



## Ozone weekend effect in Santiago, Chile

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### ABSTRACT

The study examined weekday–weekend differences in ozone, NO<sub>x</sub> (NO and NO<sub>2</sub>) and VOC concentrations in Santiago, Chile, from 1999 to 2007. The results provide evidence for the occurrence of an atmospheric phenomenon that produces higher ozone concentrations during weekends despite lower concentrations of ozone precursors. This phenomenon is known as the weekend effect (WE).

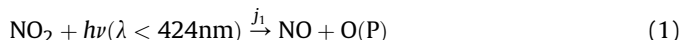
The overall ozone decrease since the spring of 2004 was a consequence of the implementation of several urban pollution control measures. Although these measures caused a decline in the number of days that exceed the national standard from two-thirds to one-third of summer days, the WE, which became statistically significant beginning in September 2004, could not be eliminated. Furthermore, VOC/NO<sub>x</sub> ratios decreased during the same period (2004), especially in the most industrialized area of Santiago. Similarly, under these regimes, the VOC/NO<sub>x</sub> ratios were higher on Sundays than on weekdays and caused higher ozone concentrations on Sundays.

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### 1. Introduction

Ozone is a secondary photochemical oxidant formed naturally by biogenic sources. Typical background ozone concentrations vary from 25 to 45 parts per billion (ppb) (Altshuller and Lefohn, 1996). However, anthropogenic emissions may increase ozone levels in or near metropolitan areas; the resultant ozone can be harmful to human health and plant life and can damage materials (Lee et al., 1996; Leiva et al., 2011).

Ozone is produced in the troposphere by the photolysis of NO<sub>2</sub> at wavelengths less than 424 nm (Blacet, 1952). The oxygen atom reacts with O<sub>2</sub> to produce O<sub>3</sub>. However, NO reacts rapidly with O<sub>3</sub> to regenerate NO<sub>2</sub>.

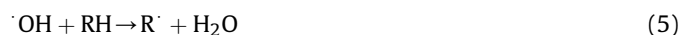


These reactions occur rapidly and establish a steady–state equilibrium for the ozone concentration according to the following NO–photostationary state equation (Leighton, 1961):

$$[\text{O}_3] = \frac{j_1}{k_3} \times \frac{[\text{NO}_2]}{[\text{NO}]} \quad (4)$$

where  $j_1$  is the photolysis rate of NO<sub>2</sub> to NO and O,  $k_3$  is the rate constant for the reaction of O<sub>3</sub> with NO, [NO<sub>2</sub>] is the concentration of nitrogen dioxide, [NO] is the concentration of nitric oxide and [O<sub>3</sub>] is the concentration of ozone. However, reactions (1) and (3) result in the cycling of NO and NO<sub>2</sub> on a typical timescale of minutes, with no net effect on ozone. A pathway leading to the net production of NO<sub>2</sub> without the destruction of ozone is required for ozone to accumulate.

This pathway was not understood until Greiner (1967) elucidated the key role of OH in the oxidation of organic compounds and two other groups, Heicklen et al. (1969) and Stedman et al. (1970), suggested that OH and HO<sub>2</sub> radicals were responsible for both the oxidation of the organics and the oxidation of NO to NO<sub>2</sub> according to the following reactions.



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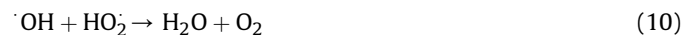
The  $\text{NO}_2$  produced by reactions (7) and (9) can produce ozone, and reactions (8) and (9) re-create radicals that can initiate another cycle.

After the key role of radical reactions with VOC and  $\text{NO}_x$  in the formation of ozone in the troposphere was understood, it became clear that ozone formation depends on the VOC/ $\text{NO}_x$  ratio. At low VOC/ $\text{NO}_x$  ratios, OH reacts predominantly with  $\text{NO}_2$ , removing radicals and retarding  $\text{O}_3$  formation.



Under these conditions, a decrease in  $\text{NO}_x$  concentration favors ozone formation because more OH is available to initiate  $\text{O}_3$  production through the oxidation of organic molecules. This low VOC/ $\text{NO}_x$  ratio, or VOC limitation, during the week is a necessary condition for the WE (Fujita et al., 2003a).

By contrast, high VOC/ $\text{NO}_x$  ratios favor the reaction of OH with VOC, which generates new radicals that accelerate  $\text{O}_3$  production. However, at a sufficiently low concentration of  $\text{NO}_x$ , or at a sufficiently high VOC/ $\text{NO}_x$  ratio, a further decrease in  $\text{NO}_x$  favors termination reactions that remove free radicals from the system, retarding  $\text{O}_3$  formation.



Thus, at a given VOC level, the  $\text{NO}_x$  mixing ratio produces a maximum amount of ozone (Fujita et al., 2003a; 2003b).

