

Variations of ground-level O₃ and its precursors in Beijing in summertime between 2005 and 2011 (acp-2013-977)

Response to Referee #1

Zhang et al.

5 *Zhang et al. present a time-series of measurements of NO_x, VOC and ozone taken between 2005 and 2011 at a single location in Beijing. They show that both ozone and total oxidants (ozone, NO₂, and other reservoir species of reactive nitrogen) have been increasing while both NO_x and VOC were decreasing. The authors discuss their measurements in the context of emission control strategies which have been implemented*
10 *in Beijing, and of other measurement data for Beijing, including satellite measurements. I would like to see some discussion of how well the measurement site at PKU is representative of the rest of Beijing. The authors describe the situation of the site and its local sources well, but I would like to see some wider context here.*

Response: Yes, the representativeness of the site is indeed a key issue for a study on
15 **variation. The monitoring site on campus of Peking University locates about 20 km northwest of the Tiananmen Square. The site was selected to be built on the 6 floor of a building, about 18 m above ground surrounded by the Zhongguancun Avenue and the 4th-ring road with high traffic density. Ozone chemistry had been measured at the site from 1982 (Shao et al., 2006). This site was considered to be representative for the**
20 **urban environment of Beijing city after an intensive campaign in Beijing where the air pollutants including ozone and PM_{2.5} were measured in August at more than 10 sites in Beijing. And this was the reason why Peking University chose this site as a long-term observatory for air pollution and climate change in 2004. This site has been used in several large-scale field campaigns for air quality program in North China Plain, including**
25 **the one for 2008 Beijing Olympics. The description of the site and measurement**

technologies at the site could also be seen elsewhere (Wehner et al., 2008;Zhang et al., 2012).

For this work, we compiled ambient ozone and its precursors' mixing ratios in Beijing from 2005 to 2011 for a trend analysis of ozone chemistry.

5 *Using measurements and a simplified model, the authors calculate the total oxidant production rate in Beijing between 2001 and 2011. It is not clear to me which data are used before 2005, as the authors' own dataset only begins in 2005. The authors should mention more explicitly which data are used as input to their model.*

10 **Response: The data of ozone and its precursors (NO/NO₂, VOCs) were from our measurements at the site on campus of Peking University. The data used in the model before 2006 were from literatures: the publication (Wang et al., 2012) summarized VOCs in Beijing between 2000 and 2007; NO_x (NO, NO₂) in Beijing were summarized from the data in Beijing Municipal Environmental Monitoring Center (Tang et al., 2009). The data source and the way we performed the data processing were explained in our revised**
15 **version.**

Using this method, the authors calculate an increase in P(Ox) from 2001 to 2006, consistent with the observed increase in ozone, but their calculation of a basically unchanged P(Ox) between 2006 and 2011 is not consistent with observations. The authors discuss this discrepancy in terms of the limitations of their method, in particular the lack of
20 *comprehensively speciated VOC input data including formaldehyde and other OVOCs. The authors suggest that better measurement of OVOCs for Beijing are required to better understand recent ozone production, which seems like a reasonable recommendation due to their role in oxidant production through their photolysis and associated radical production.*

25 **Response: Thanks for the comment. The discrepancy between calculated P(Ox) and observed Ox could result from two aspects of limitations in this method. One is the lack of some reactive VOC species like ethene and formaldehyde etc.. The other one is the**

role of regional background of ozone. If the contributions from regional ozone and its precursors also change significantly, it will be problematic to explain ozone or Ox trend only by this formula. We examined the change in regional background and surmised that the influence could be minor comparing with photochemistry in Beijing area. We will perform more quantitative studies on VOCs reactivity and regional background ozone.

Elsewhere in the paper (Sect. 3.2), the authors mention the possibility of increased regional ozone production in the North China Plain due to changing emissions patterns, in particular the increased NO_x emissions associated with power stations in this region. In my opinion the authors should give more weight to the possibility that ozone pollution in Beijing is becoming more of a regional problem, than just a matter of local photochemistry.

Response: Fully agree. Ozone pollution in Beijing could be more influenced by regional change due to stringent control of air quality in Beijing. However, it is difficult to quantify this regional contribution precisely. We made a simplified estimation based on the work of Meng et al. (2009) and Wang et al. (2009) about variations of ozone background in the Northern or Eastern China. Ozone in these two remote sites increased by 1.0 ppbv yr⁻¹ and 0.58 ppbv yr⁻¹, respectively. We assumed that regional ozone background in the North China Plain increased at the rate between 0.58-1.0 ppbv yr⁻¹. Therefore, changes of regional background may account for 22-38% of total 2.6 ppbv yr⁻¹. This was explained in the text. As the central government is pushing harmonized regional development in Beijing-Tianjin-Hebei area, the regional air quality will be more required for further studies.

In general, the paper is clearly and concisely written and certainly suitable for publication in ACP once the authors address the above minor concerns.

Response: Appreciate the encouragement.

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Response to Referee #2

Zhang et al.

This paper reports ground-based measurements of O₃, NO_x, VOCs and meteorological parameters from a central Beijing site over the period 2005 – 2011, which encompasses transient emissions reductions associated with the Olympic Games in 2008. In brief, significant positive trends for O₃ and O_x are reported, alongside negative trends for NO_x and VOCs, in all cases with significant transient downward perturbations during the Olympics period. The trends in O₃ and O_x are interpreted in terms of changing regional levels of O₃ / O_x, changing local urban decrement from NO_x emission reductions, and changing local chemical ozone production from VOC oxidation.

Response: Thank you for the comments. The background, objective and main findings of our work are well summarized.

