OZONE LEVELS ASSOCIATED TO THE PHOTOCHEMICAL SMOG IN SANTIAGO OF CHILE. THE ELUSIVE ROL OF HYDROCARBONS

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ABSTRACT

Santiago of Chile presents, in autumn and summer, high levels of oxidants and, in particular of ozone. Peculiar features of this phenomenon are a strong dependence of the contamination with the daily maxima temperature and a weekend effect, comprising relatively high ozone levels in spite of reduced emissions of its precursors. A common explanation of these effects could be an increase in the VOCs/NOx ratio. In order to test this possibility we perform la multiparametric analysis of Santiago's historical data. This data treatment corroborates a robust dependence of maxima ozone levels with temperature and a moderate weekend effect. In fact, ozone levels in weekend days are similar to those of working days, in spite of significantly reduced primary emissions (29 % of NOx and 20 % of CO). However, no increase in VOCs/NOx ratios, measured at the early morning rush out hours, is observed in high temperature days. On the other hand, the data suggest a moderate increase of the VOCs/NOx ratio in week ends. This would indicate that other factors beyond a simple increase in VOCs levels contribute to the above mentioned peculiarities of oxidant levels in the urban atmosphere of Santiago

Key words: Ozone, Santiago of Chile, VOCs/NOx ratio, weekend effect.

INTRODUCTION

High ozone levels are present in Santiago of Chile during spring, summer and autumn. [1, 2, 3] These high ozone levels reach their maximum values at early afternoon hours and are attributable to the photo-mediated oxidation of hydrocarbons and nitrogen oxides.

Two characteristics of the maxima ozone levels are noticeable:

i) a high dependence with the daily maximum temperature. [2]

ii) during weekends the maximum ozone levels are similar and even higher than those measured during weekdays in spite of reduced emissions during the weekend days.[4,5]

These two peculiarities are not exclusive of Santiago of Chile, and have not been conclusively explained. A positive correlation between maximum daily temperature and ozone levels has been reported previously in Santiago,[2] Malaga (Spain),[6] Lovozero (Russia), [7] Belgrade (Serbia), [8] Maryland (USA), [9] Tokyo (Japan).[10] . This dependence has been frequently explained in terms of changes in the rate constants of the processes involved in the chain oxidation of volatile organic compound (VOCs) and nitrogen oxides (NOx),[11] the relationship between temperature and solar radiation, [9] urban heat island effects[10] and/or in terms of a relationship between atmospheric stability and ground-level temperatures.

Decreased emissions of primary pollutants (VOCs and NOx) during weekends should decrease the amounts of secondary oxidants (ozone, PAN) during these days. However, this naive prediction is frequently not fulfilled and similar, and even lower ozone concentrations, have been reported during weekdays. This apparent anomalous effect has been reported in Santiago (Chile),[2] Cairo (Egipt),[4] Kathmandu valley (Nepal),[5] California (USA),[12] Hyogo (Japan),[13] Norwestern Spain,[14] and Lovozero (Russia).[7] The California Air Resources Board [15]described three main potential causes of the weekend effect: i) reduction in NOx emissions; ii) changes in NOx emissions time profiles; iii) increase in solar radiation associated to reduced amounts of air suspended particles. Khoder [4] has suggested that the weekend effect could result from changes in the VOCs/NOx emission ratio.

Ozone formation in Santiago is VOCs controlled [16] and hence increases when the VOCs to NOx ratio increases. It can be postulated that, due to contribution of biogenic emissions and evaporation, the VOCs/NOx ratio could increase during weekends and high temperature days. Then, the temperature and weekends effect could have a common origin. Data aimed to test this assumption are evaluated in the present communication.

DATA COLLECTION

The following analysis is based on data collected in the MACAM 2 net quality network operated by CONAMA from December 2009 to March 2010 at Parque O´Higgins station,(POH), located down town Santiago City. Some data obtained in Las Condes station, (LC), was also employed for comparison. This station is located in the periphery of the city and presents the highest ozone levels. NOx were measured with a Thermo Fisher Scietific Analyzer, model 42i Hi NO-NO_2 (Limit detection (LD) < 50 ppt; ± 1% precision. Ozone was measured with a Photometric ozone analyzer, Thermo Environmental Instruments, model 49i (LD 0.25 ppb; ± 1% precision). CO was measured using a Thermo 48i TLE (LD 0.04 ppm; ± 1% precision). Non-methane hydrocarbons (VOCS) were measured employing methane and total non methane analyzer, Synspec alpha 115 instruments (LD 100 ppb < 0.1% precision. Measurements were averaged for one hour periods. All instruments are periodically calibrated by CONAMA.

