The Evolution of Photochemical Smog in the Metropolitan Area of Santiago de Chile

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ABSTRACT

In November and December 1996 the PHOTOCHEMICAL CAMPAIGN took place in the Metropolitan Area of Santiago de Chile and covered a range of simultaneous measurements of meteorological parameters and air chemical compounds, including ozone, carbon monoxide, nitrogen oxides, peroxyacetyl nitrate (PAN), and online nonmethane hydrocarbons (NMHC) in the range of C_4–C_{12}. Measurements were obtained at a downtown site and a receptor site. In addition to high ozone concentrations, Santiago faces high PAN values that can reach to more than 20 ppbv. It is estimated that more than 50% of the daytime maximum of ozone and almost all PAN are formed within the urban plume. Ozone : PAN ratios for diurnal maxima were about 7.7. The behavior of PAN is linked strongly to anthropogenic species, especially aromatic compounds, whereas biogenic NMHC also may contribute to afternoon ozone concentrations. The ethylbenzene : m-xylene ratio can be used as a good indicator for the effect of anthropogenically related hydrocarbon chemical reactions that lead to the formation of secondary pollutants. Using this ratio, mixing ratios for hydroxyl radical (OH) were calculated. Mean diurnal maximum OH mixing ratios were about 2.9×10^6 molecules per centimeter cubed.

1. Introduction

Photochemical smog episodes are widespread phenomena in urban regions worldwide where increased levels of nonmethane hydrocarbons (NMHC) and nitrogen oxides (NO_x) may be found from various anthropogenic sources (Nelson et al. 1983; Seinfeld 1989; Field et al. 1992). Meteorological influences such as sunny and warm weather conditions, along with stagnant wind patterns, favor the formation of secondary pollutants, that is, ozone (O_3) and peroxyacetyl nitrate (PAN) through effective photochemical consumption of NMHC and NO_x in these areas (Chameides et al. 1992; Bowman and Seinfeld 1994). These conditions may be encountered very often in the Metropolitan Area of Santiago de Chile (Santiago R.M.) during summer (CONAMA 1996). Located at a latitude of 33°27′S, the climate of the Santiago basin is marked by intensive global radiation and daytime temperatures between 30° and 35°C at this time of the year. In addition, its specific orographic situation close to the highest mountain ranges of the Andes to the east and the Cordillera de la Costa to the west leads to the development of a very persistent valley–mountain breeze system that favors the enhancement of primary compounds emitted in this agglomeration from the activities of its more than 5 million inhabitants. Trapped in this basin, these precursors eventually will build up photooxidants in the course of the day.

Despite the fact that Santiago frequently faces pollution episodes with very high ozone concentrations, little knowledge about NMHC in the ambient air of Santiago has been available so far. For PAN, another harmful secondary compound, no data for Santiago R.M. existed. As demonstrated by Singh (1987) and

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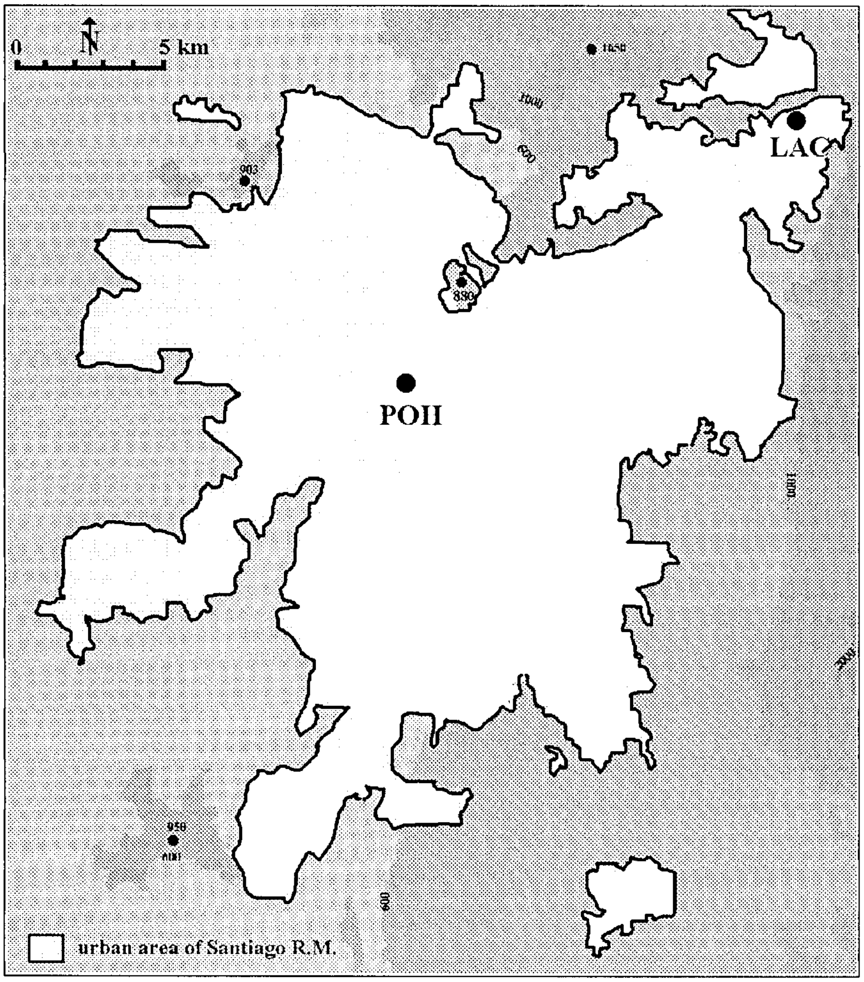

FIG. 1. Measurement sites in Santiago de Chile during the PHOTOCHEMICAL CAMPAIGN (LAC: Las Condes; POH: Parque O'Higgins).

Rappenglück et al. (1993), PAN is well known to be a far better indicator for photochemical processes than is ozone. PAN is an important indicator for NMHC-driven photochemical reactions since the PAN molecule consists of nitrogen dioxide (NO_2) plus a hydrocarbon combined. Thus PAN may be formed only in ambient air that contains NO_x and sufficient hydrocarbon precursors. Important NMHC precursors are the so-called BTEX aromatics (benzene, toluene, ethylbenzene, and the m-/p-/o-xylenes). As outlined by Rappenglück et al. (1998), they comprise a unique group of NMHC. Some of the BTEX aromatics (e.g., toluene and m-xylene) are important species with respect to both their urban atmospheric mixing ratios and their reactivity-based concentrations (Chameides et al. 1992). In particular, xylene isomers may convert large amounts of nitric oxide (NO) to NO_2 (Simpson 1995).

Here some important results of the PHOTOCHEMICAL CAMPAIGN that took place in the Santiago R.M. during November and December 1996 are reported. In addition to measurements of meteorological parameters and routinely measured air trace gases such as ozone, carbon monoxide (CO), and NO_x, this campaign included concurrent in situ online NMHC measurements at two urban sites in Santiago de Chile, along with continuous PAN measurements at one suburban site. In this paper, attention will be given primarily to the evolution of photochemical smog episodes in Santiago R.M. by describing some important case studies in detail. Relationships between specific NMHC and other precursors will be shown and their impact on the formation of photooxidants will be discussed.

2. Experimental setup

For the PHOTOCHEMICAL CAMPAIGN, two ground-based measurement sites were chosen (Fig. 1). These two locations (the distance between these sites is approximately 18 km) were selected to provide a better insight into the distribution and the possible degradation of ozone-related hydrocarbon species within the Santiago area. One set of instruments was installed in a facility of the network of the Servicio Salud del Ambiente Region Metropolitana (SESMA) close to a side entrance of Parque O'Higgins (POH) located almost in the center of Santiago [540 m above mean sea level (MSL)]. This site should provide adequate data for an urban airmass fingerprint. The other instrumentation was set up in a mobile home facility of SESMA in the recreation area El Estadio El Corfo in the suburban area of Las Condes (LAC) on the northeast side of Santiago R.M. (802 m MSL). This site is located in the small Mapocho valley leading to the Andes range. Since summertime wind circulations (mountain–valley breeze conditions) are determined by orographical structures, the small valley in Las Condes forces wind flow patterns that come from the center of Santiago and pass the measurement site at LAC. Usually this pattern happens for some hours during the afternoon under prevailing mountain–valley breeze conditions. In these cases, LAC faces air masses that have originated in the center of Santiago and have undergone photochemical processes en route.

