

Responses to referee #2:

The paper deals with the ozone production in two densely populated and highly industrialized regions in VR China also presenting speciated hydrocarbon measurements of the two regions. The paper contains interesting material from a part of the world from which information regarding air pollution is still sparse. I only recommend publication if the following points are modified or considered in a careful way.

We highly appreciate the referee's instructive suggestions. We have addressed each concern as below and corresponding revisions have been made in the manuscript.

Main points:

1. The authors point out that "In general, the ozone problem in Shanghai is on urban scale" (see page (p) 9163, line 17-18) ... Whereas "By contrast, the ozone problem in Tianjin is a regional problem" (see p. 9163, line 18-20): I don't believe, that this general conclusion can be deduced from the presented ground-based measurements because they only refer to very few ground-based receptor sites covering only limited sampling times. However, (only) when additionally including the NO₂ satellite measurements of OMI presented Figure 1 one might argue, that the related photooxidant problem is expected to extend over a much larger area in the Tianjin region (Beijing and surroundings) than the area of Shanghai.

We thank the referee for this comment and the valuable suggestion. We agree with the referee that discussions involving OMI NO₂ satellite data displayed in Figure 1 would help reinforce above conclusions, which we have drawn from ozone probability distributions on basis of in-situ measurements at five sites over NCP and two sites in the Shanghai region. We have added more discussions to the end of the third paragraph in Section 3.1: "Generally, NO₂ (NO_x) pollution is more severe in the NCP region than in the YRD as illustrated by OMI NO₂ tropospheric column amounts in Fig. 1. Besides, average distributions of OMI NO₂ exhibit clear differences in NO₂ concentrations within the Shanghai region, in contrast to the high-NO₂ belt over the entire Tianjin-Beijing region. This might also imply that ozone issues in Tianjin are probably on a regional scale, while on an urban scale in Shanghai."

2. I would prefer to describe the field measurements of the organic compounds as Non-Methane hydrocarbon measurements (NM-HC) instead of VOC-measurements because the term VOC (Volatile Organic Compounds) is much broader than hydrocarbons also including carbonyls, chlorofluorocarbons, hydrogenated chlorofluorocarbons, etc. which are not measured nor discussed in this paper.

Thank you for pointing out this more precise description. We have revised it in the manuscript.

3. It might be valuable to check the English by a native English speaker.

Thank you for this suggestion. We have worked hard on improving the interpretations by carefully reading the manuscript through for several times and corresponding corrections have been made.

4. Do what extend differs the submitted paper from the papers of Ran et al., 2009 and Ran et al., 2011? Are the measurements discussed in this paper the same as presented in the earlier papers? If yes which aspects are new in the submitted paper? I expect clarification in this question in the last paragraph of the introduction (not only learning in the middle of the paper that several aspects were already discussed the earlier papers, e.g. p. 9173, line 17; p. 9174, line 9; p. 9174, line 17; p. 9178, line 13-15).

We appreciate the referee's helpful comments. We should have clarified such points in introduction instead of revealing them later in the manuscript.

A dataset that provided grounds for discussions and results in Ran et al. (2009) involved in-situ measurements of ozone and its precursors in urban Shanghai (site Xujiahui as in this paper) from June 2006 to June 2007. We had a 24-h integrated whole-air sample and a 3-h integrated one (6:00-9:00 a.m.) on each day for non-methane organic compounds analysis. But this is the first time we employed a dataset of ozone, NO_x and NMHCs at a suburban site Jinshan in summer 2009 in Shanghai to perform a comparative study in ozone formation between the urban center and suburb. Also, the intensive NMHC samplings (8 samples per day) make it possible to examine their diurnal characteristics, in spite of a rather short sampling period (about one week).

In the Tianjin region, we carried out an intensive field campaign in summer 2009 at a suburban site. A part of the measurements (only one month in the summertime) has been discussed in Ran et al. (2011) to explore the characteristics of NMHCs and its effect on ozone production inside the city clusters over the polluted NCP. Then we particularly conducted another field campaign at an urban site of Tianjin in summer 2010, hopefully to improve our understanding of photochemistry in Tianjin as well as Shanghai by performing the comparative study inside both regions as well as between them.

We have revised the last paragraph in introduction as "In this paper, observations regarding ozone and its precursors from an intensive field campaign in summer 2010 in urban Tianjin and from routine monitoring in summer 2009 in both urban and suburban Shanghai were comparatively analyzed and discussed, with the dataset from the 2009 Haze in China (HaChi) summer campaign in suburban Tianjin (Ran et al., 2011). This would hopefully cast more light on understanding and handling current ozone problem in the two megacities."

