Reviewer 5:

This paper describes the microplastics in the coarse and fine aerosol fractions from five different sources in northern China, quantified using pyrolysis GC/MS. A selection of common plastic additives was also detected. The oxidative potentials of filter extracts were determined using a DTT assay. Livestock breeding and plastic burning were found to produce the largest potential hazards of the five sources tested. This work represents an important study in a growing area of interest in atmospheric science, and I would recommend publication if the authors can add clarity to their methodology, QA/QC protocols, and data analysis.

Dear reviewer,

Thanks very much for taking your time to review this manuscript. We have carefully reviewed your comments and made the appropriate revisions to improve the quality of our manuscript. We have already added more details to clarify our methodology, QA/QC protocols, and data analysis. Below are our detailed responses to your comments:

Specific comments:

Line 39 “Global plastic production has gradually increased” – has it gradually or exponentially increased?

Response:

Thank you for highlighting this important distinction. Based on data from “Production, use, and fate of all plastics ever made (Sci. Adv., 2017, 3, e1700782)”, we observed that global plastic production growth accelerated significantly after 1990, with a nearly vertical rise post-2000. Thus, “exponentially increased” more accurately reflects the trend of global plastic production than “gradually increased”. We have revised the sentence as follows.

“Global plastic production has increased exponentially after 1990, resulting in serious environmental contamination.”

Reference:

Geyer, R., Jambeck, J. R., and Law, K. L.: Production, use, and fate of all plastics ever made, Sci. Adv., 3, 5, 10.1126/sciadv.1700782, 2017.

Line 43 “Current research on MPs pollution sources have primarily focused on aquatic and terrestrial ecosystems..” – I would argue that current research has started to focus much more on airborne plastics, thus, I would recommend rewording this line.

Response:

We do agree with the reviewer’s comment. This point has been revised as follows:

"Research on microplastics (MPs) pollution initially focused on aquatic and terrestrial ecosystems, but recent years have seen growing attention to atmospheric MP pollution (Allen et al., 2020)."

Reference:

Allen, S., Allen, D., Moss, K., Le Roux, G., Phoenix, V. R., and Sonke, J. E.: Examination of the ocean as a source for atmospheric microplastics, Plos One, 15, 10.1371/journal.pone.0232746, 2020.

Line 50 – I would add a qualifier in this line as the Yang et al. (2021) study used a cutoff size of

50 µm, thus, there are likely many more plastic particles produced than the values reported in the study.

Response:

Thank you for pointing this out. To clarify this limitation, we have added a qualifier to the sentence. The statement has been revised as follows.

"Yang et al. (2021) have estimated that per metric ton of plastic can ***potentially*** *produce 360 to 102,000 MPs, primarily composed of polypropylene (PP) and polystyrene (PS)."*

Reference:

Yang, Z., Lu, F., Zhang, H., Wang, W., Shao, L., Ye, J., and He, P.: Is incineration the terminator of plastics and microplastics? J. Hazard. Mater., 401, 10.1016/j.jhazmat.2020.123429, 2021.

Line 99 – Section 2.1, can the authors provide sampling dates and a map of where sampling took place (with long and lat)? This would be very helpful for future modelling studies.

Response:

We have revised the Figure S1 to indicate the sampling locations, sampling dates, and respective longitudes and latitudes for different sources (PB: Plastic Burning, FB: Fruit-bag Burning, RT: Road Traffic, AF: Agricultural Film, LB: Livestock Breeding).

