

The authors thank the referees to review our manuscript and particularly for the valuable comments and suggestions that have significantly improved the manuscript. We provide below point-by-point responses (in blue) to the referees' comments and have made changes accordingly in the revised manuscript.

Referee #1

Filters were collected at two sites in Beijing, one in what is referred to as south (39.61°N) and the other the north site (39.99°N). Based on comparing measurements of water soluble DTT_v and PM_{2.5} mass concentration and various chemical species, this research finds practically all measured parameters were substantially higher in the south vs north. However, DTT_v was similar, thus DTT_m was much higher in the north; that is the water-soluble components of the particles were concluded to be more toxic at the north site (noted in lines 209-213).

Response: Thanks for pointing this out.

In lines 247-248 of the revised manuscript, we have changed "...indicates that the intrinsic OP of PM_{2.5} was higher in the north than in the south." to "...indicates that the intrinsic OP of water-soluble components of PM_{2.5} was higher in the north than in the south."

In lines 248-250 of the revised manuscript, we have changed "...indicate that the exposure-relevant toxicity of PM_{2.5} was comparable in the two sites" to "...indicate that the exposure-relevant OP of water-soluble components of PM_{2.5} was comparable in the two sites"

In lines 264-266 of the revised manuscript, we have changed "...The differences in 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..." to "...The differences in water-soluble DTT activity of PM_{2.5} in different regions can be explained by..."

In lines 407-409 of the revised manuscript, we have changed "...indicating that the PM_{2.5} exposure-relevant toxicity was similar in the two sites and that the PM_{2.5} intrinsic toxicity was higher in the north than in the south." to "...indicating that

the exposure-relevant OP of water-soluble components of PM_{2.5} was similar in 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 authors perform a correlation and source apportionment analysis and find differences. However, no possible explanation is given for the observed differences in toxicity other than it is likely due to different species. Another possibility is raised is that the nonlinearity in the DTT assay may be having an effect (noted in the manuscript line 271-273). This seems to be a viable explanation since it is known that DTT_v response decreases with increasing concentrations of species in the extraction vial such that at high metals concentrations the assay becomes much less responsive to differences in metals concentrations. Since the metals concentrations are very high in this study, this could explain the similar DTT_v at the two sites and the higher DTT_m at the north site with lower PM_{2.5} mass concentration. Since the difference in DTT_m between the sites is a key finding of this paper and is claimed to indicate a more toxic aerosol in the north site, the possibility that it is instead driven by an artifact should be investigated in detail. There are a number of things that could be done. Redo the analysis at a constant aerosol particles mass in the extraction vial at both sites, as suggested by other investigators (Charrier, J. G., A. S. McFall, K. K. T. Vu, J. Baroi, C. Olea, A. Hasson, and C. Anastasio (2016), A bias in the “mass-normalized” DTT response – An effect of non-linear concentration-response curves for copper and manganese, *Atm Env*, 325-334). Redo the analysis at different particle masses for both sites and see how much that affects DTT_m.

Response: Thanks for the professional comment. We agree 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 response may largely depend on the concentration of PM_{2.5} in the extract, as reported in Charrier et al. (2016). We therefore re-visited the response of DTT_m to PM_{2.5} concentration in the extract using sample with high concentrations of soluble Cu and Mn (Figure R1). Similar to the results observed by Charrier et al. (2016), the DTT_m response

exhibits a non-linear decrease with increasing PM_{2.5} concentrations. It can be seen that in the range of PM_{2.5} concentrations less than 150 µg mL⁻¹, the DTT_m response is greatly affected by the PM_{2.5} concentrations. However, when the concentrations of PM_{2.5} are greater than 150 µg mL⁻¹, the DTT_m response changes 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 (> 80%) at the two sites are greater than 150 µg mL⁻¹ (ranged from 78.7 to 748.7 µg mL⁻¹, with an average value of 307.7 ± 167.9 µg mL⁻¹), therefore, the difference in PM_{2.5} concentrations in different sample extracts should have a relatively small impact on the difference in DTT_m values of the samples.

In lines 186-199 of the revised manuscript, it now reads “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.”

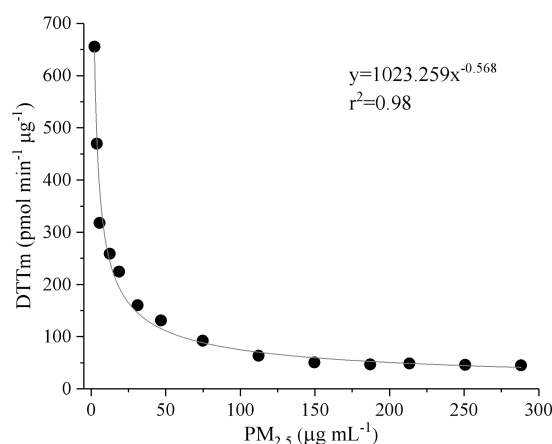


Figure R1. Measured DTT_m response as a function of PM_{2.5} concentration in the extraction solution. The Cu and Mn concentrations in this sample are 23.7 and 23.4 ng m⁻³, respectively.

In contrast to this possible limitation with the DTT assay affecting DTT_m, the results of Fig 3 showing higher correlations with Abs₃₆₅ in the north and suggesting more influence from NACs, is a possible cause for the higher DTT_m in the north. Maybe this idea could be explored more, e.g., although Abs₃₆₅ is smaller in the north what are the MACs (Abs₃₆₅/PM_{2.5} mass)? Maybe a similar analysis could be done for NACs? From a rough calculation based on Table S1, the Abs₃₆₅/mass (MAC) at the north site is 0.26 vs 0.16 at the south site. For the sum of NACs/mass, the ratio is about 2.3 at the north site and 2 at the south site, both of these suggesting that the DTT_m could be higher at the north sites due to these organic species, which could maybe be due to a higher proportion of vehicle emissions.

