



Interactive comment on “Spatial and temporal changes of the ozone sensitivity in China based on satellite and ground-based observations” by Wannan Wang et al.

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We thank the reviewers for their constructive comments and useful suggestions.

Point-by-point response to the comments: Follow your comments, our responses are written in Blue Color.

Referee #1 In their manuscript “Spatial and temporal changes of the ozone sensitiv-

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ity in China based on satellite and ground-based observations”, Wannan Wang et al. report on a study using OMI NO₂ and HCHO columns to investigate where in China photochemical ozone production is NO_x limited, and where it is VOC limited. In contrast to earlier studies using similar approaches, the classification here is based on linking satellite columns with in-situ surface ozone observations to empirically determine thresholds for the HCHO to NO₂ ratio. The method is applied to data from China for the years 2016 to 2019 to investigate changes in photochemical ozone regime. Measurements from the lockdown phase in spring 2020 are included as a test case on the effect of strongly reduced NO_x emissions. The manuscript is clearly written and fits well into the scope of ACP. The results are not really surprising but add information on a relevant topic in particular in view of what the best approach is to reduce ozone levels in China. I have however concerns with the basic approach taken to identify the NO_x and VOC limited regimes, which is the key point of this study and not trivial. In my opinion, this needs to be better explained and justified before this manuscript can be accepted for publication in ACP.

Major comment

The one new thing in this study is that the different ozone chemistry regimes are defined from measurements alone and not from models which explicitly determine it for each location. This is an interesting approach but I do not see strong justification for it in the manuscript. What the authors use in Figure 1d is a display of monthly mean ozone surface concentrations as a function of the ratio of formaldehyde to NO₂ columns. While it is tempting to look for a maximum in the ozone curve and define this as the separation between NO_x and VOC sensitive domains, this is not necessarily justified. The FNR determines the change of ozone levels in reaction to a change in NO_x or VOC concentrations, but not the total ozone concentration itself (as can clearly be seen in the graph). An argument can be made that by limiting the analysis to the highest values, we are indeed looking at local ozone chemistry and assuming that everything else remains unchanged, absolute ozone levels should reflect ozone production but more

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justification is needed to make this approach convincing. I think that adding the threshold lines in Figure 1c may help to make the argument. Thresholds are defined from this figure in a manner not clear to me but this is of course the key question: What are the correct thresholds, are they the same throughout China, are they valid in all seasons / meteorological conditions, do they change over time as emission patterns change? None of this is discussed and this needs to be added.

Response: We have derived the FNR thresholds as follows.

We focus on the average monthly ozone surface concentrations in cities in this study to reduce the effect of meteorology or regional transport events. We consider only the highest ozone value (above $160 \mu\text{g}/\text{m}^3$) to further minimize the effect of background ozone. The margin of the top 10% ozone values per city is used to cover the transitional regime. Our thresholds are derived based on the assumption that conditions are the same throughout China, spatially and temporally. To justify our approach of deriving the FNR thresholds we add the following discussion on the assumptions:

(1) We apply FNR thresholds in different latitude zones (18°N - 28°N , 28°N - 38°N , 38°N - 53°N) and add Figure S1 in the supplement. The results show higher FNR values in lower latitude zone which is in line with higher temperature and stronger solar radiation in lower latitude zone. The FNR thresholds in three latitude zones ($[3.0, 5.5]$, $[2.3, 4.3]$, $[2.1, 3.9]$) have overlapped. The results show the FNR thresholds $[2.3, 4.2]$ derived for the whole domain can represent all latitude zones.

(2) We use summertime data to derive thresholds because meteorology is favorable for O₃ formation and will result in high ozone concentrations far above the background. We have added Figure S2 in the supplement. Figure S2(a) shows that monthly O₃ concentration in winter (Dec-Jan-Feb) will seldom exceed $160 \mu\text{g}/\text{m}^3$ and are less suitable for deriving the FNR thresholds. Based on application of FNR thresholds $[2.3, 4.2]$ derived by summertime data to winter observations shown in Figure S2(a), it is a reasonable assumption that our observation-based FNR thresholds derived using

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summertime data also apply during winter. Figure S2(b) indicates that FNR thresholds $[2.3, 4.2]$ derived using summertime data will be valid for all seasons.

