Response to Reviewers' Comments

Dear Editor and Reviewers,

Thank you very much for your efforts in handling and evaluating our submission.
The review comments are very helpful for improving the original manuscript. We have carefully considered them and tried to address all of these comments in the revised version of the manuscript. Attached are the detailed point-by-point responses to the review comments. For clarity, the reviewer's comments are listed below in *black italics*, while our responses and changes in the manuscript are highlighted in blue and red, respectively.
We look forward to receiving a further evaluation of our work.

Best regards,
Guy Brasseur and co-authors

General Comments

The authors have chosen to look at the impact of emissions changes on January and July ozone in China. The manuscript is improved over the first draft, however there are still some organizational changes that could be made to improve the impact of this paper. Specifically, shifting the discussion to first focus on absolute ozone changes, and then focus on the drivers of those changes, could help avoid inconsistencies. Finally, the way the paper is written, it is not clear why the 'TOTAL' case belongs in the supplement instead of the main paper. The paper would be more impactful as well if the abstract clearly spelled out the big picture relationship between their emission scenarios, and the impact on both gas and aerosol-phase. Currently the abstract only discusses ozone but none of the complexity related to aerosol impacts, for example on HO2 uptake.

Author's reply: Thanks for your insightful suggestions. (1) We have improved the organization of our manuscripts with the first focus on the discussion of absolute ozone changes, followed by the explanation of the drivers for the ozone changes. The structure of our paper is shown as follows (See Line 159 to 164 in Text).

"In Section 3, we analyze the response of near-surface concentration of ozone to the specified emission reductions. Further, we determine the drivers responsible for the resulting ozone changes; these include changes in the concentrations of ozone precursors, of the intermediates including the oxidized VOCs (OVOCs) and in the level of secondary aerosols. We also discuss the changes to be expected in the ozone formation regimes. Finally, we describe the sensitivity of the atmospheric oxidative capacity (*AOC*) to the reduction in the emissions."

(2) The results of TOTAL case have been moved from supplementary materials to main text. (3) The abstract has also been improved with comprehensive description of the impact of emission reduction to ozone changes with both gas and aerosol-phase reactions, and shown it below:

"Despite substantial reductions in anthropogenic emissions, ozone (O3) pollution remains a severe environmental problem in urban areas of China. The reduction in the emission of pollutants affects formation of ozone through the changes in concentrations of O3 precursors and intermediates species as well as in the oxidation capacity of the atmosphere. However, the underlying mechanisms driving O3 changes are still not fully understood. Here, we employ a regional chemical transport model to quantify the changes in the formation of ozone as well as other secondary pollutants to a specified emission reduction (50%) for winter and summer conditions (January and July 2018). Our results indicate that, in winter, a 50% decrease in nitrogen oxide (NOx) emissions leads to an increase in surface O3 concentrations of 15%−33% on average across China. In summer, the concentration of O3 increases by up to 17% in the areas limited by the level volatile organic compounds (VOCs), while it decreases by 3%−12% in NOx-limited areas. The increase in the ozone concentration is associated with a reduced NOx-titration effect and higher levels of hydroxyl (OH) due to a reduced loss from

reactions with nitrogen dioxide (NO2). With a 50% reduction in anthropogenic VOCs (AVOCs) emissions, the O3 concentration decreases across the entire geographic area, with reductions of 4%−10% in South China during winter and 8%−20% in urban areas during summer. When combining the reductions in NOx and AVOCs emissions, the ozone response in urban areas (VOC-limited) is determined by the positive effect of NOx emission reduction in winter and the negative effect of AVOCs emission reduction in summer. An exception is found in the response during summertime in South China, where the role of biogenic VOCs in ozone formation is crucial due to relatively high temperatures and the existence of vegetation surroundings.

Summertime increases in the concentration of oxidized VOCs (OVOCs), particularly aldehydes and alcohols, are attributable to the reduction in NO_x emissions. This enhancement subsequently enhances the atmospheric oxidative capacity through the photolysis of OVOCs and the oxidation of alkenes by OH radicals; it favors the formation of ozone. A significant decrease in particulate nitrate and in secondary organic aerosols is derived following the reduction in NO_x and AVOCs emissions, respectively. These reductions in the aerosol concentration contribute to O_3 formation, through enhanced levels of hydroperoxyl (HO_2) radicals associated with a reduced loss via aerosol uptake, and a diminished aerosol extinction. To effectively mitigate ozone pollution in urban areas, simultaneous reductions in the emission of NO_x and specific VOCs species should be applied, especially regarding alkenes, aromatics, and unsaturated OVOCs, including methanol and ethanol."

