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An Urban Photochemistry Study in the Metropolitan Region of Santiago de Chile

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1. INTRODUCTION

It is well known that urbanized zones represent areas where significant amounts of gaseous pollutants and particulate matter are released into the atmosphere. In particular in tropical and subtropical regions, where intensive global radiation and high daytime temperatures are usually observed, very dynamic metropolitan areas exist nowadays and both their number and their size are continuously growing.

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 million inhabitants Santiago de Chile can be regarded as a medium sized agglomeration among the megacities in the world, its orographic location in a poor 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. Frequently, Santiago de Chile faces high concentrations of ozone and peroxyacetyl nitrate (PAN) (e.g. Rappenglück et al., 2000).

During spring time of the year 2002 a field experiment was carried out in the Metropolitan Area of Santiago de Chile focusing on three representative monitoring sites located along a virtual axis through this area that allowed to observe upwind, downtown and downwind conditions. Three consecutive days 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, non methane hydrocarbons (NMHC) and oxygenated volatile organic compounds (oxy-VOC)) were obtained at these sites. This paper addresses the importance of specified 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 anthropogenic and biogenic hydrocarbons to the formation of secondary species in the Santiago basin.

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2. EXPERIMENTAL SETUP AND FIELD RESULTS

In accordance with 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 suburban receptor site were chosen (Fig. 1). 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 (ElMo) about 30 km upwind the urban area. This site was designated to provide hydrocarbon input data for initializing our model runs.

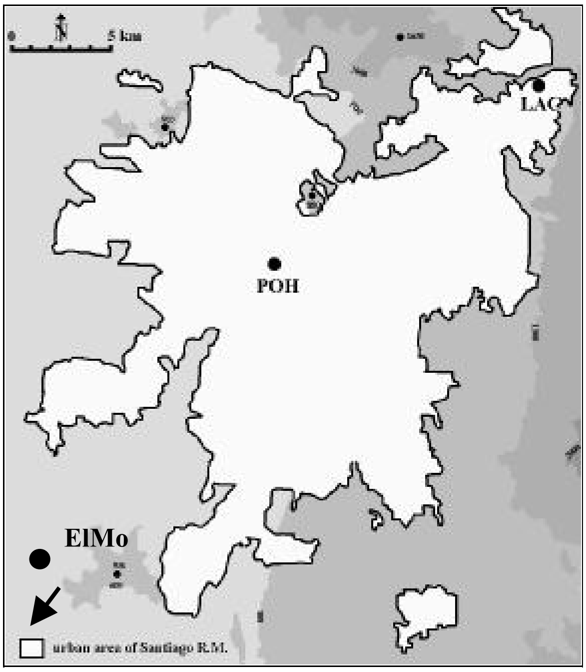

Fig. 1. Measurement sites during the field experiment from Oct 30 – Nov 1, 2002 (ElMo: El Monte; POH: Parque O´Higgins; LAC: Las Condes).

During the field experiment from October 30 – November 2, 2002, canister samples (1L 2-valve electropolished stainless steel canisters) for CO and non methane hydrocarbons in the range from C_2-C_9 and DNPH cartridge samplings for aldehydes and ketones were taken at all three sites. Canister samples were taken every two hours starting from 8:00 a.m. to 8:00 p.m.. Cartridges were filled for 4 hours during the intervals 8:00-12:00 a.m., 12:00 a.m. – 4:00 p.m., and 4:00 – 8:00 p.m..

3. MODEL APPROACH

The model used in this study was a Lagragian box model. Trajectories were calculated from wind fields generated by the fifth-generation Penn State/NCAR Mesoscale Model (MM5, Grell et al. 1994). The horizontal grid spacing was 2 km, and only winds from the first sigma level (about 17 m above surface) were considered. The box height was given by the MM5 output for the mixing layer height, for which a minimum of 100 m was considered. With an increase in the mixing layer height mixing of clean air masses from aloft into the box were assumed. The gas phase of model was treated by the RADM2 mechanism (Stockwell et al. 1990). Aerosols were treated according to MADE/SORGAM mechanism (Ackermann et al., 1999, Schell et al., 2001). Emission inventories included mobile, area, and point sources. Biogenic sources are not considered in the inventories.

