Anonymous Referee #1

We thank the reviewers for the careful reading of the manuscript and helpful comments. The reviewer's comments are accordingly addressed in the revised manuscript. We think that the paper is significantly improved following the reviewer's suggestions.

In this manuscript, Tie et al. provides an overview of the field experiment conducted in the Shanghai megacity during September 2009. Ozone and related trace gas as well as PM2.5 were measured at several ground sites during the campaign, and the data obtained from the two sites (Pudong (PD) and Dongtan (DT)) are used for this study. A regional chemical/dynamical model, WRF-Chem, is also applied to simulate the distributions and variations of ozone and related trace gases in the Shanghai region, and results are compared with measurements at the two sites. Model sensitivity tests are performed to evaluate the effect of emission ratio of NOx/VOC on ozone formation in the region. The manuscript addresses the scientific questions that are within the scope of ACP and it is certainly well suitable for this special issue. The measurement items in this study are relatively complete (though short-lived radicals are missing), providing a valuable dataset for the first time for the study of ozone chemistry in the Shanghai megacity. My major concerns and questions arise from the model analysis of this work. I think the manuscript should/could be improved by increasing the links between the more practical or sensible source emissions and model simulations as well as between the measurement data and model analysis.

Specific comments

1) The source emission distributions of primary pollutants in the Shanghai region are not clearly presented in the manuscript. I would suggest that the authors provide an additional figure showing the regional emission distributions of primary pollutants (NOx, VOCs, CO) and perhaps biogenic VOCs in the inner domain (right panel of Fig.1). What emission inventory used for the model simulations of this study is not clearly stated in the manuscript. The authors only refer to their previous work of Tie et al. (2009b) (should be Tie at al. (2009a)), where the TRACE-P inventory of gaseous pollutants developed by Streets et al. (2003) for the year 2000 had been applied. The question is: are there any great changes in the source emissions from 2000 to 2009 for the Shanghai region? Note that an emission inventory for the Yangtze Delta region has been developed recently (Huang, et al. ACP, 4105-4120, 2011).

   To address the reviewer's comments, we add more emission distributions (NOx, and VOCs) in Figure 1 (now it is Fig 1b). The biogenic VOC emission distribution can be seen in a separated paper (in this special issue), i.e., Figure 1 of Geng et al., (2011). According to the reviewer's comments, we also add some texts to clarify our emission development in the Shanghai region. The emission was initially based upon the work of Streets et al. (2003), especially the spatial distributions. However, several previous works have made some improvements for the emission data. For example, Tie et al. (2009a), Geng et al. (2009), and Geng et al. (2008) used the WRF-Chem model to

extensively compared with the measurements and to improve the emission inventory. The high resolution (1km x 1km) urban surface data (photographed by airplane) is also applied to improve the horizontal emission distribution. We should note that this high-resolution emission is only limited in the city of Shanghai (from 121E to 122E in longitude, and 30.5N to 31.5N in latitude). As a result, the emission inventory has been improved and can be represented for the current emission inventories in Shanghai. The total emission of CO, NOx, and VOCs is listed in Table 1 of Tie et al. (2009a). We have added these clarifications in the revised paper.

2) Where is the center point of urban Shanghai in the right panel of Fig.1, BS, XJH, PD or other place? It may not sound to describe the cost site DT as "remote" site. How many distances are the PD and DT sites from the city center? It would be nice if a km scale is given in the right panel of Fig.1. While the main focus of this study is the megacity impacts on the regional ozone formation, no observations at a suburban or rural site downwind of Shanghai were performed or presented. As demonstrated in Fig.13, maximum ozone is simulated to occur at about a distance of about 100 km from the city center. Could the measurement dataset of this study be applied to access such model-simulated plume evolution process?

The center point of Shanghai is at 31.234°N/121.472°E. The PD and DT sites are at 31.219°N/121.550°E and 31.469°N/121.939°E, respectively. The DT station is located in a wetland area at the coast of Shanghai, which is relatively remote from the city. The distances from the center of Shanghai to PD and DT are 7.1 km and 54.8 km, respectively. According to the suggestion of the reviewer, we have added the km scale in Fig. 1. In this study, our measurement sites are located in nearby the city, and cannot track the long-distant plume. As we mentioned in the paper, we used the measurements in the city to evaluate the model, and then used the model to extend to a long-distant plume study.