Specific points:

Abstract: 5. Page (p) 9163, line 9: I suggest to write: Two intensive ... at an urban and a suburban site of Tianjin and in Shanghai, in addition to ...

Thank you. Ozone and NO_x are routinely measured in Shanghai. We therefore described here as "Two intensive field campaigns ... at an urban and a suburban site of Tianjin, in addition to routine monitoring of trace gases in Shanghai ..."

Introduction: 6. p. 9163, line 26: The references of Streets and Waldhoff, 2000 and Klimont et al., (2001) seem rather old to me and I suggest to use more recent references, possibly referring to Van der A, R. J., et al. (2008), Trends, seasonal variability and dominant NO_x source derived for a ten year record of NO₂ measured from space, *J. Geophys Res.* 113, D04302, doi:10.1029/2007JD009021?

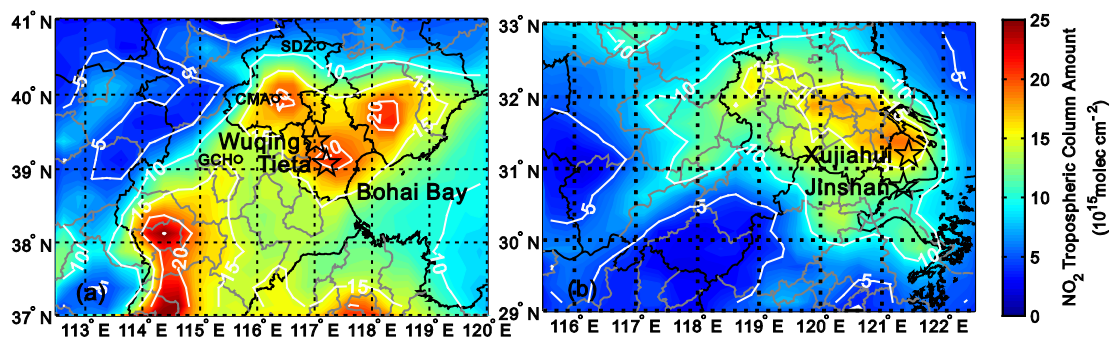
We appreciate the referee's suggestion. In addition to the recommended paper, we also refer to Van der A, R. J. et al. (2006), Detection of the trend and seasonal variation in tropospheric NO₂ over China, *J. Geophys Res.*, 111, D12317, doi:10.1029/2005JD006594.

Experiments and methodology: 7. p. 9165, line 16: How large is the spatial extension of NCP? Is the region 115°E to 114°E/37°N to 38°N part of NCP?

The NCP covers about 409,500 square kilometers, including parts of several provinces in China. The NCP is larger than what we have shown in figure 1. However, the Beijing-Tianjin-Bohai Bay city clusters and the surrounding areas (parts of Hebei Province) we have shown here are most densely populated and industrialized in the NCP.

8. p. 9165, line 16: I cannot see the Bahai Bay in Fig. 1a.

We have added the text 'Bohai Bay' in Fig. 1(a).



9. p. 9167, second paragraph: hydrocarbon sampling: The period of sampling is rather short (about one week, not simultaneously at the sites) so that the representativity of the measurements is restricted because of the variability due to meteorology.

Thank you. We agree with the referee that NMHC characteristics are influenced by meteorology, which could restrict the representativeness of the data, especially in our case (short sampling period, not simultaneously sampled). In the third paragraph in Section 3.2, we discussed the variability of NMHC and meteorological data. Analysis revealed local emissions dominated in the two urban centers during the sampling period. Easterly/Southeasterly winds often prevailed in Jinshan in summer, also the case for the sampling period. Therefore, we reckon a good representativeness of NMHC samples at these three sites. The exception is site Wuqing, where a change in synoptic system was

observed during the sampling period (Wind speed and direction shown in figure 4 in Ran et al., 2011). Accordingly, distinct compositional variations of NMHCs were observed and analyzed therein.

10. p. 9167, second paragraph: You might refer to regarding analytical technique to Ran et al., 2009 (if applicable).

Thank you. We have refereed to Ran et al. (2009).

11. p. 9168, second paragraph, starting at line 6: Is this selection of measurements based on meteorological conditions only applied to O₃, NO_x and CO measurements or also to NM-HC measurements?

