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Atmospheric Chemistry and Physics Discussions

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.

General comments:

The paper provides a substantial contribution to the understanding of photochemical ozone production in China. Instead of looking directly at ozone precursors (NOx and VOCs) in the field, it is demonstrated here that information on the photochemical regime can be derived from satellite data of NO2 and HCHO column densities. In this context, the authors develop a method to discriminate between VOC and NOX de-

pendence using characteristic monthly HCHO/NO2 column density ratios from satellite observations. An important aspect of this approach is that they contrast satellite-based HCHO/NO2 ratios for a large number of ground-based ozone measurements and derive characteristic thresholds for VOC or NOx dependence of ozone formation. In the last part of the paper, the developed methodology is applied to the exceptional situation of the COVID-19 lockdown in late winter 2020 in China. The increase in ozone concentrations observed for numerous areas in eastern China was contrasted with the parallel observed decrease in NO2 column densities, and resulting changes for the pre/post lockdown photochemical regimes prevailing in China were derived from the satellite-based HCHO/NO2 ratios. The authors conclude by pointing out that China's future ozone reduction strategy should in any case be accompanied by a parallel VOC reduction control in addition to the focus on NOx reductions that has prevailed so far. The paper is well written and structured and clearly identifies the scientific sources used. The authors make a clear distinction between their own contributions and adequately acknowledge previous work from the literature. Overall, the following ratings are given: Scientific significance: Excellent (4) Scientific quality: Good (3) (see comments) Presentation quality: Excellent (4)

Special comments:

Line 113: The authors point out that only data from the afternoon are used to determine the HCHO/NO2 ratios in order to describe the peak of photochemical ozone production. However, HCHO is a trace gas that is both emitted and photochemically formed in parallel with ozone production. Would the authors please comment on why they do not distinguish between directly emitted HCHO and photochemically formed HCHO. Shouldn't only photochemically formed HCHO be a measure of the intensity of ozone formation? And would it not be possible to draw conclusions about the proportion of directly emitted HCHO (e.g. from vehicle exhaust gases) from additional "satellite winter data" to be evaluated?

Response: We presented the level of ozone formed from photo-oxidation of total mea-

sured HCHO only, not differentiating the contributions from different sources. HCHO (no matter from directly emitted or from secondary formation) as an important precursor of ozone, the contribution to ozone formation was evaluated with in situ observations of ozone in our study. Previous modeling studies derive the thresholds by simulating the response of surface ozone to an overall reduction in NOx or NMVOC emissions with coarse resolution models, which best capture regional as opposed to local O3-NOx-VOC sensitivity. Our thresholds derived with in situ observations should be more indicative of the local ozone chemistry, including HCHO photochemical formation and the effect of NOx titration over urban areas.

HCHO exhibits significant seasonal variations: the concentrations observed in autumn and summer were higher than those in winter and spring. Due to the higher temperature and stronger solar radiation in summer, the higher concentration level of HCHO mainly results from the intense photo-oxidation of VOCs, while direct anthropogenic emissions (e.g. vehicle exhaust gases) may be more important in winter. However, the discrepancy between summer and winter is not prominent in all regions, which may be associated with the relatively smaller temperature difference and the unfavorable vertical diffusion conditions in winter. For example, in Shenzhen (a typical city located in the Pearl River Delta), the ambient daytime HCHO is dominated by anthropogenic secondary formation (about 39%) in all seasons, while anthropogenic primary sources contributed the most during the winter (18%) and spring (20%) in terms of seasonal variation (Wang et al., 2017).

We added the following to the discussion of our manuscript at line 387-389: “We presented the level of O3 formed from photo-oxidation of total measured HCHO only, not differentiating the contributions from different sources (directly emitted or photochemical formed). Due to the higher temperature and stronger solar radiation in summer, the higher concentration level of HCHO mainly results from the intense photo-oxidation of VOCs.”

Line 120: The authors point out that they use solar zenith angles of < 80 to determine

the monthly HCHO/NO2 column density ratios. However, due to the finite pixel size, the intensity of HCHO production depends on the integral solar radiation lasting for several hours. Therefore, should not different HCHO/NO2 ratios be used due to the enormous extent of the study area (< 20_N - > 45_N)?

Response: All satellite data is used in this study. However certain filters had to applied to select qualitatively good data. These criteria will not affect the amount of data very much.

We added the following at line 120: “We select QA4ECV NO2 daily observations following the recommendations given in the Product Specification Document (Boersma et al., 2011) for this data product.”

Line 129: The authors point out that the monthly mean values of the HCHO column densities of (0.05 * 0.05) have been converted to the pixel size for NO2 of (0.125*0.125). Can it be excluded that this procedure leads to significant changes in the HCHO/NO2 ratios (after all, the ratio of the column densities of HCHO/NO2 contains the quotient of the precursor (NO2) and the product of photochemical processing. The adaptation of the HCHO pixel size to that of NO2 could lead to a systematic underestimation of the HCHO column densities. Would the authors please comment on this?

Response: Satellite-based HCHO and NO2 products used in this study have the same original pixel size. Because they are measured by the same instrument OMI, but they are disseminated in different grids. It is fair to make the resolution of both products the same. We do not intent to present analysis on street-level, but we show results for averages on city-level. For this the resolution of 0.125*0.125 degree is good match. To avoid systematic impact caused by the division operation we only consider grids of monthly HCHO columns higher than 2 $\times$ 10 15 molecule/cm2 (detection limitation) and NO2 columns more than 1.5 $\times$ 10 15 molecule/cm2 (which are defined as polluted regions).

