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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozone weekend effects in the Beijing–Tianjin–Hebei metropolitan area, China" *by* Y. H. Wang et al.

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Response to S. Madronich's comments: We are very grateful to S. Madronich for the constructive suggestions and for the proposed corrections to improve our paper. Here, all the issues raised had been addressed. According, the manuscript had been modified. General comments: This is a nice data set with good geographic and temporal coverage of observations of key tropospheric pollutants ozone, NO and NOx, PM. A main result and the focus of this paper is that surface ozone is equal or even larger on weekends, despite lower precursor emissions. This ozone weekend effect (OWE) is widely known in North America and Europe, but has not been documented in this region. The analysis and interpretation is rather brief and leaves

open the opportunity to address many interesting questions. As the authors correctly recognized, this type of data can provide deep insights into chemical processing, and so I offer consideration of the following four possible starting points toward this goal:

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1. The authors focus on the reaction O3 + NO -> NO2 + O2 (1) to explain how O3 responds to diurnal and weekly variations in emissions, but don't consider the reaction OH + NO2 -> HNO3 (2) This is a very powerful termination reaction that removes a member from each of the Ox, HOx, and NOx families. Stephens et al. are misquoted here as saying that reaction (1) causes the OWE, while in fact their analysis supports reaction (2) as more important in Mexico City, with ozone formation specifically sensitive to the fraction of radicals lost via Reaction (2) vs. other radical losses (e.g. 2HO2 -> peroxide), as predicted theoretically by Kleinman (2005). To see the relative importance of these two reactions in your case, you could look at the weekend effect for Ox = O3 + NO2. Specifically: It appears that you have data for NOx and NO, so you can calculate NO2 = NOx - NO. Does Ox = O3 + NO2 have a weekend effect? Response:Thanks for the comments. We agree with that the reaction (2) are more important for the OWE in Mexico City, as Stephens. S et al. (2008) addressed. We cited Stephens's work here to illustrate the different day of OWE in Mexico City and BTH region. According to your suggestion, we look at the weekend effect for Ox=O3+NO2 to see the relative importance of the two reactions in our case. The result showed that some sites (LF, LTH, BJT, TJT, YJ and QA) have positive Ox weekend effect, while the other sites (YF, BD, TG and SQL) have negative Ox weekend effect. As showed in figure below, the weekly variations of Ox are different from site to site. There were no consistent maximum or minimum values that occurred on a fixed day. For example, the maximum Ox concentration at LF site occurred on Saturday, while that at BD site occurred on Wednesday. We think high level of NOx pollution at these sites should be responsible for these negative Ox weekend effect.

Figure1 Weekly variations of Ox concentration anomalies at these sites 2. Small and even slightly negative values of the OWE (defined as the % O3 change) may still imply

ACPD
13, C6920–C6927, 2013

inhibition by NOx, because weekend reductions in CO and VOCs alone would yield substantially lower ozone. They are offset by the lower weekend NOx ,which tends to increase ozone. Thus a small value of OWE, even OWE<0, should not be equated to "no weekend effect", for which ozone would decrease by the same relative (%) amount as its precursors. Response: We accepted your suggestion. A small value of OWE, even a negative OWE is not meaning “no weekend effect”. We corrected our statements in our manuscript. 3. As already suggested by another reviewer, the daytime and nighttime values should not be averaged, especially at the surface. Surface observations at night tend to be particularly unreliable due to poor mixing and local perturbations. Response: We accepted your suggestion. 24-hour averaged surface ozone values may be not reliable in characterizing ozone photochemistry due to poor mixing and local perturbations at night. Accordingly, we recalculated weekly variations of surface ozone anomalies using daytime 08:00-18:00 (Beijing time) value at all sites. The new result showed that there is still OWE over BTH area. However, the maximum ozone concentration occurred at Sunday, while the minimum ozone concentration occurred at Wednesday or Friday. This indicates that the difference of ozone concentration during weekend and weekday maybe from photochemical production. We also modified this part in revised manuscript.

Figure2 Weekly variations of surface ozone anomalies at these sites

4. The night-time NO and O3 values are themselves very interesting but a bit strange: Comparing figures 4 (ozone) and 5 (NO): How can 10-20 ppb O3 coexist with 20-30 ppb NO at night? Reaction (1) is very rapid (a few minutes) and whichever (NO or O3) is in excess will destroy the other one completely. Therefore the non-zero night values of BOTH NO and O3 must be artifacts, e.g. of averaging air parcels containing some NO and zero O3, with airparcels containing zero NO and some O3. Is this true? And given that at night O3 and NO control each other, why is the variability of NO so much larger than that of O3? Response: Thanks very much for your suggestion. As you just indicated, the reaction (O3 + NO -> NO2 + O2) is very rapid. No matter which is in

