Response to reviewer:

We greatly appreciate the reviewer' thoughtful comments, suggestions, and recognition of the value and significance of our study. We have carefully addressed all the comments, and a detailed item-by-item response to the comments of the reviewer is given below. The original comments are in black and our responses are highlighted in blue. Additionally, we have included the revised paragraph following each response to demonstrate the changes made.

Comments:

The manuscript reports the impacts of control measures on environmentally persistent free radicals (EPFRs) and reactive oxygen species (ROS) in Beijing during the 2015 China Victory Day Parade period. The findings reveal the changes in sources and formation processes of EPFRs and ROS in different control period. The paper is well organized and the topic is interesting for the control of hazardous species. However, some issues should be modified before publication, specific comments are as follow:

1. Abstract: You should provide the variation of the main sources before and after CP period as a comparison for those during the CP period.

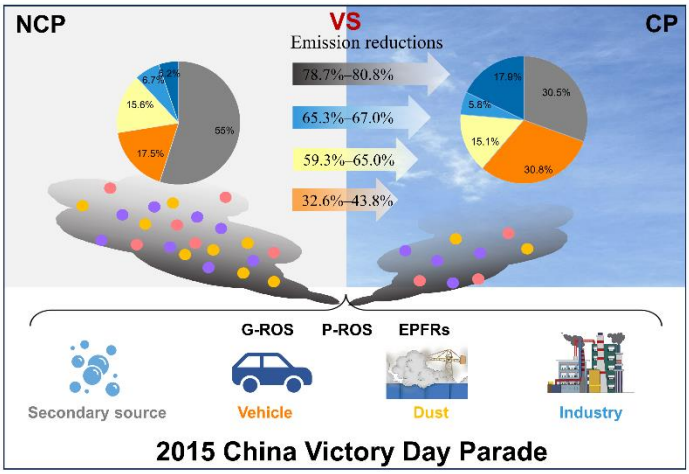
Response: Thank you very much for your valuable advice. According to your suggestion, we have added the variation of different sources during control period (CP) and non-control period (NCP) in Line 37–39, which are now described as follow:

"The "Parade Blue" days were largely attributed to the dramatic reduction in secondary aerosols, which were also largely responsible for EPFRs and ROS reductions. The source-sector based concentrations of $PM_{2.5}$, EPFRs, G-ROS, and P-ROS during CP were reduced by 78.7%–80.8% from secondary aerosols, 59.3%–65.0% from dust sources, 65.3%–67.0% from industrial emissions, and 32.6%–43.8% from vehicle emissions, compared to the cases during NCP."

2. Graphical abstract: The resolution of figure is too low.

Response: We are extremely grateful for pointing out this problem. We have

reworked graphical abstract to improve the resolution of figure are the same as follows:



Graphical abstract

3. Line 36: "correlations", between what?

Response: Sorry for the confusion. Actually, "correlations" here refers to the correlations between EPFRs and ROS. Considering the word-count limitation of the abstract, we have deleted this sentence and now described as follow:

"The "Parade Blue" days were largely attributed to the dramatic reduction in secondary aerosols, which were also largely responsible for EPFRs and ROS reductions. The source-sector based concentrations of $PM_{2.5}$, EPFRs, G-ROS, and P-ROS during CP were reduced by 78.7%–80.8% from secondary aerosols, 59.3%–65.0% from dust sources, 65.3%–67.0% from industrial emissions, and 32.6%–43.8% from vehicle emissions, compared to the cases during NCP."

4. Line 67: this sentence should be rewritten more clearly.

Response: Thank you for your careful review. We apologize for not describing it clearly. We have re-written this sentence in Line 71 as the follows:

"Thus, investigating the variations in the levels and sources of ROS are vital for understanding the mechanism of ROS formation and their effect on human health."

5. Line 87: it is not clear here, the sampling information here are for PM?

Response: Sorry for the confusion. Indeed, all ambient samples, not just $PM_{2.5}$ samples, were collected on the rooftop of a five-floor building at the Institute of Remote Sensing and Digital Earth, Chinese Academy of Sciences. According to your comment, we have made the modifications in Line 91 and also moved the information on monitoring of gaseous pollutant to this paragraph, and details are as follows:

"All sampling were conducted on the rooftop of a five-floor building at the Institute of Remote Sensing and Digital Earth, Chinese Academy of Sciences (117.39°E, 40.01°N), which is located between the fourth and fifth ring road in northern Chaoyang District, Beijing, China and is surrounded by residential buildings and Olympic Forest Park. A total of 76 $PM_{2.5}$ samples including 38 daytime (8:00–20:00) and 38 nighttime (20:00–8:00 the next day) samples were collected on prebaked quartz filters using Digital high-flow sampler (DHA-80, Digital, Switzerland) with a flow rate of 500 L/min from August 13 to September 19, 2015. The samples were wrapped in aluminum foil and then stored in a refrigerator at -20°C until analysis. Real-time SO_2, NO_2, and O_3 concentrations were simultaneously monitored online by an SO_2 analyzer (Model 43i, Thermo Scientific, USA), NOx analyzer (Model 42i, Thermo Scientific, USA), and ozone analyzer (Model 49i, Thermo Scientific, USA), respectively."

