

An urban photochemistry study in Santiago de Chile

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Abstract

During spring time 2002 a field experiment was carried out in the Metropolitan Area of Santiago de Chile at three monitoring sites located along a SW–NE transect that represents upwind, downtown and downwind conditions, respectively. Three consecutive days (30 October–01 November 2002) reflecting different photochemical and meteorological conditions were selected. These days included two workdays and one holiday and thus the effect of different primary emissions could be investigated. A variety of trace gas measurements (O_3 , NO_x , CO, volatile organic compounds (VOC)) were obtained at these sites. Alkanes represent the largest VOC fraction at all sites, followed by aromatics and alkenes, the smallest fractions are represented by the alkynes or isoprene. Regarding reactivity ranking propene equivalent values show that during morning hours, alkenes are the most reactive compounds, at noon, aromatics are dominant, and in the afternoon isoprene becomes important. Alkanes do not contribute more than 20% to the total air mass reactivity despite being present at the higher concentration levels. Regarding liquefied petroleum gas (LPG) impacts, we find a threefold decrease of concentrations at the eastern side of the city—and no significant trend at Downtown Santiago—which we ascribe to a switch to natural gas in the higher income eastern side of town. The generation of ozone impacts above 50 ppbv is mainly due to anthropogenic traffic-related hydrocarbons. In addition, traffic emissions are contributing most to the formation of secondary organic aerosols (SOA). A model study was carried out, applying a Lagrange trajectory model coupled with photochemical and aerosol modules. The model results are in good agreement with the observations. Additionally, the relative contribution of the respective hydrocarbons to the ozone production in an air parcel along the trajectory was computed. The model also indicates SOA formation by means of oxidation of higher alkanes, alkenes, and aromatics, the latter being the major contributors to those secondary pollutants.

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1. Introduction

It is well known that urban zones represent areas at which significant amounts of gaseous pollutants and particulate matter are released into the atmosphere. In particular, in tropical and subtropical regions, with intensive global radiation and high daytime temperatures, very dynamic metropolitan areas exist nowadays and both their number and size are continuously growing. These megacities often suffer from severe critical loadings of a variety of air pollutants. High concentrations of ozone and related photooxidants as well as of particulate matter are causing health effects, ecological damages and economic losses. These impacts are not only restricted to the urbanized areas themselves, pollution plumes also stretch over larger regions downwind of these agglomerations (Corsmeier et al., 2002; Rappenglück et al., 2004) and may even be observed at surface sites far away from the emission sources (e.g. Wotawa and Trainer, 2000; Forster et al., 2001; Rappenglück et al., 2003).

Located at a latitude of 33°27'S the Metropolitan Area of Santiago de Chile (Santiago R.M.) represents a subtropical site and is exposed to persistent stable meteorological conditions during spring and summertime. Though with about 5.5 million inhabitants Santiago de Chile can be regarded as a medium sized agglomeration among megacities in the world, its orographic location in a poorly ventilated basin at the rim of the highest mountain ranges of the Andes, where almost only valley-mountain-breezes control the distribution of pollutants, is quite unique (Rutllant and Garreaud, 1995, 2004; Garreaud et al., 2002; Garreaud and Rutllant, 2003). Frequently, Santiago de Chile faces high concentrations of ozone and peroxyacetyl nitrate (PAN) (Rappenglück et al., 2000; Rubio et al., 2004).

Over the last decade, knowledge about the air quality of Santiago de Chile has grown substantially. Investigations have focused on the specific urban conditions and climatological issues related to smog events in Santiago (Ihl et al., 1998; Ihl-Tessmann, 1998; Romero et al., 1999), on aerosols (Ortiz et al., 1993; Rutllant and Garreaud, 1995; Cahill et al., 1996; Artaxo et al., 1999; Morel et al., 1999; Didyk et al., 2000; Perez et al., 2000; Kavouras et al., 2001; Tsapakis et al., 2002) and on the implications of non-methane hydrocarbons (NMHC) in the evolution of photochemical smog (CENMA, 1999; Rappenglück et al., 2000; Chen et al., 2001; Monod et al., 2001). However, these studies were still restricted to the analysis of experimental fieldwork. A few statistical forecast models (Jorquera et al., 1998, 2000; Perez et al., 2000), receptor modeling study of ambient volatile organic compounds (VOC) (Jorquera and Rappenglück, 2004), and box model approaches (Jorquera, 2002a, b) have been carried out. Recently, three-dimensional numerical studies investigating the summertime circula-

tions and the air pollution dispersion (Schmitz, 2004) in the Santiago basin were presented. However, no investigations involving sophisticated numerical photochemistry models have been applied so far.

During spring time 2002 a field experiment was carried out in the Metropolitan Area of Santiago de Chile at three monitoring sites located along a SW–NE transect that includes upwind, downtown and downwind conditions, respectively. Three consecutive days reflecting different photochemical and meteorological conditions were selected (for details concerning meteorological conditions see Fig. 1). These days included two workdays and one holiday and thus the effect of different primary emissions could be investigated. A variety of trace gas measurements (O_3 , NO_x , CO, NMHC and oxygenated volatile organic compounds (oxy-VOC)) were obtained at these sites. While the earlier study by Rappenglück et al. (2000) focused on online measurements of NMHC for several weeks and was restricted to hydrocarbons $>C_3$ due to technical reasons, the present study applied canister samplings to obtain a comprehensive insight into the diurnal variations of very high volatile NMHCs. Both the well-resolved NMHC speciation and the temporal resolution of 2 h allowed us to collect additional information about NMHC photochemistry in Santiago de Chile. This paper addresses the importance of specific hydrocarbon classes with regard to their different ozone formation potentials during the daytime. In addition, numerical model studies are applied to investigate the contribution of hydrocarbons to the formation of secondary species, including the formation of secondary organic aerosol (SOA) in the Santiago basin.

2. Experimental setup

Following the investigations described in Rappenglück et al. (2000) the urban measurement sites Parque O'Higgins (POH) as a downtown site and Las Condes (LAC) as a well-documented suburban receptor site (CENMA, 1999; Rappenglück et al., 2000; Jorquera and Rappenglück, 2004) were chosen (Fig. 2). Both sites belong to the routine monitoring network of the Servicio Salud del Ambiente Region Metropolitana (SESMA) and are equipped with analyzers for ozone, CO, NO_x and sensors for meteorological parameters. In addition to these two sites, we set up a background site in the small village El Monte (EIMo) about 30 km upwind of the urban area. This site was designated to provide hydrocarbon input data for initializing our model runs. During the field experiment from 30 October–2 November 2002, canister samples for CO and NMHC in the range from C_2 – C_9 and cartridge samplings for aldehydes and ketones were taken at all three sites. Canister samples were taken at 8:00 a.m., 10:00 a.m., 12:00 a.m.,

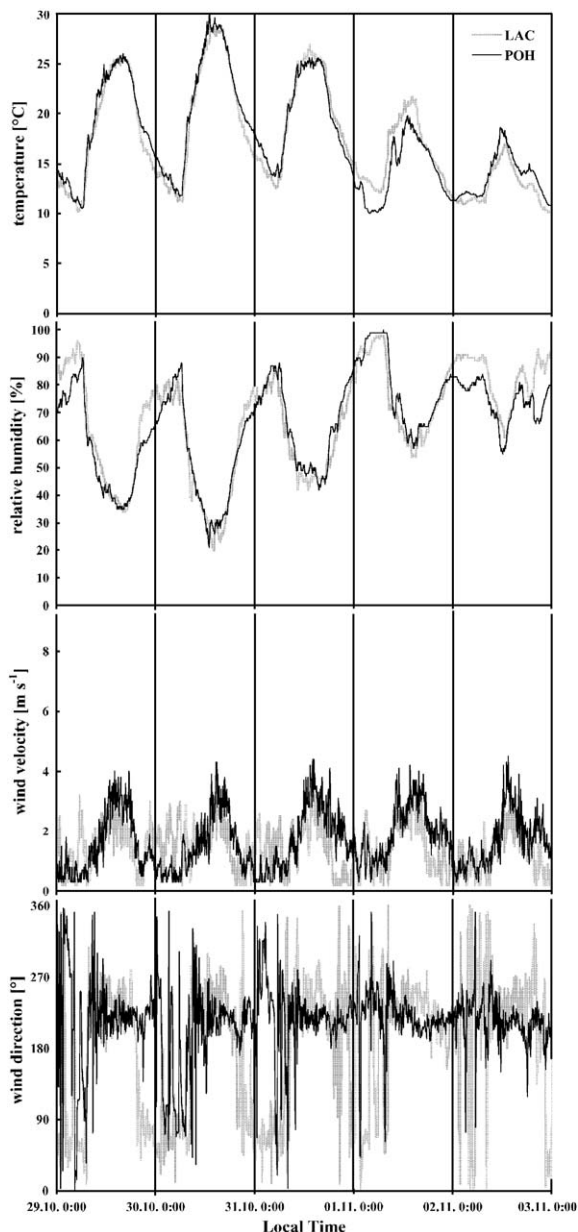


Fig. 1. Time series for temperature, relative humidity, wind velocity and wind direction as measured at Parque O'Higgins (POH) and Las Condes (LAC) from 29 October–2 November 2002. According to measurements obtained at the University of Chile located Downtown Santiago no precipitation occurred in the time period of the field campaign. Maximum solar radiation was 1000 W/m² on 30 October, 900 W/m² on 31 October, and 700 W/m² on 1 November 2002.

2:00 p.m., 4:00 p.m., 6:00 p.m., and 8:00 p.m. (flushing time about 10 min). Cartridges were filled for 4 h during the intervals 8:00–12:00 a.m., 12:00 a.m.–4:00 p.m., and 4:00–8:00 p.m. Samples were taken at a height between 2

and 3 m above ground. At POH and LAC, samples were taken close to the existing SESMA monitoring network units that are about 200 m (LAC) and 500 m (POH) away from traffic lanes. The LAC site is located in a recreational area, the POH site is located in the center of a downtown park area. The EIMo site was set up in a private garden lot of a residential area. The only road with some traffic is about 200 m away.

