Pergamon

Atmospheric Environment Vol. 31, No. 14, pp. 2147–2162, 1997
Published by Elsevier Science Ltd

PII: S1352-2310(96)00359-7
1352-2310/97 $17.00 + 0.00

NOCTURNAL CLEANSING FLOWS IN A TRIBUTARY VALLEY

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(*First received* 12 *September* 1995 *and in final form* 12 *November* 1996. *Published May* 1997)

Abstract—During photochemical air pollution episodes in the Lower Fraser Valley (LFV) near Vancouver, BC, daytime upvalley flows carried polluted air, with high ozone (O_3) concentrations, into tributary valleys to the north of the LFV. Nighttime flows out of the valleys had low O_3 concentrations, according to surface measurements, and also had low aerosol concentrations, as measured by a scanning Doppler lidar. Analysis of lidar scan data showed that the flows were highly complex, that the relatively clean flow was confined to the lower levels (lowest ~500 m) of the valley, and that regions of strongest outflow were also the regions of "cleanest" air. Measurements of NO_2 concentrations well above background levels in the outflow indicate that it was formerly polluted air from which O_3 and aerosols had been removed. Possible removal mechanisms were found to be dry deposition in the katabatic (downslope) flows down the valley sidewalls, in agreement with a previous study in a Swiss valley, or fast chemical reactions with NO and NO_3. Nearly horizontal lidar scans showed that the valley exit flows penetrated into the LFV, where they merged with the downvalley/land–breeze system along the Fraser River. Published by Elsevier Science Ltd.

Key word index: Ozone, katabatic flow, dry deposition, downvalley flows, valley outflow jets, Doppler lidar, Vancouver, BC.

1. INTRODUCTION

The diurnal heating cycle at the Earth surface produces flow up and into valleys during the day, and down and out of valleys at night. In the valley of the lower Fraser River, east of Vancouver, BC, this has been thought to contribute to increases in the concentrations of photochemical pollutants from day to day during high-ozone (O_3) episodes lasting several days, by a recirculation of pollutants. According to this view, polluted air from the Lower Fraser Valley (LFV) is advected into mountain valleys to the north during the day, only to be carried back into the LFV by downvalley flows at night. Pollution from the current day adds to that from previous days, resulting in progressively higher pollutant levels in the LFV as an episode continues.

The flow of polluted air into Pitt Lake valley, one of the major tributaries of the LFV, during the daytime is documented in another study (McKendry *et al.*, 1997). In the present paper we investigate the nighttime portion of the cycle to see whether polluted air is indeed being brought back down into the LFV by nocturnal flows departing Pitt Lake valley. We present results from surface instrumentation deployed at the mouth of the Pitt Lake valley during the Pacific 93 oxidant measurement campaign, showing that nighttime air flowing downvalley was relatively clean of O_3 and NO, consistent with results reported for a Swiss valley (Broder and Gygax, 1985), and also relatively clean of isoprene, a reactive biogenic hydrocarbon (with a minor automotive contribution) that contributes significantly to O_3 production. We also present (1) an ozonesonde ascent from an island in Pitt Lake showing the relationship between the vertical distribution of O_3 and the nocturnal flow, and (2) vertical scans from a Doppler lidar aimed toward Pitt Lake valley, showing the relationship between vertical profiles of aerosol content of the air and the structure of the flow.

The role of nocturnal flows in redistributing pollutants between sunset and sunrise on the next day is

also an important part of the diurnal cycle. Flows spilling out of Pitt Lake and other valleys at night penetrate into the LFV, and thus affect the nocturnal transport of pollutant species in the larger river valley. Nearly horizontal, low-elevation azimuth scans with the Doppler lidar address this by showing the horizontal structure and temporal behavior of these flows on the night of 4–5 August 1993. The lidar has proved to be very useful for studying flows in complex terrain (Banta and Olivier, 1991; Banta *et al.*, 1995, 1996; Clark *et al.*, 1994).

This study is the second time that Doppler lidar has been used to study the fine-scale structure of nocturnal outflow from a valley. Lidar scan data were recently used to study flow out of a canyon in Colorado as part of a wintertime tracer study at the Rocky Flats Plant (Banta *et al.*, 1995, 1996; Levinson and Banta, 1995). In the present work, features similar to those found at Rocky Flats were also found in the summertime environment of southwestern British Columbia.

2. LOCALE, WEATHER, AND INSTRUMENTATION

2.1. *Topography and weather*

A description of the topography of the LFV, the mountain ranges in the vicinity, and the tributary valleys of the LFV is given in this issue by Steyn *et al.* (1997). Pitt Lake, essentially at sea level, forms the floor of a large tributary valley that is the subject of this study. Figure 1 shows the location of this valley, the Doppler lidar site, and the fast chemistry site at Harris Road. The two roads out of the valley, along the valley floor near Pitt Lake, have little traffic at night. Thus, nocturnal flow out of the valley would show little evidence of recent emissions from within the valley.

The major photochemical pollution episode during Pacific 93 occurred from 1 to 6 August 1993. Weather for the episode period was dominated by a strong anticyclone producing strong subsidence and weak northeasterly flow in the midtroposphere, as described by Steyn *et al.* (1997) and Pottier *et al.* (1997).

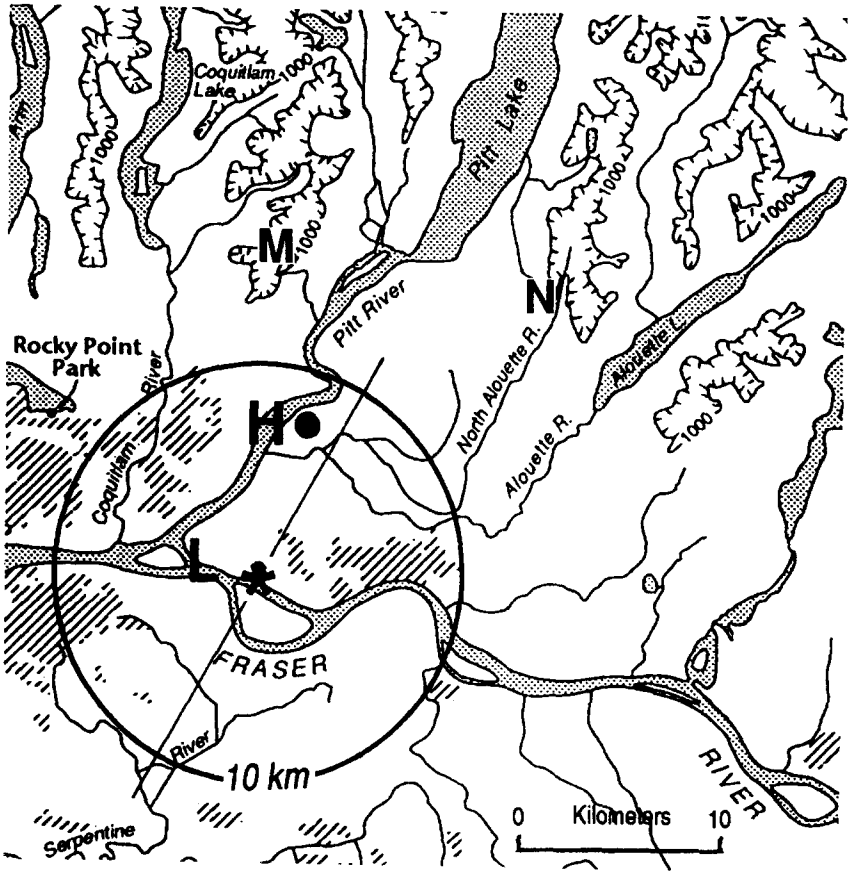

Fig. 1. Map showing the Fraser River Valley east of the city of Vancouver. Cross hatching denotes the most heavily populated areas. Complex terrain to the north of the Fraser River Valley, including the Pitt Lake region, is shown, with the 1000 m contours indicated. Location of sensors used in this study include H, the Harris Road surface chemistry site, and L, the Doppler lidar site at Pitt Meadows airport. M and N indicate mountain ridges seen in lidar scans. The circle indicates a 10 km range ring, and the line toward Pitt Lake indicates 30° azimuth.

Because of the lack of major urban centers, air to the north of the LFV is quite free of urban pollutants.

Of interest for the current case study was the occurrence of a thunderstorm passing to the north of the lidar from east to west on 4 August 1993, resulting in a thunderstorm outflow that affected the region in late afternoon. The lidar recorded an abrupt windshift and a north–south aerosol backscatter boundary passing its site at 1700 PST. Aerosol backscatter increased behind the boundary (i.e. in the gust front air), most likely because higher wind speeds there picked up surface dust. Thunderstorm outflows generally originate at midtropospheric levels, where air is considerably cleaner than at the surface.

2.2. *Doppler lidar*

A Doppler lidar is an active remote sensing system similar to a Doppler radar, except that the atmospheric scatterers are aerosol particles instead of hydrometeors. The Doppler lidar was developed by the Environmental Technology Laboratory (ETL) of the National Oceanic and Atmospheric Administration's Environmental Research Laboratories. It transmits a beam of eye-safe infrared light at a wavelength of 10.59 μm, a fraction of which is scattered back to the instrument. The intensity and frequency of the returned signal are recorded. Backscatter intensity is related in a complex way to the concentration and other attributes of aerosol particles. From the frequency, a Doppler or radial velocity u_r is calculated. The combined use of lidar velocity and backscatter analyses to study a prescribed forest fire is described by Banta *et al.* (1992), and the use of velocity data to study sea breezes is described by Banta *et al.* (1993) and Banta (1995).

