

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. Below 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

Reviewer 1:

General Comments

This paper contains very lengthy descriptions of model responses to changes in emissions of NO_x, VOCs, and both in China. The goal of the paper is to help policymakers mitigate ozone increases in urban areas. However, this message gets lost in the lengthy descriptions throughout the paper. The authors should consider significantly shortening their descriptions with a focus on how their findings can clarify the impact of policy measures that either reduce NO_x, VOCs, or both. Do we need a description of changes in pRO_x, pO_x, OH reactivity, NO_x reactivity, and AVOC? Could a subset of the plots provided with a focus on high ozone and PM_{2.5} areas suffice? What is the message the authors want to give regarding PM_{2.5}?

The authors should also better explain their finding that the combined reduction of NO_x and AVOC emissions has a larger effect on both ozone and PM_{2.5} than the sum of the reductions of NO_x and AVOC separately. Currently, it reads for example that the best 'value' to be gained in reducing P(O_x) in summer is reducing NO_x. This is also said on line 390. Overall, the authors have too much detail on specific changes in their model, and insufficient description of the broader new understanding gained or policy-insights developed.

The authors have a modeling setup that could provide insight into the benefits of different types of emissions reductions and help us gain insight into the impacts of the reductions in aerosol on ozone concentrations. The aerosol impacts on ozone could be the most interesting part of this paper but the manuscript as written is far too lengthy and lacks clear and concise messaging. The authors describe many model metrics (pRO_x, pO_x, AVOC) but it is not clear what different insights are gained from each one, or if a singular metric would suffice to describe the relevant model impacts. If the authors are able to revise the paper to increase the value of their scientific analysis and refine their messaging, then it would be appropriate for publication.

Author's reply: We would like to thank the reviewer for so carefully reading our manuscript and for making all the comments. Based on these comments, we significantly condensed our paper, which was judged to be lengthy. We have condensed the description of our model results and have focused on providing insights about how to mitigate ozone increase in urban China. Regarding the metrics used in this paper to characterize the photochemical environment, we only kept the changes in the Atmospheric Oxidative Capacity (AOC) in the main text and moved a reference to the other metrics to supplement. Regarding PM_{2.5}, we largely shortened the description on the changes in PM_{2.5} due to emissions reduction and elaborated on how the changes in the aerosol load affect the ozone formation. The structure of the new version of the paper is expressed in the paper as follows (Line 158-166 in Text).

“This paper is structured as follows. Section 2 introduces the setups of the model system

and describes the simulations performed for specified reductions in the emissions of primary pollutants. In Section 3, we first analyze the response in the near-surface concentration of ozone precursors and intermediate to primary emission reduction. We also discuss the changes in the ozone formation regime. Further, we derive the associated changes in ozone, and aerosols to emission reductions. Finally, we describe the sensitivity of the atmospheric oxidative capacity (AOC) to the reduction in emissions. A summary and implication for policy making of our study is provided in Sec. 4.”

Specific Comments

Intro: I would expect that in VOC-limited areas, decreasing NO_x would result in higher OH from reduced loss of OH to OH + NO₂ to HNO₃. Thus, HO₂ would be higher from increased VOC oxidation. Is the aerosol uptake effect on NO₂ from reduced nitrate aerosol really larger?

Author’s reply: Based on our results and regarding the increased concentration of HO₂, it is difficult to compare the contribution of the VOC oxidation by enhanced OH with the contribution of a reduced aerosol uptake. To clarify the underlying reasons for the summertime ozone increase, we changed the sentence in the introduction as follows (Line 55-58 in Text).

“This O₃ increase is associated with a reduced NO_x-titration effect and with higher levels of hydroxyl (OH) and hydroperoxyl (HO₂) radicals due to a reduced loss by reactions with nitrogen dioxide (NO₂) and by a decreased aerosol uptake”.

Line 110 – “nitration” should be “titration”. Also, please clarify the meaning of this statement “and the competition between NO₂ and VOC for OH radicals”.

Author’s reply: We corrected the mistake and deleted the unclear statement. The sentence is changed to (Line 111-113 in Text):

“In VOC-sensitive regimes, the reduction in the NO_x abundance tends to enhance the ozone formation due to the weakening of NO titration and the reduced loss of OH radical reacted with NO₂”.

Line 214 – “Validated” implies the model was correct in the companion study while there were a variety of model shortcomings described such as overestimated summertime NO₂ and PM_{2.5}. It would be better to describe how any model biases impact the conclusions rather than call the model “validated”.

Author’s reply: We added one sentence in the text, regarding the discussion of the aerosol effect on the ozone formation (Line 504-508 in Text):

“An overestimation in the concentration of NO_2 and $\text{PM}_{2.5}$ has been simulated for the baseline conditions, which can possibly lead to a higher reduction in aerosol concentration, especially in the concentration of NO_3^- . This overestimation potentially affects the aerosol-related changes in ozone formation.”

Line 237 – Has anyone done a weekend/weekday analysis of ozone to see whether ozone goes up or down when NO_x is reduced on the weekends, assuming that is the case in China? A quick search found studies like this: <https://www.sciencedirect.com/science/article/pii/S1474706518302110>, or <https://www.nature.com/articles/s41598020-64111-3>. If so, please cite those studies here as support for your spatial distribution of regimes.

Author’s reply: These two references as well as the reference to Tonnesen and Dennis, 2000 are added to our manuscript to support our description on the ozone sensitivity regimes.

Line 312 – Can you explain why that is?

Author’s reply: The higher value of $P(\text{RO}_x)$ in the TOTAL case (with the emissions reduction in NO_x , AVOCs, NH_3 , SO_2 , and CO) relative to the level in the N+A case (with the emission reduction in NO_x and AVOCs) is due to the higher concentration of OVOCs (Figure 1a) and of ozone (Figure 1b), whose photolysis produces more photochemical radicals.