Measurements of NMHC have already been reported for Santiago de Chile. They either focused on online quasi-continuous measurements of C₄–C₁₂ NMHCs (Rappenglück et al., 2000) or applied canister measurements for the detection of C₂–C₆ (Universidad de Concepción, 1998; CENMA, 1999; Chen et al., 2001, Monod et al., 2001). For the field experiment in the year 2002 we sought a compromise between the high temporal resolution of 30 min reported by Rappenglück et al. (2000) and the good chromatographical resolution of high volatile C₂–C₄ NMHCs obtained by the other authors. In our study we used 1 L 2-valve electropolished stainless steel canisters made exclusively by our provider Fäth, Eschau-Hobbach, Germany. For sampling we applied standard operating procedures developed and recommended by the Global Atmosphere Watch World Calibration Center for Volatile Organic Compounds. Briefly, as an inlet a stainless steel tubing (about 2 m) was connected to the pressurization metal bellows pump employing an inline PTFE membrane filter (pore size 0.45 µm; stainless steel filterholder). The tubing was primarily used to destroy ozone prior to entering the canister (according to a method by Koppmann et al., 1995) and the filter to protect the pump and canisters from particles and aerosols. For sampling, a canister was attached downstream to the pump. The canister was flushed with ambient air and repeatedly pressurized and released prior to the actual sampling by a final pressurization (about 3 bar). The pressurization steps were controlled via a pressure gauge connected to the pump. After filling, valve closing and plugging of valve inlets the canisters were ready for shipping. Altogether, about 80 canisters were filled during the experiment and sent back to Germany for subsequent analysis for CO and C₂–C₉ NMHCs in the laboratory at the Institute of Meteorology and Climate Research (IMK-IFU) in Garmisch-Partenkirchen. Storage time was kept as short as possible and most of the canisters were analyzed in November 2002. According to Habram (1998) who extensively studied the temporal behaviour of hydrocarbons in the canisters we used in this project, no significant deviations occur within this short storage time, in particular, if humidity levels in the canisters are sufficiently high (McClenny et al., 1991). For this reason, our standard procedure prior to canister shipping to the field campaign always involves flushing with ambient air (Rudolph et al., 1990). In order to account for the stability of the canister samples, a

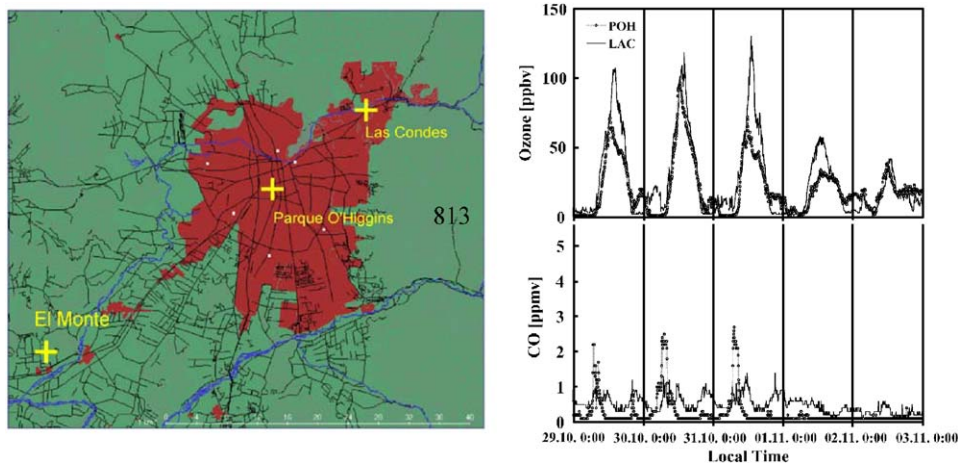


Fig. 2. Left side: location of the measurement sites during the field experiment from 30 October–1 November 2002 (ElMo: El Monte; POH: Parque O'Higgins; LAC: Las Condes). Right side: ozone and CO time series at POH and LAC.

standard canister containing 70 hydrocarbons accompanied the canister shipment throughout the time of the field campaign and storage, however it remained sealed all the time. Measurements before and after shipping showed deviations for C_2 – C_9 hydrocarbons that are within the calibration error of our NMHC analysis system. We also applied internal consistency checks as outlined in Parrish et al. (1998) and Bottenheim and Sheppard (1995). As a standard our laboratory analysis of the canister samples includes the determination of CO (for method description see below). Canister CO values obtained in Santiago agreed perfectly with online CO instruments of the SESMA monitoring sites and thus proved the quality of our ambient air sampling.

CO mixing ratios in the canisters were determined by a HgO detector after separating CO from other gases on a column packed by molecular sieve 13X (3 cm \times 2.2 mm ID) according to a method by Seiler et al. (1980). NMHCs were analyzed by a gas chromatographic (GC) method by Habram et al. (1998). The procedure is briefly summarized as follows: Up to 8 canisters were mounted to a 16-port Valco valve. This valve is controlled by the GC software to take sequential samples (400 ml) from all canisters and inject them into the analytical cycle. The set of canisters included 6 ambient air samples, one calibration canister containing benzene and *n*-butane in nitrogen, and one canister containing 70 NMHC compounds in nitrogen for identification purposes. Both canisters were filled from corresponding gas cylinders provided by Messer Griesehm, Krefeld, Germany, and the National Center for Atmospheric Research, NCAR, Boulder, CO/USA, and were in the ppbv-range. The quantification of individual NMHC species was based on the *n*-butane response factor. The two species, benzene and *n*-butane, were used to check the consistency and stability of the

calibration gas itself. In order to remove water the sample passed an empty PFA tube (300 mm \times 0.25 mm ID) at -30°C . Subsequent preconcentration of the sample was accomplished with a commercial sample preconcentration trap (SPT) made by Varian (800 mm \times 2.1 mm ID) and filled with Carbopack[®] BHT. The SPT was kept at -120°C using liquid nitrogen. The sample was desorbed at 200°C and injected into the GC (Varian 3600CX) with He (purity 99.999%) as the carrier gas. For the separation two columns run in parallel were used: C_2 – C_4 NMHCs were separated by a PLOT column GasPro GSC (17 m \times 0.32 mm ID; Astec, Whippany, NJ, USA); for the separation of C_4 – C_9 hydrocarbons a CP-SIL 5 CB column (50 m \times 0.25 mm ID, 1 μm df; 100% Dimethylpolysiloxane, Chrompack, Middelburg, Netherlands) was used. Both columns were placed in one oven. A multiramp temperature program was used: -30°C (2.5 min hold, $3.5^\circ\text{C}/\text{min}$ to -13°C , $20^\circ\text{C}/\text{min}$ to 8°C , $5^\circ\text{C}/\text{min}$ to 70°C , $10^\circ\text{C}/\text{min}$ to 240°C (10 min hold). The entire temperature program has a length of 50 min. The hydrocarbons of the sample were detected by a flame ionisation detector (FID) that was kept at 250°C . For the FID H_2 (purity 99.999%) and synthetic air was used. Precision of this system is less than 0.9% for compounds in the range between 5 and 50 ppbv. For aromatic compounds the precision for the same concentration range is 1% for benzene and toluene, 2% for ethylbenzene and 3% for the xylenes. The detection limit is between 10 and 15 pptv for most compounds for a sample volume of 400 ml. Within the German Tropospheric Research Focus (TFS) this GC system passed comprehensive independent quality assurance procedures and agreed to the instruments of the experienced participants within $\pm 20\%$ for most compounds (Volz-Thomas et al., 2002).

Carbonyls were sampled over 4 h periods at a flow rate of 1 l/min onto 2,4-dinitrophenylhydrazine adsorbent cartridges (LpDNPH S 10, Supelco, Bellefonte, PA, USA) by the procedure described by the manufacturer (Supelco, 1996), eluted with 5 ml of acetonitrile in a vacuum manifold system and determined by HPLC on an automated Shimadzu system (SCL-10A VP controller, LC-10AT VP pump, FCV-10AL VP mixer, DGU-14A degassing unit, Rheodyne injector with 20 μ l sample loop, Shim-pack VP-ODS column, 250 mm length, 4.6 μ m particle size, SPD-UV-VIS detector set at 360 nm and a CLASS-VP data system). The following mobile phases were used: A: Water/acetonitrile/tetrahydrofuran (60/30/10); B: water/acetonitrile (70/30). Gradient program was: 0 min—100% A, 1 min—100% A, 10 min—0% A, 30 min—0% A, 31 min, flow rate set at 1.5 ml/min. Quantification was made in the external standard mode, using dilutions at 5 levels (0.09–1.2 μ g/ml of each carbonyl) of a TO11/IP-6A Aldehyde/Ketone DNPH Mixed Standard (Supelco).

3. Model approach

The model used in this study was a Lagrangian box model. Trajectories were calculated from wind fields generated by the fifth-generation Penn State/NCAR Mesoscale Model (MM5, Grell et al., 1994) by hourly interpolation. The horizontal grid spacing was 2 km, and only winds from the first sigma level (about 17 m a.g.l.) were considered. The box height was given by the MM5 output for the mixing layer height. For very stable conditions a minimum of 100 m was considered. With an increase in the mixing layer height entrainment of clean air masses from aloft into the box were assumed. Furthermore, it is assumed that the box is always completely mixed. The gas phase of the model was treated by the RADM2 mechanism (Stockwell et al., 1990). Aerosols were treated according to the MADE/SORGAM mechanism (Ackermann et al., 1999; Schell et al., 2001) which treats SOA formation explicitly by the oxidation of higher alkanes, alkenes, and aromatics. As input data the model needs as input data initial conditions and emissions according to its trajectory. Initial data were obtained as described below. Emission inventories included mobile, area, and point sources. Biogenic sources are not considered.

