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## Weekly patterns of México City's surface concentrations of CO, NO<sub>x</sub>, PM<sub>10</sub> and O<sub>3</sub> during 1986-2007

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**Mexico City pollution  
weekend effect**

S. Stephens et al.

# Weekly patterns of México City's surface concentrations of CO, NO<sub>x</sub>, PM<sub>10</sub> and O<sub>3</sub> during 1986–2007

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 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 ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), particulate matter smaller than  $10\ \mu\text{m}$  ( $\text{PM}_{10}$ ), and ozone ( $\text{O}_3$ ) collected hourly over 22 years (1986–2007) at 32 urban monitoring locations were analyzed. Morning concentrations of CO,  $\text{NO}_x$ , and  $\text{PM}_{10}$  are lower on Saturdays and even more so on Sundays, compared to workdays (Monday–Friday), while afternoon  $\text{O}_3$  concentrations change minimally and are occasionally even higher. This weekend effect is empirical evidence that photochemical  $\text{O}_3$  production is  $\text{NO}_x$ -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  $\text{CO}/\text{NO}_x$  and  $\text{VOC}/\text{NO}_x$  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  $\text{NO}_x$ -related compounds, some of which (e.g. peroxy acyl nitrates) can contribute to the regional  $\text{NO}_x$  budget. While VOC emission reductions would be most effective in reducing local  $\text{O}_3$  production,  $\text{NO}_x$  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-

ACPD

8, 8357–8384, 2008

## Mexico City pollution weekend effect

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



tative of current and future conditions in other megacities undergoing rapid economic development. The city's tropical high altitude location ( $19^{\circ}$  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,

**Mexico City pollution  
weekend effect**

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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<sub>3</sub> to emission changes is provided by the weekend-workday differences in the emissions of O<sub>3</sub> precursors, and the resulting differences in O<sub>3</sub> concentrations. Generally, emissions of NO<sub>x</sub> and VOCs are lower on weekends, while in many locations (though not all) the weekend O<sub>3</sub> 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<sub>2</sub> 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<sub>3</sub> 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<sub>x</sub>, CO (as a proxy for VOCs), O<sub>3</sub> and PM<sub>10</sub> (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.

**Mexico City pollution weekend effect**

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 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<sub>3</sub>, NO<sub>x</sub>, NO<sub>2</sub>, CO, SO<sub>2</sub>, TSP, and PM<sub>10</sub>, 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<sub>3</sub>, NO<sub>x</sub>, CO, and PM<sub>10</sub> 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<sub>x</sub> and O<sub>3</sub>, allowed values were between 2 ppb and 1 ppm, for CO between 10 ppb and 100 ppm, and for PM<sub>10</sub> between 0.1 and 1000 μg/m<sup>3</sup>. 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<sub>x</sub>, and PM<sub>10</sub>, and between 11 a.m. and 5 p.m. for O<sub>3</sub>. The intent of this averaging was to capture the bulk of the chemical precursors from the morning rush-hour and the resultant afternoon O<sub>3</sub>, rather than specific maxima or exceedances

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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<sub>3</sub> values in 2007 was computed by calculating the 2007 average Wednesday O<sub>3</sub>, then the 2007 average Sunday O<sub>3</sub>, 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<sub>x</sub>, O<sub>3</sub>, and PM<sub>10</sub> surface concentrations are shown in Fig. 1, averaged for all stations and all days over 2001–2007. For CO, NO<sub>x</sub>, and PM<sub>10</sub> 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<sub>x</sub> because of its short photochemical lifetime, and smallest for PM<sub>10</sub>, 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-

## Mexico City pollution weekend effect

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Mexico City pollution  
weekend effect**