Response: Thanks for your careful reading and suggestions. The mass absorption coefficients (MACs) of water-soluble organic compounds at wavelength of 365 nm (MAC₃₆₅) is Abs₃₆₅/WSOC, the MAC₃₆₅ was 2.4 ± 0.3 and 1.5 ± 0.5 m² gC⁻¹ in the south and north, respectively. The sum of NACs/WSOC was 3.1 ± 1.8% and 1.5 ± 0.6% in the south and north, respectively. These trends were similar to the Abs₃₆₅ and NACs concentrations, which were also higher in the south than in the north, as discussed in Section 3.1 of the manuscript. Therefore, this study

didn't further analyze and discuss the differences in MACs and NACs/WSOC between the two sites.

Overall, this the results of this paper are interesting, but more analysis is needed.

Specific comments.

In Section 2.1 please state: What is the actual distance between sites (I get 42 km).

How many samples were collected at each site? State this

Response: Thanks for pointing this out. You are right, the distance between the two sites is about 42 km and a scale bar has been added to Figure S1 (Figure R2). 31 samples were collected at each site.

In lines 110-111 of the revised manuscript, it now reads "...The distance between the two sampling sites is about 42 km."

In line 117 of the revised manuscript, it now reads "...31 samples were collected at each site."

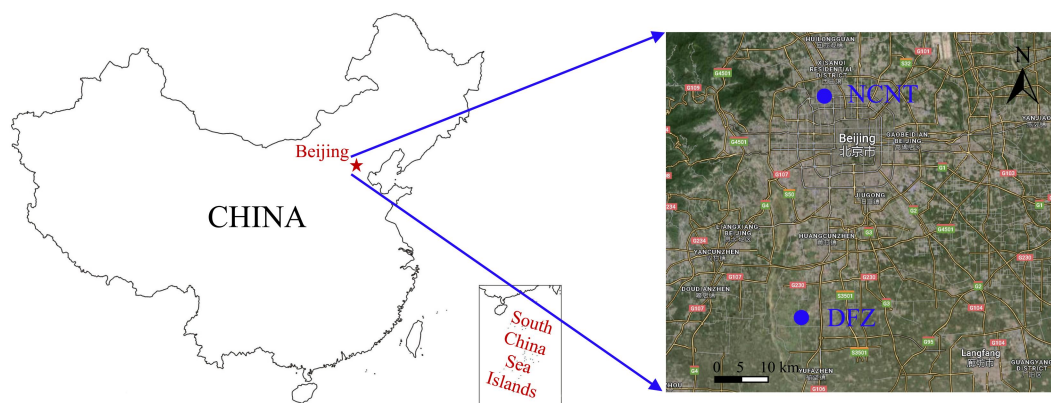


Figure R2. Map of the sampling sites. NCNT and DFZ are abbreviations for the north (the National Center for Nanoscience and Technology) and south (the Dingfuzhuang village, Daxing district) sites of Beijing, China, respectively. The left panel from Ministry of Natural Resources of China, and the right panel from Google Maps.

In Fig 2, were the protocols for the DTT analysis for the studies shown the same across all these studies?

Response: Thanks for pointing this out. The studies shown in Figure 2 mainly considered that their sampling time was similar to that of this study, and DTT assay was used. The study in Beijing (CP), China, and Gwangju, Korea didn't described the extraction solvent and method of samples in the DTT assay (Oh et al., 2023). The protocols of the DTT analysis for most of the rest studies were similar. Except for the study in Beijing (IAP), China (Campbell et al., 2021), which extracted the samples with methanol and controlled the concentration of PM_{2.5} in reaction to ~ 20 µg, other studies had used a constant filter area for each sample, and extracted with water. Except for the studies in Xi'an (Wang et al., 2020b) and Guangzhou (Yu et al., 2022c), China, which extracted the samples by vortexing and agitation, respectively, and the study in Delhi, India (Puthussery et al., 2022), which measured the DTT activity using their automated online DTT activity measurement instrument, other studies extracted the samples by ultrasonic. A previous study reported that the difference in OP of water-soluble PM_{2.5} measured by DTT assay was little for sample extracted by ultrasonic and shaking (Gao et al., 2017). Therefore, we have now removed the studies in Beijing, China, and Gwangju, Korea (Campbell et al., 2021; Oh et al., 2023) in Figure 2 (Figure R3).

In lines 254-255 of the revised manuscript, we have changed "...the DTT_v values measured in Beijing (Campbell et al., 2021; Oh et al., 2023; this study)" to "...the DTT_v values measured in Beijing in this study..."

In lines 258-259 of the revised manuscript, we have changed "...higher than that in Xi'an, Nanjing, Hangzhou, Guangzhou, and Shenzhen in China, and Gwangju in Korea..." to "...higher than that in Xi'an, Nanjing, Hangzhou, Guangzhou, and Shenzhen in China..."

