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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 39 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 proportional to those of 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.

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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 representative 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

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several other concentration ratios as indicators of NO_x or VOC sensitivity involving, in addition to O_3, total reactive nitrogen (NO_y) as well as photochemically produced formaldehyde (CH_2O), nitric acid (HNO_3), and hydrogen peroxide (H_2O_2). The VOC or NO_x sensitivities can also be assessed from chemistry-transport modeling simulations, in which the emissions of VOCs and NO_x are varied around central estimates and the response of O_3 concentrations is examined.

For México City the VOC or NO_x sensitivity has been a subject of considerable debate. Molina et al. (2002a) reviewed ambient VOC/NO_x measurements, emission inventories, and smog chamber experiments with captive air, to conclude that O_3 formation appeared to be NO_x sensitive. They however recognized that this evidence is not conclusive because of the relative scarcity of VOC/NO_x measurements and over-simplifications inherent in representing the full ozone photochemistry by this simple ratio; they also noted that VOC concentrations have been decreasing more rapidly than those of NO_x over the previous decade, so the chemical regime may have been changing. Measurements of several sensitivity indicators (O_3, NO_x, and NO_y) were made 14–25 April 2004 at a location within México City (Santa Ursula) by Torres-Jardón (2004), with their ratios indicating VOC-sensitive conditions. During MILAGRO, Nunnermacker et al. (2008) measured H_2O_2 concentrations typically below 1 ppb in urban overflights by the G-1 aircraft and at the T1 suburban supersite, consistent with a VOC-sensitive, high NO_x regime. One modeling study (West et al., 2004, see their Fig. 6) found that increasing VOC emissions by as much as a factor of four resulted in O_3 increases of only 12–25%, while more recent modeling studies (Lei et al., 2007, 2008; Tie et al., 2007) found much stronger VOC sensitivity.

A separate empirical assessment of the response of O_3 to emission changes can be obtained 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; Qin et al., 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), in Chile (Jorquera et al., 2000), Switzerland (Brönnimann and Neu, 1997), France (Pont and Fontan, 2001), the UK (Jenkin et al., 2002), Greece (Riga-Karandinos et al., 2006), India (Debaje and Kakade, 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. Torres-Jardón (2004) found that at the Santa Ursula station during 1–30 April 2004 weekend NO concentrations (6–9 a.m.) were 37% lower than on workdays, while maximum O_3 concentrations were only 10% lower, consistent with a VOC-limited regime.

Here, we examine for México City the weekly patterns over 22 years (1986–2007) of NO_x, carbon monoxide (CO, as a proxy for VOCs), O_3 and PM_{10} (PM smaller than 10 μm, since 1993) concentrations analyzed from surface measurements at 39 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 Methods

2.1 Data availability

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 US Environmental Protection Agency, and a recent report concluded that the monitoring system is overall accurate and well implemented (GDF, 2004). A data screening procedure was implemented to eliminate possible values falling far outside realistic bounds. For NO_x, NO_2, 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 ACO, ARA, CHA, LLA, LPR, LVI, NET, PER, SAG, SJA, VIF, XAL), north-west (*NW* for ATI, AZC, CAM, CUI, EAC, IMP, TAC, TLA, TLI, VAL), south-west (*SW* for

CUA, PED, PLA, SUR, TPN), south-east (*SE* for CES, COY, CHO, TAH, TAX, UIZ), and center (*CT* for BJU, HAN, IZT, LAG, MER, MIN). To represent each day by a single value, the average of the three highest values at each station 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 and NO_2. 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 of regulatory thresholds. For some considerations, values were also averaged over three longer time periods, specifically 1986–1992, 1993–2000, and 2001–2007. The availability of the data is summarized in Table 1, which gives the number of valid days summed over the stations of each sector, for each year. The data record is clearly more complete in the recent years, particularly for PM_{10} and NO_x.

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).