We have selected a subset of data from ozone and NO_x measurements based on meteorological conditions. This selection was however not applied to NMHCs, given that the periods of sampling were rather short. To make it clear, we have rephrased the last sentence in this paragraph as “Selected ozone and NO_x data were used in section 3.3 to analyze their diurnal cycles under photochemistry-dominant circumstances.”

Results and discussion: 12. p. 9172, Characterization of hydrocarbon measurements: only averages of NM-HC are presented in the paper: I suggest also to summarize the distribution of the individual hydrocarbon concentrations NM-HC, possibly as tables in an annex – e.g. presenting together with mean values the largest and smallest concentrations measured for the individual compounds at the 4 sites.

Here we provide a table below summarizing the mean, max and min concentrations of each measured NMHC species at the four sites. Since what we are concerned about is the total reactivity of the measured mixture and species that contribute largest to the total reactivity thus are crucial for ozone production as discussed in section 3.2, the individual information is not shown in the manuscript.

Species/ppbC	Xujiahui			Jinshan			Tieta			Wuqing		
	Urban Shanghai			Suburban Shanghai			Urban Tianjin			Suburban Tianjin		
	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
Propene	1.6	4.0	0	1.1	9.3	0	6.0	18.8	0	5.2	21.4	0
1-Butene	0.6	1.8	0	0.5	5.4	0	3.2	10.0	0	3.3	13.5	0
1,3-Butadiene	0.3	0.9	0	0.7	19.6	0	0.8	3.1	0	0.8	28.6	0
cis-2-Butene	0.4	1.4	0	0.2	1.1	0	4.2	14.0	0	7.8	30	0
trans-2-Butene	0.5	1.6	0	0.3	1.4	0	4.7	16.3	0	9.1	29.8	0
1-Pentene	0.4	0.9	0	0.1	0.5	0	1.0	8.6	0	1.0	7.5	0
Isoprene	0.5	2.5	0	1.0	4.3	0	1.6	6	0	8.6	65.7	0
2-Pentene	0.3	1.3	0	0.1	0.5	0	0.0	0.4	0	0.4	7.0	0
Propane	10.5	20.9	2.9	2.8	12.5	0	11.4	34.0	0	19.2	105.8	2.1

