

Point-by-Point Responses to the Comments from Reviewers

Manuscript ID: egusphere-2024-37

Manuscript Title: “Critical contribution of chemically diverse carbonyl molecules to the oxidative potential of atmospheric aerosols”

The corresponding authors: Prof. Jitao Lv and Prof. Yawei Wang

Responses to the Comments from Anonymous Referee 2:

Comments:

Li et al., utilized FT-ICRMS technology with their established screening procedure enabling a high-throughput screening of carbonyl molecules in ambient aerosol samples. They further linked these data with the DTT activity of water-soluble organic matter and found a positive correlation between carbonyl molecules and DTT activity. By employing several statistical tests and modeling, they proposed oxidized aromatic compounds containing the carbonyl group could be used as potential markers of atmospheric oxidative stress. Overall, I think these data are beneficial and the results are of great importance. I would recommend publication after the following concerns are addressed.

Response: We sincerely appreciate your positive comments. We have made careful revisions according to your comments and provided a point-by-point explanation for each comment.

1. *A significant correlation between DTT_{OC} and the number of carbonyl molecules was observed; however, the molecular intensity of carbonyls was not taken into account. I suggest the authors should consider weighing the effects of intensity and examine how it may affect the correlation.*

Response: Thanks for your suggestion, your point is similar to that of reviewer 1's comment 6.

Both the number and the number proportion of carbonyl molecules were positively correlated with DTT_{OC} (Pearson's $r = 0.55$, $p < 0.01$; and Pearson's $r = 0.63$, $p < 0.001$), whereas an insignificant or negative correlation was observed between those of non-carbonyls and DTT_{OC} (Pearson's $r = -0.26$, $p = 0.185$; and Pearson's $r = -0.63$, $p < 0.001$). We also performed a correlation analysis between DTT_{OC} and the normalized molecular intensities of carbonyls or non-carbonyls of each sample. Insignificant correlation was observed between the normalized molecular intensities of all carbonyls or non-carbonyls and DTT_{OC}. However, a significant positive correlation between the normalized molecular intensities of carbonyls and DTT_{OC} was obtained (Pearson's $r = 0.56$, $p < 0.01$) when sulfur-containing molecules were excluded (Figure R1 c). Sulfur-containing molecules in aerosols often displayed extremely high ionization efficiencies, leading to unreasonably high intensities of S-containing molecules detected by FT-ICR MS (Xie et al., 2022). When considering normalized molecular intensities in correlation analysis, it is more reasonable to exclude sulfur-containing molecules. The related revision and discussion have been added at lines 268-271 and Figure S14 in the revised manuscript.

In fact, it is a great challenge to quantification of mass data obtained by FT-ICR MS, as the peak intensity in a mass spectrum is not only determined by the initial concentration but also by the ionization efficiency of molecules. Using statistics based on the number of molecules can avoid the effect of ionization efficiency, but the concentration difference between molecules is ignored. For the statistics of molecular groups, we assume that their concentrations are normally distributed, so the number of detected molecules is to some extent representative of the abundance of this molecular group. Because of the uncertainty introduced by sulfur-containing molecules, we revised and used statistical methods based on the number of molecules rather than molecular intensities when analyzing the proportions of different molecular groups. The related revisions are presented in Figures 4, S9, S10, S11, S12, and S17.

