

Seasonal dependence of peroxyacetylnitrate (PAN) concentrations in downtown Santiago, Chile

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RESUMEN

El ozono y el nitrato de peroxiacetilo (PAN) son contaminantes secundarios de origen fotoquímico. Es por lo tanto esperable que alcancen sus máximas concentraciones en periodos de alta irradiación solar (primavera y verano). Sin embargo, en la ciudad de Santiago de Chile se presentan altas concentraciones de PAN en época de otoño. Los promedios del valor máximo diario son: 4.0 ± 1.7 ppb, en otoño (mayo y junio); 0.9 ± 0.5 ppb en invierno (julio y agosto); 1.9 ± 1.0 ppb en primavera (octubre y noviembre) y 3.1 ± 1.4 ppb en verano (enero y marzo). En otoño, los valores integrados del perfil diario de concentración son también considerablemente mayores que en otros periodos del año (promedio del perfil diario: 38 ppb-hora en mayo y 13 ppb hora en enero). Este comportamiento se relacionaría con la menor estabilidad térmica del PAN en verano. Este factor, junto a la alta estabilidad atmosférica y menores alturas de la capa de mezcla en los meses de otoño, explicaría los altos niveles de concentraciones medidos en periodos de baja irradiación solar.

ABSTRACT

Peroxyacetylnitrate (PAN) and ozone are considered typical photochemical secondary pollutants and, as such, are expected to reach higher concentrations in periods of high irradiance (summer). However, in Santiago, PAN highest values are reached in autumn. The average of daily maximums are: 4.0 ± 1.7 ppb in autumn (May and June); 0.9 ± 0.5 ppb in winter (July and August); 1.9 ± 1.0 ppb in spring (October and November); 3.1 ± 1.4 ppb in summer (January and March). In autumn the integrated daily values are also considerably higher than in other periods (averages of 38 ppb h in May and 13 ppb h in January). This behavior is related to a lower PAN's thermal stability in summer. This factor, together with an increased atmospheric stability and lower height of the mixing layer in autumn explains the high levels measured in periods of relatively low solar irradiance.

Keywords: PAN, downtown Santiago City, photochemical smog.

1. Introduction

Peroxyacetylnitrates are photochemical products with important roles in local and regional atmospheric chemistry (Kourtidis *et al.*, 1993; Williams and Grosjean, 1990; Nielsen *et al.*, 1981; Rembges *et al.*, 2001; Gaffney and Marley, 1993). Peroxyacetylnitrate (PAN) is the most abundant compound of the family, and concentrations as high as several ppb have been measured in polluted urban atmospheres (Rappenglück *et al.*, 1993; Gaffney *et al.*, 1999; Rappenglück *et al.*, 2000). At these levels, PAN is very toxic to vegetation and humans, being a potent lachrymator (WHO, 1996; En-Jang and Ming-Huei, 1995; Taylor, 1969). In addition, PAN can be transported, mostly during night time and/or in winter time due to the lower ambient temperatures, thus becoming a free radical source far away from emission areas (Crutzen, 1979; Derwent and Jenkin, 1991; Gaffney and Marley, 1993; Suppan *et al.*, 1998; Aneja *et al.*, 1999).

PAN has been considered a better indicator of photochemical smog episodes than ozone (Bottenheim *et al.*, 1994; Rappenglück *et al.*, 2003), due to its negligible natural background and the fact that its depletion by new nitrogen oxides (NO) emissions must be preceded by its thermal cleavage and can be considerably slower than that of ozone removal. Summer daily profiles of PAN have been determined in several highly polluted cities, and most studies indicate that daily maxima of ozone and PAN take place at hours of high irradiance. These maxima increase with temperature and are closely correlated (Wunderli and Gehring, 1991; Sillman and Samson, 1995; Rubio *et al.*, 2004). The ratio of the maximum daily values (PANmax / Ozone-max) tends to increase when the maximum daily temperature increases.

Seasonal changes in PAN levels have been less studied. In remote sites, maximum PAN mixing ratios have been observed in winter time, a result related to the increased PAN's thermochemical stability (Gaffney and Marley, 1993). Also, relatively high PAN mixing ratios have been reported during autumn on windless clear-sky days (Aneja *et al.*, 1999; Pippin *et al.*, 2001; Rembges *et al.*, 2001). To explain these results it has been proposed that air masses can reach conditions of high NO_x mixing ratios and high levels of volatile organic compounds (VOC), conditions that would favor PAN production. In order to assess the behavior of the PAN/ozone ratio under conditions of low solar irradiance and temperature (that would disfavor their production) and high atmospheric stability and low height of the mixing layer (that would favor the accumulation of primary pollutants) we have measured oxidant concentrations in Santiago de Chile atmosphere in different periods of the year. The data obtained are presented and discussed in the present communication.