2.2 Analytic derivation of fractional radical loss from NO_x chemistry

The weekend-workday differences in the concentrations of CO, NO_x, O_3, and PM_{10} can be used to estimate the fraction of the radicals lost via NO_x chemistry, which in turn provides an indication of whether the O_3 production is VOC or NO_x sensitive. The derivation of this fraction and the underlying approximations are presented here. Kleinman (2005) has shown that the instantaneous O_3 production rate, P_{O3}, is related to instantaneous NO_x and reactivity weighted hydrocarbon (or VOC) concentrations and the radical production rate Q by:

$$\frac{\mathbf{d}\ln P_{O3}}{\mathbf{d}\ln\,[NO_x]}=\frac{2-\frac{3L_N}{Q}}{2-\frac{L_N}{Q}} \tag{1}$$

$$\frac{\mathbf{d}\ln P_{O3}}{\mathbf{d}\ln\,[VOC]}=\frac{\frac{L_N}{Q}}{2-\frac{L_N}{Q}} \tag{2}$$

$$\frac{\mathbf{d}\ln P_{O3}}{\mathbf{d}\ln Q}=\frac{1}{2-\frac{L_N}{Q}} \tag{3}$$

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. It should be noted that Eqs. (1–3) more strictly represent the production of total odd oxygen, $O_x=O_3+NO_2$ (Sillman, 2008; Kleinman, L., priv. comm., 2008). These equations can be used to predict the response of O_3 or O_x to changes in NO_x and VOC emissions. With the simplified notation

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

the change in O_x concentration can be expanded as:

$$\delta P_{O_x}\sim\frac{\delta P_{O_x}}{\delta NO_x}\delta NO_x+\frac{\delta P_{O_x}}{\delta VOC}\delta VOC+\frac{\delta P_{O_x}}{\delta Q}\delta Q= \tag{5}$$
$$\frac{\left(2-\frac{3L_N}{Q}\right)\delta NO_x+\left(\frac{L_N}{Q}\right)\delta VOC+\delta Q}{2-\frac{L_N}{Q}}$$

where in the last equation for the sensitivities to NO_x, VOCs, and Q (Eqs. 1–3) were used. This equation can be solved for L_N/Q:

$$\frac{L_N}{Q}=\frac{2\delta P_{O_x}-2\delta NO_x-\delta Q}{\delta P_{O_x}+\delta VOC-3\delta NO_x} \tag{6}$$

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_x production, δP_{O_x}, is reflected to first order in the build-up of the afternoon O_x concentrations considered here, so that $\delta P_{O_x}\sim\delta O_x$. Second, as further discussed below, we assume that the weekend effect for VOC reactivity is similar to that for CO, $\delta VOC\sim\delta CO$. Third, 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:

$$\frac{L_N}{Q}=\frac{2\delta O_x-2\delta NO_x-\delta J}{\delta O_x+\delta CO-3\delta NO_x} \tag{7}$$

where all the terms on the right hand side can be measured or at least estimated from the weekend effect.

Table 1. Number of station-days reported in each city sector

Year	CO					O_3					NO_x					PM_{10}				
	NE	SE	SW	NW	CT	NE	SE	SW	NW	CT	NE	SE	SW	NW	CT	NE	SE	SW	NW	CT
1986	474	405	432	451	900	426	234	427	154	460	200	243	199	0	329	0	0	0	0	0
1987	550	643	511	563	1303	436	252	532	175	662	4	134	274	0	572	0	0	0	0	0
1988	410	691	539	675	1603	341	317	672	55	757	0	0	341	0	580	0	0	0	0	0
1989	673	696	567	645	1513	299	345	587	150	795	158	227	357	0	624	0	0	0	0	0
1990	813	770	618	555	1389	564	536	656	407	1086	276	315	321	0	648	0	0	0	0	0
1991	771	775	653	355	1340	430	584	661	396	1172	275	288	331	0	473	0	0	0	0	0
1992	782	583	644	538	1420	578	557	667	617	1236	291	302	311	27	552	236	134	119	0	259
1993	822	828	664	1262	1825	652	961	757	796	1678	485	273	323	460	1165	817	280	339	0	658
1994	1445	1092	722	1456	2545	1092	1456	1449	1092	1820	659	332	343	683	1300	1000	364	345	0	671
1995	2184	1456	728	1820	2912	1092	1456	1456	1092	1820	756	978	698	919	1728	1456	728	364	0	1092
1996	1921	1193	728	1820	2912	1092	1456	1456	1092	1820	887	945	717	987	1741	1340	670	335	0	1005
1997	1820	1092	728	1820	2912	1092	1456	1456	1092	1820	683	850	680	922	1706	1456	728	364	0	1092
1998	1820	1092	728	1820	2912	1092	1456	1456	1092	1820	1006	1073	716	1315	2084	1456	728	364	0	1092
1999	1820	1091	728	1787	2906	1092	1454	1451	1056	1815	1023	1029	725	1235	2062	1456	728	364	0	1092
2000	1439	1061	890	1681	2742	1078	1429	1566	1030	1781	1058	1023	866	1278	1994	1186	847	680	202	1124
2001	1418	1068	1000	1689	2831	1076	1429	1726	1071	1811	1025	1062	1003	1334	2065	1339	991	1012	325	1333
2002	1355	1020	1069	1567	2778	1026	1382	1734	1088	1776	1023	1032	1075	1253	2118	1058	890	1073	341	1091
2003	1414	1042	1075	1752	2795	1039	1429	1581	1061	1777	1069	1061	1061	1384	2107	1359	872	1064	345	1323
2004	1409	1041	1061	1765	2863	1058	1428	1446	1082	1799	1026	1051	1079	1406	2118	1431	724	1078	359	1132
2005	1430	1076	1068	1712	2498	1062	1646	1595	1054	1446	1059	1075	1066	1402	1824	1430	838	1081	363	1049
2006	1013	668	978	1041	2293	1010	1757	1708	1031	1228	1023	1040	990	1359	1560	1356	1004	906	346	874
2007	986	860	1055	979	1847	1065	1895	1784	1023	1070	1051	1085	1026	1377	1399	1389	1036	1044	364	822