Specific Comments

Abstract – The authors make no mention of their conclusions related to aerosol changes.

Author's reply: added as follows.

"A significant decrease in particulate nitrate and in secondary organic aerosols is derived following the reduction in NO_x and AVOCs emissions, respectively. These reductions in the aerosol concentration contribute to O_3 formation, through enhanced levels of hydroperoxyl (HO_2) radicals associated with a reduced loss via aerosol uptake, and a diminished aerosol extinction."

Line 258 – The authors state "A distinct increase in the surface mixing ratio of HO2 radical is derived in southern China (by up to 5 pptv or 60%; Fig. 1b). This enhancement is related to the increased mixing ratio of the OH radical found in urban areas, resulting in enhanced HO2 levels via VOCs oxidation, and a reduced HO2 loss via the aerosol uptake, as the aerosol load is reduced (see Sect. 3.2.3) (Song et al., 2021)." However, the increased HO2 appears to be present almost everywhere, while the increase in OH is highly localized to urban areas as the author's state. The authors

should be clearer that the broader increase in HO2 must be due to the reduced HO2 loss via aerosol uptake. If the authors tracked production from that chemical pathway, they could show a map of that rate decrease which could help. The authors could also consider a plot of the decrease in PM2.5.

Author's reply: We agree with your suggestion for the broader impact of aerosol decrease on the enhanced levels of HO_2 radicals. We changed the statement with emphasis on the broader impact of aerosol uptake of HO_2 and shown it below (Line 337-342 in text).

"A distinct increase in the surface mixing ratio of the HO_2 radical is derived in South China; it reaches 5 pptv or 60% (Fig. 2e). This increase contributes to a higher ozone level through the reaction between HO_2 and NO. The enhancement in the urban HO_2 concentration results from the increased levels of the OH radical via VOCs oxidation. The reduction in the aerosol load derived in South China as a result of the reduced NOx emission is responsible for the reduced loss of HO_2 by aerosol uptake (see Sect. 3.2.3)."

Figure 1&2 – I would suggest adding the 'TOTAL' case to Figure 1 and Figure 2. Figure S4b appears to be mislabeled as January instead of July.

Author's reply: changed.

Line 304 – What do you mean by "These changes are affected by meteorological parameters including the temperature, the water vapor abundance, and the solar radiation intensity, which affect the oxidative processes (Dai et al., 2023)." Is meteorology not the same in both simulations?

Author's reply: The statement here is trying to compare the seasonal difference in radial's distribution. To clarify the statement, we change the description and show it below (Line 396-399 in text).

"The spatial shift in the distribution of radical changes from South China in winter to North China in summer is influenced by seasonal patterns of meteorological parameters, including temperature, water vapor abundance, and solar radiation intensity, which affect the atmospheric oxidative processes (Dai et al., 2023)."

Line 342 – It looks like the abundance of OVOCs is reduced in "all" regions, not "most" regions.

Author's reply: we changed the statement to all regions.

Line 347 – Can you explain why this is? "The decrease is the most pronounced in the

concentration of ketones" Why does the concentration of alcohols for example not seem to change at all? Is the model budget of alcohol really dominated by BVOCs, and if so, could that really be correct?

Author's reply: Reasons for the large changes in ketones are due to the relevant speciation for ketones are mainly from anthropogenic emissions. We added a table (Table S2) to show the speciation for specific OVOCs. For the changes in alcohols, an increase can be found in the urban areas in NO_x cases in summer (Figure S9c). When AVOCs emission reduced by 50%, the alcohol concentration decreased in a large part of China (Figure S13a). Limited change in alcohol can only be found at Guangzhou sites (Figure 4g), which is due to the relatively high BVOCs concentration at the sites.

Line 376 – Is it more effective OVOC production? Or biogenic emission of OVOCs? Maybe a budget for OVOCs (AVOC vs. BVOC vs. secondary production) would help?

Author's reply: We added a figure of alcohol to show the potential changes in the contribution of BVOCs to OVOCs. To clarify the statement, we change the sentence to (Line 474-479 in text)

"This seasonal difference is attributable to the higher photochemical formation of OVOCs during summertime, which is favored by the higher levels of temperature, solar radiation, as well as the temperature-dependent biogenic emissions. The smaller decrease in alcohols concentration (from 1.5 ppbv in winter to 0.5 ppbv in summer; Figure S13) is also supportive to our founding, as its summertime formation is highly dependent on the photochemically reactions with BVOCs (Zhang et al., 2023)."