Attributes of the lidar have been summarized by Post and Cupp (1990). The velocity accuracy is 60 cm s^{-1} r.m.s., range gates are at 300 m intervals, and the pulse repetition frequency (PRF) is 10 Hz. In this study three shots were averaged for each velocity estimate, giving an effective PRF of 3 1/3 Hz. For the first 3 days of the episode the transmitted power of the lidar was variable, resulting from hardware difficulties. Absolute backscatter values from scans more than an hour or so apart thus may not be comparable, but within a given scan, relative intensities can be used to infer regions of high and low aerosol concentration.

The lidar can scan in azimuth or elevation to reveal the horizontal variability and the vertical structure of the flow. Full 360° azimuth scans can be used to calculate vertical profiles of the horizontal winds using the velocity-azimuth display (VAD) technique described by Browning and Wexler (1968). Profiles determined from the lidar in this way for Pacific 93 have been reported by Olivier *et al.* (1994), McKendry *et al.* (1997), and Pottier *et al.* (1997).

In this study the lidar was located on a dike at the south edge of the Pitt Meadows airport (L in Fig. 1). When scanning to the north, it had to look over the roof of an airport building, which intercepted the lidar beam below ~0.2° elevation. The three-dimensional volume scan used here consisted of a sequence of vertical slices taken toward Pitt Lake. Sectors were scanned from 0 to 5° elevation, repeating at 0.5° azimuth intervals from 26 to 30° azimuth (Fig. 2). Scans were performed slowly (0.5° s^{-1}) to obtain high resolution (0.167° in elevation, for a vertical resolution of 29 m at 10 km range). These volume scans were analyzed in two ways: first as vertical, along-the-beam cross sections of the flow coming out of Pitt Lake valley, indicated as OP in Fig. 2, and second as cross-beam vertical cross sections, indicated as AB in Fig. 2. Because the low-level flow was into or out of the valley, these also represented streamwise and cross-stream cross sections, respectively.

2.3. *Ozonesonde and surface chemistry instrumentation*

The ozonesonde was an ozone sounding system attached to a tethersonde, as described by McKendry *et al.* (1997). It provided profiles of ozone and meteorological variables (pressure, temperature, humidity, and wind direction and speed) to heights of ~1000 m AGL. Ozone measurements were available every 10 s, and calibration comparisons in the field indicated an r.m.s. error of less than 11 ppb.

Although ozonesonde profiles were not taken at night during Pacific 93, profiles were occasionally available for evening or early-morning hours. Also, during the following summer (August 1994) nighttime profiles, one of which will be presented in Section 3.1, were taken at the Pitt Lake site as a part of a separate

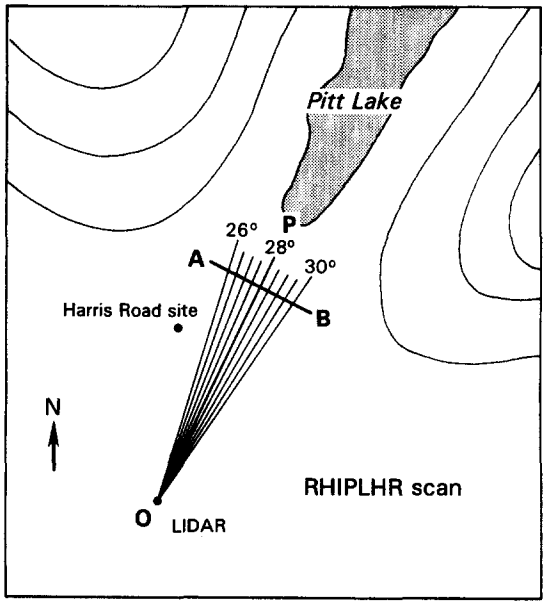

Fig. 2. Diagram of the high-resolution volume scan performed regularly by the ETL Doppler lidar during the Pacific 93 study. Each ray toward Pitt Lake represents a vertical slice scan. Vertical, along-the-beam cross sections of flow coming out of Pitt Lake valley (OP) and beam-perpendicular vertical cross sections (AB) were used for analyzing lidar volume scans.

investigation. Surface-station data at the mouth of the Pitt Lake valley indicate that nocturnal outflow was a recurrent phenomenon on nights of the episode week. Hence, data from other O_3-episode nights (even from different years) should be comparable with those taken on the present case study night of 4/5 August 1993.

The surface "fast chemistry" instrumentation at the Harris Road site (H in Fig. 1) is described in this issue by Li *et al.* (1997) and Steyn *et al.* (1997). NO, NO_2, and NO_x were measured at that site by O_3-chemiluminescence, O_3 by UV absorption, CO by gas correlation, and peroxyacetyl nitrate (PAN) by gas chromatography using electron-capture detection. Isoprene and carbonyl compounds were measured using an automated gas chromatograph/mass spectrometer (GC/MS) system, as described by Biesenthal *et al.* (1997). In the current study, "local" sources will refer to those sources, in the northeastern LFV but outside the Pitt Lake and other tributary valleys, whose effects could be detected at the Harris Road site.

3. RESULTS

Figure 3 shows the behavior of surface winds at the Harris Road site for afternoons and evenings of 4 days during the ozone episode period of 1–6 August. Southerly or southwesterly afternoon flow into the Pitt Lake valley shifted to northerly flow out of the valley at about 1800–1900 PST on each day. Later, between ~2100 and 2200 PST, the northerly flow ceased, becoming light with a variable direction until sunrise. This light-and-variable flow was shallow, since lidar observations (presented in Sections 3.1 and 3.2) indicated northerly outflow below ~600 m AGL from Pitt Lake most of the night. That the lidar saw only northerly flow indicates that the light-and-variable surface flow must have been only a few tens of meters deep at most. This surface flow most likely represented a shallow pool of cold air near the river resulting from local drainage off nearby land surfaces, similar to the thin katabatic-flow layer described by Banta *et al.* (1995, 1996).

3.1. *Vertical flow structure*

Vertical cross sections of along-valley wind speed during several stages of the flow into and out of Pitt Lake valley are given in Fig. 4, analyzed from the high-resolution volume scan described in Section 2.2. They show a 600 m deep layer of downvalley flow forming by midnight. To investigate further the flow structure near the valley mouth, we averaged lidar data in the horizontal between 8 and 9 km (solid bar at the bottom of the panels of Fig. 4) to form vertical profiles of u_r and aerosol backscatter measured by the lidar. These profiles are shown in Fig. 5 for the period from midafternoon on 4 August to noon on 5 August, negative values indicating flow out of the valley.

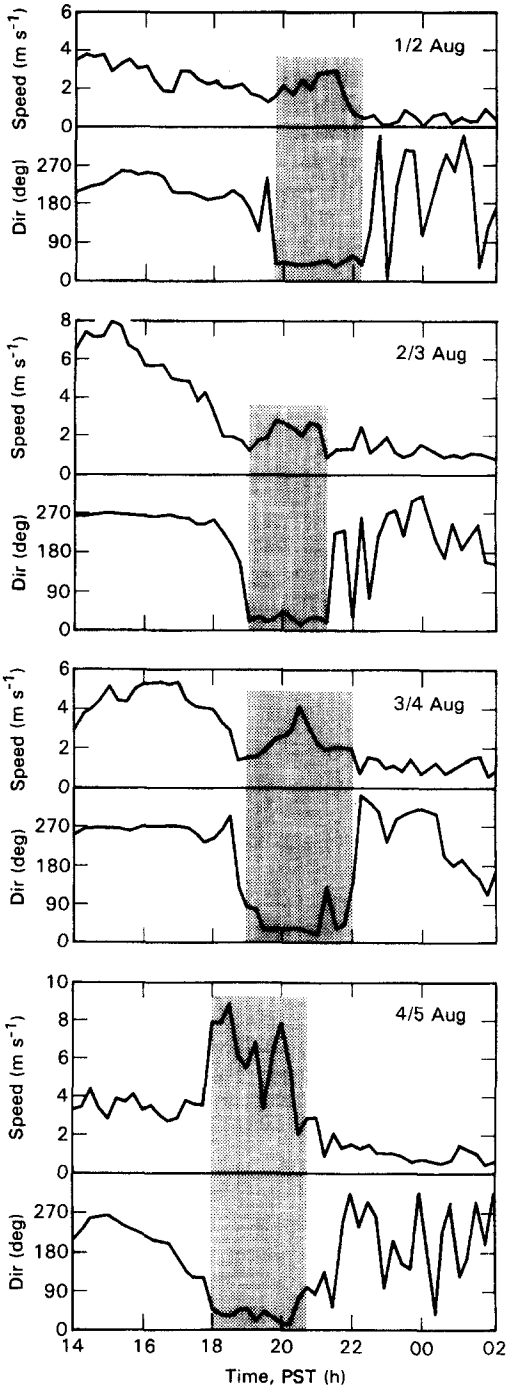

Fig. 3. Surface wind measurements from the Harris Road site. Shading indicates northerly flow or Pitt Lake valley outflow.