At both sites, SESMA routinely measures ozone, CO, NO_x, and meteorological parameters with commercial instruments. Ozone was measured with a Beckman Model 950 instrument; CO with a Monitor Labs, Inc., ML9830 analyzer; and NO_x with a Monitor Labs, Inc., ML9841A analyzer. These devices were equipped with Teflon filters (3–5 μm). SESMA routinely carries out calibration procedures. The monitoring network of SESMA has been approved by TÜV Rheinland, Inc., a certification and testing company. For the PHOTOCHEMICAL CAMPAIGN, the University of Munich equipped both measurement sites with gas chromatographic (GC) systems (Siemens AG RGC 402) for quasi-continous online NMHC measurements in the range of C_4–C_{12} with a temporal resolution of 30 min. For further experimental details see Rappenglück et al. (1998). For the Santiago measurements, calibration procedures were carried out with a special 27-component hydrocarbon mixture calibration gas cylinder in the ppbv range provided by the National Physical Laboratory, United Kingdom. For PAN measurements, one Scintrex, Limited, LPA-4 PAN analyzer was installed at the suburban site LAC, at which large concentrations of secondary pollutants could be expected. Experimental details for the LPA-4 and results from different field campaigns already have been described elsewhere (Blanchard et al. 1990; Jakobi 1994, 1998; Suppan et al. 1998; Ziomas et al. 1995). At LAC, atomic oxygen photolysis rates ($J_{O(^1D)}$) were measured by MeteoConsult GmbH. with a commercially available filter radiometer.

3. Results and discussion

Aromatic compounds composed a large part of the total NMHC that were found in ambient air of Santiago de Chile during the PHOTOCHEMICAL CAMPAIGN. From the whole NMHC dataset as presented in Table 1 for the suburban site LAC, it can be estimated that, on a parts per billion of carbon (ppbC) basis, up to 30% of total NMHC may be attributed to BTEX compounds. Similar results apply to POH. This result is in good agreement with similar investigations in other urban areas (Sexton and Westberg 1984; Field et al. 1992; Rappenglück et al. 1998). Table 2 gives a survey of BTEX results obtained in different city studies worldwide. Though BTEX values may vary depending on the measurement site (roadside, downtown, suburban) BTEX values for Santiago de Chile lie in the range that is typical for many urban areas. This result also applies specifically to toluene and benzene. The toluene : benzene ratio values imply that traffic emissions play an important role in this urban area as they do in many other urban areas (Wathne 1983; Roberts et al. 1984; Singh et al. 1985; Rappenglück et al. 1998).

Figure 2 depicts time series for toluene and for ozone at both measurement sites, along with time series for PAN and for photolysis rates of $J_{O(^1D)}$ obtained at LAC, covering the entire PHOTOCHEMICAL CAMPAIGN. In this figure, toluene is taken as a surrogate for NMHC. Maximum ozone concentrations were about 50–60 ppbv at POH, whereas at LAC peak ozone concentrations reached up to 150 ppbv (1 h). Mixing ratios of PAN were high, with maximum concentrations of up to 20.7 ppbv (5 min). Comparably high results have been reported from U.S. sites (Grosjean et al. 1993). Very recently, in 1997, PAN values of more than 30 ppbv were observed in Mexico City (Gaffney et al. 1998). PAN showed pronounced diurnal variations. In almost all cases, PAN peaks appeared between 1200 and 1500 LT. Ozone : PAN ratios for diurnal maxima were about 7.7. Although these ratios represent low concentrations, similar values have been found in laboratory experiments (Leone and Seinfeld 1984). Atmospheric measurements at times show higher values for summertime periods (Grosjean et al. 1993). Grosjean et al. considered the average ozone : PAN ratio observed at ozone maximum and report ozone : PAN values ranging from 15 to 20. In these cases, however, there is also often a very good correlation found between concurrent ozone and PAN maxima. As shown in Suppan et al. (1998), for instance, diurnal maxima of PAN and ozone must not necessarily coincide. It strongly depends on the location of the measurement site and its exposure to the urban plume. Therefore we assumed that an ozone : PAN ratio that only takes into account their corresponding diurnal maxima is a reasonable and representative quantity. Ozone : PAN ratios usually show different values mainly because of the thermal instability of PAN. This fact applies both to the seasonal behavior of ozone : PAN ratios for a specific site, as demonstrated by Grosjean et al. (1993), and to the spatial variability shown by Kourtidis et al. (1993), which implies increasing ozone : PAN ratios with growing distances from the precursor sources. In addition, according to Kourtidis et al. (1993), observations suggest that increasing NO_x values coincide with

TABLE 1. Results of hydrocarbon measurements at Las Condes, Estadio El Corfo, sorted by their median values.

NMHC compound	Median (ppbv)	Mean value (ppbv)	Max (ppbv)	*n**
n-butane/1-butene/t-2-butene	3.94	5.15	145.99	1135
Toluene	3.13	3.48	14.19	1145
i-pentane	2.27	3.36	121.56	1134
Benzene	1.25	1.44	9.66	1130
n-pentane/2-methyl-1-butene	1.21	1.70	56.07	1133
c-2-butene	1.00	1.27	39.55	1120
m-xylene	0.99	1.17	6.55	1144
Methylcyclopentane/t-3-methyl-2-pentene	0.75	0.94	9.92	1127
o-xylene	0.66	0.74	3.49	1146
t-2-pentene/isoprene/c-2-pentene	0.62	0.79	19.98	1114
n-hexane	0.50	0.58	8.40	1135
Nonane	0.46	0.52	3.17	1131
1,2,4-trimethylbenzene	0.43	0.48	2.02	1146
p-xylene	0.43	0.48	2.34	1131
Methylcyclohexane	0.43	0.47	2.22	1129
3-methylpentane	0.40	0.52	8.38	1112
Ethylbenzene	0.39	0.45	2.13	1143
p/m-ethyltoluene	0.37	0.42	1.52	1143
n-heptane	0.33	0.36	2.26	1132
n-decane	0.27	0.33	5.00	1116
2-methylhexane	0.27	0.31	2.37	1136
n-octane	0.26	0.29	1.09	1133
2,3-dimethylpentane	0.21	0.30	2.99	1099
t-2-hexene/2-methyl-2-pentene	0.18	0.22	3.77	1072
c-2-hexene	0.16	0.32	3.16	38
2-methylheptane	0.16	0.19	0.70	1130
Mesitylene	0.16	0.19	0.95	1146
Ethylcyclohexane	0.13	0.15	0.64	1111
3-methylheptane	0.13	0.16	0.66	1128
Nonene	0.13	0.16	1.18	1126
1-hexene	0.12	0.19	2.70	618
o-ethyltoluene	0.11	0.13	0.49	1121
Styrene	0.11	0.12	0.58	1135
Undecane	0.11	0.15	2.88	894
2,4/2,5-dimethylhexane	0.10	0.12	0.51	1028
1-heptene	0.09	0.14	2.12	694
1-octene	0.09	0.10	0.59	1062
n-propylbenzene/dodecane	0.08	0.10	0.53	1119
Limonene	0.08	0.09	0.25	436
Cyclohexane	0.06	0.08	1.29	745
2,3,4-trimethylheptane	0.05	0.06	0.23	754
Cumene	0.04	0.05	0.20	591
p-cymene	0.04	0.04	0.22	130
i-butylbenzene	0.04	0.04	0.14	348

* Number of evaluated analyses above detection limit.

decreasing ozone : PAN ratios. This finding may partly explain the relative low ozone : PAN ratios found in Santiago, since even at receptor sites high concentrations of nitrogen oxides were observed, as will be outlined later. In the investigations in Santiago, linear regression analysis for diurnal maximum values yields $[O_3] = 72.7 + 1.6[PAN]$, where [ ] indicates mixing ratio. Correlation coefficient r is only about 0.3. This result suggests either that formation–removal processes are slightly different for both species, or that atmospheric mixing processes (e.g., downward mixing processes) have a differential impact on ozone and PAN mixing ratios. In any case, the results for Santiago show that strong photochemical processes involving reactive hydrocarbons exist in this urban area.

The pattern of the time series for toluene as shown in Fig. 2 reveals another important feature: toluene time series are totally different at both sites. At POH there are sharp increases of toluene at times, usually during morning hours; no specific diurnal variation is visible at LAC (Fig. 2). Generally speaking, diurnal patterns of primary species reflect emissions, transport and dilution, and chemical removal. The emissions of anthropogenic compounds mostly will follow traffic patterns or industrial releases, but transport and dilution are influenced by the synoptic weather circulation, the superimposed local mountain–valley breeze circulation that often occurs in the area of Santiago, and the spatial and temporal variation of the mixing height. Chemical removal will occur through reaction with the hydroxyl (OH) radical for all NMHC, some NMHC react with O_3, and some react with the nitrate (NO_3) radical.

TABLE 2. Comparison of median and maximum (in parentheses) values for aromatic hydrocarbon mixing ratios for various cities. For Athens (1994) and Santiago (1996) separate results for p-xylene (*) and m-xylene (**) were available.

