VERTICAL NITROGEN DIOXIDE AND OZONE CONCENTRATIONS MEASURED FROM A TETHERED BALLOON IN THE LOWER FRASER VALLEY

J. T. PISANO,*† I. MCKENDRY,‡ D. G. STEYN‡ and D. R. HASTIE*

* Centre for Atmospheric Chemistry and Centre for Research in Earth and Space Science, York University, 4700 Keele St., North York, Ont., Canada M3J 1P3; † UNISEARCH Associates, 222 Snidercroft Rd, Concord, Ont., Canada L4K 1B5; and ‡ Department of Geography, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Y6

Abstract—A series of vertical profiles of temperature, relative humidity, NO_2 and O_3 were determined in the Lower Fraser Valley, British Columbia, as part of the PACIFIC '93 field study. Data from one day show very structured vertical distributions of all parameters in the morning, as expected from the limited vertical mixing under the nocturnal inversion. NO_2 concentrations of 20 ppbv were observed 300 m above the surface, while the surface concentrations were ~ 2 ppbv. Ozone and nitrogen oxide chemistry were observed at all altitudes throughout the PBL. Titration of O_3 by NO to produce NO_2 was observed in layers above the ground, under the influence of the NBL. An increase in odd oxygen throughout the PBL, during the morning and early afternoon, shows "smog chemistry" is occurring even though the ground-based O_3 measurements suggest this day was not particularly chemically active. However, once the NBL has dissipated, the ground-based measurements seem representative of the entire PBL. © 1997 Elsevier Science Ltd.

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1. INTRODUCTION

The action of sunlight on anthropogenic nitrogen oxide and hydrocarbon emissions results in exceedances of local ground-level ozone standards in, and downwind of, many urban areas (NRC, 1991; Reid et al., 1995; Volz-Thomas, 1992). In many of these areas, research programs have been initiated to understand, and ultimately control, the ozone concentrations.

Two of the key compounds in tropospheric oxidation chemistry are ozone and nitrogen dioxide. Ozone is the target oxidant, both in chemical and epidemiological studies. It has the highest concentration of the oxidants and has been shown to have deleterious effects on human health (Lippmann, 1989) and plant productivity (Heck et al., 1988; Adams et al., 1989). Nitrogen dioxide is a criteria pollutant but seldom reaches concentrations deemed hazardous. It is most important because its photolysis is the only net source of tropospheric ozone. No other compound can photolyze at wavelengths longer than 320 nm to yield the oxygen atoms necessary for ozone production. However, net ozone production can only occur when the NO, from the photolysis, reacts with a peroxy radical to regenerate NO_2. Therefore, NO and NO_2 are catalysts for the production of ozone.

Ozone and nitrogen dioxide concentrations are routinely measured in air-pollution-monitoring networks and at ground stations during intensive field campaigns but, like almost all species, there is only limited vertical distribution information. Such data are necessary for both initialization and testing of computer models, especially in areas with complex terrain, which produce a very complex local meteorology such as the Swiss plateau and the Lower Fraser Valley. Above ground, measurements of trace species have been made from hydrogen balloons (Dommen et al., 1995), tethered balloons (Hoff et al., 1995), kites (Balsley et al., 1994), a motor glider (Dommen et al., 1995) but most often from aircraft. The speed of aircraft and their limited flying hours mean they are better suited to obtaining information on the spatial variability of species rather than the details of the vertical structure.

The PACIFIC'93 field study aimed to obtain a comprehensive data set for use in understanding the chemistry in the Lower Fraser Valley (LFV), British Columbia, Canada and for use in the associated modelling activities. This valley has a very complex terrain located on a coast, surrounded by mountains up to 1000 m and with a number of tributary valleys in the immediate vicinity. In this paper we report results

from a tethered balloon program conducted as part of this study, which aimed to obtain concentrations of ozone and nitrogen dioxide along with temperature, humidity, wind speed and direction as a function of height throughout the boundary layer. Of particular interest was the evolution of the profiles throughout the day, under the impact of nocturnal inversions and the morning and evening rush hour traffic.

2. EXPERIMENTAL

2.1. Instrumentation

Vertical profile measurements described here were obtained from 3 instruments, an NO_2, an O_3 and a meteorological sonde, attached to a tethered balloon capable of reaching an altitude of 1 km above the surface.