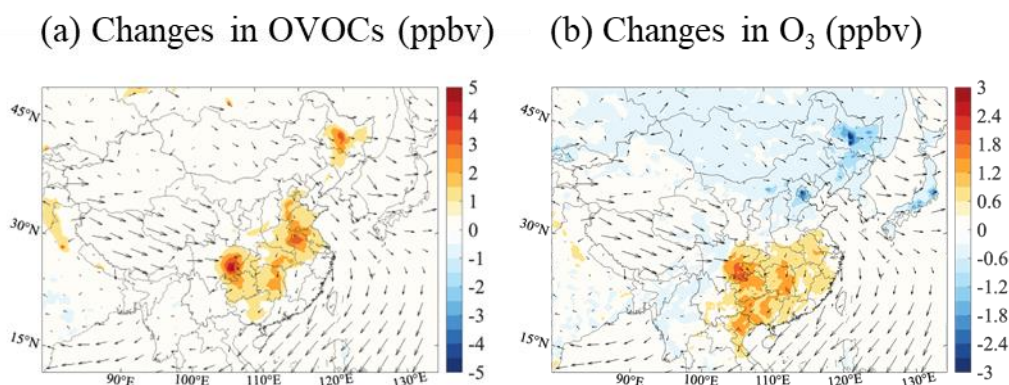


Figure 1. Changes in the concentration of OVOCs and ozone at the surface due to the emissions reduction in TOTAL case relative to N+A cases for January 2018.

Section 3.2: This goes into great detail on how the budgets of radicals change, and I find it difficult to see what the overall conclusion is that is either policy-relevant or novel. Instead, it just reads like a helpful description of the model behavior which may be useful for other modelers but is not necessary in the main text. In that case, the paper could be shortened by a quick summary of the major effects (less NO_x = less loss to

HNO₃, less VOCs = less pROx from OVOCs, less CO = more pROx due to higher OH etc) and moving the majority of the discussion to the supplement. If not, the authors need to better state the importance of their description.

Author's reply: Following your suggestions, we deleted the details dealing with the description of the changes in the radical's budget and condensed it with the description of the changes in the surface mixing ratios OH and HO₂ radicals in response to emissions reduction (in section 3.1.1).

Line 390 – Can the authors be more specific about the meaning of “further enhanced”? Why should policy makers bother if most of the impact is from NO_x?

Author's reply: Based on our results, the impact of NO_x emissions reduction on the production of radicals is larger than the impact of AVOCs emissions reduction. The decrease in radical due to reduced NO_x emissions can be partially counteracted by the reduced AVOCs emissions in the urban areas. As shown in Figure 2a, the reduction in NO_x leads to a decrease in the OH radical of the non-urban areas (NO_x-limited) in southern China, while an increase in the OH radical in urban areas (VOC-limited), results from the reduced loss by the reaction with reduced NO₂. The reduction in AVOCs leads to decreases in the OH radicals mixing ratio (Figure 2b), due to the reduced VOC oxidation. As the reduction in NO_x emission alone is not sufficient for reducing the concentration of the OH radical in all geographical areas in China, a concomitant reduction in AVOCs emissions is needed. More details can be found in Section 3.1.1 of our paper.

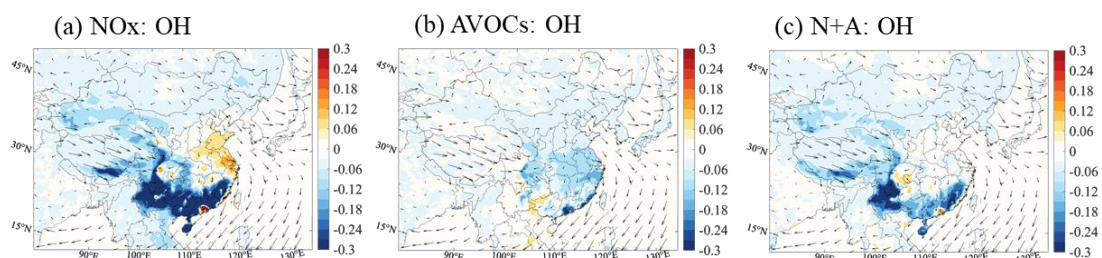


Figure 2. Changes in the averaged daytime surface mixing ratio of the OH radical (a-c, Unit: 0.1 pptv) in response to a 50% reduction in NO_x emissions (a; NO_x case), in anthropogenic VOCs (AVOCs) emissions (b; AVOCs case) and in NO_x and AVOCs emissions (c; N+A case) relative to the BASE case for January of 2018.

Line 392 – The authors state that reductions in ‘specific AVOCs’ are needed but so far they have only discussed AVOCs as a whole.

Author's reply: In our simulations for the present study, we only considered the reduction in AVOCs emissions as a whole without partitioning between species. However, we discussed the impact of AVOCs emissions reduction on specific VOCs

(hydrocarbons and OVOCs), listed in Section 3.1.2; and the changes in the contribution of the reactions of specific VOCs with OH and ozone to the Atmospheric Oxidative Capacity in Section 3.3.

Line 424 – The increase in OH in Hong Kong appears very strong as well.

Author's reply: We selected four city sites (Beijing, Shanghai, Guangzhou, Chengdu sites) to discuss the changes in OH radical. As the location of Hong Kong site is close to the Guangzhou site, we deleted the description for the Hong Kong sites in the main text.

Line 473 – Does the model really have $\text{NH}_3 + \text{OH}$ as a significant sink of OH? If the authors are referring to its impact on SIA and thus HO_2 uptake, this is not clear.

Author's reply: Our model includes the reaction between NH_3 and OH, but it is not a significant sink of OH. The increase in OH radical represented here is mainly due to the less consumption by reduced CO concentrations. We changed the statement as follows (Line 284-293 in Text):

“When accounting for the additional reduction in other anthropogenic emissions (NH_3 , SO_2 , and CO) (*TOTAL* case), the mixing ratio of the OH radical is positively modified, relative to the results in the combined case (*N+A* case). As shown in Fig. S4a, the mixing ratio of the OH radical is enhanced in the PRD and SCB regions (by up to 22%). This increase is due to the lowered consumption of the OH radical by the reduced concentration of carbon monoxide (CO) (Fig. S5a), due to its reduced emissions (Fig. S1d). For the HO_2 radicals, the additional reduction in the other emissions also contributes to a larger mixing ratio, with a pronounced increase in southern China (by up to 18%; Fig. S4c). This increase in the HO_2 radical mixing ratio is due to the increase in the oxidation of the VOCs by the OH radical and the reduced aerosol uptake of HO_2 associated with the decrease in the aerosol load”.

Paragraph starting on line 567 – This discussion is again very lengthy. The figure appears to show that the most important message is that NO_x reductions in July alone result in ozone decreases in several major cities (Beijing, Shanghai, Hong Kong?) while adding in AVOC reductions causes the cities to also see an ozone decrease.

Author's reply: To structure our description, we discussed the ozone changes due to emissions reduction in winter and summer conditions separately. We also summarized the specific ozone changes at four urban sites in Table 1 (Table 2 in Text). and the relevant statement of ozone changes is shown below (Section 3.2.2 in Text).