Sites	Benzene (ppbv)	Toluene (ppbv)	Ethylbenzene (ppbv)	m/p-xylene (ppbv)		o-xylene (ppbv)
Los Angeles 1979[a]	6.0	11.7	2.3	4.6		1.9
	(27.9)	(53.4)	(27.7)	(50.0)		(12.7)
San Jose 1985[b]	12.4	21.2	6.2	13.1		5.7
	(23.4)	(64.0)	(14.5)	(25.3)		(11.0)
Munich 1993[c]	3.0	5.7	1.2	2.9		1.1
	(14.9)	(32.1)	(9.5)	(31.5)		(10.1)
Munich 1994	2.8	4.6	0.6	2.2		0.8
	(13.8)	(25.0)	(4.2)	(15.3)		(5.5)
Athens 1994[d]						
Center	9.5	16.8	3.3	2.9*	6.2**	4.3
	(61.2)	(103.5)	(19.2)	(18.4)	(39.0)	(27.5)
Suburb	1.6	3.6	0.8	0.7*	1.2**	0.8
	(23.5)	(55.5)	(13.0)	(8.6)	(19.1)	(12.7)
Mexico City 1993[e]	3.5;5.8	12.1;29.8				
Santiago de Chile 1995[f]		16.5		5.3		3.1
Santiago de Chile 1996						
Parque O'Higgins (POH)	0.7	2.1	0.2	0.2*	0.5**	0.4
	(24.9)	(56.3)	(5.6)	(7.1)	(16.2)	(9.4)
Las Condes, El Estadio El Corfo (LAC)	1.3	3.1	0.4	0.4*	1.0**	0.7
	(9.7)	(14.2)	(2.1)	(2.3)	(6.6)	(3.5)

[a] Singh et al. (1985). Mean value reported in place of median.
[b] Singh et al. (1992). Mean value reported in place of median.
[c] Rappenglück and Fabian (1997).
[d] Rappenglück et al. (1998).
[e] Blake and Rowland (1995). Two samples (0600, 1200 LT) taken at the center of Mexico City.
[f] Blake and Rowland (1996). One sample (1100 LT) taken at Plaza del Inca.

The mean diurnal variation of toluene for both sites is plotted in Fig. 3. Presumably, the toluene pattern in the center (POH) is controlled mainly by the diurnal variation of traffic, since pronounced peaks occur during the morning rush hours. Previous studies (CONAMA 1996) show that diurnal variations of CO, a compound that predominantly is emitted by traffic, exhibit two peaks during wintertime: one in the morning hours and one during evening hours. On the whole, CO follows the pattern of the traffic emissions in Santiago. In summertime, the pattern of traffic emissions is almost identical (CONAMA 1996), but CO concentrations exhibit only one peak during the early morning hours. The second peak in the evening vanishes because of stronger ventilation during summertime. This feature coincides with the toluene observations in this study.

At LAC, the variation of toluene is smaller, but the average values are relatively high in comparison with those of POH. The reason is that at POH toluene values are very low during afternoon hours—often lower than at LAC. This difference may be explained by the persistent mountain–valley breeze that forces a specific diurnal variation of the wind pattern. Recently the wind regime in Santiago de Chile has been described thoroughly by Ihl-Tessmann (1998). The main results of this work are clearly reflected in the current measurements. Figure 4 displays time series for wind direction and wind velocity for POH and LAC as observed during the PHOTOCHEMICAL CAMPAIGN (upper panel). The lower panel shows a subset for 28 November–5 December 1996. These figures show that the downtown site predominantly faces southwesterly winds, whereas the LAC site is influenced by mountain–valley breezes. During early morning hours the wind velocity is low. Along with a low mixing height and strong emission rates, this low wind speed leads to an accumulation of primary species within the urban boundary layer. This phenomenon is reflected clearly by the toluene pattern at POH. The same processes apply to LAC. During daytime hours, however, a mountain–valley breeze develops due to solar radiation. Wind velocity increases and wind direction turns to southwest, leading both to a ventilation of the inner urban area near POH and to a transport of polluted air masses to LAC. At this time, toluene values at POH are very low. LAC, however, faces polluted air masses coming from the center of Santiago. Thus, toluene mixing ratios still may remain relatively high and often even increase shortly after noontime. Usually this phenomenon is extraordinary for measurement sites that are close to emission sources such as traffic that show clear diurnal variations but may be encountered downwind from these sources, usually in suburban areas. These transport mechanisms from downtown Santiago through the Mapocho valley to the LAC site have been confirmed by back-trajectory analysis carried out by CONAMA (1996).

Since there exists a well-defined source–receptor relationship because of a persistent mountain–valley

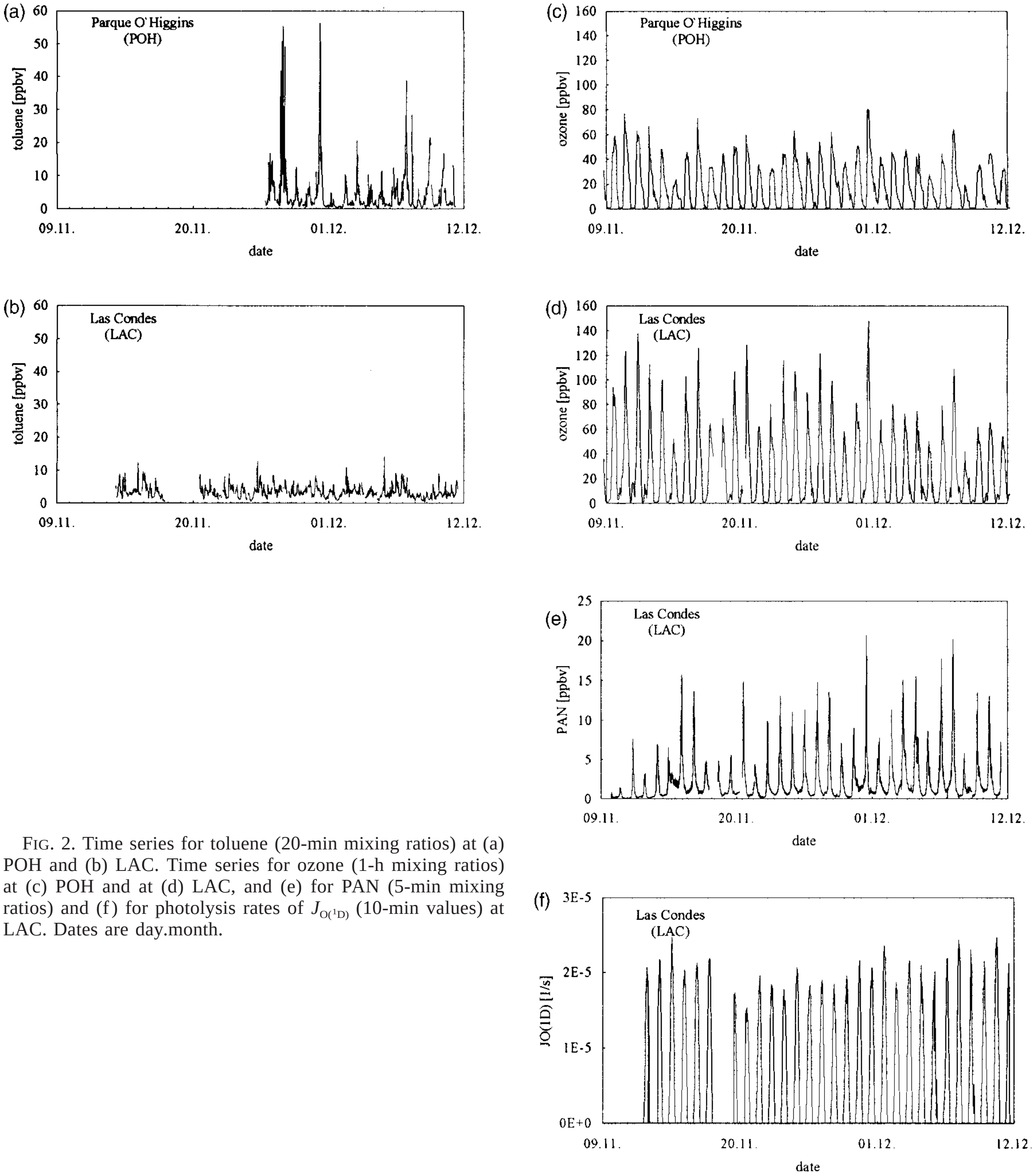

FIG. 2. Time series for toluene (20-min mixing ratios) at (a) POH and (b) LAC. Time series for ozone (1-h mixing ratios) at (c) POH and at (d) LAC, and (e) for PAN (5-min mixing ratios) and (f) for photolysis rates of $J_{O(^1D)}$ (10-min values) at LAC. Dates are day.month.

breeze system, time-dependent photochemical processes within the urban plume can be investigated using specific ratios of species. As demonstrated by Rappenglück et al. (1998) in Athens, Greece, during the Mediterranean Campaign of Photochemical Tracers-Transport and Chemical Evolution (MEDCAPHOT-TRACE), the ethylbenzene : m-xylene (e:m) represents an adequate quantity to assess urban photochemical behavior. These two species have some properties in common. They are emitted by the same sources (mainly traffic) in the same quantities and their only important atmospheric removal process is the reaction with OH. They differ only in their reactivity toward OH. Thus photochemical influences should lead to an increase of e:m, because m-xylene reacts faster with OH than does ethylbenzene. During nighttime, however, their ratio remains stable, since no chemical removal takes place for the lack of OH.