ACPD
13, C6920–C6927, 2013

excess will destroy the other one completely. This kind of situation is correct with air parcels containing some NO and O3. However, we used two years data of NO and O3 in the study. The variation pattern, O3 and NO concentrations are averaged values, so we think 10-20 ppb O3 can coexist with 20-30 ppb NO at night after the averaging. NO is a primary pollutant that comes directly from consumption of fossil fuels, such as on road vehicles. The daily variation of NO is related to human activities. For example, NO has high concentrations on morning and evening rush hours. Ozone is a secondary pollutant that comes from photochemical production. Its variation pattern and concentration is affected by its precursors (NOx, VOCs). Moreover, ozone has a longer lifetime than NO in the atmosphere. All of these make variability of NO so much larger than that of O3. **********

Minor issues: 13046/15: do you mean CO is a proxy for VOCs? Response: Yes, we use CO as a proxy for VOCs here. 17: VOC-regime -> VOC-limited regime Response: Thank you. We added the word “limited” in this sentence. 22: delete "in" Response: We deleted “in” in the sentence. 13047/24: The citation Randall et al. 1998 is incorrect here and in the bibliography where it is given as Randall and Robert, 1998. Actually Randall and Robert are the first names of the authors, and their correct names are: R.S. Cerveny and R. C. Balling Jr. Response: We are sorry for our mistake. The citation has been corrected as “Cerveny and Balling, 1998”. 13050/11: was -> were Response: Thanks a lot. We corrected the word. 13052/1: highly factory located area -> highly industrialized area 1: inner land -> inland Response: We corrected the two phrases as you suggested. 5: There are 2 possible reasons why the OWE is small at these locations: The one given in the paper is that non-industrial emissions persist on weekends. The other is that the NOx/VOC ratio may be much lower and therefore does not show a OWE Response: We agree with the explanation. The detailed interpretations have been addressed in 3.2.1. Figure 2 caption: manitude -> magnitude Response: We corrected the word. 13: what are the uncertainties of these estimates? From Fig 3, seem large. Response: Thanks for your comments. Firstly, the calculation of vertical OWE in this high platform was based on weekly variations of their ozone

ACPD
13, C6920–C6927, 2013

concentration. From Fig 3, we can see that high platform has minimal weekly variations, while low platform has maximum weekly variations. Also, the calculation was based on weekend and weekday difference. 13053/10: level -> levels Response: We corrected the word.

8: How can the NO+O3 reaction lead to "an accumulation of ozone late of Sunday night and early Monday morning"? The reaction is removing ozone (at least temporarily), not accumulating. Response: We agree with the comment that NO+O3 reaction lead to removing ozone, not accumulating. The original sentence in the MS is “It is widely accepted that the OWE in urban areas is partly attributed to a decrease in titration (NO+O3→NO2 +O2) (Fishman et al., 1978; Altshuler et al., 1995; Fujita et al., 2003; Murphy et al., 2007; Stephens et al., 2008; Tang et al., 2009), which can lead to an accumulation of ozone late of Sunday night and early Monday morning”. Considering the reaction (OH + NO2 -> HNO3), we changed the sentence as “It is widely accepted that the OWE in urban areas is partly attributed to a decrease in titration (NO+O3→NO2 +O2) (Fishman et al., 1978; Altshuler et al., 1995; Fujita et al., 2003; Murphy et al., 2007; Tang et al., 2009) and the reaction (OH + NO2 -> HNO3) (Stephens et al., 2008) , which can lead to an accumulation of ozone late of Sunday night and early Monday morning” 9-13: The diurnal cycle in O3 supports a photochemical origin, but does not provide any support for the statement that the reaction NO+O3 is the reason for the OWE. It is also consistent with OH+NO2. Response: We accepted your suggestion. We corrected the statement in our manuscript. 23: The assertion that "surface ozone mainly came from transition of upper atmosphere"is probably wrong. My guess is that most of the odd oxygen (O3 + NO2) is made in the PBL, but high NO levels near the surface keep O3 low at night. Response: Thanks very much for your comments. According to numerical simulation by Tang (2010) and vertical measurements by Chen et al. (2013) over Beijing area, transition from upper atmosphere (nearly 1km) is a main source of surface ozone. We also think NO2 is made in the PBL, and high NO levels near the surface keep O3 low at night. 13055/13: lesson -> less Response: We are sorry for our mistake. The word has been corrected. 13056/29: radiation that photo-

ACPD
13, C6920–C6927, 2013

chemical reaction needs -> radiation needed for photochemical reactions. Response: We accepted your suggestion. 13057/8: The BJT site shows OWE = 8.1% (from Table 2). If UV at this site is higher on weekends by 5.4%, as said here, then this explains most of the BJT OWE, since in these high NOx conditions the production of O3 scales linearly with photolysis coefficients. Even half of that UV change, e.g. 2.7% as a vertical average over the PBL, would be a significant fraction of the OWE (but see major comment 2 about what constitutes a small OWE) Response: We agree with your idea. In this study, we first use lots of surface atmospheric measurements data to investigate OWE in this heavy pollution region in China. We also tried to find possible reasons to explain it. Our analysis is somewhat brief as you said and we will do more detailed mechanism work to study OWE in future. 17: again, it is not just the NO+O3 reaction. Response: We accepted your comments. 21: (a proxy of CO) -> (using CO as a proxy) Response: We accepted your suggestion.

