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# Ozone and peroxyacetylnitrate in downtown Santiago, Chile

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**Abstract**

Peroxyacetylnitrate (PAN) and ozone have been measured during spring and early summer in downtown Santiago during 2002 and 2003. Although the values are lower than those reported at a site located downwind from the center of the city, ozone levels frequently surpass the air quality standard ( 80 ppb, 1 h or 60 ppb, 8 h mobile average), and PAN levels as high as 22 ppb have been measured. Ozone and PAN levels strongly correlate between them and with the maximum daily temperature. This dependence is not due to a direct relationship between temperature and irradiance, and allows a prediction of critical days from the temperature forecast. In fact, in days with temperatures below 29 °C, ozone quality standard is surpassed only 16% of the time, and PAN reaches values above 5 ppb only 7% of the measured days. On the other hand, when the temperature reaches above 29 °C, ozone surpass the quality standards 87% of the days and PAN values are above 5 ppb 83% of the measured days.


## 1. Introduction

Santiago City, due to relatively high emissions and unfavorable atmospheric and geographic conditions, suffers from high contamination levels (Artaxo et al., 1999; Rappenglück et al., 2000; Didyk et al., 2000). During winter, the main contamination is due to primary emissions: particulate matter, sulfur dioxide and $NO_x$. On the other hand, in late spring and early summer are frequent episodes of photochemical smog with relatively high levels of photochemical oxidants, such as ozone and peroxyacetylnitrate (PAN) (CONAMA, 1998; Rappenglück et al., 2000).

The highest levels of ozone have been measured in Las Condes, located in the predominant downwind direction (SW) from downtown (CONAMA, 1998; Jorquera et al., 1998; Rappenglück et al., 2000). In this quarter, the Chilean air quality standard of 80 ppb (hourly average) or 60 ppb (mobile 8 h average) is surpassed almost every day (CONAMA, 1998). Also, relatively high PAN levels have been measured at this location during a single monthly campaign carried out from 10 November to 10 December, 1996 (Rappenglück et al., 2000).

PANs are photochemical products with important roles in local and regional atmospheric chemistry (Kourtidis et al., 1993; Williams and Grosjean, 1990; Nielsen et al., 1981). PAN is the most abundant compound of the family, and values as high as several ppb have been measured in urban atmospheres

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(Rappenglück et al., 1993,2000; Gaffney et al., 1999). At these levels, PAN is a very toxic and lachrymator compound (Taylor, 1969; WHO, 1996). In addition, PAN can be transported during nighttime and be a free radical source far away from the locus of main primary emissions (Crutzen, 1979; Suppan et al., 1998; Aneja et al., 1999; Derwent and Jenkin, 1991). Furthermore, it has been considered as a better indicator of photochemical smog than ozone (Rappenglück et al., 2003; Bottenheim et al., 1994), due to its negligible natural background, and the fact that its time of depletion by new NO emissions is associated to its cleavage and can be considerably longer than that of ozone. PAN's small photolytic constant at ground level and relatively low reactivity with hydroxyl radicals and water solubility contributes to its stability, particularly at low temperatures. On the other hand, at temperatures higher than ca. 20 °C it readily decomposes with a complex kinetics whose rate is mainly determined by the $NO/NO_2$ ratio.

In downtown Santiago de Chile episodes of high ozone do not reach levels as high as in Las Condes, due probably to the continuous input of NO from the public and private mobile sources (CONAMA, 1998). However, there are not at present evaluations of PAN levels in this part of the city. In the present communication we report these data, together with companion results obtained regarding ozone levels. We discuss the similarities and differences of these results with those previously reported in Las Condes to establish the main differences between a location of high emissions and a location that can be considered as a receptor of the early morning emissions from downtown Santiago.

## 2. Experimental

PAN was measured at the Universidad de Santiago of Chile campus (USACH) by gas chromatography employing a capillary column and electron capture detection (GC-PAN from Meteorologieconsultgmbh, Germany) with 25 ppt detection limit (Volz-Thomas et al., 2002). The equipment provides real time measurements, 24 h a day, a value each 10 min. A calibration system for PAN is based upon the photolysis of acetaldehyde in presence of NO in a flow reactor. The