4. RESULTS AND DISCUSSION

Fig. 2 shows the diurnal variation of ozone and CO at POH and LAC from October 30 – November 1, 2002. CO is almost exclusively emitted by traffic exhaust. Since its reactivity to OH is moderate 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. Highest ozone values were reached at LAC on October 31 (129 ppbv) and at POH one day before (96 ppbv).

The persistent feature in both the meteorological conditions and the 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, however on generally slightly elevated background concentrations. Fig. 2 clearly shows that on November 01 CO levels are decreasing significantly due to changed emission conditions on this holiday. Considering the ozone time series of these three days it is worth to note that each day exhibited specific features that represent a nice data base for modelling studies: on the first day (October 30, 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 tremendous (61 ppbv). Moreover the temporal varia-

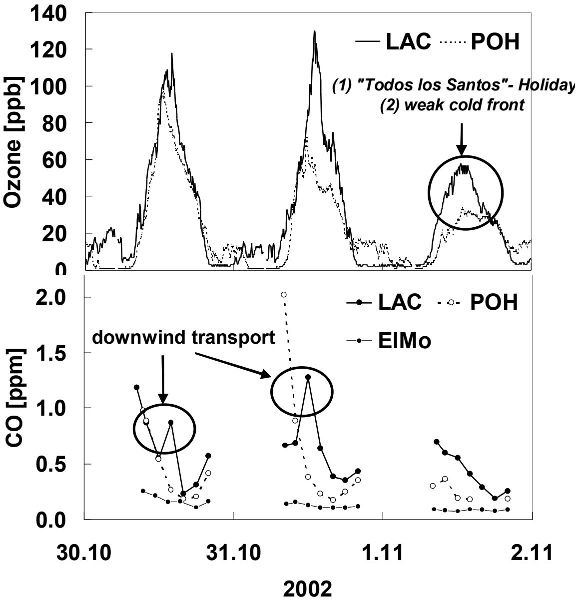

Fig. 2. Diurnal variations of ozone (upper panel) and CO (lower panel) at the sites Parque O´Higgins (POH) and Las Condes (LAC) from Oct 30 – Nov 1, 2002. In the lower panel CO data from the El Monte site (ElMo) is also shown.

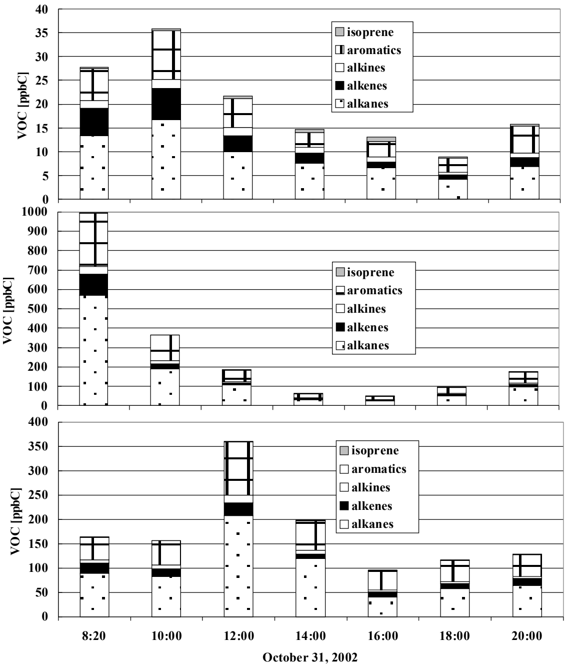

Fig. 3. Diurnal variations of NMHC fractions at ElMo (upper panel), POH (central panel), and LAC (lower panel) on October 31, 2002. Note the different scales.