4. Results and discussion

4.1. General observations

Fig. 2 shows the temporal variation of ozone and CO as obtained by the routine SESMA observations at POH and LAC in October and November 2002. CO is almost

exclusively emitted by traffic exhaust. Due to its moderate reactivity to OH CO is a good tracer for atmospheric dispersion processes, in particular, for transport studies and investigations concerning the diurnal variation of thermal inversions or the diurnal evolution of turbulent processes. According to Fig. 2 a 3-day episode with increasing day-to-day maximum ozone values can be easily identified between 29 and 31 October 2002. Highest ozone values were observed at LAC on 31 October (129 ppbv) and at POH the day before (96 ppbv). The persistent feature of meteorological conditions and primary emissions during these days is reflected in the CO time series. While the POH site experiences strong diurnal variations with well-shaped morning hour peaks and low concentrations in the afternoon, the LAC site shows moderate diurnal variations with slightly higher background concentrations.

Our field experiment covered the last 2 days of the aforementioned ozone episode (30–31 October 2002) and included the subsequent holiday (01 November 2002) when emission conditions changed drastically. Considering the ozone time series of these 3 days, it is worth noting that each day exhibited specific features that represent a nice data base for modeling studies: on the first day (30 October 2002), the shape of the diurnal variation of ozone is quite similar for POH and LAC and maximum ozone values only differ by 20 ppbv. On the second day, the difference in maximum ozone values is much higher (57 ppbv). Moreover, the temporal variations are different: at both sites a shoulder in the ozone time series develops in the afternoon. This feature appears to be the typical photochemical smog condition in Santiago and was found frequently in the 1996 study (Rappenglück et al., 2000). The last day (01 November 2002) is marked by a sharp decline in ozone maximum values at POH (33 ppbv) and LAC (57 ppbv). On the whole, the shape of the diurnal variations appears to be broader, a typical urban plume peak, however, is not present on this day.

In Table 1 results of some selected VOCs along with CO obtained within the field experiment are listed. Maximum concentrations for primary hydrocarbons and CO occur at the downtown site POH. Though maximum mixing ratios at LAC are lower than at POH, often, the median values at the suburban site are higher than in the downtown area. Contrary to both urban sites the upwind site ElMo displays median values that are generally up to ten times lower than in the urban area and thus represents typical background values for air masses entering the Santiago basin. Some hydrocarbons often reach very high concentrations, even at the ElMo site. These are the alkanes propane, *n*-butane, and *i*-pentane, species that are typically found in liquefied petroleum gas (LPG) and that have been identified in substantial amounts elsewhere (Blake and Rowland,

Table 1

Statistical parameters for CO and some selected VOCs at the sites Parque O'Higgins (POH), Las Condes (LAC) and El Monte (ElMo). Data in (ppbv), unless otherwise stated

Species	Median			Maximum			Number of samples		
	POH	LAC	ElMo	POH	LAC	ElMo	POH	LAC	ElMo
CO (ppmv)	0.30	0.55	0.11	2.02	1.28	0.25	19	21	20
Ethene	1.91	2.82	0.70	17.83	8.05	2.39	19	21	20
Acetylene	1.66	3.06	0.44	17.64	7.78	1.91	19	21	20
Propane	5.66	7.91	0.66	84.52	23.16	8.00	19	21	20
<i>n</i> -Butane	1.56	1.73	0.12	12.51	4.34	3.73	19	21	20
<i>i</i> -Pentane	1.05	2.36	0.21	11.60	5.20	6.95	19	21	20
Isoprene	0.34	0.18	0.09	0.88	0.34	0.37	19	21	20
Benzene	0.38	0.95	0.19	4.00	2.06	0.50	19	21	20
Toluene	1.59	2.28	0.19	13.52	5.99	1.15	19	21	20
Ethylbenzene	0.27	0.52	0.04	3.19	1.25	0.40	19	21	19
<i>m,p</i> -Xylene	0.70	1.46	0.12	10.50	3.24	1.12	19	21	20
<i>o</i> -Xylene	0.39	0.72	0.12	4.78	1.71	0.76	19	21	19
Formaldehyde	3.09	7.11	1.43	6.69	12.33	2.72	9	8	9
Acetaldehyde	2.92	5.05	1.88	6.59	11.68	4.64	9	8	9
Acetone	3.03	3.43	1.18	4.71	8.47	2.10	9	8	8
Propionaldehyde	0.44	0.89	0.07	0.94	1.37	0.26	9	8	7
Crotonaldehyde	0.12	0.18	0.11	0.65	0.40	0.20	9	8	3
Butyraldehyde	0.39	0.62	0.46	0.55	0.90	0.73	9	8	6
Benzaldehyde	0.11	0.19	0.12	0.30	0.27	0.16	9	8	3
Isovaleraldehyde	0.02	0.20	b.d.	0.20	0.46	b.d.	8	8	b.d.
Valeraldehyde	0.43	0.39	0.43	0.66	0.72	0.91	9	8	9
Hexaldehyde	0.15	0.11	b.d.	0.21	0.17	b.d.	9	8	b.d.

1995). Also, for Santiago de Chile high mixing ratios of propane between 131 and 136 ppbv have been detected (Chen et al., 2001). According to Chen et al. (2001), elevated concentrations of propane also coincided with high levels of *i*-butane and *n*-butane between 5:00 a.m. and 9:00 a.m., indicating the same type of emission source, namely LPG. Other previous studies in the year of 1996 applying online measurement techniques with a temporal resolution of 30 min also revealed significant amounts of C₄-alkanes in the urban air of Santiago de Chile (Rappenglück et al., 2000).

Aromatic compounds are primarily emitted by traffic (exhaust, gasoline evaporation) and in minor amounts also from their use as solvents. For the two urban sites of our study the results indicate maximum values ranging from 2 ppbv (LAC) up to 4 ppbv (POH) for benzene, and 6 ppbv (LAC) up to 13 ppbv (POH) for toluene. Earlier studies (Blake and Rowland, 1995) report more than 16 ppbv for toluene at a site known as Plaza del Inca for one 11:00 a.m. sample. In June and November 1996 two field experiments were carried using canister samples (Chen et al., 2001; Monod et al., 2001). The results show a range of 1.4 ppbv (urban)–17.6 ppbv (traffic) for benzene and 5.4 ppbv (urban)–28.1 ppbv (traffic) for toluene. According to the results from a field experiment in 1998 (v. Baer, priv. comm.) the average

concentration levels of toluene ranged between 6 ppbv (LAC) and more than 10 ppbv (POH) (6 samples; sampling time between 11:00–12:00 a.m.). Results from the 1996 study using an online measurement technique show maximum values for benzene between 10 ppbv (LAC)–25 ppbv (POH) and for toluene between 14 ppbv (LAC) and 56 ppbv (POH) (Rappenglück et al., 2000). It is important to note that usually minimum anthropogenic NMHC values can be expected during daytime due to enhanced turbulent processes, the maximum height of the mixing layer and photochemical transformations. Thus the hour of the sampling time is an essential information when different data sets are compared.

Ratios of NMHCs often reflect photochemical processes due to their different atmospheric lifetimes. These ratios are expected to vary with the distance from an emission source to a receptor site. For the Santiago sites we found that at POH the ratio between toluene and benzene is about 3:1, whereas at LAC it is 2:1, and at ElMo almost 1:1. This spatial distribution is often found in urban areas and surrounding urban–rural transition zones (Rappenglück et al., 1998; Rappenglück and Fabian, 1999; Winkler et al., 2002). Both aromatic compounds only react with OH during daytime with toluene reacting significantly faster with OH than

benzene. Usually, a ratio between 2.5:1 and 3:1 is observed close to emission sources, e.g. traffic. A ratio of 1:1 is typical for background sites. In these regions species originating from urban pollution have already been photochemically removed from the atmosphere, while biogenic hydrocarbons, e.g. isoprene, are likely to become very important. In our field experiment, however, highest isoprene mixing ratios were observed at POH due to the vegetation in this downtown park area, whereas maximum isoprene values were lower in LAC and in EIMo.

Table 1 also lists results of carbonyl measurements. On a ppbC basis the three carbonyls formaldehyde, acetaldehyde and acetone make up about 70% of all measured carbonyls at both urban sites, whereas at EIMo this amount is slightly lower (about 60%). Maximum carbonyl concentrations are usually observed at the suburban LAC site, indicating the impact of both primary and secondary carbonyls. According to Shepson et al. (1991), the acetaldehyde/propionaldehyde ratio may be an adequate criterion to assess anthropogenic pollution. High ratios of about 20 indicate clean air, whereas ratios around 1 were found for polluted air in Los Angeles, for instance. Though based on a limited data set, our results show that the EIMo site can be regarded as a background site (acetaldehyde/propionaldehyde ratio almost 40) for the air masses that are likely to enter the Santiago basin due to the prevalent meteorological flow conditions, whereas the urban sites are mostly impacted by anthropogenic sources with acetaldehyde/propionaldehyde ratios varying from 8.51 (POH) to 6.42 (LAC).

4.2. Diurnal variations

During the field experiment canisters were always sampled between 8:00 a.m. and 8:00 p.m., e.g. during daytime when the mixing height reaches its maximum and photochemical processes are strongest. Therefore, concentration levels of primary emitted species are expected to be lower during this period of time than during nighttime as observed in previous studies in the urban area of Santiago (CENMA, 1999; Rappenglück et al., 2000). However, species emitted by biogenic sources usually reach maximum mixing ratios during daytime due to the enhanced activity of the vegetation.

Canister samples were routinely screened for their CO content. As outlined before carbon monoxide is well suited for transport studies due to its moderate reactivity. Fig. 3a displays the canister results for CO for the three sites POH, LAC and EIMo during the field experiment. At EIMo almost no clear diurnal variation is visible. In addition, often, the mixing ratios are below 150 ppbv. On 1 November 2002, they even do not surpass 100 ppbv, indicating clean air. This is in good

agreement with the previous statement about carbonyl measurements at EIMo. At the two urban sites POH and LAC maximum CO values typically occur during the morning hours. In POH the lowest values (down to 174 ppbv) are always observed at noontime. Such low values are not observed at LAC any time. However, the LAC site is usually affected by the urban air plume at noon due to the local wind system in the Mapoche valley where LAC is located (Rappenglück et al., 2000). This prevalent flow system explains the lowest acetaldehyde/propionaldehyde ratios found among these three sites. The third day of this field experiment is different from the previous days. Overall, the concentration levels are lower and no pronounced diurnal variation is discernible. This is likely due to the fact that the last day was a holiday and therefore only moderate emissions occurred.

