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Weekly patterns of México City's surface concentrations of CO, NO_x, PM_{10} and O_3 during 1986–2007

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Abstract

Surface pollutant concentrations in México City show a distinct pattern of weekly variations similar to that observed in many other cities of the world. Measurements of the concentrations of carbon monoxide (CO), nitrogen oxides (NO_x=NO+NO_2), particulate matter smaller than 10 μm (PM_{10}), and ozone (O_3) collected hourly over 22 years (1986–2007) at 32 urban monitoring locations were analyzed. Morning concentrations of CO, NO_x, and PM_{10} are lower on Saturdays and even more so on Sundays, compared to workdays (Monday–Friday), while afternoon O_3 concentrations change minimally and are occasionally even higher. This weekend effect is empirical evidence that photochemical O_3 production is NO_x-inhibited, and to the extent that emissions of CO are correlated with reactive volatile organic compounds (VOCs), it is VOC-limited, at least in the urban areas for which the monitoring stations are representative. The VOC-limitation has increased in the past decade, due to decreases in the concentrations of CO (and presumably VOCs) and consequent decreases in the CO/NO_x and VOC/NO_x ratios. Enhancements of photolysis frequencies resulting from smaller weekend aerosol burdens are not negligible, but fall short of being an alternate explanation for the observed weekend effect. The strength of the weekend effect indicates that local radical termination occurs primarily via formation of nitric acid and other NO_x-related compounds, some of which (e.g. peroxy acyl nitrates) can contribute to the regional NO_x budget. While VOC emission reductions would be most effective in reducing local O_3 production, NO_x emission reduction may be more important for controlling regional oxidants.

1 Introduction

The atmosphere of México City has received considerable scientific attention in recent years, foremost because of concerns about the potential health effects of air pollutants on its ~20 million inhabitants, and also because it may be to some extent represen-

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tative of current and future conditions in other megacities undergoing rapid economic development. The city's tropical high altitude location (19° N, 2.2 km above sea level) is conducive to fast photochemistry forming secondary pollutants such as ozone (O_3) and particulate matter (PM). Several intensive measurement campaigns have characterized the main aspects of the meteorology and chemical composition, including MARI (LANL/IMP, 1994), IMADA/AVER (Doran et al., 1998), MCMA-2003 (Molina et al., 2007), and in 2006 MILAGRO (Molina et al., in preparation, 2008). An air quality monitoring network was established in 1986, and has helped document long-term reductions of some pollutants following the institution of various emission-reduction programs (INE, 1998).

One of the issues most relevant to the design of emission reduction policies for urban areas is whether the formation of O_3 is more sensitive to emissions of nitrogen oxides (NO_x) or volatile organic compounds (VOCs). It is well known (e.g. Finlayson-Pitts and Pitts, 1986) that O_3 formation depends non-linearly on these emissions, and is maximal when VOC/NO_x molar ratios are in the range of 5–15, the exact value depending on various conditions. At higher VOC/NO_x ratios, O_3 production is limited by, and therefore sensitive to, the available NO_x. At lower ratios it is limited by VOCs and, at sufficiently high NO_x, even inhibited by any additional NO_x (due to the reactions $NO+O_3 \rightarrow NO_2+O_2$ and $OH+NO_2 \rightarrow HNO_3$). However, O_3 formation is also sensitive to other factors such as detailed VOC speciation and environmental conditions, so the direct measurement of VOC/NO_x ratios is insufficient to establish whether the chemical regime is VOC- or NO_x-limited. Sillman (1995) proposed using several other concentration ratios as indicators of NO_x or VOC sensitivity involving, in addition to O_3, total reactive nitrogen (NOy), as well as photochemically-produced formaldehyde (CH_2O), nitric acid (HNO_3), and hydrogen peroxide (H_2O_2). Unfortunately these chemical species have not been measured routinely in México City, and the few available measurements are too variable to assess spatially or temporally averaged sensitivities. Thus such assessments have been limited to modeling studies in which the emissions of VOCs and NO_x were varied around central estimates and the response of O_3 concentrations was examined,

sometimes with conflicting results (West et al., 2004; Lei et al., 2007; Tie et al., 2007).

A more empirical assessment of the response of O_3 to emission changes is provided by the weekend-workday differences in the emissions of O_3 precursors, and the resulting differences in O_3 concentrations. Generally, emissions of NO_x and VOCs are lower on weekends, while in many locations (though not all) the weekend O_3 concentrations are minimally lower, or even higher, than on workdays. Observations of this effect have been made at many locations throughout the world, e.g. for the US in New York and New Jersey (Cleveland et al., 1974; Bruntz et al., 1974), the Baltimore-Washington area (Lebron, 1975; Jacobson, 1975), Southern California (Blanchard and Tanenbaum, 2003; Fujita et al., 2003; Chinkin et al., 2003), Central California (Blanchard and Fairley, 2001; Marr and Harley, 2002; Murphy et al., 2007), Northern California (Altshuler et al., 1996), Atlanta, Chicago, and Philadelphia (Pun et al., 2003), and Phoenix (Atkinson-Palombo et al., 2006); in Canada near Vancouver (Pryor and Steyn, 1995) and Toronto (Beaney and Gough, 2002), Switzerland (Brönnimann and Neu, 1997), France (Pont and Fontan, 2001), the UK (Jenkin et al., 2002), Greece (Riga-Karandinos et al., 2006), and Nepal (Pudasainee et al., 2006). A weekend effect in the NO_2 column amount has also been detected by a satellite-based instrument over urban and industrial regions of the US, Europe, and Japan (Beirle et al., 2003). For México City, Muñoz et al. (2007) have shown statistically significant variations in O_3 concentrations as a function of day of the week for the years 1990–2006.

Here, we examine for México City the weekly patterns over 22 years (1986–2007) of NO_x, CO (as a proxy for VOCs), O_3 and PM_{10} (since 1993) concentrations analyzed from surface measurements at 32 urban locations (see Sect. 2). The differences between workdays (Monday-Friday) and weekends (Saturday and Sunday) are shown in Sect. 3, while Sect. 4 discusses possible reasons for these patterns in terms of our understanding of the prevailing photochemical regime. The implications for urban and regional air quality are discussed in Sect. 5.