“*Winter conditions.* In January, the 50% reduction in NO_x emission enhanced the surface ozone concentrations, with the largest increase derived in the YRD and PRD

regions (15-20% (8-10 ppbv); Fig. 6a). During wintertime, a large part of China is under a VOC-sensitive regime. Therefore, the reduced titration of ozone by reduced NO (Fig. S13a; Fig. S2c) favors an increase in the ozone concentration. If AVOCs emissions are reduced by 50%, the surface ozone is reduced by 4-10% (2.0 to 8.0 ppbv; Fig. 6b) in the southern part of China. This ozone decrease is associated with the reduced concentration of HO_x radicals and hence a reduction in the ozone production by the HO₂ + NO reaction (Fig. S14a).

In the combined emission reduction case, the ozone response in VOC-limited areas follows the positive changes found in the NO_x-reduction case, with an ozone increase of 3.0-7.5 ppbv (4-9%) in North China and in some urban regions in South China (Fig. 6c). Simultaneously, a slight ozone decrease is derived over the southern coast of China (2.0-4.5 ppbv; 5-8%). In these areas, the ozone sensitivity is under the control of the NO_x. The ozone decrease is dominant by the negative ozone response to the AVOCs emissions reduction. With further emission reduction of the other species, an ozone increase (3-5 ppbv (4-6%); Fig. S5g) relative to the combined case is calculated in the southern part of China.

Summer condition. In July, under the reduction in the NO_x emissions, an increase in the surface ozone concentration of up to 10 ppbv (17%) is calculated in the urbanized regions of NCP, YRD, and PRD (Fig. 6d). These areas are typically located in VOC-limited areas (Fig. 5); thus, the ozone increase is explained by the reduced ozone titration (Fig. S13b). At the same time, in NO_x-limited areas, the calculated surface ozone concentration is reduced by 2 to 8 ppbv (3-10%), as a result of reduced photochemical formation under lower NO_x concentrations. With the reduction of AVOCs emissions, the surface ozone concentration decreases by up to 8.0-12.0 ppbv (8-20%; Fig. 6e) in whole areas of China. A spatial shift in the ozone decrease, from the southern regions in winter to the northern regions in summer occurs under this condition; this change is consistent with the spatial distribution of the reduction in the mixing ratio of the HO₂ radical, which contributes to the ozone production by its reaction with nitric oxide (Fig. S14b).

When combining the 50% reduction in the NO_x and AVOCs emissions, the surface ozone concentration decreases by up to 12 ppbv (15%; Fig. 6f) in NO_x-sensitive areas. In VOC-sensitive areas, the surface ozone concentration also decreases, as the increase of ozone associated with the positive impact of the reduction in NO_x emissions is smaller than the negative effect resulting from the reduction in the AVOCs emissions. This is explained by the fact that the loss of ozone due to the reduced NO_x level is rapidly compensated by the photochemically ozone formation processes, since the ozone production rate is accelerated by the high temperature and photolysis rate during summertime (T. Wang et al., 2022). One exception can be found at the Guangzhou site, where ozone slightly increases by 0.5 ppbv (Fig. S15), which can be explained by the increasingly important role of naturally emitted BVOCs species in the oxidation processes when anthropogenic emissions are reduced (see Sec. 3.3). When the emission reduction is applied to all species under consideration, the ozone changes (Fig. S5h)

relative to the combined case are smaller than the changes in winter, due to a consistently smaller reduction in aerosol concentrations (see Sec. 3.2.3).”

Table 1. Ozone changes due to reduction in emissions in urban sites (in percentage)

Location	Sites name	Ozone changes in winter condition (Mean \pm SD)			
		NO _x ^a	AVOCs ^b	N+A ^c	TOTAL ^d
North	Beijing	25.0 \pm 25.2 ^e	-2.5 \pm 1.3	22.0 \pm 32.8	20.0 \pm 19.5
East	Shanghai	33.2 \pm 35.3	-18.2 \pm 13.5	21.8 \pm 20.5	22.7 \pm 18.8
South	Guangzhou	21.4 \pm 22.6	-17.1 \pm 11.2	7.1 \pm 3.2	10.0 \pm 3.5
West	Chengdu	21.3 \pm 23.8	-9.4 \pm 8.5	14.1 \pm 8.3	20.3 \pm 13.5
Location	Sites name	Ozone changes in summer condition (Mean \pm SD)			
		NO _x	AVOCs	N+A	TOTAL
North	Beijing	6.4 \pm 3.8	-21.8 \pm 19.2	-5.5 \pm 4.2	-7.3 \pm 5.0
East	Shanghai	17.1 \pm 12.8	-22.9 \pm 20.8	-2.9 \pm 2.1	-2.6 \pm 1.5
South	Guangzhou	15.0 \pm 13.1	-14.5 \pm 13.5	1.3 \pm 1.0	1.3 \pm 0.9
West	Chengdu	5.5 \pm 4.5	-14.5 \pm 10.2	-5.5 \pm 2.0	-4.5 \pm 1.9

a-d. Sensitivity cases with a 50% reduction in NO_x emissions (NO_x), AVOCs emissions (AVOCs), NO_x and AVOCs (N+A), and other species (NO_x, AVOCs, CO, NH₃, SO₂) under consideration (TOTAL).

e. Values are displayed in the average ozone changes during daytime (06:00-19:00) in percentage with the standard deviation as the error bar. (ozone changes = (case value -base-line case) *100).

Line 599 – How do reduced AVOCs impact nitrate, sulfate, and ammonium? It is not clear from this sentence.

Author’s reply: The aerosol decrease due to the reduction in AVOCs emissions is attributed to the decrease in SOA, with minor impact on SIA. We changed the statement as follows (Line 502-505 in Text):

“With a 50% reduction of AVOCs emissions, the changes in the aerosol concentration are smaller than with the 50% reduction in NO_x emissions, with a decrease of less than 4% (5 $\mu\text{g m}^{-3}$; Fig. 7b), which predominantly results from the reduction in SOA (Fig. S18a).

Line 628 – How much does photolysis increase in your model with reduced aerosol?

Author's reply: The photolysis increases by about 5-20% in winter and 3-10% in summer, as shown in Figure 3 (Fig. S20 in Text). We added some description of aerosol-related increase in photolysis and its potential impact ozone formation in the text shown below (Line 534-541 in Text).