3) There have been numerous studies on regional ozone in the Yangtze Delta region including both measurements and model simulations, e.g. the results from the CHINA-MAP project. These previous studies should have been recognized and reviewed in the manuscript. Certainly, the authors might argue that in contrast to previous studies, their focus is on the Shanghai megacity where their super sites are located. If so, I would suggest that "urban" (instead of "regional") ozone formation be emphasized in the title as well as the body of the text.

We have added some previous studies of ozone formation in the Yangtze Delta region. We think that our paper provide both the information of ozone formation in the urban and regional scale. In the text, we try to modify some words to combine the both urban/regional effects in the revised paper.

4) While most species are generally well simulated with comparison to the mean values of measurements, the variability of some important species such as O3 is not well predicted. Scatter plots of measured and simulated mixing ratios of important species would be helpful to see the performance of the model and at least they can be given in

the Supplement. Scatter plots showing the correlations of some species with CO (Figs. 8-10) are not necessary to appear in the formal manuscript since no much more information can be learned by this investigation than from emission inventories.

Combine with the comments from reviewer1 (he/she also think the correlation of species with CO (Figs. 8-10) are not necessary), we have deleted the Figs 8-10. Because the most information are provided in the formal text, and the paper is relatively long. We decide don't add the supplement in the paper.

5) In this study, the observational data are used merely for evaluating the model performance with respect to the simulation of the species' mixing ratios. In-depth analysis with measurement data can be done to look at the chemical character of the city plume as revealed by observations. Otherwise, it may not be entirely sufficient to be a campaign overview paper.

In the revised paper, we try to weak the word of the "review paper". We shift the review tone to a comprehensive analysis of the field data and modeling study. As a result, we change the words from "overview" to "information".

6) The mean value of simulated HNO2 is nearly an order of magnitude smaller than its measured mean value over the experimental period. The effects of such HNO2 biases on simulated ozone should be quantified. How about the diurnal cycles of simulated HNO2 and other reactive nitrogen species with comparison to the measurements?

In the revised paper, we show the diurnal cycle of HONO. Figure 7 shows the averaged diurnal variation of HONO in PD. The concentration of HONO was at the maximum in the early morning (0.8 ppb) and rapidly reduced to 0.2 ppb in noontime. The maximum HONO was also consistent with the soot concentrations, which may suggests that there is possible impacts by nitrogen heterogeneous reactions occurring on the soot surface. However, this is a very complicated process, and need to be carefully studied. This issue is out of focus of this paper. According to our previous study (Tie et al., 2007). The ozone formation in the morning was very small. As a result, the impact of early morning high HONO on ozone formation should not be significant. We have stated this in the revised text.

How was PM2.5 sampled and analyzed for this study? While the PM2.5 concentrations are simulated, does the model include the effect of aerosols on ozone chemistry? Note that measured PM2.5 could reach as high as 100 g m-3 at the PD site, which might have considerable impacts on ozone formation through heterogeneous reactions and photolysis rate changes. There are few analysis and discussion about the simulation of aerosol formation in the manuscript. If no feedback on ozone chemistry from aerosols is included in the model, the authors may consider skipping over the parts about PM2.5 (both measurement and modeling results) in the manuscript.

In the current WRF-Chem model, we use the FTUV (fast TUV) mode for the photolysis calculation. The FTUV mode includes the impact of aerosols on ozone chemistry (Tie et al., 2005). Due to high aerosol concentrations in China, the impact of aerosols on the photolysis and ozone chemistry is a very interesting topic. However, this will be a

very complex process, a comprehensive analysis should be individually performed. We are planning another separated paper to address this issue. In the revised paper, we have clarified the reviewer's points.

