Reviewer 3:

Liu et al. investigated the characteristics, source profiles, and health risks of airborne microplastics and plasticizers emitted from plastic burning, fruit bag burning, road traffic, agricultural film, and livestock breeding sources in Guanzhong Plain, Northern China. Knowledge on the characteristics of atmospheric microplastics in Northern China is currently limited. This study provides important insights for source tracking and risk assessment of these emerging contaminants. I recommend this paper to be published after minor revisions.

Dear reviewer,

Thanks very much for taking your time to review this manuscript. We sincerely appreciate your constructive suggestions for improvement. We have carefully considered each of your comments and have revised the manuscript accordingly to improve the quality of our manuscript.

1. Many plasticizers were used in the manufacturing of plastics. The focus of this study is PAEs, BPs and BPA. Please provide the reason for selecting these three groups of plastics to study.

Response:

The selection of BTs, PAEs, and BPA as the focus of our study is driven by their widespread use, ubiquitous in the environment and potential health risks.

Phthalate esters (PAEs) are the most widely used plasticizers globally, dominating the plastic additive market. He et al. (2020) demonstrated that during 2007-2017, the annual global production of PAEs increased from 2.7 million tons to 6 million tons. Moreover, China is recognized as the largest importer of PAEs worldwide. Benzothiazoles (BTs) are extensively used in automotive tires and agrochemicals. High concentrations of BTs were discovered in the street runoff, suggesting that these tire material-related compounds can persevere in the environment (Zhang et al., 2018). Exposure to BTs may result in central nervous system depression, liver and kidney damage, dermatitis, and pulmonary irritation (Ginsberg et al., 2011). Bisphenol A (BPA) as a common industrial chemical component in many products, has steadily grown over the last 50 years (Corrales et al., 2015). Growth of global production has consistently ranged between 0% and 5% annually (Corrales et al., 2015). PAEs and BPA considered as endocrine disruptors, are demonstrated to impair reproductive function and development in laboratory animals (Wang et al., 2018).

Despite the well-documented health risks associated with these plasticizers in laboratory settings, there is a significant gap in understanding their real-world emissions and health impacts. In this study, we aim to fill this gap by investigating the emission characteristics of these plasticizers from various sources and evaluating their potential health impacts based on real-world concentration levels.

The related sentences have been revised as follows.

"Plasticizers are widely used in the production of plastics in order to achieve the desired material properties (Demir and Ulutan, 2013). Since plasticizers are not chemically bound to the plastic products, they can easily diffuse into the surrounding environment during the life-time (Yadav et al., 2017; Demir and Ulutan, 2013). PAEs,BTs, and BPA are the most common plastic additives that are ubiquitous in the environment and pose potential health risks. Phthalate esters (PAEs) are the most widely used plasticizers globally, dominating the plastic additive market. He et al. (2020) demonstrated that during 2007-2017, the annual global production of PAEs increased from 2.7 million tons to 6 million tons. Moreover, China is recognized as the largest importer of PAEs

worldwide. Benzothiazoles (BTs) are extensively used in automotive tires and agrochemicals. High concentrations of BTs were discovered in the street runoff, suggesting that these tire material-related compounds can persevere in the environment (Zhang et al., 2018). Exposure to BTs may result in central nervous system depression, liver and kidney damage, dermatitis, and pulmonary irritation (Ginsberg et al., 2011). Bisphenol A (BPA) as a common industrial chemical component in many products, has steadily grown over the last 50 years (Corrales et al., 2015). Growth of global production has consistently ranged between 0% and 5% annually (Corrales et al., 2015). PAEs and BPA considered as endocrine disruptors, are demonstrated to impair reproductive function and development in laboratory animals (Wang et al., 2019).