In Fig. 3b diurnal variations of total NMHC observed at all three sites are shown for the case of 31 October. For POH Fig. 3b reveals maximum values for the early morning hours POH (e.g. almost 1000 ppbC in the morning hours of 31 October). Minimum levels occur between 2:00 and 6:00 p.m. At LAC concentrations persistently remain at elevated values throughout the day (between 200 and 300 ppbC) and reach maximum values between noon and 2:00 p.m. At EIMo, however, variations are limited and the concentrations seldom surpass 50 ppbC.

Speciation of NMHCs shows that anthropogenic VOCs usually correlate well with CO (not shown here in detail). Temporal variations of benzene best match those of CO. R^2 ranges from 0.86 (POH) to 0.96 (LAC). For both of these compounds traffic exhaust represents the main emission source. Propane, however, displays stronger diurnal variations than benzene and CO. R^2 is 0.70 (LAC)–0.79 (POH), indicating other important sources. Propane may be typically found in LPG. As can be expected the diurnal variations of isoprene, the only biogenic hydrocarbon determined in the canister samples, are different and coincide with solar radiation and the ambient temperature.

In Fig. 3c diurnal variations of total aldehydes are presented for all three sites for the case of 31 October. Again, higher values for the urban sites are found throughout the field experiment. At the background site diurnal variations with a noontime peak indicate the prevalence of secondary carbonyls at this time of the day. The same feature holds for the suburban LAC site though at significantly elevated concentrations suggesting an additional strong background of primary carbonyls. The possible impact of primary carbonyls can be best seen in the morning hour samples when radiation processes are still low: in most cases carbonyl values at LAC and POH show the same levels (about three times higher than at EIMo). Later at POH both strong ventilation and lower emission

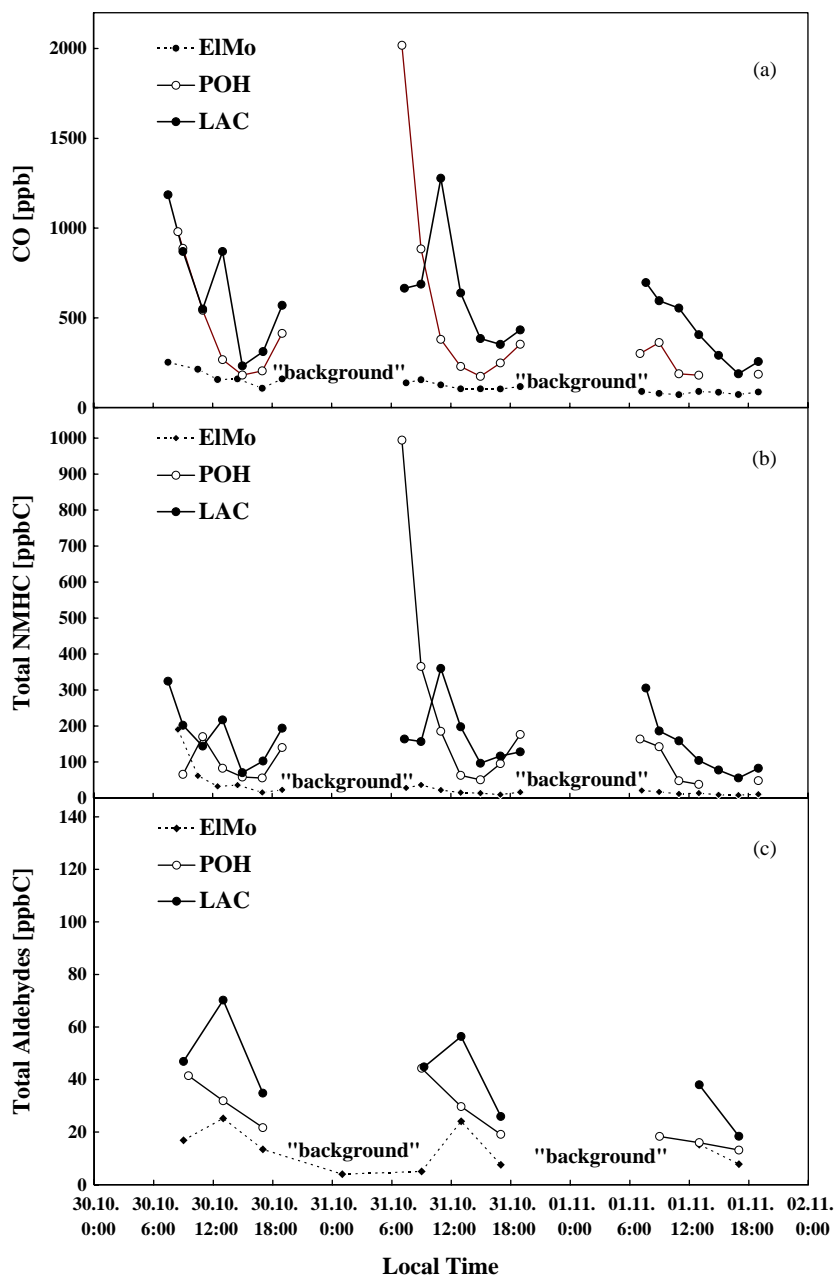


Fig. 3. Diurnal variations of CO (a) and the total amount of NMHC (b) as obtained by canister samplings, and diurnal variations of the total amount of carbonyls (c) as determined by the DNPH-method at the POH, LAC, and EIMo from 30 October–1 November 2002.

rates lead to overall lower carbonyl levels that are not compensated by enhanced formation of secondary carbonyls, whereas at the LAC site both local formation of secondary carbonyls and the passage of the urban plume containing primary and secondary carbonyls lead to a build-up of strong carbonyl peak at noon.

4.3. Discussion of reduction of LPG emissions

The use of LPG remains to be an important source in Santiago de Chile. The situation resembles Mexico City where very high amounts of propane, *n*-butane and *i*-butane could be detected in urban air (Blake and Rowland, 1995, 1996). Results obtained in 1998 (v. Baer,

priv. comm.) reveal very high values of propane, even at noontime (mean values of about 21 ppbv in LAC and 41 ppbv in POH). Also, in our measurements mixing ratios of more than 22 ppbv for propane could be observed in LAC at noontime, when the urban plume passed this area. However, at POH such high values of propane could not be found at noon (up to 13 ppbv on 31 October). By comparison, in fall and winter seasons—under poor ventilation conditions in the basin—a measurement campaign carried out by CEN-MA (1999) found mixing ratios for propane up to 80 ppbv at LAC during nighttime; while at 8:00 a.m. the propane levels were already down to 20 ppbv at the same site. This latter value resembles our values obtained for the same hour at LAC. This also suggests that during our springtime field experiment in 2002 the NMHC values were significantly higher during nighttime.

It was expected that a reduction in LPG impacts would have been affected by the introduction of natural gas, imported from Argentina since 1997 (Corvalán et al., 2003). To obtain a numerical estimate of that reduction, we took as baseline the data taken late in 1996 (Rappenglück et al., 2000, 15 days at POH and 25 days at LAC) and compared them with the 2002 data. Since in 1996 the online measurement technique was not capable of measuring species $<C_4$, we used the following surrogate mix: $SLPG = n\text{-butane} + \text{butene isomers} + i\text{-pentane}$ to compare both years at both sites, following Chen et al. (2001). To discount the traffic contributions to that mixture, we used the fact that aromatic compounds (AROM) are essentially emitted by traffic sources, so the following equation was used to estimate the non-traffic contribution to SLPG:

$$\{SLPG\}_{\text{NON-TRAFFIC}} = SLPG - \left(\frac{SLPG}{AROM} \right)_{\text{MIN}} \times AROM. \quad (1)$$

Scatter plots of SLPG against AROM at both sites and campaigns—not shown here—indeed showed a minimum slope, that is, a signature of the influence of a source that has a higher amount of aromatic compounds relative to SLPG—i.e., the traffic emissions. Furthermore, plots of non-traffic SLPG against CO (or AROM) measurements—not shown here—display a distinctive uncorrelated relationship, a proof that the approach of Eq. (1) works. The non-traffic SLPG data do not display a particular temporal pattern, showing up at all times in any given day; we ascribe this behavior to the intense LPG use both in residential and commercial cooking activities. At POH site non-traffic SLPG concentrations did not change significantly between 1996 and 2002 ($9 \mu\text{g}/\text{m}^3$ in both cases). On the other hand, at LAC site we found a significant reduction of non-traffic LPG from 15 to $5 \mu\text{g}/\text{m}^3$ between 1996 and 2002, that is, a 65% reduction. Since the distance between those two

sites is small, our comparison neglects chemical transformations along the transport pathway. Also, since the sources behave like low-level area sources, emission densities control impacts, so we conclude that in 1996 there was more LPG consumption on the eastern side of town than in Downtown, and the opposite trend was observed in 2002. This spatial redistribution is explained by socioeconomic causes: the LAC station is within the highest income population of Santiago, so it is the place at which the switch to natural gas for residential use started in 1997 and has been almost 100% completed. By contrast, at POH site the switch to natural gas is yet to be completed. These results—based on ambient campaigns—are consistent with the official statistics of fuel sales at Santiago (SEC, 2004); the total sales in 1998 and 2002 were 485 and 453 kton, respectively, showing a modest overall decrease in LPG use at Santiago. Our analysis shows that there has been a reallocation of LPG impacts across the city, being dependent upon socioeconomic factors.

