Variations of ground-level O_3 and its precursors in Beijing in summertime between 2005 and 2011 (No. acp-2013-977)

Response to Referee #2

Zhang et al.

This paper reports ground-based measurements of O3, NOx, 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 Ox are reported, alongside negative trends for NOx and VOCs, in all cases with significant transient downward perturbations during the Olympics period. The trends in O3 and Ox are interpreted in terms of changing regional levels of O3 / Ox, changing local urban decrement from NOx 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/Ox/NOx/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 NOx 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 / Ox. 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/Ox 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.

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 NOx is partitioned strongly into NO2 at these ozone levels (mean NO2:NO ratio of 5 – 6) –the NOx-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(NO+O3)/j(NO2) 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.

Response: Thank you for your valuable comments. We agree that considering the NO_x-O_3 pseudo steady state (PSS) could be better to evaluate the O_3 changes due to variation of NO and NO_2. Then the steady-state ozone would be calculated via:

$$[O_3]pss=J(NO_2)[NO_2]/(k_1[NO])$$

In which, $J(NO_2)$ is the photolysis rate of NO_2, and k_1 is the rate constant of O_3 with NO. Then the ozone trend due to reaction cycling of NO-NO_2-O_3 (including the effects of NO titration) can be affected by two terms: $[NO_2]/[NO]$ ratio and $J(NO_2)$. NO_2 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 [NO_2]/[NO] ratio (0-1%/yr). The changes of J(NO_2) 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 NO_2 for ground (Ammar et al., 2010), but if this decreasing visibility were resulted from increasing hygroscopic aerosols, the photolysis rate coefficient J(NO_2) for the upper air will increase (Madronich, 1987). Thus, J(NO_2) should be also decreasing or remain stable in the period of this study. Combined the trends of [NO_2]/[NO] ratio and J(NO_2) together, O_3 should be decreasing or remain unchanged due to the reaction cycling of NO-NO_2-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 O3/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 ppbv yr^{-1}, respectively. We assume that regional ozone background in the North China Plain increased at a rate between 0.58-1.0 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 NOx and VOC reductions over the 2001 – 2011 period, (b) the implications of these trends for future O3 and that (c) the observed trend in O3 is opposite in sign to that predicted by the P(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.

Other Comments

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

Response: This is true. As the dataset used in this work is for longer term, the NO_2 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 NO_2 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 HNO_3 by GAC (gas/aerosol collector)-IC, we found that PAN and gas-phase HNO_3 were the main contributors to the differences between Mo converter and photolysis instrument for NO_2.

Hence, our NO_2 levels in this work were somehow overestimated, but still comparable with the trends obtained from satellite retrieval. So trend analysis based on the Mo 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 NO_2 by Mo converter contained some of PAN and HNO_3, we think that the sum of NO_2+O_3 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 (Chou et al., 2011). It is suggested that NO_y will change non-linearly as to abatement of NOx emissions. Variations of NOz could consequentially influence the trend of Ox. 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.

-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.

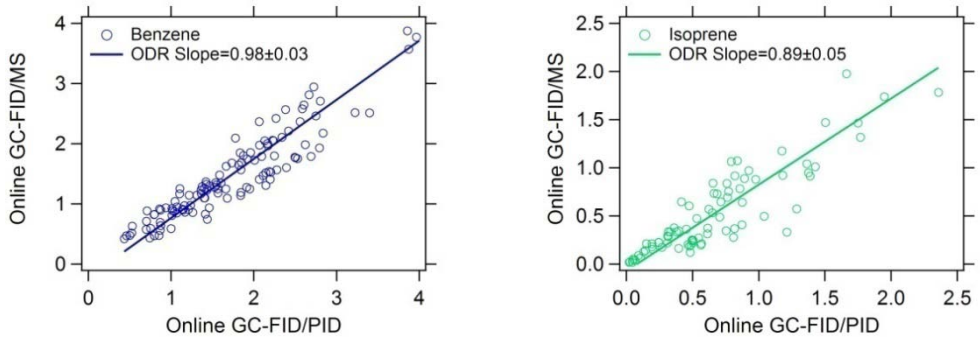

Figure S1 Inter-comparison among GC-FID/PID (GC955 811 or 611 series), GC-MS/FID at PKU site in 2010. Isoprene (right) represents C3-C6 species detected by GC955-811 VOC analyzer and benzene (left) represents C6-C9 species detected by GC955-611 VOC analyzer. Green and blue lines represent orthogonal distance regression (ODR) between two instruments.