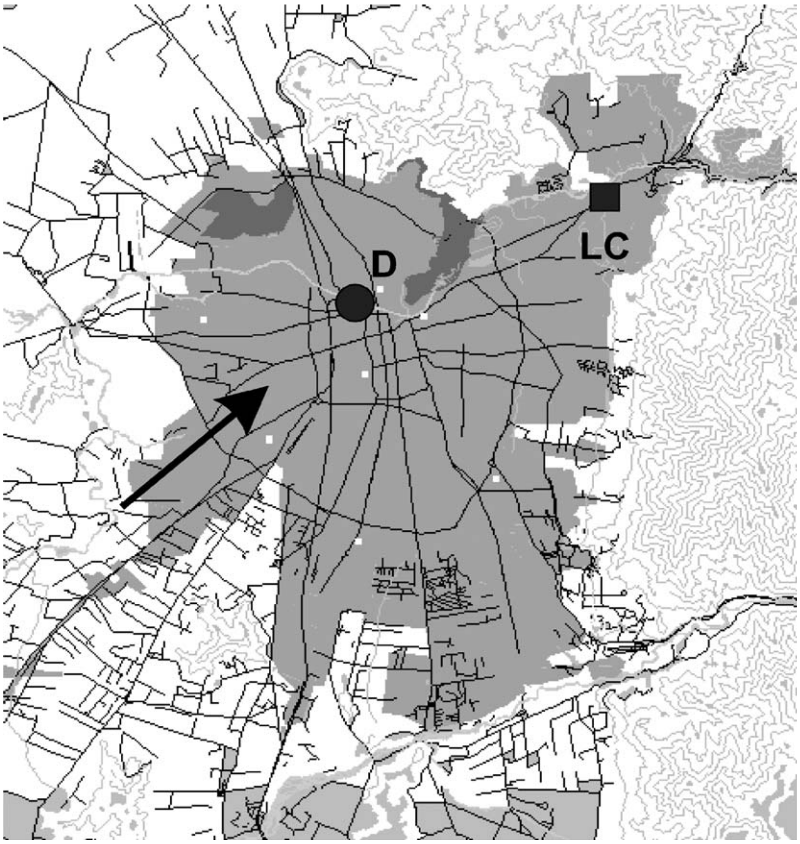


Fig. 1. Map of Santiago City. The approximate locations of the Las Condes (LC, ■) and downtown (D, ●) sampling sites are indicated in the figure. The arrow indicates the main wind direction during daytime.

reaction yield for PAN is 92± 2%. The estimated precision in PAN determinations is 5–6%.

Ozone, ambient temperature and radiation levels were determined at less than 100 m from the PAN monitor location. Ozone was continuously determined with a DOAS type automatic equipment, (OPSIS). The estimated error in ozone determinations was ±3–5%.

Solar radiation (total UV-A) was measured with a PMA 110 UV-A detector for solar light. This detector has a spectral response ranging from 320 to 400 nm, with a broad peak around 370 nm.

Carbon monoxide levels were continuously measured at a CONAMA monitoring station located 2 km from the USACH campus. Simultaneous measurements of ozone and sulfur dioxide, performed at the CONAMA station and the USACH campus, were very similar, indicating that data obtained in both sites can be directly compared. The localization of the sampling sites is indicated in Fig. 1. Measurements were carried out in spring and early summer during the years 2002 and 2003.

## 3. Results and discussion

Typical daily profiles of ozone and PAN are shown in Fig. 2. The profile obtained for a typical primary contaminant, carbon monoxide, is also included in this figure. The sharp morning peak observed for this contaminant is compatible with its predominant emission from mobile sources and Santiago's rush hour. On the other hand, the maximum obtained at the early afternoon for PAN and ozone is characteristic of the photochemical smog. The time of occurrence of this maximum is quite reproducible. This is emphasized by data shown in Fig. 3, corresponding to a whole week of continuous monitoring. The fraction of events with maximum at a given time is shown, in a hourly basis, in Fig. 4. This figure shows that PAN values sharply peak before 13 h. On the other hand, the ozone profile is slightly wider, with maximal between 11 and 16 h. This difference, that is observed most of the days, can be explained in terms of PAN instability, in particular at times of high ambient temperature. Furthermore, it is