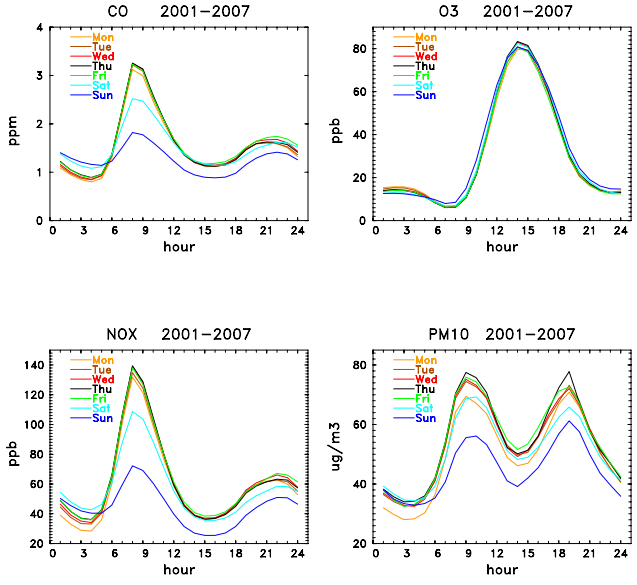

Fig. 1. Diurnal cycle of CO, NO_x, O_3, and PM_{10} in México City, averaged for all stations over 2001–2007.

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 relatively large evening PM_{10} peak occurs 1–2 h earlier than the CO and NO_x secondary peaks, and may be due to temporal overlap between evening rush hour emissions and remaining secondary aerosols produced during the daytime, wind-related dust in the late afternoon (de Foy et al., 2008) or biomass burning plumes advected into the basin from surrounding areas late in the day (Moffet et al., 2007). Ozone concentrations increase rapidly during the late morning when photochemical radical production rates are largest (Volkamer et al., 2007) and peak in the early afternoon.

The weekend effect for CO, NO_x, and PM_{10} is seen clearly in Fig. 1 with the smaller morning peaks on Saturday and Sunday, compared to workdays (Monday–Friday). Early afternoon values are similar on workdays and Saturday, but distinctly 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. For O_3, a much smaller weekend effect, if any, is seen 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, have somewhat lower O_3 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

Table 2. 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} $\mu g\,m^{-3}$		
	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

[a] 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.

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 (Fujita et al., 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 et al., 2002b). 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 2 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 Saturday or Sunday for only 5 of these 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. The SW sector is particularly interesting, with relatively low morning CO, NO_x, 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). 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 no such reductions are seen in O_3, except in the SW sector and there only 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; de Foy et al., 2008).