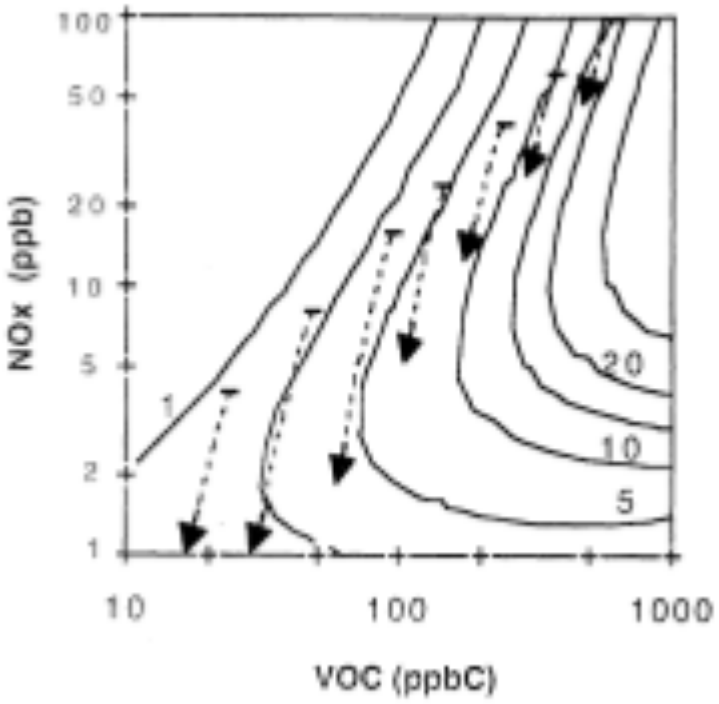
7) The authors use the ratios of CH2O/NOy to identify whether the ozone formation is under the VOC-limited or NOx-limited conditions in the Shanghai region. Based on what chemical principle or for environmental conditions did Silliman (1995) propose this method? Can the CH2O/NOy ratio threshold value (0.28) derived by Silliman (1995) be applied to the Shanghai region since the chemical character of Shanghai can be quite different? The authors also give a discussion about the effect of the concentration and emission ratios of NOx/VOC on ozone formation in Shanghai compared to Mexico City. Are there any quantitative connections of these NOx/VOC ratios to the concentration ratios of CH2O/NOy for the Shanghai region? CH2O is an oxidation product of VOCs, and NOy are the oxidation products of NOx or both NOx and VOCs (e.g. PAN). Can the NOx/VOC ratios be used to evaluate the ozone formation regime since CH2O was not measured in this study? Nevertheless, an in-depth analysis should have been performed to address these issues.

According to the study of Sillman (1995), a correlation of O_3-NOx-VOC sensitivity with an indicator of HCHO/NOy is calculated by a photochemical model. The indicator correlation is based on a series calculation with varying rates of anthropogenic and biogenic emissions and meteorology. The results suggest that when the ratio of CH_2O/NOy is smaller than 0.28, the ozone formation is under the VOC-limited condition, while a ratio of CH_2O/NOy larger than 0.28 indicates ozone formation that is under the NOx-limited condition. We have used another method suggested by Kleinman et al. (2003), which used the calculation of radical budget to determine the ozone sensitivity to VOC and NOx. The comparison of the two methods is very similar, indicating that the Sillman's method is very robust and suitable for the ozone sensitivity study. These texts have been added in the revised paper.

8) The authors performed 4 different model runs to study the effect of the NOx/VOC emission ratio on regional ozone formation in the Shanghai region. It is not clear how they changed the NOx/VOC emission ratios for model simulations (maybe I missed something in the manuscript). Are the NOx emissions changed with a constant VOC emission, or the VOC emission changed with a constant NOx emission? It is quite difficult to understand that Run-R3 (also Run-R4) can represent either a reducing NOx emission case or an increasing VOC emission case unless two simulations were performed for Run-R3. Are the emissions in the entire model domain changed? Are the biogenic VOC emissions changed? How about the situations if NOx and/or VOC emissions are reduced, e.g. by 50%? Nevertheless, I do not think such simple model sensitivity tests without practical emission scenarios could provide highly valuable formation for the understanding of ozone formation in this region, not mention to the planning of ozone control strategies.