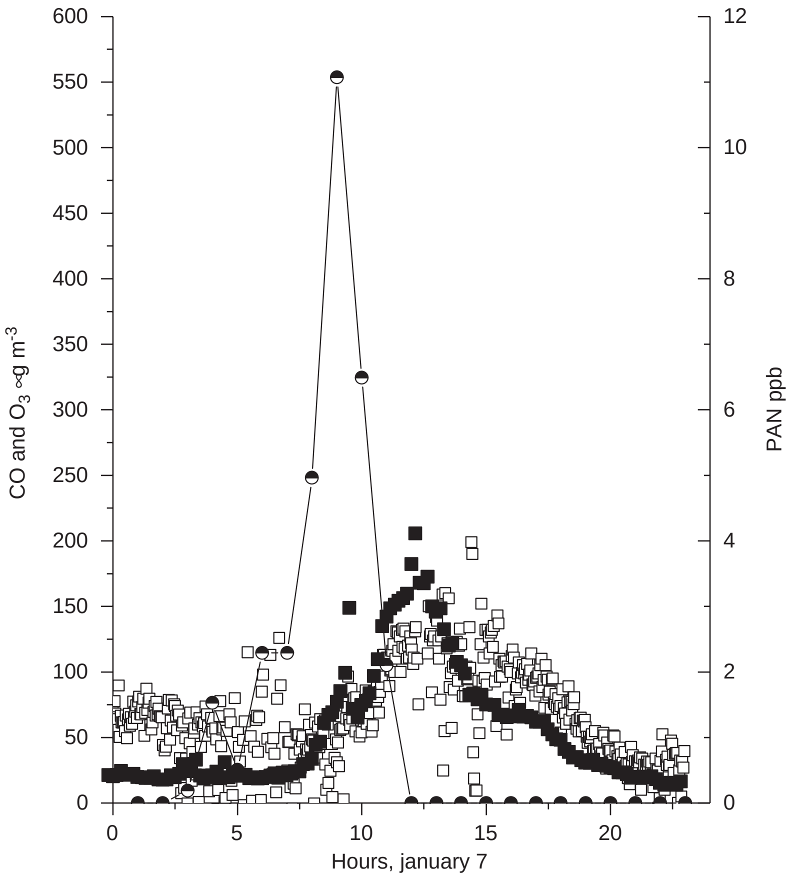


Fig. 2. Daily profiles of ozone (□) and PAN(■) measured on January 7, 2003 at the station located at the Universidad de Santiago campus. For comparison is included the daily profile of CO (◒) measured by the CONAMA network (downtown station).

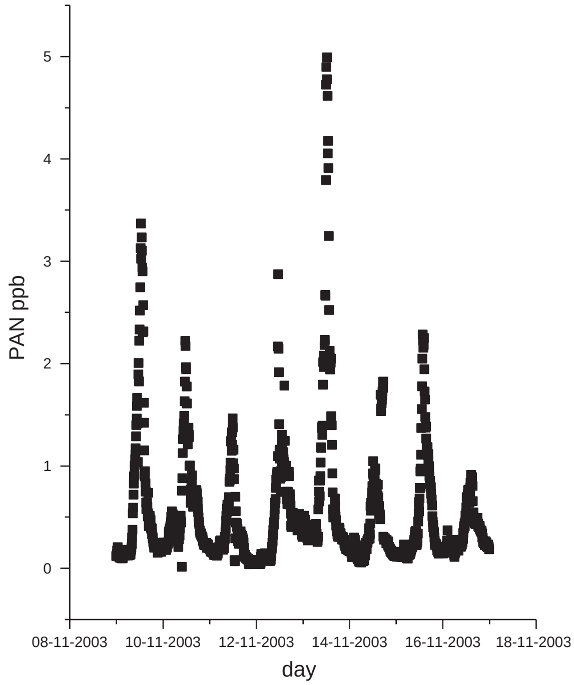


Fig. 3. Daily profiles of PAN measured from 8 November to 18 November, 2003, at the Santiago's University campus.

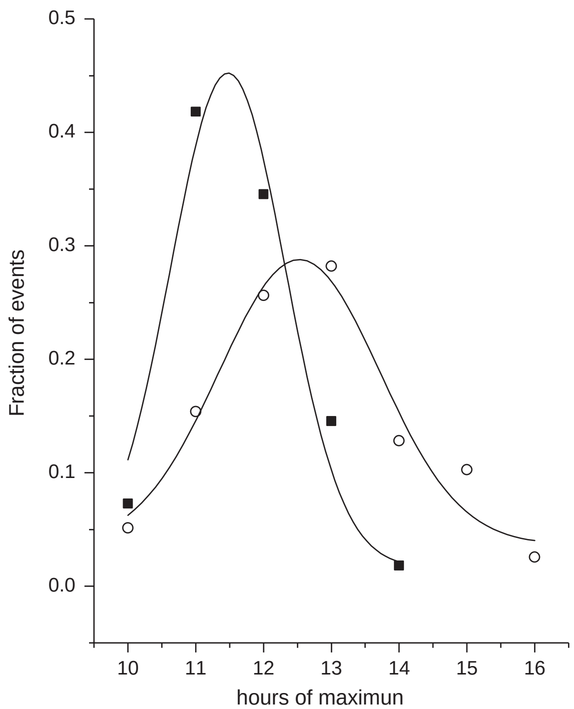


Fig. 4. Hours of maximum PAN (■) and ozone (○) levels. Data presented as the fraction of events with maximum at the indicated hours.