The key value in the paper is the clear and unambiguous trends in O₃/O_x/NO_x/VOCs presented for this (highly populous) location, the striking impact of the transient policies brought in around 2008, and the predictions of the impact of trends in NO_x and VOC emissions upon ozone production rates to date and looking ahead to the future; the paper makes a significant contribution to the public record of pollution trends and possible impact of air quality policies in this locale. I have some comments regarding the discussion and attribution for these trends (see below), and suggest that this aspect of the paper be significantly expanded to fully do the measurements justice. I have also made some more minor suggestions re presentation of the results and technical corrections.

Response: Thanks, and the manuscript will be modified according to the comments carefully.

-Cause of the increases in O₃ / O_x. If changes in deposition (land use ?) and meteorology may be neglected, three factors could contribute to the observed increased in O₃ : reduced urban decrement from lower NO emissions; reduced regional O₃/O_x levels, and reduced local ozone production.

Response: We agree with your comments of ozone variations. Our discussion involves three potential factors: NO titration effect, local ozone production, and regional ozone contribution. But it is not easy to separate these parts based on the observed ozone dataset. We tried to make some efforts to estimate their contributions in p1031 line 8-19.

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The first of these is dismissed on the basis that the NO trend (-0.2 ppb yr⁻¹) is much smaller than the O₃ trend (+2.6 ppb yr⁻¹). However, this argument neglects that NO_x is partitioned strongly into NO₂ at these ozone levels (mean NO₂:NO ratio of 5 – 6) –the NO_x-O₃ PSS needs to be taken into account to make this argument. Interestingly the data appear to show a shift in the PSS – the NO/NO₂/O₃ daily mean values imply a reduction in the inferred $k(\text{NO}+\text{O}_3)/j(\text{NO}_2)$ values of around 10%. Possibly there is some contribution from trends in visibility to the NO₂ photolysis frequency; alternatively this would suggest a similar order reduction in mean peroxy radical levels.

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Response: Thank you for your valuable comments. We agree that considering the NO_x-O₃ pseudo steady state (PSS) could be better to evaluate the O₃ changes due to variation of NO and NO₂. Then the steady-state ozone would be calculated via:

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$$[\text{O}_3]_{\text{pss}} = J(\text{NO}_2)[\text{NO}_2]/(k_1[\text{NO}])$$

In which, J(NO₂) is the photolysis rate of NO₂, and k₁ is the rate constant of O₃ with NO. Then the ozone trend due to reaction cycling of NO-NO₂-O₃ (including the effects of NO titration) can be affected by two terms: [NO₂]/[NO] ratio and J(NO₂). NO₂ decreased by 4% per year and NO decreased by 3-4% per year (for NO decreased by 0.2 ppbv/yr, average NO in the daytime is 5-6 ppbv). It results a constant or slightly decrease trend of [NO₂]/[NO] ratio (0-1%/yr). The changes of J(NO₂) are more uncertain. Previous studies found that both sunshine hours and visibility in the NCP areas have been decreasing in the past decades (Yang et al., 2009;Zhang et al., 2011). Decreasing visibility will reduce light intensity which directly decreased the photolysis rate of NO₂ for ground (Ammar et al., 2010), but if this decreasing visibility were resulted from increasing hygroscopic

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aerosols, the photolysis rate coefficient $J(\text{NO}_2)$ for the upper air will increase (Madronich, 1987). Thus, $J(\text{NO}_2)$ should be also decreasing or remain stable in the period of this study. Combined the trends of $[\text{NO}_2]/[\text{NO}]$ ratio and $J(\text{NO}_2)$ together, O_3 should be decreasing or remain unchanged due to the reaction cycling of $\text{NO}-\text{NO}_2-\text{O}_3$. We modified the discussion in the revised manuscript.

It would be nice if the authors could present more data to substantiate the changes (or lack thereof) in regional O_3/Ox levels – if other datasets exist. Even with the data mentioned, the regional contribution could account for up to 40% of the observed trend, which (with the urban decrement effect) would leave an important, but not dominant, role for local photochemistry.

Response: Yes. Regional background is an issue of our great concern. Ozone pollution in Beijing could never be only the matter of its own. Variations from regional contribution could impact observed ozone trend in Beijing. However, it is difficult to quantify this regional contribution precisely. We made a simplified estimation based on scarce results in the literature, including work of (Meng et al., 2009) and (Wang et al., 2009) about variations of ozone background in the Northern or Eastern China. Ozone in these two remote sites increased by 1.0 ppbv yr^{-1} and $0.58 \text{ ppbv yr}^{-1}$, respectively. We assume that regional ozone background in the North China Plain increased at a rate between $0.58-1.0 \text{ ppbvyr}^{-1}$. Therefore, changes of regional background may account for 22-38% of total 2.6 ppbv yr^{-1} . Then, other part should come from ‘local’ photochemistry including emissions from downtown, suburban, and surrounding areas of Beijing. Now we expect a new project, which will be conducted in both Beijing (urban site) and Hebei (regional site) to improve our understanding about this issue. We will strengthen discussion about regional variations and its impacts.

The calculation of photochemical production is an approximation, but is useful here in highlighting (a) the changes in trend of NO_x and VOC reductions over the 2001 – 2011 period, (b) the implications of these trends for future O_3 and that (c) the observed trend in O_3 is opposite in sign to that predicted by the $P(\text{Ox})$ analysis !The authors need to address

this contradiction in rather more detail – either in terms of shortcomings in the P(Ox) calculation (e.g. neglect of reactive intermediates such as OVOCs – although these wouldn't change the sign of the trend calculated) – or in terms of the conclusion regarding importance of local photochemistry vs regional abundance. Is a trend in monoterpene / BVOC abundance – not measured other than isoprene – possible ?