Typical midafternoon aerosol and wind profiles, such as in Fig. 5a, show dirty air (i.e. with high backscatter) below 500 m and an upvalley (positive) flow of ~4 m s^{-1} below 400 m, diminishing with height to the top of the profile (900 m AGL). Nighttime profiles of u_r (e.g. Figs 5b–d) show flow out of the valley exceeding 5 m s^{-1} to a depth of 400–600 m, indicating a valley exit or outflow jet, with evidence of

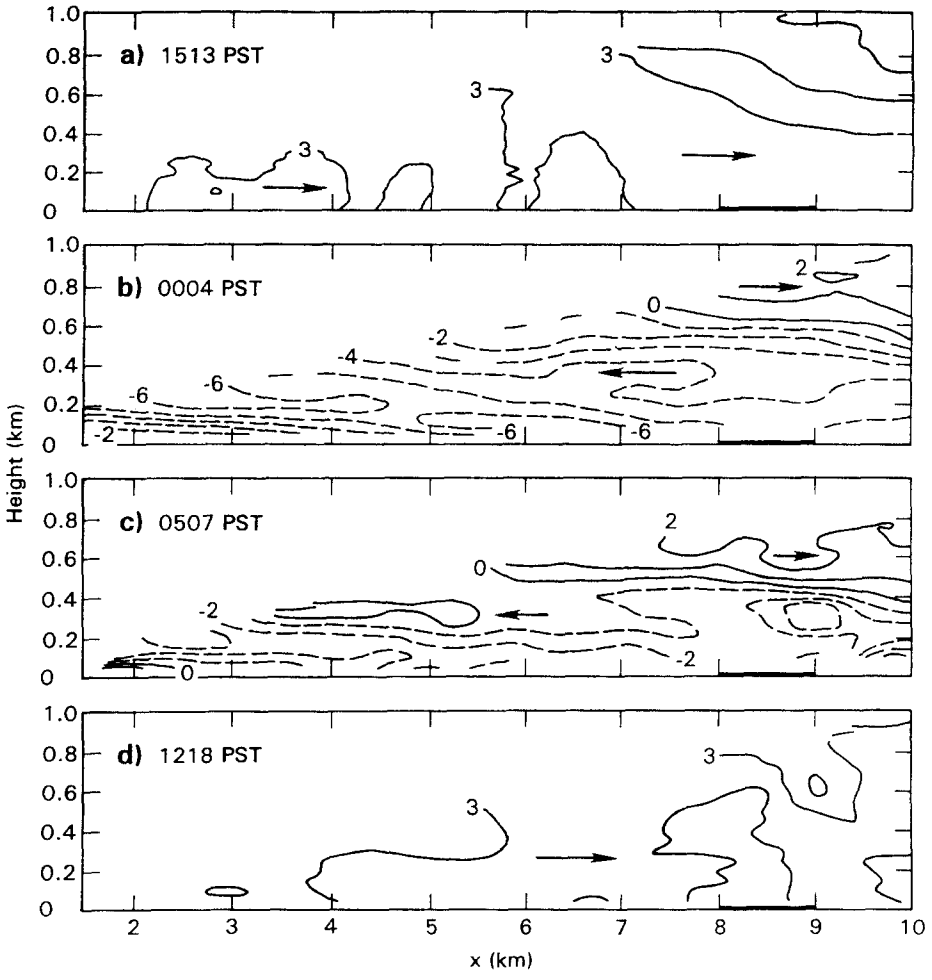

Fig. 4. Vertical cross sections of lidar radial velocities for 4/5 August 1993 along the 28° azimuth, line OP in Fig. 2. The lidar is at (0,0). Positive values (solid contours) represent flow away from the lidar (upvalley), and negative values (dashed contours), flow toward the lidar (downvalley). The bold line from 8 to 9 km (along the x-axis) shows the region where data were averaged for the profiles in Fig. 5.

lighter flow near the surface after 2053 PST. After midnight the flow was variable, and the profiles indicate weak flow after 0200 PST (Figs 5e–f). However, information from other scans, such as those presented in the next section, indicates that the valley efflux was strong at times during the midnight-to-dawn period. Aerosol backscatter profiles show that the valley outflow air was clean of aerosol compared with the air above 500 m. After sunrise (0646 PST, Fig. 5g) the flow began to reverse, but the low-level air was still clean. Later, however, profiles taken just after noon (Fig. 5h) show a 3–4 m s^{-1} flow carrying dirty air from the LFV into the tributary valley below 500 m.

Figure 5 shows a strong correlation between air with low aerosol backscatter and valley out-flow as the diurnal wind systems evolve in time. Figure 6, which gives cross sections *across* the flow analyzed from the 0004 PST volume scan, shows that the outflow and aerosol distribution are not uniform across the flow, and that the strongest values (5–6 m s^{-1}) of the outflow jet in the lower right of the velocity panels correlate with the lowest backscatter values. These measurements were just outside the valley, and the strongest outflows represent the air most recently in the valley.

O_3 profiles from inside the valley show many similarities to the aerosol backscatter profiles. Although no ozonesonde profiles were taken at night during 1993, a nighttime O_3 profile is available from an O_3-episode night during the 1994 campaign. The O_3 profile in Fig. 7, taken at 0124 PST on 31 August 1994, shows low-O_3 air below 300 m, where the lidar showed low backscatter. The association between high values of aerosol backscatter and high O_3 concentration (and between low-aerosol layers and low-O_3 layers) has been previously reported in the Los Angeles basin (McElroy and Smith, 1993) and has also been strikingly documented in other analyses of Pacific 93 data (McKendry *et al.*, 1997). However, we must note that this association only applies to

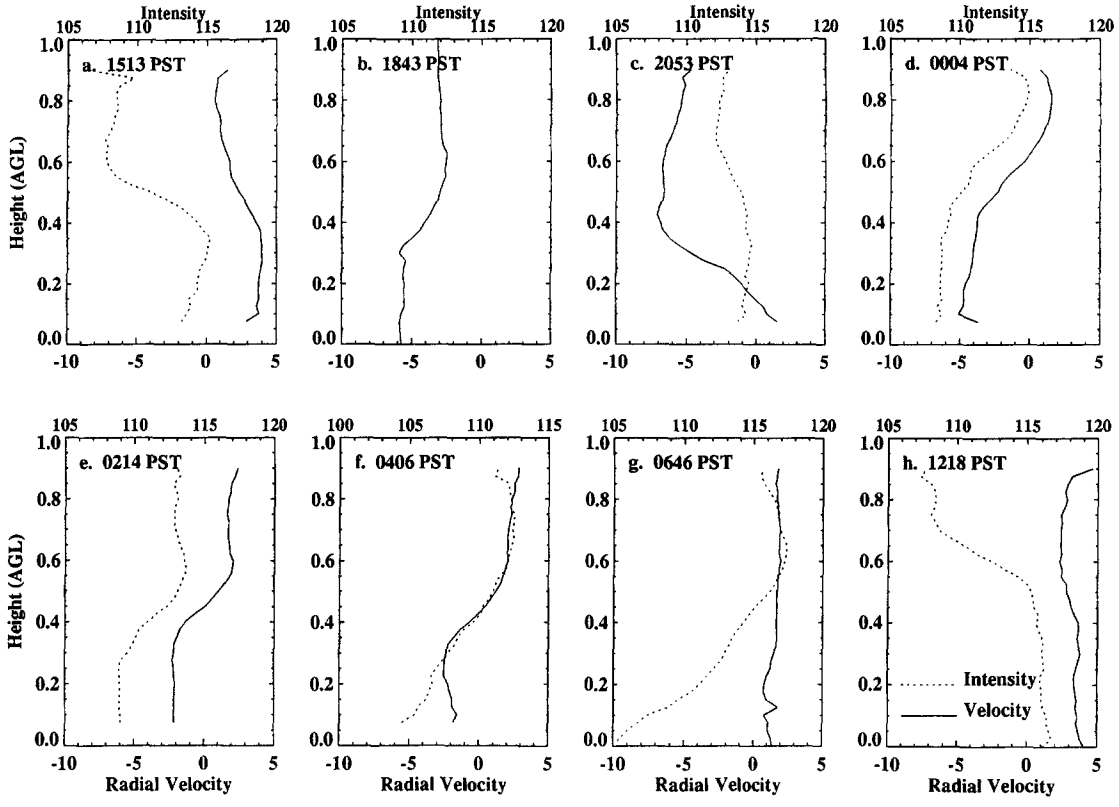

Fig. 5. Profiles of radial velocity (solid lines) and backscattered signal intensity (dashed lines) averaged over 1 km. Averages were derived from the vertical cross sections shown in Fig. 4 for 4/5 August 1993. The lower x-axis gives the radial velocity scale (m s^{-1}), and the upper x-axis, intensity (arbitrary dB units).

urban-polluted air. The thunderstorm outflow air, which originated in the unpolluted midtroposphere, also showed high values of aerosol backscatter from wind-lofted surface dust. Thus, one must use caution in using aerosol backscatter as an indicator of high-ozone air.

These results were based on analysis of data from one night (4/5 August 1993), selected because continuous lidar observations were available all night. More limited sets of nighttime observations were also available for the two previous nights of 2/3 and 3/4 August. These indicate outflow behavior very similar to that in the present case study: low values of aerosol backscatter in the low-level outflow, and higher backscatter in the air above.

3.2. *Effects on flow in the LFV*

Downvalley flow exiting Pitt Lake brought air that was low in aerosol (as shown in Section 3.3.1), O_3, and NO into the LFV. An important issue is how far this air is transported into the LFV, because this affects the sunrise distribution and concentrations of pollutants leftover from the previous day of the episode. Doppler lidar scans at low elevation angles, sweeping through a full 360° in azimuth, provide insight into behavior of the flow from Pitt Lake and other valleys as well as the main flow along the axis of the Fraser River valley. Figure 8 shows a sequence of these scans for the night of 4/5 August.

Afternoon flow during the episode period was typically into Pitt Lake valley, as exemplified by Fig. 8f, for 1338 PST on 5 August. This day is shown because the thunderstorm on the afternoon of 4 August made the flow behavior somewhat atypical for part of the late-afternoon period.

During the early part of the night, before ~0130 PST, the scans exhibit two streams of flow with a component toward the lidar, one north–northeast (NNE) and another east of the lidar (Figs 8a and b). The jet from the NNE (i.e. from the direction of Pitt valley) was strong and persistent during this period at 7–8 m s^{-1}, varying in width and height. The flow from the east, representing the downvalley/land breeze along the axis of the LFV, varied in strength from 0 to 4 m s^{-1}.