2. Experimental

PAN, toluene, ozone, nitrogen dioxide and UV-A irradiance were measured at the Universidad de Santiago de Chile (USACH) campus, near downtown Santiago city.

Toluene (detection limit 1.3 ppb; precision 8%), ozone (detection limit 1.5 ppb; precision 4%) and nitrogen dioxide (detection limit 0.5 ppb; precision 6%) were measured at 7.5 m height with a

DOAS automatic instrument (OPSIS) with 453 meters optical path length. The instrument provides a measurement every 10 minutes.

PAN was measured by gas chromatography employing a phenylmethyl polysiloxane/dimethyl polysiloxane capillary column and electron capture detection (GC-PAN from Meteorologieconsult GmbH, Germany) with 25 ppt detection limit (Volz-Thomas *et al.*, 2002). Sampling was performed at 3 meters altitude above ground, and the equipment provides real time measurements, 24 hours a day, every 10 minutes. The calibration system is based on the photolysis of acetone in presence of NO in a flow reactor, with a reaction yield for PAN of $92 \pm 2\%$. The estimated precision in PAN determinations was 9%. The technique has been validated in inter-comparison experiments (Schrimpf *et al.*, 1995).

Solar radiation (total UV-A) was measured with a PMA 110 UV-A detector from Solar Light Co. This detector has a spectral response in the 320 to 400 nm range, with a broad peak around 370 nm.

CO and NO concentration values were obtained from the local Government Monitoring Network. Data were taken from monitoring stations located at Parque O'Higgins and/or Cerrillos (henceforth denoted as POH and CER), ~0.2 km from the USACH campus. These data were obtained with a NO_x/NO monitor Labs model 9811, limit of detection 0.5 ppb, and precision 1 ppb, and a CO monitor Labs model 9830, limit of detection 0.06 ppm, precision 0.1 ppm. Dews were collected and measured as previously described (Rubio *et al.*, 2002)

3. Results and discussion

Measurements were carried out during October 2004 and November and December 2003 (spring), January and March 2004 (summer), April, May and June 2004 (autumn), and July, August and September 2004 (winter). Monthly averages of maximum daily PAN values are given in Table I. Rainy days have not been considered in these averages. The values given in this table are considerably smaller than those previously reported by Rappenglück *et al.* (2000), at a sampling site (Las Condes) located ~12 km east of downtown. This difference can be related to the different location of the sampling sites. This is evidenced when ozone levels reported by Rappenglück *et al.* (2000) in Las Condes and POH are compared. It is noticeable that in POH, a sampling site near to the USACH campus, ozone values are considerably smaller than those measured in Las Condes.

The data of Table I, as well as other relevant measurements, are summarized in Table II and in Figure 1. The results obtained for toluene, CO and NO_x are those expected given the higher stability and lower mixing layer during cold time. However, it is noteworthy that maximum values are observed in late autumn and early winter (May and June). On the other hand, the behavior of ozone is that expected for a typical secondary pollutant generated in photochemical smog episodes, with maximum values in summertime and early autumn (November to April). As well, the behavior of PAN is intermediate between that of a primary pollutant and ozone, with maximum values during autumn. The tendency of PAN to accumulate in cold weather (relative to ozone) is further emphasized if the ratio PAN/ozone is considered (Fig. 2). This figure clearly shows a noticeable

increase in PAN to ozone (maximum values) ratios during May and June, relative to summertime. Furthermore, the PAN diurnal peak is considerably wider in May than in summertime (Fig. 3 for one day example), leading to considerably larger integrated daily PAN values during late autumn. Averages of the integrated values, excluding rainy days, are given in Table III.

Table I. Monthly averages of maximum daily values of PAN (ppb).

Month	n	Average value	Maximum value	Minimum value
Nov	21	2.2 ± 1.4	5.6	0.5
Dec	30	2.3 ± 1.4	7.6	0.5
Jan	15	2.0 ± 0.56	3.1	1.1
Mar	29	3.7 ± 1.67	6.7	0.8
Apr	30	2.9 ± 1.80	6.1	0.4
May	21	4.1 ± 1.80	7.1	0.6
Jun	7	3.8 ± 1.12	5.9	2.2
Jul	8	0.9 ± 0.7	1.8	0.1
Aug	31	0.8 ± 0.37	1.5	0.1
Sep	23	1.6 ± 1.1	3.9	0.1
Oct	30	1.7 ± 1.0	3.7	0.2

n = number of measurements. Rainy days not considered.