Isobutane	4.0	10.9	0	2.0	10.7	0	7.2	23.6	0	8.7	22.6	0.5
Butane	5.6	11.9	1.1	2.7	13.9	0	10.6	32.4	0.8	10.1	28.2	1.4
Isopentane	8.2	16.4	2	2.3	11.3	0	20.7	60.4	0	18.1	85.4	2.65
n-Pentane	10.0	35.2	0	3.3	16.9	0	26.0	50.4	5.6	24.4	114.8	5.1
2,2-Dimethylbutane	0.1	0.4	0	0.0	0.6	0	0	0	0	0	0	0
Cyclopentane	0.4	1.5	0	0.1	0.8	0	0.1	2.0	0	0.8	4.3	0
2,3-Dimethylbutane	0.5	1.0	0	0.3	1.6	0	3.9	17.0	0	1.2	4.4	0
2-Methylpentane	2.4	4.6	0.9	1.4	11.4	0	2.0	14.4	0	4.2	14.0	0
3-Methylpentane	1.5	3.1	0	1.2	9.8	0	1.3	8.9	0	3.0	9.1	0
n-Hexane	2.8	6.4	0	2.9	18.8	0	15.0	45.2	2.9	47.8	258.5	4.0
2,4-Dimethylpentane	0.9	1.9	0	0.5	3.4	0	0.7	22.0	0	0.1	2.5	0
Methylcyclopentane	1.0	2.1	0	0.5	3.8	0	0.5	3.6	0	1.2	5.9	0
Cyclohexane	0.3	0.9	0	0.8	16.5	0	4.7	9.6	0	13.8	99.4	0.7
2-Methylhexane	0.7	2.0	0	0.4	2.1	0	0.4	3.9	0	1.8	10.7	0
2,3-Dimethylpentane	0.2	0.8	0	0.2	0.8	0	1.4	36.8	0	16.6	109.9	0
3-Methylhexane	0.8	2.1	0	0.5	2.3	0	0.1	2.9	0	45.3	110.4	0
2,2,4-Trimethylpentane	0.1	0.2	0	0.1	3.2	0	0.9	4.6	0	0.8	1.1	0
n-Heptane	1.1	2.1	0	0.7	3.2	0	6.0	17.8	0	5.4	119	0
Methylcyclohexane	0.4	0.8	0	0.1	0.9	0	0.3	4.2	0	0.1	1.1	0
2,3,4-Trimethylpentane	0.1	0.7	0	0.0	0.3	0	0.0	1.1	0	0	0	0
2-Methylheptane	0.2	0.5	0	0.1	0.3	0	0	0	0	0.0	0.5	0
3-Methylheptane	0.4	2.0	0	0.3	1.7	0	0	0	0	0.1	1.4	0
n-Octane	0.4	2.1	0	0.3	1.2	0	0	0	0	3.9	81.4	0
Nonane	0.5	3.9	0	0.2	0.6	0	0	0	0	0.6	2.4	0
n-Decane	0.6	3.2	0	0.2	1.1	0	0	0	0	3.1	8.9	0
n-Dodecane	0.3	1.1	0	0.2	1.1	0	0	0	0	0	0	0
n-Undecane	0.4	2.1	0	0.2	0.8	0	0	0	0	1.4	29.4	0
Styrene	1.2	4.2	0	0.5	2.5	0	6.4	18.3	0	5.6	13.0	3.7
Benzene	6.0	17.9	2.5	4.5	20.7	0	32.2	55.6	9.3	23.2	71.4	6.9
Toluene	20.4	66.7	5.3	48.6	203.6	1.1	53.6	110.5	18.0	43.9	127.9	16.5
Ethylbenzene	11.9	26.2	2.7	4.8	27.4	0	21.7	61.6	1.7	10.3	21.3	5.4
m,p-xylene	14.1	41.9	3.8	8.0	51.0	0.7	30.4	91.8	3.4	21.7	51.0	9.8
o-Xylene	3.4	10.2	0	2.0	12.9	0	8.7	26.6	0	6.9	12.9	4.0
Isopropylbenzene	0.1	0.4	0	0.2	1.9	0	0.0	0.6	0	4.2	8.4	0
n-Propylbenzene	0.4	0.9	0	0.2	1.6	0	1.9	63.3	0	3.6	6.7	0
1,3,5-Trimethylbenzene	0.4	0.8	0	0.2	0.9	0	1.6	18.4	0	3.9	5.7	3.2
1,2,4-Trimethylbenzene	1.2	3.0	0	0.6	4.1	0	7.5	28.7	0	6.9	13.7	4.3
1,2,3-Trimethylbenzene	0.4	0.9	0	0.2	1.2	0	0	0	0	5.6	9.5	0
m-Ethyltoluene	1.0	2.7	0	0.5	2.1	0	2.5	36.5	0	7.4	12.5	6.1
p-Ethyltoluene	0.9	2.1	0	0.4	1.0	0	5.3	21.8	0	13.2	25.5	0
o-Ethyltoluene	0.3	0.7	0	0.2	0.7	0	0	0	0	4.8	8.1	0
m-Diethylbenzene	0.2	0.6	0	0.1	0.3	0	0	0	0	2.6	8.6	0
p-Diethylbenzene	0.5	7.5	0	0.2	1.2	0	0.1	1.9	0	5.4	9.8	4.3

13. p. 9172, Tab. 1: For me it is quite remarkable (and could/should be explicitly mentioned in the manuscript), that the total amount of hydrocarbons in ppb is substantially larger at Wuqing than at Tieta despite the fact that Tieta is the urban site and Wuqing is the suburban site in the Beijing area (see e.g. Table 1) which is explained by the authors by the (large) evaporation of alkanes at Wuqing.

We agree with the referee and greatly appreciate this suggestion. We have indicated this point as “Evaporation of solvents used ... Xylenes(7%). Due to such large evaporation of heavy alkanes from industrial processes in this area, it is unsurprising yet noteworthy that total NMHC concentration at Wuqing is substantially larger than that at the urban site Tieta.”

14. p. 9174, line 27: do you mean “...Jinshan is a sparsely populated (instead of located) residential area”.

Yes, we have corrected the typo. Thank you very much.

15. Table 3: How is “background” for NO_x defined?

We thank the referee for this comment. We realize the term “background” here is confusing and inappropriate. We have revised it as “average”.

Conclusions: 16. Last paragraph: I strongly recommend to include the NO₂ satellite measurements shown in Figure 1 to underline the argument that the photooxidant problem extends over a larger area in the Tianjin region than in the Shanghai region (comp. point 1).

We appreciate the referee’s suggestion and have revised the manuscript accordingly following Main point 1. “Finally, it is found that ozone problem extends over a larger area in the Tianjin region than in the Shanghai region based on both in-situ ozone measurements and OMI NO₂ observations.”