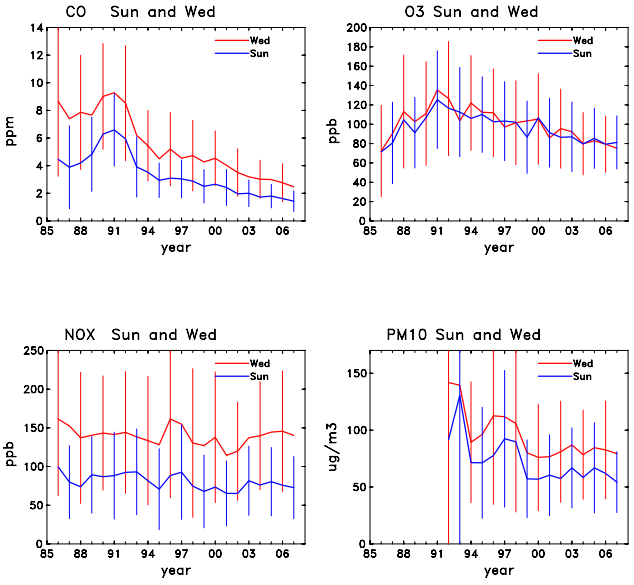

Fig. 2. Long term trends in the concentrations of CO, NO_x, and PM_{10} in the morning (average of the three highest concentrations between 7 a.m. and 12 noon) and O_3 in the afternoon (average of the three highest concentrations between 11 a.m. and 5 p.m.) averaged over all stations for Wednesdays (red)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

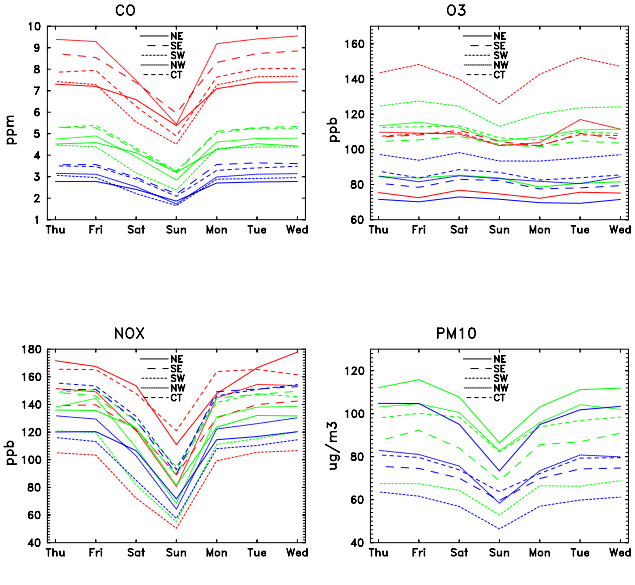

Fig. 3. Weekly patterns of the concentrations of CO, NO_x, and PM_{10} in the morning (average of the three highest concentrations between 7 a.m. and 12 noon) and O_3 in the afternoon (average of the three highest concentrations between 11 a.m. and 5 p.m.), by city sector (see legend). Averages are given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

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.

Seasonal variations are influenced by the dry (November–March) and wet (May–September) seasons. For 2001–2007 (Fig. 6) concentrations of CO, NO_x, and PM_{10} were largest during January and February, while O_3 peaked in March and April when solar actinic fluxes are higher. Lower values during the wet season are understood in terms of convective ventilation and wet removal. The relative amplitudes of the weekend effect show complex seasonal behavior (Fig. 7) for reasons that are not entirely clear but may include a number of factors such as holiday activities (December) and regional influence from biomass burning in the late dry season (March–May). For 1986-1992 and 1993–2000 (not shown), the general seasonal patterns were similar with concentrations of CO and NO_x peaking in January and February, O_3 peaking in May, and no clear seasonal trend of the relative weekend changes.