2 Data availability and analysis

Continuous monitoring of air pollutants in México City began in 1986 with the establishment of several networks (INE, 1998), now numbering 39 stations, to measure surface concentrations of O_3, NO_x, NO_2, CO, SO_2, TSP, and PM_{10}, and surface meteorology. Hourly data are archived by the Government of México City (SIMAT, 2007). The performance of the air quality monitoring network has been reviewed periodically by the U.S. Environmental Protection Agency, and a recent report concluded that the monitoring system is overall accurate and well implemented (GDF, 2004). Here we use a subset of the data, specifically the concentrations of O_3, NO_x, CO, and PM_{10} from 32 stations (the other 7 had insufficient data records for our analysis). A data screening procedure was implemented to eliminate possible values falling far outside realistic bounds. For NO_x and O_3, allowed values were between 2 ppb and 1 ppm, for CO between 10 ppb and 100 ppm, and for PM_{10} between 0.1 and 1000 $\mu g/m^3$. These wide ranges should not be construed as actual data ranges, but rather are merely additional steps to screen out possible artifacts.

The large record of surface measurements allows the analysis and interpretation of temporal patterns on many time scales, including daily, weekly, seasonal, and long-term variations. Some averaging was carried out to reduce the effects of temporal and spatial variability and thus to bring out the more persistent temporal patterns, as follows. Values from individual stations were averaged together by five city sectors (see SIMAT, 2007 for a map), specifically north-east (*NE* for stations ARA, CHA, LVI, NET, SAG, VIF, XAL), north-west (*NW* for ATI, AZC, CUI, EAC, IMP, TAC, TLA, TLI, VAL), south-west (*SW* for PED, PLA, SUR, TPN), south-east (*SE* for CES, COY, CHO, TAH, TAX, UIZ), and center (*CT* for BJU, CUA, HAN, LAG, MER, MIN). To represent each day by a single value, the average of the three highest values was taken, between 7 a.m. and 12 noon for CO, NO_x, and PM_{10}, and between 11 a.m. and 5 p.m. for O_3. The intent of this averaging was to capture the bulk of the chemical precursors from the morning rush-hour and the resultant afternoon O_3, rather than specific maxima or exceedances

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of regulatory thresholds. For some considerations, values were also averaged over three longer time periods, specifically 1986–1992, 1993–2000, and 2001–2007.

In all cases, relative changes (percents) were calculated as the deviations between average absolute values, rather than as the average of relative changes between individual values. For example, the average difference (%) between Sunday and Wednesday O_3 values in 2007 was computed by calculating the 2007 average Wednesday O_3, then the 2007 average Sunday O_3, and finally computing the percent difference between them (as opposed to computing the percent difference between each Wednesday and the previous or following Sunday, and then averaging the percent differences over the entire year). This procedure reduces the influence of short-term fluctuations in the weekend effect. Weekly patterns were also analyzed by Fourier multiple regression with nine fitting coefficients (average plus sines and cosines with periods of 7, 7/2, 7/3, and 7/4 days). This yielded the amplitude (positive or negative) of the weekly pattern, and its relative size (percent) compared to the average. Standard deviations (1σ where shown) were estimated using bootstrap resampling with replacement (Efron and Tibshirani, 1993).

3 Results

The diurnal cycles of CO, NO_x, O_3, and PM_{10} surface concentrations are shown in Fig. 1, averaged for all stations and all days over 2001–2007. For CO, NO_x, and PM_{10} the maximum values occur during the morning rush hours, followed by a decrease in the late morning due to lower emissions and the rapid growth of the planetary boundary layer (PBL) as recently reviewed by Shaw et al. (2007), a secondary maximum from the evening rush hours, and lower values at night due to decreased activity. The mid-day decreases are largest for NO_x because of its short photochemical lifetime, and smallest for PM_{10}, likely due to photochemical formation of secondary aerosols. The weekend effect is evidenced by the smaller morning peaks on Saturday and Sunday, compared to workdays (Monday–Friday). Early afternoon values are similar on work-

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days and Saturday but lower on Sundays. Increases in CO and NO_x are seen in the late evening on Friday and Saturday and persist into the early hours of the following day, as expected from increased weekend evening activities. Ozone shows a single maximum in the early afternoon stemming from its photochemical production, but a much smaller weekend effect, if any, with values on Saturday and Sunday as high as those on workdays, and (as discussed below) occasionally even higher. The evenings of Friday and Saturday, and the early hours of the following day, are somewhat lower than on other nights, consistent with the higher NO_x levels and O_3 loss by the reaction $NO+O_3 \rightarrow NO_2+O_2$. Also notable is the earlier rise in O_3 concentrations on Sunday morning relative to other days, resulting from the earlier time that O_3 concentrations exceed those of NO, i.e. an earlier NO-O_3 cross-over as already seen in other studies, e.g., in Azusa, California (Lawson, 2003).

The long-term behavior is shown in Fig. 2, where the morning maxima in CO, NO_x, and PM_{10}, and the afternoon maximum in O_3 are given for Wednesday and Sunday, averaged over all stations. Average CO values decreased sharply in the early 1990s following the closing of a major industrial facility in the city, and continued to decline most likely due to reductions in traffic-related emissions (Molina and Molina, 2002). NO_x and PM_{10} values have decreased some since the beginning of the record but show little or no change in the last decade. Ozone values peaked in the early 1990s and continue to decrease. Lower values are seen on Sunday relative to Wednesday for CO, NO_x, and PM_{10}, but not for O_3. Table 1 compares the workday averages with Saturday and Sunday values. For CO, NO_x, and PM_{10}, Saturday values generally fall between the workday and Sunday values, while for O_3 they are frequently highest (on 9 out of the 22 years). Workday O_3 was higher than either on Saturday or Sunday for only 5 of the years, and not since 1994.

The detailed weekly patterns are shown in Fig. 3, averaged separately for each city sector (CT, NE, NW, SW, SE) over 1986–1992, 1993–2000, and 2001–2007. Considerable variation is noted by sector, even for the same years. Nevertheless, values of CO, NO_x, and PM_{10} are consistently lower on Saturday and more so on Sunday, compared

to the other days of the week, while for O_3 no such reductions are seen in the most recent data, and only in the SW sector during the earlier years. Variations between workdays are much less prominent, with some indication of increases of CO, NO_x, and PM_{10} in the early part of the week (Monday to Thursday) but with considerable variability, in agreement with meteorological studies that indicated nearly complete ventilation of the basin on a daily basis, with little day-to-day accumulation of pollutants (e.g., Fast and Zhong, 1998; deFoy et al., 2007).