6. Line 98: "elementary" should be "elemental".

Response: Thanks for your kind reminder. We have replaced "elementary" with "elemental" in Line 105 according to your suggestion.

"Organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ were measured by a thermal/optical carbon analyzer (model RT-4, Sunset Laboratory Inc. USA)."

7. Line 104: it should be "Real-time SO_2, NO_2, and O_3 concentrations".

Response: Thanks for your kind reminder. We have revised it in Line 97 as follow:

"Real-time SO_2, NO_2, and O_3 concentrations were simultaneously monitored online by an SO_2 analyzer (Model 43i, Thermo Scientific, USA), NOx analyzer (Model 42i, Thermo Scientific, USA), and ozone analyzer (Model 49i, Thermo Scientific, USA), respectively."

8. Line 176: “spin” should be “spins”

Response: Thank you very much for your valuable advice. We have corrected it in Line 182 as follow:

“but much higher than that in Chongqing (7.0×10^{13} spins/m^3) in 2017–2018 (Qian et al., 2020)”

9. Figure 6: The horizontal axis should be changed to continuous time.

Response: Thank you for your careful review. According to your suggestion, we have revised the horizontal axis label in figure 6 to continuous time as follow:

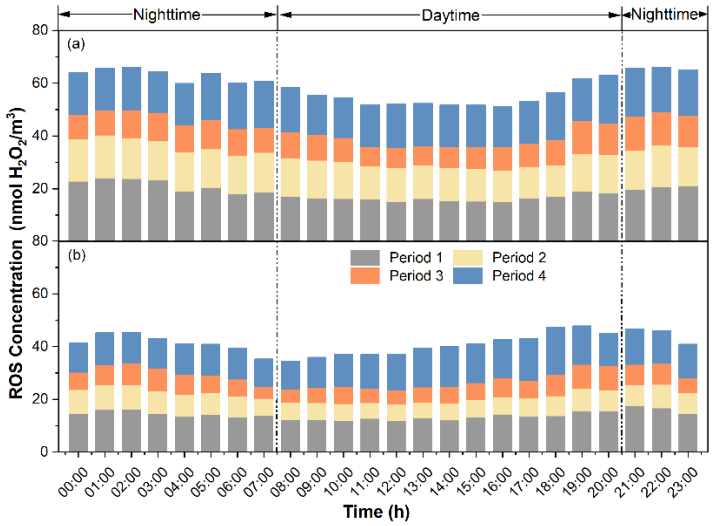


Figure 6: Diurnal variations in concentrations of (a) G-ROS and (b) P-ROS during the four pollution periods.

10. Line 202-210: The authors should provide some discussions of the comparison of reduction effects in G-ROS and P-ROS during control periods.

Response: Thank you for pointing out this problem in the manuscript. We have added a comparison of reduction effects of G-ROS and P-GOS in Line 213-215 as follows:

“The ROS activity obtained here was expressed in nmol H_2O_2 equivalents m^{-3}. As shown in Figure 4, the average concentrations of G-ROS and P-ROS were 17.2 nmol

H_2O_2/m^3 and 13.6 nmol H_2O_2/m^3, respectively, during NCP, decreased to 13.8 nmol H_2O_2/m^3 and 7.25 nmol H_2O_2/m^3 during period 2, and further decreased to 10.3 nmol H_2O_2/m^3 and 7.02 nmol H_2O_2/m^3 during period 3. The concentrations of ROS during CP were comparable to those observed in urban America (Wang et al., 2011) and rural China (Zhao et al., 2023; Huang et al., 2016). It is noteworthy that the impact of the control measures on G-ROS and P-ROS was different. Compared with NCP, the percentage decrease in G-ROS during CP was 24.1%, which was lower than that in P-ROS (46.9%). This difference may be related to the complex formation and transformation mechanism of G-ROS. These results further suggested that the decrease in gaseous pollutants was lower than that in particulate pollutants."