4.4. Case study: 31 October 2002

As outlined before the second day of the field experiment, 31 October 2002, showed the most dynamic diurnal variations in photochemical relevant species and well-defined differences between the rural, the downtown and the suburban receptor site, e.g. an increase of O_3 within a short distance between POH and LAC from 72 to 129 ppbv. In addition, trajectory analysis revealed source–receptor linkages between these sites. Fig. 4 shows the time series of various photochemically relevant species on 31 October for the LAC site. The local rush hour peak at around 7:00 a.m. can be clearly identified based on the strong NO peak up to 70 ppbv. Afterwards O_3 commences its steady increase. Between 11:30 a.m. and 0:30 p.m. a significant enhancement of NO_2 levels of the same order than the early rush hour peak occurs. However, the NO values remain almost constant at 20 ppbv. Both observations suggest that these levels of nitrogen oxides are not caused by local emissions, but rather due to the passage of the downtown urban plume. At the same time CO reaches its daytime maximum (and presumably carbonyls, but the long sampling times did not allow to resolve this peak). Moreover, the ethylbenzene/*m,p*-xylene stays at the same level, conserving typical urban traffic fingerprints which remain undisturbed while photochemical processing is still overcompensated by high precursor emissions. As mentioned before ratios of hydrocarbons are indicators for photochemical processes. The ratio between ethylbenzene and *m,p*-xylene is an important example since they have the same sources and are emitted in typical patterns (Monod et al., 2001). In addition, their atmospheric degradation pathway only occurs through the reaction with the OH radical.

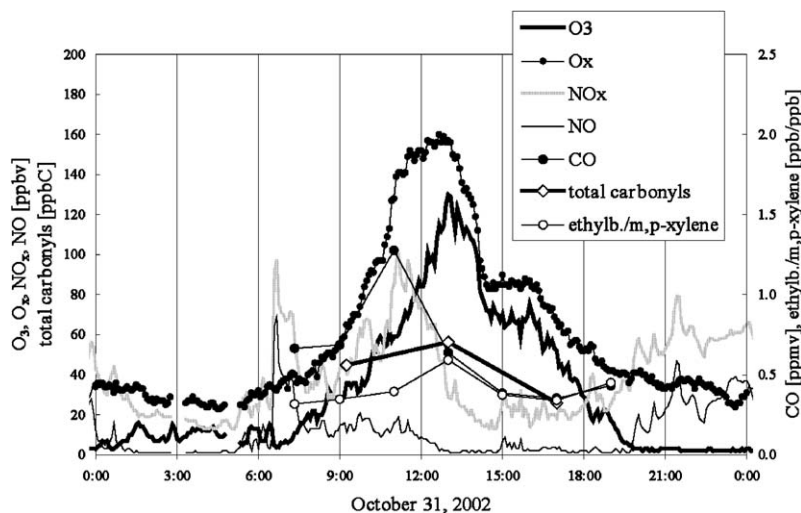


Fig. 4. Temporal variations of O_3 , O_x , NO_x , NO , CO , and the ethylbenzene/*m,p*-xylene ratio at LAC on 31 October 2002.

However, in this aspect the aromatic compounds differ significantly, since xylenes, in particular *m*-xylene, reacts pretty fast with OH than ethylbenzene or benzene, for instance. Rappenglück et al. (2000) used the ratio between ethylbenzene and *m*-xylene in their Santiago study. In the field experiment 2002 it was only possible to determine the sum of *p*- and *m*-xylene. Fig. 4 displays evolving maximum values for ethylbenzene/*m,p*-xylene ratio around noontime, i.e. when photochemical processing of the urban plume is strongest and is able to produce secondary products very effectively as can be identified in the coinciding daytime peaks of the total carbonyls and ozone. The entire time window when photochemical processes are highly due to anthropogenic emissions (high levels of NO_2 and CO , high levels of anthropogenic hydrocarbons) is closely associated with the broad O_x -peak ($[O_x]: [O_3] + [NO_2]$) between 10:00 a.m. and 2:00 p.m. O_x reaches maximum values up to 160 ppbv indicating a potential for higher O_3 values in further downwind areas. During this time window solar radiation and ambient temperature also reach their daytime maximum fostering photochemical processes. After 2:00 p.m. a shoulder in the ozone time series develops lasting for another 2–4 h. These levels are most likely due to the impact of biogenic hydrocarbon emissions on top of reduced anthropogenic precursors.

Fig. 5a shows that the alkanes represent the largest NMHC fraction at all sites, the second one being the aromatics and the third one being the alkenes. The smallest fractions are represented by the alkynes or isoprene. Sometimes the isoprene fraction is larger than the alkyne fraction. Moreover, the isoprene fraction peaks in the afternoon, e.g. at POH and ElMo. The fraction of the aromatics ranges between 20% and 40%

of the total NMHC, a typical range for urban areas. Studies of the propene equivalent according to Chameides et al. (1992) show a temporal sequence in terms of photochemical impacts of the different NMHC fractions: during morning hours, the alkenes are the most important ones (Fig. 5b). At noon aromatics are dominant, and in the afternoon isoprene becomes important. It is also supposed that other biogenic NMHCs augment this contribution as indicated by the field experiment of 1996 (Rappenglück et al., 2000) and expected by studies focusing on biogenic emission estimations for this area by CENMA (1998). Alkanes do not contribute more than 20% to the total air mass reactivity, despite being present at high concentration levels mainly due emissions of LPG (e.g. propane). That value is in good agreement with the findings of Chen et al. (2001). Together with the alkynes the fraction of the alkanes does not play a crucial role during the day, at least within the basin of Santiago, i.e. without considering any impacts downwind of the Santiago basin due to regional transport.

In addition to the non-methane hydrocarbons, Fig. 6 includes CO and aldehydes for the corresponding sampling intervals for the DNPH cartridges. CO contributes to the total propene-equivalent around 5% at POH and LAC, and can reach up to 10% at the rural ElMo site. Aldehydes contribute largely to the total propene-equivalent at all sites. Moreover, their contribution reaches maximum values at photochemical active times around noon. At POH and LAC 1/3 of the total reactivity is due to carbonyls, at ElMo even up to 2/3. We may also specify the contributions of some selected hydrocarbons on the background of this comprehensive presentation. At ElMo the BTEX

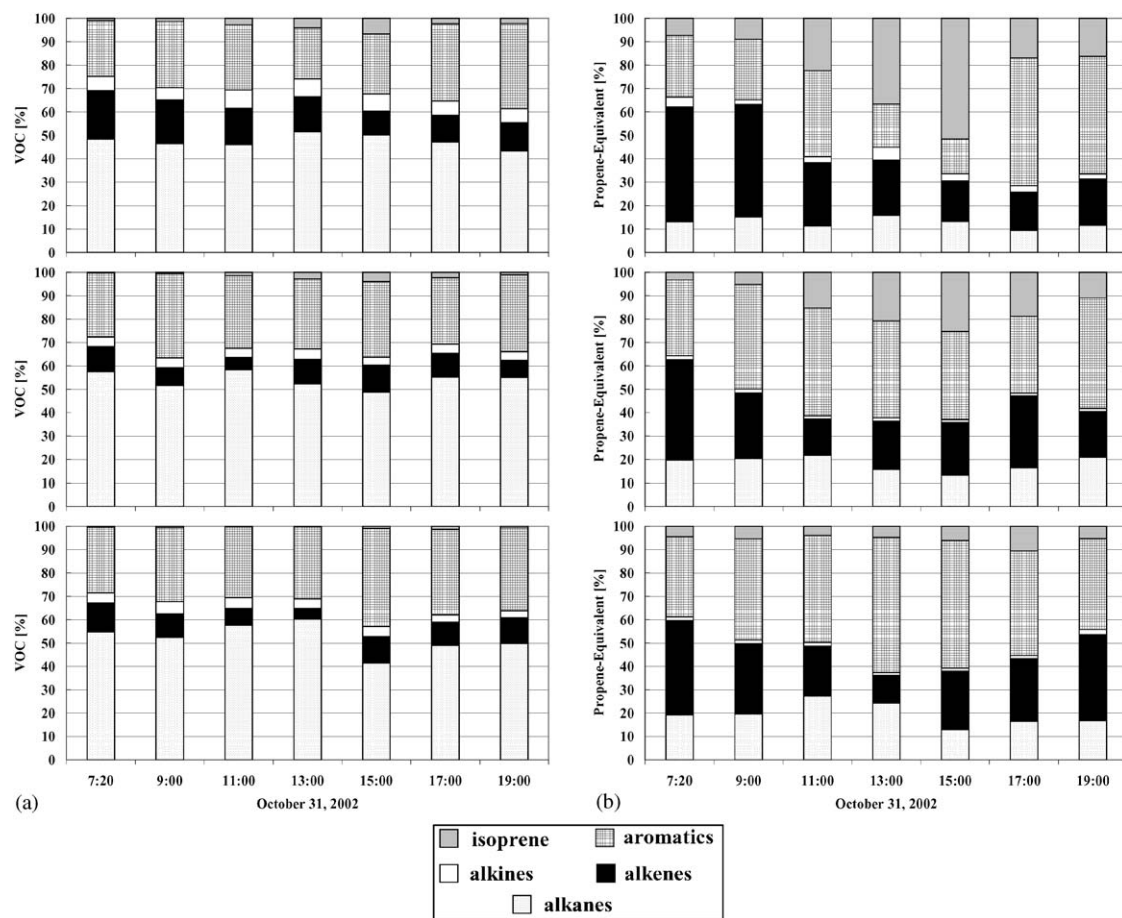


Fig. 5. (a) Temporal variations of NMHC fractions at the sites ElMo (upper panel), POH (central panel), and LAC (lower panel) on 31 October 2002, normalized to the amount of total NMHC. (b) Temporal variations of the propene equivalent corresponding to each NMHC fraction normalized to the propene equivalent of total NMHC at ElMo (upper panel), POH (central panel), and LAC (lower panel) on 31 October 2002.

fraction, i.e. the some of benzene, toluene, ethylbenzene, and the *m*-, *p*-, *o*-xylenes, range between 5% at noon and up to 15% in the morning hours, whereas at the downtown POH site values are between 10% and 31% for the same time periods. At LAC there is almost no diurnal variation in the BTEX fraction (17–18%). As a single compound, toluene was the most important species among the BTEX fraction (up to 10% at POH). The group of xylenes usually showed twice the values of toluene. Concerning LPG compounds propane alone showed low values as expected around 0.5–2.1%. Taking the entire C₃–C₄ class including alkanes and alkenes their contribution oscillated between 6.8 (noon) and 17.0% (morning hours) and did not show significant variations among all sites.