The amplitudes of the weekend effect, derived from the data shown in Fig. 3 using the harmonic regression described in Sect. 2, are shown in Figs. 4 and 5. For CO, the amplitude (ppm) has decreased in approximate proportion to the decrease in average concentrations (see Fig. 2), so that on a relative basis (%) the weekend reductions have remained relatively constant at 40–50%. Relative reductions in NO_x have also remained relatively constant, ranging between 40 and 60% in the last decade, while the PM_{10} weekend effect amplitude is variable between 10 and 40%. In contrast, the O_3 weekend effect amplitude shows a positive trend, with values in the –20 to 0% range in the late 1980s, increasing to 0 to +10% in the last few years. This long-term positive trend for O_3, coupled with the relative constancy of NO_x, CO, and PM_{10} relative weekend effect, has important implications for understanding the VOC-NO_x-UV regime of México City's photochemistry, as will be discussed below. Some variations between the different urban sectors are seen in Figs. 4 and 5 but the qualitative features of the weekend effect are present in all sectors and are quantitatively more similar in recent years.

The seasonal behavior of the weekend effect amplitudes is shown in Figs. 6–7. For CO, NO_x, and PM_{10} the amplitudes are more negative during the dry season (November–March) with the exception of December which is likely influenced by holiday activities. The less negative absolute amplitudes during the wet season (May–September) are easily understood in terms of convective ventilation and wet removal leading to generally lower levels of pollutants, but the reasons for reductions in relative (%) amplitudes are less clear. The O_3 concentrations show no obvious seasonal

patterns in either absolute or relative amplitudes.

4 Discussion

México City's surface observations show a definite pattern over weekly periods: CO, NO_x, and PM_{10} morning concentrations are smaller on weekends relative to workdays, by ca. 40–50%, 40–60%, and 10–40%, respectively; O_3 afternoon weekend concentrations are not much smaller, and are sometimes even larger, than the workday values, with differences increasing from –20 to 0% in the late 1980s, to 0 to +10% in the past decade. These observations of the weekend effect offer the opportunity to better understand the chemical regime responsible for the formation of O_3. The central issue is to explain why O_3 concentrations remain relatively unchanged on weekends, relative to workdays, when precursor emissions are considerably lower. Lawson (2003) summarized the possible reasons in terms of six hypotheses: (1) Lower weekend NO_x emissions, leading to less NO_x inhibition of O_3 formation if under VOC-limited conditions, (2) later timing of NO_x emissions on weekends, (3) carryover of previous day pollutants at the surface, (4) carryover of previous day pollutants aloft, (5) higher weekend VOC emissions, and (6) higher weekend photolysis frequencies due to less aerosol.

The first hypothesis, that workday O_3 production in México City is VOC-limited and NO_x-inhibited, appears to be the most plausible explanation for the observed weekend effect. It is important to note that direct VOC measurements were not used in our analysis. Such measurements for México City are relatively sparse and from only a few locations (e.g. Blake and Rowland, 1995; Velasco et al., 2007). The spatial and temporal variability of the weekend effect is rather large even within the much more comprehensive CO data set (e.g. Fig. 3), and would be much more difficult to quantify with the limited available VOC record. On the other hand, VOCs are several times more reactive (with respect to OH radicals) than CO in México City (see, for example, Fig. 3 of Madronich, 2006), so an open issue is whether variations in CO can be used as a proxy for variations in VOC reactivity. Some support for this comes from observations of robust CO vs. VOC correlations during the MILAGRO field campaign (deGouw et al., in

prep., 2008), as well as measurements in Southern California showing similar relative workday to Sunday reductions by 16–30% for VOCs and 12–32% for CO (Lawson, 2003). Thus, it is highly likely that the observed weekend CO reduction in México City was accompanied by roughly proportional reductions in VOC reactivity. The sensitivity of O_3 production to VOC changes is always positive (albeit small at low NO_x), while it can be either positive or negative with respect to NO_x changes, the negative values representing NO_x inhibition of O_3 production in the VOC-limited regime (e.g. Kleinman, 2005). In this regime, hypothetical reductions in only VOC emissions would lead to lower O_3, while equally hypothetical reductions in only NO_x emissions would lead to higher O_3. The near equality of workday and weekend O_3 then most likely arises from the simultaneous decreases in VOC and NO_x emissions and their opposing effects on the O_3 production rates. For this reason, it can be concluded that workday O_3 production in México City appears to be VOC-limited.

The other hypotheses (2–6) for explaining the weekend effect are not supported by the observations. Timing of the NO_x emissions (hypothesis 2) is not very different on weekend mornings than on workdays (see Fig. 1). Similarly, Marr and Harley (2002) showed that change in timing of emissions is only a minor contributor to the weekend effect in Central California. Carryover of pollutants from the previous day (hypotheses 3 and 4) is small, as can be seen in Fig. 3, consistently with meteorological studies suggesting nearly complete daily ventilation of the basin (e.g. deFoy et al., 2007). The possibility of higher weekend VOC emissions (hypothesis 5) has been examined for California where outdoor cooking and lawn mowing are common weekend activities, but even there it was not supported by detailed emissions inventories (Chinkin et al., 2003); it seems equally unlikely for México City given the large weekend decrease in CO. The workday to weekend increase in photolysis frequencies (hypothesis 6), owing to the heavier workday aerosol loading, merits some consideration. Castro et al. (2001) showed that surface NO_2 photolysis frequencies (J_{NO_2}) were reduced in México City by 20–30% compared to outside the city, and more recent measurements during the MILAGRO campaign show comparable reductions in actinic fluxes at ultraviolet wave-

lengths (Madronich et al., in prep., 2008). Weekend reductions in PM_{10} are seen to be in the range 10–40% (Fig. 3), which if applied to the J_{NO_2} reductions found by Castro et al. give an outside range of weekend enhancement of photolysis rates between 2% and 12% at the surface. Vertically averaged values in the PBL would be expected to be somewhat smaller, so that the resulting enhancement in O_3 production is small although not negligible.

