Interactive comment on **"The IPAC-NC field campaign: a pollution and oxidization pool in the lower atmosphere over Huabei, China"** ***by J. Z.*****. Ma et al.: Reply to Anonymous Referee #1**

We thank the anonymous referee for his/her constructive comments. Below the referee comments and the author responses.

Referee comments

Ma et al. presented ground and airborne measurements of atmospheric pollution in the Northern China region. As the authors discussed in the introduction section, Not only in regional standpoints but also in global standpoints, atmospheric chemistry of the Northern China region should be well characterized, considering its impacts towards air-quality and climate in regional and global scales. However, published in-situ measurement results so far, especially very close to the emission regions have been very limited. In that perspective, Ma et al.'s comprehensive ground and airborne measurement dataset should be widely available to the atmospheric chemistry community. This purpose is very well fit with the aims of Atmospheric Chemistry and Physics and this special issue. Based on the measurement dataset, authors conducted constrained box model calculations to understand regional oxidation capacity, which I believe a scientifically interesting work. However, the ways to present the results and comparisons with previous studies can be far much better than as presented in the manuscript is right now. Therefore, I recommend for authors to reorganize presentations of analysis results for publication to ACP.

Author Responses

We thank the referee for favorable considerations of our manuscript. As suggested by the referee, we have reorganized the manuscript substantially. The parts on comparisons between regional modeling and satellite retrieved tropospheric NO_2 and on secondary organic aerosol formation have been removed. Detailed descriptions of the chemical box model have been moved from Sect. 3.4 to Sect. 2.2. We tried to improve the manuscript according to the referee comments as can be seen below.

Referee comments

Major Points for Reconsideration

1) Overall, the authors tried to address too many scientific questions with a limited dataset. For example, in section 2.2., the authors discussed NO2 from modeling and satellite products. The results, as presented in Figure 3, clearly showed that the modeling results significant underestimated the satellite observation results. The reasons could potentially suggest problems in many different aspects of modeling both chemistry and emission characterizations, which can be easily summarized as a separate research paper. However, the authors only discussed a few sentences about the differences. Moreover, these emission-regional model products were not even discussed in the results-discussion section. Therefore, the insufficient regional modeling and satellite intercomparison discussion as current is appeared only distraction for developing ideas to the main points of this article. I strongly urge authors to remove this part. In addition, I suggest for the authors not to discuss about regional secondary organic aerosol forming potential in this paper. The dataset, presented in this work is too limited to discuss aerosol chemistry. On the ground, there was no aerosol measurement. In addition, the airborne measurement suite only contains aerosol physical parameter measurements. Moreover, the gas-phase measurement dataset does not contain any oxidation products such as sulfuric acid or oxygenated organic compounds (rather only hydrocarbons). These limitation on the measurement dataset can potentially cause significant uncertainty in discussion on secondary organic aerosol formation. Last but not least, the box-model, presented in this study is for gas phase chemistry not for multi-phase chemistry. In this context, I suggest that the authors should more focus on predicting oxidation capacity in the North China region and discuss about its implications.

Author Responses

Following the referee's suggestions, we have removed the parts on comparisons between regional modeling and satellite retrieved tropospheric NO_2 and on regional secondary organic aerosol forming potential. Instead, in Sect. 2.2 of the revised manuscript, we

show the regional distribution of NO_x and their source attributions in the PBL, simulated by our regional model. This may help the readers to understand the general 'chemical weather' conditions during the field campaign. We do not give more discussions on the regional model products in the Results-discussion section; otherwise, we may departure too much from the main points of the manuscript, i.e., the regional pollution characteristics and oxidation capacity of the lower atmosphere over the Huabei region.

Referee comments

2) All over the text, the authors compared the model calculated values with the previously reported actual measurements. Thoughtful care should be taken in the comparisons between measurement and model products. This is especially true for OH that have shown significant discrepancies between model and measurements. Moreover, the authors compared with the model derived OH profile in the heavily polluted North China region and measured OH profiles from relatively clean North Pacific and Gulf regions and extremely clean the rain-forest region. Especially the argument, derived from these improper comparisons, appeared in the bottom page 27721 can mislead readers. The authors cannot simply argue that pollutants are "efficiently" oxidized due to high model derived OH concentration. The whole argument either should be eliminated or supported by more comprehensive chemical transport model calculations.

Author Responses

In this paragraph we focus on the vertical distribution pattern of OH. It is true that there have been significant discrepancies between modeled and measures OH, but this is the case largely for low-NOx and high-VOC conditions and the model generally underestimates OH. High aromatics concentrations were measured over Huabei as shown in our manuscript, indicating that our model might underestimate the OH levels over Huabei, as discussed ahead of this paragraph (Page 18, Line 18-21 of the revised manuscript): "*Unaccounted OH recycling remains to be a challenge, and it is conceivable that our model also underestimates OH, in particular because the chemistry of aromatics has similarities with that of isoprene, which has been identified as a molecule that efficiently recycles OH (Lelieveld et al., 2008)*". Regarding to the statement that

pollutants are “efficiently” oxidized, we do not mean that the pollutants are well removed before transporting to the Pacific. Instead, we mean that the oxidizing rates are higher in Huabei because both higher concentrations of pollutants and OH over the region, which are favorable for the formation of regional photochemical smog and grey haze-fog. We have changed this sentence to “*Higher OH concentrations in the lower atmosphere over Huabei, one of the most severely polluted regions in Asia, compared to those over the Pacific indicate that primary pollutants are oxidized more efficiently in Huabei than over the Pacific towards North America. Such an enhancement in the oxidation capacity of the lower atmosphere over Huabei can also promote the formation of ozone and secondary aerosols in the region*” (Please see Page 19, Line 2-6 of the revised manuscript).