11. Line 271-273: Why the percentage contribution from vehicle emissions increased?

Response: Thank you very much for your question. The percentage contribution of vehicle exhaust emissions increased during the control period. On the one hand, this is attributed to the concentration decrease from this sector was smaller than those from the other major source sectors, especially factors related to secondary aerosols. On the other hand, the sampling site in this study is located near traffic arteries and are highly influenced by the traffic source. The World Athletics Championships held at the National Stadium (known as the Bird's Nest) during period 2, which resulted in a significant increase in traffic flow near the sampling site. As a result, the percentage contribution from vehicle emissions increased significantly during control period. The corresponding revision has been provided in Line 282–285 as follows:

"The percentage contribution from vehicle emissions actually increased because the concentration decrease from this sector was smaller than those from the other major source sectors (especially the factor of secondary aerosols, as discussed below). Further, the smaller decrease in concentrations from vehicle emissions may be attributed to the World Athletics Championships held at the National Stadium (known as the Bird's Nest) during period 2, which resulted in a significant increase in traffic flow near the sampling site. As a result, the percentage contribution from vehicle emissions increased significantly during CP."

12. Conclusions: In the conclusion section, the authors should include some recommendations for future research needs on ROS and EPFR.

Response: Thank you very much for your valuable advice. We have added some recommendations for future research on EPFRs and ROS in the conclusions section, which are now described as follows:

"The short-term air quality control measures on hazardous substances during the 2015 China Victory Day Parade in Beijing reduced the concentrations of EPFRs by 18.3%, G-ROS by 24.1%, and P-ROS by 46.9% during CP compared to NCP. Overall, the decrease in EPFRs and ROS was smaller than those for most other measured pollutants (e.g., $PM_{2.5}$, EC, elements, and SO_2). Although particle matter-based air quality control measures have performed well in achieving "Parade Blue", it is difficult to simultaneously reduce the negative impacts of atmosphere on human health. Given that EPFRs and ROS exhibited a significant positive correlation (p<0.01) with EC, secondary inorganic ions, NO_2, and Cd, controlling emissions of these chemical species would benefit the reduction in EPFRs and ROS pollution. The sources of EPFRs and ROS differed between day- and nighttime. EPFRs were mainly from vehicle exhaust emissions and atmospheric oxidation processes in the daytime and vehicle exhaust emissions and fossil fuel combustion in the nighttime. Vehicle exhaust, secondary aerosols, and metals from fuel combustion processes were important sources of G-ROS and P-ROS in the daytime, while vehicle exhaust and coal combustion emissions were the major contributors of P-ROS in the nighttime. The predominant sources of $PM_{2.5}$, EPFRs, G-ROS, and P-ROS during NCP were secondary aerosols, followed by vehicle emissions, but vehicle emissions surpassed secondary aerosols to become the predominant source of these chemical species during CP. The control measures implemented during CP reduced source-sector based concentrations of $PM_{2.5}$, EPFRs, G-ROS, and P-ROS by 78.7%–80.8% from secondary aerosols, 59.3%–65.0% from dust sources, 65.3%–67.0% from industrial emissions, and 32.6%–43.8% from vehicle emissions, compared to the cases during NCP. Results from this study will benefit the development of future air quality management policies targeting EPFRs and ROS.

However, the generation and transformation processes of EPFRs and ROS involve multiple complex chemical reactions, further in-depth studies are still needed to gain a complete understanding of the formation pathways of EPFRs and ROS under different environmental conditions. For example, it is necessary in future to conduct smog chamber or flow tube experiment to simulate the photochemical reactions and oxidation processes of EPFRs and ROS in the atmosphere, as well as their interactions with different chemical species. In addition, substantial efforts are needed to develop the pretreatment and analytical methods to separate various EPFRs and gain the detailed information such as g-tensors and hyperfine splitting constants to identify the specific structures of the radicals, consequently clarifying the link between EPFRs and ROS."

13. Line 390: Please check the references and unified format.

Response: Thank you for your careful review. We have carefully checked the format of all references and made the modifications in References list. Some examples of modified references are shown below:

"Borrowman, C. K., Zhou, S., Burrow, T. E., and Abbatt, J. P.: Formation of environmentally persistent free radicals from the heterogeneous reaction of ozone and polycyclic aromatic compounds, Phys. Chem. Chem. Phys., 18, 205–212, http://dx.doi.org/10.1039/C5CP05606C, 2016.

Chen, Q., Sun, H., Wang, J., Shan, M., Yang, X., Deng, M., Wang, Y., and Zhang, L.: Long-life type — The dominant fraction of EPFRs in combustion sources and ambient fine particles in Xi'an, Atmos. Environ., 219, 117059, http://dx.doi.org/10.1016/j.atmosenv.2019.117059, 2019c.

Guo, X., Zhang, N., Hu, X., Huang, Y., Ding, Z., Chen, Y., and Lian, H.: Characteristics and potential inhalation exposure risks of $PM_{2.5}$–bound environmental persistent free radicals in Nanjing, a mega–city in China, Atmos. Environ., 224, 117355, http://dx.doi.org/10.1016/j.atmosenv.2020.117355, 2020."