Figure 5 emphasizes the specific behavior of the e:m ratio. In this presentation, median diurnal variations of the e:m ratio at LAC, calculated median values for P_{OH} (the primary production rate of OH), and OH concentrations are plotted. It is obvious that during nighttime

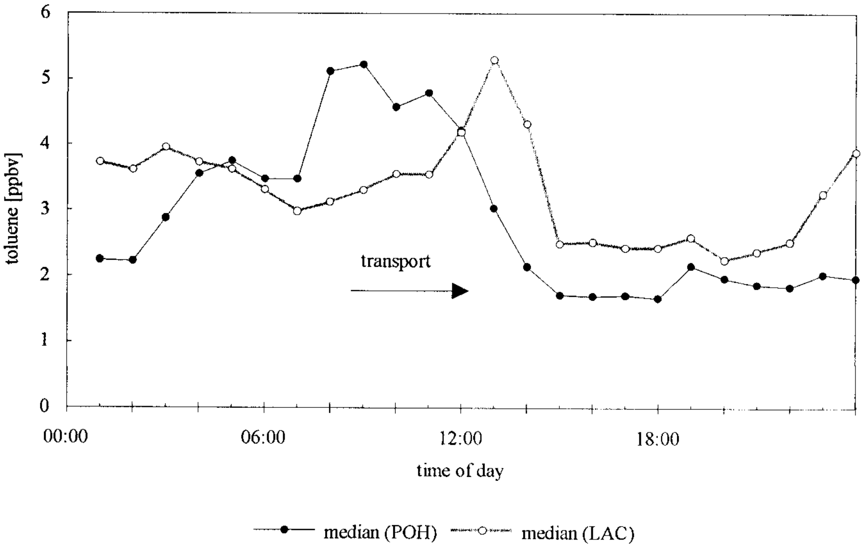

FIG. 3. Mean diurnal variation (LT) of toluene at the center (POH) and at the suburban measurement site (LAC).

the value of the e:m ratios at LAC is very constant. It reflects emission processes in Santiago R.M. During daytime, however, photochemical processes that lead to the formation of secondary species take place under the influence of solar radiation.

Photochemical degradation for a species A that is subject only to reaction with OH (k is reaction rate) during transport time t from the source to the receptor site is given in the form

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_\mathrm{A}[\mathrm{OH}]t}. \tag{1}$$

Thus the temporal variation of a ratio of two species A and B can be described by

$$\ln \frac{[\mathrm{A}]/[\mathrm{B}]}{[\mathrm{A}]_0/[\mathrm{B}]_0} = -(k_\mathrm{A} - k_\mathrm{B})[\mathrm{OH}]t. \tag{2}$$

According to model calculations of McKeen and Liu (1993), dilution processes may have an effect on NMHC ratios. Foremost this effect applies to NMHC, which differ in their sources and/or source strengths. With use of the e:m ratio these effects are negligible, since both species originate from the same sources with almost the same quantities (Nelson et al. 1983).

An assumption of mean wind velocities at LAC of about 1.8 m s^{-1} will result in a travel time of 2.78 h between POH and LAC. The OH reaction rates for ethylbenzene and m-xylene are 7.1×10^{-12} and 23.6×10^{-12} cubic centimeters per molecule per second, respectively. According to (2), mean maximum diurnal OH concentrations of about 2.9×10^6 molecules per centimeter cubed can be calculated. This concentration represents a lower limit for OH concentrations, since emissions also may occur along the trajectory of the air mass. However, the main emission sources are concentrated in downtown Santiago. LAC already is located at the outer boundary of the urbanized area. Calculations for the o-xylene : m-xylene ratio gave almost the same result, whereas the p-xylene : m-xylene ratio yielded much higher OH concentrations. The benzene : toluene ratio did not prove to be a suitable quantity for such calculations either. A probable reason for this different behavior might be that emission profiles are too different.

To make estimations of OH concentrations that are independent of NMHC ratios, a theoretical approach given by Poppe et al. (1995) was used. Under the assumptions of high NO_2 mixing ratios ($NO_2 \gg 1$ ppbv), OH concentrations may be calculated by

$$[\mathrm{OH}] = (P_\mathrm{OH} + P_{\mathrm{HO}_2})/(k_1[\mathrm{NO}_2]), \tag{3}$$

with P_{HO_2} being the primary production rate of hydroperoxy radical and k_1 being the reaction rate of

$$\mathrm{NO}_2 + \mathrm{OH} + \mathrm{air} \rightarrow \mathrm{HNO}_3 + \mathrm{air} \tag{4}$$

to produce nitric acid (HNO_3). The production rate P_OH is determined by the following reaction scheme:

$$\mathrm{O}_3 + h\nu \rightarrow \mathrm{O}(^1\mathrm{D}) + \mathrm{O}_2 \quad \text{and} \tag{5}$$

$$\mathrm{O}(^1\mathrm{D}) + \mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{OH}, \tag{6}$$

where J_{O_3} and k_2 are the photolysis rate and reaction rate of (5) and (6), respectively, $h\nu$ is the energy from solar radiation (h is Planck's constant and ν is the frequency of the electromagnetic wave of solar radiation), $O(^1D)$ is an excited oxygen atom, O_2 is an inert oxygen molecule, and H_2O is water. The competing reactions are

$$\mathrm{O}(^1\mathrm{D}) + \mathrm{O}_2 \rightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{O}_2 \quad \text{and} \tag{7}$$

$$\mathrm{O}(^1\mathrm{D}) + \mathrm{N}_2 \rightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{N}_2, \tag{8}$$

