

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

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**Abstract**—A series of vertical profiles of temperature, relative humidity,  $\text{NO}_2$  and  $\text{O}_3$  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.  $\text{NO}_2$  concentrations of 20 ppbv were observed 300 m above the surface, while the surface concentrations were  $\sim 2$  ppbv. Ozone and nitrogen oxide chemistry were observed at all altitudes throughout the PBL. Titration of  $\text{O}_3$  by NO to produce  $\text{NO}_2$  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  $\text{O}_3$  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.

**Key word index:** Ozone, nitrogen dioxide, vertical profiles, photochemistry, PACIFIC '93.

## 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  $\text{NO}_2$ . Therefore, NO and  $\text{NO}_2$  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  $\text{NO}_2$ , an  $\text{O}_3$  and a meteorological sonde, attached to a tethered balloon capable of reaching an altitude of 1 km above the surface.

The  $\text{NO}_2$  sonde operates by detecting the chemiluminescence produced when gas-phase  $\text{NO}_2$  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  $\text{NO}_2$  occurs. A photomultiplier (PMT) detects the resulting chemiluminescence. To remove the known interference from  $\text{O}_3$ , an  $\text{O}_3$  trap (Unisearch Associates Inc,  $\text{O}_3$  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  $\text{NO}_2$  (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  $\text{NO}_2$  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  $0.5 \text{ m s}^{-1}$ , 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  $\text{NO}_2$  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  $22 \mu\text{l min}^{-1}$  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  $\text{O}_3$  sonde (AIR). This is an electrochemical cell which measures the oxidation of iodide by  $\text{O}_3$ . 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 ( $49^\circ 26' 15'' \text{N}$ ,  $122^\circ 31' 20'' \text{W}$ ) 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  $\text{NO}_2$  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  $\text{NO}_2$  sonde with those of the  $\text{O}_3$ /meteorological sondes were conducted. In total there were 21 flights in which  $\text{NO}_2$  measurements were attempted, of which 2 were aborted due to high winds. Of the 19 successful flights the  $\text{NO}_2$  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  $\text{NO}_2$  sonde.

## 3. RESULTS AND DISCUSSION

The most extensive  $\text{NO}_2$  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  $\text{NO}_2$  profiles on that day.

The  $\text{O}_3$  and  $\text{NO}_2$  concentrations measured at the surface at the Harris Road site on 1 August are shown in Figs 1b and 2b. The  $\text{O}_3$  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  $\text{NO}_2$  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  $\text{O}_3$  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

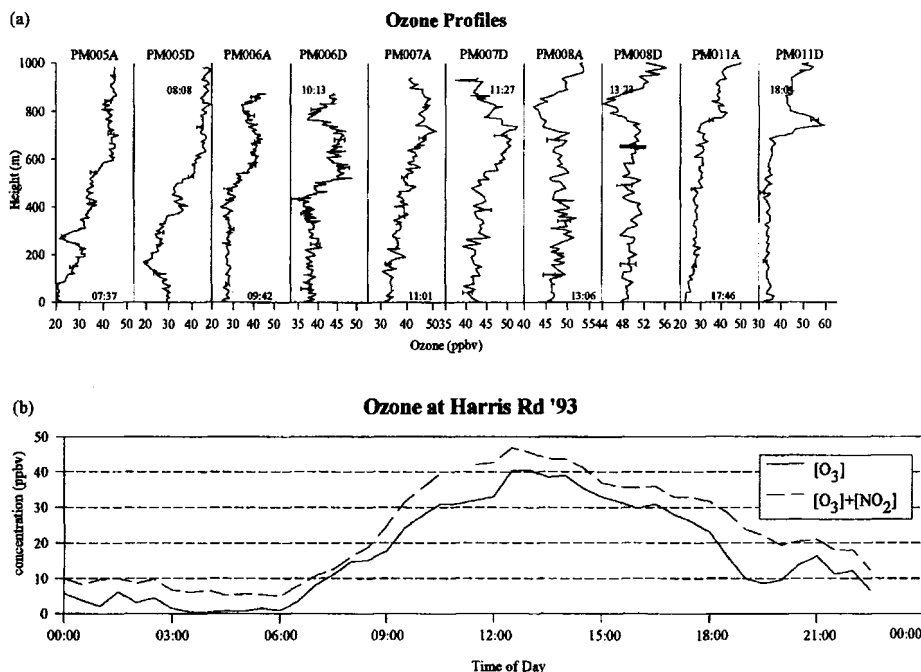


Fig. 1. Ozone profiles (a) and ground-level ozone concentrations (b) measured on 1 August 1993. The error bars on the profiles represent the precision of the individual measurements.

