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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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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:

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 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?

2. Small and even slightly negative values of the OWE (defined as the % O3 change) may still imply 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.

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.

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?

_____ Minor issues:

13046/15: do you mean CO is a proxy for VOCs?

17: VOC-regime -> VOC-limited regime

22: delete "in"

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.

13050/11: was -> were

13052/1: highly factory located area -> highly industrialized area 1: inner land -> inland

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

Figure 2 caption: manitude -> magnitude

13: what are the uncertainties of these estimates? From Fig 3, seem large.

13053/10: level -> levels

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.

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

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.

13055/13: lesson -> less

13056/29: radiation that photochemical reactin needs -> radiation needed for photochemical reactions.

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)

17: again, it is not just the NO+O3 reaction.

21: (a proxy of CO) -> (using CO as a proxy)

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