Previous studies have investigated the emission characteristics of plasticizers from various sources. Simoneit et al. (2005) illustrated that the major plasticizers detected in particulate matters (PMs) from open-burning of plastics were dibutyl phthalate (DBP), diethylhexyl adipate (DEHA), and diethylhexyl phthalate (DEHP). Zeng et al. (2020) reported phthalate concentrations in greenhouses air were higher than that in ambient air. Liu et al. (2023) found that phthalates were the most dominant plasticizer compositions in tunnel PM2.5, accounting for 64.8% of the detected plasticizers. Zhang et al. (2018) demonstrated that tire material-related compounds, benzothiazole (BT) and 2-hydroxybenzothiazole (2-OH-BT) were the major compounds in both tire and road dust samples. The majority of existing studies on atmospheric MPs and plasticizers have focused on analyzing the emission characteristics of individual source and lacked a comprehensive and comparative analysis of the MPs emission profiles of various sources."

Reference:

Corrales, J., Kristofco, L. A., Steele, W. B., Yates, B. S., Breed, C. S., Williams, E. S., and Brooks, B. W.: Global Assessment of Bisphenol A in the Environment: Review and Analysis of Its Occurrence and Bioaccumulation, Dose-Response, 13, 29, 10.1177/1559325815598308, 2015.

Demir, A. P. T. and Ulutan, S.: Migration of phthalate and non-phthalate plasticizers out of plasticized PVC films into air, Journal of Applied Polymer Science, 128, 1948-1961, 10.1002/app.38291, 2013.

Ginsberg, G., Toal, B., and Kurland, T.: Benzothiazole Toxicity Assessment In Support Of Synthetic Turf Field Human Health Risk Assessment, J. Toxicol. Env. Health Part A, 74, 1175-1183, 10.1080/15287394.2011.586943, 2011.

He, M. J., Lu, J. F., Wang, J., Wei, S. Q., and Hageman, K. J.: Phthalate esters in biota, air and water in an agricultural area of western China, with emphasis on bioaccumulation and human exposure, Sci. Total Environ., 698, 9, 10.1016/j.scitotenv.2019.134264, 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.

Simoneit, B. R. T., Medeiros, P. M., and Didyk, B. M.: Combustion products of plastics as indicators for refuse burning in the atmosphere, Environ. Sci. Technol., 39, 6961-6970, 10.1021/es050767x, 2005.

Wang, Y., Zhu, H. K., and Kannan, K.: A Review of Biomonitoring of Phthalate Exposures, Toxics,

7, 28, 10.3390/toxics7020021, 2019.
Yadav, I. C., Devi, N. L., Zhong, G., Li, J., Zhang, G., and Covaci, A.: Occurrence and fate of organophosphate ester flame retardants and plasticizers in indoor air and dust of Nepal: Implication for human exposure, Environmental Pollution, 229, 668-678, 10.1016/j.envpol.2017.06.089, 2017.
Zeng, L.-J., Huang, Y.-H., Chen, X.-T., Chen, X.-H., Mo, C.-H., Feng, Y.-X., Lu, H., Xiang, L., Li, Y.-W., Li, H., Cai, Q.-Y., and Wong, M.-H.: Prevalent phthalates in air-soil-vegetable systems of plastic greenhouses in a subtropical city and health risk assessments, Sci. Total Environ., 743, 10.1016/j.scitotenv.2020.140755, 2020.
Zhang, J., Zhang, X., Wu, L., Wang, T., Zhao, J., Zhang, Y., Men, Z., and Mao, H.: Occurrence of benzothiazole and its derivates in tire wear, road dust, and roadside soil, Chemosphere, 201, 310-317, 10.1016/j.chemosphere.2018.03.007, 2018.
Zhang, H., Yang, R. F., Shi, W. Y., Zhou, X., and Sun, S. J.: The association between bisphenol A exposure and oxidative damage in rats/mice: A systematic review and meta-analysis, Environmental Pollution, 292, 9, 10.1016/j.envpol.2021.118444, 2022.

2. The authors mention ROS formation in the text for several times. You use DTT consumption rate to represent oxidative potential. Note that DTT consumption rate is not equal to ROS formation. Some chemicals can consume DTT without the formation of ROS during interaction.

Response:

Thank you for the reviewer's insightful comments. DTT consumption rate indeed reflects oxidative potential rather than directly measuring ROS formation. We have carefully revised the manuscript to consistently use the term "oxidative potential (OP)" rather than "ROS formation." The revised paragraph is as follows:

"Figure S3 demonstrates the oxidative potential capacity of $PM_{2.5}$ and PM_{10} from five sources. Overall, $PM_{2.5}$ exhibits a generally higher level of oxidative potential than PM_{10}."