S. Stephens et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

days and Saturday but lower on Sundays. Increases in CO and NO<sub>x</sub> 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<sub>x</sub> levels and O<sub>3</sub> loss by the reaction NO+O<sub>3</sub>→NO<sub>2</sub>+O<sub>2</sub>. Also notable is the earlier rise in O<sub>3</sub> concentrations on Sunday morning relative to other days, resulting from the earlier time that O<sub>3</sub> concentrations exceed those of NO, i.e. an earlier NO-O<sub>3</sub> 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<sub>x</sub>, and PM<sub>10</sub>, and the afternoon maximum in O<sub>3</sub> 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<sub>x</sub> and PM<sub>10</sub> 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<sub>x</sub>, and PM<sub>10</sub>, but not for O<sub>3</sub>. Table 1 compares the workday averages with Saturday and Sunday values. For CO, NO<sub>x</sub>, and PM<sub>10</sub>, Saturday values generally fall between the workday and Sunday values, while for O<sub>3</sub> they are frequently highest (on 9 out of the 22 years). Workday O<sub>3</sub> 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<sub>x</sub>, and PM<sub>10</sub> are consistently lower on Saturday and more so on Sunday, compared

**Mexico City pollution  
weekend effect**

S. Stephens et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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<sub>x</sub>, and PM<sub>10</sub> morning concentrations are smaller on weekends relative to workdays, by ca. 40–50%, 40–60%, and 10–40%, respectively; O<sub>3</sub> 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<sub>3</sub>. The central issue is to explain why O<sub>3</sub> 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<sub>x</sub> emissions, leading to less NO<sub>x</sub> inhibition of O<sub>3</sub> formation if under VOC-limited conditions, (2) later timing of NO<sub>x</sub> 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<sub>3</sub> production in México City is VOC-limited and NO<sub>x</sub>-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

### Mexico City pollution weekend effect

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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<sub>3</sub> production to VOC changes is always positive (albeit small at low NO<sub>x</sub>), while it can be either positive or negative with respect to NO<sub>x</sub> changes, the negative values representing NO<sub>x</sub> inhibition of O<sub>3</sub> production in the VOC-limited regime (e.g. Kleinman, 2005). In this regime, hypothetical reductions in only VOC emissions would lead to lower O<sub>3</sub>, while equally hypothetical reductions in only NO<sub>x</sub> emissions would lead to higher O<sub>3</sub>. The near equality of workday and weekend O<sub>3</sub> then most likely arises from the simultaneous decreases in VOC and NO<sub>x</sub> emissions and their opposing effects on the O<sub>3</sub> production rates. For this reason, it can be concluded that workday O<sub>3</sub> 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<sub>x</sub> 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<sub>2</sub> photolysis frequencies ( $J_{\text{NO}_2}$ ) 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-

**Mexico City pollution  
weekend effect**

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Mexico City pollution weekend effect

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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:

$$d \ln P_{O_3} / d \ln [NO_x] = [1 - (3/2)L_N/Q] / [1 - (L_N/Q)/2] \quad (1)$$

$$d \ln P_{O_3} / d \ln [VOC] = [(1/2)L_N/Q] / [1 - (L_N/Q)/2] \quad (2)$$

$$d \ln P_{O_3} / d \ln Q = (1/2) / [1 - (L_N/Q)/2] \quad (3)$$

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

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

the change in  $O_3$  concentration can be expanded as:

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

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,  $\delta P_{O_3}$ , 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  $\delta Q$  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  $\delta J$  is probably an upper limit to  $\delta Q$ . 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  $\delta CO$ ,  $\delta NO_x$ ,  $\delta J$ , and  $\delta O_3$ . 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  $\delta CO$ ,  $\delta NO_x$ ,  $\delta J$ , and  $\delta O_3$  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  $\delta J$  of 0.02 (filled

## Mexico City pollution weekend effect

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



symbols) or 0.12 (open symbols) to bracket the weekend enhancement of photolysis rates estimated from PM<sub>10</sub> 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 than Saturday-Sunday values as expected from more intense NO<sub>x</sub> 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  $\delta\text{CO}$ ,  $\delta\text{NO}_x$ , and  $\delta\text{O}_3$  (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<sub>3</sub> 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<sub>3</sub> values, as less change in NO<sub>x</sub> inhibition of O<sub>3</sub> 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<sub>3</sub> in México City is VOC-limited and NO<sub>x</sub>-inhibited. This is particularly clear for workdays, as reflected in high  $L_N/Q$  values for the workday-to-Saturday changes. Whether the NO<sub>x</sub> inhibition also persists on Sundays is less clear, and we note that early afternoon NO<sub>x</sub> values are significantly lower on Sundays (see Fig. 1), but not on Saturdays, relative to workdays. Since early afternoon NO<sub>x</sub> is mostly

