

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

I thank the authors for addressing the comments from the first review. I have two issues I wish the authors consider.

Overall, I am still concerned with the use of variable concentrations in the extraction vial that may be affecting the results and leading to erroneous conclusions. The authors response based on plotting DTT_m vs $PM_{2.5}$ mass and stating that at high $PM_{2.5}$ mass concentrations DTT_m does not depend on mass is not highly convincing, in part because one is dividing by a large number ($PM_{2.5}$ mass). The authors ideally should re-evaluate some of the filters (if some fraction of the filters remain). Example, redo the DTT analysis for say three to four different concentrations of PM in the reaction vial including the concentration recommended in a number of publications and see if this affects DTT_m . If there are no filters to redo some further analysis, then state that. Overall, this issue is noted in the manuscript so readers can assess for themselves if this is a significant limitation with this study or not. I find the new added explanation given rather weak, but I do not feel it should hold up the publication of this work since it has been noted.

Response: Thank you for your professional comments and valuable suggestions.

Figure S2 shows the effect of $PM_{2.5}$ concentration in the reaction vial on DTT_m ($PM_{2.5}$ concentration in the reaction vial changed from 2 to 300 $\mu\text{g mL}^{-1}$, including the concentration recommended in previous publications) (Figure R1). The concentration of $PM_{2.5}$ in the reaction vial does indeed have an impact on DTT_m . In the range of $PM_{2.5}$ concentration in the reaction vial less than 150 $\mu\text{g mL}^{-1}$, the DTT_m response decreased significantly with the increase of $PM_{2.5}$ concentration in the reaction vial. However, when the concentration of $PM_{2.5}$ in

the reaction vial is greater than $150 \mu\text{g mL}^{-1}$, the DTT_m response changes little ($< 12\%$) with the increase of $\text{PM}_{2.5}$ concentration in the reaction vial. Because most samples did not have enough filters to redo further analysis, therefore, not every sample was analyzed for the effect of $\text{PM}_{2.5}$ concentration in the reaction vial on DTT_m response. However, in this study, most of samples ($> 80\%$) had a concentration of $\text{PM}_{2.5}$ in the reaction vial greater than $150 \mu\text{g mL}^{-1}$, therefore, the difference in $\text{PM}_{2.5}$ concentration in reaction vial of different samples should had a relatively small impact on the difference in DTT_m values of different samples.

To make the expression clearer, in lines 186-204 of the revised manuscript, it now reads, “Considering that for samples containing a significant amount of substances whose DTT response is non-linear with $\text{PM}_{2.5}$ concentration (e.g., Cu, Mn), the DTT_m value depends on the concentration of $\text{PM}_{2.5}$ added to the reaction solution... The response of DTT_m to $\text{PM}_{2.5}$ concentration added to the reaction solution was analyzed using sample containing high concentrations of soluble Cu and Mn (Figure S2). When the $\text{PM}_{2.5}$ concentration added to the reaction solution is less than $150 \mu\text{g mL}^{-1}$, the DTT_m response is greatly affected by the difference in added $\text{PM}_{2.5}$ concentration; however, when the $\text{PM}_{2.5}$ concentration added to the reaction solution is greater than $150 \mu\text{g mL}^{-1}$, the DTT_m response is less affected by the difference in $\text{PM}_{2.5}$ concentration ($< 12\%$). In this study, the concentration of $\text{PM}_{2.5}$ added to the reaction solution of most samples from the two sites was greater than $150 \mu\text{g mL}^{-1}$ (ranged from 78.7 to $748.7 \mu\text{g mL}^{-1}$, with an average of 408.9 ± 164.1 and $206.6 \pm 95.0 \mu\text{g mL}^{-1}$ in the south and north, respectively), therefore, the difference in $\text{PM}_{2.5}$ concentration added to the reaction solution of different samples should had a relatively small impact on the difference in DTT_m values of different samples.”

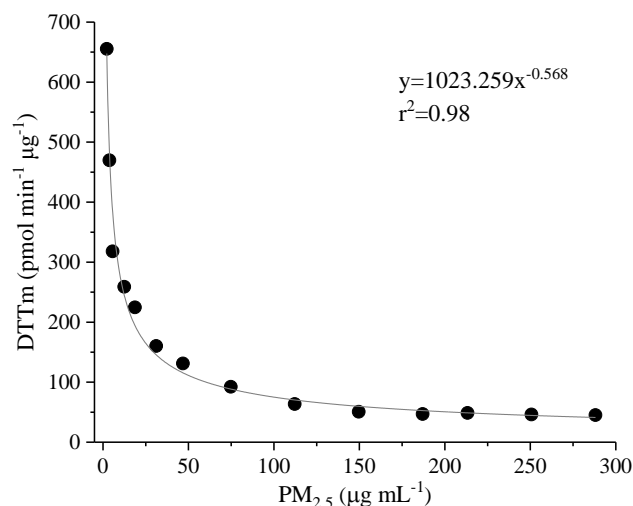


Figure R1. Measured DTT_m response as a function of PM_{2.5} concentration in the reaction vial.