4 Discussion

4.1 Hypotheses for the weekend effect

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

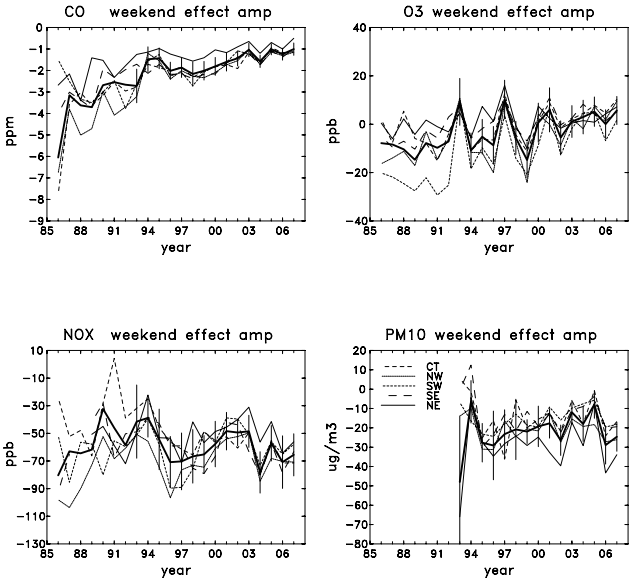

Fig. 4. Amplitude (absolute concentration) of the weekend effect for CO, NO_x, PM_{10}, and O_3. Thick line is the average of all stations, while individual thin lines (legend in lower right panel) give results by sector.

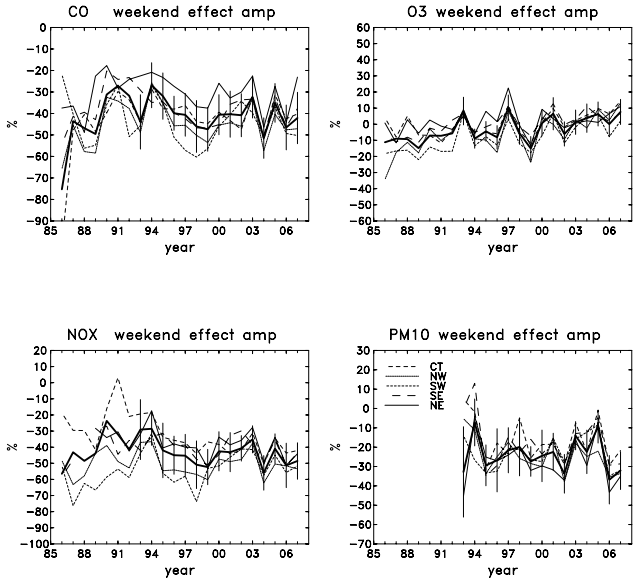

Fig. 5. Amplitude (relative, %) of the weekend effect for CO, NO_x, PM_{10}, and O_3. Thick line is the average of all stations, while individual thin lines (legend in lower right panel) give results by sector.

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 is VOC-limited and NO_x-inhibited, appears to be the most plausible explanation for the observed weekend effect in México City. 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. 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 arises from the simultaneous decreases in VOC and NO_x emissions and their opposing effects on the O_3 production rates.

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; Raga et al., 2001; Arriaga-Colina et al., 2004; Velasco et al., 2007; and references therein). 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. Mexico City's mobile sources account for ∼98% of CO emissions, but only ∼40% of VOC emissions with the balance mostly from area sources such as solvent use and painting (Molina et al., 2002a). Whether the emissions from these area sources decrease on weekends by a similar fraction as mobile sources is uncertain. Some support for this comes from observations of robust CO vs. VOC correlations during the MILAGRO field campaign (deGouw, J. 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 (Blanchard and Tanenbaum, 2003).

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, consistent with meteorological studies suggesting nearly complete daily ventilation of the basin (e.g. deFoy et al., 2008). 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

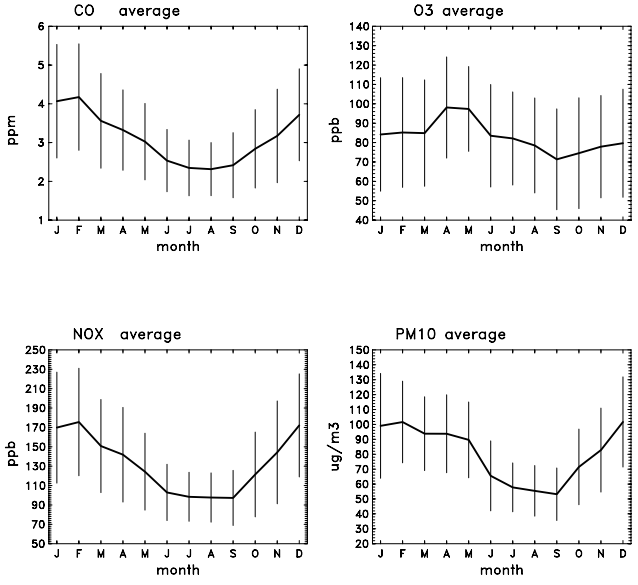

Fig. 6. Seasonal variation of the concentrations of CO, NO_x, and PM_{10} in the morning (average of the three highest concentrations between 7 a.m. and 12 noon) and O_3 in the afternoon (average of the three highest concentrations between 11 a.m. and 5 p.m.), for the years 2001–2007.