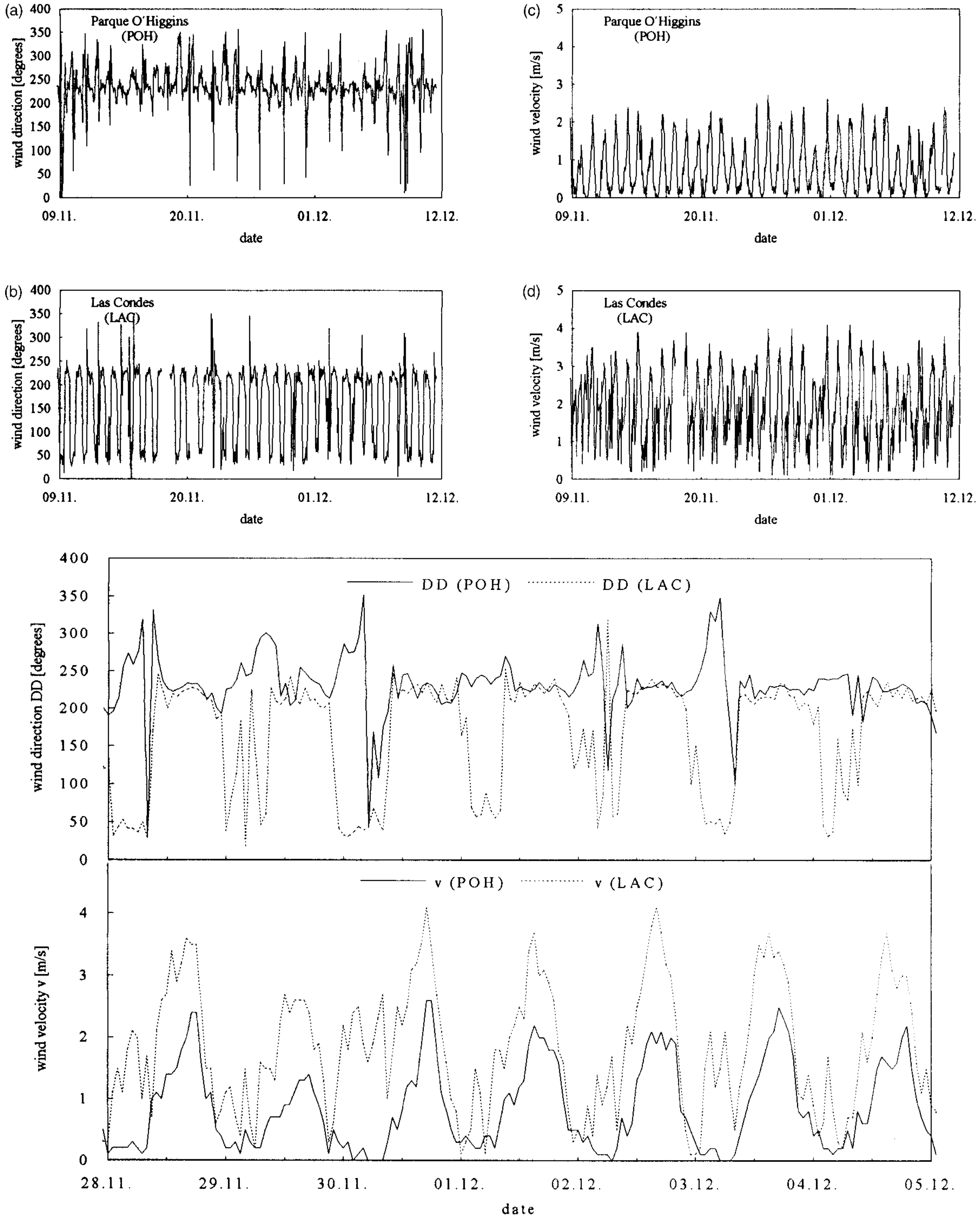

FIG. 4. (upper panel) Time series for wind direction (1-h values) at (a) POH and (b) LAC. Time series for wind velocity (1-h values) at (c) POH and at (d) LAC. (lower panel) Subset of the time series for wind direction and wind velocity at POH and LAC for 28 Nov–5 Dec 1996. Dates are day.month.

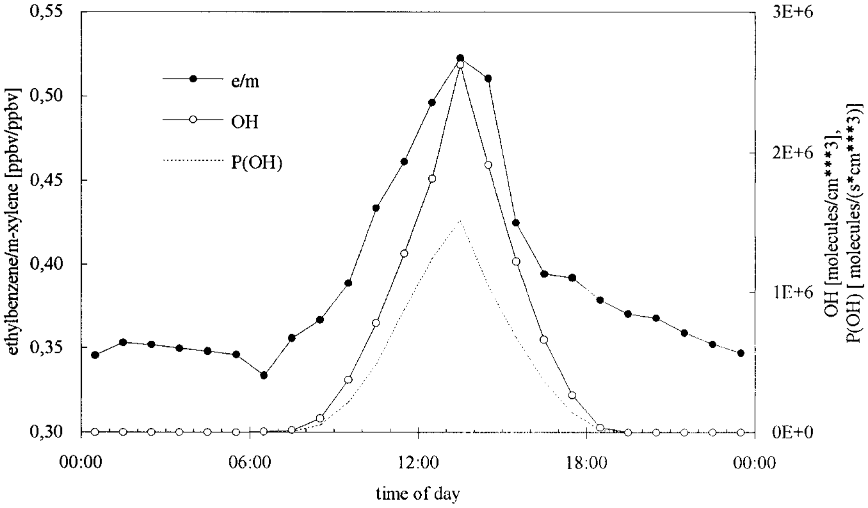

FIG. 5. Median diurnal variation (LT) of the e:m ratio, the primary OH production rate *P*(OH), and OH concentrations at the suburban measurement site (LAC) of Santiago.

with reaction rates k_3 and k_4, respectively [O(^{3}P) is a ground-state oxygen atom and N_2 is an inert nitrogen molecule]. The primary production rate P_{OH} can be calculated by

$$P_{OH} = 2J_{O_3}[O_3]k_2[H_2O]/(k_2[H_2O] + k_3[O_2] + k_4[N_2]). \qquad (9)$$

All the variables in (9) were available at LAC. The results for P_{OH} are plotted in Fig. 5. They show a good relationship to the e:m ratio. Here P_{HO_2} represents the HO_2 production rate through the photolysis of formaldehyde (HCHO):

$$P_{HO_2} = 2J_{HCHO}[HCHO]. \qquad (10)$$

The rate P_{HO_2} was not measured at LAC, but the following assumptions were made: photolysis rate J_{HCHO} was suggested to have the same diurnal shape as $J_{O(^1D)}$. For formaldehyde, we assumed the same diurnal variation, taking into account that Seinfeld (1989) reports only a fraction of 20% is emitted directly (predominantly by mobile sources), whereas the biggest fraction is formed photochemically. Differential optical absorption spectroscopy measurements carried out at a roof platform in the center of Santiago from July until November 1991 show a mean diurnal maximum of about 13 ppbv for formaldehyde at this site (Oyola and Romero 1992). The entire time series of formaldehyde, however, shows a slight decrease from July to November, indicating lower formaldehyde maximum concentrations in November. Results from other urban/suburban areas, for example, Brazilian urban environments (Grosjean et al. 1990), show a similar range for formaldehyde values. Therefore, we supposed a maximum median diurnal concentration for formaldehyde of about 10 ppbv for the LAC site to be a plausible value for the model approach. Calculated median diurnal OH concentrations are plotted in Fig. 5. Maximum values are about 2.6 × 10^6 molecules cm^{-3}, only slightly lower than those obtained by the e:m ratio method. In the current model approach, the effect of the photolysis of nitrous acid (HONO) was not included. According to new findings published by Ammann et al. (1998), photolysis of HONO may be a stronger source for direct formation of OH than previous investigations indicated. HONO, however, is important only during early morning hours. Its influence on OH concentrations during subsequent hours probably is of minor importance.

The results for Santiago imply that reactive NMHC play an important role in this urban area. Photochemical formation of PAN and ozone strongly depends on the specific hydrocarbon precursors and their availability to take part in competitive reactions versus OH, O_3, and NO_3. These nonlinear processes also depend on the amount of hydrocarbons that is present in ambient air and the NMHC:NO_x ratios. Some hydrocarbons, the alkenes, also may destroy ozone, but they never destroy PAN. The effect of alkenes is ambiguous (Isidorov 1990); their effect on ozone destruction becomes relevant when O_3–alkene reactions are more likely to occur than are OH–alkene reactions, for example, when a high concentration of ozone is present in ambient air, or when reactions with OH are limited, as may be the case during the morning hours. Though C_2–C_3 NMHC could not be measured with the system, the NMHC results suggest that high concentrations of C_2–C_3 should be present in the ambient air of Santiago. This suggestion is supported by results from canister samplings reported by Blake and Rowland (1996). The influence of ethene and propene on the ozone mixing ratios in Santiago in the course of the day, however, still needs to be addressed in further investigations.

Figure 6 demonstrates the differences between the behavior of ozone and PAN during a period with strong solar radiation every day. In addition, Fig. 4 displays

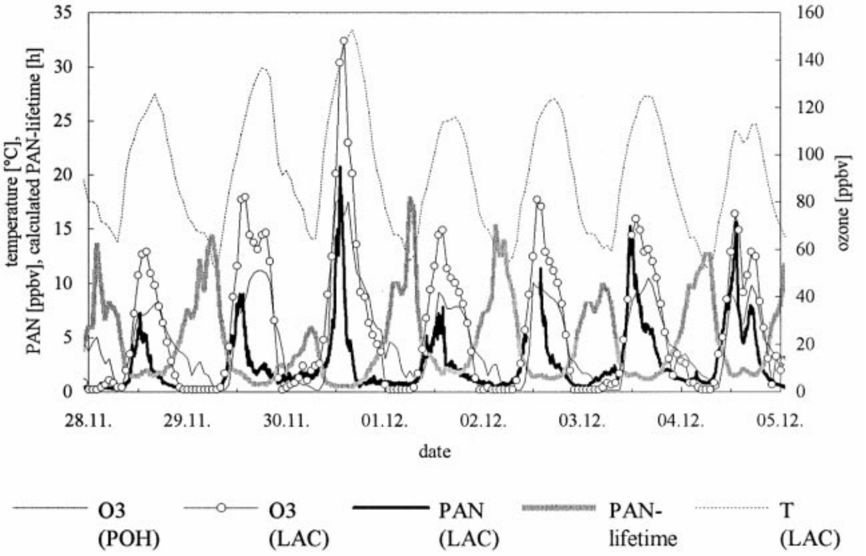

FIG. 6. Time series for ozone (O3) at POH and ozone, PAN, PAN lifetime, and temperature (T) at LAC. Dates are day.month.

the wind patterns for this period and indicates that the LAC site usually is under urban influence in the afternoon. Diurnal ozone variations at POH and LAC look similar, but ozone mixing ratios at LAC are up to 100% higher than in the city, indicating high photochochemical activity within the urban plume. PAN diurnal variations are different. Although they increase at almost exactly the same time of day as ozone, PAN mixing ratios then decrease rapidly. Ozone concentrations stay at the same level for another 2–3 h. PAN peaks always occur well before the diurnal temperature maximum. PAN degradation occurs through the following reactions:

$$CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO + NO_2, \qquad (11)$$

$$CH_3C(O)OO + NO_2 \rightarrow CH_3C(O)OONO_2, \quad \text{and} \qquad (12)$$

$$CH_3C(O)OO + NO \rightarrow CH_3C(O)O + NO_2, \qquad (13)$$

with k_5, k_6, and k_7 being the reaction rates for (11), (12), and (13), respectively. Based on these reactions, the lifetime of PAN can be calculated according to Ridley et al. (1990) as

$$\tau_{\mathrm{PAN}} = \frac{1}{k_5}\left(1 + \frac{k_6[\mathrm{NO_2}]}{k_7[\mathrm{NO}]}\right). \qquad (14)$$