The lidar scan at 0149 PST (Fig. 8c) shows a very complex flow pattern. Flow with a component toward the lidar appeared in three directions: the north–northwest (NNW) from the direction of the Coquitlam Lake valley, the east–northeast (ENE) from the direction of the Alouette Lake valley, and the southeast, representing the flow along the Fraser River. Flow from Pitt Lake seemed to be emerging aloft at this time. The flows from the north all appear

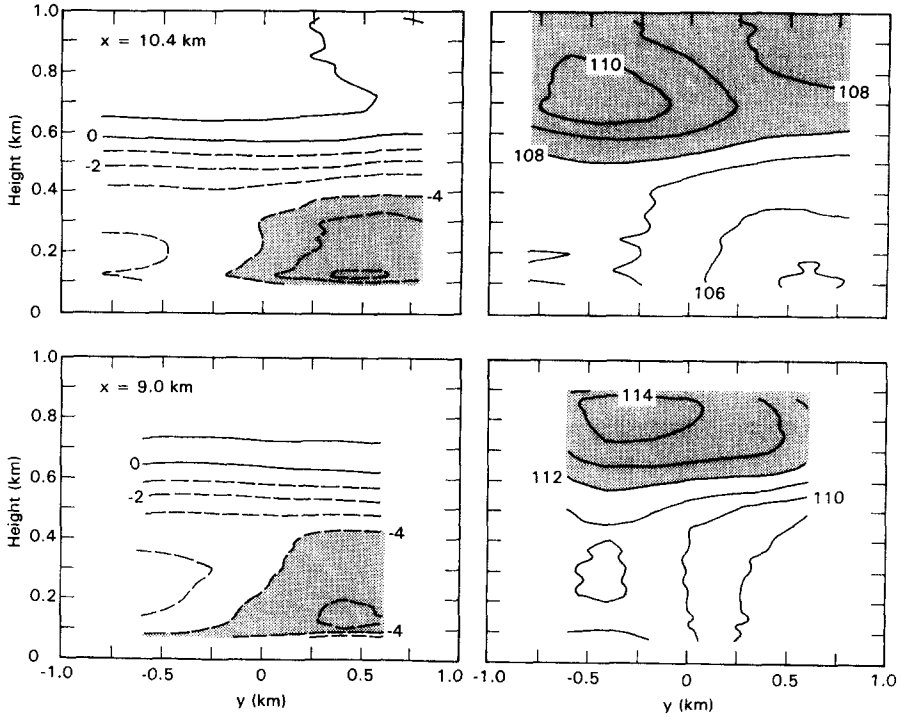

Fig. 6. Cross-flow vertical cross sections from the 0004 PST high-resolution lidar volume scans on 4/5 August 1993, shown schematically in Fig. 2 as line AB. The top two plots show contours of u_r (left, m s^{-1}) and backscattered signal intensity (right, dB) 10.4 km from the lidar. The bottom two plots show similar contours from the same volume, but at a distance of 9 km from the lidar. Radial velocities > 4 m s^{-1} and areas of highest backscatter are shaded.

to have been converging into the flow down the Fraser River valley in the vicinity of the lidar, whence they depart as a single flow to the west. This confluence pattern lasted less than 1 h, because it had not formed on the 0118 PST lidar scan and was gone by the 0232 PST scan (Fig. 8d). The rapidly changing nature of these flows is similar to the highly transient features found in nighttime outflow-jet flows in Colorado by Banta *et al.* (1995, 1996).

For the next 2 h after 0232 PST, lidar scans show a steady pattern, with a flow component of ~ 5 m s^{-1} toward the lidar from the NNE, flow away from the lidar of 6 m s^{-1} to the WSW, and light, seemingly unorganized flow elsewhere (Fig. 8e). This pattern suggests that the jet from Pitt Lake valley passed to the northwest of the lidar site, joined with the flow down the LFV, and proceeded westward down the Fraser valley. As dawn approached, a scan at 0533 PST (not shown) indicates light flow in all directions. After sunrise, upvalley flow began, and Fig. 8f shows the flow into Pitt Lake valley in early afternoon. Lidar scans on the other afternoons of the O_3 episode indicate flow patterns very similar to this panel, as one would infer from the afternoon winds just outside the mouth of the valley in Fig. 3.

3.3. *Chemistry measurements*

Measurements of a wide variety of chemical species were taken at the Harris Road surface site just outside the mouth of the Pitt Lake valley. During daytime when turbulent mixing is strong, measurements at one location are often representative of a larger area. At night, however, mixing is suppressed, and flows often occur in layers or in structures such as the jet described in Section 3.2. This is especially true in complex terrain. Such flow structures often alternate in advecting air with different origins and different histories past the sensors. For example, Fig. 6 shows that the fastest moving core of the jet from Pitt Lake valley contains the cleanest air. Therefore, as this jet meanders back and forth over the measurement site, fluctuations in O_3 concentration with time should appear in the time series. Such fluctuations thus do not necessarily represent changes in how the chemistry is proceeding, but more likely represent unmixed flows with different histories.

Meteorologically, the shaded regions in the surface wind data of Fig. 3 divide the afternoon and night into three periods that may be characterized as follows: (1) an afternoon well mixed period, (2) an early-evening period of northerly outflow, in which meteorology and chemistry variables showed strong fluctuations, and (3) a nighttime period of light-and-variable winds at the surface. Light winds during this final period imply that meteorological and chemistry effects near the surface were confined to the local area, minimizing longer-range advection effects.

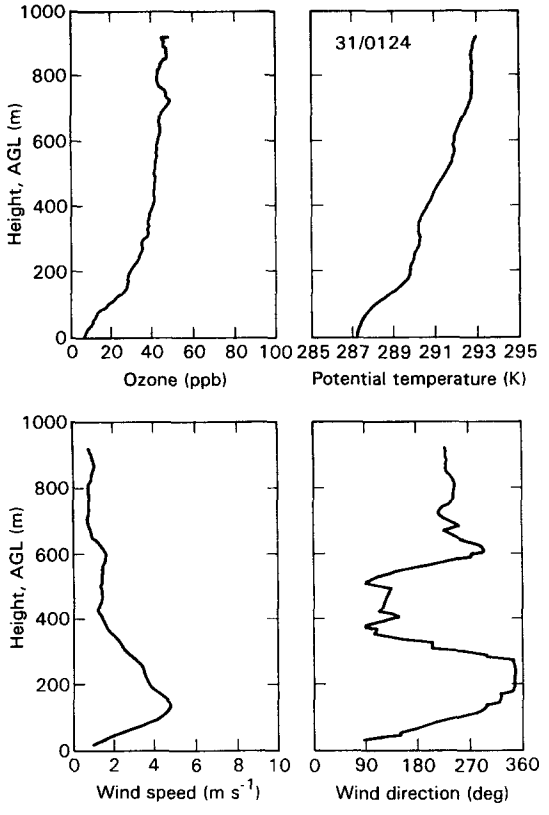

Fig. 7. Profiles of ozone, potential temperature, wind speed, and wind direction from a tethersonde launched from a site on Little Goose Island, in Pitt Lake at 0124 PST, on 31 August 1994.

3.3.1. *Ozone decay.* Surface O_3 measurements at the Harris Road site typically show concentrations decreasing from late afternoon until after midnight. On at least three of the four nights a significant portion of this decrease tended to occur around the 1800–2200 PST period (Fig. 9). We consider three major processes that lead to concentration reductions, namely, deposition, chemical reaction, and dilution.

Deposition can consist of moist or dry removal processes. Moist removal was probably not a factor in the present cases, because low-level clouds and fog were absent, and a water surface such as Pitt Lake is very inefficient in removing O_3 (Galbally and Roy, 1980). Dry deposition occurs mainly at the Earth surface, and an important removal mechanism occurs when a chemically reactive species, such as O_3, comes in contact with vegetation and soil. This process occurring along valley sidewalls has been observed elsewhere (Broder and Gygax, 1985) and must be a candidate in the present case as a mechanism responsible for low O_3 concentrations in the valley exit jet. Because of the similarity in distribution between aerosols and O_3, the same arguments apply to aerosols. Furthermore, this mechanism may be responsible for the rapid evening losses of several other hydrocarbons and PAN, as described in the next section, assuming that they all have relatively similar deposition velocities.

Titration with NO is an important chemical reaction affecting atmospheric O_3 during photochemical pollution episodes:

$$O_3 + NO \rightarrow NO_2 + O_2 . \quad (1)$$

For instance, when photochemistry stops as the sun sets behind mountain ridges, O_3 and NO rapidly react on a time scale of a few minutes, and the species with the lower concentration, often NO, is totally consumed. Titration can also be seen in local combustion source activity, in which freshly produced NO produces a rapid decrease in $[O_3]$. (When such activity is suspected, an increase in CO concentration is further evidence for the presence of local combustion sources.) Other possible chemical removal processes are described in the next section.

A conservative tracer of oxidant is the sum of the concentrations of O_3 and NO_2. Defined as O_x (Volz *et al.*, 1988), it is conserved during titration, because each molecule of O_3 converts to one molecule of NO_2. Hence, it can be used to assess whether O_3 is decreasing due to processes other than titration by NO. A plot of O_x during the first four days of August is shown in Fig. 10.

To assess the effects of dilution, one must consider the behavior of a species, such as CO, that is relatively chemically inert in the atmosphere. The concentration of CO is plotted in Fig. 10 for the 1–5 August period; it will be used later in this section to assess dilution and source effects.

A useful measure related to air-mass age and origin is the ratio NO_x/NO_y where NO_x represents the sum $NO + NO_2$ and NO_y is the sum of all odd-nitrogen species (including e.g. PAN and HNO_3). When this ratio is high (> 0.9), much of the NO_y is reactive nitrogen oxides, indicating an unaged air mass and often high concentrations of fresh pollution with a high potential for reductions in O_3 by chemical reaction. Lower values ($\lesssim 0.6$) indicate aged air in which most reactive nitrogen oxides have been transformed to stable end products, with no recent input of NO_x (Olszyna *et al.*, 1994). Plots of NO and NO_x/NO_y are shown in Fig. 9.