**Mexico City pollution  
weekend effect**

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



NO<sub>2</sub>, the Sunday reductions in NO<sub>x</sub> imply that total O<sub>x</sub> (=O<sub>3</sub>+NO<sub>2</sub>) is lower than on workdays and Saturdays, even with O<sub>3</sub> relatively unchanged. Therefore Sunday's O<sub>x</sub> concentrations may be both VOC and NO<sub>x</sub>-sensitive.

One possible confounding factor is that NO<sub>x</sub> and VOC emissions in one part of the city may be transported over a few hours by urban scale circulations to produce high O<sub>3</sub> 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<sub>3</sub> weekend effect, while the CO and NO<sub>x</sub> 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<sub>x</sub> concentrations have remained largely unchanged. A decrease in the VOC/NO<sub>x</sub> 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<sub>x</sub>-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<sub>3</sub> 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.

**Mexico City pollution  
weekend effect**

S. Stephens et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## 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

### Mexico City pollution weekend effect

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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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## Mexico City pollution weekend effect

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Mexico City pollution  
weekend effect**

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Mexico City pollution  
weekend effect**

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Mexico City pollution  
weekend effect**

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Table 1.** Concentrations of CO, O<sub>3</sub>, NO<sub>x</sub>, and PM<sub>10</sub> in México City on workdays (M-F), Saturday (Sat), and Sunday (Sun); 3-h daily maxima<sup>a</sup> averaged over all stations and days of year.

Year	CO ppm			O <sub>3</sub> ppb			NO <sub>x</sub> ppb			PM <sub>10</sub> mg m <sup>-3</sup>		
	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<sub>x</sub>, and PM<sub>10</sub>, and between 11 a.m. and 5 p.m. for O<sub>3</sub>.