“This decrease in the aerosol burden weakens the aerosol extinction effect and therefore enhances the photochemical formation rate of radicals and ozone. As shown in Fig. S20 a-d, the photolysis rate increases (by 5-20%) in southern and central China during winter due to the aerosol decrease induced by the emission reductions. The highest increase in photolysis rates results from the joint emission reduction in NO_x and AVOCs (Fig. S20c). The increase of the photolysis rates in summer is not as distinct as the increase during wintertime due to the more limited reduction of the aerosol burden during summer (Fig. S20e-h).”

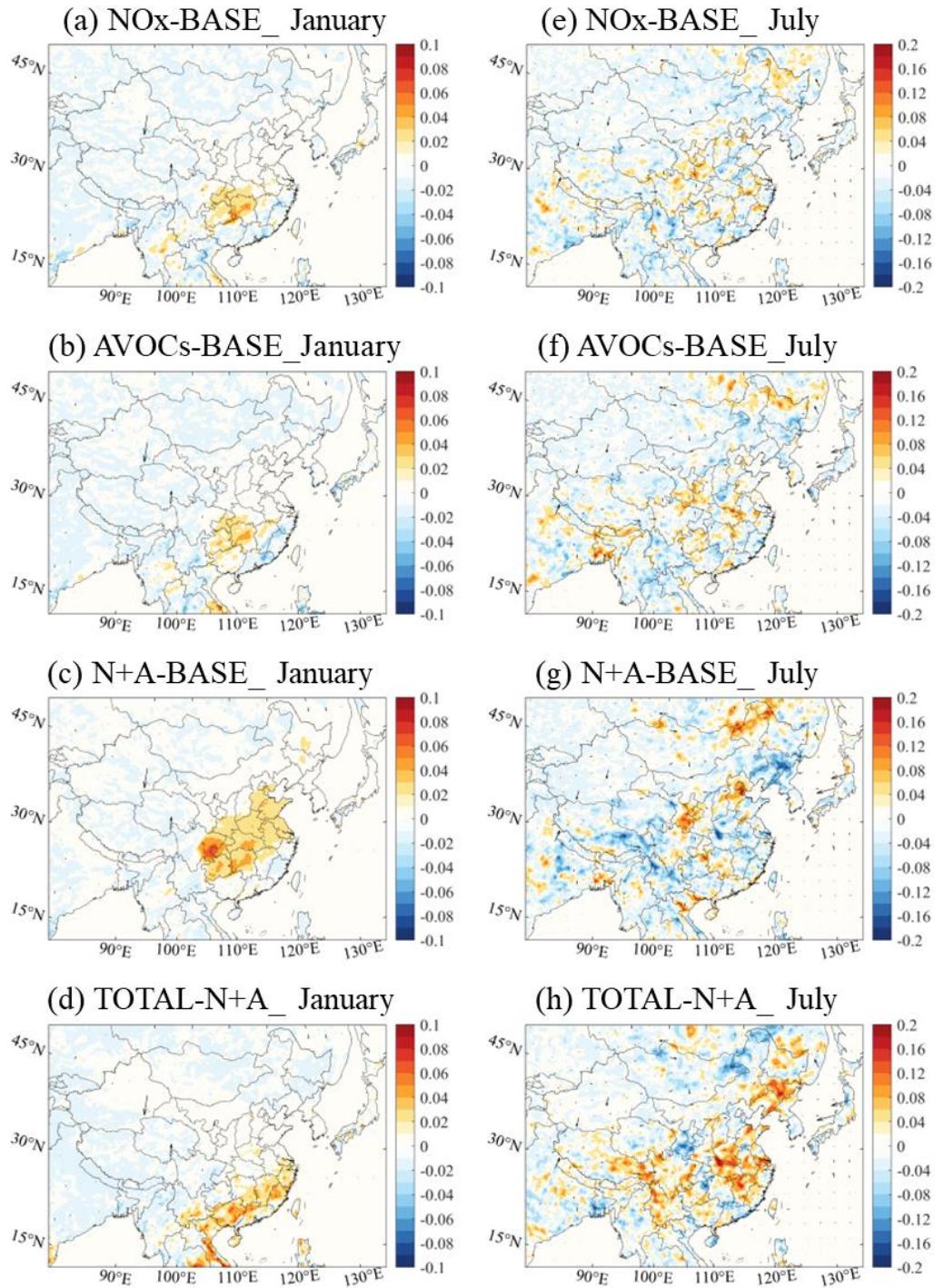


Figure 3. Changes in the total photolysis rate (a-d) [Unit: s^{-1}] due to the emission reduction in NO_x (a,e), AVOCs (b,f), NO_x and AVOCs (N+A)(c, g) relative to the BASE case and TOTAL case relative to N+A cases (d, h) in January (a-d) and July (e-h) of 2018.

Figure 13 – What is in ‘Other’ that is impacted in your ‘TOTAL’ case? This category is a surprisingly large fraction of model PM_{2.5} and thus deserves more discussion. Overall, Fig. 13 contains a lot of information but is barely discussed.

Author's reply: The large decrease in the aerosol load for the "TOTAL" case is due to the reduction in the sulfate and ammoniate particulates, as the emissions of SO₂ and NH₃ are reduced in this case. The relevant description is shown below (Line 510-514 in Text):

"With a further reduction in other emissions, the decrease in the concentration of aerosol is deeply enhanced; this is the case for the concentration of NH₄⁺ (919a), SO₄²⁻ (Fig. S19b), and NO₃⁻ particles (Fig. S19c). The concentration of the gas-phase precursors, NH₃ and SO₂, is considerably reduced, which affects the process of acid replacement (Meng et al., 2022) and hence the level of NO₃⁻."

Line 645 – Why have a schematic for reduction in NO_x emissions, but not AVOC emissions, and the combination of the two?

Author's reply: We changed the schematic and show it below.