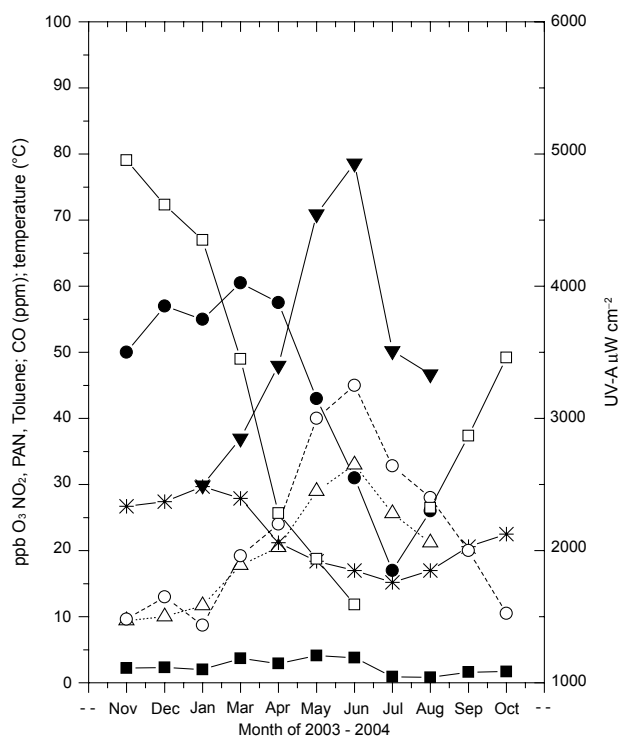


Fig. 1. Monthly average of daily maximum concentrations of toluene (Δ), PAN (\blacksquare), ozone (\bullet), nitrogen dioxide (\blacktriangledown), carbon monoxide (\circ), temperature ($*$) and UV-A radiation (\square).

Table II. Average maximum daily values of PAN, ozone, CO, toluene, NO₂, temperature, UV-A radiation.

Month	PAN ppb	O ₃ ppb	CO ppm	Toluene ppb	NO ₂ ppb	NO ₂ /NO*	T °C	UV-A μW cm ⁻²
Nov	2.2	50	0.96	9.4	---	2.4	26.7	4726
Dec	2.3	57	1.13	10.0	---	4.4	27.4	4670
Jan	2.0	55	0.87	11.7	30	5.2	29.7	4349
Mar	3.7	60	1.92	17.8	37	7.7	27.9	3450
Apr	2.9	57	2.40	20.5	48	2.4	21.2	2283
May	4.1	43	4.0	29.0	71	2.9	18.4	1936
Jun	3.8	31	4.5	33.0	79	1.2	18.8	1592
Jul	0.9	17	nm	25.6	50	1.3	15.2	---
Aug	0.8	26	2.8	21.2	47	2.0	22.5	2323
Sep	1.6	---	2.0	---	---	4.5	20.6	2868
Oct	1.7	---	1.05	---	---	5.0	22.5	3460

*Values measured at the time of daily maximum PAN concentrations.

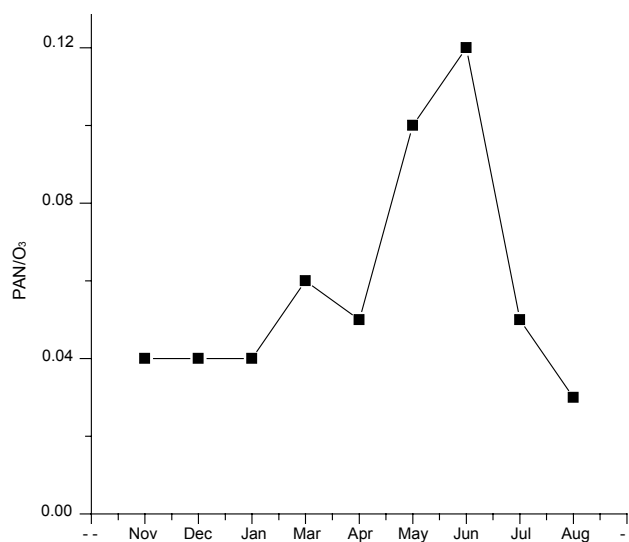


Fig. 2. Monthly average of PAN/O₃ values. Ratios were obtained employing the maximum daily concentrations of each compound.

