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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Weekly patterns of México City's surface concentrations of CO,NO_x, PM_{10} and O_3 during 1986–2007" *by* S. Stephens et al.

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1. General comments This paper uses the difference between weekday and weekend concentrations of O_3, CO and NO_x to draw inferences concerning ozone-precursor sensitivity. The presentation is thorough and the authors are careful to include caveats and uncertainties. This is one of the most successful attempts to use "observation-based methods" to obtain evidence on how ozone formation in polluted regions depends on NO_x and VOC. I recommend publication.

In addition, the paper presents an innovative use of Kleinman's L_n/Q formula to interpret the weekday/weekend results. This is especially important because it provides a

basis for evaluating the significance of the weekday/weekend difference and for identifying uncertainties. This is a useful new method of analysis that should be used in future studies.

The paper presents strong evidence that ozone in Mexico City is primarily sensitive to VOC rather than NO_x. Nonetheless, I think that there are important additional reasons to question the result. I urge the authors to add caveats based on the concerns described below, and possibly do some additional analysis to address them.

I also think there are some minor errors in the authors' use of L_n/Q. I urge them to correct these. I also want to suggest a small extension of the authors' L_n/Q analysis, which might give it greater significance.

The changes and extensions suggested here are recommendations rather than requirements for publication.

1. Specific comments

(a) Ozone-precursor sensitivity

The main limitation of the weekday/weekend analysis is that it is based only on the multi-year average for diurnal peak O_3 and does not account for day-to-day variations. The multi-year average includes many days with relatively low O_3 and low photochemical production rates due to unfavorable meteorology (for example, cloud cover). These days are likely to have O_3 strongly inhibited by NO_x, in part because the "NO_x titration effect" (O_3+NO$\rightarrow NO_2$) is larger relative to photochemical production and in part because lower photolysis rates lead to higher ratios of L_n/Q. As a result, the weekday-weekend difference in O_3 is biased by the low-ozone days. The long-term average may obscure a situation that includes NO_x inhibition on days with low O_3 and NO_x-sensitive ozone production on days with high O_3.

Similarly, the multi-year analysis does not distinguish between conditions characterized by fresh NO_x and VOC emissions as opposed to photochemically aged air. This

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distinction is analogous to the distinction between cloudy and sunny days. Fresh emissions are associated with low O_3 and a strong NO_x inhibition effect, while photochemically aged air is more likely to have high O_3 and NO_x-sensitive ozone production. The multiyear average (showing no change in weekend vs. weekday O_3) may represent a combination of NO_x-inhibition in air dominated by fresh emissions and NO_x-sensitive ozone production in aged air with the highest O_3.

The data set provides some evidence in support of these concerns. Figure 3 shows a significant decrease in O_3 on weekends in the SW city sector. This sector has the highest O_3 and the lowest NO_x, suggesting greater photochemical aging. The difference between SW and other sectors may point to larger differences between high-O_3 and low-O_3 conditions. Similarly, Figures 6 and 7 show that O_3 decreases on weekends during the month of March, which I believe is the month with the highest O_3. By contrast, O_3 increases on weekends during much (though not all) the rainy season.

I urge the authors to modify the discussion to include these concerns. The multiyear average data does not exclude the possibility that many events with high O_3 also have NO_x-sensitive conditions. This is an important caveat for the conclusions of the paper.

This issue may also explain why model-based studies such as West et al. (2004) found NO_x-limited conditions or mixed NO_x-VOC sensitivity (p. 8370, line 18). The modeling studies typically focus on events with the highest O_3.

One way to address this concern is to show results for weekday versus weekend O_3 (as in Figures 2 through 7) based on the 75^{th} percentile O_3 rather than the average O_3, or to show results for weekday versus weekend average O_3 only for days with O_3 above the median value in each data ensemble. This is not necessary for publication, but it may be a way to find evidence on this issue.

(b) L_n/Q analysis

The L_n/Q analysis is especially useful because it provides a way to evaluate weekday-

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weekend differences on a more quantitative basis. As shown in the text, it also provides a way to address uncertainties due to differences in aerosol loading between weekdays and weekends.

Two minor errors should be corrected.