interesting to note that the fast decay in PAN levels, taking place between 13 and 15 h (period of maximal temperature), can be important in increasing the width of the early afternoon ozone pick. The afterwards decay of ozone can be easily explained in terms of increased NO emissions during afternoon rush hours and the decrease in irradiance. If the present data are compared to that derived from the 1996 campaign in Las Condes (Rappenglück et al., 2000), it can be concluded that the maximum in PAN takes places almost 1 h early downtown than in Las Condes. Furthermore, in this location the distribution of time for ozone is sharper and is centered at the same time than the PAN maximal (Rappenglück, personal communication). Small differences in temperature (lower in Las Condes) and less primary emissions (particularly NO) in LC could account for the differences.

Since both ozone and PAN have a photochemical origin, a fair relationship between the maximum values of both contaminants could be expected (Schrimpf et al., 1998; Rembges et al., 2001). If this were so, the easier ozone measurement could be employed as a simple indicator of PAN levels. The type of correlation obtained is shown in Fig. 5. The data show a fair correlation that can be best fitted to a monoexponential function. A similar, albeit smaller, correlation was observed in Las Condes (Rappenglück personal communication). Furthermore, a comparison of both sets of data (Table 1) shows that the absolute PAN levels and the ratio PAN/ozone are considerably larger in Las Condes. This can be due both to differences in location and changes in emission patterns from mobile sources during the time elapsed between both campaigns (Jorquera et al., 2000; CONAMA, 2003). However, it has to be considered that the non-linear correlation between ozone and PAN (Fig. 5) implies that not a clear meaning can be given to PAN/ozone average ratios. This non linear behavior could be due to the fact that in days of low photochemical smog the maximum PAN values tend to zero, while the maximum ozone values are similar to those of the natural background.

It has been frequently reported that ozone levels increase when the temperature increases (Wunderli and Gehrig, 1991; Sillman and Samson, 1995), a result that has been related to PAN instability (Sillman and Samson, 1995). In fact, thermal cleavage of PAN

$$CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO^* + NO_2^* \quad (1)$$

will contribute to ozone formation by reaction of the peroxyacetyl radical with NO (at low $NO_2$/NO ratios)

$$CH_3C(O)OO^* + NO \rightarrow CH_3C(O)O^* + NO_2 \quad (2)$$

followed by

$$CH_3C(O)O^* \rightarrow CH_3^* + CO_2 \quad (3)$$

Methyl radicals will ultimately lead to the production of $NO_2$ and, hence, ozone. Similarly, under conditions of low $NO_x$ levels, the peroxyl radical formed in Eq. (1) could react with hydroxyperoxyl radicals

$$CH_3C(O)OO^* + HOO^* \rightarrow CH_3C(O)OOH \quad (4)$$

leading to the formation of acetylhydroperoxide, whose subsequent decomposition would contribute to NO oxidation. On the other hand, due to its instability, the dependence of PAN levels with temperature is more complex (Sillman and Samson, 1995), but positive correlations between PAN and mean daily temperature (Wunderli and Gehrig, 1991) or maximum daily temperature (Schrimpf et al., 1998) have been reported. The same type of correlation is observed for the present data, both for ozone (Fig. 6A) and PAN (Fig. 6B). This is a very interesting result since it could imply that the temperature forecast could be employed as a very simple, although rough, predictor of daily maximum ozone and PAN levels. This predictive capacity is emphasized by the data collected in Table 2. It is interesting to note that, in spite of the lower emissions expected during Sundays and holidays, the data obtained in these days follow the same tendency than that of working days. The data presented in Fig. 6B comprise all measured days ($N = 70$) but two days with suburban fires around Santiago. During these two days the measured ozone and PAN levels were considerably higher than those expected from the maximum daily temperature and were not included.