RESULTS AND DISCUSSION

In order to assess the effect of weekends upon the primary emissions, CO and NOx levels measured at the POH station during the morning rush hours were analyzed by a multiparametric equation considering their concentrations as dependent variables and the maximum temperature and the type of day as independent variables. To fulfill this aim, days were characterized by arbitrary numerals (0 for week ends and 1.0 for week days):

$$CO = a_{CO} + b_{CO}\,T + c_{CO}\,(day) \quad (1)$$

$$NOx = a_{NOx} + b_{NOx}\,T + c_{NOx}\,(day) \quad (2)$$

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Table 1. Coefficients derived from multiple correlations given by Eqns. (1) and (2) in ppbv.

	A	b	c
CO	-1189.9 ± 449.8 p = 0.094	65.14 ± 10.13 p<0.0001	163.57 ± 94.69 p = 0.0869
NOx	-183.79 ±73.01 p = 0.0133	9.14 ± 2.46 p = 0.00032	52.19± 15.42 p = 0.00095
VOCs	-11.56 ± 0.171 p = 0.946	5.472 ± 5.764 p = 0.344	22.482 ± 35.79 p = 0.535
O_3	-65.240 ± 8.560 p< 0.0001	4.179 ± 0.288 p<0.0001	1.0097 ± 1.802 p = 0.576

The values of the coefficients of Eqns. (1) and (2) are collected in Table 1. The values of coefficient **c** indicate a positive correlation with the type of day for CO and NOx. The fact that these coefficients are positive implies that emissions are higher during week days. In fact, the data of Table 1 indicate that during weekends the levels during the morning rush hours are reduced in 188 ppbv and 52.8 ppbv for CO and NOx, respectively. These values amount to a reduction of 20% and 29 % for CO and NOx, respectively. On the other hand, it is interesting to note that there is not a significant reduction in VOCs emission during weekends, pointing to an increase in the VOCs/NOx ratio during these days.

A peculiar feature of the coefficients given in Table 1 is the high significance of the contribution of b values, implying that larger values of morning NOx and CO levels are observed in days of high maxima temperatures. This is probably due to meteorological factors such as cloud covering. In particular clear skies (and hence high maxima temperatures) are usually related to cold nights with significant radiative inversions. However, this effect is not observed regarding VOCs emissions. This is probably due to the numbers of sources that contribute to VOCs levels.

A similar multiparametric relation was applied to ozone data:

$$O_3 = a_{O3} + b_{O3}\, T + c_{O3}\,(day) \qquad (3)$$

The values and significance of the coefficients obtained with this data treatment are included in Table 1. These data show a strong positive dependence with the temperature, as reported in previous works.[2] On the other hand, no correlation with the type of day is observed. These effects are visualized in Figure 1 for the data collected in park O'Higgins. In this figure is evident the strong dependence of ozone maxima levels with temperature. On the other hand, the data obtained during weekends and weekdays are randomly distributed validating the conclusions derived from the coefficients given in Table 1.

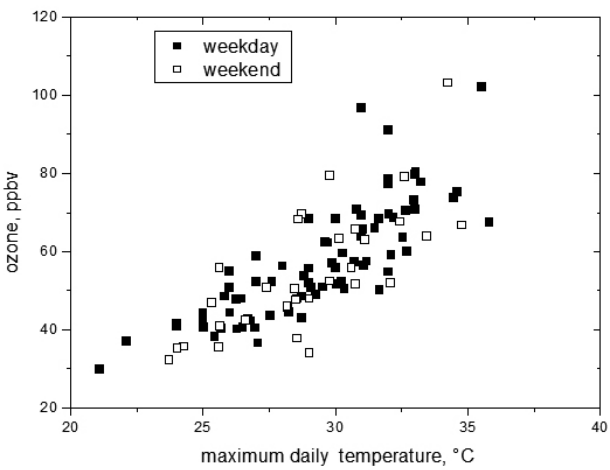

Fig.1: Relationship between ozone maxima levels and maximum daily temperature collected in park O'Higgins.

Taken together, the dada discussed in the former section indicate that smaller emissions in precursors (CO and NOx) during weekends are not translated to lower ozone levels during the day. Since the levels of ozone are VOCs controlled,[16] a plausible explanation could be an increase in the VOCs/NOx levels in weekends and or in high temperature days. These changes could be due to evaporation of solvents and or a significant contributions of biogenic emission VOCs that will be unaltered during week ends. In order to test these possibilities, we apply to the data a multiparametric relationship involving the ratio VOCs/NOx as dependent variable and temperature and type of day as independent variables (ppbv):

$$R = VOCs/NOx = a_R + b_R\, T + c_R\,(day) \qquad (4)$$

a= 4.204 ± 2.005 p=0.0384
b= -0.0688 ±0.0677 p= 0.311
c= -0.6708±0.4250 p = 0.1175

These values imply that there is not a simple relationship between the VOCs/NOx ratio and the temperature and/or the type of day.