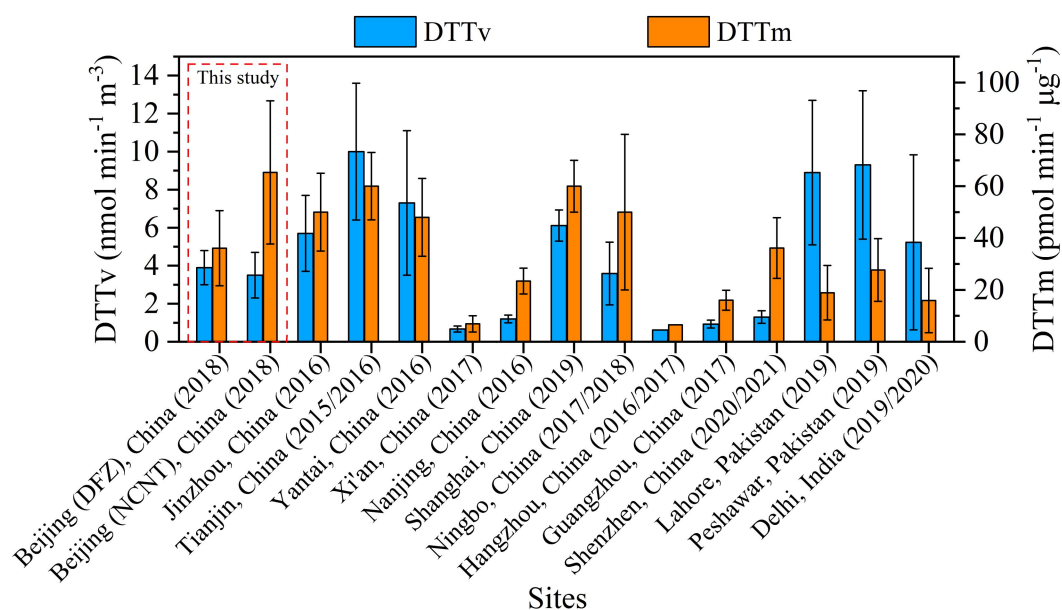


Figure R3. Comparison of DTT_v and DTT_m values of water-soluble PM_{2.5} measured in this study with those measured in other areas of Asia during similar period.

Estimate the mass of PM_{2.5} in the extract that was used for the DTT analysis, show a summary comparing the two sets of data, S and North. (This relates to the comment about possible artifacts related to non-linear response of the assay to metals).

Response: In lines 186-199 of the revised manuscript, it now reads “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 have had a relatively small impact on the difference in DTT_m values of the samples.”

In Figure 2, is this comparison just WS DTT for all data shown. Be clear on what is being compared. Does the China data in Figure 2 support the findings of a difference in this paper.

Response: Thanks for the professional comment. We rechecked the comparative studies in Figure 2 and removed the studies in Beijing, China, and Gwangju, Korea (Campbell et al., 2021; Oh et al., 2023), which were not WS DTT. Due to the differences in chemical composition, sources and atmospheric formation processes of water-soluble PM_{2.5} in different regions, the differences in DTT activity in other regions in Figure 2 were not all similar to that in this study. The DTT_v of Xi’an ($0.7 \pm 0.2 \text{ nmol min}^{-1} \text{ m}^{-3}$) and Guangzhou ($0.9 \pm 0.2 \text{ nmol min}^{-1} \text{ m}^{-3}$), China was comparable, while the DTT_m of Guangzhou ($16.0 \pm 0.2 \text{ pmol min}^{-1} \mu\text{g}^{-3}$) was much higher than that of Xi’an ($6.9 \pm 3.2 \text{ pmol min}^{-1} \mu\text{g}^{-3}$) (Wang et al., 2020b; Yu et al., 2022c), which was similar to the situation in this study.

In lines 252-253 of the revised manuscript, we have changed “Figure 2 shows the comparison of DTT_v and DTT_m values measured in this study...” to “Figure 2 shows the comparison of water-soluble PM_{2.5} DTT activity measured in this study...”

In lines 254-255 of the revised manuscript, we have changed “...the DTT_v values measured in Beijing (Campbell et al., 2021; Oh et al., 2023; this study)” to “...the DTT_v values measured in Beijing in this study...”

In lines 258-259 of the revised manuscript, we have changed “...higher than that in Xi’an, Nanjing, Hangzhou, Guangzhou, and Shenzhen in China, and Gwangju in Korea...” to “...higher than that in Xi’an, Nanjing, Hangzhou, Guangzhou, and Shenzhen in China...”

PMF analysis. Is n=31 (approximately) sufficient for a robust analysis? Justify.

Response: A 62 (total number of samples collected in the south and north, Beijing) × 23 (number of species) matrix was inputted into PMF. The number of samples was higher than the number of species, approaching the ratio of at least 3:1 proposed by Belis et al. (2019). Besides, previous study has reported that if the variances among samples are significant, it can obtain physically meaningful PMF results (Sun et al., 2011).

In lines 206-209 of the revised manuscript, it now reads “...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 correlation analysis is interesting, but a more mechanistic analysis, eg maybe doing more experiments with the filter samples, as noted above, would add strength to the conclusions. Example, the sentence on line 363-366 in the Conclusions (“The results indicate that in the north trace elements and water-soluble organic compounds, especially BrC...”) is a strong statement simply based on correlations.

Response: Thanks for the professional comment. Certainly, it will be interesting and helpful to understand the mechanisms of the influence of trace elements and organic compounds on the OP of water-soluble PM_{2.5}. However, the focus of this study was the district differences in water-soluble PM_{2.5} OP and its connection with organic compounds, trace elements and sources. The mechanisms of the influence of trace elements and organic compounds on the OP of water-soluble PM_{2.5} was not the objective of this study. Due to the chemical composition of water-soluble PM_{2.5} is very complex, the DTT response of only a few compounds has been studied (Charrier and Anastasio, 2012; Xiong et al., 2017), and there is no study on the mechanisms by which brown carbon (BrC) affects the OP of PM_{2.5}. Besides, the interactions between metals and organics, as well as between organics and organics, also affect the DTT consumption of particulate matter (Yu et al., 2018), making it more difficult to understand their

influence mechanisms. Each of these aspects require intensive studies in the future.