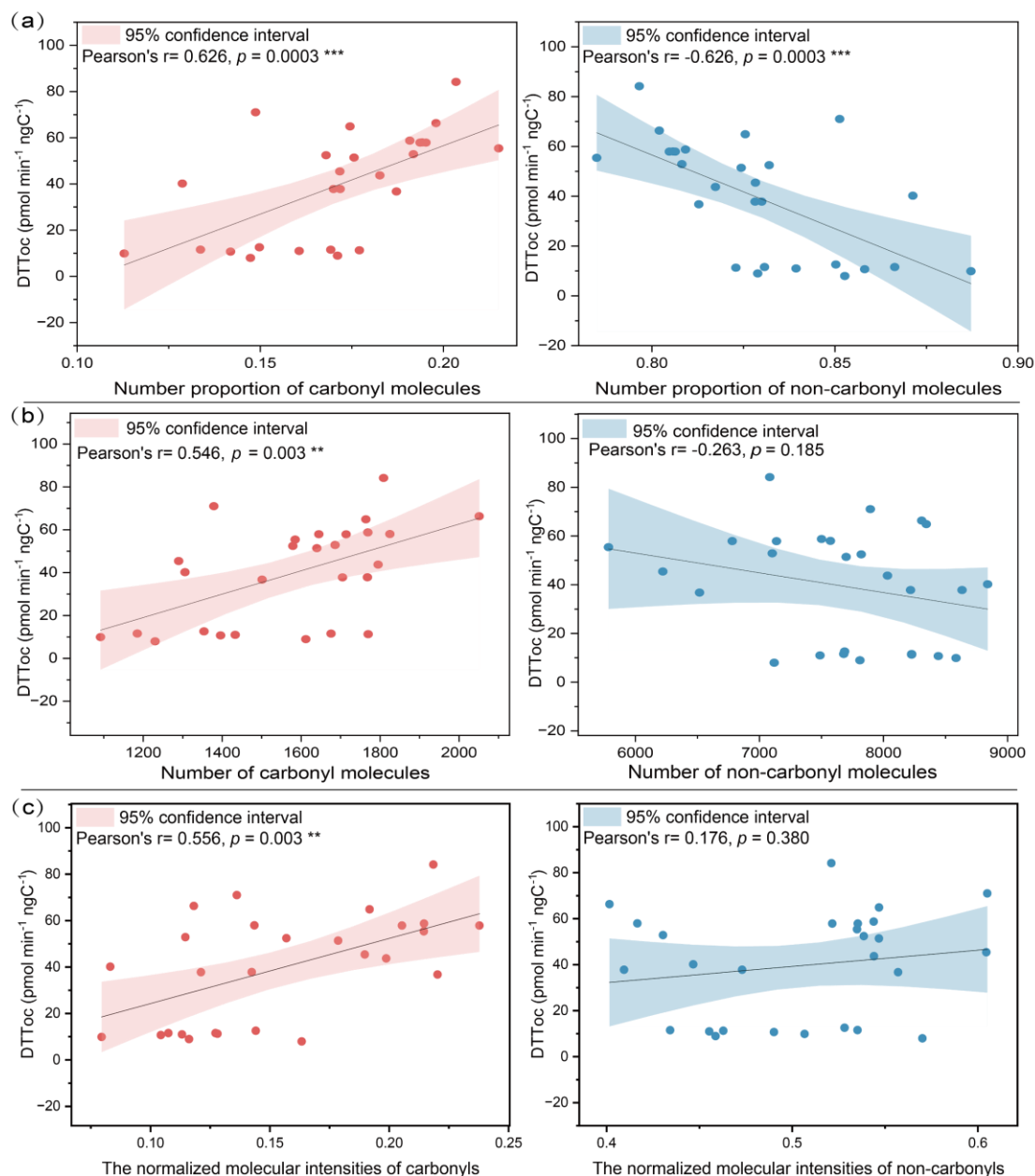


Figure R1. (a) Correlation analysis between the number proportion of carbonyl and non-carbonyl molecules and DTToc. (b) Correlation analysis between the number of carbonyl and non-carbonyl molecules and DTToc. (c) Correlation analysis between the normalized molecular intensities of carbonyl and non-carbonyl molecules (sulfur-containing molecules were eliminated) and DTToc.

Reference:

Xie, Q., Su, S., Dai, Y., Hu, W., Yue, S., Cao, D., Jiang, G., and Fu, P.: Deciphering ¹³C and ³⁴S Isotopes of Organosulfates in Urban Aerosols by FT-ICR Mass Spectrometry, *Environ. Sci. Technol. Lett.*, 9, 526–532, <https://doi.org/10.1021/acs.estlett.2c00255>, 2022.

2. *The authors utilized Suwannee River natural organic matter and diesel soot to validate a decrease in DTT activity after the removal of carbonyls. I suggest the authors should discuss why similar experiments were not performed using real*

ambient WSOM. If feasible, conducting additional experiments to demonstrate a substantial decrease in DTT activity after removing carbonyls for ambient WSOM is recommended. Such results would enhance the credibility of the findings. At the very least, the representatives of Suwannee River natural organic matter and diesel soot should be discussed in the manuscript.

Response: Thanks for your thoughtful comments. Similar to comment 9 of reviewer 1, we have performed additional experiment to verify whether NaBH₄ treatment can reduce the DTT activity using ambient-collected OA samples (PM_{2.5} = 52.55 μg m⁻³). As shown in Figure R2, after NaBH₄ treatment, the DTT activity of the real OA sample reduced by about 60%, which was consistent with the results using model samples. And the corresponding discussion was added at lines 308-311 and Figure S15 of the revised manuscript.