We consider briefly whether the observed weekend changes in CO, NO_x, and O_3 are consistent with current photochemical understanding. Kleinman (2005) has shown that the instantaneous O_3 production rate, P_{O_3}, is related to instantaneous NO_x and reactivity weighted hydrocarbon (or VOC) concentrations and the radical production rate Q by:

$$dlnP_{O_3}/dln[NO_x] = [1 - (3/2)L_N/Q]/[1 - (L_N/Q)/2] \quad (1)$$

$$dlnP_{O_3}/dln[VOC] = [(1/2)L_N/Q]/[1 - (L_N/Q)/2] \quad (2)$$

$$dlnP_{O_3}/dln\ Q = (1/2)/[1 - (L_N/Q)/2] \quad (3)$$

where L_N is the radical loss due to NO_x chemistry (e.g. $OH+NO_2 \rightarrow HNO_3$, and reactions of organic peroxy radicals with NO to form organic nitrates) rather than other processes (e.g. formation of peroxides at low NO_x). Because radical lifetimes are short, the radical production rate Q is essentially equal to the total radical loss, so that the ratio L_N/Q is the fraction of the radical loss that occurs via NO_x chemistry, with values larger than 0.5 for VOC-limited conditions, and smaller than 0.5 for NO_x-limited conditions. Furthermore, the radical production rate Q is proportional to photolysis frequencies J (e.g., J_{NO_2}), as these initiate photochemistry by fragmenting relatively stable molecules into highly reactive fragments. With the simplified notation

$$\delta X \equiv dln[X] = \text{relative (percent) change in } X (\text{e.g. } X = [O_3], [NO_x], [CO], Q) \quad (4)$$

the change in O_3 concentration can be expanded as:

$$\delta P_{O_3} \sim (\delta P_{O_3}/\delta NO_x)\delta NO_x + (\delta P_{O_3}/\delta VOC)\delta VOC + (\delta P_{O_3}/\delta Q)\delta Q$$
$$\sim [(2 - 3L_N/Q) \quad \delta NO_x + (L_N/Q) \quad \delta VOC + \delta Q]/[2 - (L_N/Q)] \quad (5)$$

where in the last equation Eqs. 1–3 for the sensitivity to NO, VOCs, and Q were used. This equation can be solved for L_N/Q:

$$L_N/Q = (2\delta P_{O_3} - 2\delta NO_x - \delta Q)/(\delta P_{O_3} + \delta VOC - 3\delta NO_x) \quad (6)$$

The terms on the right hand side can be estimated from the weekend effect with some additional approximations. First, we assume that the weekend effect for the instantaneous O_3 production, δP_{O_3}, is reflected to first order in the build-up of the afternoon O_3 concentrations considered here, so that $\delta P_{O_3} \sim \delta O_3$. Second, and as already discussed above, we assume that the weekend effect for VOC reactivity is similar to that for CO, $\delta VOC \sim \delta CO$. Finally, we assume that the change in the radical production rate is due mostly to changes in photolysis frequencies, so that $\delta Q \sim \delta J$. On this last point, we note that δQ also depends on the availability of photo-labile species, such as O_3, CH_2O, and HONO, which however are not likely to be larger on weekends, so δJ is probably an upper limit to δQ. With these approximations, Eq. (6) can be rewritten as:

$$L_N/Q = (2\delta O_3 - 2\delta NO_x - \delta J)/(\delta O_3 + \delta CO - 3\delta NO_x) \quad (7)$$

The algebraic form of Eq. (7) permits any negative or positive value of L_N/Q (from $-\infty$ to $+\infty$) for independently selected combinations of δCO, δNO_x, δJ, and δO_3. However, the photochemical interpretation of L_N/Q, as the fraction of radical termination effected by NO_x chemistry, limits its possible values to the range 0–1. The question then is whether the observed weekend effect values of δCO, δNO_x, δJ, and δO_3 are consistent with this chemical interpretation. Figure 8 shows the L_N/Q values calculated from the observed CO, NO_x, and O_3 (taken from Table 1) for workday-Saturday (circles) and Saturday–Sunday (squares), with assumed values for δJ of 0.02 (filled

symbols) or 0.12 (open symbols) to bracket the weekend enhancement of photolysis rates estimated from PM_{10} changes, as discussed above. The values are rather scattered but clearly fall near or within the chemically permissible range (except for 1986, not shown in the figure, where values as high as ~2.7 were obtained, probably because of relatively few data in the first year of the network). Moreover, the L_N/Q values are generally between 0.5 and 1.0 as expected for a VOC-limited regime; the workday-Saturday values are somewhat higher that Saturday-Sunday values as expected from more intense NO_x inhibition on workdays; and a slight upward trend in L_N/Q is seen, especially for the last decade, as expected from the decreasing trend in concentrations of CO (and presumably VOCs). However, such temporal variations should be viewed with caution, because the uncertainty in L_N/Q is about ±30%, as estimated by error propagation in quadrature through Eq. (7) of the standard deviations in δCO, δNO_x, and δO_3 (ca. 10%, 10%, and 7%, respectively, from Fig. 5).

The effect of photolysis frequencies on L_N/Q is also shown in Fig. 8. The net production of O_3 is photon-limited in all but the most pristine parts of the troposphere. Weekend enhancements in J-values can provide a partial explanation for the persistence of high O_3 values, as less change in NO_x inhibition of O_3 production is needed to explain the observations, leading to smaller values of L_N/Q as seen in the figure. The values of L_N/Q do remain mostly in the VOC-limited regime (>0.5) even with the maximum estimated enhancement in J-values (12% workdays to Saturday, plus 12% Saturday to Sunday). However, the sensitivity to changes in J-values is seen to be significant, and emphasizes the need for accurate long-term observations of the urban ultraviolet environment.

Overall, the analysis of the weekend effect provides observation-based evidence that the production of O_3 in México City is VOC-limited and NO_x-inhibited. This is particularly clear for workdays, as reflected in high L_N/Q values for the workday-to-Saturday changes. 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 (see Fig. 1), but not on Saturdays, relative to workdays. Since early afternoon NO_x is mostly

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NO_2, the Sunday reductions in NO_x imply that total O_x ($=O_3+NO_2$) is lower than on workdays and Saturdays, even with O_3 relatively unchanged. Therefore Sunday's O_x concentrations may be both VOC and NO_x-sensitive.

One possible confounding factor is that NO_x and VOC emissions in one part of the city may be transported over a few hours by urban scale circulations to produce high O_3 concentrations in other parts of the city, under some specific meteorological conditions as noted by de Foy et al. (2005). Our use of city-wide averages evidently smoothes over such spatial variations, and in any case the weekend effect was noted to be qualitatively similar in all city sectors (see Figs. 3 and 4), so it is unlikely that such circulations would alter our conclusion about VOC-limitation. Another interesting result is the detection of a long-term positive trend in the O_3 weekend effect, while the CO and NO_x weekend fractional reductions have remained essentially constant (see Fig. 4 for concentrations, or Fig. 8 for L_N/Q). This is associated with the long-term decrease in CO concentrations, presumably correlated with decreases in VOC concentrations, while NO_x concentrations have remained largely unchanged. A decrease in the VOC/NO_x ratio implies a shift toward more VOC-limited conditions over the decades examined here. Earlier modeling studies using three-dimensional chemistry-transport models (CTMs) suggested a NO_x-limited regime (Molina and Molina, 2002; West et al., 2004), while more recent CTM studies indicated a VOC-limited regime (Tie et al., 2007; Lei et al., 2007). It has been so far unclear whether this discrepancy is due to improvements in the models, or to changes in the actual emissions. Our observation of a long term positive trend in the O_3 weekend effect provide at least a partial explanation for the different modeling results, suggesting a more VOC-limited regime for the recent years. It should be cautioned, however, that our use of CO as a proxy for VOC reactivity may be less valid over very long time periods, because of possible long-term changes in the detailed speciation of the many components that make up the reactive VOC mixture.