The shading in Figs 9 and 10 divides the afternoon into the three meteorological periods, as in Fig. 3. During period 1, the afternoon well-mixed period, O_3 and NO coexisted as a result of photolysis of NO_2, late-afternoon increases in NO and NO_2 from afternoon traffic, and the beginning of the reductions in O_3 and NO by titration. Also during this period polluted air was mixed to the top of the boundary layer (~ 600 m AGL), and some dilution occurred as indicated by the decrease in CO. Decreases in O_3 were therefore largely due to recent titration and dilution.

During period 2, when the northerly outflow jet reached the surface, many processes were occurring.

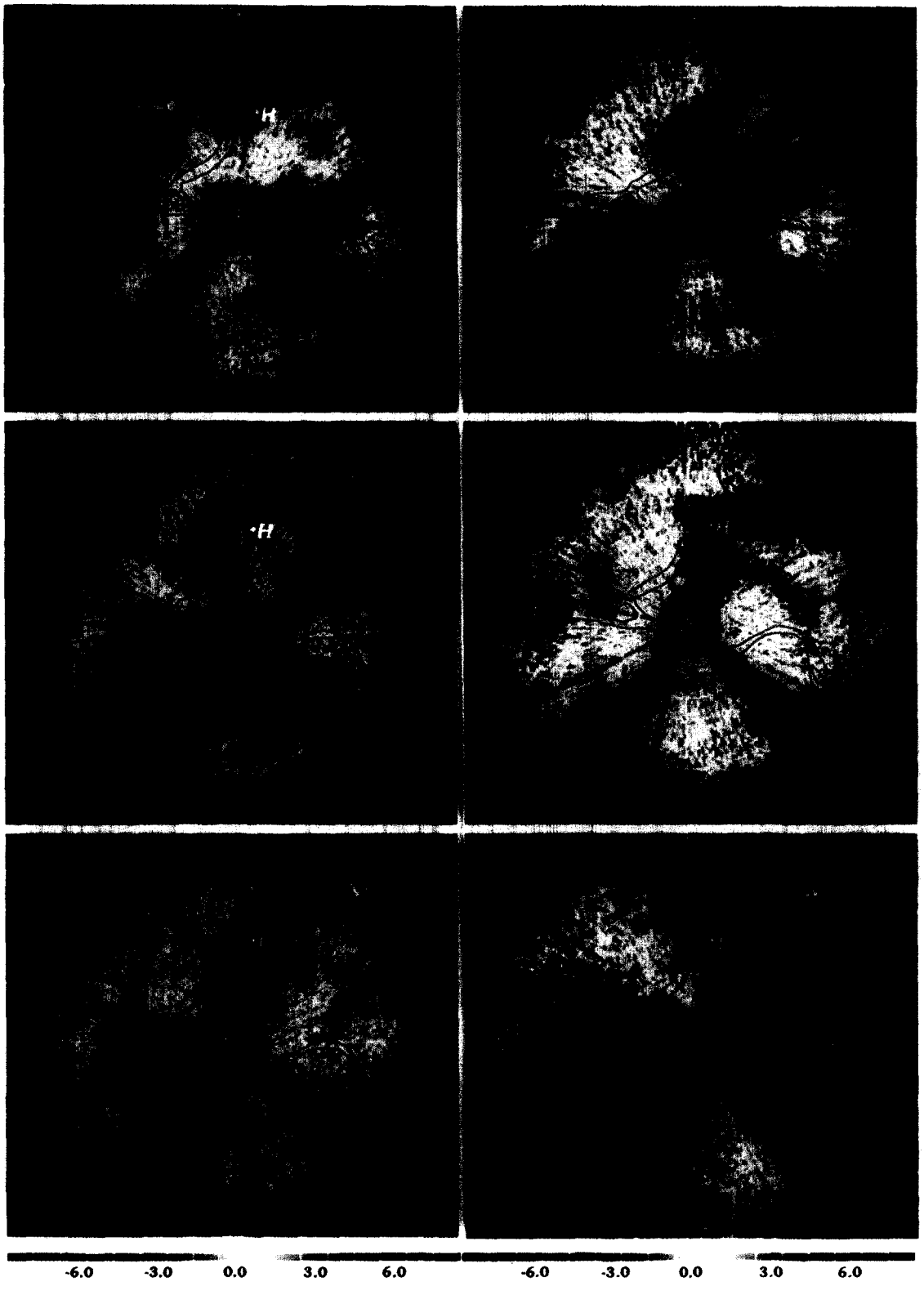

Fig. 8. Nearly horizontal plots of lidar-derived radial velocity from low-elevation scans in azimuth ("PPI" scans), with north at the top, for 4/5 August 1993. The lidar L is at the center of each plot and range rings are 5 km apart. The Harris Road site is indicated by H, and mountain ridges referred to in Fig. 1, by M and N. Negative velocities (greens, blues, and purples) indicate flow toward the lidar, and positive velocities (reds and yellows), flow away from lidar. The Fraser and Pitt Rivers are outlined in blue.

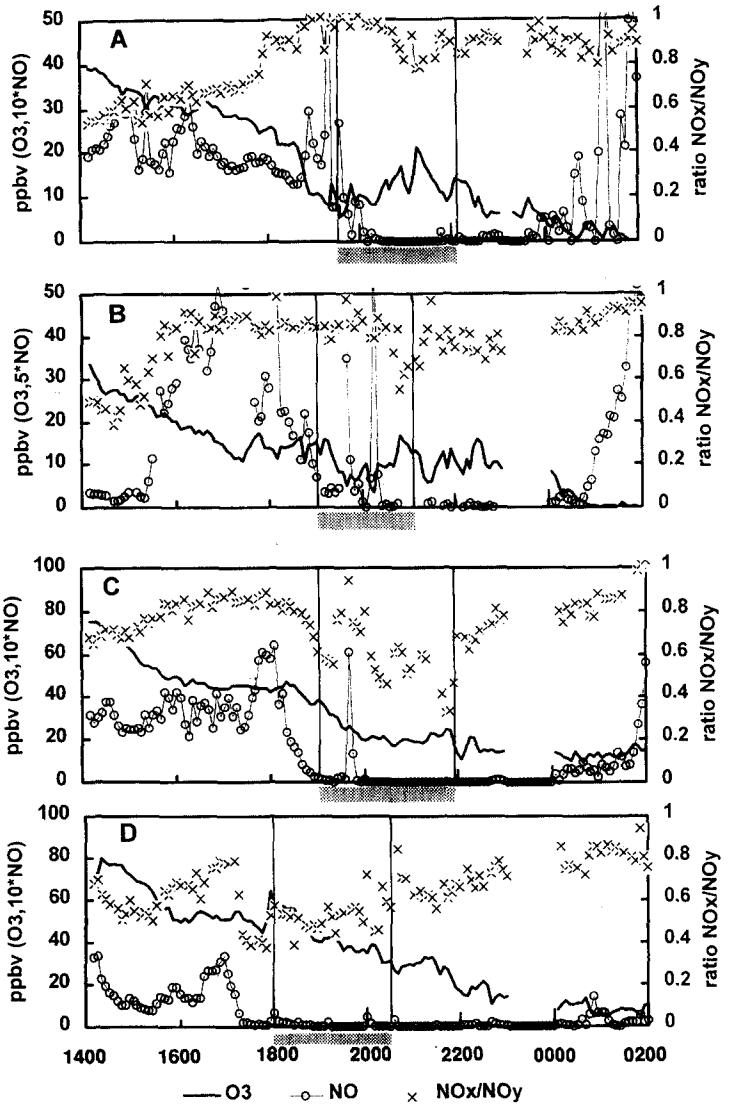

Fig. 9. *Left axis*: Mixing ratios of O_3 (solid line) and NO (circles, multiplied by 10) at the Harris Road site, for the same times (PST) as Fig. 3. *Right axis*: NO_x/NO_y ratio (x). The shaded bar denotes the period of northerly outflow from Pitt Lake valley, referred to as period 2 in the text. (a) 1/2 August, (b) 2/3 August, (c) 3/4 August, and (d) 4/5 August 1993.

Dilution, however, should be suppressed in the stable nighttime flow, making it difficult to transport clean air from above the level of the daytime mixed layer at 600 m all the way down to the surface. Although strong ambient flow over complex topography could produce such vertical transport, the ambient flow during the episode was light, and terrain-induced vertical transport was probably not significant. Inspection of Fig. 10 shows a CO burst at ~2000 PST on the first three evenings. Except for this notable feature, CO tended to level off during the period of the outflow jet on at least three of the nights, affirming that dilution was a minor effect.

On 1/2 August the CO burst contained fresh pollution, with NO_x/NO_y ratios near 1.0. Reductions in O_3 during this period can thus be attributed to titration by NO, but the accompanying decline in O_x signifies that another process, dry deposition, was also active. On 4/5 August, a night with much stronger outflow winds than the others, no significant CO burst occurred. Low values of NO_x/NO_y indicate that the outflow contained photochemically aged air, implying that O_3 concentrations were not being reduced significantly by reaction with NO. O_3 and O_x declined together during period 2, again typical of dry deposition. Summarizing, the O_x behavior suggests that dry deposition was responsible for O_3 losses in the outflow on both nights, whereas NO_x/NO_y behavior shows that reaction with NO was an additional significant O_3 sink on 1/2 August but was negligible on 4/5 August.