3. It is interesting that PMMA, PET, PE, PAEs, and BPA showed a positive correlation with oxidative potential. I encourage the authors to further discuss the possible mechanism which would help readers to understand their health impact.

Response:

The observed positive correlation between polyethylene terephthalate (PET) and oxidative potential (OP) may be mechanistically explained through environmentally persistent free radicals (EPFRs) (Zhang et al., 2024). EPFRs can form in MPs with conjugated aromatic-ring structures under thermal or photochemical aging conditions (e.g., high temperature/solar irradiation) (Yuan et al., 2022; Zhu et al., 2019). Previous studies have demonstrated that OP of particulate matter exhibits positive correlations with the concentration of EPFRs (Huang et al., 2021; Li et al., 2023). EPFRs can directly participate in redox reactions or mediate reactive oxygen species (ROS) generation to enhance the consumption of DTT (Yang et al., 2024). Therefore, PET and other MPs showing a positive correlation with OP may be attributed the formation of EPFRs.

Previous studies (Yu et al., 2022; Lin and Yu, 2019) have shown that organic compounds with a similar structure to PAEs (containing a benzene ring) can form complexation with metal ions (e.g., Mn^{2+}, Fe^{2+}, etc.), and this complexation can accelerate the consumption of DTT. Since atmospheric particles contain a certain amount of metal ions, we speculate that the strong correlation between PAEs and the OP of PM may be due to this reason.

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 PM2.5, ACS Earth Space Chem., 5, 1865-1875, 10.1021/acsearthspacechem.1c00135, 2021.

Li, H., Chen, Q. C., Wang, C., Wang, R. H., Sha, T., Yang, X. Q., and Ainur, D.: Pollution characteristics of environmental persistent free radicals (EPFRs) and their contribution to oxidation potential in road dust in a large city in northwest China, J. Hazard. Mater., 442, 11, 10.1016/j.jhazmat.2022.130087, 2023.

Lin, M. F. and Yu, J. Z.: Effect of metal-organic interactions on the oxidative potential of mixtures of atmospheric humic-like substances and copper/manganese as investigated by the dithiothreitol assay, Sci. Total Environ., 697, 10, 10.1016/j.scitotenv.2019.134012, 2019.

Liu, S. J., Huang, W. L., Yang, J. J., Xiong, Y., Huang, Z. Q., Wang, J. L., Cai, T. T., Dang, Z., and Yang, C.: Formation of environmentally persistent free radicals on microplastics under UV irradiations, J. Hazard. Mater., 453, 10, 10.1016/j.jhazmat.2023.131277, 2023.

Yang, X., Liu, F. B., Yang, S. Q., Yang, Y. L., Wang, Y. A., Li, J. J., Zhao, M. Y., Wang, Z., Wang, K., He, C., and Tong, H. J.: Atmospheric evolution of environmentally persistent free radicals in the rural North China Plain: effects on water solubility and PM2.5 oxidative potential, Atmos. Chem. Phys., 24, 11029-11043, 10.5194/acp-24-11029-2024, 2024.

Yu, Q., Chen, J., Qin, W. H., Ahmad, M., Zhang, Y. P., Sun, Y. W., Xin, K., and Ai, J.: Oxidative potential associated with water-soluble components of PM2.5 in Beijing: The important role of anthropogenic organic aerosols, J. Hazard. Mater., 433, 12, 10.1016/j.jhazmat.2022.128839, 2022.

Yuan, Z. H., Huang, Q. J., Wang, Z. Q., Wang, H., Luo, J. M., Zhu, N. W., Cao, X. D., and Lou, Z. Y.: Medium-Low Temperature Conditions Induce the Formation of Environmentally Persistent Free Radicals in Microplastics with Conjugated Aromatic-Ring Structures during Sewage Sludge Pyrolysis, Environ. Sci. Technol., 56, 16209-16220, 10.1021/acs.est.2c04453, 2022.

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.