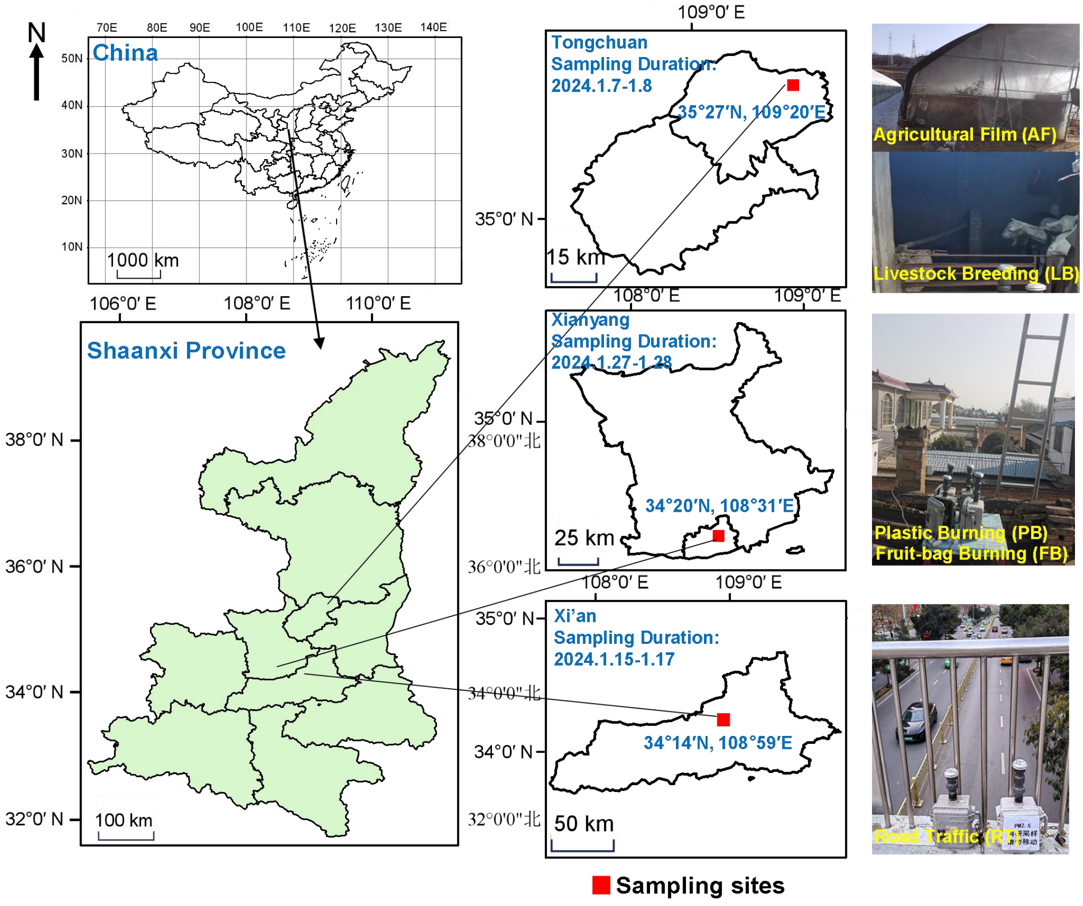

Figure S1 Sampling sites for different sources (PB: Plastic Burning, FB: Fruit-bag Burning, RT: Road Traffic, AF: Agricultural Film, LB: Livestock Breeding).

Line 121 – what was the material of the air cassettes used? And did it influence the final results?

Response:

The air cassettes used in our study were made of glass, a material selected for its chemical inertness to ensure no interference with experimental results. Each cassette was thoroughly rinsed with ethanol absolute before use.

Line 122 – did filter weighing follow any published standard and was static electricity neutralised prior to weighing?

Response:

The filter weighing process in our study was conducted in accordance with the Chinese National Standard GB/T 39193-2020 and the reference “Chemical characterization of $PM_{2.5}$ in heavy polluted industrial zones in the Guanzhong Plain, northwest China: Determination of fingerprint source profiles (Sci. Total Environ., 2022, 840, 156729).”, which provide detailed protocols for the determination of particulate matter mass concentration in ambient air, ensuring the reliability of our filter weighing procedures. We used anti-static instrument (ANTIST-kit-un, MettlerToledo, Switzerland) to neutralize static electricity prior to weighing the filters.

Reference:

Wang, Z. X., Xu, H. M., Gu, Y. X., Feng, R., Zhang, N. N., Wang, Q. Y., Liu, S. X., Zhang, Q., Liu, P. P., Qu, L. L., Ho, S. S. H., Shen, Z. X., and Cao, J. J.: Chemical characterization of $PM_{2.5}$ in heavy polluted industrial zones in the Guanzhong Plain, northwest China: Determination of fingerprint source profiles, Sci. Total Environ., 840, 9, 10.1016/j.scitotenv.2022.156729, 2022b.

Line 124 – please provide more detailed information on how the field blanks were treated/collected.

Response:

We have provided the information on how the field blanks collected in Lines 163-166.

“The field blank of each type of source was synchronously collected with active sampling. Unused filters (the same batch as sampling filters) were loaded into identical sampling devices, which were placed adjacent to operational samplers for the entire duration of one sampling event.”

Line 125 – Several studies have found that nitrile gloves can potentially influence pyrolysis GC/MS analysis of polymers, particularly PE. Please discuss.