Response: Thanks really for the in-depth thinking. Actually we had thought for long on how to compute the 11 years change of ozone chemistry. We found we were not capable to do the full simulation due to the lack of emission inventory and meteorological parameters for such a long time. We ended up with a simple model for the change of oxidants production, which could give us some hints for the change of ozone chemistry, as mentioned by the point (a) and (b) by the reviewer.

As to the point (c), we considered that the calculated P(Ox) was only the perspective of local chemistry to look at the change of observed Ox. Current calculation of P(Ox) could result from two aspects of limitations: One is for the Ox local production, we aware that we lacked some reactive VOC species, such as ethene concentrations were not measured in all years, and we did not know precisely the levels of formaldehyde, and then trends of HCHO and other important OVOCs remained unclear. We believe that by using current VOC species for our model, we captured more than 70% of the reactivity of hydrocarbons, and missed all the contribution of reactive intermediates. We will try to include these OVOCs to see how they will influence the calculation in the following studies. The other one is changing of regional background. It would be very interesting to simulate the change of regional background ozone and to see how it will affect our measured trends of O_x. But in this work our approach is to derive the growth rate of regional ozone based on literatures' values, and to presume regional growth rate as a constant in the past decade.

Except isoprene, our measurements don't contain monoterpene or other BVOCs. Generally ambient mixing ratios of monoterpenes were much lower than that of isoprene and their reactivity were also lower (Atkinson and Arey, 2003). From our

measurements on isoprene, which was used as a tracer for biogenic emissions, we did not find an evident trend. As the isoprene emissions from vegetation were influenced by both temperature and light intensity, while monoterpene emissions mainly controlled by temperature, we guess that monoterpene levels might also have no distinct trend.

5 *Other Comments*

-The NO₂ data are obtained using a Mo converter instrument. As the authors correctly comment, such systems suffer from positive interference from NO_y. How might this affect the analysis? The interference will not be 100% for all NO_y species.

10 **Response: This is true. As the dataset used in this work is for longer term, the NO₂ concentrations were measured by using Mo converter instrument at the beginning of the observatory, therefore we kept the running of the device till now. We had the NO₂ instrument based on principle of photolysis just last year. The inter-comparison between these two gave about 10-20% difference depending on the photochemical status. Using the simultaneous measured PAN by GC-ECD and gas-phase HNO₃ by GAC**
15 **(gas/aerosol collector)-IC, we found that PAN and gas-phase HNO₃ were the main contributors to the differences between Mo converter and photolysis instrument for NO₂.**

Hence, our NO₂ levels in this work were somehow overestimated, but still comparable with the trends obtained from satellite retrieval. So trend analysis based on the Mo
20 converter instrument could be acceptable. For the calculation of production rate of oxidants ($P(O_x)$), we defined $O_x = NO_2 + O_3$, as measured NO₂ by Mo converter contained some of PAN and HNO₃, we think that the sum of NO₂+O₃ might be all right for total oxidants.

The mixing ratio of NO_y decreased significantly from 45 ppbv in 2006 to 20 ppbv in 2008
25 (Chou et al., 2011). It is suggested that NO_y will change non-linearly as to abatement of NO_x emissions. Variations of NO_z could consequentially influence the trend of O_x. One study revealed that ozone production efficiency in Los Angeles area didn't change

significantly during the past 50 years but oxidation of NO_x into PAN or HNO_3 enhanced (Pollack et al., 2013). Therefore we fully agree that it is necessary to have in-parallel NO_y , photolysis-based NO_2 , PAN, gas-phase HNO_3 measurements in our follow-up studies in future years, in order to make odd-nitrogen chemistry precisely.

5 -VOC measurements – not clear if these were all online measurements (instruments present in Beijing) or offline measurements (samples taken to their respective laboratories).

Response: All VOC data taken into trend analysis in this study were from online measurements. The instruments involved in this study were operated by different laboratories between 2005 and 2011, we organized systematic quality assurance and quality control for these instruments before applied in the campaign for this work. We also did offline measurements for some years as part of QA/QC. The QA/QC procedures were described elsewhere (Liu et al., 2008;Shao et al., 2009).

Please define all abbreviations where first used. Please be more precise re the comparisons between the instruments – “most” measurements in agreement – which /how many weren’t, and by how much?

Response: Accepted. (a) We defined all abbreviations in revised version. (b) We modified the description of VOCs measurements. Our VOC data were done by three laboratories: Peking University (PKU), NOAA Aeronomy lab, and Research Center for Environmental Changes, Academia Sinica of Taiwan (RCEC). During each campaign we conducted calibration of instrument and inter-comparisons when two labs involved. Two ways of inter-comparisons were preformed: first is check of VOC standards used by different labs, second is the measurement of the same blind samples by different labs. The standard deviations for VOC standard check were less than 10% for all species except for isoprene (which was around 15%), ratios of PKU results and RCEC results varied between 0.87 and 1.11 for all measured species, the inter-comparison between PKU lab and NOAA lab agreed between 0.85-1 (Liu et al., 2008;Shao et al., 2009). Fig. S1 and S2 illustrate inter-comparison of measurement results in 2010 by GC-FID/PID and

GC-FID/MSD both in PKU lab. Different measurements show good consistency in time-series data, regression and bias analysis also demonstrate acceptable ratios between them. We were confident that the VOC data in this work were obtained under reliable QA/QC procedures.