The NO_2 sonde operates by detecting the chemiluminescence produced when gas-phase NO_2 reacts with a luminol solution in the presence of oxygen (Maeda et al., 1980; Wendel et al., 1983). The instrument is a smaller lightweight version of the detector described in Schiff et al. (1986) and has been fully described in Pisano et al. (1996). It will only be discussed briefly here.

Ambient air is pumped through a reaction chamber where it contacts a wick continuously wetted with a luminol solution on which the reaction of luminol with the NO_2 occurs. A photomultiplier (PMT) detects the resulting chemiluminescence. To remove the known interference from O_3, an O_3 trap (Unisearch Associates Inc, O_3 scrubber) is placed in the inlet line. The instrument is calibrated on the ground and the zero baseline is regularly tested for drift, in-flight, by supplying scrubbed ambient air from a small compressor. This response of this sonde has been fully characterized and algorithms developed to account for low-level non-linearity (at concentrations less than 2.8 ppbv) and the signal dependence on both pressure and temperature. The technique has a known interference from PAN. Studies with a similar instrument, using an identical luminol solution, showed the response of the technique to peroxyacetyl nitrate (PAN) is 25% that towards NO_2 (Drummond et al., 1989). The maximum PAN concentration observed at the ground at the time of the data reported here was 0.75 ppbv (J. Bottenheim, personal communication), so the maximum interference was 0.18 ppbv and since this is much lower than any NO_2 data reported here, was neglected. The sonde is integrated with a radiosonde to give supporting pressure, temperature and relative humidity data. The PMT signal, the meteorological data and a number of housekeeping signals are telemetered to the ground every 5 s using the transmitter from the radiosonde. For an average ascent rate of approximately $0.5 \, m \, s^{-1}$, this corresponds to a data point every 2.5 m.

During the field study, sonde calibrations were conducted, before and after each flight, using a 10.6 ppbv NO_2 standard from a permeation tube. Changes in instrument sensitivity were less than 5% over the sampling period. The in-flight zero measurements represented about 6% of the total data and indicated negligible baseline drift. The instrument sensitivity is dependent on the luminol flow but this remained within 20% of the optimal $22 \, \mu l \, min^{-1}$ over 95% of the time so little data was lost due to flow fluctuations.

An AIR meteorological sonde measured wind direction, wind speed, wet and dry bulb temperatures, and external pressures. The height of the balloon was determined using the altimeter equation. Ozone was measured using a commercial Brewer-Mast O_3 sonde (AIR). This is an electrochemical cell which measures the oxidation of iodide by O_3. The use and calibration of these sondes can be found in McKendry et al. (1996).

2.2. Field study

Measurements were made at the Harris Road site (49°26'15"N, 122°31'20"W) during the PACIFIC '93 field study held in Vancouver, British Columbia. This was the site at which the most active chemistry was expected, and was the most heavily instrumented site. For complete details of the study and the site, see Steyn et al. (1996). The vertical profile package was installed on an AIR tethered balloon and NO_2 surroundings were conducted for a total of 5 days. During the first 3 days a balloon large enough to carry all three sondes was used, but for the last 2 sampling days a smaller balloon was used and so alternating flights of the NO_2 sonde with those of the O_3/meteorological sondes were conducted. In total there were 21 flights in which NO_2 measurements were attempted, of which 2 were aborted due to high winds. Of the 19 successful flights the NO_2 sonde produced data on 15 flights, yielding 29 profiles. The loss of data was due primarily to difficulties encountered with telemetry. Of the 29 profiles, 4 were on 26 July, 14 on 1 August, 5 on 2 August and 6 on 5 August. The altitude and meteorological information for the 6 profiles on 5 August were generated from data taken by the radiosonde that was incorporated with the NO_2 sonde.

3. RESULTS AND DISCUSSION

The most extensive NO_2 data were obtained on 1 August (see above) where measurements were obtained over the entire day. The discussion below will concentrate on seven flights (numbers 04, 05, 06, 07, 08, 10, and 11 in (A)scent and (D)escent) that yielded NO_2 profiles on that day.

The O_3 and NO_2 concentrations measured at the surface at the Harris Road site on 1 August are shown in Figs 1b and 2b. The O_3 data show the common diurnal profile with a nighttime minimum, from losses of ozone under the nocturnal inversion, and an early afternoon maximum, from the combination of transport and photochemistry. However, the maximum concentration observed was only 42 ppbv so 1 August was not a day in which high ozone concentrations were generated. Similarly, the NO_2 concentration was below 10 ppbv for most of the day, whereas it exceeded 35 ppbv on 3 and 4 August (H. A. Wiebe, personal communication). Thus, examination of these diurnal profiles would point to a low pollution, low ozone production day.