Response:

We sincerely appreciate the reviewer’s insightful comment. We fully acknowledge this concern and have taken multiple precautions in our experiment to minimize any possible interference.

Firstly, we cleaned the gloves with ethanol absolute before the experiment. This effectively removed potential contaminants from the gloves, minimizing their interference with the pyrolysis GC/MS analysis.

Secondly, we used stainless steel tweezers to handle the filter membrane throughout the experiment, avoiding direct contact between the gloves and the filters. This further ensured the reliability of the analysis results.

Moreover, the blank experiment was also conducted with gloves on, and the results from the blank experiment have been subtracted. This step effectively eliminated the potential interference that might be caused by the gloves, ensuring the accuracy of the final results.

Line 138 – Please provide explicit details of preparation of samples, instrument configurations, and QA/QC protocols in this manuscript rather than referring to another paper. In regards to QA/QC, please provide information on positive and negative controls, the amount of analytes detected in background samples, and any subtractions that were completed to produce the final values. Addition to the supplemental would be a satisfactory placement for this information.

Response:

We do agree with the reviewer's comment. We have now incorporated the QA/QC protocols into Section 2.3 of the Methods. Additionally, the detailed sample preparation procedures and instrument configurations are provided in the Supplemental Information. The specific information is as follows:

"Quality assurance/Quality control (QA/QC)

The flow rates of all samplers were calibrated using a mass flowmeter (Model 4140, TSI, Shoreview, MN, USA) before and after each sampling cycle. All quartz filters used in this study were preheated at 800°C for 3 h to remove any potential contaminants and then cooled before use. To minimize experimental error, sampling was conducted in duplicate for each particle size of each source. For the chemical measurements, one in every 10 samples was reanalyzed for quantity assurance purposes, and the SD errors of replicate trials were within 10% for the pyrolysis analyses. Calibration curves were established using reference standards. The linearities of the standard calibration curves were > 0.987. The standard deviations of the pyrolyzed standard were within 94.1% to 98.3%. Background contamination (Table S3) was monitored by processing operational blanks (unexposed filters) simultaneously with field samples."

*"**Appendix 1** Analysis of Microplastics*

In the quantification of miccroplastic (MPs) contents, 0.526 cm^2 of a filter sample was folded with ferromagnetic pyrofoil (F670, Japan Analytical Industry Co., Ltd, Tokyo, Japan) using a clean flip head tweezer. The pyrofoil was loaded onto a Curie-point pyrolyzer (JHS-3, Japan Analytical Industry Co., Ltd) coupled with a GC/MS (7890GC/5975MS. Agilent Technology) system, and was rapidly heated to 670°C at 5 s. The interface between Curie point and GC injection port was 300°C. The pyrolyzed compounds were separated with a DB-5ms capillary column (30 m × 0.25 mm × 1 μm film thickness; J&W Scientific, USA). The initial the GC oven temperature was at 50°C for 5 min, increase at a rate of 25°C min^{-1} to 300 °C, and then hold at the final temperature of 310°C for 10 min. The carrier gas was ultra-high purity helium (He). The mass selective detector (5975, Agilent Technology) was at a full scan mode from 30 to 500 amu under electron ionization (EI) at a voltage of 70 eV and an ion source temperature of 230°C. Peaks were identified from the known fragmentation, mass spectra, and retention times of the target pyrolysis products of detected MPs (Table S1). Calibration curves were prepared using the reference standards. All standards excepting rubbers (99%, JSR Corporation) were purchased from Dupont (≥ 98%, USA). The linearities of the standard calibration curves were > 0.987. As markers for butadiene rubber (BR) (e.g., vinylcyclohexene) have interferences from SBR, BR is not quantified independently; instead, the sum of SBR and BR is reported to reduce uncertainties."

Line 140 – please provide manufacturer information on the thermal desorption unit used.

Response:

The statement has been revised as follows.

"An in-port thermal tube (78 mm long, 4 mm I.D., 6.35 mm O.D., Agilent Technology, USA) coupled with a GC/MS system (7890GC/5975MS, Agilent Technology, USA) was utilized to analyze phthalates."

Line 142 (and elsewhere) – please provide supplier information and purity for all chemicals used in the study.

Response:

The supplier details and purity of all chemicals used in this study have been added to the Methods section.

"An in-port thermal tube (78 mm long, 4 mm I.D., 6.35 mm O.D., Agilent Technology, USA) coupled with a GC/MS system (7890GC/5975MS, Agilent Technology, USA) was utilized to analyze phthalates, including dimethylphthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), bis(2-ethylhexyl)phthalate (DEHP), and di-n-octyl phthalate (DnOP) All PAEs were purchased from Sigma-Aldrich (≥ 98%, Steinheim, Germany)."