Although at POH and LAC NO_2 data were obtained by chemiluminescence instruments, with a molybdenum catalyst, that detect the sum of NO_2, PAN, HNO_3, minor constituents, it is suggested that NO_2 constitutes by far the biggest fraction most of the time. Only in a few cases may the fraction of the other compounds become important. In these cases, τ_{PAN} calculation based on (14) may be too high and may be regarded as an upper limit for PAN lifetime. The only important interference with the NO_2 signal may take place during midday in the case of PAN and during the afternoon hours in the case of HNO_3, the respective times of day when these species exhibit their diurnal maximums. For HNO_3, no data were available. HNO_3 measurements (Kitto and Harrison 1992; Pio et al. 1992) show that, as far as average concentrations are concerned, HNO_3 represents 5%–10% of the NO_2 concentration. HNO_3 interferences should be of minor relevance. The contribution of PAN to the NO_2 signal, and hence its effect on (14) may be assessed by taking the example of 30 November 1996 (Fig. 7), an episode day with maximum PAN values (this day will be discussed later in detail). With the assumption that the analyzer has the same sensitivity to both NO_2 and PAN, the contribution of PAN to the NO_2 signal will be more than 20% between 1000 and 1500 LT, with maximum contributions at noon of about 75%, based on hourly averages. According to Fig. 7, there are only slight diurnal variations in NO_2 mixing ratios. As outlined above, it is suggested that apart from the midday time period NO_2 constitutes by far the biggest fraction during the rest of the day. At noon there is a peak in the NO_2 signal. It occurs, however, at exactly the same time that other precursors such as CO and toluene also exhibit their diurnal maximums. The assumption that PAN is detected quantitatively by the analyzer and will contribute 75% to the NO_2 signal at midday would lead to a sharp decline in NO_2 values, down to 5 ppbv for 2 h. Although PAN interferences cannot be ruled out completely, it therefore is plausible to assume much lower contributions to the NO_2 signal. As far as effects on lifetime calculations according to (14) are concerned, an assumption of 75% lower NO_2 values at noon will result in 30% shorter PAN lifetimes

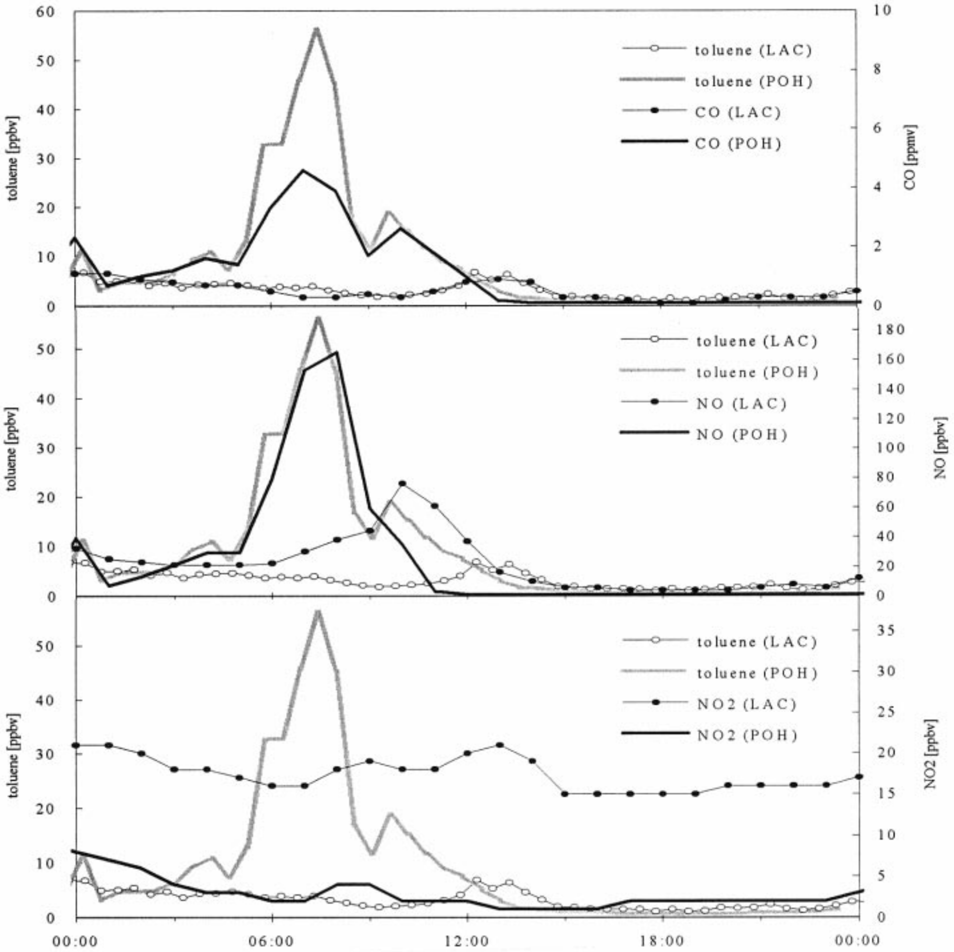

FIG. 7. The photochemical episode of 30 Nov 1996. Diurnal variation (LT) of toluene, CO, NO, and NO_2 at POH and LAC.

at 1300 LT. Between 1200 and 1300 and 1300 and 1500, the effect will be about 15%. It can be concluded that, overall, PAN contributions to the NO_2 signal will only lead to a limited reduction in PAN lifetime, when calculation is based on (14). Strictly speaking, in these very few cases τ_{PAN} calculations represent an upper limit for PAN lifetime. As a consequence, it also means that PAN lifetime is expected to be somewhat shorter, indicating that even stronger photochemical processes are necessary to maintain high PAN levels.

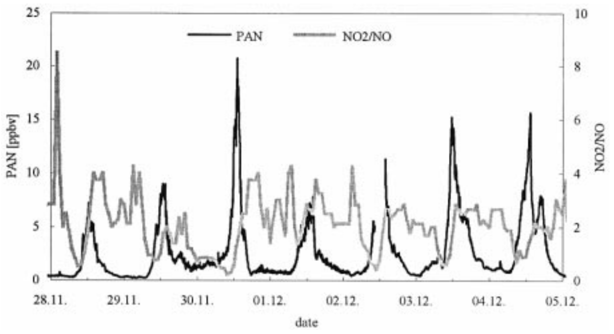

FIG. 8. Time series for PAN and NO_2:NO ratio at LAC. Dates are day.month.

The lifetime of τ_{PAN} is displayed in Fig. 6. Obviously, temperature plays a crucial role in the degradation process of PAN through thermal decomposition [(11)]. During the daytime, especially during periods of high PAN concentrations, PAN lifetime is between 30 min and 1 h. Lifetime starts to increase in the late afternoon when peak PAN concentrations are past and concentration is close to 1 ppbv. During nighttime, τ_{PAN} increases to 10–15 h, enough to stabilize PAN at a concentration of about 1 ppbv until the next day. Figure 8 shows that the NO_2:NO ratio usually has daytime minimums when PAN concentrations start to increase. This minimum coincides with the arrival of the urban plume, which contains high amounts of precursors. Although the lifetime of PAN is very low at this time of day, PAN values increase rapidly, presumably because of high NMHC precursors in the urban plume. According to Fig. 8, the

NO_2:NO ratio increases within an hour. Obviously, this increase seems to contradict the point of view taken when Lagrangian assumptions are made: within a given air parcel, the formation of PAN is expected to consume NO_2, resulting in a decrease of the NO_2:NO ratio. However, LAC actually faces an intermediate state of the urban plume that has not yet undergone complete photochemical processing. Precursors such as NO and NMHC still are present. Conversion of NO to NO_2 in the presence of NMHC continues. As a consequence, the NO_2:NO ratio may increase subsequently. Secondary compounds already have been formed in considerable amounts in the plume. Even higher concentrations of ozone could be expected farther downwind. PAN, however, is obviously subject to an effective removal mechanism, although increasing NO_2:NO ratios after noon suggest longer lifetimes. Therefore, it is not certain that PAN concentrations continue to rise farther downwind. In this study, LAC is a suitable measurement site because of its pronounced mountain–valley breeze system. Farther downwind, the landscape becomes diverse. Flow regimes are much more complex.