tions 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 (November 01, 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 Fig. 3 diurnal variations of NMHC fractions are displayed at all three sites for the case of October 31. Isoprene is the only compound in these presentations that is exclusively of biogenic origin. For POH fig. 3 reveals maximum values for the early morning hours. Minimum levels occur between 2:00 – 6:00 p.m.. At LAC there is a maximum peak between noon and 2:00 p.m.. Though maximum values occur at POH (almost 1.000 ppbC in the morning hours of October, 31), it is obvious that at LAC concentrations persistently remain at elevated values throughout the day (between 200-300 ppbC). At El Monte, however, variations are limited and the concentrations seldom surpass 50 ppbC.

During the field experiment canister 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. Primarily, the atmospheric transport is controlling the distribution of pollutants to downwind sites. In general, the LAC site is a well-documented receptor site (CENMA, 1999; Rappenglück et al., 2000).

Speciation of NMHCs show that anthropogenic VOCs usually correlate well with CO (not shown here in detail). Temporal variations of benzene match best those of CO. For both of these compounds traffic exhaust represents the main emission source. Propane, however, displays stronger diurnal variations than benzene and CO. Propane may be typically found in LPG. The use of this gas remains to be an important source in Santiago de Chile. Nethertheless, comparisons with previous NMHC results (CENMA 1999; Rappenglück et al., 2000) indicate a significant reduction in LPG emissions over the last years. As

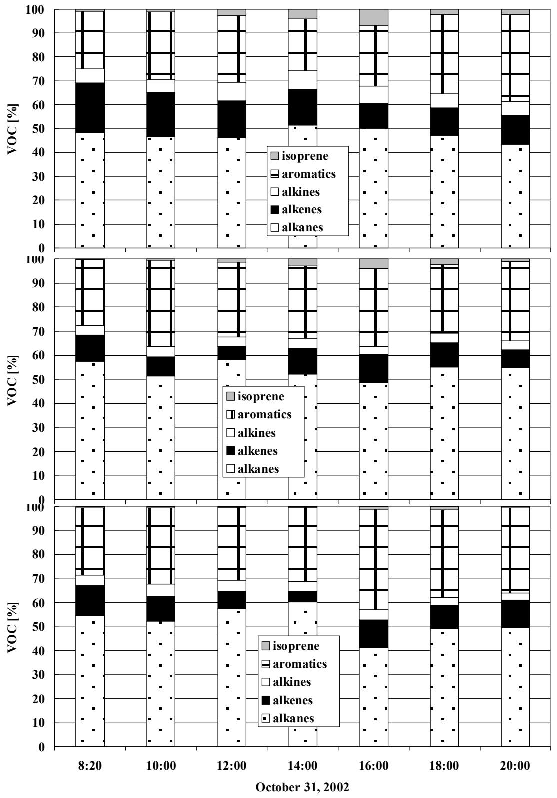

Fig. 4. Diurnal variations of NMHC fractions at the sites ElMo (upper panel), POH (central panel), and LAC (lower panel) on October 31, 2002, normalized to the amount of total NMHC.