In our previous studies (Tie et al., 2007; 2009), we find that the absolute values of NOx and VOCs cannot be used to determine the regimes of ozone formation. This is

also being found from the NOx-VOC-ozone relationship. For example, Figure 1 of Sillman (1999) (see the following plot) shows that when NOx concentrations are between 10 and 100 ppbv, which was often the values measured in the Shanghai region. If the VOC concentrations increase from 100 to 500 ppbv, the ozone concentrations are rapidly increased.



In the revised manuscript, we also clarify the calculation of the emission ratio of NOx/VOC. In our study, the rate of NOx emission is fixed, and the emission ratio of NOx/VOC is increased or decreased by changes of the rate of VOC emission. For example, the default emission ratio is 0.4. The emission ratios of 0.8, 0.2, and 0.1 are changed the VOC emission by decreasing VOC emission by a factor of 2, and increasing by a factor by 2, and 4, respectively. The changes in VOC emission are only limited to the anthropogenic emission in all domain. This clarification is included in the revised manuscript.

9) In the Summary section, the conclusions based on wind directions in Highlights 1 and 4 are limited to the case of this study (summertime in Shanghai). These results are too local to be referred by other studies. Highlight 3 may not be necessary to be a conclusion, as mentioned above. There is neither measurement nor model simulation to support the conclusion about the contribution of biogenic isoprene emissions to ozone formation as stated in Highlight 5. Of course, Fig.16 provides some highlights, but it would be more convincing if a model sensitivity study had been performed.

We have changed texts to address the reviewer's comments. We add some texts to address the local effects in highlights 1, and removed the highlights 3 as suggested by the reviewer.

Technical corrections

1) Abstract and Introduction: The full name of an abbreviation should be given when it is firstly used, e.g. NOx and VOC.

Addressed

2) P1676, L21: Tie et al. (2009) should be Tie et al. (2009a)?

Corrected.

3) P1677, L29: participants?

Changed

4) P1678, L22: the Institute of Chinese Meteorological Science? Not found in the author's affiliations.

Corrected.

5) Fig.1: There are three large red points, instead of two, all of them referring to the super sites? Where are the white points? A description of observational stations in the panel is needed. A distance scale in km should be given.

Corrected and added.

6) Fig.2: This plot may be not necessary. Otherwise, the distributions of major pollutants (CO, NOx, NOy and O3) as well as RH at the two sites (PD and DT) can be shown and discussed in the text.

7) P1680, L21 and L 24: should be Tie et al. (2009a).

Corrected

8) P1682, L6, "polluted period" and "clean" period": it may not be suitable to saying so, merely according to the observations at one site.

We re-defined to "north wind period" and "east wind period"

9) P1683, L28–P1684, L1, "It shows that.....during the experiment". What do you mean? One should know if PAN and MPAN are measured by the instrument performance itself.

The text is changed.

10) P1684, L1-4: The NOx/NOy ratios of 0.92 and 0.99 are mean values. How about the variations and the minima?

The variation and minima are added.

11) Fig. 11: it would be better to show both measured and calculated ages for PD with one panel and calculated ages for DT with another panel. There appear larger differences between measured and calculated ages at PD, indicating that the plume feature is not well captured by the model.

According to the suggestion, we changed the Fig. 11 (now Fig. 8) to combine the age measured and calculated age plots in PD and DT in a separated plot.

12) P1691, L20: should be Tie et al. (2009a).

Corrected.

13) P1691 and Fig. 16: What is OH reactivity and how it was calculated? The unit should be given in the figure. Note that OH reactivity is different from the ozone forma-tion potential.

OH reactivity is defined by several previous studies. For example, the R-4 of Apel et al. (2010) (see below)

$$\sum_{i}^{n} k_{(\mathrm{VOC}_i+\mathrm{OH})}[\mathrm{VOC}_i] \qquad \text{(R4)}$$

In the revised manuscript, we add the units of the OH reactivity of (1/s).

14) P1692, L12, "In addition to.....": should be rewritten.

Changed.

15) Figs. 12, 14-17, the same model domain should have been used, the latitudes and longitudes should have been labeled, and the PD and DT sites marked out.

Changed.

16) It might not be necessary to put all the original version of figures into the Supplement. Interactive comment on Atmos. Chem. Phys. Discuss., 13, 1673, 2013.

This comment is taken in the revised version.