Table III. Average integrated daily values of PAN and ozone in January (summer) and May (autumn). Values expressed in ppb per hour.

Pollutant/month	January	May
Ozone	586	245
PAN	13	38

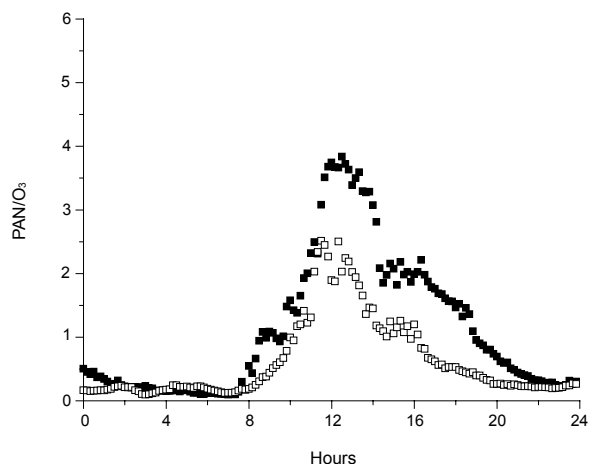


Fig. 3. Daily profile of PAN, in January 9, 2003 (\square) (summertime) and May 3, 2004 (\blacksquare) (autumn time).

The high values of PAN observed in autumn are at first sight puzzling for a secondary pollutant if it is considered that during this time period UV-A irradiance is minimum (Fig. 1). A plausible explanation for these high PAN levels is based on an increased amount of early morning precursors, as evidenced for the NO_x , CO and toluene levels. These increased levels can be ascribed to the higher stability and lower mixing layer heights of the atmosphere during cold time (Rutland and Garreaud, 1995). However, this factor should affect both ozone and PAN values and can not fully explain per se the increase in PAN to ozone ratios. A factor that could explain these results is the higher thermochemical stability of PAN during late autumn. In fact, average maximum temperatures are around 30 °C in January and 18 °C in May. This temperature difference implies a nearly five times slower rate of PAN thermal decomposition (Finlayson-Pitts and Pitts, 2000). This slower decomposition rate can explain the higher PAN / ozone ratios and wider PAN peaks during cold weather. Furthermore, it could explain why during autumn and winter PAN nighttime levels are considerably larger than in summertime (Table III). It is interesting to note that, for ozone, the opposite trend is observed (Table IV). The low nighttime values of ozone can be understood in terms of an increased titration by emitted NO under conditions of high atmospheric stagnation.

Table IV. Nighttime (from 0 to 8 hours) monthly averages of PAN and ozone (ppb).

Pollutant	January	May
PAN	0.2	0.85
Ozone	10	2

Another factor that could favor PAN accumulation is the NO_2/NO ratio, since its increase can increase both PAN production and its thermal stability. These values are also given in Table II.

PAN stability can be calculated if the temperature and NO_2/NO ratios are known. As expected, the PAN stability is considerably higher in cold weather. Monthly average values of PAN lifetimes at the moment of its maximum concentrations were: May, 337 minutes; August, 276 minutes; October, 200 minutes; January, 93 minutes. However, differences in PAN stability per se can not explain the high PAN concentrations measured in autumn since, when all measurements are considered, it is not observed a significant correlation between PAN lifetimes and maximum daily values (data not shown). It can be then concluded that a combination of factors, including high atmospheric stability, relatively high NO_2/NO ratios and increase PAN stability can explain the high PAN values and PAN /ozone ratios observed in autumn, particularly when daily integrated values are considered.

In order to assess the relevance of early morning precursors accumulation (measured by the morning maximum CO value), temperature and NO_2/NO ratios, a multiparametric test comprising these three independent variables was applied to all the set of individual values.

$$\text{PAN (ppb)} = \text{cte} + a T + b \text{NO}_2 / \text{NO} + c \text{CO}$$

In this equation “cte” is a parameter without a clear physical meaning that should take into account the average contribution of other factors to PAN values (cte = -1.5244 ppb). The three coefficients obtained, and the degree of confidence of their contribution, were:

$$a = 0.1137, \text{ppb}/^\circ\text{C}, p < 0.0001$$

$$b = 0.0947, \text{ppb}, p < 0.001$$

$$c = 0.5038, \text{ppb/ppm}, p < 0.0001$$

showing that the three factors considered are important in determining PAN values. In particular, the dependence on the amounts of precursors could explain why maximum PAN values are observed in autumn, where maximum levels of CO and toluene have been determined (Table II and Fig. 1).

