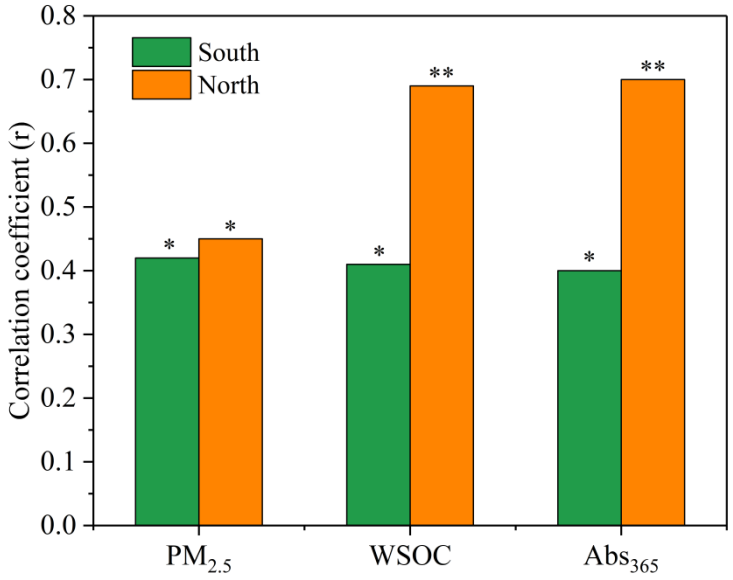

781

782 **Figure 3.** Correlation coefficients between DTT_v and $PM_{2.5}$, WSOC, and Abs_{365} in the

783 south and north of Beijing (* indicates correlation is significant at the 0.05 level, and

784 ** indicates correlation is significant at the 0.01 level).

785

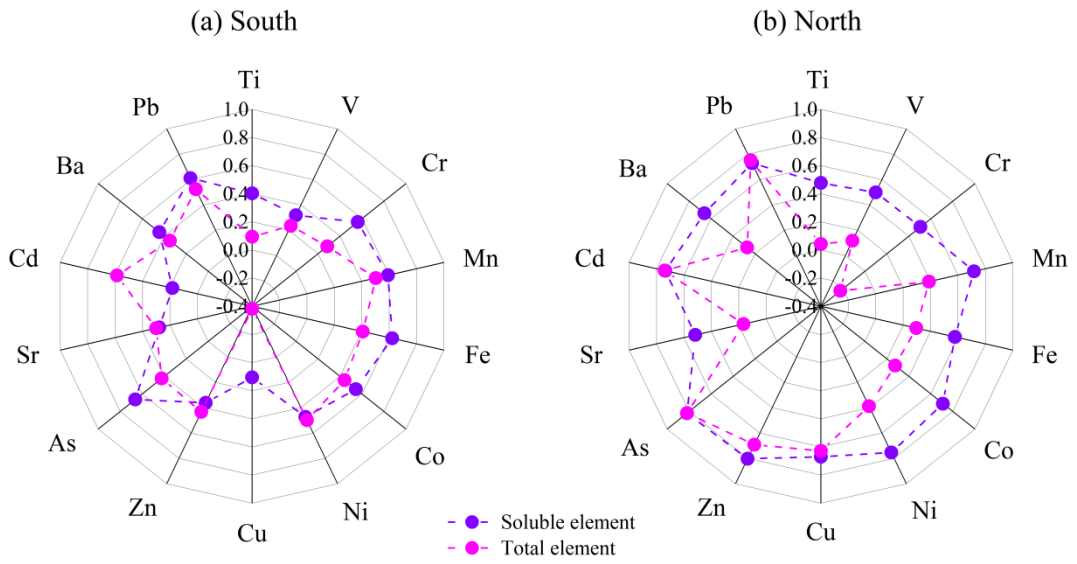

Figure 4. Correlation coefficients between DTT_v and elements in the (a) south and (b) north of Beijing.

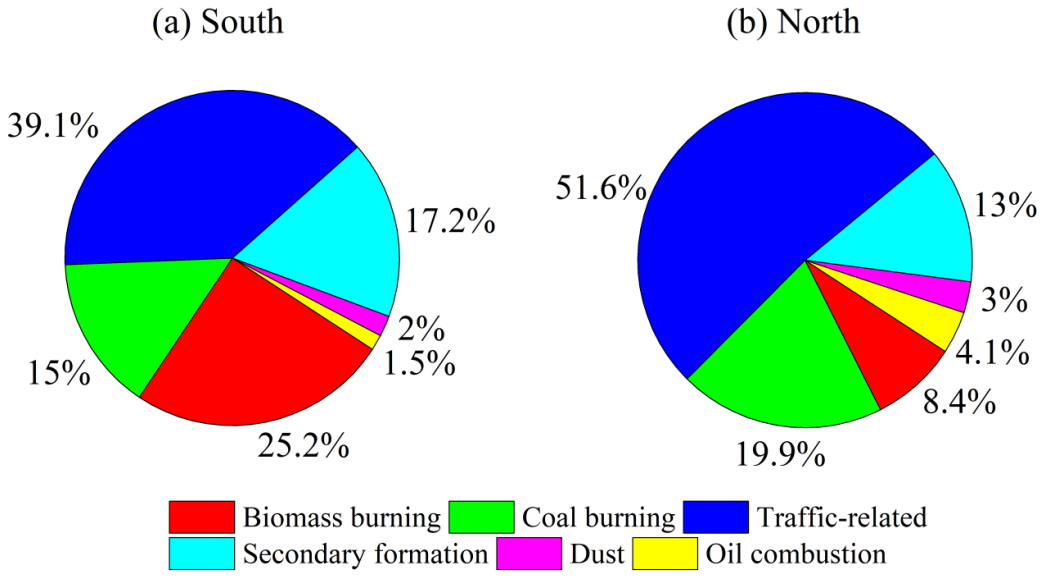

Figure 5. Contributions of resolved sources to DTT_v in the (a) south and (b) north of Beijing.