Atmos. Chem. Phys. Discuss., 8, S5042–S5051, 2008
www.atmos-chem-phys-discuss.net/8/S5042/2008/

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.

S. Stephens et al.

Received and published: 18 July 2008

Reply to comments by Sanford Sillman
by S. Madronich et al.

We thank Sillman for the many useful comments, particularly with respect to the interpretation of L_N/Q in the context of the weekend effect.

[Sillman] General comments
This paper uses the difference between weekday and weekend concentrations of O_3, CO and NOx 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 NOx 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.

[Reply] The data collected over the past two decades by Mexican researchers is truly an outstanding resource, and our study has tapped only a small fraction of its information content. Opportunities for many more detailed analyses abound.

The paper presents strong evidence that ozone in Mexico City is primarily sensitive to VOC rather than NOx. 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.

The points raised by Sillman are very relevant, so we have done some additional sensitivity studies and corrected the minor errors in L_N/Q. The effects are small and the main conclusion is unchanged, that O_3 production is primarily sensitive to VOCs and NOx-inhibited.

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Interactive Comment

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 NOx, in part because the "NOx 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 NOx inhibition on days with low O_3 and NOx-sensitive ozone production on days with high O_3.

Because we used average values including all days, we disagree slightly that "the weekday-weekend difference in O_3 is biased by the low-ozone days", but we agree strongly that it is also interesting to consider the subset of high ozone days. We have added calculations for the 25% of days having the highest ozone concentrations (upper 75th percentile), and added the calculated L_N/Q for this subset to Figure 8. The results show that O_3 production is VOC-limited and NOx-inhibited even for the high O_3 days. The following text was added:

The L_N/Q values discussed so far were based on the average of all days for which data were available, and it is not obvious a priori that VOC limitation and NOx inhibition persist also for very high O_3 episodes. To test this, we selected the upper 75th percentile having the highest ozone concentrations (i.e. 25% of days, separately for workdays, Saturdays, and Sundays) and recalculated L_N/Q for this subset. Figure 8 shows that values of L_N/Q for the high O_3 days are still in the VOC-limited and NOx-

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inhibited range for most years, although with more scatter and an anomalous value for 1991 probably due to large intra-annual emission changes as already mentioned in Section 3. It should be noted that selecting a subset of the days introduces additional scatter and possible bias because: (1) Sample size is reduced, e.g. for the upper 75th percentile only 13 weekends are available per year. (2) While yearly averages include all days, a subset may sample workdays and weekends from different weeks, thus amplifying variability from seasonal dependences. (3) When the selection is made on the basis of high O_3, some days with high NOx may be excluded precisely because O_3 formation is NOx inhibited. This bias is more frequent on workdays because they are more strongly NOx-inhibited (indeed, for 2007 Saturday NOx values were actually higher than for workdays for the 75th percentile O_3 subset, while for all-day averages, shown in Table 2, Saturday NOx is lower as expected).

Similarly, the multi-year analysis does not distinguish between conditions characterized by fresh NOx and VOC emissions as opposed to photochemically aged air. This distinction is analogous to the distinction between cloudy and sunny days. Fresh emissions are associated with low O_3 and a strong NOx inhibition effect, while photochemically aged air is more likely to have high O_3 and NOx-sensitive ozone production. The multiyear average (showing no change in weekend vs. weekday O_3) may represent a combination of NOx-inhibition in air dominated by fresh emissions and NOx-sensitive ozone production in aged air with the highest O_3.

We don't think photochemical aging is affecting our results, except perhaps for the SW sector in the early years (see below). We use NOx and CO concentrations measured in the morning, before significant photochemical processing occurs. These precursors are then correlated with O_3 maxima in the afternoon. If we focused on a single station or sector, it would indeed be inappropriate to correlate morning precursors and

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afternoon O_3 because basin circulations can advect air to different parts of the city as it ages photochemically. But by using basin-wide averages, this problem is reduced.

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 NOx, 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.

We agree, but note that during 2001-2007 the SW sector no longer shows a weekend O_3 decrease, and has become rather more similar to the other sectors. This may be due to urban expansion (see also comment by Referee 1) with a shift from NOx-limited to VOC-limited regime for this sector. The following text was added:

The SW sector is particularly interesting, with relatively low morning CO, NOx, and PM_{10} but high afternoon O_3 concentrations, indicating substantial contributions from advection during photochemical hours from other sectors, in agreement with the frequent "O_3-South" episodes described by deFoy et al. (2005) and the confluence lines discussed by Cruz Nuñez and Jazcilevich Diamant (2007).

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.

O_3 actually peaks in April and May, as shown in Fig. 6 (which now shows average concentrations rather than changes, as suggested below by Sillman). The high O_3 days were already examined as described above and were found to have a similar

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VOC sensitivity. The following text was added:

Concentrations of CO, NOx, and PM_{10} are largest during January and February, while O_3 peaks in March and April when solar actinic fluxes are higher.

(b) L_N/Q Analysis: Two minor errors should be corrected. First, the authors have interpreted PO_3 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 Ox (=O_3+NO_2). Kleinman's PO_3 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 NOx titration. PO_3 should therefore be interpreted as Ox rather than O_3. Therefore, the δO_3 in Equation (7) (p. 8368) should be replaced by δOx. As pointed out in the text (p. 8370, line 1) the reduction in Ox 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 NOx-sensitive to VOC-sensitive O_3 may occur at L_N/Q lower than 0.5 in locations with high NOx.)