References

- Belis, C., Larsen, B. R., Amato, F., Haddad, I. El, Favez, O., Harrison, R. M., Hopke, P. K., Nava, S., Paatero, P., Prévôt, A., Quass, U., Vecchi, R., and Viana, M.: European Guide on Air Pollution Source Apportionment with Receptor Models, JRC References Report, March, 88, 1–170, <https://doi.org/10.2788/9307>, 2019.
- Campbell, S. J., Wolfer, K., Uttinger, B., Westwood, J., Zhang, Z. H., Bukowiecki, N., Steimer, S. S., Vu, T. V., Xu, J., Straw, N., Thomson, S., Elzein, A., Sun, Y., Liu, D., Li, L., Fu, P., Lewis, A. C., Harrison, R. M., Bloss, W. J., Loh, M., Miller, M. R., Shi, Z., and Kalberer, M.: Atmospheric conditions and composition that influence PM_{2.5} oxidative potential in Beijing, China, *Atmos. Chem. Phys.*, 21, 5549–5573, 10.5194/acp-21-5549-2021, 2021.
- Charrier, J. G. and Anastasio, C.: On dithiothreitol (DTT) as a measure of oxidative potential for ambient particles: evidence for the importance of soluble transition metals, *Atmos. Chem. Phys.*, 12, 9321–9333, 10.5194/acp-12-9321-2012, 2012.
- Charrier, J. G., McFall, A. S., Vu, K. K.-T., Baroi, J., Olea, C., Hasson, A., and Anastasio, C.: A Bias in the “Mass-Normalized” DTT Response – An Effect of Non-Linear Concentration Response Curves for Copper and Manganese, *Atmos. Environ.*, 144, 325–334, 2016.
- Gao, D., Fang, T., Verma, V., Zeng, L., and Weber, R. J.: A method for measuring total aerosol oxidative potential (OP) with the dithiothreitol (DTT) assay and comparisons between an urban and roadside site of water-soluble and total OP, *Atmos. Meas. Tech.*, 10, 2821–2835, 10.5194/amt-10-2821-2017, 2017.
- Oh, S. H., Park, K., Park, M., Song, M., Jang, K. S., Schauer, J. J., Bae, G. N., and Bae, M. S.: Comparison of the sources and oxidative potential of PM_{2.5} during winter time in large cities in China and South Korea, *Sci. Total Environ.*, 859,

160369, 10.1016/j.scitotenv.2022.160369, 2023.

- Puthussery, J. V., Dave, J., Shukla, A., Gaddamidi, S., Singh, A., Vats, P., Salana, S., Ganguly, D., Rastogi, N., Tripathi, S. N., and Verma, V.: Effect of Biomass Burning, Diwali Fireworks, and Polluted Fog Events on the Oxidative Potential of Fine Ambient Particulate Matter in Delhi, India, *Environ. Sci. Technol.*, 56, 14605-14616, 10.1021/acs.est.2c02730, 2022.
- Sun, Y., Zhang, Q., Zheng, M., Ding, X., Edgerton, E. S., and Wang, X.: Characterization and Source Apportionment of Water-Soluble Organic Matter in Atmospheric Fine Particles (PM_{2.5}) with High-Resolution Aerosol Mass Spectrometry and GC-MS, *Environ. Sci. Technol.*, 45, 4854-4861, <https://doi.org/10.1021/es200162h>, 2011.
- Wang, Y., Wang, M., Li, S., Sun, H., Mu, Z., Zhang, L., Li, Y., and Chen, Q.: Study on the oxidation potential of the water-soluble components of ambient PM_{2.5} over Xi'an, China: Pollution levels, source apportionment and transport pathways, *Environ. Int.*, 136, 105515, 10.1016/j.envint.2020.105515, 2020b.
- Xiong, Q., Yu, H., Wang, R., Wei, J., and Verma, V.: Rethinking Dithiothreitol-Based Particulate Matter Oxidative Potential: Measuring Dithiothreitol Consumption versus Reactive Oxygen Species Generation, *Environ. Sci. Technol.*, 51, 6507-6514, 10.1021/acs.est.7b01272, 2017.
- Yu, H., Wei, J., Cheng, Y., Subedi, K., and Verma, V.: Synergistic and Antagonistic Interactions among the Particulate Matter Components in Generating Reactive Oxygen Species Based on the Dithiothreitol Assay, *Environ. Sci. Technol.*, 52, 2261-2270, 2018.
- Yu, Y., Cheng, P., Li, Y., Gu, J., Gong, Y., Han, B., Yang, W., Sun, J., Wu, C., Song, W., and Li, M.: The association of chemical composition particularly the heavy metals with the oxidative potential of ambient PM_{2.5} in a megacity (Guangzhou) of southern China, *Environ. Res.*, 213, 113489, 10.1016/j.envres.2022.113489, 2022c.

Referee #2

This study explored the sources of aerosol oxidative potential – quantified through the DTT assay – at two sites in Beijing. Daily PM_{2.5} filters were collected at both sites for a period of one month. In addition to DTT, water-soluble organics, water-soluble and total metal concentrations, and certain organic markers were measured. PMF was applied in an attempt to apportion the DTT response to different sources. Overall, the manuscript topic is certainly relevant for ACP and some of the results are novel and insightful. However, there are several places where key conclusions are not robustly supported by the data. There are many places where more nuanced analysis is needed.