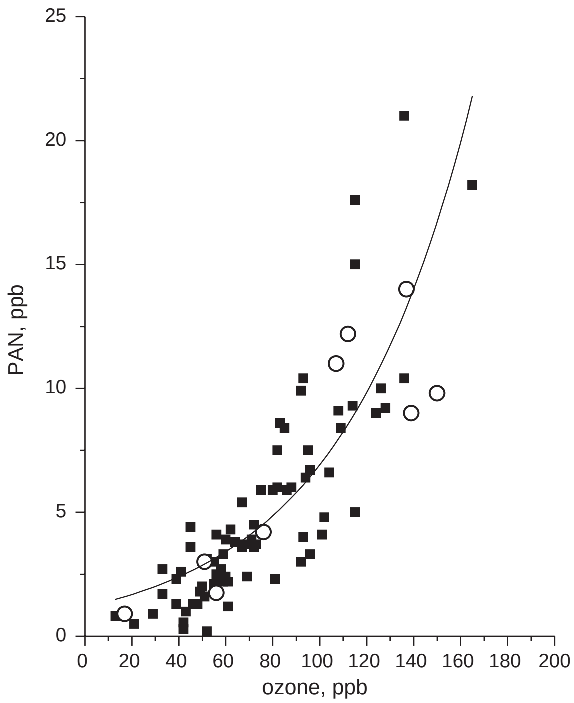


Fig. 5. Relationship between the maximum levels of ozone and PAN. (■) working days; (○) Sundays and holidays. Data obtained at the University campus during September, October and December 2002, and January and November, 2003. $N = 86$. The line shows the best exponential fit: $[PAN] = A \exp(B\,[ozone])$ with $A = 1.28$ ppb ; $B = 0.017\,(ppb)^{-1}$.

In order to assess the impact of the emissions and the atmospheric stability on PAN and ozone levels, we have plotted their daily maximum against CO concentrations, both at the early morning maximum (Fig. 7) and at the time of the peak of the secondary contaminants (data not shown). The data of Fig. 7 show a significant relationship between the early morning CO levels and the early afternoon maximum values of ozone and PAN. This relationship between early morning levels of primary contaminants and early afternoon ozone levels has been frequently reported and easily understood in terms of a photochemical oxidants formation through mechanisms involving hydrocarbons and $NO_x$ oxidation (Stephens, 1969; Bottenheim et al., 1994). It is interesting to note that holidays and Sundays values tend to concentrate in the upper part of the distribution, indicating that the decrease in primary emissions (as measured by CO levels) is not directly reflected in the maximum ozone and PAN levels. Several explanations, among them an increase in the VOC/$NO_x$ ratio due to the permanence of the biogenic emissions, can be advanced to account for this "Sunday" effect (Fugita

Table 1
PAN (average, minimum, maximum) levels and PAN/ozone ratio (average) measured in downtown Santiago (D) and in Las Condes (LC)

| Date | Site | Average (ppb) | Maximum (ppb) | Minimum (ppb) | PAN/$O_3$ (ppb) |
|---|---|---|---|---|---|
| September 2002 | D | 2.8 | 3.9 | 0.5 | 0.05 |
| October 2002 | D | 1.8 | 3.8 | 0.2 | 0.057 |
| December 2002 | D | 5.3 | 9.8 | 2.4 | 0.06 |
| January 2003 | D | 6.4 | 22 | 2.3 | 0.10 |
| November 2003 | D | 2.3 | 8.0 | 0.55 | 0.043 |
| November 1996 | LC | 9.4 | 21 | 1.5 | 0.095 |
| December 1996 | LC | 5.8 | 20 | 5.9 | 0.17 |

LC data taken from Rappenglück et al., 2000.