Mexico City pollution weekend effect

S. Stephens et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

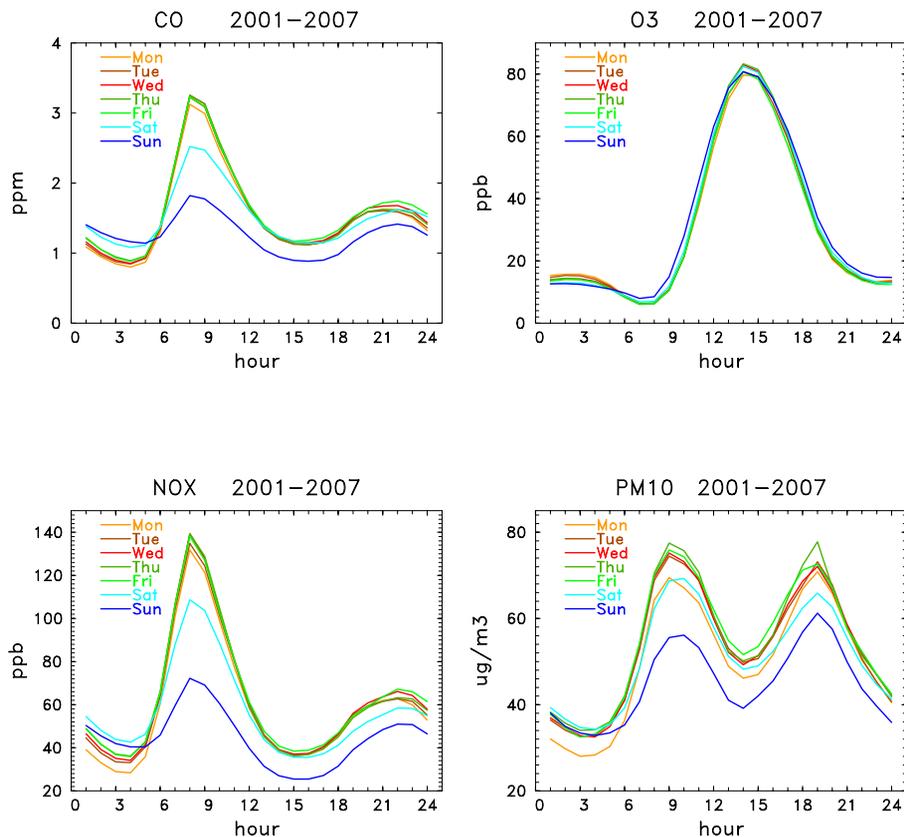
Printer-friendly Version

Interactive Discussion



Mexico City pollution  
weekend effect

S. Stephens et al.

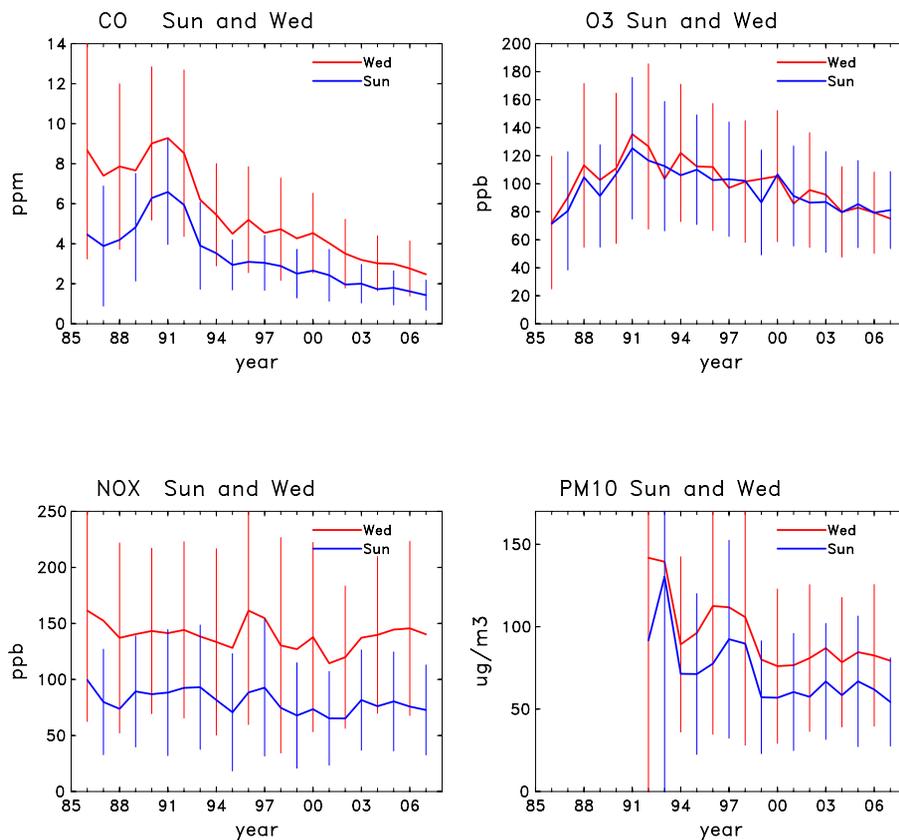


**Fig. 1.** Diurnal cycle of CO, NO<sub>x</sub>, O<sub>3</sub>, and PM<sub>10</sub> in México City, averaged for all stations over 2001–2007.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Mexico City pollution  
weekend effect