4. Figure 2 shows that the composition profile of $PM_{2.5}$ and PM_{coarse} from different sources can be very different. Did you consider the impact of particle size in risk assessment?

Response:

We did consider the effect of particulate matter particle size in our risk assessment. Specifically, we compared the difference in risk indices for PM_{10} and $PM_{2.5}$. As shown in Figure S2, for the same source, the difference in non-carcinogenic risk for different particle sizes is small. This suggests that the effect of particle size on MPs induced health risk is relatively limited. Therefore, in the Discussion section, we focused more on comparing the differences in health risk between sources rather than particle sizes.

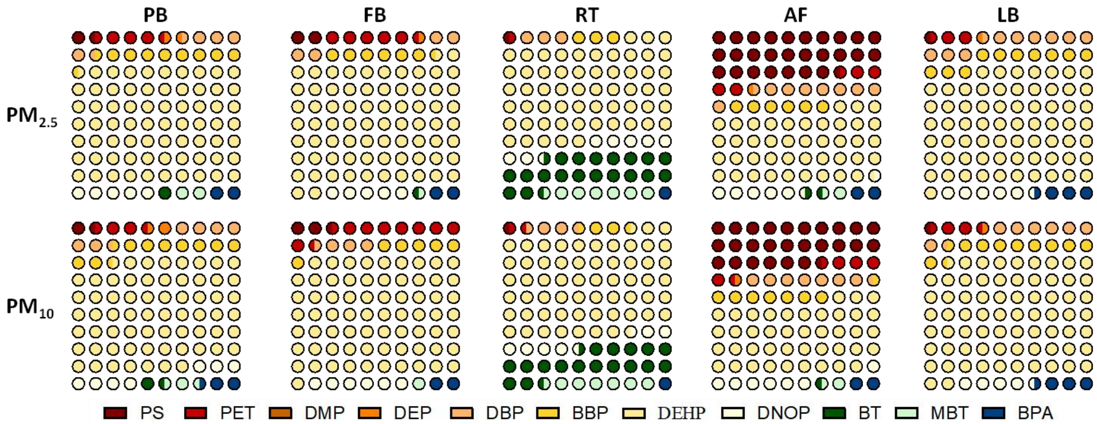

Figure S2 The non-cancer risks of MPs and plasticizers from five sources (PB: Plastic Burning, FB: Fruit-bag Burning, RT: Road Traffic, AF: Agricultural Film, LB: Livestock Breeding).

5. Line 51, Agricultural activities are also a significant contributor to atmospheric MPs?

Response:

Thank you very much for your valuable comment. Although agricultural activities are not a direct source of microplastics (MPs), they serve as a significant indirect contributor to atmospheric MPs. due to the use of plastic mulch films and other related plastic products, as well as the deposition of MPs in agricultural soils transported via atmospheric and surface runoff pathways, MPs are present in the soil (Lakhiar et al., 2024). Agricultural activities, by increasing soil disturbance, may cause the resuspension of MPs into the atmosphere. In this way, agricultural activities indirectly contribute to atmospheric MPs. For example, the paper "Activities of Microplastics (MPs) in Agricultural Soil: A Review of MPs Pollution from the Perspective of Agricultural Ecosystems" clearly indicates that agricultural machinery operations, such as plowing and harvesting, can disturb the soil and expose MPs to the air. These particles can then be released into the air by wind.

Reference:

Jin, T. Y., Tang, J. C., Lyu, H. H., Wang, L., Gillmore, A. B., and Schaeffer, S. M.: Activities of Microplastics (MPs) in Agricultural Soil: A Review of MPs Pollution from the Perspective of Agricultural Ecosystems, J. Agric. Food Chem., 70, 4182-4201, 10.1021/acs.jafc.1c07849, 2022.

Lakhiar, I. A., Yan, H. F., Zhang, J. Y., Wang, G. Q., Deng, S. S., Bao, R. X., Zhang, C., Syed, T. N., Wang, B. Y., Zhou, R., and Wang, X. X.: Plastic Pollution in Agriculture as a Threat to Food Security, the Ecosystem, and the Environment: An Overview, Agronomy-Basel, 14, 36, 10.3390/agronomy14030548, 2024.