Fig. 7 shows the top 20 hydrocarbon species ranked by their fraction of the total propene-equivalent at the various sampling times at LAC on 31 October 2002. It is

important to keep in mind the diurnal variations of the absolute NMHC concentrations as shown in Fig. 3b and the diurnal variation of other species as given in Fig. 4. Throughout the day the *m,p*-xylenes are the most important species in terms of their contribution to the total propene-equivalent reaching their maximum at 11:00, i.e. the time when the urban plume passed the LAC site. This plume is primarily enriched in traffic exhaust-related hydrocarbons, i.e. aromatics such as the xylenes and toluene, and the alkenes ethene and propene. Also alkanes, e.g. nonane—a compound associated with diesel exhaust in the Santiago basin (Jorquera and Rappenglück, 2004), *i*-pentane—a tracer for evaporative losses—and even the slow reacting LPG-related propane are found among the top 10 most important NMHCs in this reactive urban plume. The contribution of isoprene, which is always found among the top five reactive species, is surpassed by most

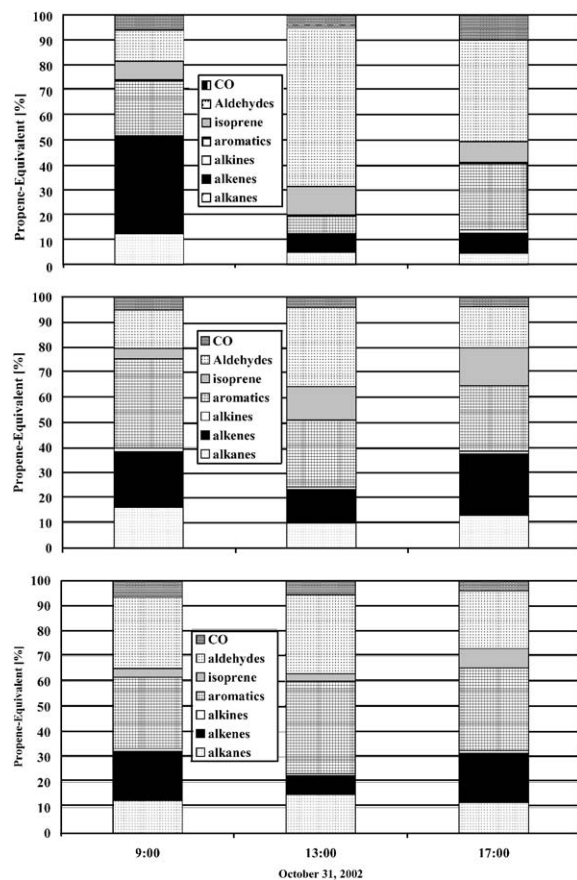


Fig. 6. The same as Fig. 4, right side; however, this presentation includes oxygenated species (CO, carbonyls).

traffic-related species at the time of the impact of the urban plume (it ranks fifth), but plays major role in the afternoon, when it ranks second to *m,p*-xylenes (15:00 and 17:00) and reaches its daytime maximum at 17:00. As already suggested in Rappenglück et al. (2000), this may be the dominant reason for the afternoon ozone shoulder of about 75 ppbv. However, the excess ozone of more than 50 ppbv ozone or 75 ppbv O_3 , respectively, is most likely due to anthropogenic hydrocarbons. The contribution of isoprene to ozone formation is limited because isoprene emission rates are lower due to reduced radiation in the afternoon and also, nitrogen oxide levels are lower at daytime.

Photochemical processes lead to the degradation of primary NMHC and the formation of secondary species, e.g. ozone and carbonyls. Fig. 8 shows some selected carbonyls along with ozone time series obtained at POH and LAC on 31 October 2002. At both sites carbonyls correlate well with ozone (Fig. 8a). At LAC carbonyl concentrations are higher than at POH. This also coincides with higher ozone levels. For formaldehyde

and acetaldehyde we tried to roughly estimate the fraction of primary carbonyls and carbonyls formed as secondary products in photochemical processes using the concept outlined in Possanzini et al. (2002). In our case we assumed that the 9:00 a.m. carbonyl sampling at POH is entirely represented by primary carbonyls in the early rush hour period. This is a rough estimation as this statement covers a time period of 4 h sampling in the morning hours, assuming only a negligible fraction of secondary on the background of significant emissions on primary precursors (see CO in Fig. 3a and total NMHC in Fig. 3b). Contrary to Possanzini et al. (2002), who took toluene as a reference surrogate for traffic emissions, we took CO that is exclusively related to traffic exhaust, and calculated the ratio ρ of primary carbonyls to CO at 9:00 a.m. for the POH yielding a formaldehyde/CO ratio = 0.0061 and a corresponding acetaldehyde/CO ratio = 0.0052 and determined the photochemical fraction of carbonyls as follows:

$$\frac{[\text{carbonyl}]_{\text{photochemically produced}}}{[\text{carbonyl}]_{\text{ambient air}}} = 1 - \rho \frac{[\text{CO}]_{\text{ambient air}}}{[\text{carbonyl}]_{\text{ambient air}}} \quad (2)$$

We assumed that the values for ρ are valid throughout the metropolitan area of Santiago de Chile. The results of our calculations are shown in Fig. 8b. These results reveal a strong diurnal variation for POH with about 50% fraction of secondary formaldehyde and almost 70% fraction of secondary acetaldehyde in ambient air at noontime. In the afternoon there is a decrease to 23% and 33%, respectively. Possanzini et al. (2002) report somewhat higher fractions for Rome, but this may be most likely due to the fact that the Rome measurements were taken in the midst of summertime (late July), whereas our measurements were taken in springtime and the secondary fraction of carbonyls is very sensitive to the season (Possanzini et al., 2002). At the LAC site higher fractions are found in the morning and in the afternoon, whereas lower fractions are observed at noontime. This appears plausible, because the urban plume passes the LAC site at noon thus limiting the fraction of secondary species. In the afternoon there is almost no decrease in the fraction of secondary formaldehyde. This is most likely due to the enhanced impact of isoprene, an important biogenic precursor for formaldehyde (Shepson et al., 1991). Shepson et al. showed that at sites dominated by the impact of isoprene emissions a formaldehyde/acetaldehyde ratio up to 10 could be observed. Our results show that this ratio is about 1.0 at POH and 1.9 at LAC on 31 October 2002 (Fig. 8c). Fig. 8c shows that (i) the formaldehyde/acetaldehyde ratio at LAC is higher than at POH and (ii) higher isoprene mixing ratios are observed at POH than at LAC. This indicates that apart from biogenic contributions, anthropogenic NMHC precursors likely

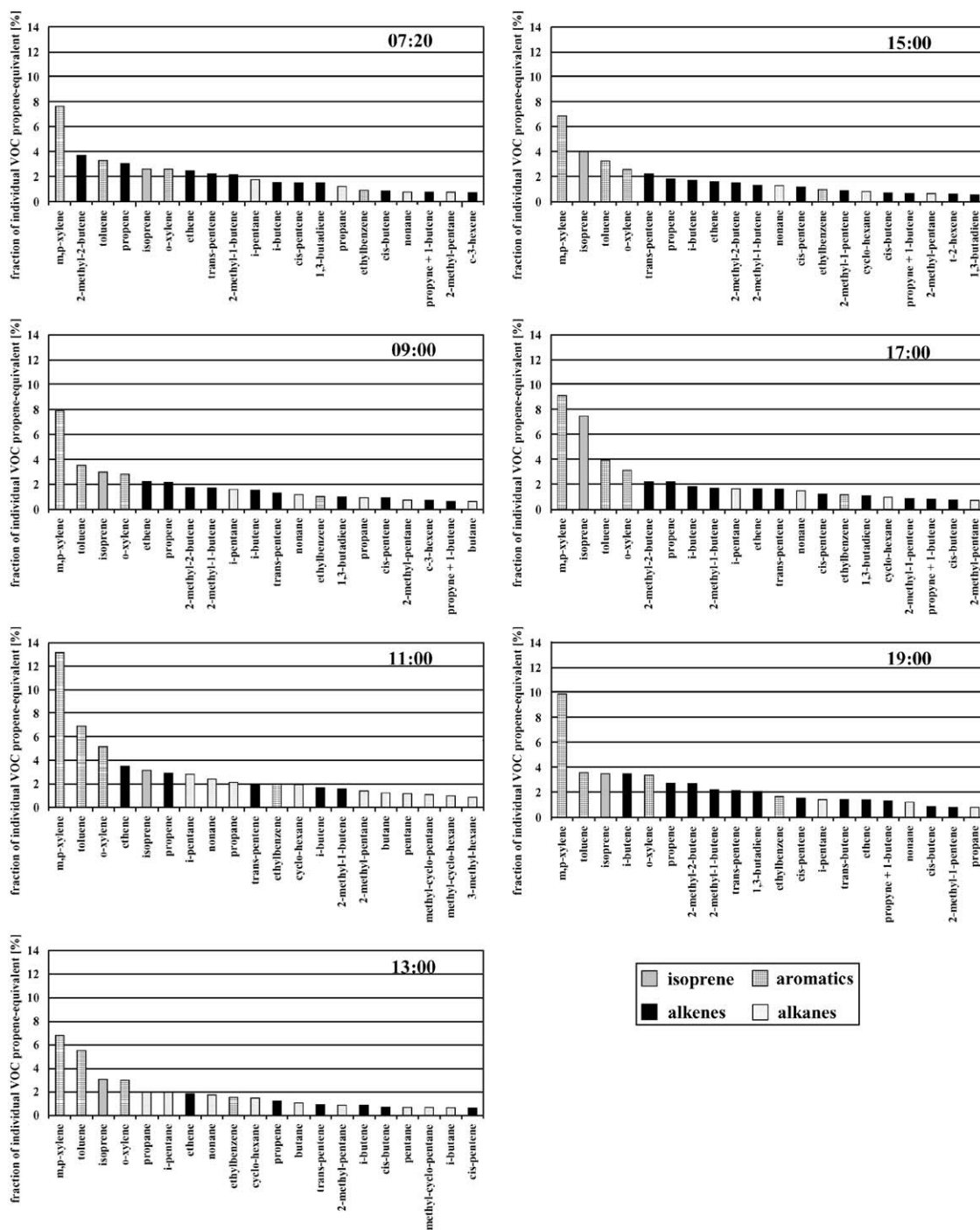


Fig. 7. The top 20 hydrocarbon species ranked by their fraction of the total propene-equivalent at the various canister sampling times at LAC on 31 October 2002.