These atmospheric chemical mechanisms for ozone formation can be observed in an urban weekly cycle in which changes in precursor concentrations occur between weekdays and weekends. Slightly lower or higher urban ozone concentrations have been reported in some cities of North America, Europe and Asia during weekends (Atkinson-Palombo et al., 2006; Blanchard et al., 2008; Brönnimann et al., 2002; Geng et al., 2008; Jiménez et al., 2005; Parra et al., 2008; 2009; Pudasainee et al., 2006; Shan et al., 2008), despite the substantial reduction of  $\text{NO}_x$  emissions due to lower emissions from traffic and industrial sources. This phenomenon is known as the WE (Dodge, 1977). An appropriate understanding of WE conditions may provide effective strategies for atmospheric urban pollution control (Duan et al., 2008; Gros et al., 2007).

Although other hypotheses have been proposed, such as pollutant carryover near the ground or aloft, higher weekend VOC emissions, or greater photolysis due to decreased emissions of fine particles, the  $\text{NO}_x$  reduction hypothesis is the most consistent explanation (Fujita et al., 2003a, 2003b). Given reaction (3), a decrease in NO emissions results in less  $\text{O}_3$  titration, which results in higher morning  $\text{O}_3$  on weekends. By contrast, less  $\text{NO}_2$  results in more OH to initiate  $\text{O}_3$  production because inhibition of termination reaction (10) favors faster  $\text{O}_3$  accumulation on weekends (Heicklen et al., 1969). Other researchers have also concluded that the primary cause for higher ozone on weekends is the reduction in  $\text{NO}_x$  emissions in a VOC-limited chemical regime (Blanchard, 2001; Blanchard and Tanenbaum, 2006; Heuss et al., 2003; Lawson, 2003; Marr and Harley, 2002; Yarwood et al., 2003).

In this work, ozone trends were analyzed for urban areas of Santiago, Chile ( $33.5^\circ \text{S}$ ,  $70.6^\circ \text{W}$  see Fig. 1), which has historically experienced the most severe  $\text{O}_3$  pollution in Chile. Levels as high as 174 ppb (1-hr) have been measured. This city counts more than six million people within a topographical valley located 500 m above sea level (Instituto Geográfico Militar, 1979; Morales, 2006).

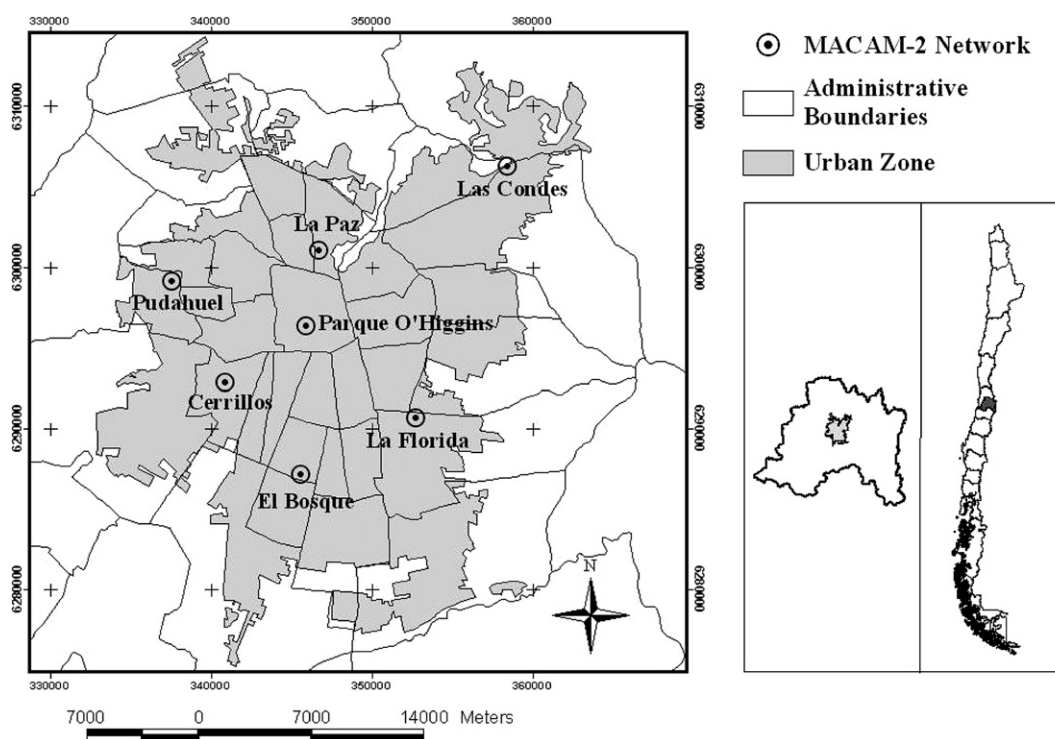


Fig. 1. Monitoring network of Santiago, Chile. Cerro Navia is not included.