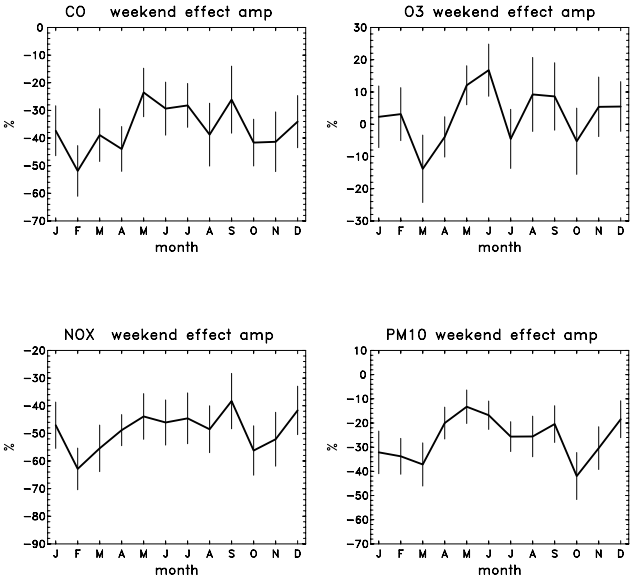

Fig. 7. Seasonal variation of the weekend effect (relative amplitude), for the years 2001–2007.

(hypothesis 6), owing to the heavier workday aerosol loading, merits some consideration. Castro et al. (2001) showed that surface NO_2 photolysis frequencies (J_{NO2}) 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 wavelengths (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_{NO2} 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.

4.2 Evaluation of L_N/Q

We consider here whether the magnitudes of the observed weekend changes in CO, NO_x, and O_3 are consistent with photochemical understanding. In Sect. 2.2 the theoretical expectation of how these magnitudes are related to each other was derived (Eq. 7) within the approximations discussed there. 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_x. 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 changes (taken from Table 2), approximating δO_x by δO_3 and with a photolysis enhancement (δJ=0.07) in the mid range of values discussed above (sensitivity to these approximations is discussed in Sect. 4.3). The values are rather scattered but clearly fall near or within the chemically permissible range, and moreover 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 small variations should be viewed with caution, because the uncertainty in L_N/Q is about $\pm$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 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 NO_x 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 NO_x-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 Sect. 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 75% 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 NO_x may be excluded precisely because O_3 formation is NO_x inhibited. This bias is more frequent on workdays because they are more strongly NO_x-inhibited (indeed, for 2007 Saturday NO_x values were actually higher than for workdays for the 75th percentile O_3 subset, while for all-day averages, shown in Table 2, Saturday NO_x is lower as expected).

The measurement-based values of L_N/Q found here are supported by recent modeling of the April 2003 MCMA field campaign. Lei et al. (2007, 2008) analyzed the correlations between simulated radical sources and production rates of NO_z(= $NO_y - NO_x$). The slopes of these correlations are equivalent to L_N/Q and show that, during the afternoon in the Mexico City urban area, over 90% of the radicals are removed via NO_x chemistry.

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. 4 and 5), 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. 5 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 studies using three-dimensional chemistry-transport models (CTMs) suggested a NO_x-limited regime (Molina et al., 2002a; West et al., 2004), while more recent CTM studies indicated a VOC-limited regime (Tie et al., 2007; Lei et al., 2007, 2008). 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 provides 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. We note also that urban and regional development has increased greatly in the past two decades (Lezama et al., 2002), so that the monitoring stations may have been sampling a more urban chemical regime in recent years.