"Nine types of benzothiazole (97%, Thermofisher Scientific Co., LTD, Waltham, MA, United States) related compounds were quantified"

Line 154 – the extraction and concentration procedures need to be provided in detail.

Response:

Thank you for your comments. The extraction and concentration procedures were performed as detailed in Appendix 2 in Supplemental Information, including ultrasonic extraction and purification.

"The filter is transferred into a test tube, and 10 mL of a mixture of ultrapure deionized water (18 M-Ohm) and methanol (HPLC grade, Fisher Chemical, USA) (5:3, v:v) is added. The sample is extracted in an ultrasonic water bath at room temperature for 60 min. The combined extracts are concentrated and then diluted with ultrapure deionized water containing 0.2% v/v formic acid (~pH 2.5). The diluted extract is purified using an Oasis HLB Flangeless Vac Cartridge (3cc, 60 mg sorbent per cartridge, 30 μm particle size; Waters, USA)."

Line 158 – please provide method details instead of referring to a different paper.

Response:

We sincerely appreciate your suggestion. As requested, we have now provided the method details in Supplementary Information (Appendix 2). The specific information is as follows:

*"**Appendix 2** Analysis of plasticizers*

Phthalates were quantified using in-injection port-thermal desorption/mass spectrometry (TD-GC/MS) method. Aliquots of the filters (1.578 cm2) were cut into small pieces, spiked with ISs (Chrysene-d12, 96%, LGC Standard Limited, United States), and inserted into thermal tubes (78 mm long, 4 mm I.D., 6.35 mm O.D., Agilent Technology, USA) for analyses. The sample tube was directly loaded into a GC injection port (GC7890, Agilent Technology), at an initial temperature of 50°C. The temperature of injector was then ramped to 275°C for desorption in a splitless mode, while the GC oven temperature was kept at 30°C. The desorbed analytes were refocused at the column head. After the injector temperature reaches the set point, the oven program starts. The analytes were speared by an DB-5ms capillary column (30 m × 0.25 mm i.d. × 0.25 μm film *thickness; J&W Scientific). The carrier gas was ultra-high purity (99.9999%) He at a constant flow of 1.0 cm3 min-1. The MSD (5975, Agilent Technology) was full scanned from 50 to 550 amu under electron impact ionization (EI) at a voltage of 70 eV and an ion source temperature of 230°C. Identification was achieved by characteristic ion and retention times of the chromatographic peaks with those of authentic standards.*

To quantify benzothiazole and its derivatives, each of 1.578 cm2 of the filter sample was cut and spiked with an internal standard (IS) of benzothiazole-d4 (benzothiazole=d4, 95%, LGC Standard Limited, United States). The filter is transferred into a test tube, and 10 mL of a mixture of ultrapure deionized water (18 M-Ohm) and methanol (HPLC grade, Fisher Chemical, USA) (5:3, v:v) was added. The sample was extracted in an ultrasonic water bath at room temperature for 60 min. The combined extracts were concentrated and then diluted to with ultrapure deionized water containing 0.2% v/v formic acid (~pH 2.5). The diluted extract was purified using an Oasis HLB Flangeless Vac Cartridge (3cc, 60 mg sorbent per cartridge, 30 µm particle size; Waters, USA). The target analytes were eluted with 5 mL of methanol and the eluents were evaporated to 1 mL under a gentle nitrogen stream prior to analysis. The separation of target analytes was performed using an ultra-performance liquid chromatography (UPLC; ACQUITY, Waters), and both identification and quantification were accomplished using a triple quadrupole mass spectrometer (ESI-MS/MS; Xevo TQ-S, Waters). An ACQUITY UPLC BEH SHIELD RP 18 column (100 mm ×3 mm × 1.7 mm) was serially connected to a Vanguard column (BEH C18, 5 mm × 2.1 mm × 1.7 mm). The mobile phase comprises 100% methanol (A) and ultrapure deionized water acidified with 0.1% (v/v) formic acid (B) at a flow rate of 450 mL min-1. A gradient elution program was applied for the separation. The tandem MS system was operated in the positive ion multiple reaction monitoring mode. Identification was achieved by characteristic ion and retention times of the chromatographic peaks with those of authentic standards.”

Line 167 – please discuss potential for interferences with detection or any specificity testing that was completed.