Chen, P., Quan, J., Zhang, Q.,Tie, X., Gao, Y., Huang, M.: Measurements of vertical and horizontal distributions of ozone over Beijing from 2007-2010, Atmos. Environ., doi:10.1016/j. atmosenv.2013.03.026,2013

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C6920/2013/acpd-13-C6920-2013-supplement.zip

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 13045, 2013.

ACPD
13, C6920–C6927, 2013

Interactive Comment

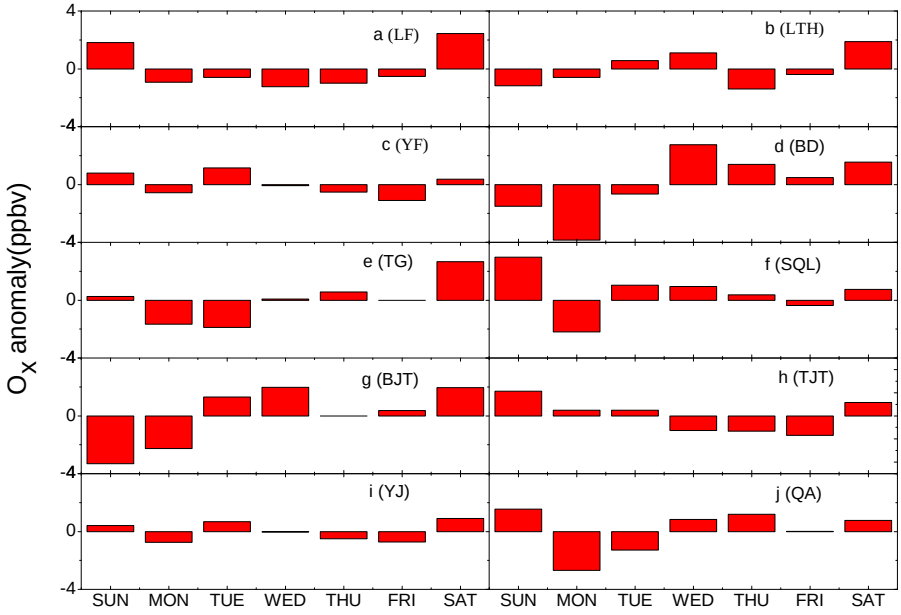

Fig. 1. Figure1 Weekly variations of Ox concentration anomalies at these sites

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ACPD
13, C6920–C6927, 2013

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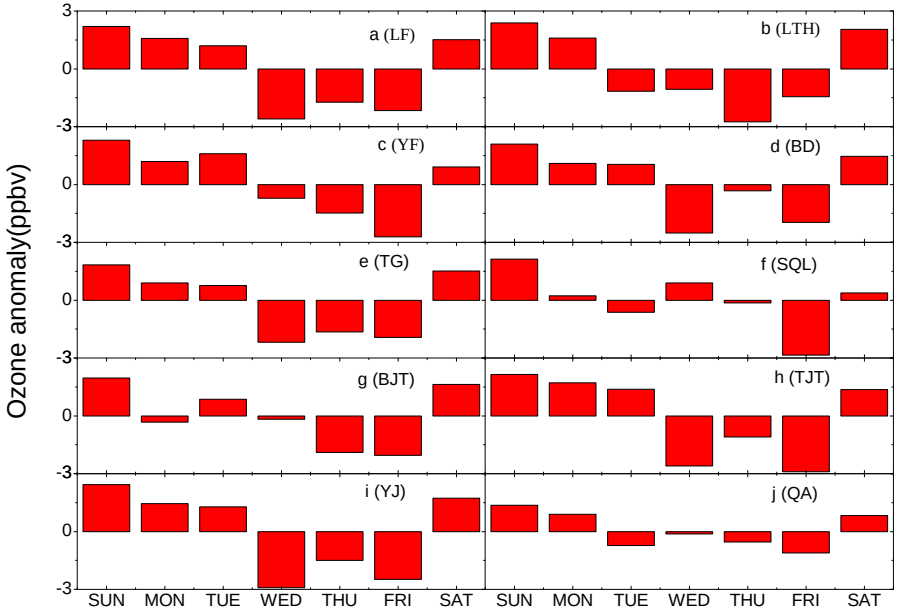

Fig. 2. Figure2 Weekly variations of surface ozone anomalies at these sites

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