Because of the limited amount of WSOM in PM_{2.5} samples, it cannot meet the needs of NaBH₄ reduction, PFBHA derivatization, FT-ICR MS analysis, and DTT activity assay. Therefore, we employed two model samples for these analyses instead of real samples. One is SRNOM obtained from IHSS because it has similar chemical composition to HULIS (Havers et al., 1998; Graber and Rudich, 2006); The other is WSOM extracted from diesel soot, as it is an important source of carbonyls in urban OA (Grosjean et al., 2001; Wang et al., 2023a). We have revised and explained the reason for choosing these two models at lines 295-298.

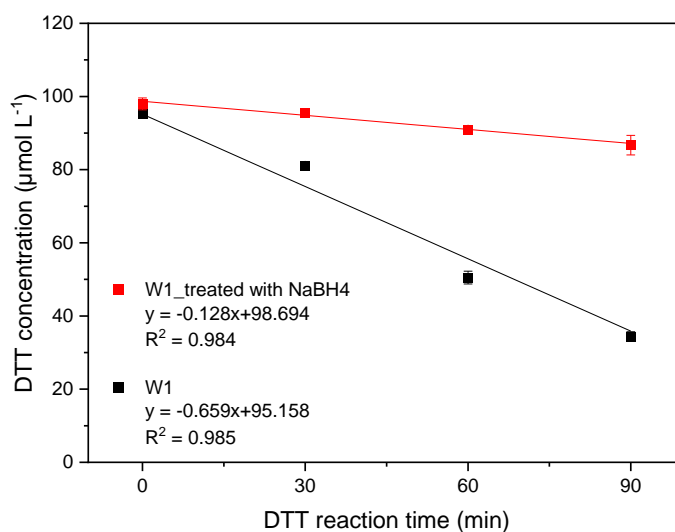


Figure R2. The DTT activity of WSOM from PM_{2.5} sample before and after NaBH₄ treatment was measured.

Reference:

Havers, N., Burba, P., Lambert, J., and Klockow, D.: Spectroscopic Characterization of Humic-Like Substances in Airborne Particulate Matter, *Journal of Atmospheric Chemistry*, 29, 45–54, <https://doi.org/10.1023/A:1005875225800>, 1998.

Graber, E. R. and Rudich, Y.: Atmospheric HULIS: How humic-like are they? A comprehensive and critical review, *Atmos. Chem. Phys.*, 6, 729–753, <https://doi.org/10.5194/acp-6-729-2006>, 2006.

Grosjean, D., Grosjean, E., and Gertler, A. W.: On-Road Emissions of Carbonyls from Light-Duty and Heavy-Duty Vehicles, *Environ. Sci. Technol.*, 35, 45–53, <https://doi.org/10.1021/es001326a>, 2001.

Wang, L., Wen, W., Yan, J., Zhang, R., Li, C., Jiang, H., Chen, S., Pardo, M., Zhu, K., Jia, B., Zhang, W., Bai, Z., Shi, L., Cheng, Y., Rudich, Y., Morawska, L., and Chen, J.: Influence of Polycyclic Aromatic Compounds and Oxidation States of Soot Organics on the Metabolome of Human-Lung Cells (A549): Implications for Vehicle Fuel Selection, *Environ. Sci. Technol.*, 57, 21593–21604, <https://doi.org/10.1021/acs.est.3c05228>, 2023a.

3. *The reported DTT_m (Figure 2) is over an order of magnitude lower than the general reported DTT_m in literature (e.g., Yu et al., *Journal of Hazardous Materials*, 2022 (10.1016/j.jhazmat.2022.128839); Campbell et al., *Atmos. Chem. Phys.*, 2021 (10.5194/acp-21-5549-2021), works for Beijing DTT activities). Please discuss the possible reasons for the difference.*

Response: Thanks for your suggestion. After recalculating for DTT_m (see the 4th question), the DTT_m range in our study is between 0.2 and 28.2 pmol/min/μg, which is consistent with the order of magnitude reported in previous literature. Figure 2 and S13 have depicted the correct values of DTT_m.