Some of these effects can be seen on the other two nights, but the situation was obviously more

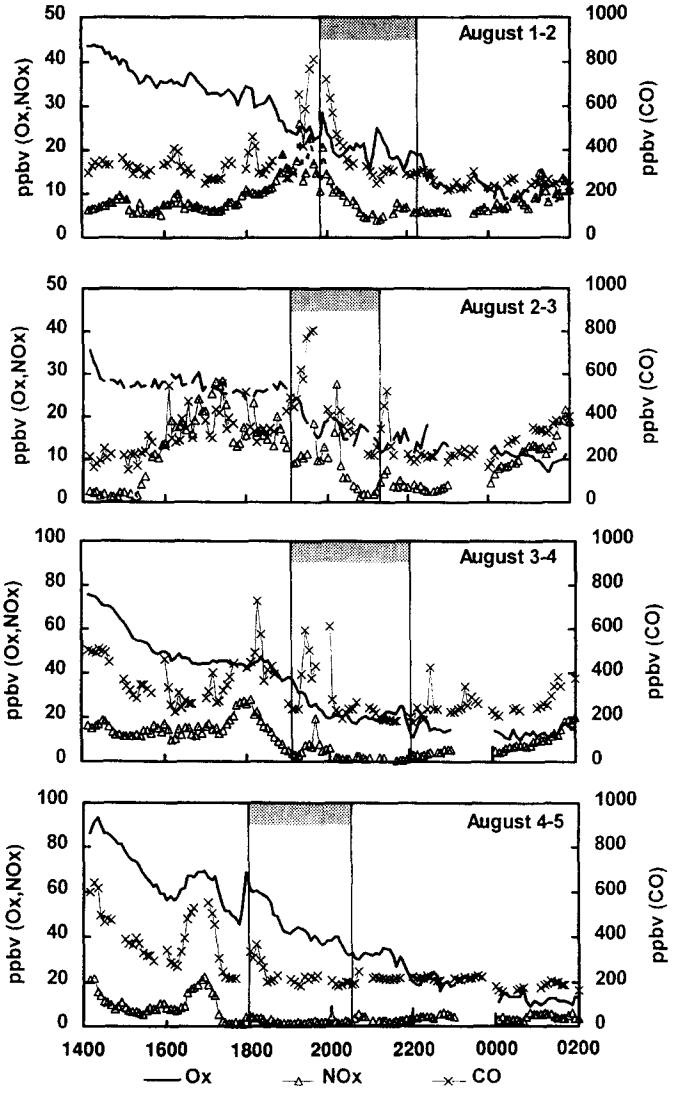

Fig. 10. Mixing-ratio measurements from the Harris Road site for O_x (solid), NO_x (triangles), and CO(x) for the same time periods (PST) as in Figs 3 and 9. The shaded bar denotes the period of northerly outflow in Fig. 3.

complicated. For example, on 3/4 August, O_3 and O_x concentrations stopped declining during the outflow after 1945 PST. A minor peak in O_3 at 2145 PST was accompanied by significantly lower NO_x/NO_y, suggesting that the O_3–O_x behavior probably resulted more from outflow meander than chemistry, and this conclusion was probably valid for most of the outflow-chemistry behavior on these two nights.

Period 3 was when the strong, low-level, nocturnal inversion decoupled the air at the surface from the outflow jet above and trapped any fresh emissions, and therefore concentrations of primary pollutants measured at the surface could rise dramatically. Evidence of local combustion source activity could be seen on some nights as increases in concentrations of CO and NO after 0100 PST. In the presence of nighttime source activity during period 3, dilution could have been important between air with very high pollutant concentrations (which would have built up by being trapped beneath the nocturnal inversion layer) and the less polluted air just above the shallow (probably < 100 m) inversion. This vertical mixing most likely would occur as a result of intermittent turbulence in this layer, as hypothesized by Banta *et al.* (1995).

3.3.2. *Isoprene decay.* Biesenthal *et al.* (1997) calculated that isoprene chemistry produces a significant fraction ($\sim 13\%$) of ozone in the LFV during daylight hours, in the process forming relatively longer-lived oxidation products, such as methyl vinyl ketone (MVK) and methacrolein (MACR). Isoprene, however, is not emitted at night, and its oxidation rate at night in the absence of NO_3 chemistry (see later in this section) is probably slower than during the day. Thus, it is of interest to investigate the nocturnal behavior of

isoprene and its major products, in part to assess the extent to which they remain in the LFV as a result of the valley outflow events.

The diurnal behavior of measured concentrations for O_3, isoprene, MVK, MACR, and acetone are shown in Fig. 11 for the period 3–5 August at the Harris Road site. Acetone is a complex species in that it is emitted by vegetation (MacDonald and Fall, 1993) and by motor vehicles and industrial processes (Singh *et al.*, 1994), and it is produced from atmospheric oxidation of a variety of hydrocarbons [e.g. propane (Atkinson, 1990)]. It is potentially useful for examining dilution effects, however, because it is a relatively long-lived species. Figure 11 shows that all the listed species exhibit rapid nighttime decays beginning at ~1800 PST.

If the declines in concentration were produced by a simple first-order process such as dilution or dry deposition, then a plot of $\ln([X]_t/[X]_0)$ vs time, where $[X]_t$ is the concentration of a chemical species at time t, should be linear with a slope equal to the decay-rate coefficient. In Fig. 12 we use data for 1800–2400 PST on 4 August to plot the logarithmic transform of the concentrations of O_3, acetone, isoprene, MVK, butanal (which is emitted directly by motor vehicles and is a product of the atmospheric oxidation of hydrocarbons such as *n*-butane), and PAN (chosen because it has no direct emission sources) vs time.

As seen in Fig. 12 the only species that exhibited simple exponential decay was O_3. A linear regression for O_3 yields $r^2 = 0.98$ with a slope or first-order decay coefficient $k_{dec} = 6.0\ d^{-1}$, corresponding to a relatively rapid decay rate of 25% h^{-1}. A similar analysis of O_3 decay for the evening of 5 August yields $k_{dec} = 6.3\ d^{-1}$ ($r^2 = 0.94$). As discussed previously, reaction with NO is unlikely to have contributed to this rapid evening O_3 decay, because NO concentrations were negligible in the aged air mass on this night. Previously (Section 3.3.1), we concluded that O_3 losses were most likely due to dry deposition, and next, in Section 3.4 we further conclude that this loss occurred along the Pitt Lake valley sidewalls.

Acetone, MVK, butanal, and PAN all exhibited exponential decay as well, but the actual decay rate leveled off by ~2100 PST. During the outflow event (1800–2100 PST) the decay in the concentration of acetone occurred at the same rate as O_3, whereas MVK, butanal, and PAN appear to have decayed faster than O_3. Shepson *et al.* (1992) found that, on average, the PAN deposition velocity is larger than that for O_3 at night. Thus, our observed relative decays of these two compounds are consistent with loss by dry deposition. Acetone, MVK, and butanal all have surface sources (automotive, other combustion, and vegetative). Their observed decay relative to O_3 is also consistent with loss by dry deposition. Hence, during period 2, we conclude that the observed reductions in concentrations of these measured species resulted from dry deposition along the Pitt Lake valley sidewalls.

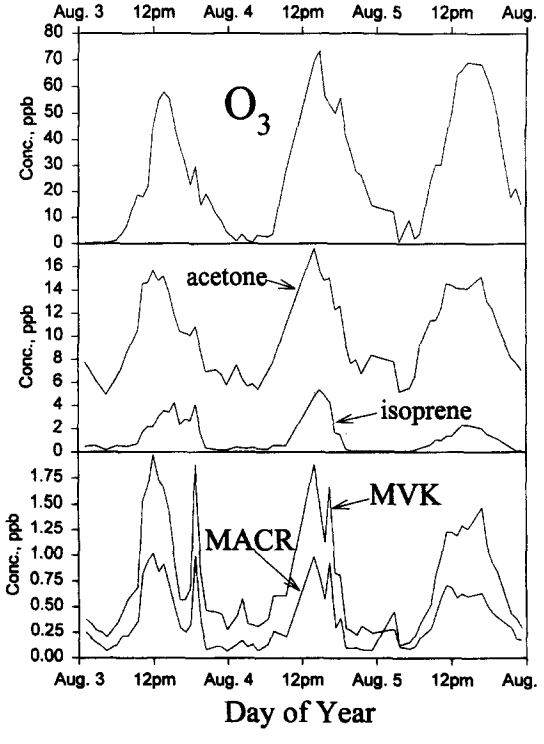

Fig. 11. Concentration time plots for O_3, acetone, isoprene, MACR, and MVK from the Harris Road site for 3–5 August 1993.

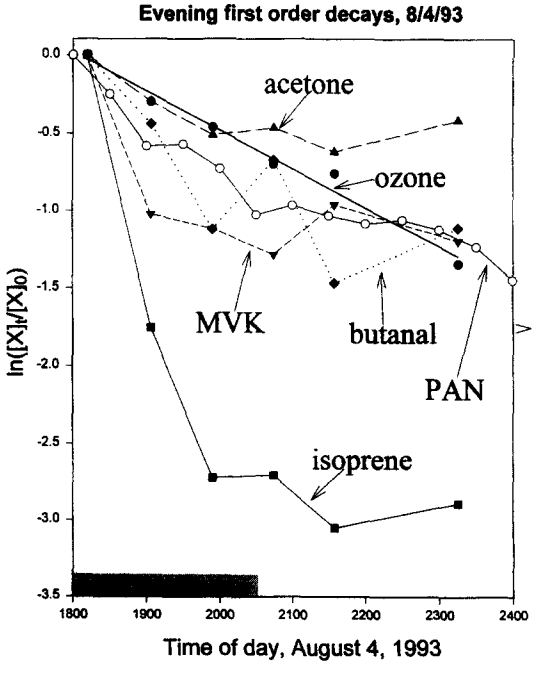

Fig. 12. First-order decays over 5 h for acetone, O_3, PAN, MVK, butanal, and isoprene on 4 August 1993. Shading denotes the period of northerly outflow (period 2).