S. Stephens et al.

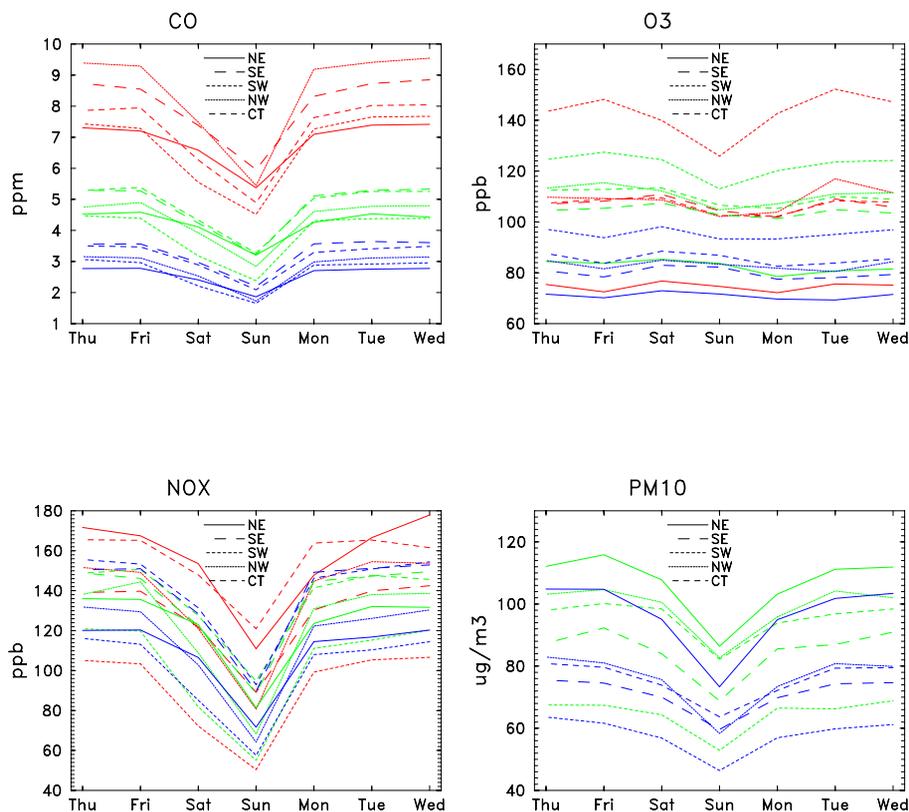


**Fig. 2.** Long term trends in the concentrations of CO, NO<sub>x</sub>, and PM<sub>10</sub> in the morning (average of the three highest concentrations between 7 a.m. and 12 noon) and O<sub>3</sub> in the afternoon (average of the three highest concentrations between 11 a.m. and 5 p.m.) averaged over all stations for Wednesdays (red) and Sundays (blue).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Mexico City pollution  
weekend effect