First, the authors have interpreted P_{O3} in Equations 1-6 (p. 8367-8) as referring to O_3. Based on the original derivations in Kleinman (2005) the term should be interpreted as O_x (=O_3+NO_3). Kleinman's P_{O3} assumes that ozone production is proportional to the summed rates of OH+VOC reactions. These reactions lead to the conversion of NO to NO_2 which ultimately produces O_3. This does not include the effect of NO_x titration. P_{O3} should therefore be interpreted as O_x rather than O_3.

Therefore, the δO_3 in Equation (7) (p. 8368) should be replaced by δO_x. As pointed out in the text (p. 8370, line 1) the reduction in O_x between weekdays and weekends is larger than the reduction in O_3. This changes the L_n/Q analysis.

(A corollary is that the transition from NO_x-sensitive to VOC-sensitive O_3 may occur at L_n/Q lower than 0.5 in locations with high NO_x.)

A second possible error is that background O_3 has not been included in the δO_3 term in Equation (7). The $_3$ represents the relative (percent) change between weekday and weekend O_3 as an approximation for the relative change in ozone production (δP_{O3}). This assumes that all the O_3 in Mexico City represents local photochemical production. In fact, O_3 in the afternoon mixed layer always includes background O_3 from outside the city, with background values equal to 20-40 ppb in Mexico. The background O_3 can be regarded as identical on weekdays and weekends, but it should be subtracted from the average O_3 to avoid bias in the relative term δO_3.

More generally, I think that the authors' innovative use of L_n/Q can be extended to illustrate some features of the weekday/weekend analysis. The weekday-weekend difference can give a clear signal for O_3-precursor sensitivity only if there is a strong

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NO_x-inhibition effect (as occurs here). If O_3 is found to decrease on weekends it may be unclear whether O_3 is sensitive to NO_x or to VOC. The authors' L_n/Q analysis can provide evidence for this, as follows.

Referring to the authors' Equation (6): if the relative change from weekday to weekend is the same for NO_x and VOC, then Equation (6) reduces to the following.

$L_n/Q = (1-\gamma)/(1-0.5\gamma)$ (6a)

where $\gamma = \delta P_{O3}/\delta NO_x$, the ratio between the relative change in P_{O3} and the relative change in NO_x. The L_n/Q approaches zero (NO_x-sensitive) as γ approaches one, meaning that the reduction in P_{O3} and NO_x are the same on a percent basis. However, for L_n/Q at 0.5 or below, the value is very sensitive to small changes or uncertainties in δP_{O3}.

This is why the use of O_x rather than O_3 and the inclusion of background O_3 is important. If the resulting L_n/Q is close to one (VOC-sensitive), there is no problem, but when L_n/Q is 0.5 or less the result may be critically dependent on these assumptions.

I urge the authors to correct the minor errors.

(c) Minor issues p. 8369, line 26+: "Whether the NO_x inhibition also persists on Sundays is less clear, and we note that early afternoon NO_x values are significantly lower on Sundays... the Sunday reductions in NO_x imply that total O_x is lower, even with O_3 relatively unchanged. Therefore Sunday's O_x concentrations may be both VOC and NO_x sensitive."

As described above, the question of O_x versus O_3 is important. However, this paragraph suggests that O_3-precursor sensitivity is shown to be different on Sundays as opposed to weekdays. I think this is incorrect. The analysis is based on the measured difference between weekdays and Sundays. This provides evidence for how a reduction in precursors would affect weekday O_3. It cannot provide evidence for how reductions in emissions affect Sunday O_3, because the Sunday measurements already

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represent the lowest precursor levels.

p. 8370, line 4: The text briefly discusses the question of geographical variation within the city (relating to the issue of fresh emissions/photochemical aging discussed above) and states that "in any case the weekend effect was noted to be qualitatively similar in all city sectors." As noted above, the weekend effect appears to be significantly different in the SW sector (from Figure 3), and this is important because the SW sector also has the highest O_3.

p. 8370, line 18: The text discusses NO_x-sensitive model results. As stated above, I think that the NO_x-sensitive model results may occur because the models have been used to simulate days with high photochemical activity, which are more likely to have NO_x-limited conditions.

Figures 6-7: It would be useful to also show the month-to-month variation in average O_3.

3. Technical correction

Figure 3 is dim and difficult to read in the current version. The figure itself is good, but the lines need to be made brighter in the final version.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 8357, 2008.