Specific Comments:

- There are significant limitations with the present study that need to be discussed, and it is definitely not “comprehensive” as the study claims. The limitations are (1) that measurements were only conducted for a period of one month, and (2) water-insoluble species were excluded from the analysis. Therefore, the discussion associated with Fig. 2 needs to be qualified. Similarly, the authors are advised against using descriptors like “exposure-relevant toxicity” and “PM_{2.5} intrinsic toxicity”. Water-insoluble components can contribute to OP (and thus the exposure and toxicity of people in Beijing), yet they were not quantified in this study. The authors should be more accurate/specific with their description of results here and the implications of their findings.

Response: Thanks for your careful reading and professional comments. We have revised the description of “comprehensive”. Due to we only collected samples simultaneously at two sites for one month, it is difficult to improve the limitation that the measurements in this study were only conducted for one month. However, in the future, we will consider conducting longer periods of simultaneously sample collection and analysis in different regions.

The studies shown in Figure 2 mainly considered that their sampling time was similar to that of this study, and DTT assay was used. We rechecked the comparative studies in Figure 2 and removed the studies in Beijing, China, and Gwangju,

Korea (Campbell et al., 2021; Oh et al., 2023), which were not extracted samples with water for DTT analysis (Figure R1). Besides, we have revised the descriptions of “exposure-relevant toxicity” and “PM_{2.5} intrinsic toxicity”, as well as the descriptions of relevant results to make these expressions more specific.

In lines 99-100 of the revised manuscript, we have changed “...provide a comprehensive comparison of...” to “...provide a comparison of...”

In lines 252-253 of the revised manuscript, we have changed “Figure 2 shows the comparison of DTT_v and DTT_m values measured in this study...” to “Figure 2 shows the comparison of water-soluble PM_{2.5} DTT activity measured in this study...”

In lines 254-255 of the revised manuscript, we have changed “...the DTT_v values measured in Beijing (Campbell et al., 2021; Oh et al., 2023; this study)” to “...the DTT_v values measured in Beijing in this study...”

In lines 258-259 of the revised manuscript, we have changed “...higher than that in Xi’an, Nanjing, Hangzhou, Guangzhou, and Shenzhen in China, and Gwangju in Korea...” to “...higher than that in Xi’an, Nanjing, Hangzhou, Guangzhou, and Shenzhen in China...”

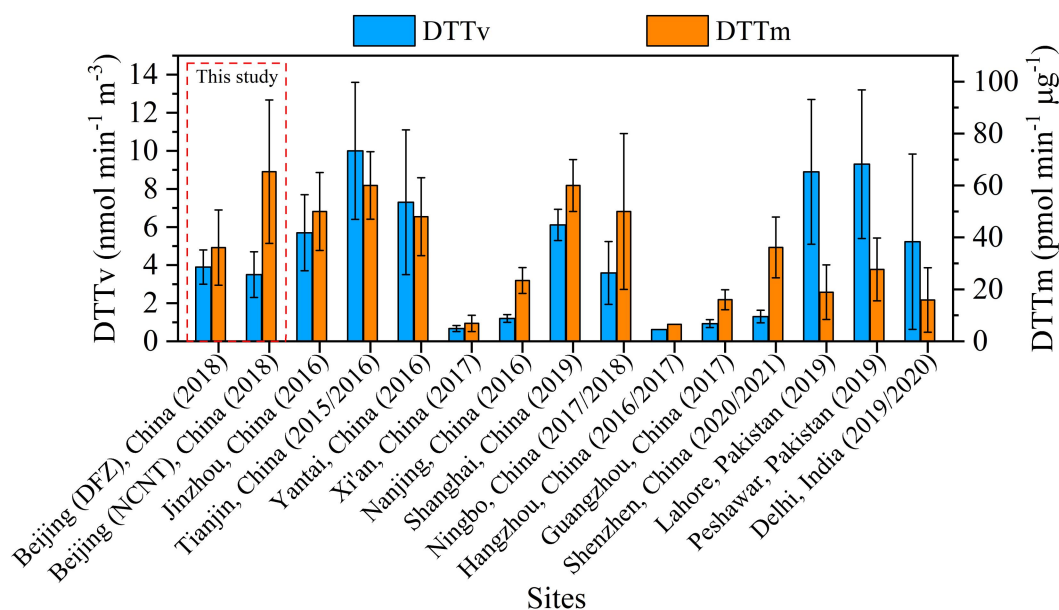


Figure R1. Comparison of DTT_v and DTT_m values measured in this study with those measured in other areas of Asia during similar period.

In lines 247-248 of the revised manuscript, we have changed “...indicates that the intrinsic OP of PM_{2.5} was higher in the north than in the south.” to “...indicates that the intrinsic OP of water-soluble components of PM_{2.5} was higher in the north than in the south.”

In lines 248-250 of the revised manuscript, we have changed “...indicate that the exposure-relevant toxicity of PM_{2.5} was comparable in the two sites” to “...indicate that the exposure-relevant OP of water-soluble components of PM_{2.5} was comparable in the two sites”

In lines 264-266 of the revised manuscript, we have changed “...The differences in 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...” to “...The differences in water-soluble DTT activity of PM_{2.5} in different regions can be explained by...”