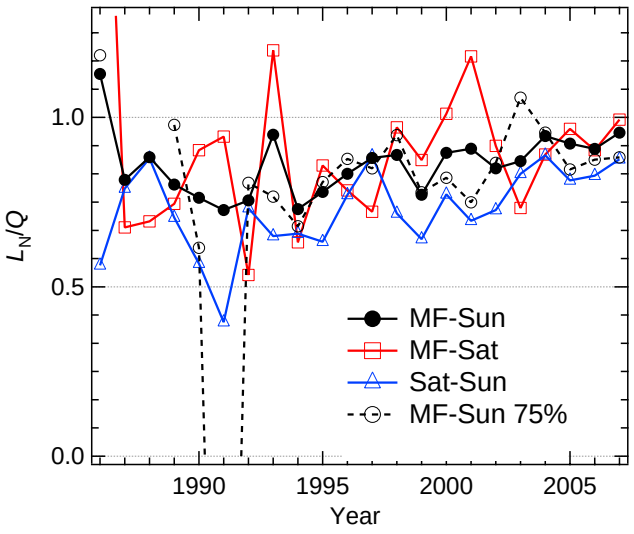

Fig. 8. Fraction of radical loss by NO_x chemistry relative to total radical loss (L_N/Q) derived from the observed weekend changes in CO, NO_x, and O_3 concentrations. Black line with solid circles is for workday (Monday–Friday) to Sunday changes; red line with open squares is for workday to Saturday, blue line with open triangles is for Saturday to Sunday changes; dashed black line with open circles is for workday to Sunday changes but including only high O_3 days (75th percentile). All calculations were made with a 7% change in photolysis rates (δJ, see text).

4.3 Sensitivity of L_N/Q

The sensitivity of estimated L_N/Q to several assumptions is presented here. For reference, we used the workday to Sunday changes, average of all days, and weekend photolysis enhancement of 7% (as in Fig. 8). We first consider the possibility that the weekend enhancements in photolysis frequencies may have been as large as 12% (δJ=0.12 rather than 0.07). Figure 9 shows that the estimated values of L_N/Q are then smaller by about 0.05. The net production of O_3 is usually photon-limited (in all but the most pristine parts of the troposphere) so that weekend enhancements in J-values contribute to the persistence of high O_3 values, and less change in NO_x inhibition is needed to explain the observations, leading to smaller values of L_N/Q. Although the values of L_N/Q do remain mostly in the VOC-limited regime ($>$0.5) even with these larger J-value enhancements, the sensitivity is seen to be significant and emphasizes the need for accurate long-term observations of the urban ultraviolet environment.

The sensitivity to using O_x 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 δO_x which

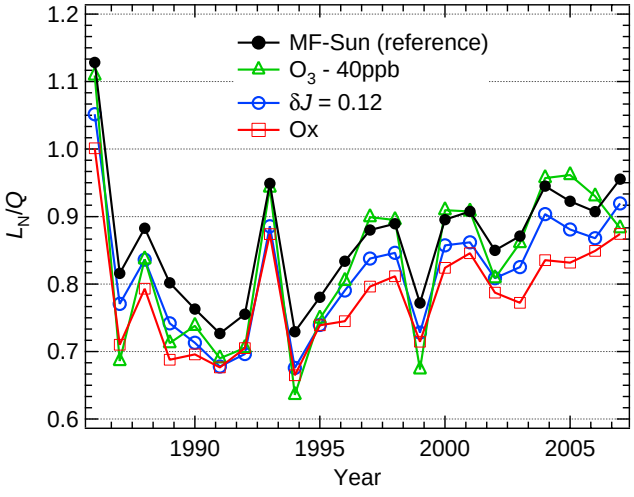

Fig. 9. Sensitivity of L_N/Q to assumed photolysis weekend enhancement of 12% rather than 7% (blue line, open circles); to a 40 ppb reduction in O_3 to account for regional background O_3 (green line, open triangles); and to using O_x (=O_3+NO_2) changes rather than O_3 changes (red line, open squares). The reference (black line, filled circles) is estimated from the workday to Sunday changes as in Fig. 8.

was then used in Eq. (7) in place of δO_3. For the workday to Sunday differences, this 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 NO_x 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 O_x 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 NO_x values on Saturday afternoons are nearly identical to those on workdays (see again Fig. 1), so δO_x is well approximated by δO_3.

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 O_x 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 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 ∼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.

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. Nitrogen chemistry accounts for most of the radical loss, with L_N/Q values (from Figs. 8 and 9) in the range 0.75 to 0.95; with these values, the normalized sensitivities of O_3 production (Eqs. 1–3) lie in the range −0.25 to −0.8 for NO_x, 0.6 to 0.9 for VOCs, and 0.8 to 0.95 for photolysis frequencies. 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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