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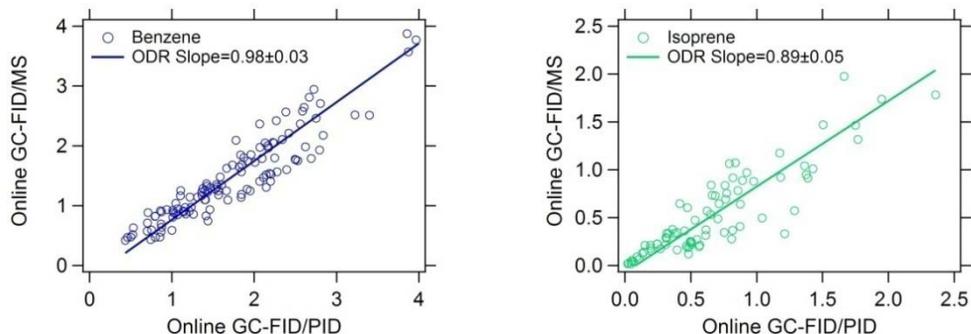


Figure S1 Inter-comparison among GC-FID/PID (GC955 811 or 611 series), GC-MS/FID at PKU site in 2010.

Isoprene (right) represents C3-C6 species detected by GC955-811 VOC analyzer and benzene (left)

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represents C6-C9 species detected by GC955-611 VOC analyzer. Green and blue lines represent orthogonal distance regression (ODR) between two instruments.

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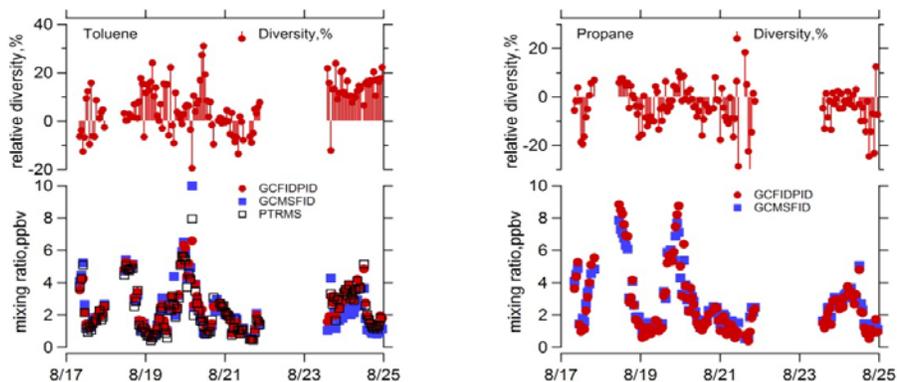


Figure S2 Time-series comparison among GC-FID/PID, GC-MS/FID and PTR-MS (if available) at PKU site in 2010. Toluene (left) and propane (right) are two of most abundant VOC species as examples and red dot and sticks represent relative differences between GC-FID/PID and GC-MS/FID, which appears less than 20% in general.

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-Fig 5 not referred to in the text

Response: The discussions regarding Fig. 5 appeared actually twice in the manuscript (p1029 line 10 and p1033 line 5). The trend of NO₂ in Fig. 5, which were derived from averages from all official monitoring sites in Beijing, showed moderate but the same direction with our data from summertime measurements. Other primary pollutants also showed decreasing trends, suggesting the representativeness and rationality of our measurements. One more reason to have Fig. 5 was to show the importance of VOCs measurements which were not routinely operated yet in the government run sites.

-The explanation of the P(Ox) equation is not clear, and needs expanding in this paper, in addition to the references given to the original derivation p.1030 first few lines –please give more specifics of the VOC trend comparison

Response: Accepted. We made several modifications: (a) the derivation and explanation of P(Ox) equation were described in details in the supplementary material, it could be too long to be included in the text; (b) We added one reference (Zhao et al., 2009) regarding the discussion in first few lines of p1030. (c) All derived trends of VOC species herein were listed in the following tables. We treated linear regressions via both means and medians of mixing ratios of VOCs. The regression performances among these species differed largely: Propene, n-Butane, i-Pentane, n-Pentane, Benzene, Toluene, and o-Xylene showed decreasing trends, whereas the rest showed no clear trends.

Furthermore, I-pentane and n-pentane usually were regarded as the trace gas for gasoline evaporation. Benzene and toluene had diverse emission sources, in which traffic emissions could also play an important role. All these evidences tend to infer that VOC emissions from gasoline vehicles in Beijing were decreasing in the past 7 years.

Table S 1 Temporal regression performances of VOC species via means

Items	Trends, ppbv/yr	95% CI, \pm ppbv/yr	r^2
Propane	-0.09	0.12	0.17
Propene	-0.06	0.02	0.65
i-Butane	-0.05	0.08	0.10
n-Butane	-0.12	0.06	0.57
i-Pentane	-0.41	0.08	0.89
n-Pentane	-0.13	0.03	0.84
t-2-Butene	-0.01	0.01	0.19
1-Butene	-0.04	0.03	0.43
c-2-Butene	-0.01	0.01	0.10
t-2-Pentene	-0.01	0.02	0.16
1-Pentene	-0.01	0.01	0.12
n-Hexane	-0.07	0.05	0.37
Benzene	-0.14	0.05	0.75
Toluene	-0.15	0.04	0.81
Ethyl-benzene	-0.04	0.04	0.27
m/p-Xylene	-0.08	0.16	0.07
o-Xylene	-0.07	0.03	0.61
isoprene	-0.01	0.04	0.03

Table S 2 Temporal regression performances of VOC species via medians

Items	Trends, ppbv/yr	95% CI, \pm ppbv/yr	r^2
Propane	-0.18	0.12	0.43
Propene	-0.07	0.02	0.87
i-Butane	-0.05	0.1	0.09
n-Butane	-0.13	0.08	0.47
i-Pentane	-0.41	0.08	0.90
n-Pentane	-0.14	0.04	0.81
t-2-Butene	-0.01	0.01	0.12
1-Butene	-0.04	0.03	0.36
c-2-Butene	-0.01	0.01	0.04
t-2-Pentene	-0.01	0.02	0.12
1-Pentene	-0.01	0.01	0.10
n-Hexane	-0.08	0.06	0.37
Benzene	-0.12	0.03	0.85
Toluene	-0.15	0.05	0.77
Ethyl-benzene	-0.03	0.04	0.20
m/p-Xylene	-0.07	0.16	0.06
o-Xylene	-0.07	0.03	0.68
isoprene	-0.01	0.04	0.03

Presentation / Minor Comments

- The English usage could be improved, although the meaning is clear throughout. The
 5 Abstract in particular would benefit from a little attention.