In lines 407-409 of the revised manuscript, we have changed “...indicating that the PM_{2.5} exposure-relevant toxicity was similar in the two sites and that the PM_{2.5} intrinsic toxicity was higher in the north than in the south.” to “...indicating that the exposure-relevant OP of water-soluble components of PM_{2.5} was similar in 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.”

- In several cases, the authors are cautioned against making the well-known mistake of confusing correlation with causation. Section 3.2 concludes that nitroaromatic compounds “could be important contributors to DTT consumption,” on the basis of their correlation with DTT_v. To my knowledge, the response of NACs in the DTT assay has not been assessed. Therefore, without this direct knowledge, it might be other components, including those not measured, that correlate with NACs that are driving the correlation. A similar comment applies to discussion surrounding Figure 4, including Line 261-262: “*the consumption of DTT from elements depend primarily on its soluble fraction instead of their total content.*” However, it was only the water-soluble fraction that was added to the

DTT assay, so it makes sense that DTT_v would have much stronger correlations with the water-soluble species. The authors are referred to the work of C. Sioutas, who has examined the response of soluble and insoluble PM fractions in the DTT assay.

Response: Thanks for your professional comments. We agree that it might be other components related to NACs driving the correlation between NACs and DTT_v.

In line 291 of the revised manuscript, we have changed "...suggesting that NACs could be important contributors..." to "...suggesting that NACs may be important contributors..."

In lines 298-301 of the revised manuscript, it now reads "...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."

In lines 305-306 of the revised manuscript, we have deleted the sentence "suggesting that the consumption of DTT from elements depend primarily on its soluble fraction instead of their total content"

- The PMF results need to be analyzed more critically, and with much more detail. For example, traffic is identified as the most significant contributor to the DTT activity in the south (39.1%). And yet, aside from hopanes, other elements attributed to traffic emissions (Ba, Sr, and Cu) seem to have very low correlation coefficients with DTT? The discussion in Section 3.3 is also confusing: the point of PMF is that it is much more sophisticated than simple linear correlations, yet the discussion here uses correlations with individual species to draw conclusions about the sources contributing to DTT_v. Then the discussion moves to the PMF output, but the connection between these is not apparent.

Response: In the south, the correlation coefficients between Ba, Sr, and Cu and DTT_v were indeed low ($r < 0.4$), however, the concentrations of soluble Ba, Sr, and Cu were higher than most of other trace elements, as described in Section 3.1. The low correlations between these trace elements and DTT_v may be due to the

nonlinear response of DTT activity to their concentrations (Charrier and Anastasic, 2012). Besides, it may be other species (e.g., quinones) from vehicle emissions contribute more to DTT_v than these trace elements, which may also be the reason for the weak correlations between these trace elements and DTT_v . Further, the acquisition of PMF results was much more sophisticated than simple linear correlations, and that the correlation between DTT_v and individual species was not directly related to PMF output. To reduce confusion, the description in Section 3.3 has been revised, and more details about the PMF analysis have been added to the Supporting Information (**PMF analysis**).

In lines 334-357 of the revised manuscript, it now reads, “This study analyzed eight organic markers... to help identify the sources of DTT activity. The correlation coefficients between DTT_v and organic markers are shown in Figure S5...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 factors were resolved and quantified using PMF model in the south and north of Beijing...”

In lines 211-212 of the revised manuscript, it now reads “More details are described in SI (PMF analysis).” For more details about PMF analysis, please see SI (**PMF analysis**).

- Many, many method details (blanks, calibration procedures, QA/QC procedures) are missing. The UV-Vis spectrophotometer model is not given. These can be included in the SI, but they are not present at all. Measurement uncertainties were an input into the PMF model (Line 174) yet these were not given for any species, nor the methodology to quantify the uncertainties.

Response: Thanks for pointing these out. All of the results reported in this study were corrected for blanks. The calibration procedures and QA/QC procedures of ICP-MS analysis for trace elements and GC-MS analysis for organic markers were shown in Supplementary Information (**ICP-MS analysis and GC-MS analysis** sections). The quality control of LWCC-UV/Vis analysis for light absorption has been added in Supplementary Information (**Calculation of absorption coefficient of BrC** section). The quality control description of DTT analysis and the model of UV-Vis spectrophotometer has been added in the revised manuscript. The method for quantifying the uncertainty of species input into the PMF model has also been added in Supplementary Information (**PMF analysis**).

In lines 134-135 of the revised manuscript, it now reads “...UV-Vis spectrophotometer (300-700 nm; Ocean Optics, USA)...”

In line 160 of the revised manuscript, it now reads “...All of the results reported in this study were corrected for blanks. ”

In lines 181-183 of the revised manuscript, it now reads “...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.”

In lines 210-212 of the revised manuscript, it now reads “...The species-specific uncertainties were calculated following Liu et al. (2017). More details are described in SI (PMF analysis).”

In **Calculation of absorption coefficient of BrC** section in SI, a paragraph has been added, it reads “The light absorption of water-soluble light-absorbing organic compounds (also known as brown carbon, BrC) were measured with an UV-Vis spectrophotometer equipped with a liquid waveguide capillary cell. During the measurement, the system was cleaned with ultrapure water ($> 18.2 \text{ M}\Omega \text{ cm}$) after each sample analysis. After cleaning, for instrument calibration, the baseline was zeroed using the Spectra-Suite software so that zero absorption was recorded at all wavelengths for ultrapure water.”

The method for quantifying the uncertainty of species input into the PMF model

please see Supplementary Information (**PMF analysis**).