3.1. Chemical and meteorological indications of boundary layer structure

The depth and structure of the planetary boundary layer (PBL) has a marked impact on the concentration and the distribution of primary pollutants. This control of primary pollutants impacts the rate of production and subsequent transport of secondary pollutants such as O_3 and particulate matter. The structure of the PBL, and the effect of the sea breeze, in the LFV has been studied extensively using meteorological parameters (Steyn and McKendry, 1988). In this study, we can add the chemical indicators to the meteorological parameters. Nitrogen dioxide is especially valuable as it is produced from the reaction of

(a)

Ozone Profiles

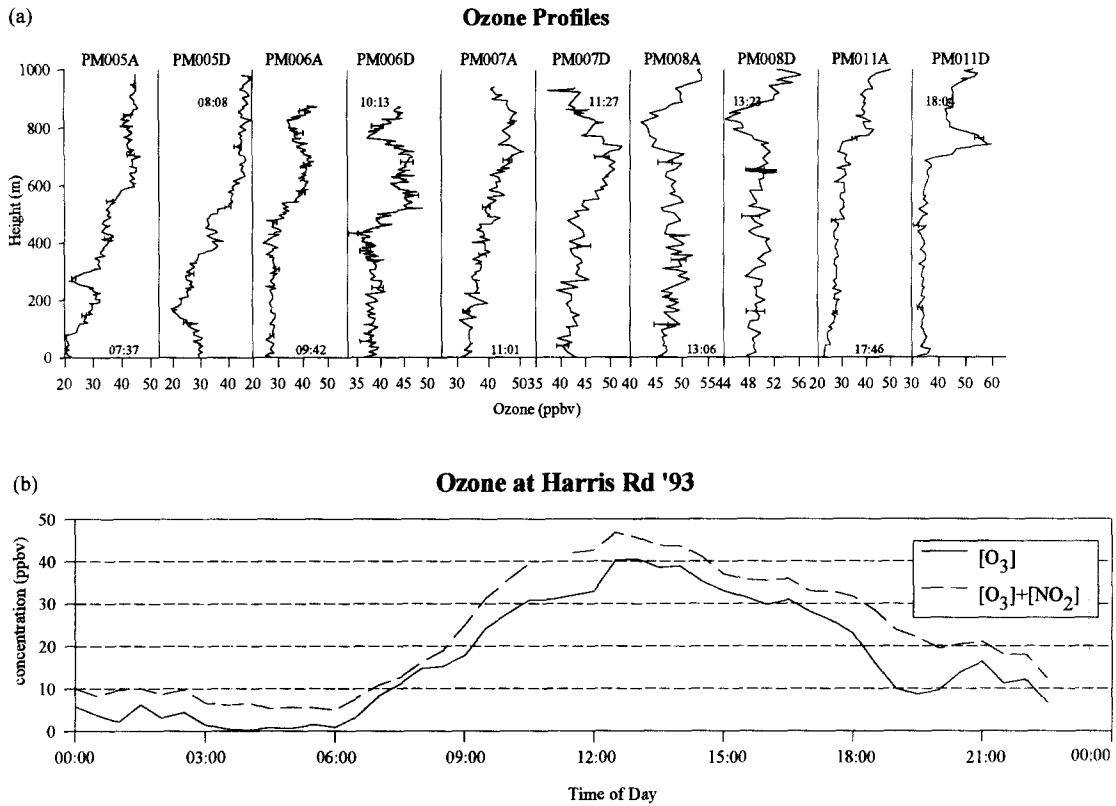

(b)

Ozone at Harris Rd '93

Fig. 1. Ozone profiles (a) and ground-level ozone concentrations (b) measured on 1 August 1993. The error bars on the profiles represent the precision of the individual measurements.

O_3 with NO released at the surface. Since there is generally excess O_3 available, we can consider NO_2 as having a surface source. Furthermore, its lifetime, with respect to oxidation, is of the order of $\frac{1}{2}$ day so its vertical distribution is an indicator of vertical mixing mechanisms. In contrast, O_3 has a long lifetime compared to vertical mixing so O_3 would be expected to have an almost constant mixing ratio through and above the PBL, provided local production and loss is limited. A small gradient induced by dry deposition to the surface would be expected.