S. Stephens et al.

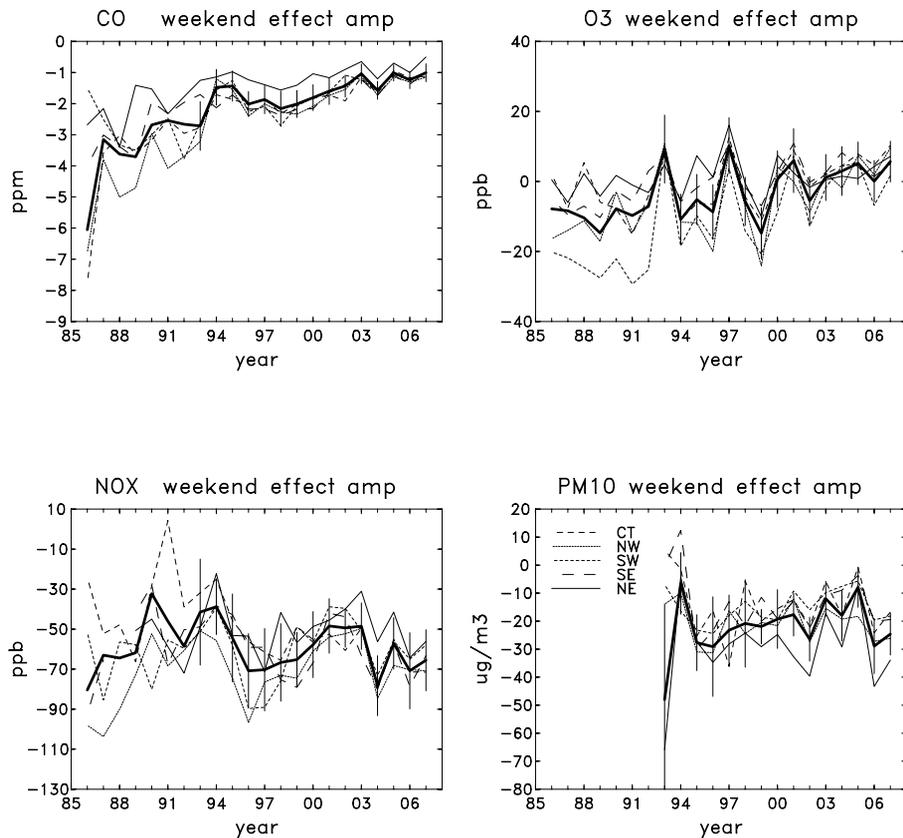


**Fig. 3.** Weekly patterns of the concentrations of CO, NO<sub>x</sub>, and PM<sub>10</sub> in the morning (average of the three highest concentrations between 7 a.m. and 12 noon) and O<sub>3</sub> in the afternoon (average of the three highest concentrations between 11 a.m. and 5 p.m.), by city sector (see legend). Averages are given for the time periods 1986–1992 (red), 1993–2000 (green), and 2001–2007 (blue).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Mexico City pollution  
weekend effect

S. Stephens et al.

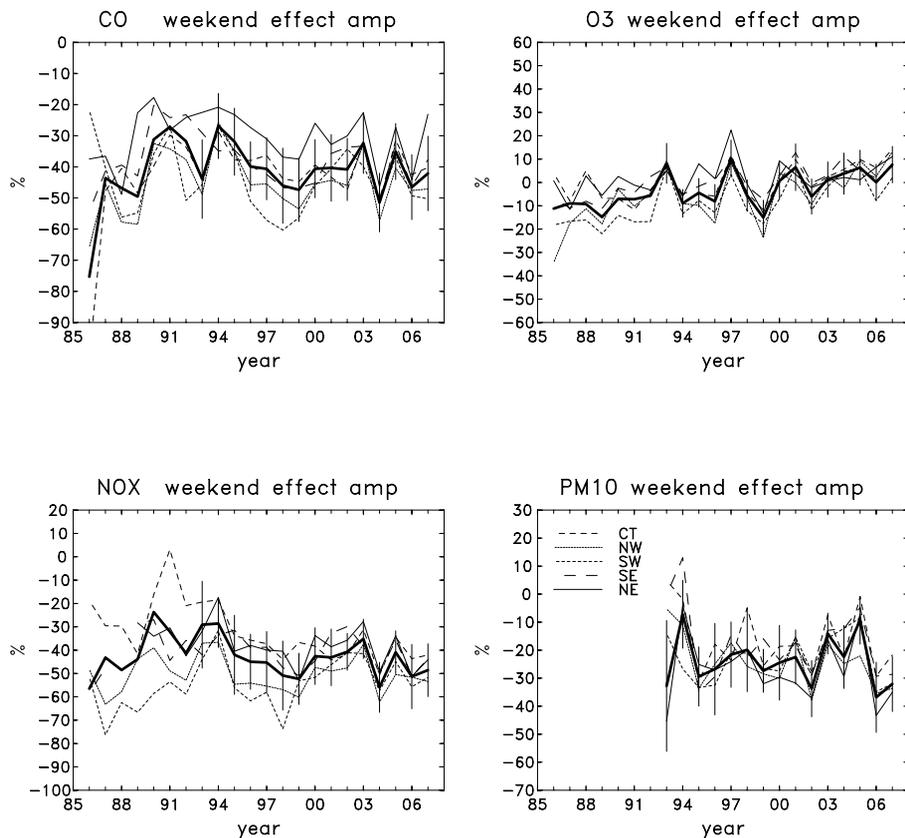


**Fig. 4.** Amplitude (absolute concentration) of the weekend effect for CO, NO<sub>x</sub>, PM<sub>10</sub>, and O<sub>3</sub>. Thick line is the average of all stations, while individual thin lines (legend in lower right panel) give results by sector.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Mexico City pollution  
weekend effect