One further clarification is requested. In response to a question the authors have added: “...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).”

I suggest writing as. A PMF analysis was performed for each site based on 31 filter samples collected at each site, and 23 species were input into each of the PMF models. The number of samples is higher than the number of species.” I believe the latter part is wrong (“and approaching the ratio of at least 3:1”) since the ratio should be 31/23 not 62/23 which does not approach 3:1.

Response: Thanks for your suggestion. In lines 210-213 of the revised manuscript, it now reads, “...For each site, 31 samples and 23 species were input into PMF model. The number of samples is higher than the number of species.”

Referee #3

In this manuscript, Yuan et al., report upon an analysis of PM_{2.5} composition and oxidative potential (OP: measured using the DTT assay), for two locations in the Beijing area. The compositional analysis is pretty extensive, including both metals and some organic species. They link their composition analysis with PMF to assess source impacts on OP.

As a measurement report, this paper achieves its goal, i.e., contributing to the databank of PM composition and OP characterization. The further analyses, including source apportionment and such, are similar to past work, and only go a little ways in to what might be done with their data. Their findings are similar to prior work as well. A major shortcoming is they tend not to answer the big question of why does OP vary so much between north and south. DTT_m is rather different between north and south, but the sources contributing to PM are rather similar (Fig. 5), one has to ask “Why?” That question is not really addressed. Why are the correlations between DTT OP and soluble elements so different as well? Is it really due to the non-linear response as a function of level? That seems a bit far-fetched as the levels are not that different, and unless that non-linearity becomes very large (which would tend to suggest criticism of any further analysis or utility of the measurements), it would not be expected to have such a large impact on the correlations. If you plot metal concentrations vs. OP, does a non-linearity appear? It should also be noted that the correlation between DTT_v and WSOC and ABS is also much less in the south: might there be something more about the measurements in the south? Given what is currently there, one might suggest some further caveats and cautions about what might be taken away from the analyses.

Response: Thanks for your professional comments. In this study, the difference of OP between the south and north of Beijing were mainly ascribed to the differences in chemical composition and sources, as well as the interactions between metals and organic compounds. We analyzed the differences in trace elements and WSOC between the south and north, which are substances that previous studies have shown to contribute significantly to DTT activity. In lines 237-240 of the revised manuscript, it reads “...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.” In lines 249-251 of the revised manuscript, it reads “...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...” The sources of DTT_v in the south and north were quantified using the PMF model. The relative contribution of each source to DTT_v may not be very different in the south and the north, but their absolute contribution difference is 1.2-3.4 times (Table R1). In lines 393-395 of the revised manuscript, it now reads “...The absolute contribution of each source to DTT_v varies by 1.2-3.4 times between the south and north of Beijing (Table S2).” Due to the complex chemical composition of water-soluble $PM_{2.5}$, and the complex effect of interactions between metals and organics, as well as between organics and organics on DTT consumption of PM (Yu et al., 2018), it is difficult to understand their influence mechanisms. Each of these aspects require intensive studies in the future. Therefore, this study only mentioned that the interactions between metals and organic compounds can also affect DTT activity. In lines 319-322 of the revised manuscript, it reads “...the interactions between metals and organic compounds also affect the consumption of DTT..., with both synergistic and antagonistic effects. For example...”

Figure R1 shows the relationship between soluble trace elements and DTT_v . Generally, the relationship between most soluble trace elements and DTT_v was more non-linear than linear. Besides, the concentration of soluble trace elements was generally higher in the south than in the north (1.3-4.1 times) (Figure R2). These results affect the differences in correlation between DTT OP and soluble elements in the south and north. In addition, the interactions between metals and organic compounds also play a role, as described above. In lines 315-318 of the revised manuscript, it now reads “...As shown in Figure 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.”