As an alternative analysis aimed to evaluate the relevance of the VOCs/NOx ratio on ozone maxima daily values, a correlation was attempted employing three independent variables and ozone levels as dependent variable

$$O_3 = a_{O3} + b_{O3}\, T + c_{O3}\,(day) + d_{O3}\,(VOC/NOx) \qquad (5)$$

The values of the coefficients derived from this treatment were: (ppbv)
A=-61.60 ± 9.06 p< 0.0001
b = 4.09 ± 0.30 p < 0.0001
c = 0.87 ± 1.90 p = 0.64
d = - 0.52 ± 0.42 p = 0.23

These values would indicate that the only relevant parameter is the temperature, and that no significant influence of the morning VOCs/NOx ratio or the type of day is observed. The lack of dependence of the VOCs/NOx ratio with the type of day (Eq 4) and its null influence on ozone levels (Eq 5) could be due to the fact that the ratio has been evaluated at the rush hour. This selection was based on the premise that rush hour emissions strongly influence the early afternoon levels of ozone[17]. However, the influence of evaporation and biogenic emissions could be relevant only during high temperature times.

In order to get further inside on the factors that regulate the high levels of ozone measured after noon, we apply to the data a multiparametric relationship (multiple regression analysis) employing ozone as dependent variable and the maximum temperature, NOx and VOCs levels measured at rush time, and the type of day as independent variables:

$$O_3 = a_{O3} + b_{O3}\, T + c_{O3}\, VOCs + d_{O3}\, NOx + e_{O3}\,(day) \qquad (6)$$

The parameters obtained, as well as their significance, are included in Table 2.

Table 2. Parameters and significances estimated employing Eqn. 6.(ppbv)

a_{O3}	b_{O3}	c_{O3}	d_{O3}	e_{O3}
-55.84 ± 8.50 P < 0.0001	3.73 ± 0.29 P < 0.0001	- 0.00029 ± 0.0046 P = 0.95	0.045 ± 0.01 P < 0.0001	-1.13 ± 1.8 P = 0.54

Several conclusions can be derived from these data:

i) There is a strong positive dependence with the maximum temperature. This is a very robust dependence that appears irrespective of the data treatment.

ii) In spite of reduced NOx emissions during weekends (Table 1), the measured ozone levels are not influenced by the type of day. It is so confirmed the "weekend effect" but this is not enough, during the tested period, to produce higher ozone levels;

iii) The correlations observed between the maximum ozone levels and the primary pollutants (VOCs and NOx) measured at rush time are rather unexpected. There is observed a strong positive correlation with NOx levels ($p < 0.0001$ and a total lack of dependence on VOCs levels ($p = 0.95$).

Interestingly, similar lack correlation of maxima ozone with morning VOC

levels were observed in Las Condes, where there are observed the highest values of ozone, presumably formed by photo oxidation of the polluted air masses transported from the center of Santiago.[18] A multi parametric regression such as (Eq 6) with maxima ozone in Las Condes, rendered no correlation with VOCs morning levels . In fact, the coefficients for VOCs as independent parameters were 0.00029 ± 0.0046 (p=0.95) and 0.00202 ± 0.0028 (p=0.388) for VOCs measured at rush time in POH and Las Condes, respectively. On the other hand, significantly correlation was found in LC ozone levels with NOx rush time values measured in POH (0.07938 ± 0.032 p= 0.0159). These correlations imply that the lack of dependence of ozone with morning VOCs and the dependence with NOx values in not restricted to POH and takes place also in a receptor site as LC.

In terms of isopleths[19] and rush time emissions, point iii) would imply that ozone levels are NOx limited in Santiago's atmosphere. This point has been a matter of discussion. Early ozone modelation [20] concluded that photochemical smog in the city was NOx limited. On the other hand, Elshorbany [16] modelated the ozone sensitivity towards VOCs and NOx , concluding that, in spite of relatively large VOCs/NOx ratios, ozone levels were VOC limited. Similarly, Seguel [21] from the fact that NOx (mean daily concentration) decreases and ozone (mean diurnal concentration; 9 to 17 h) increases during week ends concluded that secondary pollutants are VOC limited. The variety of responses could then result from the different scenarios chosen to take into account the effect of primary pollutants upon the levels of photochemical oxidants.

CONCLUSIONS

Ozone maxima daily levels are similar in weekdays and weekends, in spite of reduced NOx emissions (ca 29 %) in weekend. This implies a moderate "weekend effect) that could be attributed, at least partially, to an increase in VOCs/NOx ratio.

Of the tested variables, maximum temperature, type of day, VOCs, NOx and VOCs/NOx ratio, the strongest and most persistent correlation observed was that of maximum daily ozone concentration and maximum daily temperature.

The discussion regarding if ozone levels are NOx or VOCs controlled is still open. In particular, the answer will depend upon how ozone levels (diurnal average or maximum value) and VOCs and NOx levels (rush time or average values) are considered. Furthermore, it is important to take into account that conclusions derived from sensitivity analysis correspond to VOCs and/or NOx values constrained along all the simulation.

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