Line 175: Using the CLASS model, the authors demonstrate that photochemical ozone production can be represented in terms of O3 isopleths as a function of HCHO (as a proxi for VOC) and NO2. Shouldn't the isopleths rather represent the ozone production over a period of time instead of the total ozone concentrations shown? Elsewhere, the authors explicitly point out that they distinguish between background ozone and additional ozone production by local photochemical ozone production in the measured ozone monthly means (c. f. line 207). It is suggested to describe the non-linearity of ozone production either only schematically (in the form of a cartoon) or actually quantitatively by naming all boundary conditions (starting concentrations, radiation conditions, background ozone concentration, ...).

Response: We use a box-model to simulate the real situation in cities including background level of ozone. Our model results are indeed limited and that is why we use monthly mean data to average out transport. But we still include background ozone. For the isopleths in Figure 1c we used monthly average values of O3, HCHO and NO2.

We present atmosphere dynamic and chemistry conditions adopted in model in Table 1. We added the initial mixing ratios of chemical species are shown in Table S1 in the supplement.

We added the following at 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-NOx-VOC-HOx cycle in semirural areas (Vil'a-Guerau de Arellano et al., 2011; Janssen et al., 2012; van Stratum et al., 2012)."

Line 220: The authors plot the measured monthly means (noon) as a function of the

FNR ratio for a large number of monitoring stations. From the summer O3 monthly means > 160 ug/m3 they calculate a median for the FNR (3.28). The 20% and 80% percentiles are then used as thresholds for VOC and NOx limitation. Would the authors please comment on why it is justified to assume that thresholds can be inferred unambiguously in this way? For this, the ozone monthly means of the measuring stations used must satisfy a given frequency distribution of the photochemical regimes. (After all, it is conceivable that the Chinese O3 monitoring network contains practically only stations with NOx limitation. Then this approach (i. e. by calculating the 50% percentile of the O3 measuring stations for which O3 monthly means > 160 ug/m3 are observed) would shift the center of the transition range far into the range of NOx limitation). Would it not be more appropriate to argue that the highest photochemical ozone production must occur in the transition region? It is therefore proposed to use an isopleth plot of summertime O3 levels above 160 ug/m3 as a function of HCHO and NO2 column densities to identify the HCHO/NO2 ratio of maximum ozone production. In this way, the HCHO/NO2 ratios for NOx and VOC limitation can be determined independently of the frequency distribution of ozone monitoring stations with values above 160 ug/m3.

Response: The suggestion of the reviewer is actually exactly the approach we have applied and it is shown in Figure 1c. Apparently that has not been made clear in the original text. We have changed the explanation to the following at line 217-223:

"We calculated for each city the monthly mean surface O3 as function of the monthly column densities of NO2 and HCHO for all months during May – October from 2016 to 2019. The results are shown in Figure 1c. We only consider observations of monthly HCHO columns higher than 2 $\times$ 10 15 molecule/cm2 (detection limitation), NO2 columns more than 1.5 $\times$ 10 15 molecule/cm2 (which are defined as polluted regions) and O3 columns above 160 μg/m3 (minimizing the effect of background ozone). We then plot in Figure 1d the surface O3 concentrations as function of the FNR to determine the range of FNRs, which includes the O3 maximum for most (> 60%) cities. This range, which we define as the transition between the NOx-limited and VOC-limited

regime."

Line 315: Are the same HCHO/NO2 thresholds used for the COVID-19 lockdown periods (Jan. 2010, period I and Feb. 2020 period II) from Fig. 6c and 6d as for summer conditions? It is evident that due to the different radiation conditions alone, the ratio of directly emitted HCHO and photochemically formed HCHO (see also comment to Line 113) is significantly different in late winter than under summer conditions, so that a change in the threshold ratios for VOC- and NOx-limitation should also be expected. It is suggested that the VOC- and NOx-limitation thresholds for the COVID-19 lockdown periods should be determined independently (e.g. using the isopleth method proposed above).

Response: We agree directly emitted HCHO might be more important in winter. But the contribution of HCHO to O3 formation was evaluated with in situ observations of O3 in our study which including HCHO photochemical formation and the effect of NOx titration in the local ozone chemistry.

We use summertime data to derive thresholds because meteorology conditions (temperature, solar radiation) are favorable for ozone formation. In Figure S2(a) in the supplement we show monthly O3 concentration in winter (Dec-Jan-Feb) as function of NO2 and HCHO. It is much harder to derive the FNR thresholds from these values. We assume the thresholds derive from the summertime data can be applied in winter too. Application of FNR thresholds [2.3, 4.2] derived by summertime data to winter observations in Figure S2(a) shows it is a reasonable assumption. Hence, we used the same thresholds when analyzing the COVID-19 period.

We added the discussion above in our manuscript at line 236-238:

"Figure S2(a) in the supplement shows monthly O3 concentration in winter (Dec-Jan-Feb) which rarely exceed 160 μg/m3, 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."

Technical corrections:

Only two minor issues were found when reviewing the manuscript: - Line 68: Please replace "... to the summed rate of reactions of VOC with peroxy radicals". "... to the summed rate of reactions of VOC with OH radicals". Line 68: The reference (Sillman, 1995) does not appear in the bibliography.

Response: This reference has been added.

Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2020-1097/acp-2020-1097-AC2-supplement.pdf

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