$O_3$  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 been 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  $250^\circ$ , 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

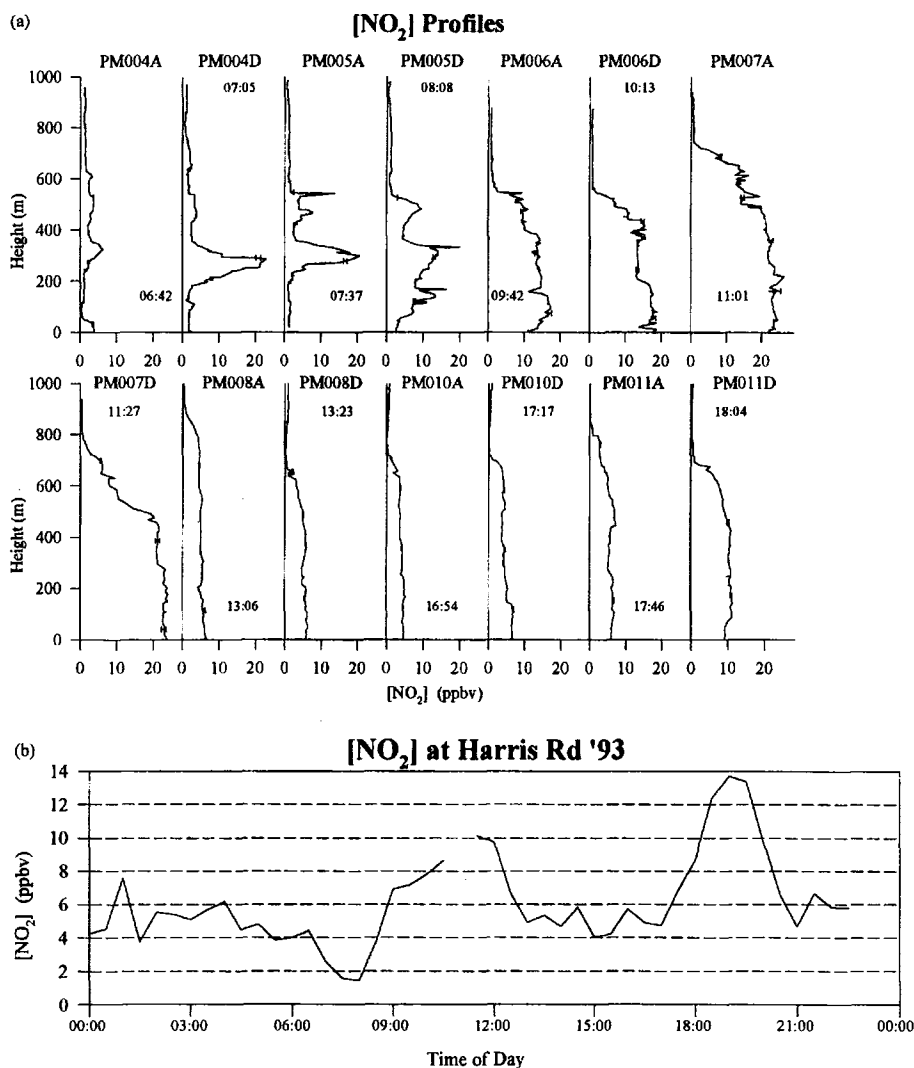


Fig. 2. NO<sub>2</sub> profiles (a) and ground-level NO<sub>2</sub> concentrations (b) measured on 1 August 1993. Error bars are as for Fig. 1.

Flight 04. The O<sub>3</sub> 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<sub>2</sub> profile on ascent is similar to the previous one with a slightly lower maximum concentration but about the same total amount of NO<sub>2</sub>. By the descent, the NO<sub>2</sub> concentration was still lower but the extent of the higher concentration was much larger so that the total amount of NO<sub>2</sub> 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<sub>2</sub>. The NO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> and O<sub>3</sub> profiles reflect this well-mixed PBL as they show very little variation in their concentrations with

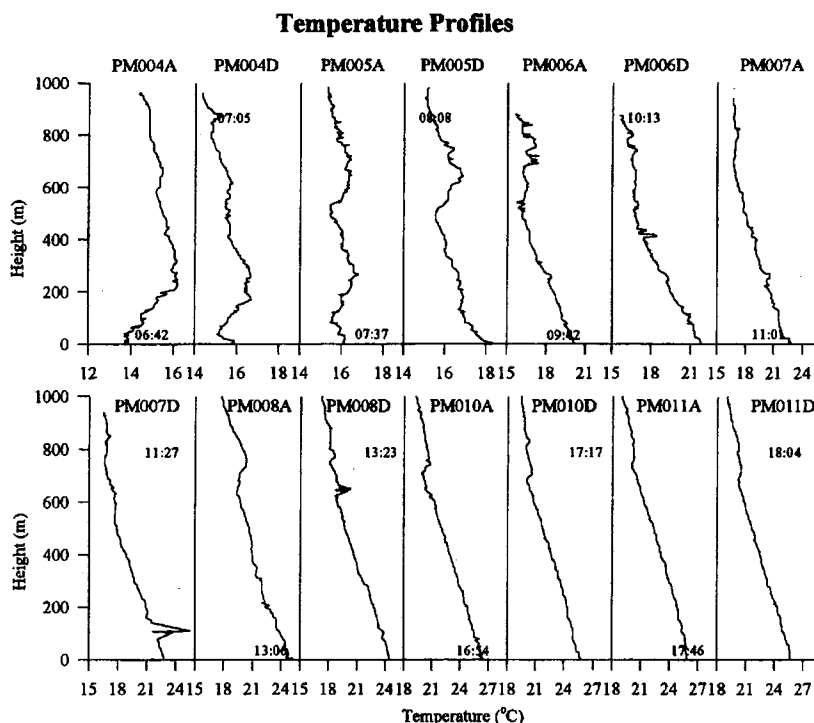
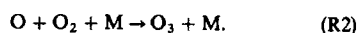
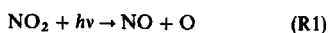