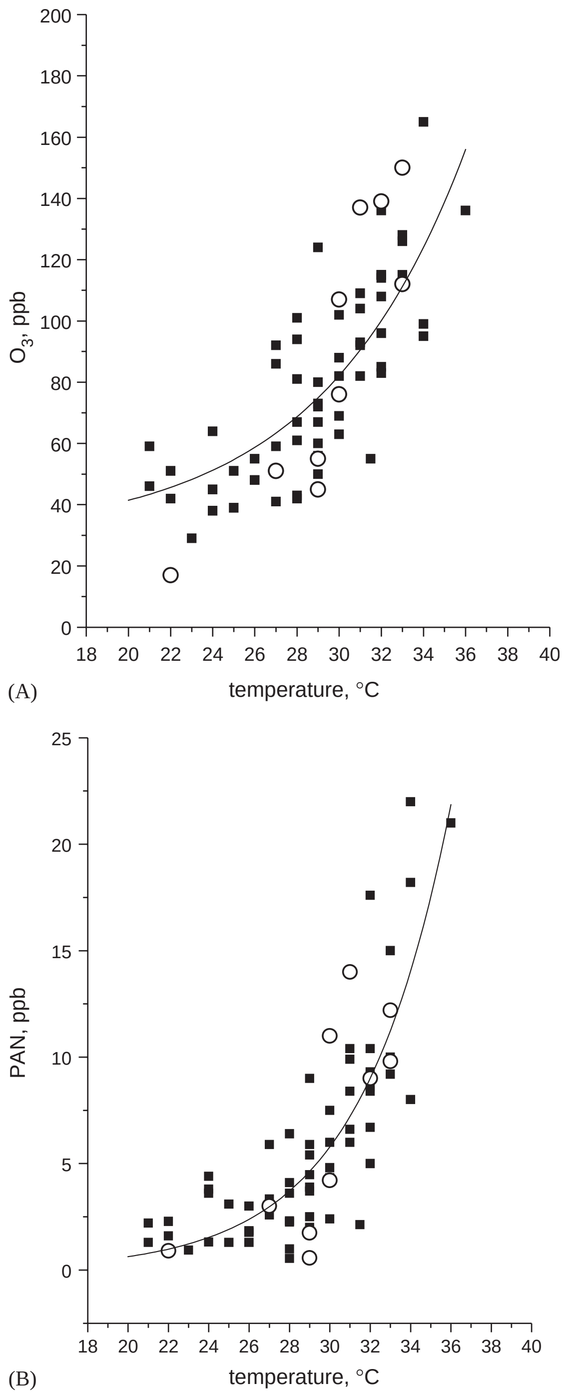


Fig. 6. Relationship between the photochemical oxidants maximum levels and the maximum daily temperature, measured in the same site and periods described in Fig. 5. (■) working days; (○)Sundays and holidays. (A) Data ($n = 70$) obtained for ozone. The line shows the best exponential fit: [Ozone] = $A$ exp ($B$ Temp) with $A = 4.03$ ppb ; $B = 0.1$ (°C)$^{-1}$. (B) Data ($N = 70$) obtained for PAN. The line shows the best exponential fit: [PAN] = $A$ exp ($B$ Temp.) with $A = 0.077$ ppb ; $B = 0.22$ (°C)$^{-1}$.

Table 2
Effect of the daily maximum temperature on the fraction of days with high levels of ozone and PAN ($N$ values indicate the number of days considered in each temperature interval)

| Condition/temperature | $T<29$ °C | $T>29$ °C |
|---|---|---|
| Ozone over 80 ppb | 0.16 ($N = 25$) | 0.87 ($N = 30$) |
| PAN over 5 ppb | 0.07 ($N = 27$) | 0.83 ($N = 30$) |

et al., 2000; Brönniman and Neu, 1997). Another significant feature of the data collected in Figs. 7A and B is the relatively large values of the ordinates, particularly for ozone. This implies that a reduction in primary emissions will be only partially reflected in the secondary contaminants levels. For example, a reduction in the morning CO levels by a factor two, from 2 to 1 mg m$^{-3}$ reduces the expected (average) ozone level from 98.1 to 83.9 ppb (14%), and the PAN level from 10.2 to 6.4 ppb (37%).

We have tried to see if early afternoon CO values (a measure of the early morning emissions and the atmospheric stability) correlated with the photochemical oxidant levels. Only a weak relationship was observed between PAN maximum values and the simultaneous CO levels (Table 3). On the other hand, no significant correlation was observed with ozone levels (Table 3). This would indicate that atmospheric stability (one the main factors leading to differences in mid-day CO levels) is not a dominant parameter in determining the photochemical oxidant accumulation. However, it is interesting to note that, both with early morning and simultaneous CO levels, PAN correlations are significantly higher than those shown by ozone data. The observed poor relationships could be due to an inverse relationship between irradiance and atmospheric stability and, hence, with carbon monoxide levels. In order to test this possibility we tried to correlate CO levels during the early afternoon with the irradiance intensity. No significant correlation was observed (data not shown).