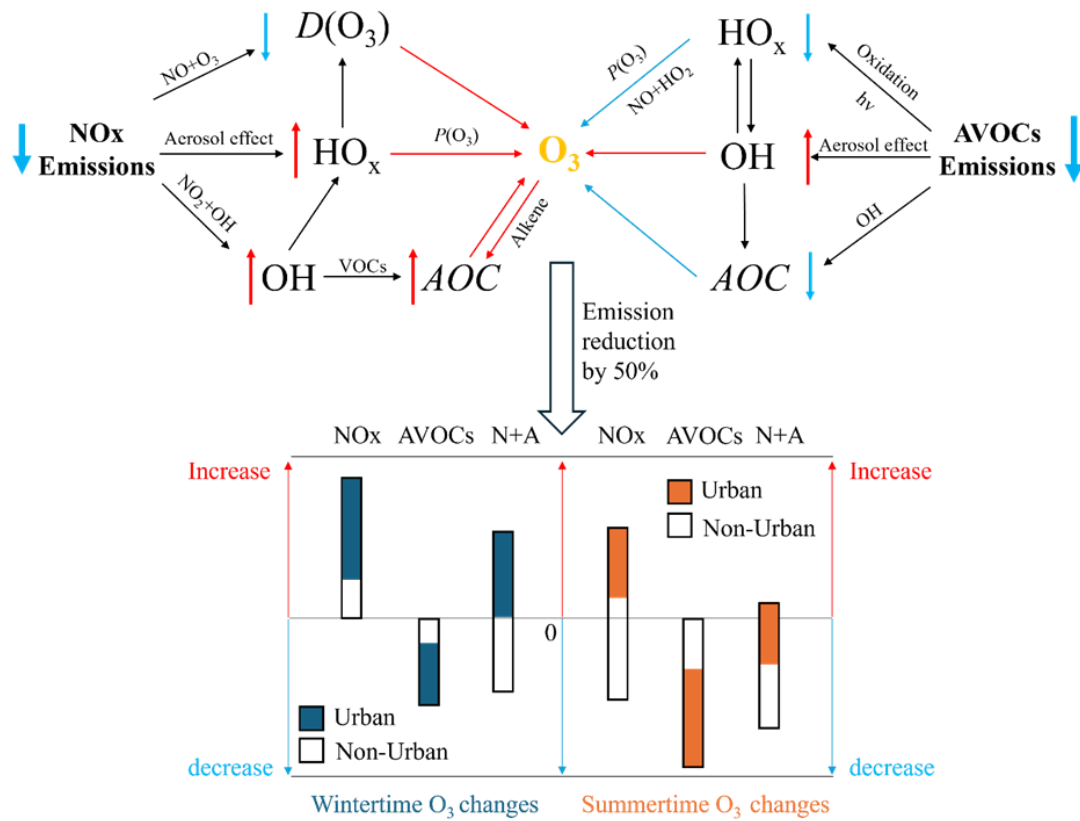


Figure 4. Schematics show the responses of oxidative processes, associated with ozone formation, to the reduction in primary emissions of NO_x and AVOCs in urban areas (VOC-limited) in winter and summer. Arrows besides the chemicals represent the changes associated with the reduction in emission. (decrease trend shown in blue; increase trend shown in red) Blue and red arrows closing to O₃ represent the positive and negative contributions to the ozone formations. AOC, P(O₃), and D(O₃) are the abbreviations of the Atmospheric Oxidative Capacity, production of ozone, and

destruction of ozone. Bar figure shows the ranges of ozone changes in whole of China (black bar), in non-urban areas (white part in the bar), and in urban areas (colored part in the bar) in three emissions cases (NO_x, AVOCs, and N+A represent the case with emissions reduction in NO_x, Anthropogenic VOCs (AVOCs), and the combined NO_x and AVOCs emissions, respectively) relative to BASE cases in winter and summer.

Section 3.4.1 – Again, I am not sure what the main message is from this lengthy section.

Author’s reply: We largely condensed the paragraph and kept the discussion about the changes in daytime AOC in response to emission reduction, as it gives us insights on the contributions from the reaction between specific VOCs with OH and O₃.

Line 755 – What is the result of the increased ozonolysis? Do we get more OVOCs that impact daytime air quality? This is said later but is not clear here.

Author’s reply: The changes in atmospheric oxidative capacity due to the increased ozonolysis are shown in Figure 5a-b. The concentration of OVOCs increases when NO_x emissions are reduced as shown in Figure 5c-d. The relevant statement in the main text is also shown below (Line 571-573 in Text).

“During nighttime (20:00 to 05:00 LST), the reduction in NO_x emissions is responsible for an increase in AOC by up to 50% (Fig. S21a). A contribution to this increase is provided by the alkene’s ozonolysis, since the concentration of ozone (Fig. 6 a) and of alkenes is enhanced (Fig. S8c).”

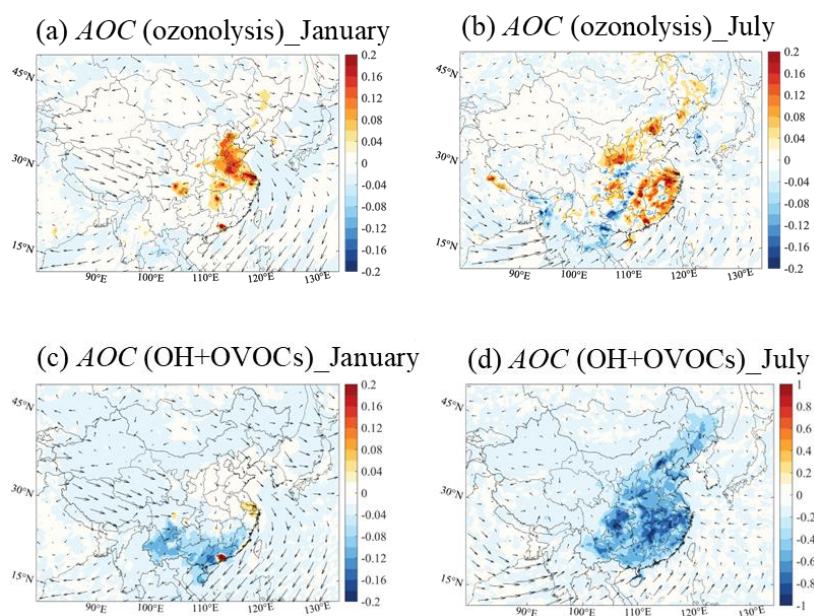


Figure 5. Changes in atmospheric oxidizing capacity (AOC, Unit: $10^6 \text{ molec. cm}^{-3} \text{ s}^{-1}$) due to the reaction between alkenes and ozone (ozonolysis) (a, b) and the reaction between OH and OVOCs (c, d) in response to the NO_x emissions case relative to the

BASE case in January (a, c) and July (b, d) of 2018.

Line 771 – Are these primary OVOCs like methanol or ethanol? Or secondary species like HCHO and acetaldehyde? If secondary, then what are their main precursors? Which ‘unsaturated OVOCs’ should be targeted?

Author’s reply: In the calculation of atmospheric oxidative capacity (AOC), the reaction related OVOCs includes all OVOCs species (primary and secondary). Considering the contributions of VOCs-related reactions to AOC increase and the increases in OVOCs species associated with NO_x emissions reduction, we suggest the reduction in the emissions of alkenes, aromatics, and unsaturated OVOCs, especially methanol and ethanol. The relevant statement is shown below (Line 687-689 in Text).