In addition, the DTT levels measured in this study were still reduced compared to previous studies. For example, this study observed a significantly lower DTT level in 2022 compared to those reported in 2016 (DTT_v = 1.9±0.3 nmol min⁻¹ m⁻³, DTT_m ≈ 10-75 pmol min⁻¹ μg⁻¹) and 2017 (5.8±7.1 nmol min⁻¹ m⁻³, DTT_m ≈ 20-160 pmol min⁻¹ μg⁻¹) for Beijing PM_{2.5} samples (Yu et al., 2022; Campbell et al., 2021). This may be attributed to China's implementation of the "Three-Year Action Plan (2018-2020)", an energy policy that gradually shifted the use of coal to natural gas and electricity for cooking and heating in rural areas, leading to livelihood-related heating and household emissions were reduced (Du et al., 2022; Li et al., 2023c). The revision was presented at lines 251-257 of the revised manuscript.

Reference:

Yu, Q., Chen, J., Qin, W., Ahmad, M., Zhang, Y., Sun, Y., Xin, K., and Ai, J.: Oxidative potential associated with water-soluble components of PM_{2.5} in Beijing: The important role of anthropogenic organic aerosols, *J. Hazard. Mater.*, 433, 128839, <https://doi.org/10.1016/j.jhazmat.2022.128839>, 2022.

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, *Atmospheric Chemistry and Physics*, 21, 5549–5573, <https://doi.org/10.5194/acp-21-5549-2021>, 2021.

Du, H., Li, J., Wang, Z., Chen, X., Yang, W., Sun, Y., Xin, J., Pan, X., Wang, W., Ye, Q., and Dao, X.: Assessment of the effect of meteorological and emission variations on winter PM_{2.5} over the North China Plain in the three-year action plan against air pollution in 2018–2020, *Atmospheric Research*, 280, 106395, <https://doi.org/10.1016/j.atmosres.2022.106395>, 2022.

Li, Y., Lei, L., Sun, J., Gao, Y., Wang, P., Wang, S., Zhang, Z., Du, A., Li, Z., Wang, Z., Kim, J. Y., Kim, H., Zhang, H., and Sun, Y.: Significant Reductions in Secondary Aerosols after the Three-Year Action Plan in Beijing Summer, *Environ. Sci. Technol.*, 57, 15945–15955, <https://doi.org/10.1021/acs.est.3c02417>, 2023c.

4. *Furthermore, based on the discrepancy between DTT_v and DTT_m in Figure 2, it appears that they cannot be converted by the equation provided by the author. For instance, to obtain the DTT_v shown in Figure 2, the DTT_m would need to be multiplied by approximately 1000 ug/m³ PM_{2.5} concentration. I recommend double-checking the data for accuracy. Additionally, please include the PM_{2.5} concentrations in Table S1, and it would be preferable to provide TOC concentration data for the air rather than in the WSOM extracts.*

Response: Thanks for your insightful comments. We have provided PM_{2.5} concentration data (μg m⁻³) at Table S1 and Figure S8.

We meticulously reviewed the calculation process of converting DTT_v to DTT_m, and we found a mistake when during conversion. In the previous manuscript, we used the product of PM_{2.5} concentration and 24-hour sampling time for calculating DTT_m. In the revised manuscript, only the PM_{2.5} concentration was used for DTT_m calculation, consistent with the equation provided at line 171. Additionally, DTT_{oc} utilized the TOC concentration of WSOC, thus remaining unaffected.

In the revised manuscript, Figures 2 and S13 depicted the correct values of DTT_m ($0.2\text{--}28.2 \text{ pmol min}^{-1} \mu\text{g}^{-1}$). Additionally, we only measured the TOC values of WSOM, hence cannot provide TOC concentration data for the air data.

5. Figure S11 will be more informative by showing the categorized groups of molecular formulas for different sampling periods instead.

Response: Thanks for your suggestion. The modified figure illustrates a comparison of the categorization of different molecular formulas in the three sampling periods (Winter, Winter Olympics, and Summer) (shown in Figure R3 below). The corresponding modifications are shown in Figure S12 in the Supporting Information.