5 Conclusions

México City experiences a weekend effect in its air quality similar to that found in many cities around the world: Although concentrations of O_3 precursors NO_x, CO, and (presumably) VOCs are significantly lower on Saturday and even more so on Sunday compared to workdays, the concentrations of O_3 change only minimally, and in some cases are even larger. This effect has become more pronounced in recent years because of significant emission reductions of CO and VOCs but relatively steady NO_x emissions. The observed weekend effect is consistent with a VOC-limited, NO_x-inhibited chemical regime for O_3 production during workdays. In this regime, any magnitude of reduction in VOC emissions would contribute to lowering ambient O_3 concentrations, while only large reductions in NO_x emissions would prove effective, with smaller incremental reductions being ineffective and possibly even detrimental by increasing local O_3 production, depending on specific location and time.

There are of course many other reasons for reducing NO_x emissions. NO_2 is per se an important pollutant, and many nitrogen-containing compounds formed in the atmosphere are noxious, e.g. nitric acid, peroxy acyl nitrates (PANs), and nitro-cresols. Furthermore, the NO_x inhibition of O_3 production is likely temporary, and by slowing the oxidative reactivity it allows more yet-to-be-reacted O_3 precursors to be exported from the city to the regional scale, including slower-reacting hydrocarbons and partly oxygenated VOCs. Many organic nitrogen species (e.g., alkyl nitrates and PANs) formed in the urban atmosphere have relatively long lifetimes and can, through later thermal or photolytic decomposition, be an important source of NO_x to the regional and global atmosphere where O_3 production is generally NO_x-limited.

This analysis was confined to the urban network of monitoring stations for which long term measurements are available, and is therefore only valid for the geographic area which these stations represent. Over the past two decades, urban expansion beyond the monitored area and suburban development make it important to understand at which point the chemical regime transitions from VOC-limited to NO_x-limited. While

this can be achieved by expansion of the long-term monitoring network, it can also be addressed by improved numerical models that have been evaluated with observations in both urban and regional chemical regimes.

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Table 1. Concentrations of CO, O_3, NO_x, and PM_{10} in México City on workdays (M-F), Saturday (Sat), and Sunday (Sun); 3-h daily maxima[a] averaged over all stations and days of year.

Year	CO ppm			O_3 ppb			NO_x ppb			PM_{10} mg m^{-3}		
	M-F	Sat	Sun	M-F	Sat	Sun	M-F	Sat	Sun	M-F	Sat	Sun
1986	8.2	6.2	4.5	72	82	71	151	136	99			
1987	7.3	5.3	3.9	91	82	80	149	116	79			
1988	7.8	6.2	4.2	112	106	104	133	108	73			
1989	7.5	6.0	4.8	99	95	91	141	117	89			
1990	8.7	7.5	6.3	110	115	106	136	116	86			
1991	9.3	7.9	6.6	135	145	125	143	118	88			
1992	8.4	7.2	5.9	124	118	116	141	121	92	131	125	91
1993	6.2	5.0	3.9	113	121	112	142	122	93	143	144	130
1994	5.5	4.7	3.5	121	117	106	135	115	81	89	92	71
1995	4.5	3.7	2.9	116	119	109	126	101	70	94	82	71
1996	5.1	4.4	3.1	107	107	102	157	138	88	108	106	77
1997	4.6	3.9	3.0	100	99	103	157	126	92	107	107	92
1998	4.7	3.8	2.9	101	108	102	129	103	74	104	104	89
1999	4.3	3.5	2.5	98	98	86	124	104	67	80	72	57
2000	4.5	3.7	2.7	103	109	106	135	113	73	75	78	56
2001	4.0	3.2	2.4	91	98	91	112	95	65	78	76	60
2002	3.5	2.8	2.0	91	93	86	121	98	65	79	68	57
2003	3.2	2.8	2.0	87	87	86	138	120	81	85	82	66
2004	3.1	2.3	1.7	78	77	79	140	107	76	80	68	58
2005	2.9	2.4	1.8	81	85	85	139	116	80	84	86	66
2006	2.7	2.2	1.6	77	79	79	137	112	75	78	70	61
2007	2.4	2.2	1.4	74	81	81	135	121	72	76	74	54

Average of each day's three highest values between 7 a.m. and noon for CO, NO_x, and PM_{10}, and between 11 a.m. and 5 p.m. for O_3.

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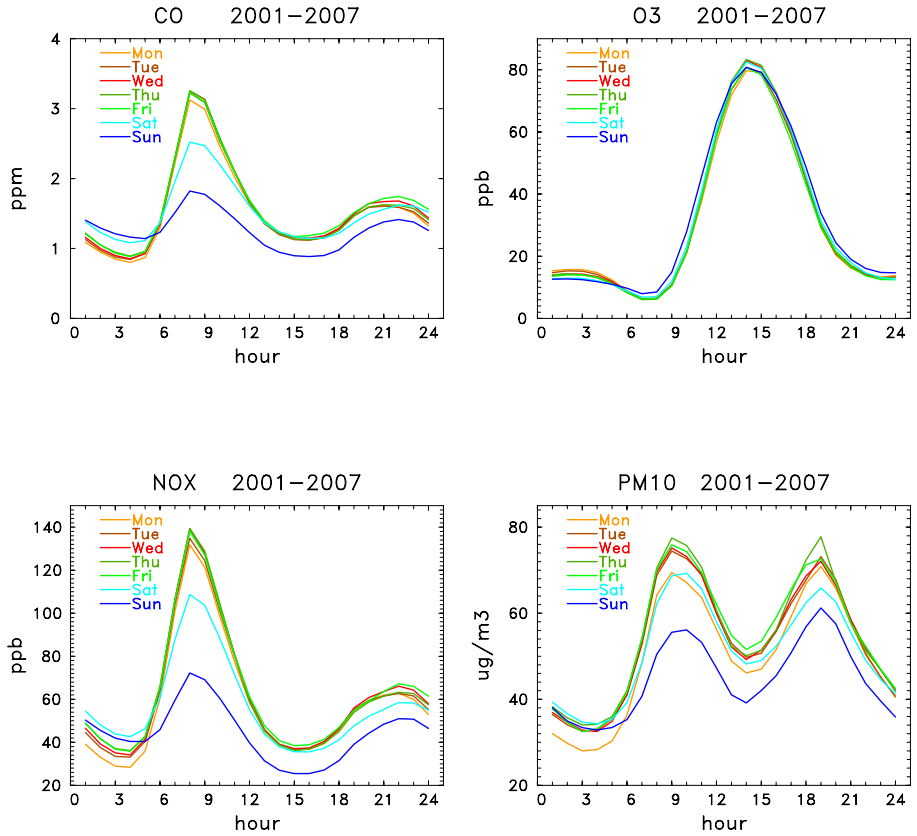