Response: Accepted. we smoothed the English of the whole manuscript especially the abstract.

-In general: ppb is a measure of mixing ratio, not concentration. Conversely, on Fig 5, mg/m³ are not units of mixing ratio.

5 **Response: Thanks and changed accordingly.**

p.1024 line 25 be precise re "one" "the other one". Dual not duel.

Response: Accepted and corrected

p.1025 line 4 "previously commercial" ?

Response: Refer to Entech 7100A preconcentrator

10 *p.1027 line 6 RO₂ or RO₂ + HO₂*

Response: RO₂, and we assumed simply that [RO₂]=[HO₂], the same simplification as literature reported (Geddes et al., 2009).

p.1027 line 7 reaction not collision

Response: Sorry for this error, we corrected.

15 *p.1028 line 22 not clear precisely which years were then included in the trend*

Response: O_x trend derived from the data measured in 2006, 2007, 2009, 2010 and 2011.

p.1030 line 23 this argument also depends upon how much C₅H₈ is present

20 **Response: Exactly. We modified the sentence (p1030 line 23-24) like this: As $k_{OH, isoprene}$ *[Isoprene] occupies a relatively large share of alkenes reactivity, variations in L_{OH} due to isoprene could introduce considerable variability into total VOC reactivity.**

Fig 7 VOCs: total ppb or ppbC ?

Response: Here the figure shows VOCs mixing ratio in ppb as shown in the right vertical axis. Recent literatures prefer to report VOC mixing ratio in ppb rather than ppbC, though ppbC could be used in approximate estimation of VOC reactivity. Instead we present calculated OH loss rate along with VOC mixing ratio.

5 **References:**

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Response to Dr. D. Parrish

Zhang et al.

This paper presents a comprehensive overview of measurements related to photochemical ozone production in the Beijing urban area in a clear and concise manner. Beijing is mega-city that currently suffers from some of the world’s most severe air quality problems. The combination of the urban emissions plus the transport of regional pollution into the city likely presents new challenges to our understanding of degraded air quality, and hence to our ability to effectively identify the most efficient control efforts. This paper provides a much-needed synthesis of important research that has been conducted into these issues including a review of that discussed in previous papers plus much that is new here. As such, I expect this paper to serve as an important reference, and as a very useful guide for future field measurements and analyses. This comment presents some suggestions intended to increase the clarity of the analysis and further increase the value of the paper.

Response: Thank you for your commendation.

The detailed information regarding Beijing ozone concentrations is particularly important; I suggest an expanded discussion. Particular suggestions include:

Response: We expanded discussion in revised version following your advice.

- Combine Figure 1 and 2 into a two-panel figure spanning a common time period:

5 2005-2011.

Response: Accepted and modified.