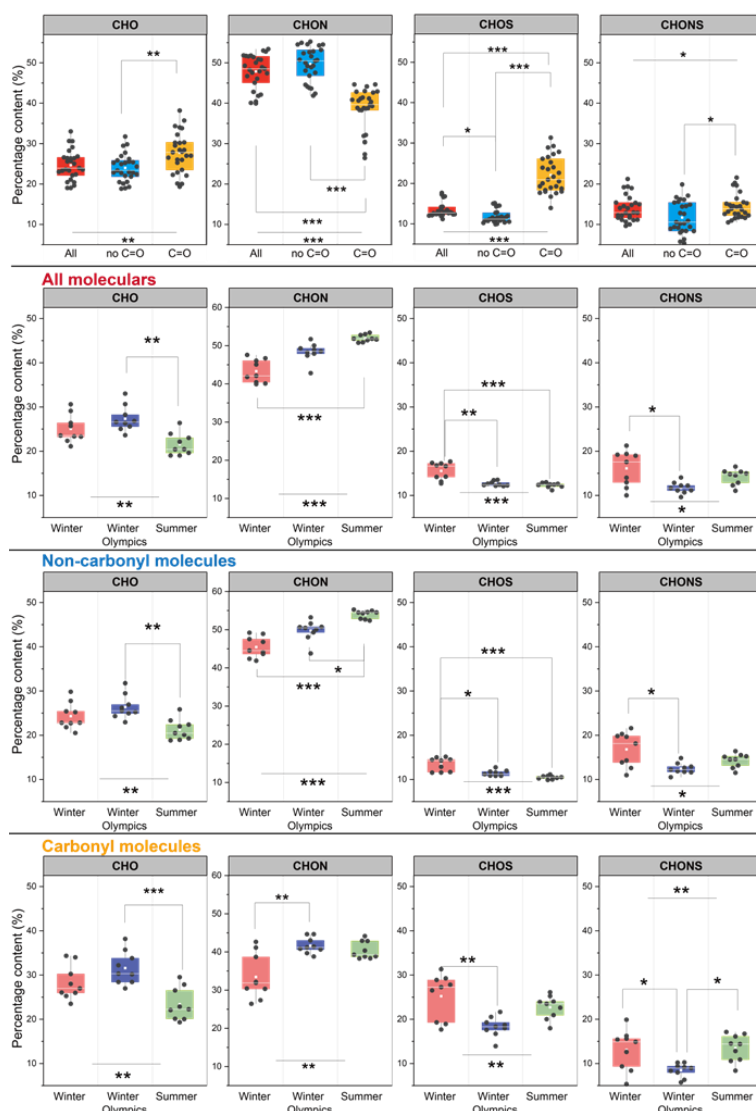


Figure R3. Differences in the percentage distribution of elemental composition based on the molecular numbers of all organic, non-carbonyl, and carbonyl molecules in winter, summer and Winter Olympics (Kruskal-Wallis tests, Differences between groups were considered statistically significant when $p < 0.05$, with $0.01 < p < 0.05$ marked by *; $p < 0.01$ marked by **; and $p < 0.001$

marked by ***).

6. *Line 244: "... This is likely due to the differences in aerosol sources in different seasons." please expand the discussion, e.g., what could be the main sources for DTT in summer and winter, respectively.*

Response: Thank you for your suggestion. In winter, fossil fuel and biomass burning is a major local source of PM_{2.5} in suburban sites, while this special combustion source aerosol in suburban sites was eliminated in summer (Steimer et al., 2020; Campbell et al., 2021). The relevant discussion was added at lines 261-263 of the revised manuscript.

Reference:

Steimer, S. S., Patton, D. J., Vu, T. V., Panagi, M., Monks, P. S., Harrison, R. M., Fleming, Z. L., Shi, Z., and Kalberer, M.: Differences in the composition of organic aerosols between winter and summer in Beijing: a study by direct-infusion ultrahigh-resolution mass spectrometry, *Atmospheric Chemistry and Physics*, 20, 13303–13318, <https://doi.org/10.5194/acp-20-13303-2020>, 2020.

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, *Atmospheric Chemistry and Physics*, 21, 5549–5573, <https://doi.org/10.5194/acp-21-5549-2021>, 2021.

7. *Line 338: "These results suggested that aromatic secondary products containing carbonyl group produced from combustion by-products in winter are potential molecular markers of atmospheric oxidative stress." Here I suggest the authors discuss the study by Liu et al., et al., 2023 (10.1021/acs.est.3c03641), where similar findings are observed for cellular oxidative stress. Also, the authors should clarify the combustion activities only occurred in winter (and also during the winter Olympic period) but not in summer.*

Response: Thank you for your comment and provide us with an excellent reference. According to Liu et al., we further highlight the role of oxygenated organic aerosols containing carbon-oxygen double bonds and aromatic structures in cellular oxidative stress, along with their higher contribution during the winter season. The revision was presented at lines 376-378 of the revised manuscript.