We replaced line 210 by:

“The overall O₃-NO₂-HCHO chemistry is also captured by satellite-based HCHO and NO₂ column in Figure 1c, where we construct the O₃ isopleth using only observations.”

We added the discussion above in our manuscript at line 231-240:

“To minimize the effect of background O₃ by transport or meteorological variability, we use monthly mean O₃ concentrations above $160 \mu\text{g}/\text{m}^3$ in summer time when the O₃ chemistry is strongest. We assume that the results are applicable for the whole of China. To check this assumption we investigate the FNR thresholds in different latitude zones (18°N - 28°N , 28°N - 38°N , 38°N - 53°N) in Figure S1 in the supplement. Generally, we conclude that the derived FNR thresholds range of $[2.3, 4.2]$ for the whole domain is a good representation for all latitude zones in China. Figure S2(a) in the supplement shows monthly O₃ concentration in winter (Dec-Jan-Feb) which rarely exceed $160 \mu\text{g}/\text{m}^3$, including the FNR thresholds derived using summertime data. Based on Figure S2(b) we assume that our FNR thresholds $[2.3, 4.2]$ derived using summertime data will be valid for all seasons.”

In addition, we added the HCHO/NO₂ threshold lines in Figure 1c to clarify our results.

Minor comments

At some point in the manuscript, a short discussion of the problems in using columnar data instead of surface concentrations is needed, as well as of the question, in how far monthly averages are representative of the highly variable concentrations and the strongly non-linear NO_x-O₃ chemistry.

Response: We agree that application of a surface-based predictor to a column-based HCHO/NO₂ requires accounting for differences in the HCHO and NO₂ vertical profiles as well as meteorology. Thus, we select satellite retrievals according to standards that

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is considered as optimal. In addition, the monthly mean HCHO/NO₂ columns are used to reduce impact of this problem. We are focusing on the average air quality related to ozone in the Chinese cities, which doesn't show extreme events, but is a useful tool for air quality management. Hence, we focus on long-term evolution in ozone sensitivity by satellite-based HCHO/NO₂.

We added the following to the discussion of our manuscript at line 383-386:

"Satellite instruments measure the vertically integrated column density, which we use as a proxy of the actual surface concentrations. To reduce the effect of short-term variability in vertical distributions caused by meteorological changes we use monthly mean averages. Therefore, our satellite-based HCHO/NO₂ method is limited to identification of long-term evolution in O₃ sensitivity, focusing on understanding the average air quality."

L111: Add that quoted resolution for OMI is at nadir.

Response: This has been adapted.

L137: Which product is used in the DESCOS algorithm – the QA4ECV product?

Response: Yes, the QA4ECV product is used for DESCOS. We have added this at line 138-139: "... from OMI observations of tropospheric NO₂ columns (the QA4ECV product discussed in section 2) by the Daily Emission estimation Constrained by Satellite Observations (DESCOS) algorithm."

L150: Please add some basic information on which type of instrument is used for the ground-based data, which measurement principle is applied and if there are possible cross-sensitivities.

Response: The concentration of ozone and NO₂ is measured by a set of continuous automated instruments. Various instruments are used. Ozone is measured by point analysers using the ultraviolet absorption spectrometry method, NO₂ is measured using the chemi-luminescence method. For open path analysers, differential optical ab-

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sorption spectroscopy is used to measure ozone and NO₂.

We clarified this by making the following modification at line 151-155: "At each monitoring site, the concentration of O₃ is measured using the ultraviolet absorption spectrometry method and differential optical absorption spectroscopy, NO₂ is measured using the chemi-luminescence method. The instrumental operation, maintenance, data assurance and quality control were conducted based on the most recent revisions of China Environmental Protection Standards (CMEE, 2013)."