“With the known contribution of the VOCs-related reactions to the AOC, the reduction in the emissions of alkenes, aromatics, and unsaturated OVOCs, especially the methanol and ethanol, should be a priority.”

Summary – Again, a greater focus on policy-relevant insights would be helpful as there are opposite effects on average compared to in the major cities.

Author’s reply: we added some policy implications for the ozone mitigation in summary as shown it below.

“Paths to mitigation. We conclude this paper by highlighting a few chemical paths that should be considered when designing a mitigation policy for a reduction of ozone in the urban areas of China. Figure 10 presents a schematic description of the chemical mechanisms involved in the chemical production of atmospheric ozone and highlights how different reaction paths tend to change the ozone abundance in response to a reduction in NO_x and anthropogenic VOC (AVOCs) emissions. This graph shows that a reduction in NO_x emissions tends to increase the ozone concentration by (1) reducing the rate of the NO + O₃ reaction (ozone titration); (2) by increasing the rate of the HO₂ + NO reaction due to an increase in the HO₂ level associated with the reduced uptake of this radical by a lowered aerosol load; (3) by an increase in the atmospheric oxidizing capacity (AOC) through OH- and ozone-related reactions. The graph also shows that a decrease in AVOCs emissions tends (1) to reduce the level of the HO_x radical and hence the ozone production by the HO₂ + NO reaction; (2) to enhance the level of HO_x due to the reduced aerosol uptake and (3) to reduce the AOC with a negative effect on the ozone concentration. The relative importance of these different chemical mechanisms varies with location and environmental conditions.

We conclude that, in winter when the background ozone concentration is low, the reduction of NO_x emissions tends to increase the level of near-surface ozone, while the reduction in AVOC emissions has the opposite effect. This conclusion applies both in rural and in urban areas. A combined reduction in the emissions of these two primary

pollutants tends to decrease the level of ozone in rural areas, but to increase ozone in urban areas. Thus, in urban areas during winter, an effective approach to reduce the surface ozone concentration is through a strong limitation in the emissions of volatile organic compounds.

In summer when the ozone level is generally high, the reduction of NO_x emissions is an effective action to reduce the ozone concentration in rural areas, but this measure is counterproductive in the NO_x-saturated urban areas where ozone is controlled by VOCs. In fact, in urban areas during this season, the mechanisms involved in ozone mitigation are complex. For example, when NO_x emissions are reduced, the atmospheric OH concentration is enhanced because of its reduced destruction by NO₂. Following this increase in the OH concentration, an increase in the level of OVOCs, whose photolysis is an important source of HO_x radicals, also leads to accelerated ozone production and further amplifies the oxidation of VOCs. In addition, the increase in AOC, linked to the reaction of OH and ozone with alkenes and the reactions of OH with OVOCs also contribute to an increase in the ozone production. Further, the reduction in the aerosol load resulting from a reduction in the emissions of aerosol precursors promotes the ozone formation by decreasing the aerosol extinction and by reducing the uptake of HO₂. If combined with a 50% reduction in AVOCs, the increase in OVOCs and AOC, due to reduced NO_x emissions, can be offset. However, the aerosol-related promotion of the level of OH and HO₂ radicals can be enhanced, highlighting the complexity of summertime ozone mitigation in urban areas.

Table 2 provides quantitative information on the response of ozone at different urban locations for January and July. In urban areas, the reduction in the level of surface ozone requires a reduction in the emissions of anthropogenic VOCs. However, for practical reasons, a 50% reduction in AVOCs emissions, as assumed in our study, is difficult to implement over a short period of time. With the known contribution of the VOCs-related reactions to the AOC, the reduction in the emissions of alkenes, aromatics, and unsaturated OVOCs, especially the aldehydes and alcohols, should be a priority. The development of efficient mitigation strategies based on the reduction of AVOCs emissions requires, however, more detailed investigations on the reactivity of individual VOCs and on their potential impact on the ozone formation.”

Line 795 – What about reduced loss of OH to OH + NO₂ which increases the ability to oxidize VOCs?

Author’s reply: We believe the increase of OH due to the reduced loss of OH reacted with NO₂ is an important pathway to the increased ozone formation. We provide a comprehensive statement about how ozone increases in VOCs-limited areas (Figure 4) and show it below (Line 644-651 in Text).

“Figure 10 presents a schematic description of the chemical mechanisms involved in the chemical production of atmospheric ozone and highlights how different reaction

paths tend to change the ozone abundance in response to a reduction in NO_x and anthropogenic VOC (AVOCs) emissions. This graph shows that a reduction in NO_x emissions tends to increase the ozone concentration by (1) reducing the rate of the NO + O₃ reaction (ozone titration); (2) by increasing the rate of the HO₂ + NO reaction due to an increase in the HO₂ level associated with the reduced uptake of this radical by a lowered aerosol load; (3) by an increase in the atmospheric oxidizing capacity (AOC) through OH- and ozone-related reactions.”

Line 830 – The reason for the greater joint impact needs to be explained.

Author’s reply: we added some explanations for the larger decrease in aerosol in the joint case with the sentence shown below (Line 505-508):

“With a joint reduction in NO_x and AVOCs (Fig. 7c), the aerosol decrease is larger than the separated effect of the individual emissions decrease, as the increase in the concentration of SOA resulting from the reduced NO_x emissions is compensated by the reduced AVOCs emissions.”

Line 853 – Refrain from discussing ‘slight’ changes to focus on the major findings.

Author’s reply: We deleted the discussion regarding slight changes.

Line 869 – Here the authors state that their goal is to help develop a strategy for metropolitan areas. If this is the goal of the paper, the authors should consider a greater focus on the impacts on cities (bar chart figures such as Fig. 4).

Author’s reply: We agree with this statement. We focused our discussion of ozone changes and relevant policy implication at four city sites, as shown in the schematics (Figure 4) of our study.

Line 869 – The authors already specifically call out categories of VOCs (alkenes, aromatics etc). Could the authors better describe what they mean by ‘more detailed investigations’ here?

Author’s reply: We elaborated more on the detailed investigation as (Line 683-685 in Text)

“The development of efficient mitigation strategies based on the reduction of AVOCs emissions requires, however, more detailed investigations on the reactivity of individual VOCs and on their potential impact on the ozone formation”

Code and data availability: This does not include the modifications made to WRF-Chem described in Dai et al., 2023 and used here.

Author's reply: We are willing to share our code upon asking, and we emphasize this in the code availability part.