S. Stephens et al.



**Fig. 5.** Amplitude (relative %) of the weekend effect for CO, NO<sub>x</sub>, PM<sub>10</sub>, and O<sub>3</sub>. Thick line is the average of all stations, while individual thin lines (legend in lower right panel) give results by sector.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Mexico City pollution  
weekend effect

S. Stephens et al.

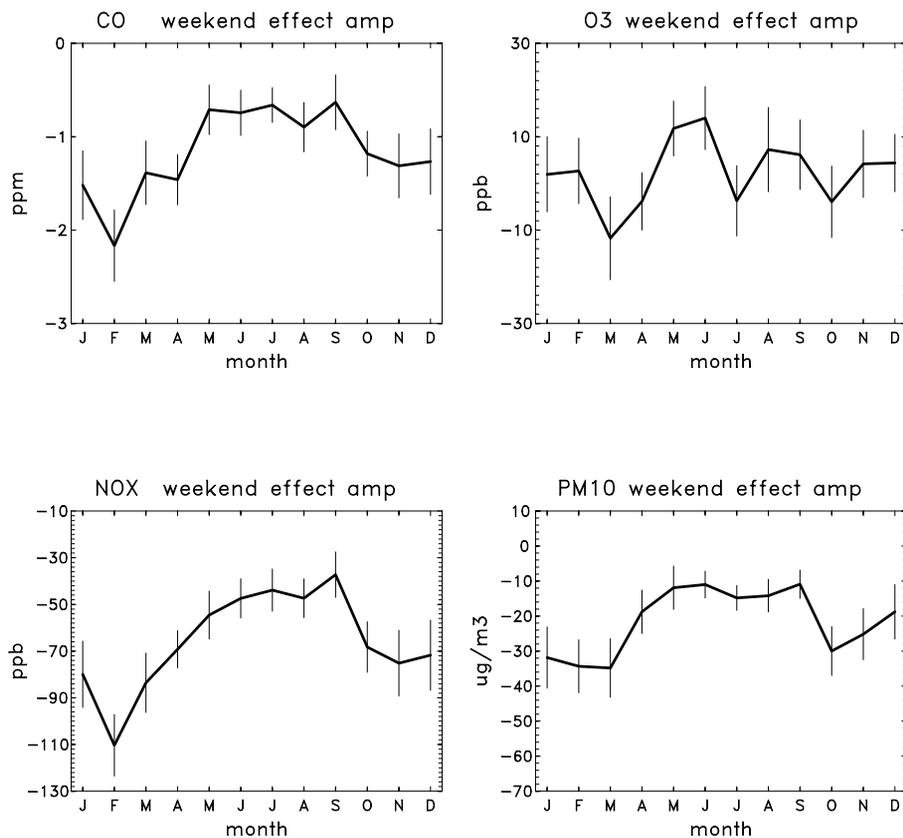
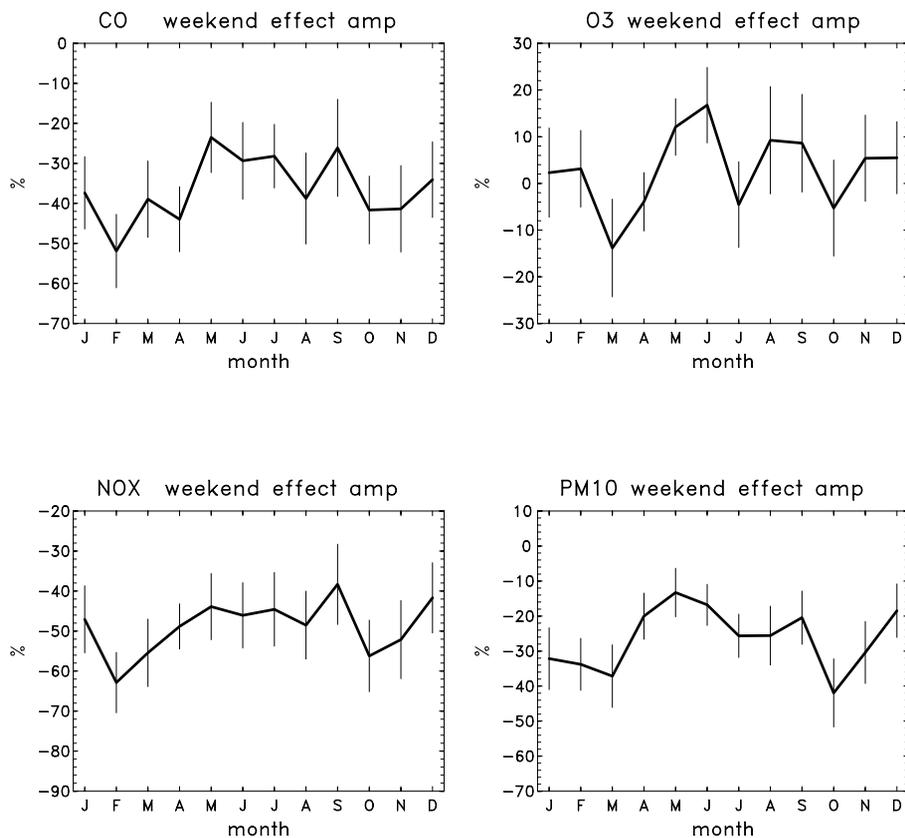