Additionally, while combustion activities are not exclusively limited to the winter season, they typically increase during winter due to heating activities in cold conditions. We clarified this point in lines 379-380 of the revised manuscript.

8. *Conclusion section: the first paragraph regarding the authors' FT-ICR-MS method was not discussed in the Results and Discussion section and is not rational to be a conclusion of this work.*

Response: Thank you for your suggestion. The section regarding the FT-ICR-MS method has been deleted.

9. *Conclusion section: aromatic carbonyl molecules are suggested as indicators of atmospheric oxidative stress. However, the second paragraph primarily discusses the possible formation sources of general carbonyl molecules, such as terpene and isoprene oxidation, which do not produce aromatic carbonyl molecules. The authors should revise the discussion to be more explicit and focused. Otherwise, the current discussion on the formation pathways of carbonyls seems to favor summer conditions, which contradicts the findings of this study.*

Response: Thank you for your insightful suggestion. The conclusion of the paper was rewritten to highlight our main research results and findings. Specifically, we highlight the significant contribution of highly unsaturated and aromatic carbonyl molecules to OP, indicating the need for more attention to the potential health risks posed by these molecules. These carbonyls primarily originate from fuel combustion, including biomass burning and fossil fuel combustion. The detailed revision was presented at lines 393-397 of the revised manuscript.

Minor comments:

1. In Figure S2 (a) and (b), the fittings for blank samples look incorrect. The fitting curves do not come across any data point.

Response: We performed linear regression on the original blank sample data once again in the origin software, and obtained a new fitted curve (Figure R4), as shown in Figure S3 in the revised supporting information.

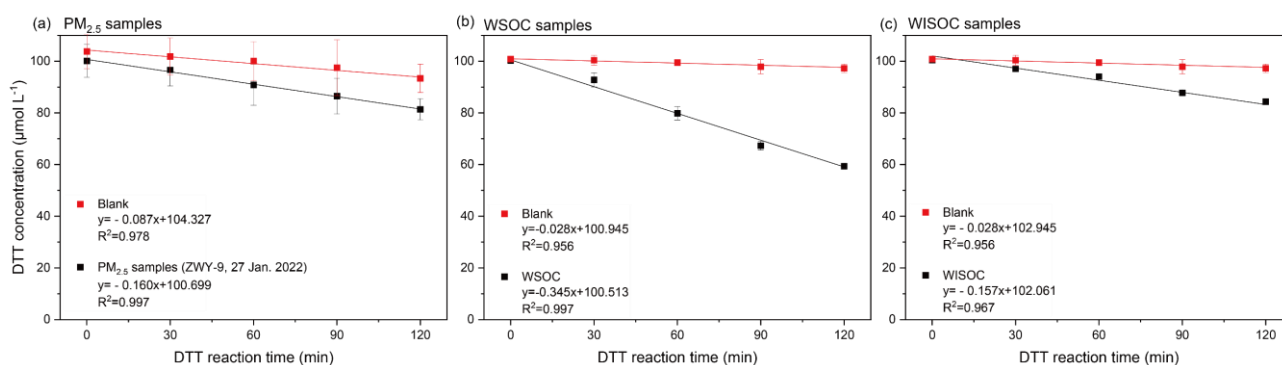


Figure R4. Reproducibility of DTT measurements of samples. (a) DTT measurements of PM_{2.5} samples and backgrounds, using the downtown site on January 27, 2022, as an example. (b) DTT measurements of a water-soluble organic carbon (WSOM) quality control sample, which was prepared containing a mixture of all WSOM samples. (c) DTT measurements of a water-insoluble organic carbon (WISOM) quality control sample, which was prepared containing a mixture of all WISOM samples.

2. Please clarify the sampling period for each sample. Was it 24-hr sampling?

Response: The sampling period for each sample was one day (24 hours), which was added to line 101 of the revised manuscript.

3. A number of typos in the manuscript, please carefully check. E.g., WSOM has been written as WOSM here and there.

Response: The manuscript has been carefully examined and all “WOSM” has been revised to “WSOM”, as at lines 133, 139 and 290.

4. Figure S11, “CHO” figure, x-axis, “oC=O” should be “no C=O

Response: The x-axis label “oC=O” has been corrected to “no C=O” in Figure S12.