- Also, I acknowledge that the methods the authors have used are widely applied in aerosol studies, however, two potential measurement artifacts need to be acknowledged and discussed. The first relates to potential compositional changes that may occur when the filters are sonicated. Sonication produces hydroxyl radicals and this can change the organic composition (e.g., Miljevic et al., 2014, and references therein). The second potential artifact relates to metal precipitation during the DTT assay. This can cause complex responses in the DTT assay that are not straightforward to interpret (Yalamanchili et al., 2023). Again, the authors have applied established methods here, but these potential effects can (and should) still be discussed.

Response: Thanks for your professional comments. In lines 166-172 of the revised manuscript, it now reads “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.”

In lines 199-202 of the revised manuscript, it now reads “...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).”

- I don't follow the explanation in Lines 270-272: why wouldn't the non-linear response also apply in the north?

Response: We agree that the non-linear response of DTT consumption to trace element concentrations was also applicable in the north. DTT consumption has a non-linear response to trace element concentration. With the the increase of trace

element concentration, the increase of DTT consumption rate decreased, therefore, the linear correlation between trace elements and DTT activity was higher in the low concentration range than in the high concentration range (Charrier and Anastasio, 2012). Because the concentration of soluble elements in the north (total of $99.2 \pm 83.4 \text{ ng m}^{-3}$) was much lower than that in the south (total of $185.4 \pm 116.7 \text{ ng m}^{-3}$), the non-linear response of DTT consumption to trace element concentrations could have greater impact on the correlations between DTT activity and soluble elements in the south than in the north.

Technical Corrections:

- Should all WSOC units be $\mu\text{g-C m}^{-3}$ (instead of $\mu\text{g m}^{-3}$)?

Response: Thanks for pointing this out. The unit of WSOC has been changed from $\mu\text{g m}^{-3}$ to $\mu\text{gC m}^{-3}$.

- Does Fig. S3 and Table S1 together indicate that only ~1-2% of Fe was soluble?

Response: Yes. The average Fe solubility in the south and north of Beijing was $1.8 \pm 1.2\%$ and $1.2 \pm 1.0\%$, respectively, which was similar to the value in Qingdao, China ($1.3 \pm 1.4\%$) (Zhang et al., 2022).

- Figure S1 needs a scale so the distance between the sites can be estimated.

Response: Thanks for pointing this out. The distance between the two sites is about 42 km and a scale bar has been added to Figure S1 (Figure R2).

In lines 110-111 of the revised manuscript, it now reads “...The distance between the two sampling sites is about 42 km.”

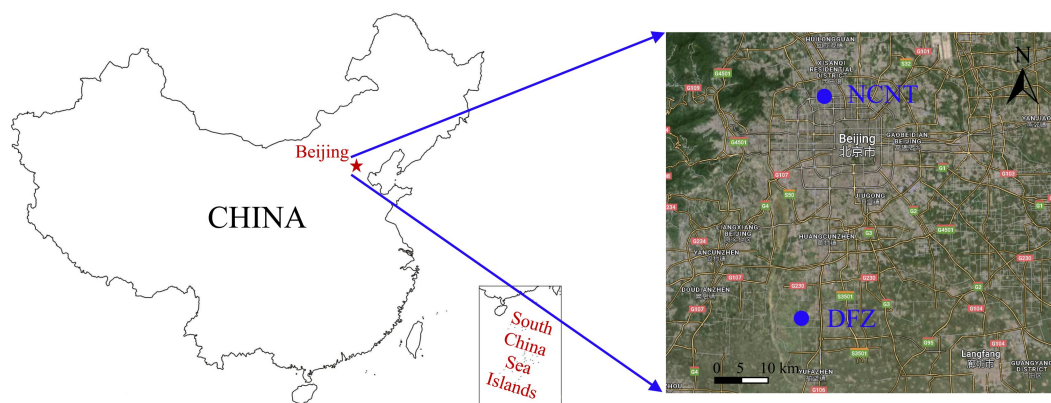


Figure R2. Map of the sampling sites. NCNT and DFZ are abbreviations for the north (the National Center for Nanoscience and Technology) and south (the Dingfuzhuang village, Daxing district) sites of Beijing, China, respectively. The left panel from Ministry of Natural Resources of China, and the right panel from Google Maps.

- Line 17-18: sentence needs clarification

Response: Thank you. In lines 17-19 of the revised manuscript, we have changed “...atmospheric fine particles, while our understanding of their relationship is still limited.” to “...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, is still limited.”

- Line 65: “organic” should be “organics”

Response: Thank you. Change made.

- Line 116: “foils” should be “foil”

Response: Because one sample was wrapped in an aluminum foil, there were multiple samples, so “foils” was used here.

- Line 134: change “were” to “was”

Response: Thank you. Change made.

- Line 141: edit sentence for clarity

Response: Thank you. In lines 144-146 of the revised manuscript, we have changed “...another filter with same size was used and digestion after added of 10 mL HNO₃ and 1 mL HF.” to “...another 47 mm diameter filter of the same sample was used and digested with 10 mL HNO₃ and 1 mL HF at 180 °C for 12 h.”

- Line 207: edit sentence for grammar

Response: Thank you. In lines 245-246 of the revised manuscript, we have changed “...may be due to that the increased PM_{2.5} in the south contains more substances...” to “...may be due to the increased PM_{2.5} in the south containing more substances...”

- Line 244: suggest changing “are coincide” to “qualitatively agree” or similar

Response: Thank you. In line 284 of the revised manuscript, we have changed “...are coincide...” to “...qualitatively agree...”

- Line 314: change “wither” to “winter”

Response: Thank you. Change made.