The agreement between calculated and experimentally determined maximum PAN values is given in Figure 4. The correlation between both parameters is:

$$\text{PAN}_{\text{cal}} = (1.46 \pm 0.13) + (0.44 \pm 0.04) \text{PAN}_{\text{exper}}$$

with $r = 0.66$ and $p < 0.0001$ for $n = 132$. However, the fact that the ordinate is significantly different from zero, and that the slope differs from 1.0 would indicate that a combination of variables and/or other non considered variables are also important. A relevant parameter could be the radiation intensity. This factor was not considered in the multiparametric relationship given its dual effect. In fact, high irradiances increase the rate of hydroxyl radical production, increasing the level of photochemical oxidants and, among them, PAN levels. On the other hand, radiation intensity decreases NO_2/NO ratios due to NO_2 photolysis, increasing the rate of PAN decomposition. Furthermore, the fact that NO_2 photolysis increases ozone values tends to favor the accumulation of this oxidant during periods of high irradiance (summer), leading to relatively low PAN/ozone ratios during summertime (Fig. 2).

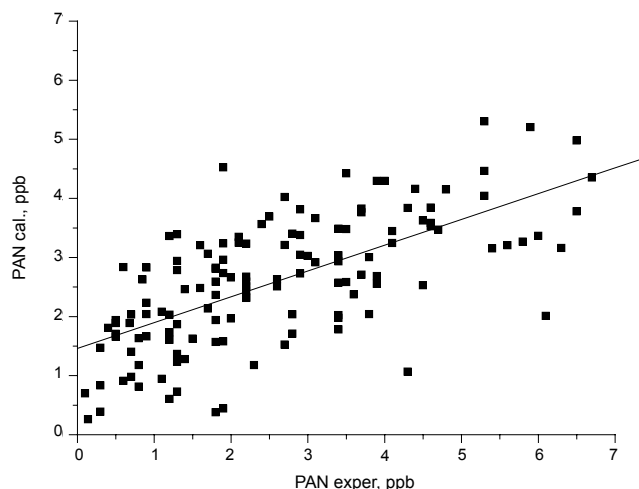


Fig. 4. Correlation between calculated and measured maximum values. Linear regression intercept (A) = 1.4625; Slope (B) = 0.4361; $R = 0.66$; number of measurement (n) = 132; $p < 0.0001$.

During May, dew events in Santiago are frequent. The presence of the wet surface could modify PAN chemistry and/or increase its production rate by an increased input of hydroxyl radicals after sunrise (Rubio *et al.*, 2002). In order to test this possibility, daily maximum PAN values were plotted as a function of the amount of collected dew water in April, May and June (Fig. 5). These data show only a very weak, not significant relationship, implying that PAN production and/or removal is almost unrelated to dew formation. This could reflect the low solubility of PAN in aqueous solutions (Gaffney *et al.*, 1989; Frenzel *et al.*, 2000).

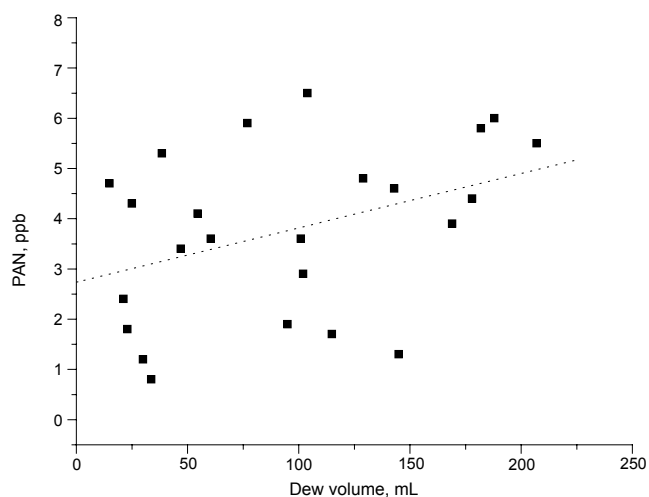


Fig. 5. Maximum daily PAN concentrations as a function of the amount of collected dew water. Linear regression intercept (A) = 2.736; slope (B) = 0.0108; $R = 0.392$; number of measurement (n) = 24 and $p = 0.058$.

4. Conclusions

High values of PAN concentrations measured in Santiago, Chile in autumn are higher than those observed in summer. These high values are due to increased levels of precursors, associated to the stability of the atmosphere, and a decreased rate of thermal decomposition.

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