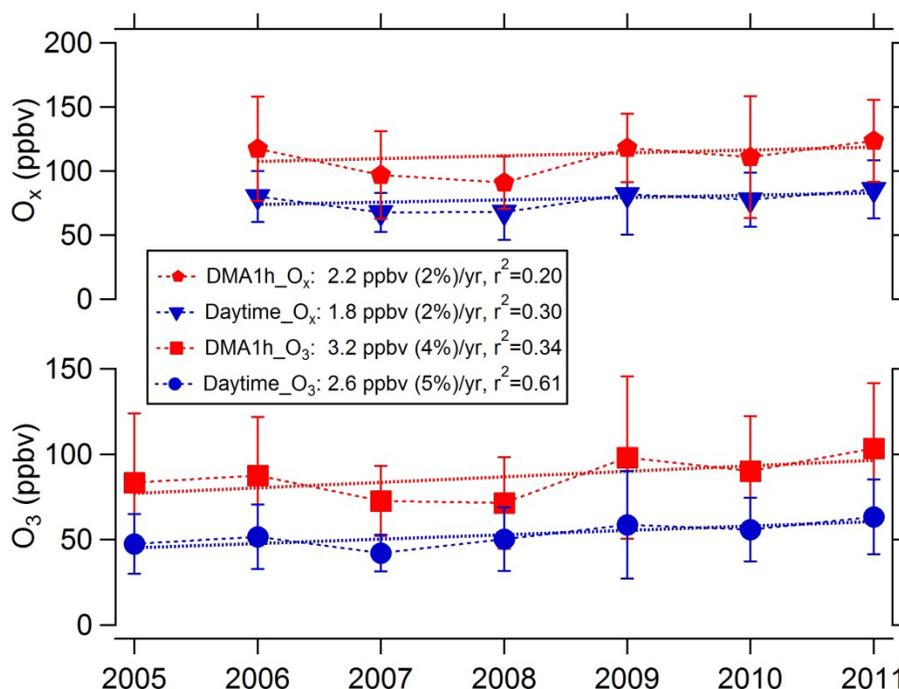


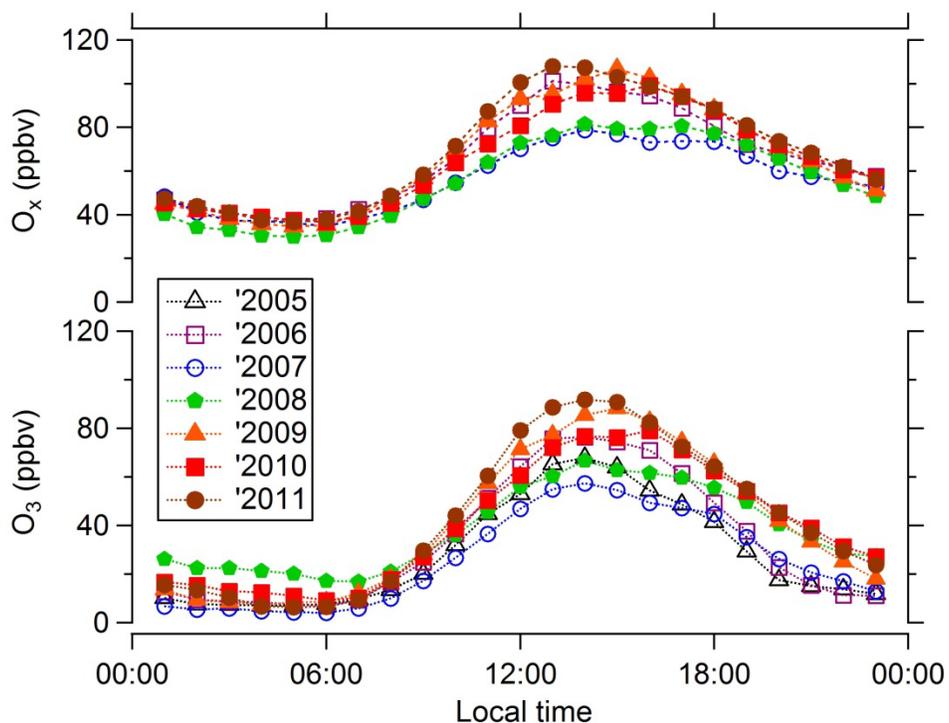
Figure S1 (Upper) Variations in daytime averages (blue triangles) and daily maximum averages (red pentagons) of total oxidants (O_x); (Lower) Variations in daytime averages (blue dots) and daily maximum averages (red squares) of ozone (O₃) in Beijing, August between 2005 and 2011

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- Include a second panel in Figure 3 that shows the diurnal cycle of Ox in the same manner as ozone in the current figure. This will more clearly illustrate the photochemical

formation of total oxidant, and minimize the influence that ozone titration by fresh NO emissions has on the diurnal cycle.

Response: Accepted and modified.

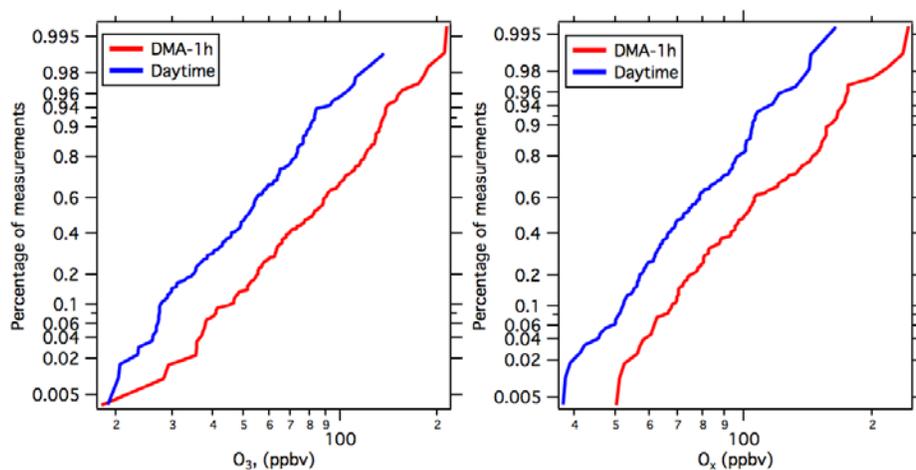


5 **Figure S2 Diurnal variations of O_x (upper) and O_3 (lower) in Beijing, August between 2005 and 2011**

- Include a figure that shows the cumulative distribution functions for ozone and for O_x (e.g., see Fig. 2.1 of Dentener et al., 2011). This would preferably be done for the daily maximum 1-hr ozone averages, since that is evidently the basis for the air quality standard in Beijing. Future studies could compare with this figure to gauge progress in improving
10 Beijing's air quality.

Response: Accepted and added. Ambient abundance of ozone and its precursors is subject to log-normal distribution (Dentener et al., 2011). We plotted expected cumulative probability from log-normal distribution at y axis with logarithmic measured ozone and O_x at x axis in Fig. S3. If ozone and O_x mixing ratios in our measurements also

obey distribution of log-normal distribution, the plotted curve in Fig. S3 should be closed to a straight line similar to the principle of P-P plot, which is just shown in Fig. S3.