Fig. 1. Diurnal cycle of CO, NO_x, O_3, and PM_{10} in México City, averaged for all stations over 2001–2007.

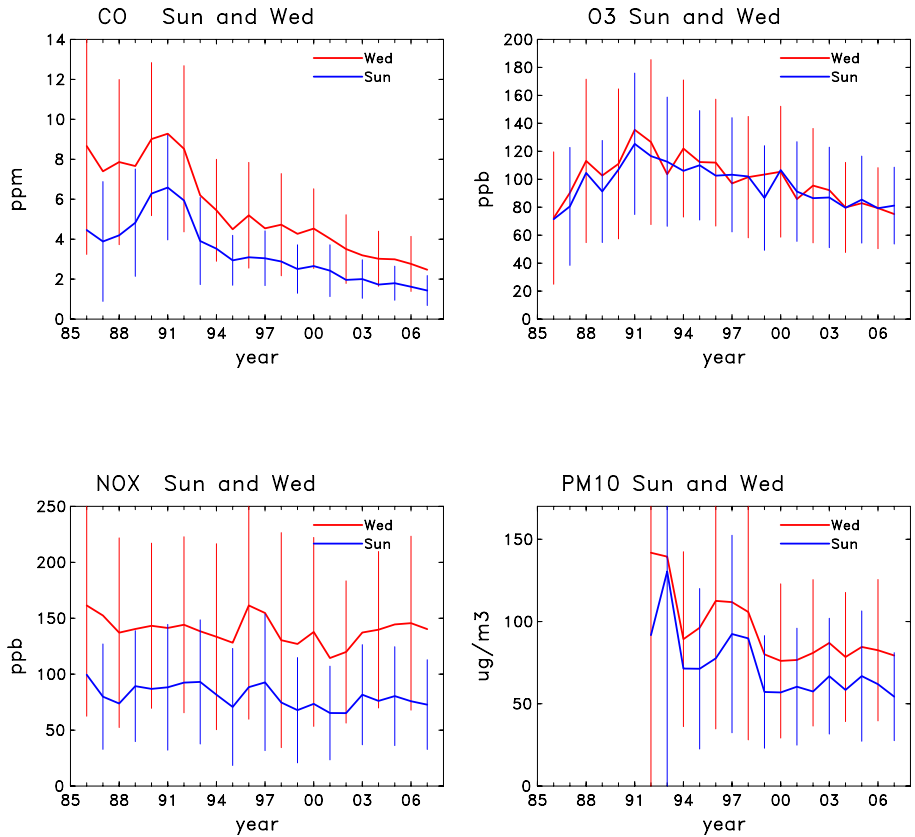

Fig. 2. Long term trends in the concentrations of CO, NO_x, and PM_{10} in the morning (average of the three highest concentrations between 7 a.m. and 12 noon) and O_3 in the afternoon (average of the three highest concentrations between 11 a.m. and 5 p.m.) averaged over all stations for Wednesdays (red) and Sundays (blue).

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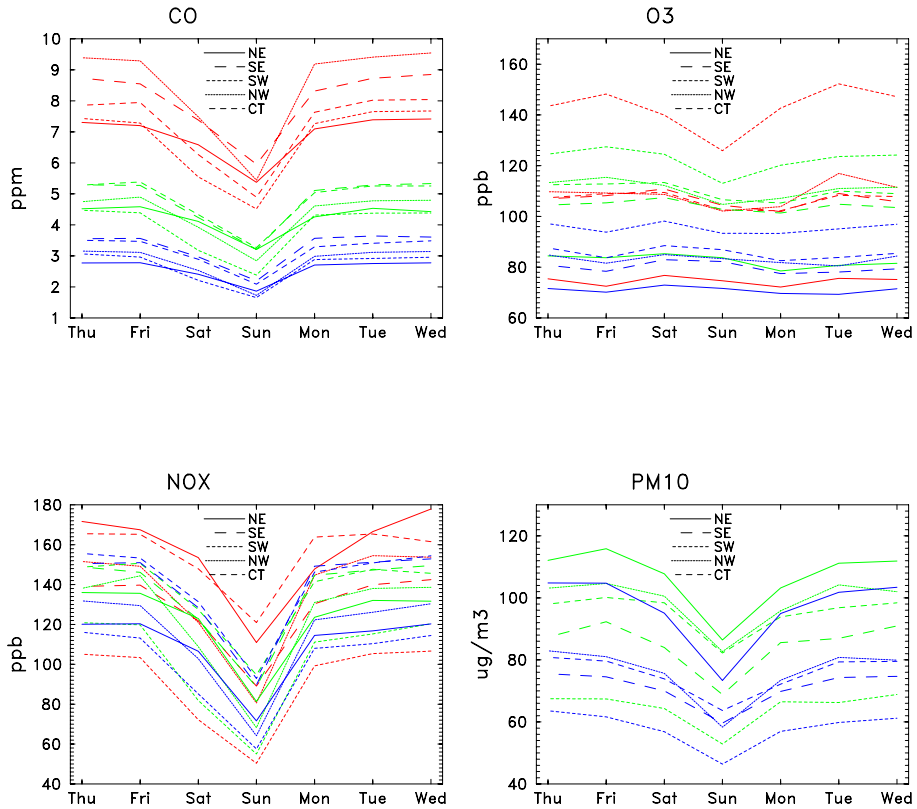

Fig. 3. Weekly patters of the concentrations of CO, NO_x, and PM_{10} in the morning (average of the three highest concentrations between 7 a.m. and 12 noon) and O_3 in the afternoon (average of the three highest concentrations between 11 a.m. and 5 p.m.), by city sector (see legend). Averages are given for the time periods 1986–1992 (red), 1993–2000 (green), and 2001–2007 (blue).