Santiago is surrounded by a ring of hills, which include the Andes and Coastal ranges. This region has a Mediterranean climate, with a complex wind pattern produced by its topography and urban surface roughness. A very persistent low-speed southwest valley-mountain breeze predominates. In addition, a semi-permanent anticyclone condition prevails throughout the year, which leads to a persistent subsidence inversion with a base between 400 and 1000 m above the city. The resulting stable atmospheric gradient reduces the dispersion of air pollutants and results in high levels of pollution in the city's urban area (Leiva et al., 2004).

## 2. Methods

### 2.1. Data and methods

In 1997, the Santiago Metropolitan Government established an ambient air quality monitoring program managed by the Ministry of Health. Eight monitoring stations distributed in the city currently measure criteria pollutants (particulate matter, ozone, nitrogen dioxide, sulfur dioxide, carbon monoxide and VOC) as well as meteorological data. All of these stations support the network identified as MACAM-2, base of the Air Quality Monitoring Program in the Santiago metropolitan area (Fig. 1 and Table 1). However, only three stations can measure O<sub>3</sub>, NO<sub>x</sub> and VOC simultaneously: Las Condes, Cerrillos and Pudahuel.

To determine the weekly pattern of ozone concentrations, we have examined the data from September 1999 to April 2007 at the Las Condes, Pudahuel and Cerrillos monitoring stations. Ozone, NO<sub>x</sub> and VOC (monitored as nonmethanolic hydrocarbon compounds, NMHC) levels were measured with continuous monitors. Ozone was measured with a 400A API monitor; NO<sub>x</sub> was measured with a 9841A Labs monitor, and NMHC were measured with a TNMH 451 DANI monitor. The validation process includes the elimination of anomalous data and checking the zero and span as described in the national regulation (Ministerio de Salud, 2008).

The most common method used to measure the WE, as described by Atkinson-Palombo et al. (2006) and the references therein, is to compare mean ozone Sunday concentrations to those observed on Wednesdays (Altshuler, 1995). In addition, some researchers analyze peak levels by day of the week (DOW); others have analyzed specific percentiles of cases (Chow, 2003). However, we do not believe that the debate on how to select a measurement technique or the best location to determine the WE is yet settled. For the purposes of this study, we analyzed the daily O<sub>3</sub> and NO<sub>x</sub> average concentrations between 9:00 a.m. and 5:00 p.m. at different sites in the metropolitan area of Santiago (Las Condes, Pudahuel and Cerrillos). The time periods studied spanned from 1 September to 30 April for the years 1999–2007 because ozone is mainly a spring–summer issue in this area. To determine whether there was a significant difference between weekday and weekend concentrations, a *t*-test was applied to each day-to-day comparative study; Student's *t*-test (pooled) for equal variance and the Welch–Satterthwaite test (unequal variance) were also performed. These tests enabled a comparison of the general tendency between the two entire considered distributions with a confidence interval of 95%. The difference was considered statistically significant when *t* was greater than the *t<sub>c</sub>* value.

To determine day-of-the-week variations in the mixing ratios of ozone precursors, we estimated the VOC/NO<sub>x</sub> ratios during O<sub>3</sub> inhibition time, between 6:00 a.m. and 9:00 a.m., for any VOC/NO<sub>x</sub> ratios within the years of interest.

## 3. Results and Discussions

### 3.1. Ambient ozone concentrations

The maximum ozone concentrations were observed in the summer and spring seasons, primarily because of higher solar

**Table 1**  
MACAM-2 network in the metropolitan area of Santiago.

Label <sup>a</sup>	Station	Latitude (S)	Longitude (W)	Altitude (m) a.s.l.
F	La Paz	33° 25' 09"	70° 38' 55"	588
L	La Florida	33° 30' 48"	70° 35' 09"	654
<sup>b</sup> M	Las Condes	33° 22' 26"	70° 31' 21"	811
N	Parque O'Higgins	33° 27' 40"	70° 39' 29"	562
<sup>b</sup> O	Pudahuel	33° 26' 06"	70° 44' 52"	553
<sup>b</sup> P	Cerrillos	33° 29' 33"	70° 42' 46"	528
Q	El Bosque	33° 32' 38"	70° 39' 50"	574

<sup>a</sup> Labels are described in Fig. 1.