Referee comments

3) The whole discussion about NO2 and NO2* is very confusing in all over the manuscript. Obviously, the discussion about potential interference from other NOy species to the NOx channel for an instrument with a thermal converter is correct and the significance of the interferences should be considered when NO2 was measured by a thermal converter equipped analyzer. However, just introducing the idea about potential interference is not enough considering the scope of this study. This is especially important when one compares datasets from an urban and a rural area just like this study. In urban areas, near NOx emission sources, a thermal converter probably works just fine. However, in rural environments away from the source regions, a significant amount of NOy potentially interferes NOx measurement with a thermal converter. I suggest that the authors should revisit the measurement and the modeling datasets and compare what are the distributions of the NO2/NOx ratios. By comparing the rations in two different datasets, more quantitative information of the potential interferences from NOy to the NOx channel can be presented. The discussion about the distribution of measured NOx should be followed after this evaluation.

Author Responses

As suggested by the referee, we revisited the measurement and the modeling datasets and compared the distributions of the NO_2/NO_x ratios. The results have been discussed in the

revised manuscript. Please see Page 13, Line 28 to Page 14, Line 2: "*We calculated NO_2 using the chemical box model (see Sect. 2.2), constrained by measured concentrations of ozone and its precursors including NO. The average daytime NO_2/NO_x ratios are estimated to be 0.74 base on our measurements and 0.72 by the modeling at Beigongda (urban site), and 0.75 by our measurements and 0.70 by modeling at Xin'an (rural site). By comparing calculated results with measurements, we estimate that about 5% of NO_x^* at Beigongda and 15% of NO_x^* at Xin'an might be affected by the interference of other NO_y species. Therefore, the modeled NO_2 values are used for the calculation of O_x in this study*". Figure 7 (Fig. 6 in the original manuscript) has been re-plotted with measured NO_2 labeled as NO_2* and O_x calculated by O_3 plus model estimated NO_2.

Referee comments

Specific issues to be addressed

Page 27702 Line 15-16 I am not sure how meaningful it is to discuss difference of 1.4e6 molecules cm-3 in OH concentration in model calculation results. We are dealing with ~40 % of differences in very reactive species that actual in situ measurement has an analytical uncertainty of more than 30 %. If the authors would like to make this as a main finding on the paper, they should justify this point.

Author Responses

We have deleted this sentence in the revised manuscript.

Referee comments

Page 27703 Line 11 Officially, the continent of America is divided by North, Central and South and Mexico is in North America as far as I know. Double check with the official geographical region!

Author Responses

We have changed it to "Central America" (Page 2, Line 17 in the revised manuscript).

Referee comments

Page 27707 Line 3 "associated with high OH": How high is really high? The OH levels from the model calculations don't seem particularly high compared with

previous measurement and model calculation results.

Author Responses

We have changed it to “associated with OH” (Page 5, Line 24 in the revised manuscript).

Referee comments

Figure 1. If readers are not familiar with geography in China, this map is little tough to read. Use a regional scale map!

Author Responses

Using a larger regional scale map could certainly help the readers to find the position of the region, but it might not be easier for them to compare model results (Figs. 2-4) and aircraft flight tracks (Figs. 6) with emission distributions (Fig. 1).We have marked out the positions of Beijing, Tianjin, Tangshan and Shijiazhuang cities and the Bohai Gulf in Figs. 1 and 3-4 of the revised manuscript. The indicated positions of Beijing and the Bohai Gulf can help the readers to find the position of Huabei in the maps of China, Asia or the world.

Referee comments

Page 27710 Line 7 “East 4th Ring Road” If readers are not familiar with Beijing, probably they cannot get an idea about proximity to the city center. Find a batter way to present this

Author Responses

We have given the distance value from this site to the Tian-An-Men Square, the center of Beijing City (Page 9, Line 13-14 in the revised manuscript).

Referee comments

Line 12 Is this Xian? or Xinan?

Author Responses

It should be Xin’an, and we have made a correction (Page 9, Line 18 in the revised manuscript).

Referee comments

Line 22 It is not clear whether NO and NO2 are detected by two separate instruments or one instrument was used for NO and NO2 measurements. If an one channel instrument was used for the airborne measurements, the authors should describe about how the data gap was handled while one channel was devoted to measure either NO or NO2.