Response:

In order to avoid fluorescence detector saturation owing to matrix components in the quantification of BPA, the excitation and emission wavelengths from 0 to 14 min were fitted at 210 and 220 nm, respectively. Besides, to eliminate potential interferences from other organic compounds in PM samples, we employed both peak purity testing and spectrum matching in the quantification of BPA. For peak purity, we set a scan threshold of 1 mAU and required a peak coverage of 95%. For spectrum matching, we established a similarity threshold of 0.98. These rigorous measures effectively confirmed the presence of BPA in the samples, free from interference from other compounds.

Line 168 – was quantification completed using an internal standard or external standard method?

Response:

Quantification of total bisphenol A (BPA) in this study was completed using an external standard method. Calibration curves for BPA were prepared using BPA standard (≥ 99%, Sigma-Aldrich, Steinheim, Germany) solutions in acetonitrile. The linearities of the standard calibration curves were > 0.987. The recoveries of bisphenol A (BPA) are in a range of 96.3%-99.3%.

Section 2.3. – With regard to the FB filters, presumably many combustion products would be produced that no longer resemble the chemical structure of the original plastic. Please discuss the potential of these compounds to influence the oxidative testing.

Response:

Thank you for your valuable comment. Our results demonstrated that PMs from combustion sources exhibited higher oxidative potential (OP) compared to non-combustion sources. This suggests that the combustion process may enhance the OP of PM. This phenomenon may be associated with the products generated from the combustion of plastics. However, as we were unable to isolate these combustion products from PM, we could not quantify the impact of polymer combustion products on the OP results.

In our study, we focused on exploring the relationship between the DTT activity of PMs and microplastics and plasticizers using a correlation method. We focused on the oxidative potential of residual microplastics and plasticizers after combustion, rather than their thermal transformation products.

We acknowledge the importance of investigating the specific contributions of combustion-derived microplastics to PM OP. In future research, we propose conducting DTT assays on standard microplastic subjected to combustion treatment, comparing with non-combusted microplastics. This approach could provide valuable insights into the role of combustion products of microplastics in altering the oxidative potential of PM.

Line 221 – since wax coatings often contain a mixture of alkanes, please discuss any potential interferences of the wax on the pyrolysis GC/MS results (e.g. PE quantification).

Response:

The reason we distinguish between plastic burning (PB) and fruit bag burning (FB) rather than classifying them as a single combustion source is that the wax layer in fruit bags cannot be separated from the plastic. This is a featured source in the Guanzhong region (This is also quite common in fruit producing areas in northern China), and local residents typically burn fruit bags directly without separating the wax.

By comparing the results of PB and FB, we found that, there were no significant differences in the composition and concentration of microplastics and plasticizers emitted from PB and FB. These results indicate that the wax coating in FB has minimal influence on the analytical results.

Line 223 – the MPs in PB and LB were 50% of the PM, was this by mass? Please clarify and also present the percentage of PM that was attributed to plastic in all scenarios.

Response:

We apologize for causing confusion to the reviewer. The 50% mentioned in original Line 223 refers to the relative proportion of coarse and fine microplastics from PB and LB, meaning that the combined mass percentage of coarse and fine microplastics is 100%. The sentence has been revised as follows.

"Notably, MPs in Plastic Burning and Livestock Breeding constituted a comparable proportion in both fine and coarse fractions, both close to 50%."

We also presented the mass proportion of microplastics in PMs from five sources in Figure S4.

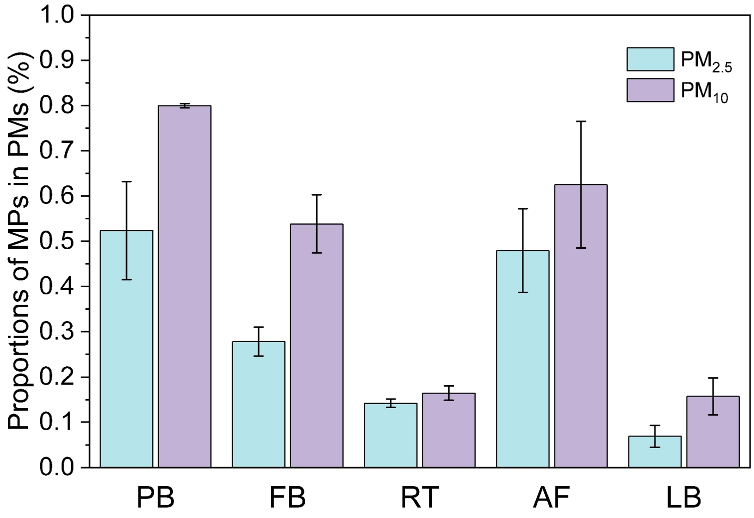

Figure S4 The mass proportion of MPs in PMs from five sources (PB: Plastic Burning, FB: Fruit-bag Burning, RT: Road Traffic, AF: Agricultural Film, LB: Livestock Breeding).