<sup>b</sup> Stations selected for the present study. Cerro Navia is not included.

radiation intensity and surface temperatures (Rappenglück et al., 2005). However, the observed peak ozone concentrations were spatially variable. The northeast sector of the city, represented by the Las Condes station, showed the highest ozone level whereas the lowest levels were measured in the west and southwest, which were represented by the Pudahuel and Cerrillos stations, respectively (Seguel A et al., 2009). The prevailing wind patterns (SW) transport ozone and its precursors to the northeast sector of the city, where higher ozone levels may exist over a larger area. Unfortunately, the monitoring resources in this area are limited.

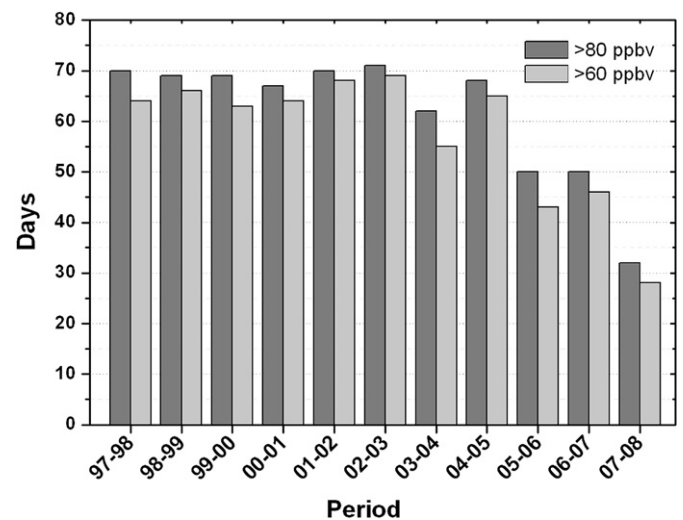
The Santiago Basin has recorded a large number of days with high pollution during the summer months (December, January and February). Although the number of days that exceed the Chilean National Ambient Air Quality Standard (NAAQS) of 80 ppb maximum hourly mean has decreased from 70 to 32 and the number of days that exceed the 61 ppb maximum 8-h average has decreased from 64 to 28, the standards are currently exceeded on more than one-third of the summer days in Santiago, Chile (Fig. 2).

### 3.2. Weekday variations

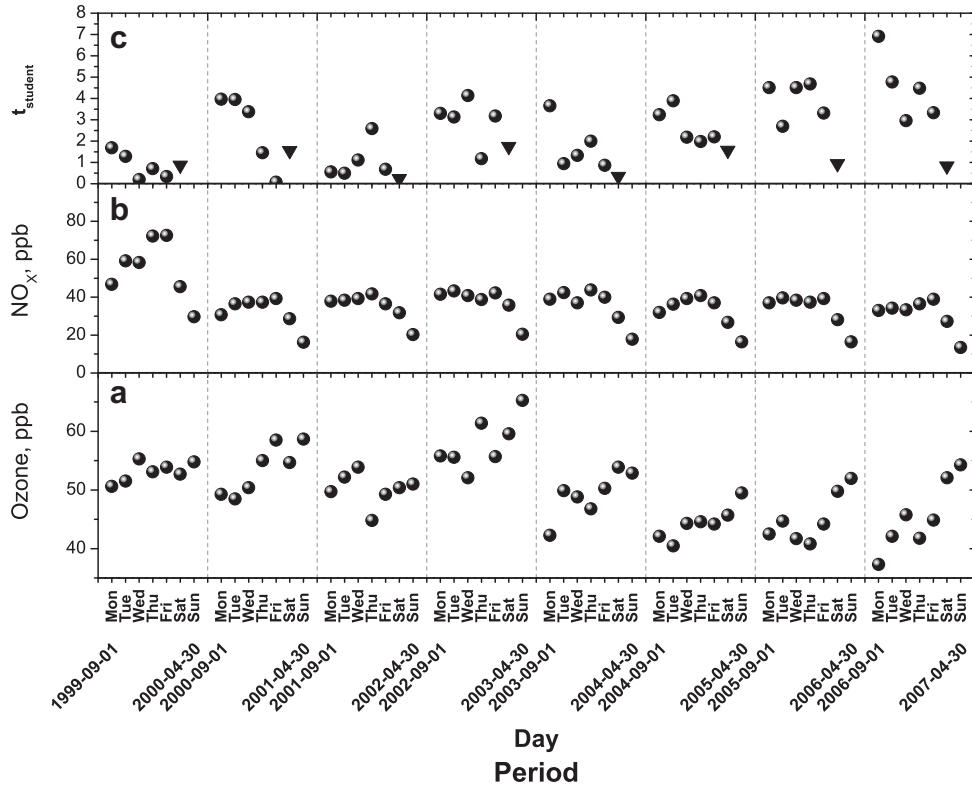
Elevated summertime ozone levels were observed on Sunday compared with Monday–Friday at three locations. As shown in Figs. 3, 4 and 5, the diurnal average ozone concentration was higher on weekends than on weekdays. Using both statistical tests (pooled and Welch–Satterthwaite), we found that the WE became statistically significant from spring 2004, when *t* was higher than *t<sub>c</sub>* by approximately 1.65-fold. This result (Student's *t*-test) was observed for all three stations studied (Figs. 3–5).