By period 3 the strong outflow winds became light and variable. Concentrations of combustion-derived species, such as CO and NO_x, tended to increase in period 3 near the surface, as local emissions were trapped within the nocturnal inversion layer, which was stronger and shallower than in period 2. Similarly, we expect an increase in the concentrations of acetone, MVK, and butanal, because these compounds are also directly emitted into the atmosphere by combustion processes. Biesenthal *et al.* (1997) and Li *et al.* (1997) argued that significant surface-source activity for acetone resulted in substantial equilibrium concentrations in period 3. Counteracting the tendency for stabilized or increased pollutant concentrations in period 3 are (1) local dry deposition in the light-and-variable drainage flows and (2) dilution of the surface species by the relatively cleaner, "scrubbed" air in the outflow jet just above the surface inversion layer. The tendency of the concentrations of acetone, MVK, and butanal to level off after 2030 PST is thus interpreted as being due to equilibrium among these processes.

PAN, on the other hand, is a species that has no direct surface source. Thus, its rapid decay from 1800 to 2030 PST (period 2) was followed by slow decay throughout the rest of the night, most likely resulting from local dry deposition. Note that for the large NO_2/NO ratios in effect at night, thermal decomposition would be an unimportant loss process for PAN.

As for isoprene, the data shown in Figs 11 and 12 indicate that it decayed much *faster* than the other species through the evening. This was consistently the case for all nights of the episode week of 1–6 August. There is currently no evidence that dry deposition occurs for isoprene, and we explore whether fast chemical removal could have been a major factor in the decay of isoprene. After sunset the OH radical concentration should be negligible ($< 1 \times 10^5$ molecules cm^{-3}), leading to an isoprene e-folding lifetime with respect to OH reaction of >28 h at night. Although isoprene also reacts with O_3, its lifetime with respect to O_3 reaction is ~ 25 h (for an O_3 concentration of 40 ppb); thus, the isoprene–O_3 reaction is a negligible sink for *both* species. Of the known isoprene reactions, the only other possibility is reaction with NO_3. Isoprene reacts rapidly with NO_3 (rate constant $k = 6.7 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}), where NO_3 is produced according to

$$O_3 + NO_2 \rightarrow NO_3 + O_2. \qquad (2)$$

NO_3 is not present during the daytime because of its fast photolysis ($J_{NO_3} = 0.2\ s^{-1}$ at noon) and its rapid reaction with NO. However, small concentrations of NO_3 could be present in the evening if NO concentrations are very low. For the evening of 4 August the initial slope of the isoprene decay corresponds to a loss rate of $\sim 0.025\ min^{-1}$. This decay rate could be caused by NO_3 reaction, if NO_3 were present at 25 ppt at ~ 1900 PST. To see whether such a mixing ratio might have been present, we conducted a simple computer model simulation for the conditions of 1800 PST on 4 August (i.e. 40 ppb O_3, 3 ppb NO_2). The maximum NO_3 that can be produced under these conditions (i.e. assuming NO_3 reacts only with isoprene and via $NO_3 + NO_2 \rightleftharpoons N_2O_5$, and ignoring reaction with NO) is ≈ 3.5 ppt. This leads to a maximum removal rate via NO_3 reaction for isoprene of $0.0035\ min^{-1}$ (i.e. 14% of the observed loss). Given that the loss via direct O_3 reaction can account for only $0.0007\ min^{-1}$ of the observed decay rate, known chemistry does not explain the magnitude of the observed isoprene decline.

In sorting out possible causes for the apparently high isoprene losses, we again need to consider the strong spatial heterogeneity of the region and the complexity of the flows. Two factors that may contribute are as follows: First, the outflow air from Pitt Lake valley was a different air mass from the afternoon LFV air mass that it replaced. As shown in Fig. 9, the outflow air for this night was more photochemically aged ($NO_x/NO_y \sim 0.5$) than that in the LFV; in other words, the air mass that traveled up the Pitt Lake Valley was more extensively processed by OH radicals. Thus, isoprene, which is much more reactive to OH than the other species shown in Fig. 12, may simply have been present at a lower concentration in the outflow air, as the outflow event began. A second factor is that we know little about the spatial heterogeneity of isoprene sources in this area, and perhaps there were fewer isoprene emitters in the Pitt Lake area.

We conclude that in the evening, reaction with isoprene was a negligible sink for O_3, and reaction with NO_3 drove only a part of the observed rapid decline in isoprene. It is unclear what is responsible for the fast decay of isoprene during the outflow events. O_3 in the LFV declined at a rate of $\sim 25\%\ h^{-1}$, and several other substances, such as PAN, acetone, and aerosols declined at comparable rates during outflow events. It is important that these effects be incorporated into any multiday simulation of oxidant formation in the LFV.

3.4. *Flow mechanisms*

Two types of nocturnal system that produce flow out of a valley are downvalley flow and downslope (katabatic) flows, as explained in the following paragraphs. The first nocturnal flow type is a simple reversal to downvalley flow as air in the entire Pitt Lake valley cools. During early stages clean air displaces polluted air in the far end of the valley, and polluted air moves out of the valley at the near end and into the LFV. Air cools fastest and thus moves fastest in the lower levels of the valley. The clean air thus travels fastest at low levels, undercuts polluted air, and emerges from the near end of the valley beneath polluted air in layers aloft that are moving out of the valley more slowly (or not at all). However, such along-valley flows take a few hours to establish themselves (Defant, 1949, 1951; Whiteman, 1990).

The second type of flow that could bring cleansed air into the valley bottom is katabatic flow down the valley sidewalls. As slope flows slip down the wooded sidewalls of the valley, vegetation and soils scavenge ozone and other pollutants. These flows converge in the bottom of the valley, forming a deeper layer of cleansed air, which then flows out of the valley. Downslope flows form earlier in the evening than down-valley flows (Defant, 1949, 1951; Whiteman, 1990), and in fact such katabatic flows form on shaded slopes in late afternoon, i.e. while it is still daylight (Urfer-Henneberger, 1970; Hennemuth and Schmidt, 1985). The significance of this process, as pointed out by Broder and Gygax (1985), is that the downslope flows continue to bring O_3-rich air down to the surface. They show that dry deposition can continue at near-daytime levels in the presence of downslope flows over complex terrain, whereas normally, over flat terrain, deposition becomes negligible at the surface under very stable nighttime conditions, owing to the inhibition of vertical transport.

We noted in Section 3.3 that surface instrumentation beyond the mouth of Pitt Lake valley measured relatively clean air in the evening soon after the flow reversed. From this rapid appearance of cleaner air, we conclude that the second flow type, katabatic flow down the valley sidewalls, was the source of the air coming out of the valley, because downslope flows form earlier in the evening than downvalley flows.

4. CONCLUSIONS

Air chemistry measurements taken just outside the Pitt Lake valley near Vancouver, BC, during a photochemical pollution episode in August 1993 showed that, whereas daytime upvalley flow carried polluted air into tributary valleys of the LFV, downvalley air pouring out of these valleys at night was cleansed of O_3, aerosols, and a variety of volatile organic compounds. This nocturnal outflow was in the form of a valley exit jet that appeared at the surface rather suddenly at $\sim$1900 PST on most episode nights, then yielded to a light-and-variable surface wind regime at $\sim$2200 PST. However, wind profiles outside the mouth of the valley from ETL's Doppler lidar showed that the jet persisted aloft nearly all night. This structure is very similar to the structure of a canyon outflow jet observed by lidar in Colorado.

The two most likely mechanisms for reducing ozone concentrations at the lower levels of the outflow jet are titration of O_3, as air flows out of the valley and over NO-producing emission sources outside the valley, and dry deposition.

Data from other Pacific 93 studies show a correlation between aerosol backscatter measured by lidar and O_3 concentration, in which regions of high backscatter and regions of high $[O_3]$ occur together in polluted air. In this study the Doppler lidar indicated air having low aerosol concentrations near the surface flowing out of the valley and air having higher aerosol concentrations above. Data from the one ozonesonde in the middle of the night (from another high-pollution episode in 1994) also showed low O_3 near the surface and higher O_3 aloft. These two observations taken together strongly suggest that a significant amount of O_3 and aerosol were removed at the surface in the valley, where few if any emission sources exist at night. The presence of several pollutant species (e.g. CO, NO_x) and the fact that the pollution at times showed signs of being aged suggests that the air was previously polluted air that had flowed into the valley during daytime, and the lack of sources in the valley implies that the mechanism for O_3 reduction for air coming out of the valley was dry deposition. The dry deposition had to be occurring along the valley sidewalls, because the floor of the valley is a water surface. Pollutants in this air could be further subjected to removal by deposition or titration outside the valley.

Careful analysis of the Harris Road chemistry measurements just outside the mouth of the Pitt Lake valley showed that on one of the episode nights (4/5 August) dry deposition along valley sidewalls was the dominant removal mechanism, in agreement with a study in a Swiss valley (Broder and Gygax, 1985). On another night (1/2 August), however, fresh emissions were present, and titration with NO and dry deposition were both significant sinks for O_3. Other nights illustrate that processes responsible for the decline of concentrations of the pertinent pollutants at night result from complex chemical interactions intertwined with complex meteorological flows. Although precise chemistry measurements of many significant species and sophisticated meteorological measurements were available for this analysis, coverage was far from complete. Thus, explanations of how chemistry and meteorology interact to produce observed behavior cannot always be complete, and occasionally may not even seem consistent. In this light it is perhaps fortunate that two cases could be found in which the interpretation was relatively straightforward.

Removal of isoprene occurred more rapidly than removal of O_3 and other pollutants, most likely through chemical reactions involving the highly reactive NO_3 radical. Less-reactive species such as NO_2 and CO, which are not subject to adsorptive loss, tended to remain constant except for occasional bursts from local sources near the Harris Road site.

These conclusions are possible because of the availability of a comprehensive set of high-quality chemistry measurements, many at fine temporal resolution. Unique to this study was the combination of these chemistry measurements with the high spatial- and temporal-resolution meteorological measurements of the Doppler lidar. Lidar scans showed unequivocally that the northerly flows in the surface observations (Fig. 3) were outflows from Pitt Lake valley, that the

clean-air outflow was confined to the lower levels of the valley, and that the flow and aerosol distribution were not uniform across the outflow.