L168: If the model is to be used in any quantitative sense, then much more information on initialisation, VOCs used, inclusion of heterogeneous reactions etc. is needed.

Response: We agree that more information on CLASS model is needed. In this study, the model is used to show ozone formation is a highly nonlinear process in relation to NO₂ and HCHO. The chemical reactions employed in model scheme are presented in van Stratum et al. (2012). VOC mainly refers to isoprene, where all its oxidation products (MVK; methyl-vinyl-ketone and MACR; methacrolein) are lumped into a single species MVK. As the scheme contains less species and equations, the computational costs are minimized while the scheme still retains the essential components of the O₃-NO_x-VOC-HO_x cycle (Vil'a-Guerau de Arellano et al., 2011).

We added the following at line 175-177 and line 185-186:

"The initial mixing ratios of chemical species are shown in Table S1 in the supplement. The initial mixing ratios data are from van Stratum et al. (2012). All other species (except for molecular oxygen and nitrogen) are initialized at zero, and modified only the concentrations of NO₂ and HCHO." "This chemical scheme is able to represent the evolution of O₃-NO_x-VOC-HO_x cycle in semirural areas (Vil'a-Guerau de Arellano et al., 2011; Janssen et al., 2012; van Stratum et al., 2012)."

L219: Sentence is not clear to me but probably touches on my main point of concern: That the way the thresholds are derived is oversimplified and not necessarily valid for

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all locations in China.

Response: Figure 1c resembles this overall O₃-NO_x-VOC chemistry based on the observations, with an uncertain, blurry transition between NO_x-limited and VOC-limited regimes, similar as represented in Figure 1a.

As mentioned in Response to Major comment, the FNR thresholds slightly shift from low latitude to high latitude zones. Our thresholds are derived based on statistical analysis covering more than half of samples (60%) to make it valid as much as possible in most locations in China.

We made the following modification at line 227-230:

“We find a relationship between FNR and the O₃ response patterns that is qualitatively similar but quantitatively distinct across cities. Taking into account the range of transitional regime, the FNR thresholds [2.3, 4.2] marking the transitional regime, are defined as the $\pm 30\%$ range from the median (3.28) covering the O₃ maximum in most (60%) studied cities.”

L303: Up to this point, only summer values have been discussed and used. Now, the method is suddenly used for winter values which is problematic and needs at least to be acknowledged and discussed.

Response: We use summertime data to derive thresholds because meteorology (temperature, solar radiation) is favorable for ozone formation. The local ozone maximum occurs in summer and monthly ozone value can reach above 160 $\mu\text{g}/\text{m}^3$ which can be thought of as a dividing line separating two different photochemical regimes.

As mentioned in Response to Major comment, Figure S2(a) in the supplement shows monthly O₃ concentration in winter (Dec-Jan-Feb) is difficult to exceed 160 $\mu\text{g}/\text{m}^3$. The winter ozone observations have limited impacts on deriving the FNR thresholds. Application of FNR thresholds [2.3, 4.2] deriving by summertime data to all seasons' observations in Figure S2(b) shows it can capture the high O₃ values as well. Hence,

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we used the same thresholds when analyzing the COVID-19 period.

We added to the text at line 339:

“Assuming that our observation-based FNR thresholds derived using summertime data also apply during winter.”

L358: Here (and earlier), the assumption is made that VOC emissions have not decreased (much) during the lockdown which would deserve a bit of discussion, in particular as a significant number of studies related to the signature of the lockdown in pollution in China is already available in the literature.

Response: We assumed VOC emissions as “rising or in steady state” when discussed the impact of NO_x emission variations on O₃ concentrations in east China between 2016 and 2019 (Line 291 in original manuscript). During lockdown period, both the anthropogenic emissions of NO_x and VOCs were reduced according to Sicard et al. (2020). The reductions of VOC emissions are generally effective in reducing O₃ concentrations. However, such air quality improvements are largely offset by reductions in NO_x emissions reductions lead to increases in O₃ concentrations due to the strongly VOC-limited conditions in the North China Plain in winter (Xing et al., 2020). Figure 6c shows most regions of eastern China belong to VOC-limited conditions before lockdown. Thus, stronger NO_x reduction than the VOC reduction resulted in significant O₃ enhancement during lockdown.