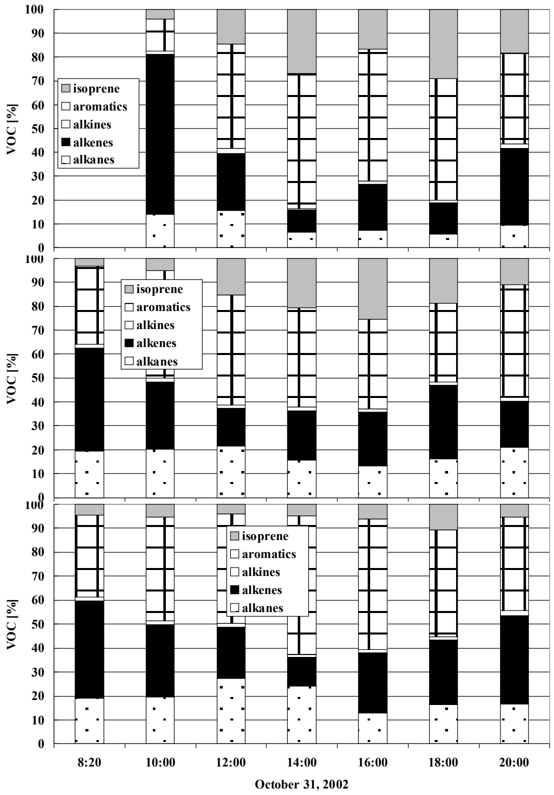

Fig. 5. Diurnal variations of the propene equivalent corresponding to each NMHC fraction normalized to the propene equivalent of total NMHC at ElMo (upper panel), POH (central panel), and LAC (lower panel) on October 31, 2002.

can be expected the diurnal variations of isoprene are different and coincide with solar radiation and the ambient temperature.

Based on absolute values the results (Fig. 4) show 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 alkines or isoprene. Sometimes the isoprene fraction is larger than the alkine fraction. Moreover, the isoprene fraction peaks in the afternoon, e.g. in POH and ElMo. The fraction of the aromatics ranges between 20-40% of the total NMHC, a typical range for urban areas.

Studies of the propene equivalent (Fig. 5) show a temporal sequence in terms of photochemical impacts of the different NMHC fractions: during morning hours the alkenes are the most important ones. At noon aromatics are dominant, and in the afternoon isoprene becomes very important. It is supposed that also other biogenic NMHCs augment this contribution as indicated by the field experiment of 1996 (Rappenglück et al., 2000) and expected by studies focusing biogenic emission estimations for this area by CENMA (1998). On the whole, alkanes - though being present at high concentration levels mainly due emissions of liquefied petroleum gas (e.g. propane) - do not contribute more than 20% to the total air mass reactivity. Together with the alkines 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 the Santiago basin due to regional transport.

Photochemical processes lead to the degradation of primary NMHC and the formation of secondary species, e.g. ozone and carbonyls. Fig. 6 shows some selected carbonyls along with ozone time series obtained at POH and LAC on October 31, 2002. At both sites carbonyls correlate well with ozone. At LAC carbonyl concentrations are higher than at POH. This also coincides with higher ozone levels. The formaldehyde/acetaldehyde ratio is about 1.0 at POH and

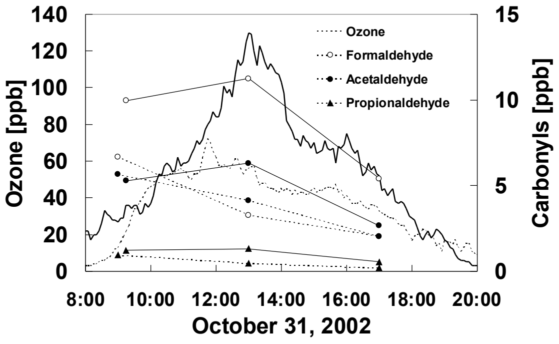

Fig. 6. Ozone and some selected carbonyls measured at POH (dashed lines) and LAC (solid lines) on October 31, 2002.

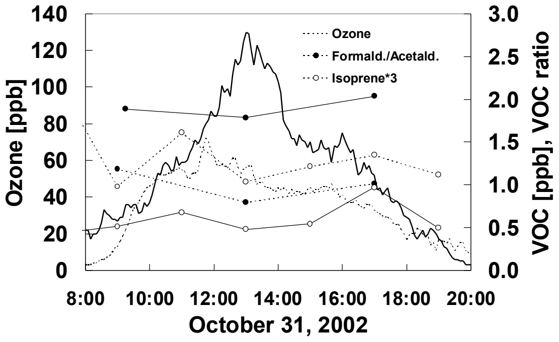

Fig. 7. Ozone, Isoprene and the Formaldehyde/ Acetaldehyde ratio at POH (dashed lines) and LAC (solid lines) on October 31, 2002.