The differences in correlation between DTT_v and WSOC and Abs in the south and north were mainly ascribed to the differences in chemical composition and sources of water-soluble PM. Of course, interactions between organics and between organics and metals could also have an impact (Yu et al., 2018). In this study, we analyzed the differences in the concentration of nitroaromatic compounds (NACs) and their correlation with DTT_v between the south and north. Due to the complex chemical composition of water-soluble organic matter, it is difficult to investigate the differences in the effects of interactions between organics and between organics and metals on DTT activity between the south and north. Therefore, there were no more measurements in the south. The analysis of this study suggests that the water-soluble $PM_{2.5}$ OP is closely related to its chemical composition and sources, and the effect of interactions between organics and between metals and organics on $PM_{2.5}$ OP is still worthy of further study. In lines 327-330 of the revised manuscript, it reads “...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.” In lines 395-397 of the revised manuscript, it reads “...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 OP of $PM_{2.5}$.”

Table R1. DTT_v values in the south and north of Beijing and the sources contributions.

	South	North
DTT _v (nmol min ⁻¹ m ⁻³)	3.9	3.5
Sources contribution to DTT _v (%)		
Biomass burning	25.2	8.4
Coal burning	15	19.9
Traffic-related	39.1	51.6
Secondary formation	17.2	13
Dust	2	3
Oil combustion	1.5	4.1
Sources contribution to DTT _v (nmol min ⁻¹ m ⁻³)		
Biomass burning	0.98	0.29
Coal burning	0.59	0.7
Traffic-related	1.5	1.8
Secondary formation	0.67	0.46
Dust	0.08	0.11
Oil combustion	0.06	0.14