influence the atmospheric carbonyl burden in Santiago, at least at this time of the year, when foliage has not yet been fully developed and biogenic emissions are still limited. This suggestion is supported by maximum

carbonyl levels at LAC at noon accompanied by slightly lower formaldehyde/acetaldehyde values, when the urban plume reaches the LAC site. However, it is worth noting that in the afternoon there is a slight increase in

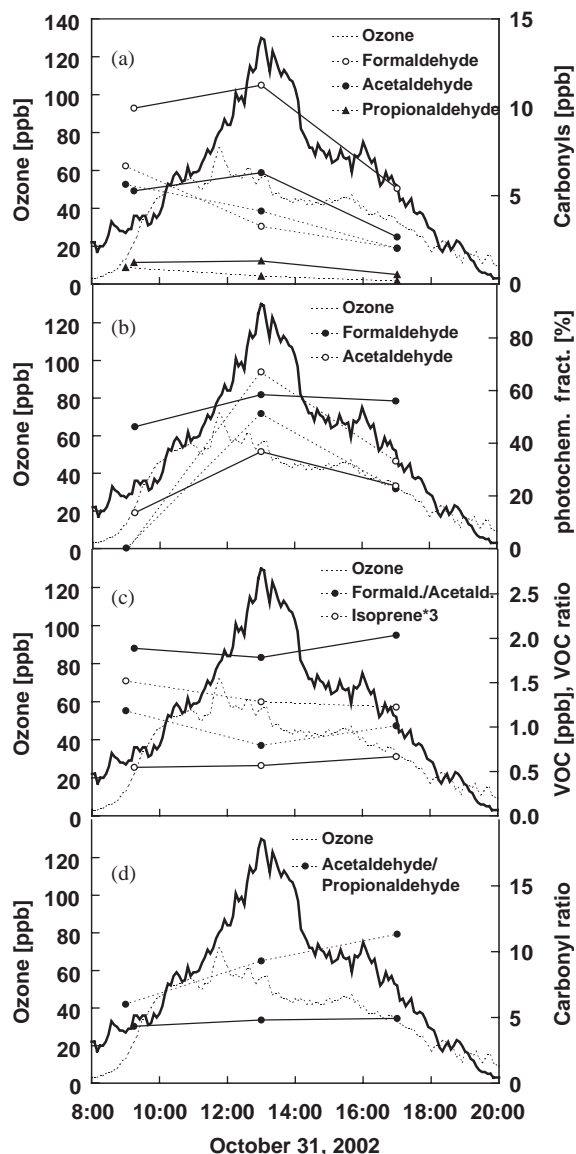


Fig. 8. Some selected time series obtained at LAC on 31 October 2002 (dashed lines refer to the POH site, solid lines refer to the LAC site): (a) ozone and some selected carbonyls, (b) ozone, and the photochemical fraction of formaldehyde and acetaldehyde, (c) ozone, isoprene and the formaldehyde/acetaldehyde ratios, (d) ozone and the acetaldehyde/propionaldehyde ratios.

both the isoprene mixing ratios and the formaldehyde/acetaldehyde ratio at both sites. Again, this may explain the extended ozone shoulder at this time of the day that is in agreement with earlier findings (Rappenglück et al., 2000). As previously discussed the acetaldehyde/propionaldehyde ratio may be used to assess the impact of anthropogenic hydrocarbon precursors (Shepson et al., 1991). Our results (Fig. 8d) show that at POH the

corresponding values are higher than at LAC and show a slight increase during the day, whereas at LAC the acetaldehyde/propionaldehyde ratio remains rather constant. These results support the suggestion that anthropogenic NMHC are important precursors. They are likely more important at LAC than at POH and at POH these compounds become even less important in the afternoon. This may be explained by the environmental (downtown park area; higher isoprene values) and meteorological conditions at that site (strong ventilation in the afternoon leading to transport of fresh air from outside of the urban area). This also coincides with the low CO values found at POH in the afternoon (Fig. 3a) and the results derived from Figs. 3b and 5.

According to Grosjean (1992), the in-situ formation of SOA occurs for low volatile hydrocarbons including alkanes, alkenes and aromatics which contain more than six carbon atoms. Low-molecular-weight carbonyls also do not contribute to SOA formation. We identified 20 species among our VOC data set that fall into this category and attempted to estimate their SOA forming potential. For this we used the numbers for the fractional aerosol coefficients and the fraction of VOC reacted as given in Grosjean (1992). In cases where no numbers were given (i.e. for 2,4-dimethyl-pentane, 2-methyl-hexane, 2,3-dimethyl-pentane, 3-methyl-hexane, and 2,3-dimethyl-2-pentane) we took as an upper limit the corresponding numbers for the alkane among our data set that was expected to yield most SOA according to Grosjean (1992). In our case this was methyl-cyclohexane. Grosjean considered a reaction time of 6 h under a daytime scenario of $[O_3] = 100$ ppbv, $[OH] = 1.0 \times 10^6$ molecules cm^{-3} , and $[NO_3] = 0$ ppbv. This is also a good approximation for the atmospheric environment of Santiago de Chile (e.g. this paper and Rappenglück et al., 2000). For the case of 31 October 2002, we considered the canister air sample taken at the POH site at 7:05 and assumed photochemical SOA formation for 6 h and calculated the expected SOA concentration at 1:00 p.m. We calculated a total SOA yield of $2.4 \mu g m^{-3}$. By far, the maximum contribution to SOA formation was caused by the *m/p*-xylenes (60.6%), followed by toluene (14.8%), *o*-xylene (12.1%), ethylbenzene (5.0%) making the aromatic fraction the most important SOA precursors. Nonane (2.1%), 3-methyl-hexane (1.6%), 2-methyl-hexane (1.5%), and methyl-cyclo-hexane (1.2%) were of minor importance. However, we have to take into account that our measurements did not include hydrocarbons with $C > 9$. Thus the SOA value of $2.4 \mu g m^{-3}$ represents a lower limit for this particular day.

4.5. Model case study

In addition to the measurements, a few model experiments were carried out. Of particular interest

were the days 30 and 31 October. Since the last day of the campaign, 1 November, was partly cloudy, and the model used in this study assumed clear sky conditions, this day could not be considered. As outlined above, on 30 October ozone concentrations at POH and LAC reached similar values, whereas on 31 October at LAC much higher values were measured than at POH. Fig. 9 shows the trajectories for LAC and POH for both days. Maximum ozone concentration on 30 October were measured at both sites at around 1:00 p.m. It can be seen (upper panel) that at this time the trajectories have their origin in the mountains and there is no direct connections between the two sites. On the other hand on 31 October maximum ozone values at POH were measured around 1:00 p.m. and at LAC at 2:00 p.m. In the lower panel of Fig. 9 only the backward trajectory which reaches LAC at 2:00 p.m. and goes through POH at around 1:00 p.m. before reaching LAC, indicating the direct connection of the two sites at this occasion.

For the trajectories, given in Fig. 9, the chemical Lagrange model was applied. Due to the lack of information on background values, all trajectories were initialized with values, as measured in EIMo in the early morning hours. Table 2 summarizes the results of these modeling experiments. With respect to the differences of maximum ozone concentrations at LAC and POH the model agrees reasonably well with the observations on 31 October. The different trajectories on both days can be assumed to be responsible for this. Errors between observations and model values can be explained by the simplification due to the model and lack of information for the initialization of the model. Also indicated in Table 2 are the model results for the production of SOA, as a result from the oxidation of alkanes, alkenes, and aromatics. According to the model the alkanes contribute to SOA at LAC with only 9% to the total, the alkenes 37% with the aromatics contributing with 54% by far the most. The contributions at POH are with 13%, 35%, and 52%, respectively, very similar. The aerosol module would be capable of treating the formation of SOA by the oxidation of biogenic precursors. However, since these precursors are not explicitly treated by the gas phase mechanism RADM2 they cannot be evaluated here. No observations of SOA are available for a comparison with the model results. Therefore, this result can only be taken as an indicator for the potential of SOA formation in Santiago.

Apart from the comparison between observed and simulated values at POH and LAC, the photochemical behavior along the trajectory would be of interest, particularly the question of how the different hydrocarbon classes contribute to the production of ozone. Fig. 10a shows the time series of the relative contributions of alkanes, alkenes, and aromatics with respect to

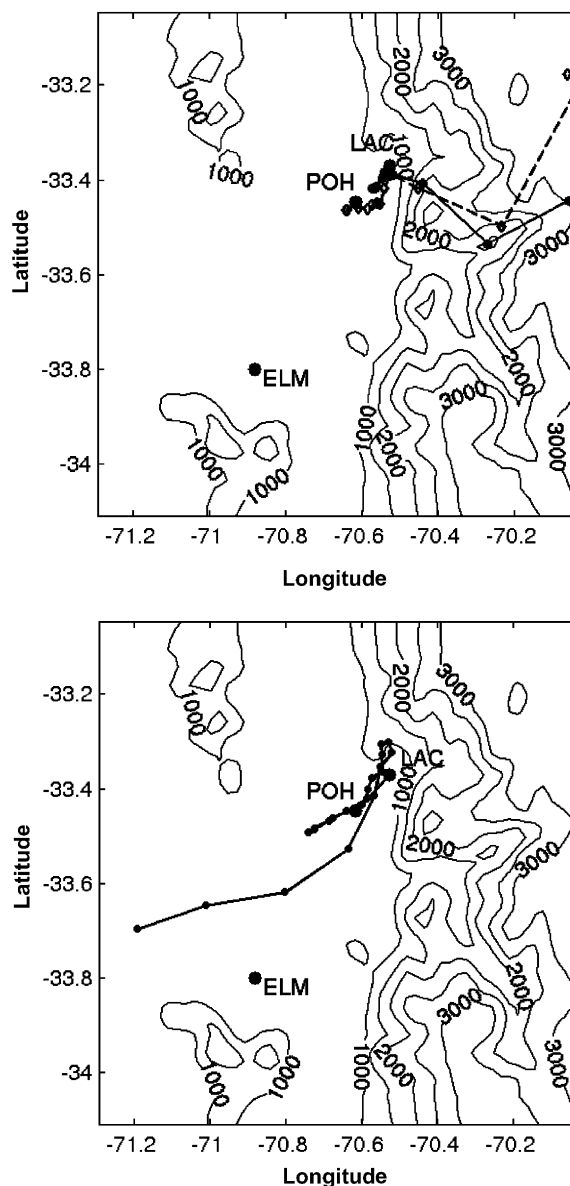


Fig. 9. Trajectories for the measuring sites LAC and POH. Markers indicate time intervals of 1 h. Upper panel: backward trajectories reaching the respective sites at 1:00 p.m. on 30 October 2002. Lower panel: backward trajectory reaching LAC at 2:00 p.m. LAC and going through POH at 1:00 p.m. on 31 October 2002. Contours indicate 500 m isohypsens.