Doppler lidar scans also revealed that the cleansed outflow jet, which was often 5–6 $m\,s^{-1}$ and occasionally reached 8 $m\,s^{-1}$, was present much of the night but would periodically show significant changes in structure or even disappear over intervals of less than 1 h. Lidar scans showed that these valley exit flows of cleansed air did penetrate deeply into the LFV, merging with the land-breeze/downvalley flow systems there. Thus, the flows apparently did have a role in mitigating high O_3 concentrations during an episode.

The valley outflow jet and thin surface inversion layer with light-and-variable flow beneath it resemble similar structures found in Colorado (Banta *et al.*, 1995, 1996). The significant changes in the structure of the outflow from Pitt Lake valley occurring over time periods of $\sim$ 30 min also agreed with findings in the Colorado study. The Colorado results were from a dry climate in winter, whereas the present study was from a moist climate in summer. The similarities thus suggest that the meteorological findings apply more generally than just to the two locations where they were studied.

Relatively high NO_2 concentrations in the out-flow would seem to favor higher production of O_3 the next day. What remained, however, was small compared with the next morning's NO_x injection. The net result of these low-level cleansing processes in the valley was often that an elevated layer of high O_3 and aerosol, similar to that described by McElroy and Smith (1993) was left behind. As they point out, such layers often fumigate as a result of surface heating the next day, causing ground-level concentrations to rise.

Although these processes at least have a role in mitigating peak O_3 concentrations during an episode, it has not been established exactly how effective they can be. It is worthwhile to note that these processes are not totally beneficial; the cleansing occurs at the expense of the sidewall vegetation, on which multiple doses of pollutants are deposited (Broder and Gygax, 1985; Zaveri *et al.*, 1995). To sort out quantitatively which of these competing processes would dominate under various conditions, it will most likely be necessary to conduct more focused field experiments and to employ sophisticated, combined mesoscale and air-chemistry numerical modeling.

Acknowledgements—The field portion of this research was sponsored by the Atmospheric Environment Service of Canada under Contract Number KM464-2-8992. We express appreciation to our colleague Ray Hoff for his advocacy for involving the lidar in Pacific 93, and for helpful insights and technical discussions on the significance of these findings. We also thank members of the lidar crews who obtained these data, including Janet Intrieri, Mike Hardesty, M. J. Post, and Ron Willis. This paper is contribution number 96-12 of the Canadian Institute for Research in Atmospheric Chemistry.

REFERENCES

Atkinson, R. (1990) Gas-phase chemistry of organic compounds: a review. *Atmospheric Environment* **24A**, 1–41.

Banta, R. M. (1995) Sea breezes shallow and deep on the California coast. *Mon. Weath. Rev.* **123**, 3614–3622.

Banta, R. M. and Olivier, L. D. (1991) Doppler lidar observations of air flow in the Grand Canyon. *Proc. 84th Annual Meeting, Air and Waste Management Association, Vol. 2, Atmospheric Monitoring and Measurement*, Paper 91-47.11. Air and Waste Management Association, Pittsburgh, Pennsylvania.

Banta, R. M., Olivier, L. D., Holloway, E. T., Kropfli, R. A., Bartram, B. W., Cupp, R. E. and Post, M. J. (1992) Smoke-column observations from two forest fires using Doppler lidar and Doppler radar. *J. appl. Met.* **31**, 1328–1349.

Banta, R. M., Olivier, L. D. and Levinson, D. H. (1993) Evolution of the Monterey Bay sea-breeze layer as observed by pulsed Doppler lidar. *J. atmos. Sci.* **50**, 3959–3982.

Banta, R. M., Olivier, L. D., Neff, W. D., Levinson, D. H. and Ruffieux, D. (1995) Influence of canyon induced flows on flow and dispersion over adjacent plains. *Theoret. appl. Climatol.* **52**, 27–42.

Banta, R. M., Olivier, L. D., Gudiksen, P. H. and Lange, R. (1996) Implications of small-scale flow features to modeling dispersion over complex terrain. *J. appl. Met.* **35**, 330–342.

Biesenthal, T., Wu, Q., Shepson, P. B., Wiebe, H. A., Anlauf, K.G. and Mackay, G.I. (1997) A study of relationships between isoprene, its oxidation products, and ozone, in the lower Fraser Valley, B.C. *Atmospheric Environment*, **31**, 2049–2058.

Broder, B. and Gygax, H. A. (1985) The influence of locally induced wind systems on the effectiveness of nocturnal dry deposition of ozone. *Atmospheric Environment* **19**, 1627–1637.

Browning, K. A. and Wexler, R. (1968) The determination of kinematic properties of a wind field using a Doppler radar. *J. appl. Met.* **7**, 105–113.

Clark, T. L., Hall, W. D. and Banta, R. M. (1994) Two- and three-dimensional simulations of the 9 January 1989 severe Boulder windstorm: Comparison with observations. *J. atmos. Sci.* **51**, 2317–2343.

Defant, F. (1949) Zur theorie der Hangwind, nebst Bemerkungen zur Theorie der Berg- und Talwinde. *Arch. Met. Geophys. Bioklim.* **A1**, 421–450. [English translation: Whiteman, C. D. and Dreiseitl, E. (1984) Alpine meteorology: Translation of classic contributions by A. Wagner, E. Ekhart and F. Defant. Pacific Northwest Laboratory, Richland WA, 121pp. (PNL-5141/ASCOT-84-3)].

Defant, F. (1951) Local winds. In *Compendium of Meteorology*, ed. T.M. Malone, pp. 655–672. Amer. Meteor. Soc., Boston, Massachusetts.

Galbally, I. E. and Roy, C. R. (1980) Destruction of ozone at the earth's surface. *Q. Jl. R. Met. Soc.* **106**, 599–620.

Hennemuth, B. and Schmidt, H. (1985) Wind phenomena in the Dischma valley during DISKUS. *Arch. Met. Geophys. Bioklim.* **B35**, 361–387.

Levinson, D. H. and Banta, R. M. (1995) Observations of a terrain-forced mesoscale vortex and canyon drainage flows along the Front Range of Colorado. *Mon. Weath. Rev.* **123**, 2029–2050.

Li, S.-M., Anlauf, K. G., Wiebe, H. A., Bottenheim, J. W., Shepson, P. B. and Biesenthal, T. (1997) Emission ratios and photochemical efficiencies of nitrogen oxides, ketones, and aldehydes in the Lower Fraser Valley during the summer Pacific 93 oxidant study. *Atmospheric Environment*, **31**, 2037–2048.

MacDonald, R. C and Fall, R. (1993) Acetone emission form conifer buds. *Phytochemistry* **34**, 991–994.

McElroy, J. L. and Smith, T. B. (1993) Creation and fate of ozone layers aloft in Southern California. *Atmospheric Environment* **27A**, 1917–1929.

McKendry, I. G., Steyn, D. G., Banta, R. M., Strapp, W., Anlauf, K. and Pottier, J. (1997) Daytime ozone concentrations over a tributary lake (submitted).

Olivier, L. D., Banta, R. M. and Hardesty, R. M. (1994) Wind flow in the Fraser River valley as measured by a pulsed CO_2 Doppler lidar. In *Preprints, 8th Joint Conf. on Applications of Air Pollution Meteorology with A&WMA*, 23–28 January, Nashville TN, pp. 329–334. Amer. Meteor. Soc., Boston, Massachusetts.

Olszyna, K. J., Bailey, E. M. and Meagher, J. F. (1994) O_3 and NO_y relationships at a rural site. *J. Geophys. Res.* **99**, 14,557–14,563.

Post, M. J. and Cupp, R. E. (1990) Optimizing a pulsed Doppler lidar. *Appl. Opt.* **29**, 4145–4158.

Pottier, J. L., Pryor, S. and Banta, R. M. (1997) Synoptic variability related to boundary layer and surface features observed during Pacific 1993. *Atmospheric Environment*, **31**, 2163–2173.

Shepson, P. B., Bottenheim, J. W., Hastie, D. R. and Venkatram, A. (1992) Determination of the relative ozone and PAN deposition velocities at night. *Geophys. Res. Lett.* **19**, 1121–1124.

Singh, H. B., O'Hara, D., Herlth, D., Sachse, W., Blake, D. R., radshaw, J. D., Kanakidou, M. and Crutzen, P. J. (1994) Acetone in the atmosphere: distribution, sources, and sinks. *J. geophys. Res.* **99**, 1805–1819.

Steyn, D. G., Bottenheim, J. W. and Thompson, R. B. (1997) Overview of tropospheric ozone in the Lower Fraser Valley, and the Pacific 93 field study. *Atmospheric Environment*, **31**, 2025–2035.

Urfer-Henneberger, C. (1970) Neurere Beobachtungen ueber die Entwicklungen des Schoenwetterwindsystems in einem V-foermigen Alpental (Dischmatal bei Davos). *Arch. Met. Geoph. Bioklim.* **B18**, 21–42.

Volz, A., Mihelcic, D., Musgen, P., Patz, H. W., Pilwat, G., Geiss, H. and Kley, D. (1988) Ozone production in the Black Forest: direct measurements of RO_2, NO_x, and other relevant parameters. In *Tropospheric Ozone*, ed. I.S.A. Isasksen, NATO ASI Series. Reidel, Dordrecht.

Whiteman, C. D. (1990) Observations of thermally developed wind systems in mountainous terrain. In *Atmospheric Processes over Complex Terrain*, ed. W. Blumen, Meteorological Monographs, Vol. 23, No. 45, pp. 5–42. Aaamer. Meteor. Soc., Boston, Massachusetts.

Zaveri, R. A., Saylor, R. D., Peters, L. K., McNider, R. and Song, A. (1995) A model investigation of summertime diurnal ozone behavior in rural mountainous locations. *Atmospheric Environment* **29**, 1043–1065.