Line 411 – There is still a lot of VOC-limited area. Instead of "tend to be converted", maybe say x% of VOC-limited is converted to transition or NOx-limited?

Author's reply: we added a table (Table S3) to show the changes in percentage of grid cell of different ozone sensitivity regimes in each case, with the added statement shown in below (Line 571 in the text):

"from 68.8% in BASE case to 71.9% in NOx case".

Line 414 – Just confirming that your HO2 uptake reaction does not produce H2O2? Does it produce H2O?

Author's reply: we added the reaction of HO_2 uptake to produce H_2O.

Line 420 – Against suggest pulling the 'TOTAL' case into the main text.

Author's reply: added.

Line 431 – Can we learn something from Guangzhou? Does Guangzhou have differences in emissions compared to the other cities that would explain why it remains VOC-limited? In the N+A and TOTAL cases, does this applies also to Shanghai? What is the difference compared to Beijing and Chengdu?

Author's reply: The reasons for the Guangzhou sites remains in VOC-limited regimes in N+A and TOTAL conditions is due to the high biogenic emissions at the surroundings of the sites. The case for Shanghai is different from Guangzhou due to the different temperature and land cover. At the sites of Beijing and Chengdu, the changes in the ozone sensitive regimes are determined by the increased production of H_2O_2 due to reduced loss of HO_2 via aerosol uptake, as the aerosol load at these two sites is at relatively high levels. To describe the underlying reasons for the changes of ozone sensitive regimes in these four sites, we improved the explanation and shown it below. (Line 590-599 in text)

"The regimes at three urban sites, which are VOC-limited in the BASE case, are modified: the ozone sensitivity at Beijing is converted to a NO_x-limited case (Fig. 7i), while the sites of Shanghai (Fig. 7j) and Chengdu (Fig. 7l) are shifted towards a Transition regime. The changes in ozone sensitivity at these three city sites result from the decreased production of HNO_3 due to reduced NO_2 as well as the increased production of H_2O_2 due to reduced HO_2 loss via aerosol uptake. The Guangzhou site remains in a VOC-limited region (Fig. 7k). Reasons for this exception can be the lower aerosol load (Fig. S17) and higher temperature-dependent biogenic VOCs emissions in the location (Dai et al., 2023), as its surroundings are covered by vegetations (Zhang et al., 2023)."

Figure 6 – Shouldn't the unit be (ppbv) not (pptv)?

Author's reply: changed.

Table 2 shows that in winter, NOx reduction results in ozone increase in all cities, and AVOC reduction results in ozone decrease in all cities. The N+A and TOTAL cases result in ozone increases in all cities. In summer, NOx reduction results in ozone increases in all cities while AVOC reduction results in decreases in all cities. In the N+A and TOTAL cases, ozone decreases in Beijing, Shanghai, and Chengdu, but not in Guangzhou. According to Figure 5, in July, in the N+A and TOTAL cases, Guangzhou and Shanghai remain VOC-limited while Beijing and Chengdu shift to transitional conditions. Given that you get a different picture from Table 2 vs. Figure 5 (in Table 2, Guangzhou stands out) but in Figure 5, Guangzhou and Shanghai are different from Beijing and Chengdu, it might help to start with the ozone changes in Table 2, and use your other analysis to explain those changes, rather than starting with

radical changes and NOx vs. VOC-limited changes.

Author's reply: we agree with these suggestions. As we mentioned in the description of structure, we first analyzed the ozone changes at the four sites in Table 2 (shown below, Line 282-292 in text), with the supported discussion in the changes of ozone sensitivity regimes (Line 590-599 in text).

"Table 2 and Figure S5 provide quantitative information on the response of ozone to emission reduction at four urban locations (Beijing, Shanghai, Chengdu, and Guangzhou) for January and July of 2018. In winter (in January), the reduction in the emission of NO_x results in ozone increases of 21.3%−33.2% in all cities, while the reduction applied to AVOCs emission results in a decrease of urban ozone levels by 2.5%−18.2%. Ozone changes in the N+A and TOTAL cases follow the ozone response found in the NO_x case, with concentration increases of 7.1%−22.0% and of 10.0%−22.7%, respectively. In summer (in July), the urban ozone responses to the NOx and AVOCs cases are similar to those derived for winter conditions. The calculated ozone concentrations increase by 5.5%−17.1% in response to the reduced NO_x emissions and decrease by 14.5%−22.9% in response to the reduced AVOCs emissions. In the N+A and TOTAL cases, the changes in the ozone concentration follow the response to AVOCs reductions: the ozone concentration decreases at the sites of Beijing (by 5.5% and by 7.3%), Shanghai (by 2.9% and 2.6%), and Chengdu (by 3% and 2.5%). An exception is found at the Guangzhou site, where the ozone concentration increases by 1.3% in both cases; this calls for a different role of the anthropogenic emissions regarding the ozone formation at this location."