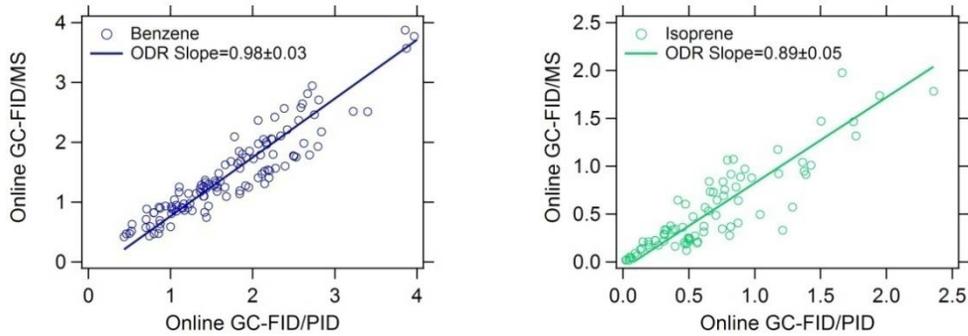
5 **Figure S3** Logarithmic plots of probability vs. measurement values in terms of ambient O_3 (left) and O_x (right) in 1-h daily maximum averages (red) and 12-h daytime averages (blue), respectively, in Beijing, August between 2005 and 2011

This paper discusses measurement intercomparisons, which are important, particularly when measurements are made with instruments designed for environments that may be different from the Beijing region. The comparison of in situ measurements of NO_2 with satellite column measurements is particularly welcome, since satellites indicate continuing increases of NO_2 over the North China Plain, while ambient NO_2 concentrations in Beijing itself are decreasing. Explicitly showing and discussing this apparent inconsistency is important. Figure 6 could perhaps be improved by expanding the scale for the NO_2 VCD, (and VCD should be defined). Additionally, the NMHC measurements were made by a variety of instruments and different groups over the years. Including more details of the intercomparisons of these measurements, perhaps in the Supplementary Material, would be useful.

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Response: Thank you for your comments. As the basis of data availability, we did make and discuss intercomparison between measurements during these years (Liu et al., 2008;Shao et al., 2009) and we expanded this part in revision especially about NMHC measurements according to the referee's comments. VCD of NO₂ within Beijing from satellite results by our estimation showed U-shape variations between 2005 and 2010 which is consist with results from ground-level monitoring (though they didn't change in the same percentage). The variations of NO₂ VCD in Beijing disagreed with trends of NO₂ VCD in the NCP. That is the point in Fig. 6. We also found some evidence of emission inventory variations to support that (Wang et al., 2012). Ozone production in vicinity of Beijing is sensitive to VOC whereas large areas in the NCP are sensitive to NO_x (Zhao et al., 2009). In such case, decease of NO_x within Beijing accompanying increase of NO_x in regional area will promote ozone photochemistry in the same direction so as to aggravate ozone pollution in Beijing. We explained meaning of VCD of NO₂ and expanded the scale of Fig. 6 in the revised manuscript.

Our VOC data were done by three laboratories: Peking University (PKU), NOAA Aeronomy lab, and Research Center for Environmental Changes, Academia Sinica of Taiwan (RCEC). During each campaign we conducted calibration of instrument and inter-comparisons when two labs involved. Two ways of inter-comparisons were preformed: first is check of VOC standards used by different labs, second is the measurements of the same blind samples by different labs. The standard deviations for VOC standard check were less than 10% for all species except for isoprene (which was around 15%), ratios of PKU results and RCEC results varied between 0.87 and 1.11 for all measured species, the inter-comparison between PKU lab and NOAA lab agreed between 0.85-1 (Liu et al., 2008;Shao et al., 2009). Fig. S1 and S2 illustrate inter-comparison of measurement results by GC-FID/PID and GC-FID/MSD both in PKU lab in 2010. Different measurements show good consistency in time-series data, regression and bias analysis also demonstrate acceptable ratios between them. We were confidant that the VOC data in this work were obtained under reliable QA/QC procedures.



5 **Figure S4 Inter-comparison among GC-FID/PID (GC955 811 or 611 series), GC-MS/FID at PKU site in 2010. Isoprene (right) represents C3-C6 species detected by GC955-811 VOC analyzer and benzene (left) represents C6-C9 species detected by GC955-611 VOC analyzer. Green and blue lines represent orthogonal distance regression (ODR) between two instruments.**

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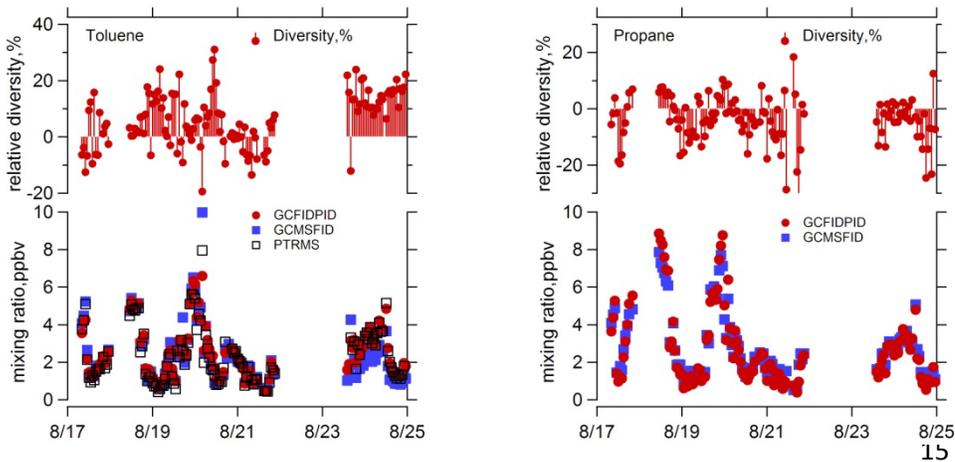


Figure S5

Time-series comparison among GC-FID/PID, GC-MS/FID and PTR-MS (if available) at PKU site in 2010. Toluene (left) and propane (right) are two of most abundant and typical VOC species as examples and red dot and sticks represent relative differences between GC-FID/PID and GC-MS/FID, which appears less than 20% in general.

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The discussion at the beginning of Section 2.4 seems to imply that ozone air quality in Beijing can be considered only from a local perspective. While the investigation of the

local photochemistry is very important, it should be more clearly emphasized that transport of regional pollution into Beijing is also important. The regional modeling of Zhao et al. [2009] and Nawahda et al. [2013] deserves more emphasis in the discussion of ground-level ozone in Beijing, although the measurements discussed in this paper cannot directly address the impact of regional transport.