Fig. 6. Seasonal variation of the weekend effect (absolute amplitude), for the years 2001–2007.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Mexico City pollution  
weekend effect**

S. Stephens et al.

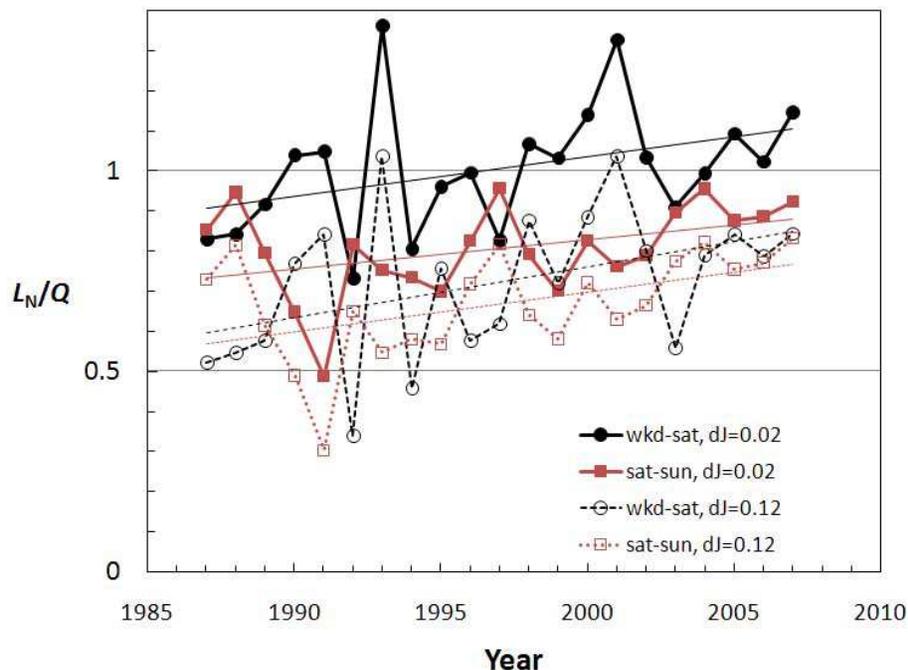


**Fig. 7.** Seasonal variation of the weekend effect (relative amplitude), for the years 2001–2007.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Mexico City pollution  
weekend effect

S. Stephens et al.



**Fig. 8.** Fraction of radical loss by  $\text{NO}_x$  chemistry relative to total radical loss ( $L_N/Q$ ) derived from the observed weekend changes in  $\text{CO}$ ,  $\text{NO}_x$ , and  $\text{O}_3$  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.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)