There are no data from true nighttime flights but the morning flights (04 and 05) are sufficiently early to capture some of the features of the nocturnal boundary layer (NBL). The temperature data from flight 04 (0642–0732 h) show the atmosphere to have a very complicated temperature structure (Fig. 3). On ascent, there is a shallow ($\sim$ 50 m) isothermal layer capped by an inversion up to $\sim$ 200 m. Another isothermal layer persists to $\sim$ 350 m followed by a temperature decrease to the top of the balloon profile. There are several discontinuities indicating there is still structure at these altitudes. The most marked of these is at $\sim$ 550–600 m, which we attribute to the top of the residual layer. The isothermal layer at 200–350 m is associated with a slightly lower relative humidity, suggesting this air has a different origin from the rest of the air sampled. On descent, a similar profile is

obtained, with the exception that the ground has heated and the isothermal layer at the surface is replaced by a 50 m deep layer with a positive lapse rate. There are no O_3 data on this flight. The NO_2 concentration shows an elevated level in the first 50 m on ascent, consistent with the surface source and the limited vertical mixing in the capped isothermal layer. This is absent on descent, consistent with the temperature change over this period which promoted vertical mixing. The most notable feature is the high ($\sim$ 20 ppbv) concentration of NO_2 within the drier isothermal layer from 200 to 350 m visible on the descent (there is very little of this seen on ascent). This feature is less than 100 m deep at $\frac{1}{2}$ maximum and accumulated quickly, with the NO_2 concentration at 220 m increasing from 2 to 20 ppbv in less than 1 h. Wind speeds at this altitude increase between ascent and descent from $\sim$ 0.5 to $>$ 3 m s^{-1} and the wind direction is 250°, indicating the NO_2 is being blown in rapidly from the southwest, the direction of suburban Vancouver. The narrow depth of the NO_2 peak points to the lack of vertical mixing, especially when compared to the rapid horizontal transport.

Flight 05 immediately followed Flight 04. The temperature profiles for 04D and 05A are very similar below $\sim$ 550 m but the latter flight shows an increase in temperature from 550 to 700 m, which accentuates the temperature inversion visible at 550–600 m in
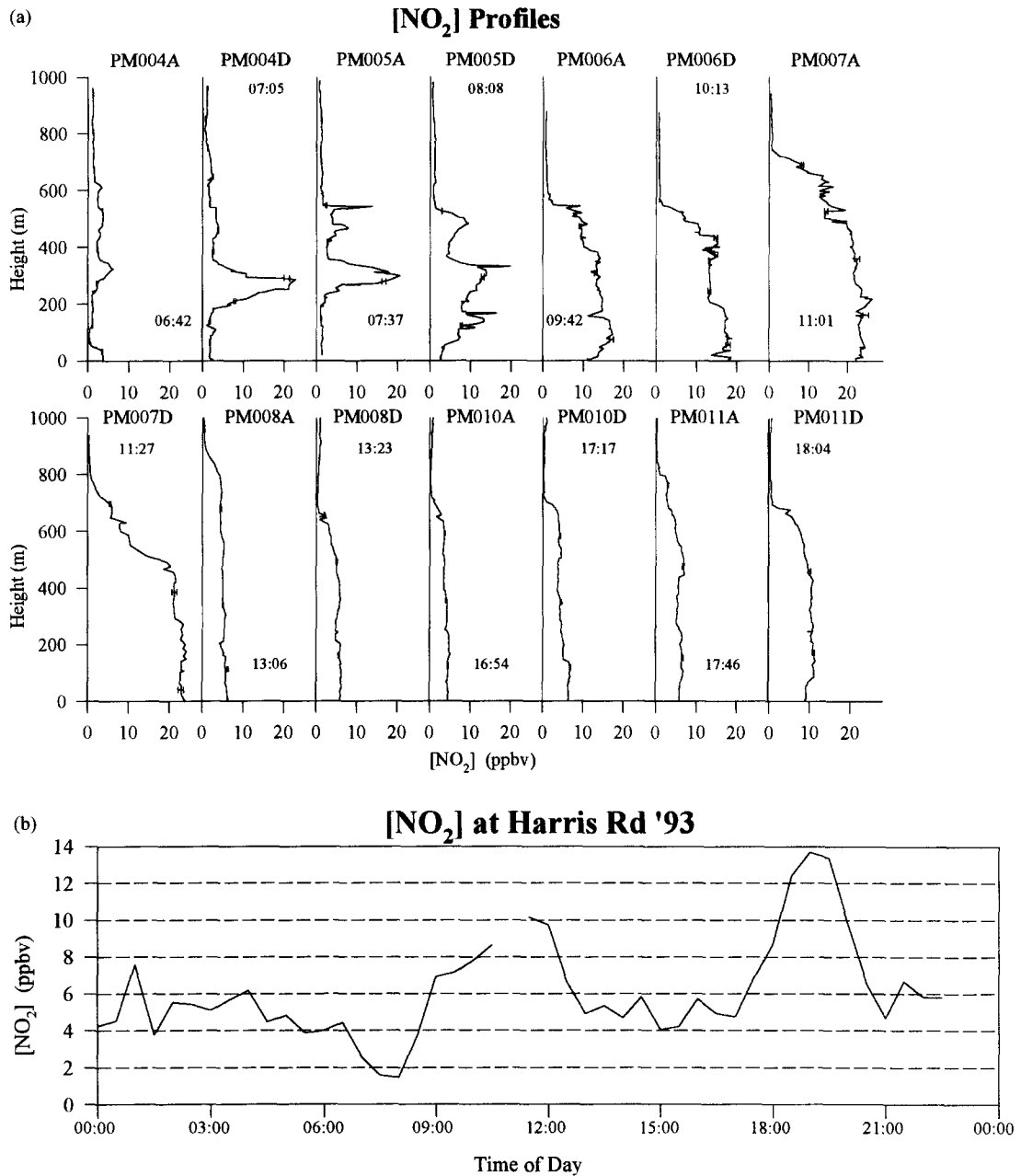
(a)