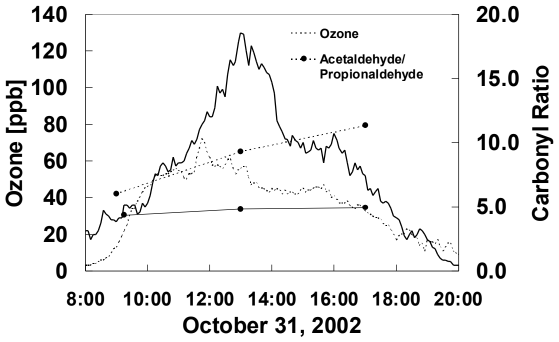

Fig. 8. Ozone and the Acetaldehyde/ Propionaldehyde ratios at POH (dashed lines) and LAC (solid lines) on October 31, 2002.

1.9 at LAC on this day. According to Shepson et al. (1991) values for this ratio may range between ≈1 (urban) and 10 (deciduous forest). Fig. 7 shows that (a) the formaldehyde/acetaldehyde ratio at LAC is higher than at POH and (b) higher isoprene mixing ratios are observed at POH than at LAC. This indicates that apart from biogenic contributions anthropogenic NMHC precursors likely influence the atmospheric carbonyl burden in Santiago, at least at this time of the year, when biogenic emissions are still limited. This suggestion is supported by maximum carbonyl levels at LAC at noon accompanied by slightly lower formaldehyde/acetaldehyde values. At this time the urban plume usually reaches the LAC site (Fig. 6). However, it is worth to note that in the afternoon there is a slight increase in both the isoprene mixing ratios and the formaldehyde/acetaldehyde ratio at both sites. This may explain the extended ozone shoulder at this time of the day that is in agreement with earlier findings (Rappenglück et al., 2000).According to Shepson et al. (1991) the Acetaldehyde/Propionaldehyde ratio may be another important 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. Our results (Fig. 8) show that at POH the corresponding values are higher than at LAC and show a slight increase during the day, whereas at LAC the formaldehyde/acetaldehyde ratio remains rather constant. These results support the suggestion that anthropogenic NMHC are important precursors. They are likley 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. 2) and the results derived ngs from Figs. 4-5.

In addition to the measurements a few model experiments were carried out. Of particular interest were the days October 30 and 31. Since the last day of the campaign, November 1, was partly cloudy, and the model used in this study assumed clear sky conditions, this day could not be considered. As outlined above, at October 30 ozone concentrations at POH and LAC reached similar values, whereas at October 31 at LAC much higher values were measured than at POH. Figure 9 shows the trajectories for LAC and POH for both days. Maximum ozone concentration on October 30 were measured at both sites at around 1:00 pm. It can be seen (upper panel) that at this time