Figure 7 – I think it would be better if 7b was on the same scale as 7a and 7c.

Author's reply: changed.

Line 499 – The meaning of this is unclear "followed by effect of NO4+".

Author's reply: we changed the statement to

"followed by the reduction in the concentration of NO_4^+."

Line 515 – Cite Dai et al., 2023 here for this model bias evaluation?

Author's reply: added.

Line 550 – Please add some discussion of the model HO2 uptake parameterization and uncertainties in the strength of this uptake (for example, is gamma 0.2 or 0.1)? Previous studies have reduced this gamma to better fit observations (e.g., Yang et al., 2023).

Author's reply: we added some description of the uncertainty in the parameterization of aerosol uptake of HO_2 and shown it below (Line 556-558 in text).

"Large uncertainties still exist in the adopted value of the uptake coefficient of HO_2 (considered as 0.1 in this study) (Yang et al., 2023). This affects the quantitative evaluation of the aerosol effects on the ozone levels and deserves further studies."

Line 555 – Can you better describe the calculation of AOC? Is there an equation you can add here?

Author's reply: we added an equation of *AOC* in the main text.

Line 557 – There is nothing in the discussion below to support this statement: "This parameter allows us to characterize the formation process of O3 and can be used as an indicator to design mitigation policies for reducing ozone pollution." I think this comes in better in the conclusions where you describe the relative importance of different VOCs to AOC. How is this different/better than the use of OH reactivity? The conclusions mention that AOC helps you to pick out "alkenes, aromatics, and unsaturated OVOCs, especially methanol and ethanol." It would help if the identification of those VOCs were discussed in Section 3.3 and not solely placed in the conclusions.

Author's reply: We agree with this suggestion. (1) First, we changed the sentence for the parameters after the description of the relative importance of different VOCs to AOC (Line 631-633 in main text). (2) Reasons for choosing the AOC parameters rather than OH reactivity are the AOC parameters is more relevant to our topic and the AOC changes due to emission reduction can not only represent the changes in radicals but also in the feedback of radicals' changes to ozone, as involved the OH and ozone-related reactions. (3) we added the description of changes in VOCs and shown it below (Line 465-467; Line 499-482 in Text).

"This result indicates that reducing anthropogenic emissions of aldehydes and alcohols may help offset the increase in OVOCs caused by the reduction in NO_x emissions."

"Considering the increases in aldehydes and alcohols levels induced by reduced NO_x emission, this result also reveals a need to reduce the primary emissions of these two OVOCs to effectively control their negative impact on ozone pollution mitigation".

Line 640 – Better to name the specific cities and instead of 'slight' give the actual increase.

Author's reply: we added the relevant statement and shown it below.

"i.e., by 0.5 ppbv or 1.3% at Guangzhou sites"

Line 651 – Does ozonolysis really have a net impact of increasing ozone levels? Just need clarification here on the suggestion that the net effect is positive.

Author's reply: The effect of ozonolysis on AOC is related to the changes in the concentration of ozone and alkenes. It is hard to answer the effect of ozonolysis on the net ozone levels based on our studies, so we change to statement to

"by an increase in the atmospheric oxidizing capacity (*AOC*) through OH-related reactions".

Line 653 – Do you mean enhance the level of OH? Otherwise, this is a nice schematic and helpful description.

Author's reply: We modified the HO_x to OH in the main text.

Line 704 – The author's state: "The modified code in the WRF-Chem model is available upon request to the corresponding author." The best practice now seems to be to put modified code on Zenodo.

Author's reply: We are happy to share our code with anyone interested in our studies. Compared to simply uploading the code to Zenodo, we prefer to engage in more communication with interested individuals and share more detailed information with them.

References

Yang, L. H., Jacob, D. J., Colombi, N. K., Zhai, S., Bates, K. H., Shah, V., Beaudry, E., Yantosca, R. M., Lin, H.,Brewer, J. F., Chong, H., Travis, K. R., Crawford, J. H., Lamsal, L. N., Koo, J.-H., and Kim, J.: Tropospheric NO2 vertical profiles over South Korea and their relation to oxidant chemistry: implications for geostationary satellite retrievals and the observation of NO2 diurnal variation from space, Atmos. Chem. Phys., 23, 2465–2481, https://doi.org/10.5194/acp-23-2465-2023, 2023.