We agree, but even with this correction L_N/Q in Mexico City is well within the VOC-limited regime. Kleniman's equations have been re-cast in terms of Ox rather than O_3. We also did a sensitivity study using Ox rather than O_3, by adding available measurements of NO_2, with results shown in the new Fig. 9. The following text was added:

The sensitivity to using Ox rather than O_3 in the analysis is shown in Fig. 9. Co-located simultaneous measurements of NO_2 and O_3 were summed to compute δOx which was then used in Eq. 7 in place of δO_3. For the workday to Sunday differences, this

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reduces the values of L_N/Q by 0.04-0.13 over the data record, as could be expected from Fig. 1 which shows that values of NOx in the early afternoon (mostly NO_2) are lower on Sunday than on other days. Although O_3 on Sundays is typically the same or even slightly higher than on workdays (Table 2), the total Ox is slightly lower due to the lower NO_2. Even with this correction, L_N/Q is still within the VOC-limited regime. For Saturdays (not shown) corrections to L_N/Q are negligible because NOx values on Saturday afternoons are nearly identical to those on workdays (see again Fig. 1), so δOx is well approximated by δO_3.

A second possible error is that background O_3 has not been included in the δO_3 term in Equation (7). The δO_3 represents the relative (percent) change between weekday and weekend O_3 as an approximation for the relative change in ozone production (δPO_3). 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.

We agree and have carried out a sensitivity study shown in Fig. 9. The effect is minor. The following text was added:

Finally, Fig. 9 shows the sensitivity of L_N/Q to an assumed 40 ppb of background O_3. The derivation of L_N/Q (Eq. 7) refers exclusively to Ox produced during the same day and does not account for any O_3 that may have been present in the atmosphere from production in previous days. The amount of background O_3 on any particular day is not well known, but ozone sondes (Thompson et al., 2008) showed concentrations above the PBL in the range of 30-50 ppb during March 2006 and 40-60 ppb during

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August - September 2006. These sondes were launched in the early afternoons and may reflect some same-day production in addition to background O_3. Thus our use of 40 ppb is probably a reasonable estimate for this sensitivity study. Figure 9 shows that the effect of background O_3 is negligible when L_N/Q values are higher than ca. 0.8, as in the recent years, but could lead to overestimation of L_N/Q by as much as 0.1 when the values are lower.

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 NOx-inhibition effect (as occurs here). If O_3 is found to decrease on weekends it may be unclear whether O_3 is sensitive to NOx 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 NOx and VOC, then Equation (6) reduces to the following.

$$L_N/Q = (1-\gamma)/(1-0.5\gamma) \qquad \textbf{(6a)}$$

where $\gamma = \delta PO_3/\delta NOx$, the ratio between the relative change in PO_3 and the relative change in NOx. The L_N/Q approaches zero (NOx-sensitive) as γ approaches one, meaning that the reduction in PO_3 and NOx 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 δPO_3. This is why the use of Ox 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.

We agree, although for Mexico City the value of L_N/Q is typically larger than 0.5 and therefore not so dependent on these assumptions. In any case, from Eq. 6a it is seen

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that for $L_N/Q < 0.5$, γ would range between 2/3 and 1, which is still a substantial range although only half of that for $L_N/Q > 0.5$ (γ between 0 and 2/3). Therefore measurements of γ could still provide useful information as to whether L_N/Q is in the VOC or NOx limited regime.

We also agree with the general comment that Eq. 6 can be used to illustrate many features of the chemical system. Perhaps one of the most interesting is the prediction of how Ox responds to changes in NOx and VOCs. With the definitions $\alpha \equiv \delta POx/\delta VOC$, $\beta \equiv \delta POx/\delta Q$, and $\gamma \equiv \delta POx/\delta NOx$, Eq. 6 (or more directly Eq. 5) can be rearranged:

$$\gamma = [2 + \beta + (\alpha - 3)L_N/Q]/(2 - L_N/Q)$$

This equation shows that γ can take positive or negative values, as expected from the competition between Ox formation from VOCs, and either formation or inhibition by NOx. The case in which NOx is lower but Ox is higher ($\gamma < 0$, e.g. the weekend effect) can occur only if $\alpha < 3 - (2 + \beta)Q/L_N$.

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

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The correction for Ox, already discussed above, is negligible for Saturdays because afternoon NOx concentrations are similar to those on weekdays. For Sundays, the lower afternoon NOx indicates that total Ox is somewhat lower. Furthermore, we showed in Fig. 8 that L_N/Q calculated from workday-to-Saturday transitions are slightly higher than those calculated from Saturday-to-Sunday transitions. For both of these reasons, we think that the workday-to-Saturday transition indicates stronger NOx inhibition than the Saturday-to-Sunday, as can also be expected from the fact that NOx is highest on workdays. The revised text should be clearer on this point.

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.

The behavior of the SW sector in the early years was addressed above.

Figures 6-7: It would be useful to also show the month-to-month variation in average O_3.
Figs. 6-7 now show averages and percent changes (we removed absolute changes).

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.
Line thicknesses have been increased.

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