From these observations, it can be concluded that PAN is formed almost completely within the urban plume. A removal mechanism of PAN based on thermal decomposition implies subsequent removal by NO. At this same time, NO reactions also should apply for ozone. In these investigations, however, simultaneous O_3 reductions were not identified. This failure may be caused by the fact that PAN decay also serves as a source for NO_2, thus compensating possible O_3 losses (Becker 1991). This mechanism may be effective at high temperatures and at high PAN concentrations. Another possible loss mechanism that recently has been discussed for air quality studies in Mexico City, that is, heterogeneous reactions of PAN on fine aerosols and in particular carbonaceous soots (Gaffney et al. 1998), has not been a focus yet in Santiago de Chile. Studies comparing air quality in various Latin American cities, however, imply similarities in regard to the high burden of particulate matter in both cities (Romieu et al. 1991). Therefore, heterogeneous removal mechanisms for PAN may not be ruled out.

For ozone formation, it is necessary to consider that part of the ozone that has been built up during the day and may be stored in the residual layer aloft. This feature primarily applies to ozone rather than PAN, since PAN concentrations already are low (about 1 ppbv) in comparison with ozone when inversion layers develop in the evening hours. On the following day, breaking up of the inversion layer leads to vertical mixing and therefore to a rapid increase in ozone mixing ratios. Investigations carried out in Athens, Greece (Suppan et al. 1998), showed that concurrent increases of ozone took place at various locations within the greater Athens area during the morning hours because of the breakup of the nocturnal inversion layer. No concurrent rises in PAN concentrations were discernible, but rather a time shift in diurnal maximums of PAN was seen. PAN mixing ratios were controlled primarily by horizontal advection of the photochemically active urban air mass. Daytime ozone production at LAC may be deduced by comparing daytime maximum ozone concentrations obtained at POH with corresponding ozone values at LAC. At the POH site, very low concentrations of precursors (even lower than at LAC) are found after noon because of effective ventilation; for example, both NO and NO_2 values are about 1 ppbv. Ozone concentrations at this time of day represent urban background values. On 29 November, maximum ozone concentrations at POH are about 50 ppbv, whereas LAC had 82 ppbv ozone. On 30 November, the corresponding values were 81 ppbv and 148 ppbv, respectively. Ozone concentrations at LAC are about 61%–83% higher than at POH.

Figure 7 also elucidates relationships among some important precursor compounds, that is, toluene, CO, and nitrogen oxides for the photochemical episode of 30 November 1996. At both sites there is a good relationship between CO and toluene, whereas NO is only in good agreement with toluene at the center site (POH). At LAC this compound peaks before toluene reaches its noon peak. The diurnal variation of NO_2 looks almost the same at both sites. At LAC there is only a slight diurnal variation and NO_2 concentrations are high throughout the day in comparison with those of POH. It indicates a high potential for the formation of ozone through NO_2 photolysis. This NO_2 feature at LAC is not very common at other urban measurement sites, but it is usually encountered along the Mapocho valley, including the LAC site. Apart from results obtained by commercial analyzers, this finding also is supported by results from NO_2 passive tubes (Oyola and Romero 1992). According to investigations carried out during July until October 1995 (CONAMA 1996), NO_2 passive tubes that were exposed at various sites throughout Santiago, including LAC, yielded mean monthly NO_2 concentrations of 61 ppbv (July), 64 ppbv (August), 46 ppbv (September), and 39 ppbv (October). Decreasing NO_2 mixing ratios in springtime also imply still lower values in November. Nevertheless, NO_2 concentrations still remain relatively high in the Mapocho valley. Intercomparisons of mean monthly NO_2 mixing ratios obtained by the passive tube method and a commercial monitor at one site of the local air pollution network showed that, during the measurement period of July–October 1995, the passive tubes in most cases yielded slightly higher NO_2 concentrations than did the commercial analyzer (CONAMA 1996).

Figure 9 summarizes the phenomena for the episode of 30 November 1996. From this figure it is quite obvious that there is a relationship between POH and LAC. The mountain–valley breeze system leads to transport of polluted air masses (e.g., as indicated by toluene and CO) from POH to LAC. Contrary to what happens at POH, the toluene maximum at LAC develops after noon. At this time, toluene concentrations at LAC are even

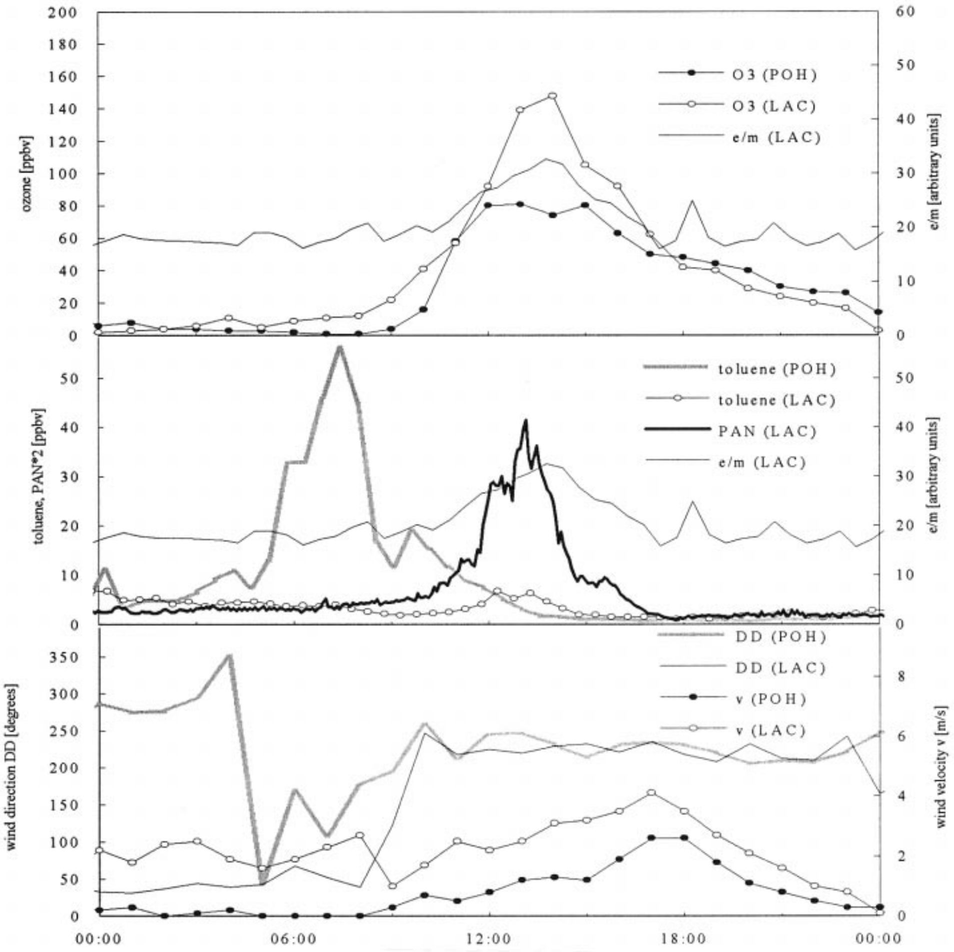

FIG. 9. The photochemical episode of 30 Nov 1996 (e/m is ethylbenzene : m-xylene and is scaled upward by a factor of 50). Time series is in LT.

higher than at POH. Moreover, along with toluene and CO, PAN and ozone also increase at LAC. The shape of the PAN peak is in good agreement with the morning-hour toluene peak at POH. For ozone the corresponding peaks do not correlate as well. The shapes of the toluene and CO curves at LAC have been transformed in comparison with their morning peaks at POH. Toluene and CO are subject to the same dilution effects on their way from downtown Santiago to LAC. Mixing ratios of toluene, however, decrease more rapidly than those of CO, presumably because of photochemical processing. The phenomena mentioned above are strong indications that PAN has been formed from hydrocarbon precursors within the urban plume en route to LAC. Also O_3 is strongly built up to almost double the value observed at POH. An important indicator for these photochemical processes is the e:m ratio measured at LAC. As long as the e:m ratio increases, O_3 and PAN concentrations at LAC also increase.

To assess the importance of different NMHC in the evolution of photochemical smog it is necessary to differentiate between anthropogenic and biogenic NMHC. Figure 10 shows plots of the diurnal variation of specific ratios between benzene as a typical surrogate for anthropogenic NMHC and two species of biogenic origin: limonene and iso.*. (Here iso.* mainly consists of isoprene but also includes t-2-pentene and c-2-pentene, since these compounds may not be separated by the GC system. However it is assumed that the alkenes form only a minor part of this sum.) These figures show that biogenic precursors gain importance in the afternoon at both sites. This result is due to high solar irradiance and high temperatures. It is important that POH is located on the border of an extended park, and the LAC site is situated in a recreation area. In both cases deciduous trees and shrubs form by far the most part of the vegetation. These trees usually emit isoprene. Contrary to the case for monoterpene emission, isoprene emission depends on both temperature and sunlight (Guenther et al. 1991). Figure 11 depicts times series for PAN and O_x ($[O_x] = [O_3] + [NO_2]$) for the same time period as shown in Figs. 4, 6, and 8. The features plotted in Fig.