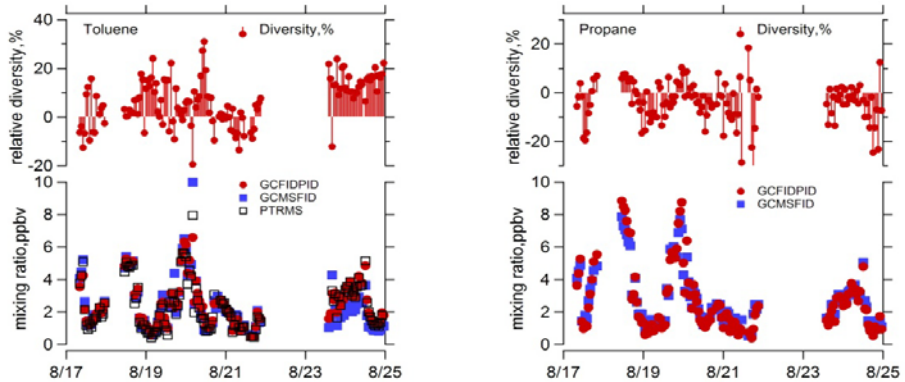

Figure S2 Time-series comparison among GC-FID/PID, GC-MS/FID and PTR-MS (if available) at PKU site in 2010. Toluene (left) and propane (right) are two of most abundant VOC species as examples and red dot and sticks represent relative differences between GC-FID/PID and GC- MS/FID, which appears less than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

-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 NO_2 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 lin es –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, ±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

5

Table S 2 Temporal regression performances of VOC species via medians

Items	Trends, ppbv/yr	95% CI, ±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 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.

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

p.1027 line 6 RO2 or RO2 + HO2

Response: RO_2, and we assumed simply that $[RO_2]=[HO_2]$, the same simplification as literature reported (Geddes et al., 2009).

p.1027 line 7 reaction not collision

Response: Sorry for this error, we corrected.

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

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.

References:

Ammar, R., Monge, M. E., George, C., and D'Anna, B.: Photoenhanced NO2 loss on simulated urban grime, Chemphyschem, 11, 3956-3961, 2010.

Atkinson, R., and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, Chem. Rev., 103, 4605-4638, 2003.

Chou, C.-K., Tsai, C.-Y., Chang, C.-C., Lin, P.-H., Liu, S. C., and Zhu, T.: Photochemical production of ozone in Beijing during the 2008 Olympic Games, Atmos. Chem. Phys., 11, 9825-9837, doi:10.5194/acp-11-9825-2011, 2011.

Geddes, J. A., Murphy, J. G., and Wang, D. K.: Long term changes in nitrogen oxides and volatile organic compounds in Toronto and the challenges facing local ozone control, Atmos. Environ., 43, 3407-3415, 2009.

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.

Madronich, S.: Photodissociation in the atmosphere: 1. Actinic flux and the effects of ground reflections and clouds, J. Geophys. Res.- Atmos., 92, 9740-9752, 1987.

Meng, Z. Y., Xu, X. B., Yan, P., Ding, G. A., Tang, J., Lin, W. L., Xu, X. D., and Wang, S. F.: Characteristics of trace gaseous pollutants at a regional background station in Northern China, Atmos. Chem. Phys., 9, 927-936, doi: 10.5194/acp-9-927-2009, 2009.

Pollack, I. B., Ryerson, T. B., Trainer, M., Neuman, J. A., Roberts, J. M., and Parrish, D. D.: 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, 2013.

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.

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.

Yang, Y. H., Zhao, N., Hao, X. H., and Li, C. Q.: Decreasing trend of sunshine hours and related driving forces in North China, Theor. Appl. Climatol., 97, 91-98, 2009.

Zhang, J., Ouyang, Z., Miao, H., and Wang, X.: Ambient air quality trends and driving factor analysis in Beijing, 1983–2007, J. Environ. Sci., 23, 2019-2028, 2011.

Zhao, C., Wang, Y., and Zeng, T.: East China plains: A “basin” of ozone pollution, Environ. Sci. Technol., 43, 1911-1915, 2009.