Reviewer 2:

Summary

The authors perform four sets of model simulations over China: a base case, a 50% NO_x emission reduction, a 50% AVOC emission reduction, and a combined 50% NO_x and 50% AVOC emission reduction. The science presented is largely sound. However, the paper currently reads as a lengthy report rather than a scientific manuscript. There is extensive repetition of conclusions in different sections of the paper, and a lot of the more impactful conclusions get lost in the details. I recommend that the authors restructure the paper around their main conclusions and science questions, rather than organizing by metric as is done currently. I also suggest that many of the minor details presented in the main text be moved to the supplement so that only text in support of the main conclusions of the paper is presented in the main text.

Major comments

As is currently written, a lot of the main conclusions and the primary storyline get lost in the details presented. In addition, a lot of conclusions get repeated in different sections. For example, a lot of the same conclusions are drawn when assessing ozone production regime (Section 3.1), odd oxygen production and destruction (Section 3.2.2), and ozone concentrations (Section 3.3.2). Uniting these sections will reduce the overall manuscript length, help highlight whether these different lines of analysis lead to consistent conclusions and help to bring the overall conclusions of the study to the forefront.

I wonder if the authors could comment on the relevance of broad NO_x and AVOC reductions in China, in contrast to reductions that vary by sector or by region. For example, are transportation sector reductions more/less likely than stationary emissions, and what might this imply for the chemistry discussed? In addition, a lot of the analysis presented highlighted changes in radical cycling related to changes in OVOC emissions. Do we expect AVOC emission reductions to be consistent across classes of VOCs, or could the effectiveness of emission reductions of OVOCs vs hydrocarbons differ? And, similarly, do we expect consistent emission reductions for VOCs with higher and lower HCHO yields? How might this impact the conclusions presented here?

Author's reply: Thank you very much for your comments that are very helpful. Based on your comments, we significantly condensed our paper, with a shortened description of the text on our model results and are focusing on insights about how to mitigate ozone increase in urban China. For the metrics related to photochemical activity, we limited our analysis to the Atmospheric Oxidative Capacity (AOC) in the main text and moved other calculated metrics to the Supplement. The structure of this paper is as follows.

“This paper is structured as follows. Section 2 introduces the setups of the model system

and describes the simulations performed for specified reductions in the emissions of primary pollutants. In Section 3, we first analyzed the response in the near-surface concentration of ozone precursors and intermediate to primary emission reductions. Then, we also discuss the changes in the ozone formation regime. Further, we derive the associated changes in ozone, and aerosols to emission reductions. Finally, we describe the sensitivity of the atmospheric oxidative capacity (*AOC*) to the reduction in emissions. A summary and implication for policy making of our study is provided in Sec. 4.”

Regarding policy to mitigate ozone, we highlight that the reduction in emissions should be implemented by regions and by the type of environment, with different strategies for the south and in the north of China and for the urban versus non-urban areas. We suggest that the reduction in NO_x emissions be coordinated with the reduction in AVOCs emissions, especially with reduction of alkenes, aromatics and unsaturated OVOC emissions, including methanol or ethanol. This conclusion is based on the contribution of these different species to the daytime oxidative capacity of atmosphere and to the secondary formation of OVOCs. The summary of our policy implication [also shown in Table 1 and Figure 1 (Table 2 and Figure 10 in Text)] is shown below.

“Paths to mitigation. We conclude this paper by highlighting a few chemical paths that should be considered when designing a mitigation policy for a reduction of ozone in the urban areas of China. Figure 10 presents a schematic description of the chemical mechanisms involved in the chemical production of atmospheric ozone and highlights how different reaction paths tend to change the ozone abundance in response to a reduction in NO_x and anthropogenic VOC (AVOCs) emissions. This graph shows that a reduction in NO_x emissions tends to increase the ozone concentration by (1) reducing the rate of the $\text{NO} + \text{O}_3$ reaction (ozone titration); (2) by increasing the rate of the $\text{HO}_2 + \text{NO}$ reaction due to an increase in the HO_2 level associated with the reduced uptake of this radical by a lowered aerosol load; (3) by an increase in the atmospheric oxidizing capacity (*AOC*) through OH- and ozone-related reactions. The graph also shows that a decrease in AVOCs emissions tends (1) to reduce the level of the HO_x radical and hence the ozone production by the $\text{HO}_2 + \text{NO}$ reaction; (2) to enhance the level of HO_x due to the reduced aerosol uptake and (3) to reduce the *AOC* with a negative effect on the ozone concentration. The relative importance of these different chemical mechanisms varies with location and environmental conditions.

We conclude that, in winter when the background ozone concentration is low, the reduction of NO_x emissions tends to increase the level of near-surface ozone, while the reduction in AVOC emissions has the opposite effect. This conclusion applies both in rural and in urban areas. A combined reduction in the emissions of these two primary pollutants tends to decrease the level of ozone in rural areas, but to increase ozone in urban areas. Thus, in urban areas during winter, an effective approach to reduce the surface ozone concentration is through a strong limitation in the emissions of volatile

organic compounds.

In summer when the ozone level is generally high, the reduction of NO_x emissions is an effective action to reduce the ozone concentration in rural areas, but this measure is counterproductive in the NO_x-saturated urban areas where ozone is controlled by VOCs. In fact, in urban areas during this season, the mechanisms involved in ozone mitigation are complex. For example, when NO_x emissions are reduced, the atmospheric OH concentration is enhanced because of its reduced destruction by NO₂. Following this increase in the OH concentration, an increase in the level of OVOCs, whose photolysis is an important source of HO_x radicals, also leads to accelerated ozone production and further amplifies the oxidation of VOCs. In addition, the increase in *AOC*, linked to the reaction of OH and ozone with alkenes and the reactions of OH with OVOCs also contribute to an increase in the ozone production. Further, the reduction in the aerosol load resulting from a reduction in the emissions of aerosol precursors promotes the ozone formation by decreasing the aerosol extinction and by reducing the uptake of HO₂. If combined with a 50% reduction in AVOCs, the increase in OVOCs and *AOC*, due to reduced NO_x emissions, can be offset. However, the aerosol-related promotion of the level of OH and HO₂ radicals can be enhanced, highlighting the complexity of summertime ozone mitigation in urban areas.