Fig. 3. Temperature profiles for the flights of 1 August.

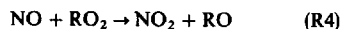
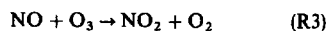
height up to the top of the PBL, with a very marked transition for the top of the PBL at ~ 550 m. The absolute values of the concentrations and the weak gradients are discussed below. For the rest of the day the PBL remains well mixed, with the depth increasing from 550 to ~ 700 m by Flight 07 (~ 1100 h) and remaining almost constant until the final descent beginning at 1821 h. This profile (11D) shows a shallower PBL and higher  $\text{NO}_2$  concentration than the ascent. The decrease in PBL depth heralds the formation of an NBL and the higher  $\text{NO}_2$  concentrations result from the greater  $\text{NO}_x$  emissions in the evening rush hour. This increase in  $\text{NO}_2$  is clearly visible in the ground-based  $\text{NO}_2$  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  $\text{O}_3$  can only be produced, in the troposphere, by  $\text{NO}_2$  photolysis.



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:



where  $\text{RO}_2$  is either an  $\text{HO}_2$  or an organic peroxy radical. Following an injection of NO into an air mass, (R3) removes  $\text{O}_3$ . At longer times, (R4) becomes appreciable, so the sequence of reactions (R1), (R2) and (R4) produce  $\text{O}_3$ . This is the so-called smog chemistry that is responsible for the production of  $\text{O}_3$ , which can be a major problem in the LFV. Vertical profiles of  $\text{NO}_2$  and  $\text{O}_3$  can yield information on the chemistry that is occurring and the altitudes of importance.

The major loss term for tropospheric  $\text{O}_3$  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  $0.5 \text{ cm s}^{-1}$  (Warneck, 1988), the lifetime of  $\text{O}_3$  in the PBL is ~ 40 h. For  $\text{O}_3$  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 chem-

istry 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  $\sim 40$  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

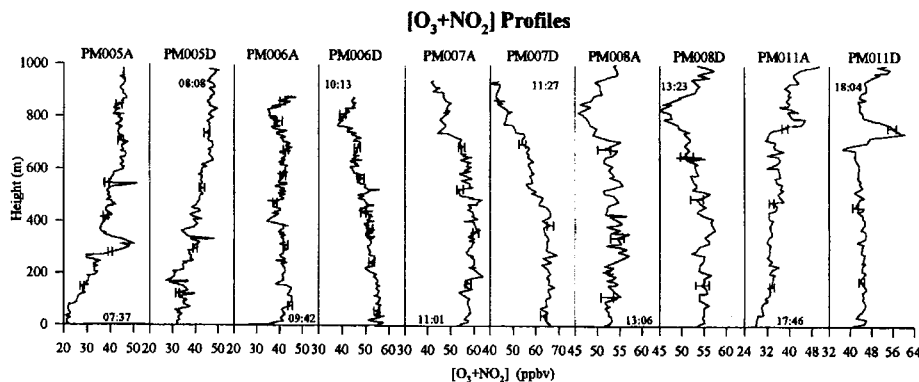


Fig. 4. Odd oxygen ( $NO_2 + O_3$ ) profiles for the flights of 1 August. Error bars are as for Fig. 1.

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<sub>2</sub> and O<sub>3</sub>. For these compounds, NO<sub>2</sub> has a surface source whereas O<sub>3</sub> has a surface sink.

Sunrise occurred at 0530 PDT on this day. In the early flights, 04 and 05, the NO<sub>2</sub> concentration in the lowest 50 m of the atmosphere matches that measured at the ground. This is especially notable since the NO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>3</sub> data for Flight 05 show the O<sub>3</sub> 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<sub>3</sub> deposition.

For Flights 06 and 07, the sonde continues to measure higher concentrations for both NO<sub>2</sub> and O<sub>3</sub> 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<sub>2</sub> and O<sub>3</sub> 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<sub>2</sub> 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<sub>3</sub> by NO to produce NO<sub>2</sub> 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<sub>3</sub> 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<sub>2</sub> are representative of the entire PBL.

*Acknowledgements*—This work was supported by an NSERC Strategic Grant. We thank K. Anlauf J. Bottenheim, and H. A. Weibe for use of their data prior to publication. This is publication #96/05 of the Canadian Institute for Research in Atmospheric Chemistry.

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