Figs. 3–5 also show that the weekday variations in NO<sub>x</sub> were inverse to those of ozone. The lowest NO<sub>x</sub> concentrations in a weekly cycle occurred on Sunday at all monitoring locations. At the Las Condes station, the NO<sub>x</sub> concentrations increased by as much as 190% on weekdays compared with weekends.

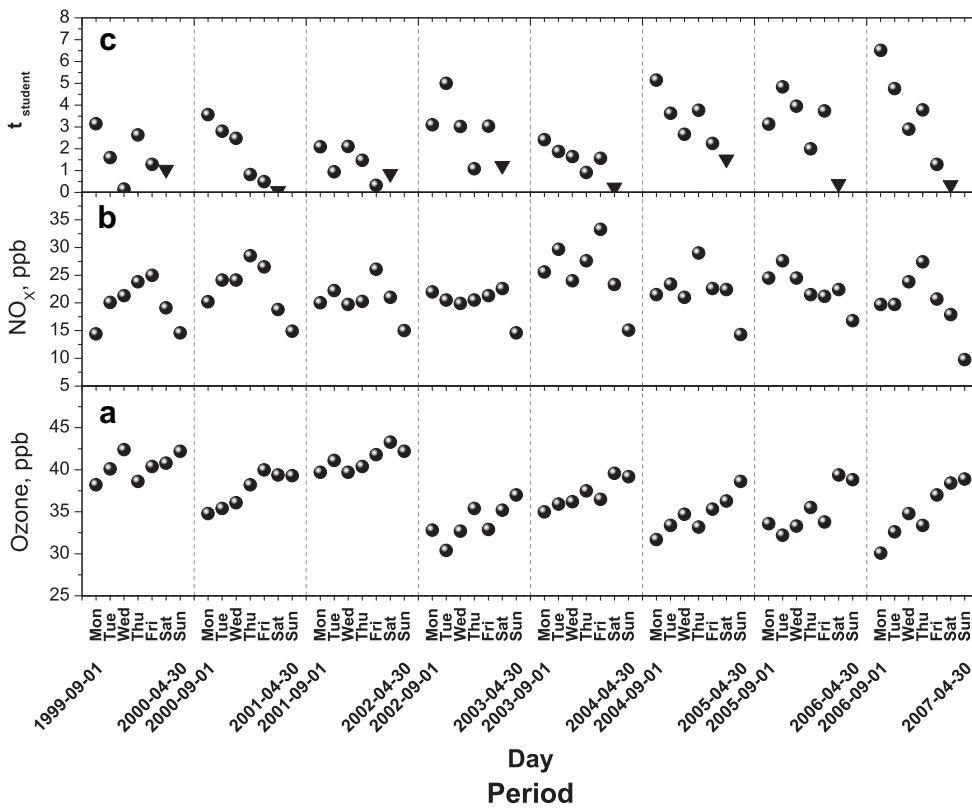
The ozone concentration also began decreasing in 2004 because several control measures were implemented to reduce the overall ozone in Santiago, Chile. At the same time, the WE became statistically significant. In December 2004, 800 old buses, 10% of the total number of buses at that time, were taken out of circulation, and



**Fig. 2.** Days exceeding the Chilean National Ambient Air Quality Standard (NAAQS) mean of 80 ppb maximum hourly and the NAAQS average of 61 ppb maximum over 8 h.



**Fig. 3.** Daily ozone average concentrations (a) and daily  $\text{NO}_x$  average concentrations (b) in a weekly cycle, determined between 9:00 and 17:00 for the 1999 to 2007 spring–summer periods (September to April), at the Las Condes station. Student's  $t$ -test was calculated for every weekday compared with Sunday (●:  $t$  Monday to Friday, ▼:  $t$  Saturday).



**Fig. 4.** Daily ozone average concentrations (a) and daily  $\text{NO}_x$  average concentrations (b) in a weekly cycle, determined between 9:00 and 17:00 for the 1999 to 2007 spring–summer periods (September to April), at the Pudahuel station. Student  $t$ -test was calculated for every weekday compared with Sunday (●:  $t$  Monday to Friday, ▼:  $t$  Saturday).