Table 2 provides quantitative information on the response of ozone at different urban locations for January and July. In urban areas, the reduction in the level of surface ozone requires a reduction in the emissions of anthropogenic VOCs. However, for practical reasons, a 50% reduction in AVOCs emissions, as assumed in our study, is difficult to implement over a short period of time. With the known contribution of the VOCs-related reactions to the *AOC*, the reduction in the emissions of alkenes, aromatics, and unsaturated OVOCs, especially the aldehydes and alcohols, should be a priority. The development of efficient mitigation strategies based on the reduction of AVOCs emissions requires, however, more detailed investigations on the reactivity of individual VOCs and on their potential impact on the ozone formation.”

Table 1. Ozone changes due to reduction in emissions in urban sites (in percentage)

Location	Sites name	Ozone changes in winter condition (Mean \pm SD)			
		NO _x ^a	AVOCs ^b	N+A ^c	TOTAL ^d
North	Beijing	25.0 \pm 25.2 ^e	-2.5 \pm 1.3	22.0 \pm 32.8	20.0 \pm 19.5
East	Shanghai	33.2 \pm 35.3	-18.2 \pm 13.5	21.8 \pm 20.5	22.7 \pm 18.8
South	Guangzhou	21.4 \pm 22.6	-17.1 \pm 11.2	7.1 \pm 3.2	10.0 \pm 3.5
West	Chengdu	21.3 \pm 23.8	-9.4 \pm 8.5	14.1 \pm 8.3	20.3 \pm 13.5
Location	Sites name	Ozone changes in summer condition (Mean \pm SD)			
		NO _x	AVOCs	N+A	TOTAL
North	Beijing	6.4 \pm 3.8	-21.8 \pm 19.2	-5.5 \pm 4.2	-7.3 \pm 5.0
East	Shanghai	17.1 \pm 12.8	-22.9 \pm 20.8	-2.9 \pm 2.1	-2.6 \pm 1.5
South	Guangzhou	15.0 \pm 13.1	-14.5 \pm 13.5	1.3 \pm 1.0	1.3 \pm 0.9
West	Chengdu	5.5 \pm 4.5	-14.5 \pm 10.2	-5.5 \pm 2.0	-4.5 \pm 1.9

a-d. Sensitivity cases with a 50% reduction in NO_x emissions (NO_x), AVOCs emissions (AVOCs), NO_x and AVOCs (N+A), and other species (NO_x, AVOCs, CO, NH₃, SO₂) under consideration (TOTAL).

e. Values are displayed in the average ozone changes during daytime (06:00-19:00) in percentage with the standard deviation as the error bar. (ozone changes = (case value -base-line case) *100).

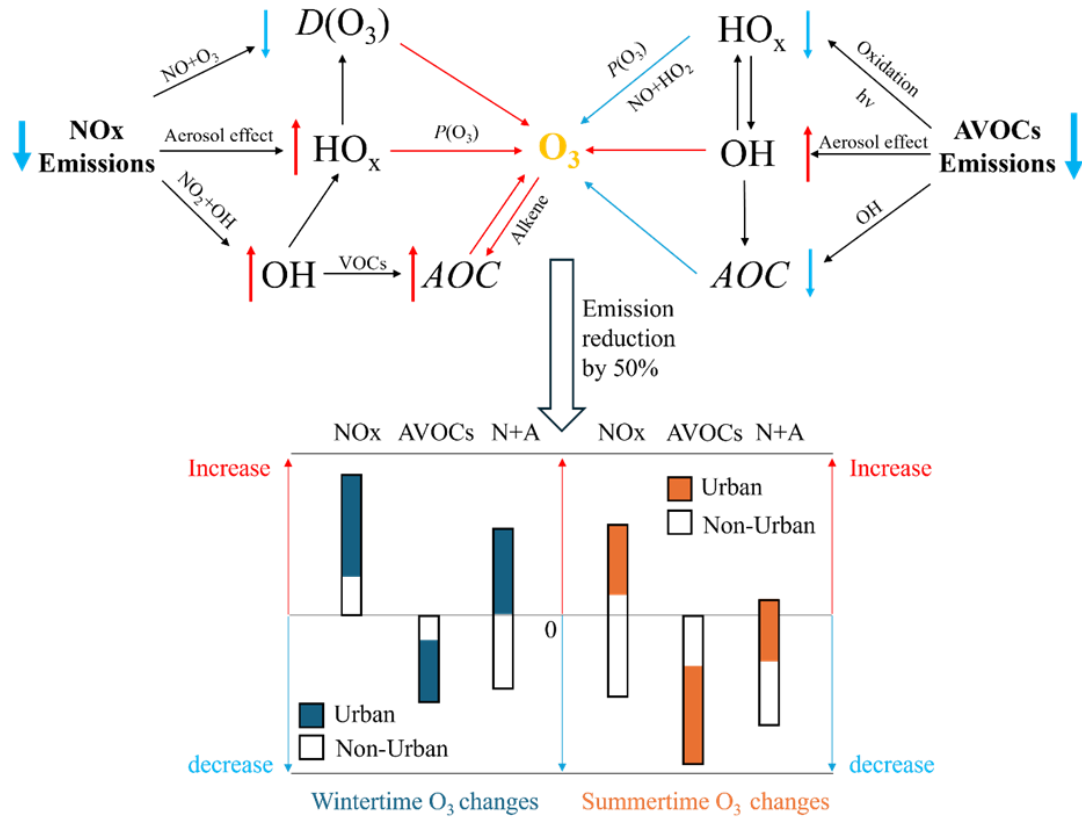


Figure 1. Schematics show the responses of oxidative processes, associated with ozone formation, to the reduction in primary emissions of NO_x and AVOCs in urban areas (VOC-limited) in winter and summer. Arrows besides the chemicals represent the changes associated with the reduction in emission. (decrease trend shown in blue; increase trend shown in red) Blue and red arrows closing to O_3 represent the positive and negative contributions to the ozone formations. AOC , $P(O_3)$, and $D(O_3)$ are the abbreviations of the Atmospheric Oxidative Capacity, production of ozone, and destruction of ozone. Bar figure shows the ranges of ozone changes in whole of China (black bar), in non-urban areas (white part in the bar) and in urban areas (colored part in the bar) in three emissions cases (NO_x , AVOCs, and N+A represent the case with emission reduction in NO_x , Anthropogenic VOCs (AVOCs), and the combined NO_x and AVOCs emissions, respectively) relative to BASE cases in winter and summer.

Minor comments

Line 110: typo (nitration vs titration)

Author's reply: Revised.

Line 236: Zhang et al, 2009 get these numbers from Tonnesen and Dennis, 2000, so Tonnesen and Dennis, 2000 should be cited here as the original citation.

Author's reply: Changed.