- Paragraph beginning on Line 337: is it accurate to qualify these as “regional” differences?

Response: Thank you. We have changed “regional” to “district”.

In line 390 of the revised manuscript, we have changed “...exhibiting obvious regional differences.” to “...exhibiting obvious district differences.”

In line 395-396 of the revised manuscript, we have changed “The large regional differences in sources of DTT_{v...} ” to “The large district differences in sources of DTT_{v...}”

References

Miljevic, B., et al., To Sonicate or Not to Sonicate PM Filters: Reactive Oxygen Species Generation Upon Ultrasonic Irradiation, *Aerosol Science and Technology*, 48: 1276-1284, 2014.

Yalamanchili, J., et al., Measurement artifacts in the dithiothreitol (DTT) oxidative potential assay caused by interactions between aqueous metals and phosphate buffer, *Journal of Hazardous Materials*, 465, 131693, 2023.

References

Campbell, S. J., Wolfer, K., Utinger, B., Westwood, J., Zhang, Z. H., Bukowiecki, N., Steimer, S. S., Vu, T. V., Xu, J., Straw, N., Thomson, S., Elzein, A., Sun, Y., Liu, D., Li, L., Fu, P., Lewis, A. C., Harrison, R. M., Bloss, W. J., Loh, M., Miller, M. R., Shi, Z., and Kalberer, M.: Atmospheric conditions and composition that influence PM_{2.5} oxidative potential in Beijing, China, *Atmos. Chem. Phys.*, 21, 5549-5573, 10.5194/acp-21-5549-2021, 2021.

Charrier, J. G. and Anastasio, C.: On dithiothreitol (DTT) as a measure of oxidative potential for ambient particles: evidence for the importance of soluble transition metals, *Atmos. Chem. Phys.*, 12, 9321-9333, 10.5194/acp-12-9321-2012, 2012.

Cui, Y., Zhu, L., Wang, H., Zhao, Z., Ma, S., and Ye, Z.: Characteristics and Oxidative Potential of Ambient PM_{2.5} in the Yangtze River Delta Region: Pollution Level and Source Apportionment, *Atmosphere*, 14, 10.3390/atmos14030425, 2023.

Gao, D., Fang, T., Verma, V., Zeng, L., and Weber, R. J.: A method for measuring total aerosol oxidative potential (OP) with the dithiothreitol (DTT) assay and comparisons between an urban and roadside site of water-soluble and total OP, *Atmos. Meas. Tech.*, 10, 2821-2835, 10.5194/amt-10-2821-2017, 2017.

Jiang, H., Xie, Y., Ge, Y., He, H., and Liu, Y.: Effects of ultrasonic treatment on dithiothreitol (DTT) assay measurements for carbon materials, *J. Environ. Sci.*, 84, 51-58, 2019.

Liu, W., Xu, Y., Liu, W., Liu, Q., Yu, S., Liu, Y., Wang, X., and Tao, S.: Oxidative potential of ambient PM_{2.5} in the coastal cities of the Bohai Sea, northern

- China: Seasonal variation and source apportionment, *Environ. Pollut.*, 236, 514-528, 10.1016/j.envpol.2018.01.116, 2018.
- Liu, Y., Yan, C. Q., Ding, X., Wang, X. M., Fu, Q. Y., Zhao, Q. B., Zhang, Y. H., Duan, Y. S., Qiu, X. H., and Zheng, M.: Sources and spatial distribution of particulate polycyclic aromatic hydrocarbons in Shanghai, China, *Sci. Total Environ.*, 584-585, 307-317, <https://doi.org/10.1016/j.scitotenv.2016.12.134>, 2017.
- Miljevic, B., Hedayat, F., Stevanovic, S., Fairfull-Smith, K. E., Bottle, S. E., and Ristovski, Z. D.: To sonicate or not to sonicate PM filters: reactive oxygen species generation upon ultrasonic irradiation, *Aerosol. Sci. Technol.*, 48, 1276–1284, 2014.
- Oh, S. H., Park, K., Park, M., Song, M., Jang, K. S., Schauer, J. J., Bae, G. N., and Bae, M. S.: Comparison of the sources and oxidative potential of PM_{2.5} during winter time in large cities in China and South Korea, *Sci. Total Environ.*, 859, 160369, 10.1016/j.scitotenv.2022.160369, 2023.
- Shen, J., Taghvaei, S., La, C., Oroumijeh, F., Liu, J., Jerrett, M., Weichenthal, S., Del Rosario, I., Shafer, M. M., Ritz, B., Zhu, Y., and Paulson, S. E.: Aerosol Oxidative Potential in the Greater Los Angeles Area: Source Apportionment and Associations with Socioeconomic Position, *Environ. Sci. Technol.*, 56, 17795-17804, 10.1021/acs.est.2c02788, 2022.
- Yalamanchili, J., Hennigan, C. J., and Reed, B. E.: Measurement artifacts in the dithiothreitol (DTT) oxidative potential assay caused by interactions between aqueous metals and phosphate buffer, *J. Hazard. Mater.*, 456, 131693, 2023.
- Zhang, H., Li, R., Dong, S., Wang, F., Zhu, Y., Meng, H., Huang, C., Ren, Y., Wang, X., Hu, X., Li, T., Peng, C., Zhang, G., Xue, L., Wang, X., and Tang, M.: Abundance and fractional solubility of aerosol iron during winter at a coastal city in northern China: Similarities and contrasts between fine and coarse particles, *J. Geophys. Res.-Atmos.*, 127, e2021JD036070, 2022.