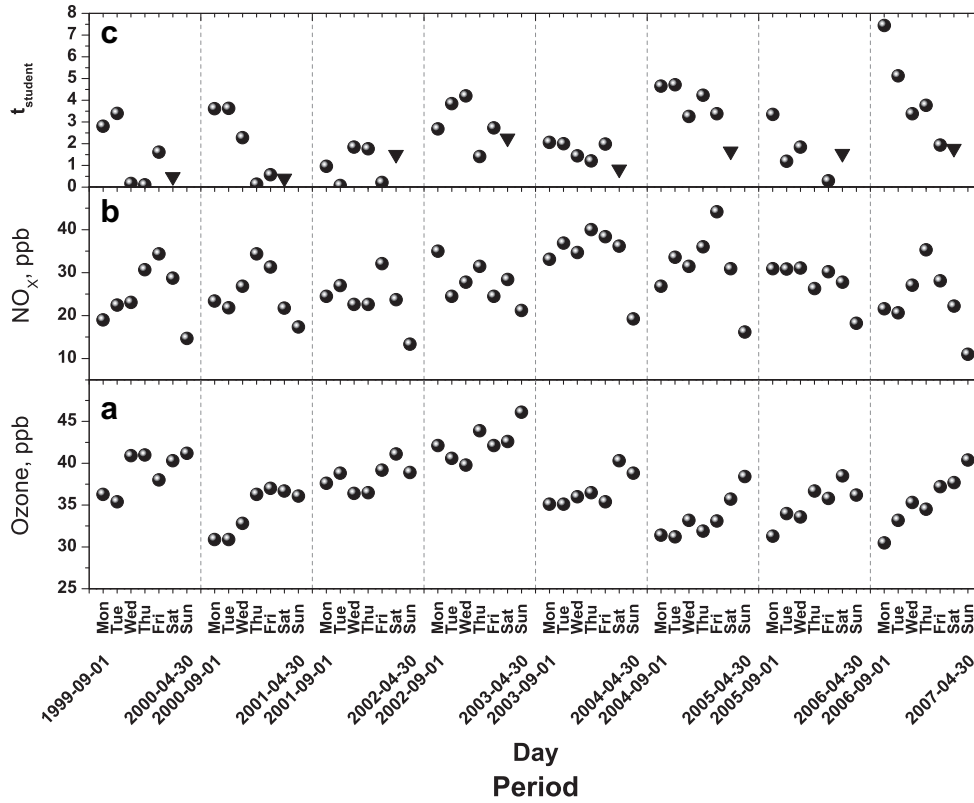


Fig. 5. Daily ozone average concentrations (a) and daily NO<sub>x</sub> average concentrations (b) in a weekly cycle, determined between 9:00 and 17:00 h for the 1999 to 2007 spring–summer period (September to April), at the Cerrillos station. Student's *t*-test was calculated for every weekday compared with Sunday (●: *t* Monday to Friday, ▼: *t* Saturday).