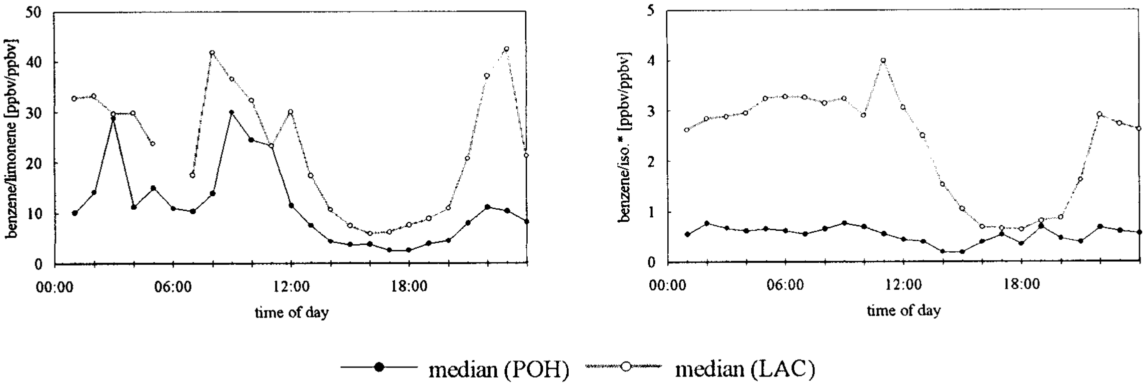

FIG. 10. Mean diurnal variation (LT) of the ratios benzene : limonene (left) and benzene : iso.* (right) at POH and LAC (iso.* includes t-2-pentene, isoprene, and c-2-pentene).

11, however, are typical for the entire campaign. In addition to PAN and O_x, some selected hydrocarbon fractions of the whole C_4–C_{12} NMHC spectrum are presented, namely, toluene/NMHC, m-xylene/NMHC, and iso.*/NMHC. These fractions are calculated on a ppbC basis. Some important results may be deduced from this figure. Usually toluene forms about 15% of all C_4–C_{12} NMHC at LAC. Almost every time when the urban plume passes the LAC site, and through the entire period when increased O_x concentrations can be observed at LAC, however, the toluene fraction also is greatly increased (20%–30%). There are only a few exceptions, especially on 30 November 1996. Within the urban plume, the m-xylene fraction decreases considerably (from about 8% to 5%). Its minimum is always reached when PAN peaks occur. After PAN decreases (but O_x levels still remain high) the m-xylene fraction rises again. Note that the lowest minimum of the m-xylene fraction appears on 30 November 1996, the day with the highest PAN values. Obviously, degradation of aromatic compounds, for instance, is strong and even leads to lower toluene fractions, in contrast with most of the other days as outlined above. The iso.* fraction usually reaches its daytime peaks in the afternoon. Since iso.* is a fast-reacting compound toward OH and O_3, iso.* may not be transported for longer times. Therefore it can be explained that sometimes when the urban plume passes LAC the iso.* fraction of NMHC becomes less (e.g., on 30 November 1996). From this fact alone it may not be ruled out that this species takes part in local production of ozone and PAN under the influence of the urban plume. It is obvious from Fig. 11, however, that iso.* starts to increase when PAN values are decreasing because of thermal decomposition. At this time, iso.* may no longer be an effective PAN precursor, but it may keep up the formation of ozone that is not subject

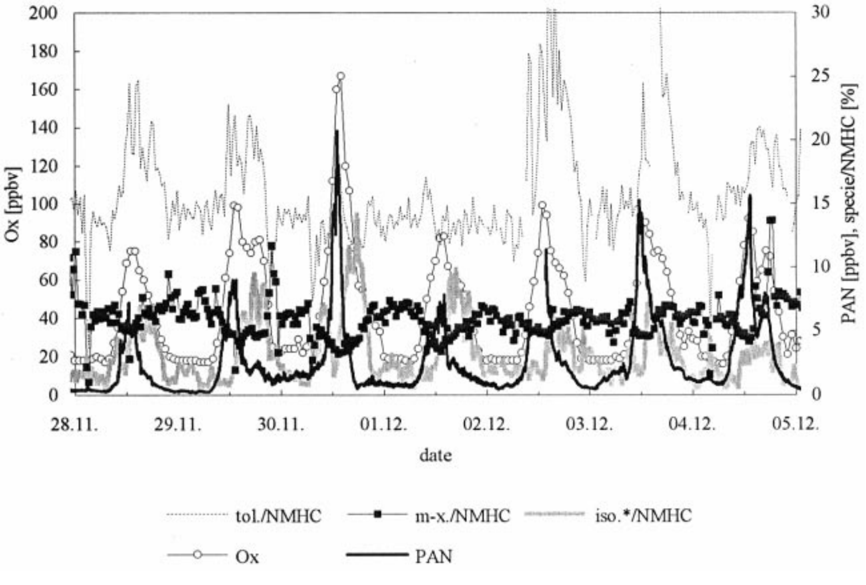

FIG. 11. Time series for O_x, PAN, and the fraction of toluene (tol.), m-xylene (m-x.), and iso.*, respectively, of all measured NMHC (C_4–C_{12}) at LAC. Dates are day.month.

to thermal decay. As a matter of fact, usually a broad O_x peak can be observed almost every day. Sometimes (e.g., on 29 November 1996) even a second afternoon O_x peak may form. In any case, this second peak never reaches the peak that is observed concurrently with the PAN peak shortly after noon.

Given the transport processes from the center of Santiago to LAC that were mentioned above, it may be concluded that anthropogenic emissions, especially traffic emissions, contribute greatly to photochemical processes in the urban area of Santiago. Biogenic NMHC may support the buildup of secondary species but mostly contribute to maintaining ozone concentrations in the afternoon when biogenic emissions reach their daytime maximum because of high temperatures and irradiance.

The results obtained in Santiago de Chile confirm studies made during MEDCAPHOT-TRACE in Athens, Greece, in 1994 where, for the first time, relationships between online BTEX measurements and secondary compounds in an urban area were investigated. Rappenglück et al. (1998) found out that the e:m ratio related well with the diurnal variation of ozone. Ozone formation, however, is more complicated than PAN formation. PAN formation is linked much more unambiguously to the abundance of hydrocarbons in ambient air and therefore often is related closely to anthropogenic pollution. During MEDCAPHOT-TRACE, PAN measurements took place at various locations but not at the sites where online NMHC measurements were available. Thus, information about BTEX–PAN relationships still was limited. In this sense, the measurements in Santiago are unambiguous, since all requirements were met: concurrent online NMHC and PAN measurements at the same site and very favorable and stable meteorological conditions. Both the MEDCAPHOT–TRACE campaign in Athens and the PHOTOCHEMICAL CAMPAIGN in Santiago de Chile show that the e:m ratio is a good indicator for the effect of anthropogenic-related hydrocarbon chemical processes.

4. Conclusions

During the PHOTOCHEMICAL CAMPAIGN in November and December 1996 quasi-continuous measurements of NMHC in the range of C_4–C_{12} together with PAN measurements were carried out for the first time in the Metropolitan Area of Santiago de Chile simultaneously at two sites (center and suburban) by means of online GC methods. Results of peroxyacetyl nitrate measurements could be obtained from the suburban site. Measurements were accomplished with standard meteorological parameters, CO, NO_x, ozone, and $J_{\mathrm{O}(^1\mathrm{D})}$.

Overall, the hydrocarbon mixture in Santiago mainly reflects emissions from traffic. The benzene : toluene ratio as a typical surrogate for this type of source is on the same order of that found in other urban areas worldwide. The distribution of NMHC within the Metropolitan Area of Santiago de Chile is controlled strongly by the mountain–valley breeze system that leads to transport of polluted air masses from the center of Santiago de Chile to the northeast suburban regions during daytime. Within the urban plume, regularly high mixing ratios of PAN can be found. Maximum concentrations reach up to 21 ppbv. The observations show that the behavior of PAN is linked strongly to anthropogenic compounds, namely, aromatic compounds (e.g., m-xylene). Biogenic precursors may contribute only to afternoon ozone concentrations since PAN thermally decomposes before biogenic precursors are emitted in large amounts. Increased ethylbenzene : m-xylene (e:m) ratios correlate very well with increased mixing ratios of secondary compounds. This ratio can be used as a good indicator for the effect of anthropogenically related hydrocarbon chemical reactions leading to the formation of secondary pollutants, since increasing concentrations of PAN and ozone are accompanied by increasing e:m ratios.

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