[NO₂] Profiles

(b)

[NO₂] at Harris Rd '93

Fig. 2. NO₂ profiles (a) and ground-level NO₂ concentrations (b) measured on 1 August 1993. Error bars are as for Fig. 1.

Flight 04. The O_3 profiles from the ascent and the descent show a constant mixing ratio from 600 to 1000 m but a steady decrease from 600 m to the surface, see below. The NO_2 profile on ascent is similar to the previous one with a slightly lower maximum concentration but about the same total amount of NO_2. By the descent, the NO_2 concentration was still lower but the extent of the higher concentration was much larger so that the total amount of NO_2 between the ground and 400 m had doubled in the 45 min between measurements. There appears to be both an onset of vertical mixing, to disperse the plume so evident in

04D and 05A, and the continued accumulation of NO_2. The NO_2 concentrations are elevated at all heights up to the temperature inversion around 550 m with little evidence for entrainment above this height. Thus, the change in the NO_2 concentration identifies the top of the PBL extremely well.

Flight 06 commenced 1 h after 05 and by that time (0942 h) the temperature profile shows a decrease from the surface to 550 m of 0.8°C per 100 m. Thus, all indications are that the NBL had dissipated. The NO_2 and O_3 profiles reflect this well-mixed PBL as they show very little variation in their concentrations with
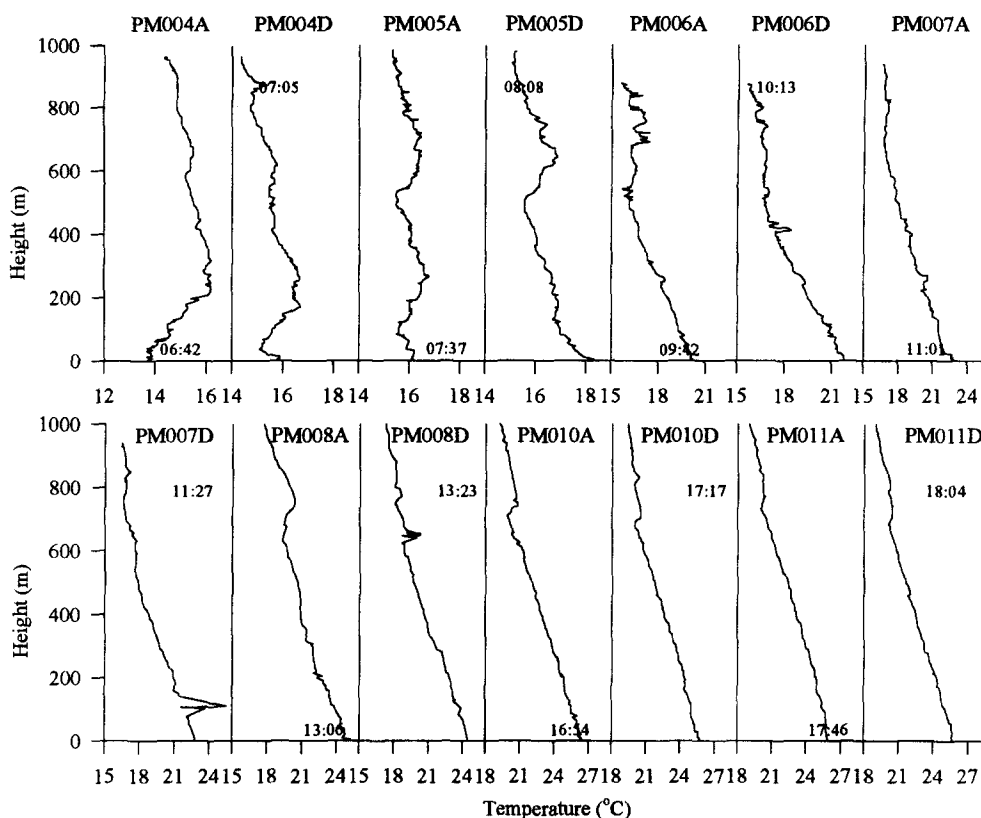
Temperature Profiles

Fig. 3. Temperature profiles for the flights of 1 August.

height up to the top of the PBL, with a very marked transition for the top of the PBL at ~ 550 m. The absolute values of the concentrations and the weak gradients are discussed below. For the rest of the day the PBL remains well mixed, with the depth increasing from 550 to ~ 700 m by Flight 07 (~ 1100 h) and remaining almost constant until the final descent beginning at 1821 h. This profile (11D) shows a shallower PBL and higher NO_2 concentration than the ascent. The