Response: Fully agree. We have never intended to draw any judgment like that only local pollutants and relevant photochemistry leads to severe ozone pollution in Beijing. We do think both global and regional background variations are constructive when analyzing ground-level ozone trends. Long-term measurement evidences of elevated ozone background in the Eastern and Southern China were reported by (Xu et al., 2008) and (Wang et al., 2009). Moreover, ozone pollution is typically a piece of regional environmental issue. Modelling of (Zhao et al., 2009) demonstrated high ozone pollution suffered in a large scale in the NCP under adverse meteorological condition. Results from (Nawahda et al., 2012) revealed ozone pollution deteriorated from 2000 to 2005 in the NCP area including the Beijing city. We added some discussion to emphasize this point. We admit that it is hard to separate explicitly results of photochemistry within Beijing and from regional transport via measurements at a single site, but we did a simplified estimation to weight contribution from variations of photochemistry and regional background.

The multi-year perspective that the authors take in this paper is very enlightening. Presenting the results of the special controls instituted in Beijing for the 2008 Olympic Games in the context of the long-term trends is particularly welcome. I suggest that the trends of ozone precursors and other primary pollutants in Figures 4, 5 and 7-9 be presented in a somewhat different manner. Ambient concentrations of these species tend to decrease exponentially in response to control efforts [see e.g., Pollack et al.,2013], so that if trends are plotted on semi-log scales, approximate straight lines are defined, and the slope of this line is directly related to the rate of decrease in percent per year.

Response: Accepted and modified these figures on semi-log scales in the revised manuscript.

5 *Finally, I suggest that the authors take the opportunity this paper provides to briefly discuss their perspective of future research that is required to arrive at a fuller understanding of Beijing's air quality issues.*

Response: Thank you for your valuable comments. Based on the insight from this work, we will persist in working on following aspects to deepen our knowledge on these issues We are continuing the measurement at PKU site to maintain and lengthen this hard-won dataset. We are finding more reliable modelling to test more effective emission control
10 **measures and working on more detailed analysis of VOC and OVOC variations in Beijing during the past decade. Our new settled measurement of OH reactivity tends to reveal direct evidence on variations of atmospheric oxidation capacity in Beijing. We also plan to conduct new series of field campaign in the North China Plain to investigate both local and regional contribution to Beijing's air quality. Other important things that can**
15 **not be addressed by this study include: (1) explicitly determination of regional ozone transportation and local chemistry to Beijing ozone trend; (2) The trend of other secondary products, e.g. PAN, HNO₃ and OVOCs; (3) Key parameter measurements including HO_x, OH reactivity. We added a paragraph in the Conclusion Section to discuss the perspective of future research for the air quality of Beijing, especially for**
20 **atmospheric photochemistry in Beijing and its surrounding areas.**

References not included in Discussion Paper

25 *Dentener, F., T. Keating, and H. Akimoto (Eds.) (2011), Hemispheric Transport of Air Pollution 2010: Part A: Ozone and Particulate Matter, Air Pollut. Stud., vol. 17, United Nations, New York. (available at: <http://www.htap.org/publications/2010report/2010FinalReport/HTAP>)*

Pollack, I. B., T. B. Ryerson, M. Trainer, J. A. Neuman, J. M. Roberts, and D. D. Parrish(2013), *Trends in ozone, its precursors, and related secondary oxidation products in Los Angeles, California: A synthesis of measurements from 1960 to 2010*, *J. Geophys. Res. Atmos.*, 118, 5893–5911, doi:10.1002/jgrd.50472.

- 5 Zhao, C., Y. Wang, and T. Zeng (2009), *East China Plains: A “basin” of ozone pollution*, *Environ. Sci. Technol*, 43, 1911–1915.

Response: Thanks for the suggestion. All of these literatures are included in the revised manuscript.

References:

- Dentener, F., Keating, T., and Akimoto, H.: Hemispheric Transport of Air Pollution 2010: Part A: Ozone and Particulate Matter in: *Air Pollut. Stud.*, 17, United Nations, New York, 2011.
- 5 Liu, Y., Shao, M., Lu, S., Chang, C.-C., Wang, J.-L., and Chen, G.: Volatile organic compound (VOC) measurements in the Pearl River Delta (PRD) region, China, *Atmos. Chem. Phys.*, 8, 1531-1545, doi:10.5194/acp-8-1531-2008, 2008.
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- 10 Shao, M., Lu, S., Liu, Y., Xie, X., Chang, C., Huang, S., and Chen, Z.: Volatile organic compounds measured in summer in Beijing and their role in ground-level ozone formation, *J. Geophys. Res.-Atmos.*, 114, D00G06, doi: 10.1029/2008jd010863, 2009.
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- 15 Wang, T., Wei, X. L., Ding, A. J., Poon, C. N., Lam, K. S., Li, Y. S., Chan, L. Y., and Anson, M.: Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994-2007, *Atmos. Chem. Phys.*, 9, 6216-6226, doi: 10.5194/acp-9-6217-2009, 2009.
- 20 Xu, X., Lin, W., Wang, T., Yan, P., Tang, J., Meng, Z., and Wang, Y.: Long-term trend of surface ozone at a regional background station in eastern China 1991-2006: enhanced variability, *Atmos. Chem. Phys.*, 8, 2595-2607, doi: 10.5194/acp-8-2595-2008, 2008.
- Zhao, C., Wang, Y., and Zeng, T.: East China plains: A "basin" of ozone pollution, *Environ. Sci. Technol.*, 43, 1911-1915, 2009.
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