Line 226 – how was the reported uncertainty calculated?

Response:

At each sampling location, we collected 2-3 replicate samples for each particle size fraction. The standard deviation was calculated to represent the uncertainty.

Line 261 – Please discuss the details of the flyover? How was this sample collection done?

Response:

The sampling was conducted on a pedestrian flyover (height: ~4 m) near the Xi’an Jiaotong University campus in Beilin District, Xi’an. The flyover spans an urban arterial road with four motorized lanes (bidirectional), two dedicated bicycle lanes. The traffic volume is substantial, with private cars being the primary type of vehicle. We did not choose to conduct sampling on the ground by the roadside in order to avoid direct interference from road dust and vehicle exhaust.

The MiniVOL samplers (Airmetrics, Springfield, OR, USA), inertial impactors, was conducted on the flyover railing (see the following photo). In order to prevent any potential interference from pedestrians on the flyover, we cordoned off an area of 1.5 meters around the sampler with caution tape and affixed signs indicating that the area was designated for scientific research purposes.

Line 394 – please cite where these compounds are accepted as carcinogens.

Response:

We have revised the sentence to include the necessary citations to support this statement.

"ILCR for the three carcinogenic compounds (BT, BBP, and DEHP) were calculated in this study (Guyton et al., 2009; Ma et al., 2020; Liu et al., 2023)."

Reference:

Guyton, K. Z., Chiu, W. A., Bateson, T. F., Jinot, J., Scott, C. S., Brown, R. C., and Caldwell, J. C.: A Reexamination of the PPAR-α Activation Mode of Action as a Basis for Assessing Human Cancer Risks of Environmental Contaminants, Environ. Health Perspect., 117, 1664-1672, 10.1289/ehp.0900758, 2009.

Ma, B. B., Wang, L. J., Tao, W. D., Liu, M. M., Zhang, P. Q., Zhang, S. W., Li, X. P., and Lu, X. W.: Phthalate esters in atmospheric PM2.5 and PM10 in the semi-arid city of Xi'an, Northwest China: Pollution characteristics, sources, health risks, and relationships with meteorological factors, Chemosphere, 242, 10, 10.1016/j.chemosphere.2019.125226, 2020.

Liu, M. X., Xu, H. M., Feng, R., Gu, Y. X., Bai, Y. L., Zhang, N. N., Wang, Q. Y., Ho, S. S. H., Qu, L. L., Shen, Z. X., and Cao, J. J.: Chemical composition and potential health risks of tire and road wear microplastics from light-duty vehicles in an urban tunnel in China, Environmental Pollution, 330, 9, 10.1016/j.envpol.2023.121835, 2023.

Line 432 – does correlation in this testing confirm causation of oxidative stress? Please discuss.

Response:

The strong correlation between these components (e.g. PET, PAEs, etc.) and DTT consumption rate only indicates that these components can promote DTT activities, suggesting their potential contribution to the oxidative potential (OP) of particulate matter. However, these results do not conclusively prove that these substances directly cause oxidative stress. Although OP exhibits a certain correlation with ROS generation, there is still a scarcity of mechanistic understanding in this area (Hwang et al., 2021; Zhang et al., 2024). We will also pay attention to this issue and conduct relevant research in the future.

Reference:

Hwang, B., Fang, T., Pham, R., Wei, J. L., Gronstal, S., Lopez, B., Frederickson, C., Galeazzo, T., Wang, X. L., Jung, H., and Shiraiwa, M.: Environmentally Persistent Free Radicals, Reactive Oxygen Species Generation, and Oxidative Potential of Highway $PM_{2.5}$, ACS Earth Space Chem., 5, 1865-1875, 10.1021/acsearthspacechem.1c00135, 2021.

Zhang, X. J., Wang, Y. D., Yao, K. X., Zheng, H., and Guo, H. B.: Oxidative potential, environmentally persistent free radicals and reactive oxygen species of size-resolved ambient particles near highways, Environ. Pollut., 341, 9, 10.1016/j.envpol.2023.122858, 2024.