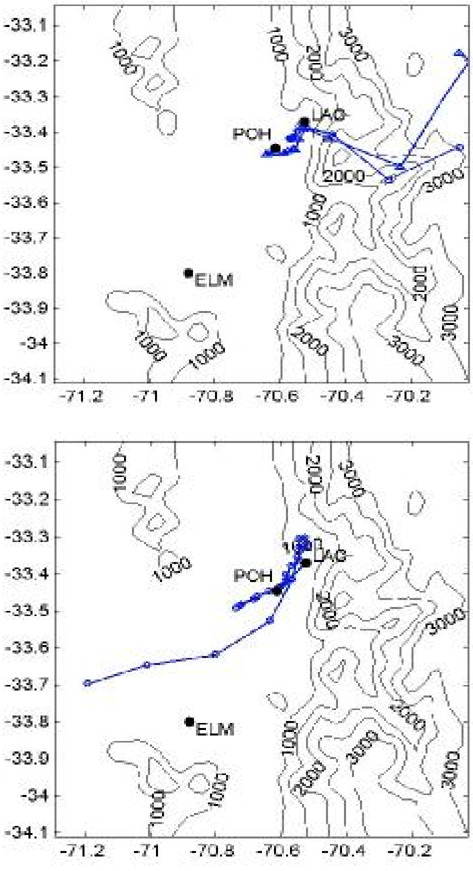

Fig. 9: Trajectories for the measuring sites LAC and POH. Markers indicate time intervals of one hour. Upper panel: Backward trajectories reaching the respective sites at 1:00 pm on October 30, 2002. Lower panel: Backward trajectories reaching LAC at 2:00 pm LAC and going through POH at 1:00 pm on October 31, 2002.

the trajectories have their origin form the mountains and there is no direct connections between the two sites. On the other hand on October 31 maximum ozone values at POH were measure aroound 1:00 pm and at LAC at 2:00 pm. In the lower panel of Fig. 9 only the backward trajectory which reaches LAC at 2:00 pm is given. However, it can be seen, that this trajectory cycles for 23 hours through the basin and the city and goes through POH at around 1:00 pm 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

	October 30		October 31	
	POH	LAC	POH	LAC (2 pm)
Ozone (ppb)	71	88	73	114
SOA (µg/m3)	4.6	5.5	2.8	3.7

Table 1: Model results for October 30 and 31 for the sites POH and LAC.

initialised with values, as measured in El Monte in the early morning hours. Table 1 resumes the results of these modeling experiments. With respect to the the differences of maximum ozone concentrations at LAC and POH the model agrees with the observations, indicating much larger differences on October 31 than on October 30. The different trajectories at both days can be assumed to be responsible for this. Also indicated are the model results for the production of secondary organic aerosols (SOA), as a result from the oxidation of olefins and aromatics. Errors between observations and model values can be explained by the simplification due to the model and lack of information for the initilisation of the model.

3. CONCLUSIONS

From October 30 – November 01, 2002, a field experiment was carried in the basin of Santiago de Chile primarily focusing on the impact of hydrocarbons on the formation of secondary compounds. The results show that based on the propene equivalent certain temporal sequences in terms of photochemical impacts of the different NMHCfractions prevail: during morning hours the alkenes are the most important ones. At noon aromatics are dominant, and in the afternoon isoprene becomes very important. On the whole, alkanes - though being present at high concentration levels mainly due emissions of liquefied petroleum gas (e.g. propane) - do not contribute more than 20% to the total air mass reactivity.

Model results indicate the strong dependency of ozone concentrations on the origin of the air masses. Trajectories for two of the three days of the field campaign show very different behaviour which is also reflected in the ozone concentrations. Furthermore, the application of a SOA module indicates a significant contributuion of anthropogenic hydrocarbons to SOA.

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4. REFERENCES

Ackermann, I.J., Hass, H., Memmesheimer, M., Ebel, A. Binkowski, F.S., Shankar, U. (1999): Modal aerosoll dynamics model for Europe: development and first applications, *Atmos. Environ.*, **32**, 2981-2999

CENMA (1998): Subprograma emisiones biogénicas, Informe Final para la CONAMA R.M.

CENMA (1999): Estudio piloto de fotoquímica, Informe Final para la CONAMA R.M.

Rappenglück B., Oyola P., Olaeta I., Fabian P. (2000): The evolution of photochemical smog in the Metropolitan Area of Santiago de Chile, *J. Appl. Meteor.*, **39**, 275-290

Schell, B., Ackermann, I.J., Hass, H., 2001, Modeling the formation of secondary aerosol within a comprehensive air quality model system, *J. Geophys. Res.*, **106**, D22, 28275-28293

Shepson B., Hastie D. R. Schiff H.I., Polizzi M., Bottenheim J.W., Anlauf K., Mackay G.I., Karecki D.R. (1991): Atmospheric concentrations and temporal variations of C1-C3 carbonyl compounds at two rural sites in central Ontario, *Atmos. Environ.*, **25**, 2001-2015