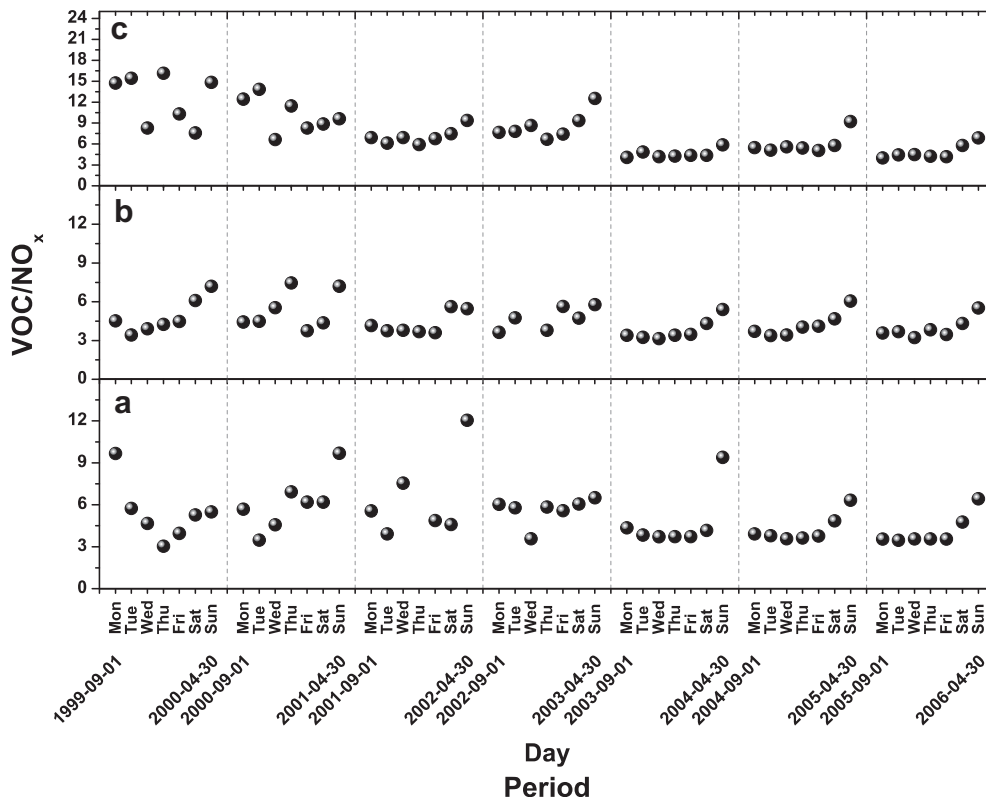


Fig. 6. VOC (NMHC)/NO<sub>x</sub> ratios determined under similar conditions of time (6:00–9:00 a.m.) and location for every spring–summer period and for each day of the week. (a) Las Condes Station, (b) Pudahuel Station and (c) Cerrillos station.

a thousand new buses began operating in October 2005. All public buses must now be equipped with high-efficiency diesel particle filters, and provisions must be made to obtain new buses (or retrofit old buses) to achieve lower NO<sub>x</sub> emissions (Lents et al., 2006). In addition, since July 2004, gasoline in the metropolitan area has contained a maximum of 30 ppm sulfur, and diesel has contained a maximum of 50 ppm sulfur. The new requirements also improved combustion and decreased BTEX (acronym that stands for benzene, toluene, ethylbenzene, and xylenes) and nitrogen content. Since January 2004, Santiago has required vapor recovery or emission-reducing systems for large gasoline storage tanks (>100 m<sup>3</sup>) for new gas stations, some older gas stations and for the tanker trucks that deliver the gasoline from large storage tanks to gas stations. In October 2005, 65% of the stations were certified. The controls implemented at that time clearly reduced overall ozone but did not reduce weekend ozone as much as weekday ozone.

### 3.3. VOC/NO<sub>x</sub> ratio

The effects of daily VOC (expressed as nonmethanic hydrocarbons or NMHC) and NO<sub>x</sub> concentrations on ozone behavior are well known. Fig. 6 shows the VOC (NMHC)/NO<sub>x</sub> ratios determined under similar conditions of time (6:00 to 9:00 a.m.) and location for every spring–summer period and for each day of the week. The period between September 2006 and April 2007 was not included because an insufficient number of measurements were collected.

Variations in the VOC/NO<sub>x</sub> ratio were observed during the week. Higher ratios on weekends could be explained by lower emissions from traffic in a city where mobile sources contribute 71% of NO<sub>x</sub> according to the last official inventory compiled in 2005 (DICTUC, 2007). By contrast, the VOC should be less variable during the week because mobile sources contribute less to the VOC than to NO<sub>x</sub>; on-road emissions represent 20% of the total VOC whereas area sources represent 73% of the total VOC. The three stations studied showed higher ratios on Sunday and Saturday than on Monday through Friday. Under this regimen, the lower ambient NO<sub>x</sub> concentration on the weekend should result in less inhibition of ozone during the weekend and less radical termination due to higher weekend VOC/NO<sub>x</sub> ratios, which leads to higher weekend ozone in Santiago, Chile.

In addition, differences in the VOC/NO<sub>x</sub> ratios were observed between the three sites and between the examined periods. The VOC/NO<sub>x</sub> ratio dropped at all sites after 2003 on both weekdays and weekends. From Fig. 6, a more drastic decrease between 2002 and 2003 and 2003 and 2004 can be distinguished, especially at the Cerrillos site. These periods coincide with a maximum industrial consumption of natural gas until the shortage in 2007. The reduction in the VOC/NO<sub>x</sub> ratio implies a significant reduction in region-wide VOC or possibly an increase in NO<sub>x</sub> at some sites. Nevertheless, these results are inconsistent with the last two official inventories (2000 and 2005) (DICTUC, 2007; National Center