decrease in PBL depth heralds the formation of an NBL and the higher NO_2 concentrations result from the greater NO_x emissions in the evening rush hour. This increase in NO_2 is clearly visible in the ground-based NO_2 data (Fig. 2) and the associated titration of ozone by the emitted NO is visible in Fig. 1.

3.2. Nitrogen oxide/ozone chemistry in the boundary layer

Nitrogen dioxide and ozone are both secondary pollutants. Their chemistry is intimately linked, as O_3 can only be produced, in the troposphere, by NO_2 photolysis.

$$NO_2 + hv \rightarrow NO + O \qquad (R1)$$

$$O + O_2 + M \rightarrow O_3 + M. \qquad (R2)$$
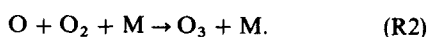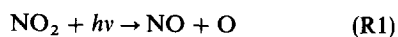
Nitrogen dioxide is produced by the oxidation of NO, which results from soil emissions and combustion. A small fraction of the oxidation is performed by molecular oxygen in the combustion exhaust but mostly it is oxidized by the gas-phase reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (R3)$$

$$NO + RO_2 \rightarrow NO_2 + RO \qquad (R4)$$
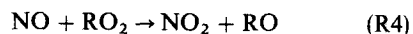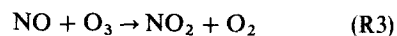
where RO_2 is either an HO_2 or an organic peroxy radical. Following an injection of NO into an air mass, (R3) removes O_3. At longer times, (R4) becomes appreciable, so the sequence of reactions (R1), (R2) and (R4) produce O_3. This is the so-called smog chemistry that is responsible for the production of O_3, which can be a major problem in the LFV. Vertical profiles of NO_2 and O_3 can yield information on the chemistry that is occurring and the altitudes of importance.

The major loss term for tropospheric O_3 is deposition to the Earth's surface. Taking a daytime boundary layer height of 700 m (from above) and a mid-latitude, continental deposition velocity of $0.5 \, cm \, s^{-1}$ (Warneck, 1988), the lifetime of O_3 in the PBL is ~ 40 h. For O_3 above the PBL, the lifetime is much longer and is determined by transport into the PBL.