total non-methane hydrocarbons (TNMHC) from 9:00 a.m. to 2:00 p.m. (Even though the trajectory was calculated for 24 h, we limit our analysis to its last 5 h, since this is due to the photochemical activity, the time period of interest.) At 9:00 a.m. the air parcel lies west to the city and, as outlined above, passes through POH at 1:00 p.m. reaching LAC at 2:00 p.m. It can be observed

Table 2
Model results for October 31 for the sites POH and LAC (in brackets measured values)

	31 October 2002	
	POH (1:00 p.m.)	LAC (2:00 p.m.)
Ozone (ppbv)	73 [56]	114 [130]
SOA ($\mu\text{g}/\text{m}^3$)	2.9	3.7
Alkanes (ppbC)	35 [33]	112 [119]
Alkenes (ppbC)	12 [7]	26 [9]
Aromatics (ppbC)	29 [19]	57 [61]
Formaldehyde (ppbv)	9 [3]	16 [11]
Other aldehydes (ppbv)	7 [4]	11 [6]

that the alkanes relative contribution is always highest during the whole time period always maintaining a contribution of at least 60%. Between 9:00 a.m. and 12:00 p.m. this contribution increases from about 60% to 80%. Between 12:00 p.m. and 1:00 a.m. it decreases rapidly from 80% to 60% again. In the last hour on the trajectory it again experiences an increase of about 67%. The relative contributions of alkenes and aromatics follow the time series of the alkanes inversely, i.e. an increase in alkanes is accompanied by a decrease in alkenes and aromatics and vice versa, with the aromatics contributing slightly more than the alkenes. While the alkanes represent the largest contribution to the TNMHC, their contribution to the production of ozone is, due to their low reactivity, less. Fig. 10b shows the time series of the relation of produced ozone ($d[\text{O}_3]$) to consumed alkanes, alkenes, and aromatics, respectively (since all $d[\text{hydrocarbon}]$ are negative and in order to obtain positive values the relations are displayed with a negative factor). It can clearly be seen that ozone is most effectively produced by the alkenes and the aromatics, with little effectivity by the alkanes. Furthermore, it is worth noting that the effectivity of alkenes and aromatics shows a dramatic increase at 12:00 a.m. and maintains very high values until 2:00 p.m. These effectivities during the last 2 h raise the question whether they also explain the dramatic increase in ozone concentrations between POH (at 1:00 p.m.) and LAC (2:00 p.m.). For this purpose the time series the production rates of O_x , O_3 , and NO_2 are plotted in Fig. 10c. It can be seen that the rates are maintained relatively constant until 12:00 a.m. Between 12:00 a.m. and 1:00 p.m. all of them experience a significant increase. After 1:00 p.m. the O_x production rate drops. This drop can be explained by a dramatic decrease in the NO_2 production rate which cannot be buffered by the increase in the O_3 production rate. The increase of the NO_2 production rate between 12:00 p.m. and 1:00 a.m. indicates both strong NO emissions and an efficient conversion from NO to NO_2 through the oxidation of

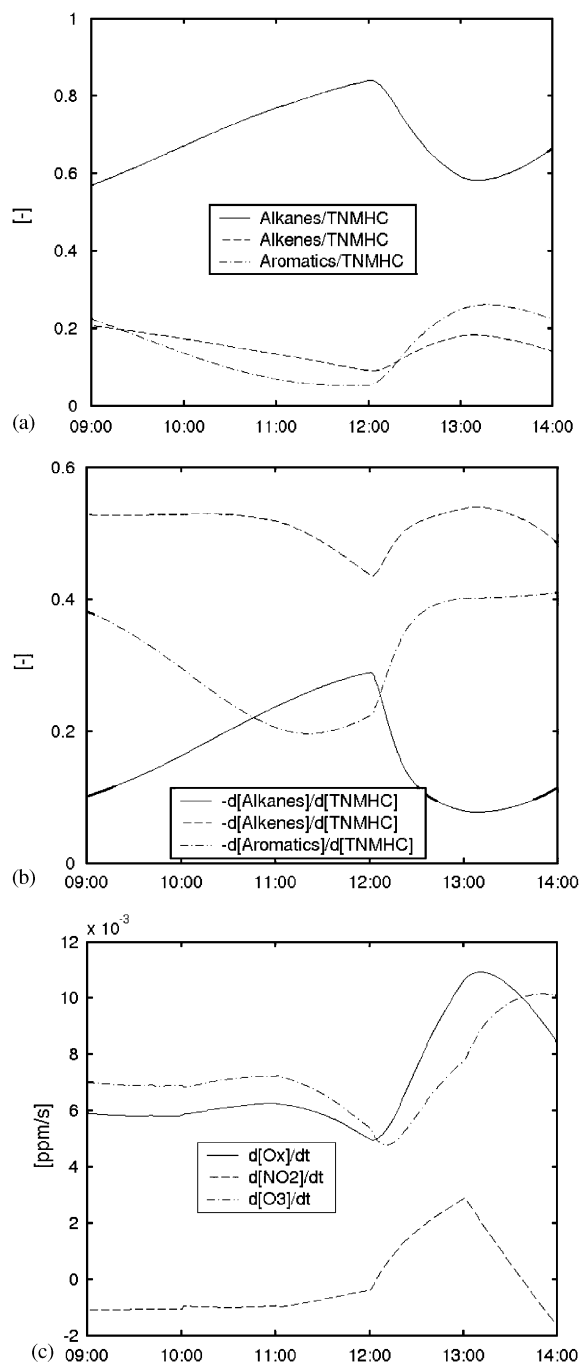


Fig. 10. Photochemical processes along the trajectory linking EIMo, POH and LAC on 31 October 2002: (a) time series of the relative contributions of alkanes, alkenes, and aromatics with respect to TNMHC from 9:00 a.m. to 2:00 p.m., (b) time series of the relation of produced ozone ($d[\text{O}_3]$) to consumed alkanes, alkenes, and aromatics, respectively, and (c) time series the production rates of O_x , O_3 , and NO_2 .

hydrocarbons (see Fig. 8c). However, first NO will most likely inhibit the ozone production (by the titration reaction of O₃ with NO) and only result in moderate ozone concentrations in POH at 1:00 am. After 1:00 am these strong primary NO emissions do not longer resist. However, the remaining NO₂ (produced through the reaction chains with the hydrocarbons) will eventually be photolyzed and thereby produce ozone or probably be incorporated in PAN species.

5. Conclusions

From 30 October–01 November 2002, an urban air quality field experiment was carried out in the basin of Santiago de Chile. Meteorological conditions during the campaign agreed well with general flow circulations reported in previous field studies and confirmed source–receptor relationships between downtown and downwind sites. The main objective of this campaign was the analysis of the impact of speciated C₂–C₉ hydrocarbons and aldehydes on the formation of secondary pollutants.

Results based on the propene equivalent show that certain temporal sequences in terms of photochemical impacts of the different VOC fractions prevail: during morning hours the alkenes are the most important ones. At noon aromatics are dominant, and in the afternoon isoprene becomes very important. Alkanes do not contribute more than 20% to the total air mass reactivity despite being present at high concentration levels mainly due emissions of liquefied petroleum gas (e.g. propane). There has been a spatial reallocation of ambient LPG impacts across the city between 1996 and 2002, from a threefold reduction on the eastern side of town to no change whatsoever at Downtown; this has been brought up by different rates of switch to natural gas since 1997. The generation of ozone impacts above 50 ppbv is mainly due to anthropogenic traffic-related hydrocarbons (*m*, *p*, *o*-xylenes, toluene, ethene, propene). Isoprene contributes to the development of an afternoon ozone shoulder at the suburban LAC site. According to their propene-equivalents aldehydes, both primary and secondary, are very important to ozone formation. SOA formation is strongly linked to traffic emissions, basically aromatic compounds. Future investigations should focus on contribution of carbonyls and of other biogenic hydrocarbons apart from isoprene to the formation of ozone and PAN. In addition, the investigation of SOA formation with a particular focus on health relevant PM_{2.5} and PM_{1.0} caused by aromatics and terpenes should be strengthened.

Model results indicate the strong dependency of ozone productivity on the origin of the air masses. Trajectories for 2 of the 3 days of the field campaign show very different behavior, which is also reflected in the ozone

concentrations. Applying the Lagrange trajectory model to a particular case it could further be shown that ozone productivity varies significantly with time and space. In this sense it could also be shown that concentrations of alkanes are always much higher than those of alkenes and aromatics along the trajectory. However, due to their higher reactivity, alkenes and aromatics contribute significantly to ozone production. A particularly high ozone production is indicated during the last hour of the simulation (from POH to LAC). This is in good agreement with the observations which indicate a strong increase in ozone concentrations from POH to LAC. Furthermore, the application of a SOA module in the Lagrange trajectory model indicates a significant contribution of anthropogenic hydrocarbons to SOA by higher alkanes, alkenes, and aromatics. The model application does not consider biogenic emissions. Since the observations indicate a significant contribution of isoprene to the photochemistry in Santiago it is strongly recommended to include these biogenic processes in further model studies (both gas phase and aerosols).

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