In order to assess if the dependence of PAN and ozone levels with the daily maximum temperature is subrogate to the dependence of the temperature with the irradiance (Schrimpf et al., 1998), we tried to correlate the secondary contaminant maximum levels with the irradiance intensity measured at noon. No positive relationship was observed (data not shown). Also, no clear relationship was observed between temperature and irradiance levels over the period (late spring and early summer) considered in the present communication. This can be easily explained since maximum irradiances take place in December, while maximum temperatures tend to concentrate in January. This leads even to anticorrelations between irradiance and temperature ($R = -0.49$, $N = 40$). On the other hand, we found a significant correlation between the early morning CO

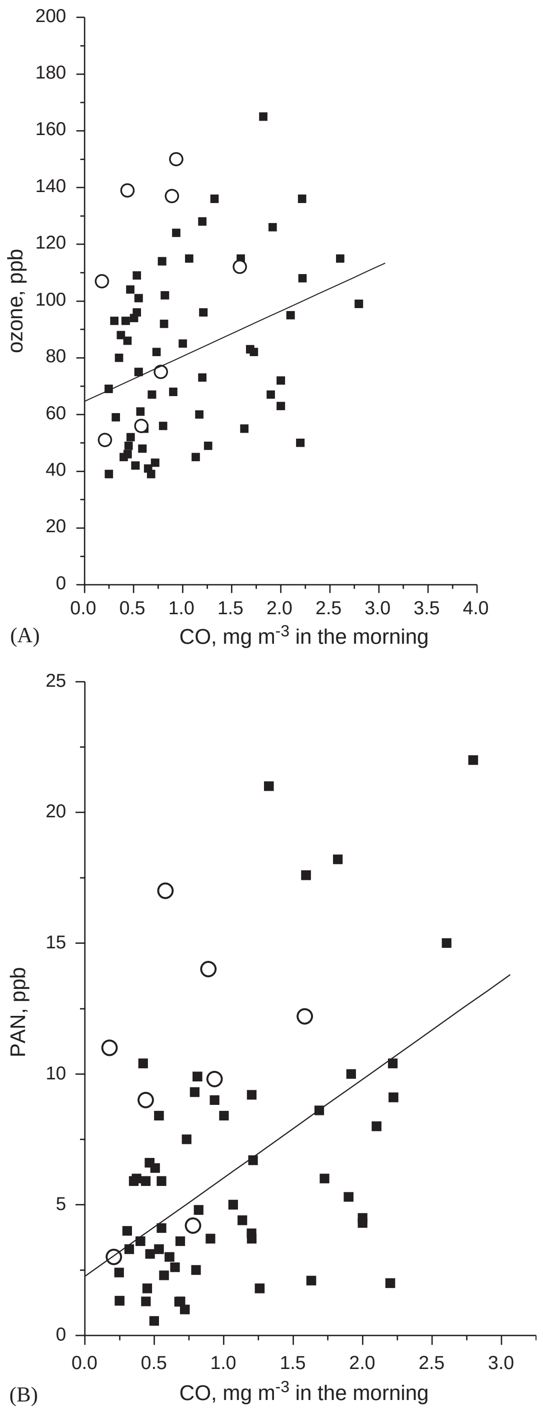


Fig. 7. Relationship between maximum levels of the photochemical oxidants and the early maximum levels of CO, (■) working days; (○) Sundays and holidays. Data obtained during September, October and November, 2002, and January, 2003. (A) Data ($N=65$) obtained for ozone. The best straight line corresponds to [ozone] = $A+B$ [CO] with $A=70$ ppb ; $B=14.2$ ppb$(\mathrm{mg\,m^{-3}})^{-1}$. (B) Data ($N=65$) obtained for PAN . The best straight line corresponds to [PAN] = $A+B$ [CO] with $A=2.9$ ppb ; $B=3.5$ ppb $(\mathrm{mg\,m^{-3}})^{-1}$.

levels and the daily maximum temperature (Fig. 8). Interestingly, holidays and Sundays tend to lay at the bottom of this distribution, as expected from the lower levels of emissions during these days. This result, together with those mentioned regarding the lack of differences among holidays and working days in oxidant levels (Figs. 6A and B) explains the relatively high values of oxidants in holidays observed in Figs. 7A and B.

The results shown in Fig. 8 imply the possibility that the dependence with temperature, observed in Figs. 6A and B, could be subrogate to the dependence of the photochemical products with the concentration of primary contaminants present during the early morning. This increase in early morning CO concentrations in days of high daily maximum temperatures could be related to the characteristics of Santiago's micrometeorology, where the presence of a coastal trough by depressing early morning mixing depths is associated with high maximum temperatures (Rutllant and Garreaud, 1995).