We clarified this at line 344-348 and line 394-396:

“During lockdown period, both the anthropogenic emissions of NO_x and VOCs were reduced. The NO_x reduction during the lockdown is higher than the VOC reduction according to Sicard et al. (2020). The reductions of VOC emissions are generally effective in reducing O₃ concentrations. However, such air quality improvements are largely offset by reductions in NO_x emissions leading to increases in O₃ concentrations due to the strongly VOC-limited conditions in the NCP in winter (Xing et al., 2020).”

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“The case study of O₃ level changes during the COVID-19 lockdown in China demonstrated that the strong reductions in anthropogenic NO_x emissions resulted in significant O₃ enhancement due to the VOC-limited regime in winter.”

L363: I guess that something should also be said about the availability of the data produced in this study.

Response: We added the following at line 405-406: “The hourly O₃ and NO₂ observations of Chinese ground stations can be accessed from third parties (<http://www.pm25.in>, <http://www.aqicn.org>).”

Figure 1: This figure needs to be revised in several ways:

1. the same colour scheme and scale should be used for model and observations;
2. the figures showing observations should not just plot the data on top of each other as this prevents readers from seeing many of them. Instead, a “heat map” type display would be more appropriate showing the binned data;
3. I’d suggest to include the threshold ratio lines also in panel 1c.

Response: We agree with the referee that it is necessary to use the same color scheme and scale for Figure 1a to 1c. Figure 1b and 1c have been adapted to “heat map”. In addition, the threshold ratio lines have been added in Figure 1c.

Figure 2: I don’t see the need for the inserted maps in particular as they depict disputed areas without relevance for the study. Figure 2: Add in caption that HCHO columns are from OMI.

Response: We removed the inserted maps in Figure 2. The caption of Figure 2 has been adapted.

Figure 3: Explain arrows in caption.

Response: The arrows represent time step from 2016 to 2019. This has been adapted.

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Figure 5: Looking at panels (b) and (c) it is clear that the ozone changes in China are not linked in a simple way to the NO_x changes: Ozone decreased very much in Neijiang in spite of very moderate NO_x decreases while it increased significantly in Guangzhou where NO_x emissions remained basically constant. In Beijing, a reduction in NO_x emissions by a factor of 2 from 2016 to 2018 had no effect on surface ozone but further reduction then leads to an increase in O₃. This needs more discussion in the text.

Response: We agree that the relationship between ozone and NO_x emission is not in such a simple way. Due to different ozone formation chemistry, opposite change of ozone occurs in Guangzhou and Neijiang with NO_x emission reduction. Because of VOC-limited chemistry condition, O₃ increases with decreasing NO_x emissions in Beijing, Shanghai and Guangzhou. NO_x-limited condition leads to decreasing O₃ with decreasing NO_x emissions in Neijiang.

Even we assumed VOC emissions as rising or in steady state, different pollutants level and VOC species across cities would affect ozone changes in quantitative. We find a qualitative relationship between NO_x emission and the O₃ response patterns conforms the nonlinear O₃-NO₂-VOC chemistry, not in quantitative sense.

We added the following at line 318-327:

“Note that we find a qualitative relationship between NO_x emission and the O₃ response patterns conform the nonlinear O₃-NO₂-VOC chemistry, not in quantitative sense. For example, the changes of NO_x emissions in Beijing (-2.17 Gg N/cell), Shanghai (-1.18 Gg N/cell), Guangzhou (-0.28 Gg N/cell) and Neijiang (-0.15 Gg N/cell) during 2016-2019 lead to different levels of O₃ changes in Beijing (10.43 μg/m³), Shanghai (7.81 μg/m³), Guangzhou (25.54 μg/m³) and Neijiang (-22.66 μg/m³). Because of the VOC-limited chemistry condition, O₃ increases with decreasing NO_x emissions in Beijing, Shanghai and Guangzhou. The NO_x-limited condition leads to decreasing O₃ with decreasing NO_x emissions in Neijiang. Compared with Beijing, NO_x emissions in

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Guangzhou remained basically constant in 2016 and 2019. But O₃ concentrations in Guangzhou increased more than in Beijing. The local O₃ formation sensitivity is helpful to present the way of O₃ response to NO_x emission, but VOC emission are needed when discussing their relationship in a quantitative way.”