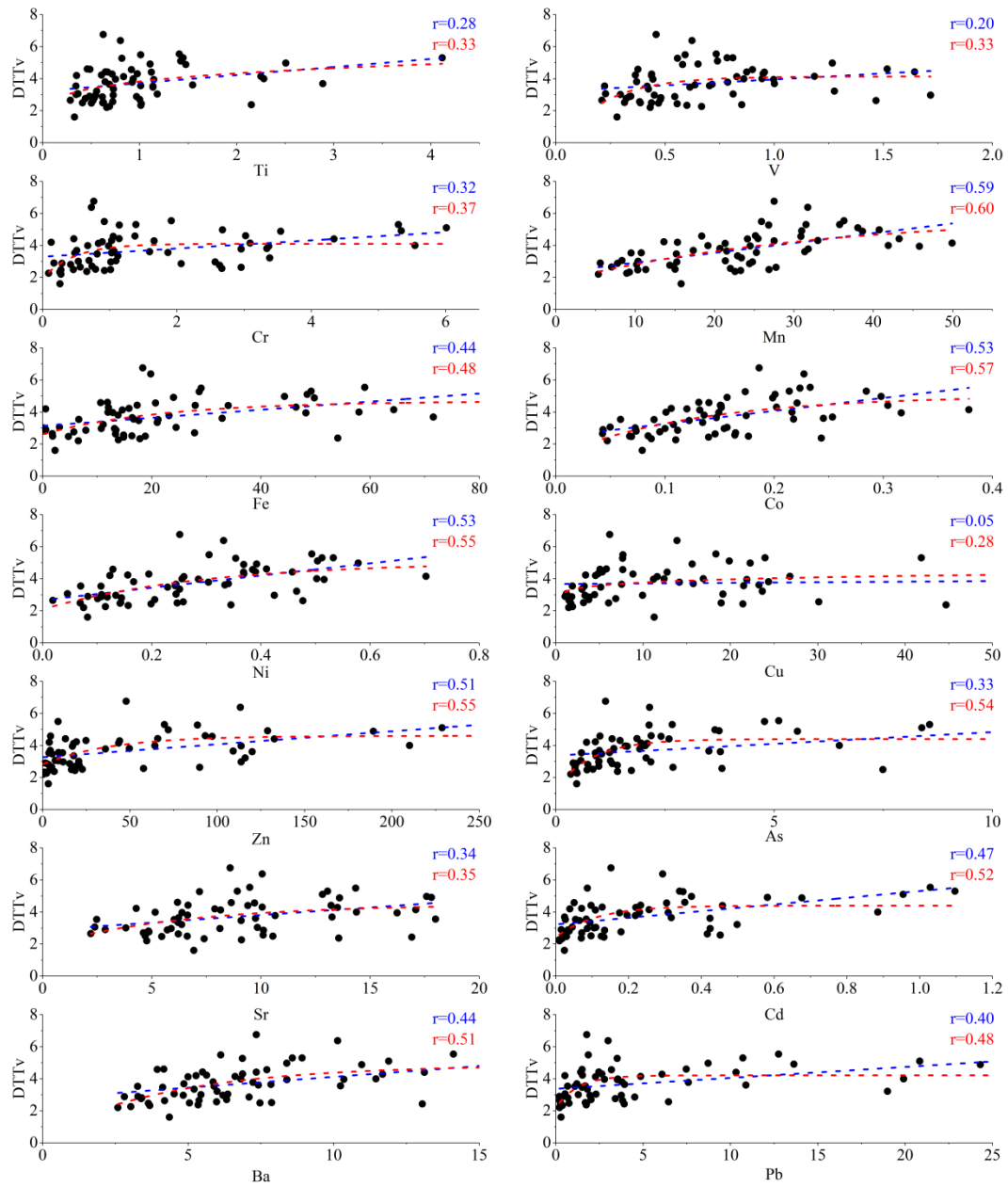


Figure R1. Relationship between soluble trace elements concentration (ng m⁻³) and DTT_v (nmol min⁻¹ m⁻³).

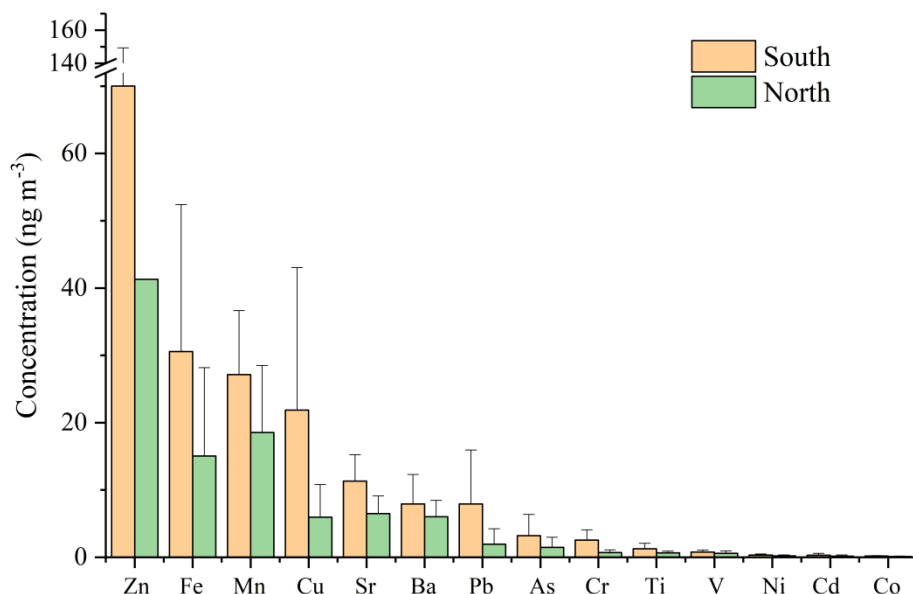


Figure R2. Concentrations of soluble elements in the south and north of Beijing.

The authors have adequately responded to the prior review. I will add, that further uncertainty analysis is suggested, and they should watch the precision with which they report their values. In particular, what is their reproducibility of sampled OP and how was reproducibility tested? Reproducibility of DTT-based OP assays is an issue: not that the measurements are “wrong”, just that they can vary by day of analysis given handling, dilution, extraction and other issues. Further, there is the issue of non-linear response brought up. Given the variability in their results and uncertainties in the methods, two significant figures are more than enough.

Response: Thanks for your careful reading and professional comments. The uncertainty analysis of organic compounds and trace elements are shown in Supporting Information (ICP-MS analysis and GC-MS analysis). For DTT analysis, for every 10 samples, select one sample to measure three times to check the reproducibility, and the relative standard deviation was lower than 5%. In lines 180-182 of the revised manuscript, it now reads “...Besides, 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%.” Further, in the revised manuscript, all data reported in this study have been changed to two significant figures.

Finally, the authors should have the manuscript grammar checked again, particularly the sections modified or added in response to the last reviews. While generally the article is reasonably good grammatically, there were some sections (e.g., the paragraph starting “Consider that for samples...”) that were in less good shape.

Response: Thank you for your suggestion. We have re-checked the grammar of the manuscript and made corresponding modifications. The paragraph starting with “Consider that for samples” now reads “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 sample containing high concentrations of soluble Cu and Mn (Figure 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 the PM_{2.5} concentration added to the reaction solution 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 difference in PM_{2.5} concentration added to the reaction solution of different samples should 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 phosphate matrix on the measured DTT values, as there is not a straightforward method to correct the artifacts caused by this phenomenon (Yalamanchili et al., 2023).” For other changes, please see the revised manuscript with modification marks.

References

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