The occurrence of the NBL isolates much of the O_3 from the surface overnight, so the real lifetime of O_3 is several days. This means that, in the absence of additional sources and sinks, the concentration of O_3 should be highest above the PBL and have a very weak gradient to a minimum at the surface.

The afternoon O_3 profiles show a well-mixed PBL which overcomes the expected gradient. However, the morning profiles (05A and D) show a gradient from 20 (30) ppbv at the surface to 45 ppbv above the PBL. This indicates that, under the PBL, O_3 is being lost at the surface, either by dry deposition or reaction with freshly emitted NO. In a predominantly urban environment, the latter would be expected to be significant, but the lack of an inverse gradient in the NO_2, which would be the product of the reactive loss (via (R3)), points towards dry deposition as being more important. This gradient is maintained by the weak vertical mixing as described above.

The layer of high NO_2 concentration seen in Flights 04D, 05A and 05D results from the titration of NO by O_3 (R3). For Flight 05, where O_3 data are available, a concurrent decrease in the O_3 concentration is evident. This titration is so prevalent in profile 05D that the O_3 actually decreases with height for the lowest 150 m.

If titration were the only process occurring, then the odd oxygen concentration (defined here as $NO_2 + O_3$) would remain constant, since the stoichiometry of reaction (R3) produces one NO_2 molecule for every O_3 molecule consumed. This is the case in Flight 05 (see Fig. 4) and in the ground-based data after 1800 h, where the odd oxygen concentration shows a gradient but without the sudden decreases seen in the O_3 concentrations. In the absence of other chemistry, the profiles should show an averaging of the concentrations throughout the PBL during the day as the vertical mixing is too fast to allow the concentration gradients to be sustained.

The presence of high concentrations of NO_2 aloft in the morning may have an impact on the overall chemistry of the region, out of proportion to their physical size. Although they are sustained by the NBL, they persist well after sunrise when there is sufficient solar radiation to initiate the hydrocarbon/NO_x chemistry. Unfortunately, there are no hydrocarbon measurements in these air masses but the coincidence of the sources, and the high NO_2 concentrations, suggest the air masses should contain high concentrations of hydrocarbons. Therefore, these regions should be chemically very active. Ozone production is not observed in these air masses, because of the lack of the time for the chemistry to become established. However, the chemistry will have begun and the concentrations of the reactive intermediates, such as radicals and aldehydes, will also be higher than the surrounding air masses. Once the NBL breaks up, this material is dispersed throughout the PBL. This will distribute the reactive intermediates into less-reactive air masses, and initiate photochemical ozone production more rapidly than would be expected if these polluted air masses had not been so entrained.

Examining the odd oxygen profiles during the day, it is clear that the total odd oxygen increases in the PBL. For Flight 06A, there is an almost constant odd oxygen concentration throughout the PBL of ~ 40 ppbv. Subsequent profiles show an increase in odd oxygen to about 60 ppbv in Flight 07. Thus, there is a 50% increase in odd oxygen concentration on this day due to the NO catalyzed hydrocarbon oxidation chemistry. From Flight 08D onwards, there is a decrease in O_3 throughout the PBL. This is consistent with the ground-level measurements for this day where the O_3 maximizes at noon and cleaner air masses appear to impact the site later in the day.

2.5. How representative are ground-based measurements?

In complex terrain, such as the LFV, there is always the question as to whether ground-based monitoring networks are measuring concentrations that are representative of those throughout the PBL. It is
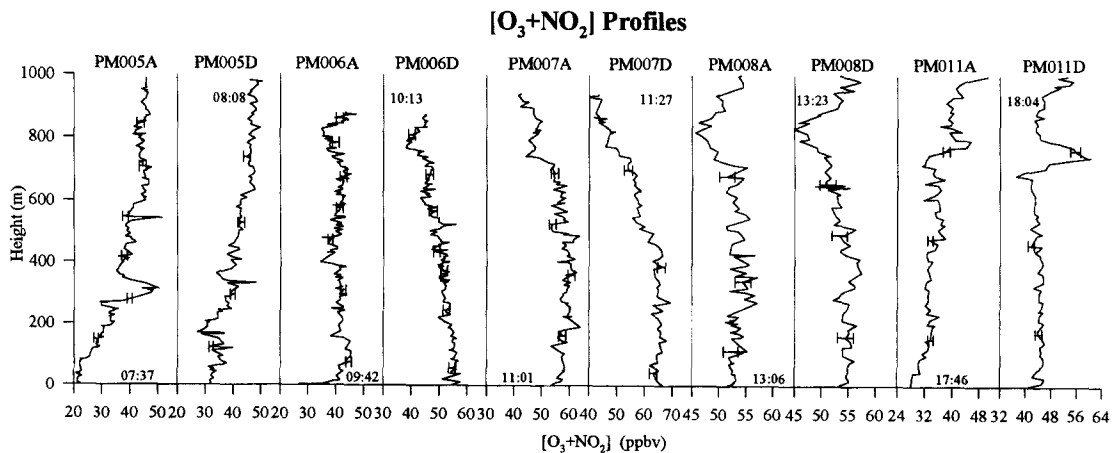