Figure 6: Define time periods in caption.

Response: This has been adapted.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2020-1097/acp-2020-1097-AC1-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-1097, 2020>.

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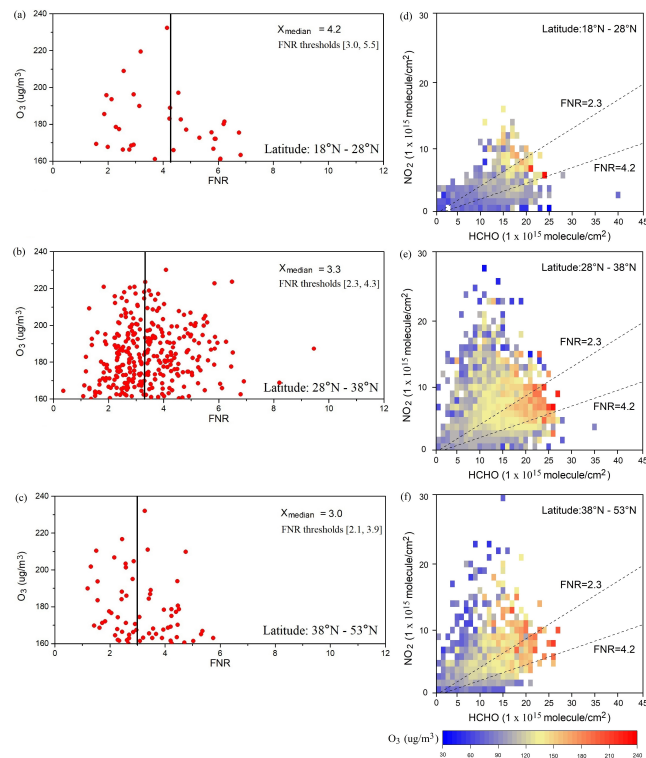


Fig. 1. FNR thresholds in different latitude zones.

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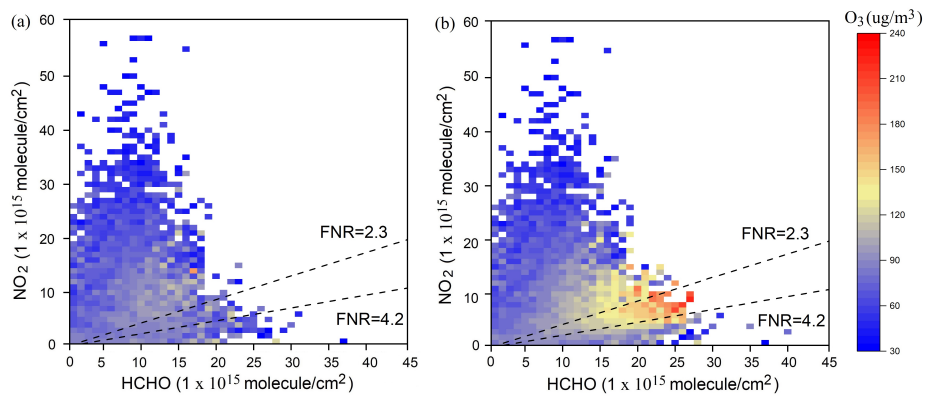


Fig. 2. (a) Monthly mean in-situ O₃ concentrations versus NO₂ columns and HCHO columns from OMI in winter (Dec-Jan-Feb) during 2016-2019.(b) same as (a), but for all season.