The relationships found in the present work are summarized in Table 3. The most noticeable feature of the present data is the strong relationship between maximum daily temperature and maximum levels of the photochemical oxidants, ozone and PAN. This strong dependence is not due to a direct relationship between temperature and irradiance, and it is particularly intriguing for PAN, that can be expected to readily decompose at higher temperatures (Atkinson et al., 1992; Finlayson-Pitts and Pitts, 1986; Bridier et al., 1991). The relationship between oxidant levels and daily temperature observed in downtown Santiago could result from a combination of several factors:

(i) A relationship between intrabasin circulation of the polluted air masses and temperature, favoring the transport of ozone to the downtown sampling site. However, the fact that a similar strong relationship between maximum ozone levels and maximum local temperature is also observed in Las Condes (data not shown) would indicate that the observed relationship takes place over all the urban area.
(ii) The particular micrometeorology of Santiago, where low mixing heights in the morning are frequently related to high early afternoon temperatures (Rutllant and Garreaud, 1995).
(iii) An increase in the VOC/$NO_x$ ratio in days of high temperature, due to an increase in hydrocarbons evaporations and biogenic emissions. In particular, it has been observed that biogenic contribution to VOCs in Santiago is maximal at the hours of highest temperatures (Rappenglück et al., 2004).

At present, it is difficult to establish the influence of these factors. Analysis of the relationship between intrabasin circulation and temperature, as well as careful

Table 3
Relationships among the variables considered in the present work

| Correlation | Type | $R$ o $R^2$ | P | CHI $^2$ |
|---|---|---|---|---|
| PAN vs. ozone | Exponential | 0.69 | | 5.76 $(ppb)^2$ |
| Ozone vs. $T$ | Exponential | 0.64 | | 399 $(ppb)^2$ |
| PAN vs. $T$ | Exponential | 0.69 | | 7.48 $(ppb)^2$ |
| Ozone vs. maximum CO | Linear | 0.30 | 0.013 | |
| PAN vs. maximum CO | Linear | 0.47 | $<0.0001$ | |
| Ozone vs. simultaneous CO | Linear | 0.14 | 0.37 | |
| PAN vs. simultaneous CO | Linear | 0.32 | 0.018 | |
| Maximum CO vs. $T$ | Exponential | 0.32 | | $0.31(mg\,m^{-3})^2$ |

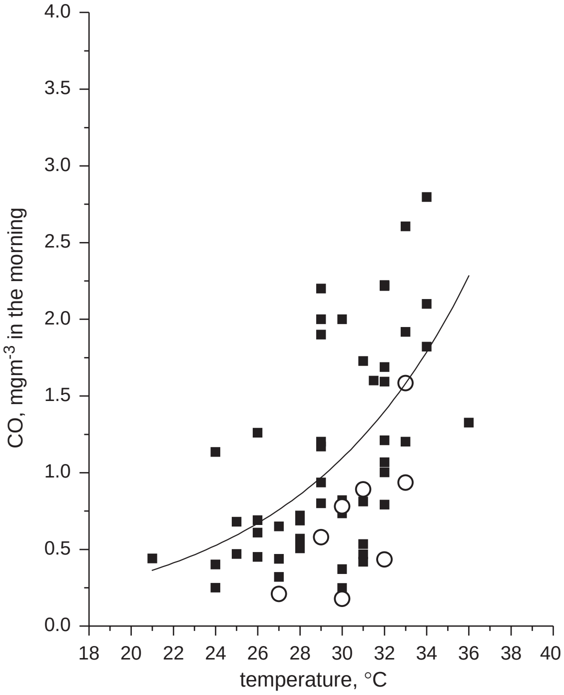


Fig. 8. Relationship between the early morning maximum levels of carbon monoxide and the daily maximum temperature. (■) working days; (○)Sundays and holidays. The line shows the best exponential fit:[CO] = $A$ exp ($B$ Temp) with $A = 0.022\,mg\,m^{-3}$ ; $B = 0.13\,(°C)^{-1}$.

simultaneous measurements of ozone, PAN, $VOC/NO_x$ ratios and biogenic VOCs levels are needed in order to assess the relevance of the above-mentioned factors. Furthermore, it has to be taken into account that the capacity of the maximum temperature forecast to predict maximal ozone and PAN levels can be employed only for periods of similar irradiation and without significant changes in the primary emission pattern. However, these considerations also apply to other approaches employed to forecast oxidant daily maximum levels (Jorquera et al., 1998).

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