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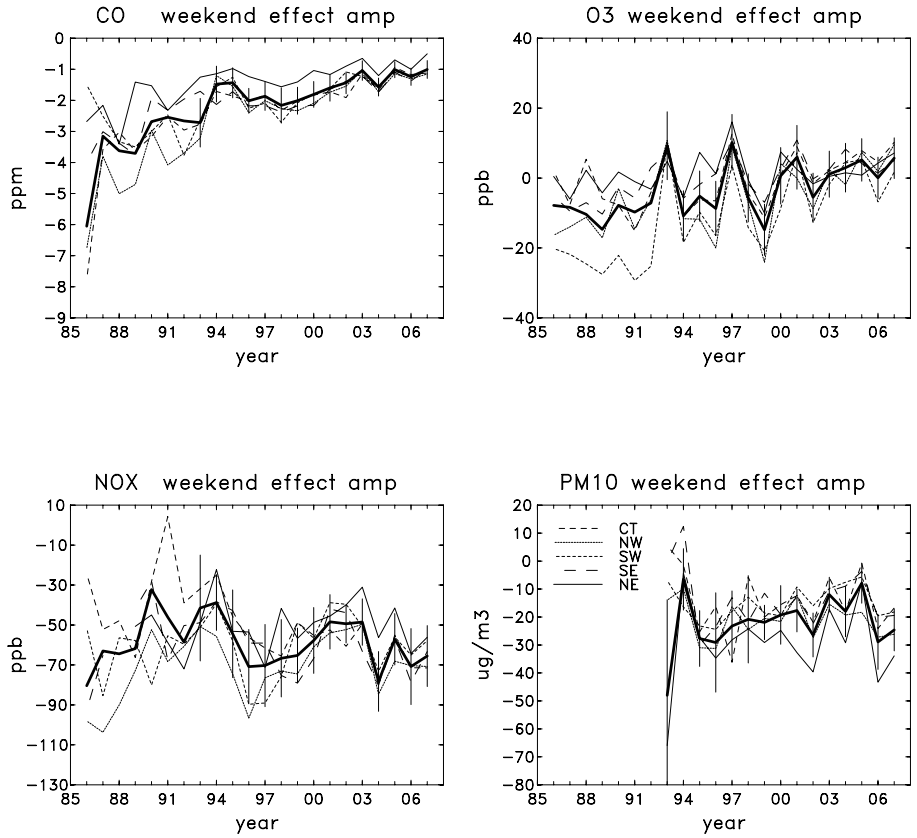

Fig. 4. Amplitude (absolute concentration) of the weekend effect for CO, NO_x, PM_{10}, and O_3. Thick line is the average of all stations, while individual thin lines (legend in lower right panel) give results by sector.

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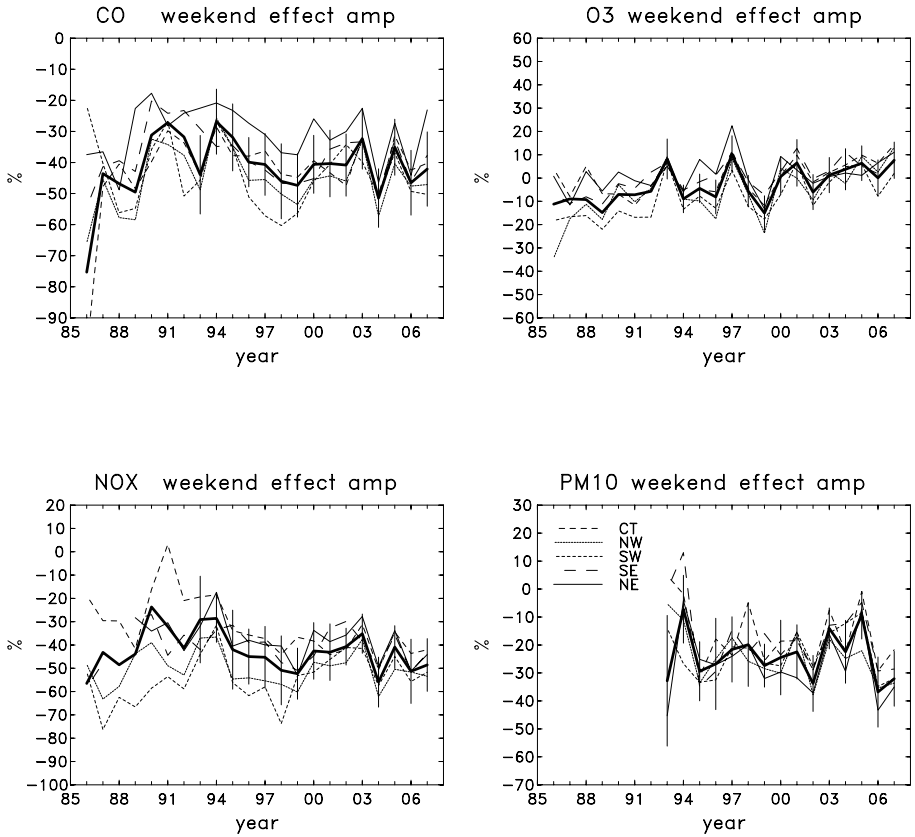

Fig. 5. Amplitude (relative %) of the weekend effect for CO, NO_x, PM_{10}, and O_3. Thick line is the average of all stations, while individual thin lines (legend in lower right panel) give results by sector.