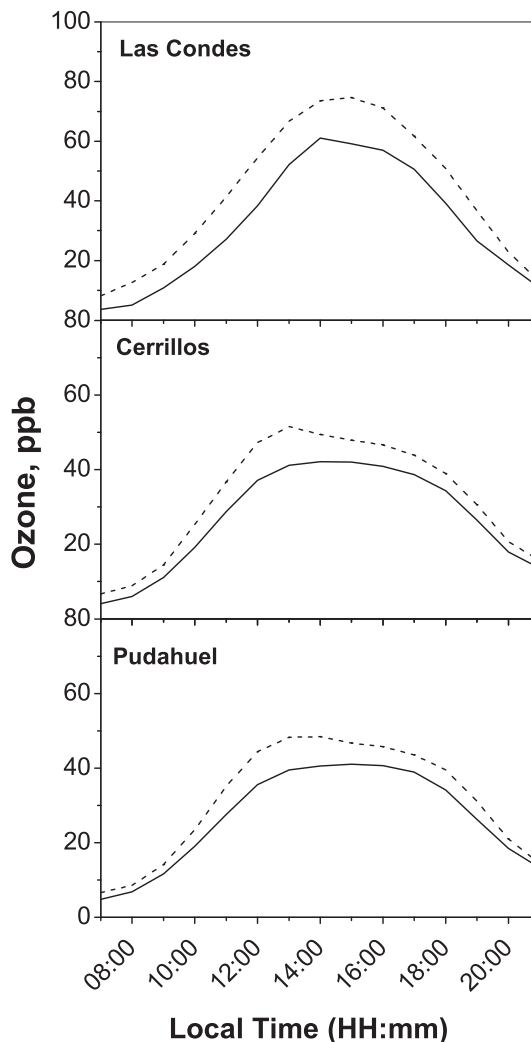


Fig. 7. Diurnal evolution of ozone concentrations for the 2006–2007 period. (—) weekday average for Monday through Thursday. (---) Sunday.

for the Environment CENMA, 2001), which reported a 29% increase in VOC and a 9% decrease in NO<sub>x</sub>, which indicates that the inventories should be evaluated and reconciled to the ambient concentration. Furthermore, as shown in Figs. 4 and 5, NO<sub>x</sub> increased after 2003 whereas ozone decreased at both sites. The ozone values are less than 40 ppb at these sites (a typical background level), which indicates that some of the decrease in ozone could be due to scavenging from increased NO<sub>x</sub>. Fig. 3 shows that Las Condes does not appear to have changed significantly since 2003, except on weekends.

### 3.4. Diurnal variations

Weekend–weekday differences in ozone concentrations were larger in Las Condes (see Table 2) than at the Cerrillos and Pudahuel stations. The latter two stations are located in areas where both residential and industrial activities occur throughout the week. In addition, the international airport is located in the Cerrillos commune. Las Condes, by contrast, is a downwind residential area where the transport of NO<sub>x</sub> emissions is expected to be much lower on weekends.

Fig. 7 shows the typical diurnal pattern observed in the city, where the maximum ozone concentration is observed between

**Table 2**  
Average weekday (Mon–Thu) to weekend (Sun) differences in ozone for the period 2006-09-01 to 2007-04-30, determined between 9:00 and 17:00.

Day	O <sub>3</sub> , ppb	%Delta
<b>Las Condes</b>		
Mon-Thu	41.8	30.1
Sun	54.3	
<b>Cerrillos</b>		
Mon-Thu	33.4	21.0
Sun	40.4	
<b>Pudahuel</b>		
Mon-Thu	32.7	18.9
Sun	38.9	

2:00 p.m. and 4:00 p.m. The figure also shows how the ozone increases on Sundays compared with weekdays for every station examined. Finally, the figure highlights the earlier accumulation of ozone on weekends because of reduced ozone inhibition. Other researchers have found that the accumulation time occurs an hour earlier on weekends compared with weekdays on the southern coast of California (Fujita et al., 2003a).

Lower NO<sub>x</sub> emissions on weekends decrease NO titration of ozone, thereby allowing O<sub>3</sub> to accumulate earlier on weekends than on weekdays. Ozone formation is also inhibited by the reaction of OH with NO<sub>2</sub>; the relatively lower NO<sub>2</sub> concentrations on weekends result in more OH radical being available to react with VOC and form additional O<sub>3</sub>. At this point, biogenic emissions become relevant because recent studies conducted in the metropolitan area show that in Las Condes, at noon, isoprene contributed to 10% of the overall ozone (Seguel, 2010).

#### 4. Conclusions

Day-of-the-week variations in ozone and its precursors were examined for the spring–summer ozone season for the years from 1999 to 2007. The maximum daily NO<sub>x</sub> mean concentration was found on Thursdays and Fridays whereas the minimum was frequently observed on Sundays. The NO<sub>x</sub> concentrations on Thursdays were 180%, 190% and 220% greater than the weekend concentrations at the Pudahuel, Las Condes and Cerrillos stations, respectively. Moreover, the VOC/NO<sub>x</sub> ratios were significantly higher on Sundays compared with weekdays.

After several urban pollution control measures were implemented in the metropolitan area, the VOC/NO<sub>x</sub> ratio on weekdays (~3.6) has increased on weekends (~6.4) since spring 2004, which has allowed higher ozone concentrations on weekends. These measures to reduce the overall ozone did not eliminate the WE. Moreover, the increasing VOC/NO<sub>x</sub> ratios, which are less than 8, are characteristic of a chemical process limited by VOC.

This WE phenomenon has been observed in many other polluted urban atmospheres, where changes in VOC/NO<sub>x</sub> ratios that occur on weekends lead to higher ozone concentrations on weekends.

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