Author Responses

The model TE42C-TL is a commercial gas analyzer produced by Thermo Scientific Inc. One instrument was used for aircraft NO and NO_x measurements during our campaign. We have given additional descriptions in the revised manuscript. Please see Page 9, Line 28 to Page 10, Line 3: *"The analyzer measures the chemiluminescence induced by the reaction between NO and O_3, the intensity of which is proportional to the NO concentration. NO_x measurements are approximated using the thermal reduction of NO_2 to NO by a heated (320°C) molybdenum converter. The 10s duty cycle of the TE42C alternates between NO and NO_x measurements. The difference between the two measurements allows the two continuous signals of NO and NO_x. Data are produced at 1 Hz, although the readings of NO and NO_x are only updated every 10s"*.

Referee comments

Page 27713 Figure 6.It is very odd that the dataset have significant nighttime NO and nighttime O3 at the same time. This seems to be a case both the urban and the rural sites. In the presence of ozone, usually NO is titrated into NO2 without solar radiation (e.g. JNO2 = 0). Provide justifications!

Author Responses

This is the consequence of a misleading presentation, but we have given a note in the revised manuscript. Please see Page 12, Line 31 to Page13, Line 1: *"It should be noted that during several days NO was very low when O_3 was very high, and vice versa. Since average values are presented, we may expect significant nighttime NO simultaneously with O_3"*.

Referee comments

Page 27715 First paragraph: It seems that the authors were trying to identify

whether the Northern China region is NOx or VOC limited regimes in ozone production. To address these issues, a lot more care should be taken. The scope of discussion is not appeared wide enough to draw the conclusion about the ozone production regime. The authors should include modeling analysis for NOx-VOCs-ozone photochemistry.

Author Responses

The ozone production regime is not the main points of this study, and we do not want to consider it as a conclusion in the manuscript. In this paragraph we focus on the oxidant levels measured at the urban and rural sites. The last sentence on comparison between the urban and rural NO_2/NO ratios has been removed in the revised manuscript.

Referee comments

Second paragraph: VOC analysis results should be presented as followings. 1) Along with concentration information, the authors should present reactivity scale information. Due to a wide range of reaction constants of various VOCs to OH in the atmosphere, A simple concentration comparison is almost meaningless. 2) By taking ratios of different VOCs with different lifetimes, the dataset may provide some VOC aging information. This is especially important for comparison between the urban and the rural sites.

Author Responses

As suggested by the referee, we calculated the reactivity of each NMHC species, L_{OH}, using measured concentration times the reaction rate constant of such species with OH. Figure 8 (Fig.7 in the original manuscript) has been updated by showing (a) measured mixing ratios of alkanes, alkenes and aromatics, (b) calculated reactivity, L_{OH}, of alkanes, alkenes and aromatics, and (c) L_{OH} and chemical lifetime, τ_{NMHC}, of individual NMHC species at the Beigongda (urban) and Xin'an (rural) sites during IPAC-NC. Comparisons and discussions have been given in the revised manuscript. Please see Page 14, Line 14 to Page 15, Line 6: "*During the IPAC-NC campaign air samples were obtained at the Beigongda and Xin'an sites for NMHC analyses, and 55 individual species were quantitatively identified (Cheng and Wang, 2010). ····· Pollution transport, e.g., from Beijing, Tianjin and Tangshan, might have a large influence on the species with* τ_{NMHC}

larger than 2 h (e.g., toluene, m,p-xylene, benzene, ethylbenzene and styrene) measured at the Xin'an site". We do not take the ratios of different VOCs with different lifetimes for aging information, considering that air masses at Xin'an (rural site) might also come from different regions than Beijing. But this is a good idea for investigating the influence of urban plume on downwind rural areas, and will be used for case studies in the future.

Referee comments

Page 27718 Line 26: Obviously, the authors calculated NO2 using the box model. Discuss about how different between model calculated NO2 and measured NO2* (or similar between them) and why

Author Responses

Please see our responses to Major points 3) above.

Referee comments

Page 27719 Line 4: Justify why the authors assumed 1.5 ppbv of formaldehyde! This could be a very important source for OH by photolysis so a correct assumption should be warranted.

Author Responses

This value is given base on measurements by other studies as referred in the manuscript. According to our simulations, photolysis of CH_2O contributed about 4-16% to the HO_2 production over Huabei. Certainly, changes in CH_2O concentration could affect OH, and hence we have performed addition sensitivity simulations assuming a 3 ppbv increase of CH_2O at the surface and a 30% increases aloft (Page 17, Line 28 to Page 18, Line 2 of the revised manuscript). The results are also presented in Fig. 12 and described in the revised manuscript.

Referee comments

Page 27720 - 27721 As pointed out above, more careful discussion is required when the authors compared model calculated OH from this study and measured OH from previous studies. Especially, many studies have reported significant discrepancies between model calculated and measured OH.

Author Responses

Please see our responses to Major points 2) above.

Referee comments

Page 27723 Reconsider the way of categorizing altitude! I would recommend that the authors reassess data based on whether the data were collected from above or below the boundary layer.

Author Responses

Our circular flights were generally carried out at different altitudes with intervals of 400-500m. So we think that the present way of categorizing altitude may be more suitable to show the vertical distributions of measured and calculated species concentrations, and also easier for readers to make comparisons with their own dataset. The boundary effect can be evaluated for case study in the future.