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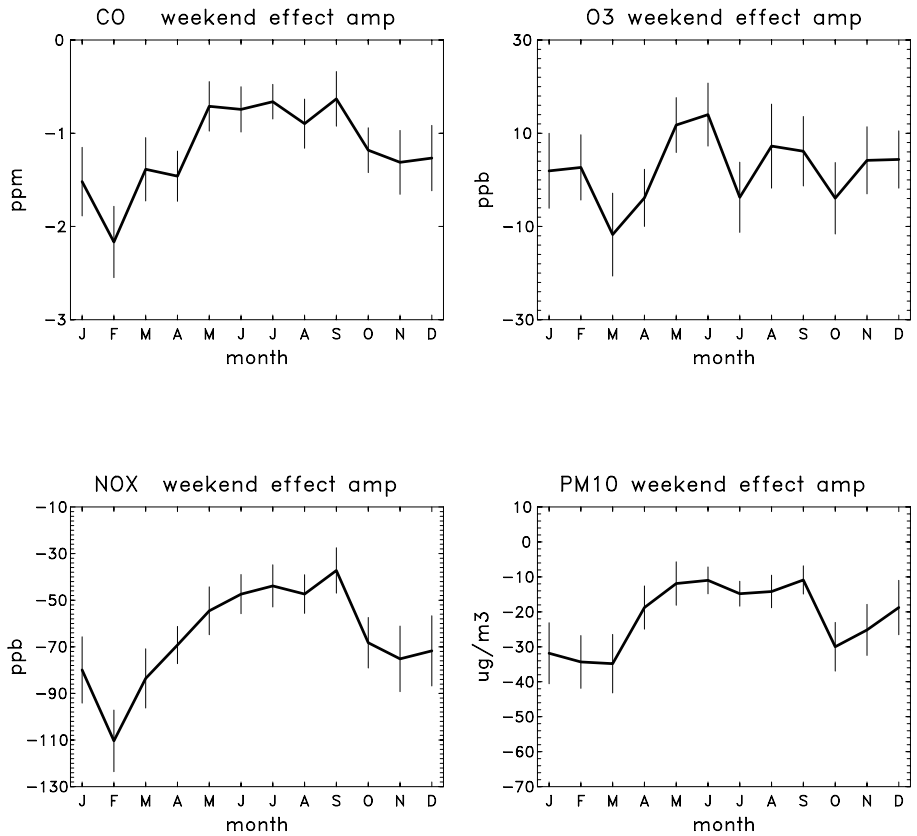

Fig. 6. Seasonal variation of the weekend effect (absolute amplitude), for the years 2001–2007.

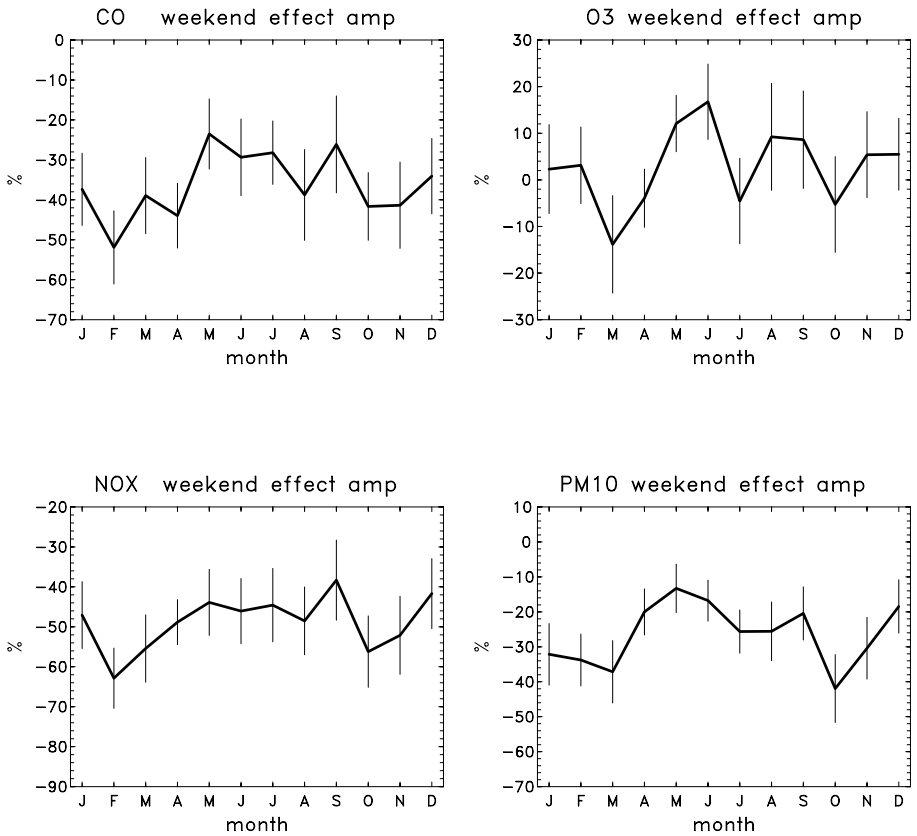

Fig. 7. Seasonal variation of the weekend effect (relative amplitude), for the years 2001–2007.

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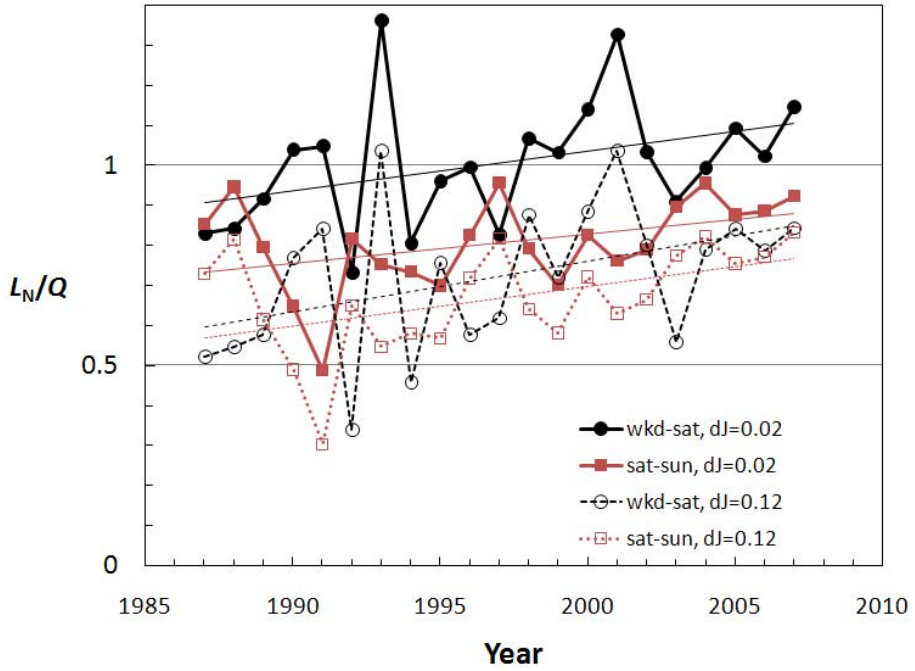

Fig. 8. Fraction of radical loss by NO_x chemistry relative to total radical loss (L_N/Q) derived from the observed weekend changes in CO, NO_x, and O_3 concentrations. Circles are for workday (Monday–Friday) to Saturday changes, while squares are for Saturday to Sunday changes, for assumed 2% (solid symbols) and 12% (open symbols) enhancements in photolysis rates (J-values). Unweighted least square linear fits are shown for visual guidance.