$[O_3+NO_2]$ Profiles

Fig. 4. Odd oxygen ($NO_2 + O_3$) profiles for the flights of 1 August. Error bars are as for Fig. 1.

generally felt that daytime measurements, after the breakup of the NBL, are truly representative because of the high turbulence, especially in the summer. The interpretation of nighttime data is more difficult because of the stratification of the atmosphere (Hastie *et al.*, 1993; Shepson *et al.*, 1992). The flights of 1 August allow us to examine this problem for both NO_2 and O_3. For these compounds, NO_2 has a surface source whereas O_3 has a surface sink.

Sunrise occurred at 0530 PDT on this day. In the early flights, 04 and 05, the NO_2 concentration in the lowest 50 m of the atmosphere matches that measured at the ground. This is especially notable since the NO_2 concentration drops markedly between the ascent and descent of Flight 04. However, the ground-based measurements (and the lowest 100 m measurements) give no indication of the high NO_2 concentrations to be found aloft in profile 04D, 05A and D, even 3 h after sunrise. For these 3 profiles only 6, 4 and 11% of the NO_2 in the PBL can be found in the bottom 100 m of the atmosphere, whereas 45, 26 and 22% are in the layer from 200 to 300 m. By the descent of Flight 05, the average PBL concentration is 8 ppbv but the ground-based measurement is still less than 3 ppbv. This may be an extreme case where the NO is emitted earlier than the measurement and entrained aloft by the buoyancy of the air (the air from combustion sources being warm) or by the need to pass over a geographical feature such as a ridge, to reach the measurement site. The O_3 data for Flight 05 show the O_3 concentration at the lowest point of the profile is a factor of 2 higher than measured at the surface. The ground-level instrument was located lower than the launch site for the balloon so it could experience a pool of cool stagnant air, and therefore have greater O_3 deposition.

For Flights 06 and 07, the sonde continues to measure higher concentrations for both NO_2 and O_3 above the surface than the ground-based instruments, even though the daytime turbulent mixing has overcome the gradients in the concentrations aloft. For the remainder of the flights, the surface concentrations match the average PBL concentrations.

These data show that once the NBL has dissipated, the ground-based measurements are representative of the entire PBL. However, at other times they can show significant deviations.

4. CONCLUSIONS

A series of vertical profiles of temperature, relative humidity, NO_2 and O_3 were determined as part of the PACIFIC '93 field study. In particular, the evolution of these profiles throughout 1 August gives a valuable picture of the meteorology and chemistry active in the area.

Early morning profiles show very structured vertical distributions of all parameters indicating as expected, limited vertical mixing under the nocturnal inversion. Elevated concentrations of NO_2 can persist

aloft with no indications of their presence in the ground-based data. Since this situation can persist for a couple of hours after sunrise, chemistry can be occurring aloft well before its presence can be detected at the ground. When the PBL deepens and becomes more turbulent, these plumes mix into the rest of the PBL. This dilution of high concentrations slows the rates of reactions, but also supplies reactive intermediates to the expanding boundary layer. The importance of these early morning high concentration air masses needs to be examined.

Ozone and nitrogen oxide chemistry is observed at all altitudes throughout the PBL. Titration of O_3 by NO to produce NO_2 was observed in layers above the ground, under the influence of the NBL. An increase in odd oxygen throughout the PBL, during the morning and early afternoon, shows "smog chemistry" is occurring even though the ground-based O_3 measurements suggests this day was not particularly chemically active.

Nighttime ground-level measurements can be explained by the presence of a NBL, and are truly decoupled from those aloft. However, once the NBL breaks up, ground-based measurements of ozone and NO_2 are representative of the entire PBL.

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