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Secondary ozone maxima in a very stable nocturnal boundary layer: observations from the Lower Fraser Valley, BC

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Abstract

The relationship between near-surface ozone concentration and the structure of the nocturnal boundary layer was investigated during a field campaign conducted in 1998 in the Lower Fraser Valley (LFV), British Columbia Canada. Despite the spatial and temporal variation in frequency and morphology, secondary nocturnal ozone maxima were shown to be an important feature of the diurnal ozone cycle throughout the LFV, and localised increases in ozone occasionally exceeded more than half the previous day's maximum concentration.

Turbulence in the nocturnal boundary layer was shown to be weak and intermittent. Vertical profiles of Richardson number and ozone concentration indicated that the temporary turbulent coupling of the residual layer to the surface layer facilitated the transport of ozone stored aloft to the surface. Despite the overall complexity of the system, results show that seven out of the 19 ozone spikes observed at the Aldergrove site coincided with turbulence associated with the development of the down-valley wind system. A further nine spikes occurred during periods when a low-level jet was identified aloft. Significantly, ozone concentrations were shown to be highly variable in the residual layer and played an important role in determining the morphology of secondary ozone maxima at the surface. Largest increases in surface ozone concentration occurred when turbulence coincided with periods when ozone concentrations in excess of 80 ppb were observed aloft.

Keywords: Low-level jet; Residual layer; Vertical mixing; Turbulence; Mesoscale flows

1. Introduction

Near-surface concentrations of photochemical pollutants exhibit a marked diurnal periodicity during summer smog episodes, with high concentrations observed during the day and low concentrations (often near zero) at night (Kleinman et al., 1994; Garland and Derwent, 1979). The characteristics of these temporal patterns are location and pollutant specific, determined by the complex interaction between precursor emissions, chemistry, depositional processes and meteorological controls on dispersion (Reitebuch et al., 2000). Ozone (O_3), a volatile secondary photochemical pollutant, is formed in the atmosphere as a result of the photodissociation of nitrogen dioxide (NO_2) a reaction that occurs only in the presence of ultra-violet light. After sunset, concentrations in the surface layer are expected to rapidly decrease as O_3 is deposited onto surfaces or chemically depleted from the atmosphere (Zaveri et al., 1995; Broder and Gygax, 1985; Colbeck and Harrison, 1985).

Despite the dominance of removal mechanisms near the surface, significant increases in nocturnal O_3 concentrations have been observed in a range of different environments (Seibert et al., 2000; Kalthoff et al., 2000; Corsmeier et al., 1997; Coulter, 1990). Increases tend to be well defined, appear as a secondary maximum or 'spike' in the data set and are followed by a substantial decrease in concentration. They typically

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occur during the summer months when anticyclonic conditions support the development of a very stable nocturnal boundary layer (NBL). The occurrence of these localised nocturnal maxima has been shown to be highly variable in time and space (Löffler-Mang et al., 1997) and as a result these events may easily be missed within data sets averaged over several days.

Nocturnal O_3 maxima may have environmental and health consequences for local populations. Recent studies have demonstrated that increased levels of O_3 concentration at night play an important role in determining the negative response of vegetation to O_3 (Musselman and Massman, 1999). The identification of vertical mixing processes operating in the very stable NBL also has implications for pollutant concentrations in the residual layer (RL) and may affect the daily temporal autocorrelation of O_3 concentrations during a pollution episode (Zhang and Rao 2000; Lehning et al., 1998; Gusten et al., 1997; Banta et al., 1997; Neu, 1995).

Given the absence of any known sources of O_3 in the NBL, any increase in concentration is likely to result from transport processes. The presence of a marked vertical gradient in O_3 concentration, combined with the prevalence of low O_3 concentrations near the surface, suggest that vertical mixing processes which temporarily couple the surface and residual layers account for these sudden increases in concentration (Corsmeier et al., 1997).

Although turbulence in the very stable NBL is typically weak, patchy and intermittent, active shear instabilities can penetrate through the RL to the surface. Turbulence typically results from shear associated with changes in wind velocity with height (Mahrt et al., 1998). One of the first studies to attribute increased O_3 concentrations in the stable layer to turbulence was conducted by Samson (1978), who related localised increases in O_3 concentration to a nocturnal low-level jet (LLJ). More recent studies by Reitebuch et al. (2000), Corsmeier et al. (1997) and Beyrich et al. (1996) confirmed the importance of the LLJ in generating sufficient turbulence to mix O_3 from the residual layer to the surface. However, with the exception of Coulter (1990) little consideration has been given to the role of other sources of turbulence (such as reversals in the mesoscale wind regime or breaking gravity waves) in the NBL.

Turbulence alone cannot account for increased surface concentration: increased levels of O_3 must also be present within the profile. Berkowitz et al. (2000) noted that relatively large increases in surface O_3 levels are preceded by the horizontal transport of aged plumes rich in O_3 aloft. However, our current understanding of the turbulent and meteorological processes controlling pollutant dispersion in the NBL has been limited by a focus on surface based measurements (Hastie et al., 1993). Thus despite a recognition of the importance of pollutant levels in the residual layer on near-surface air quality (Zhang and Rao, 2000; Bigler-Engler and Brown, 2000; Banta et al., 1998; Berkowitz and Shaw, 1997; Gusten et al., 1997), concentrations in the residual layer are typically treated as invariant in time and space (Neu et al., 1994).

Clearly the processes operating in the nocturnal boundary layer which determine the three-dimensional distribution of pollutants, surface based pollutant sinks and pollutant storage aloft may have a significant impact on near-surface concentrations at a diurnal scale. In this paper data collected during a field study conducted at Aldergrove in the Lower Fraser Valley (LFV) of British Columbia during the summer of 1998 are examined to investigate the relationship between the characteristics of the nocturnal boundary layer and near surface O_3 concentration. Data from 12 surface monitoring sites throughout the LFV are also analysed. This is intended only to ascertain whether the spikes in O_3 concentration are a local or valley-wide phenomenon. It is beyond the scope of this paper to attempt a more detailed description of processes operating throughout the LFV and our three-dimensional results refer only to the Aldergrove site.

Specifically, this paper seeks to:

- Document the spatial and temporal variability in the incidence of nocturnal O_3 spikes in a region of urbanised complex, coastal terrain.
- Emphasise the temporal variability of ozone concentrations in the residual layer.
- Utilise vertical soundings to examine the nature of, and mechanisms contributing to O_3 down-mixing events.

Due to the extent of the data set, emphasis here will be placed on one representative case study.

2. Background

2.1. The Lower Fraser Valley

The LFV is a triangular shaped valley located on the coast of the Strait of Georgia straddling the US/Canada border. It is a flat-bottomed valley, located a few metres above sea-level, and orientated approximately WNW–ESE (Fig. 1). The highest population density is found at the northwest end of the valley where the metropolitan area of Vancouver contains a population of approximately two million people. During summer months O_3 concentrations in the LFV periodically exceed the maximum acceptable national ambient air quality objective (NAAQO) of 82 ppb (Li et al., 1997). Extensive research has been conducted in the LFV on air quality issues, with much of this work summarised in Steyn et al. (1997). The site chosen for the field experiment was the

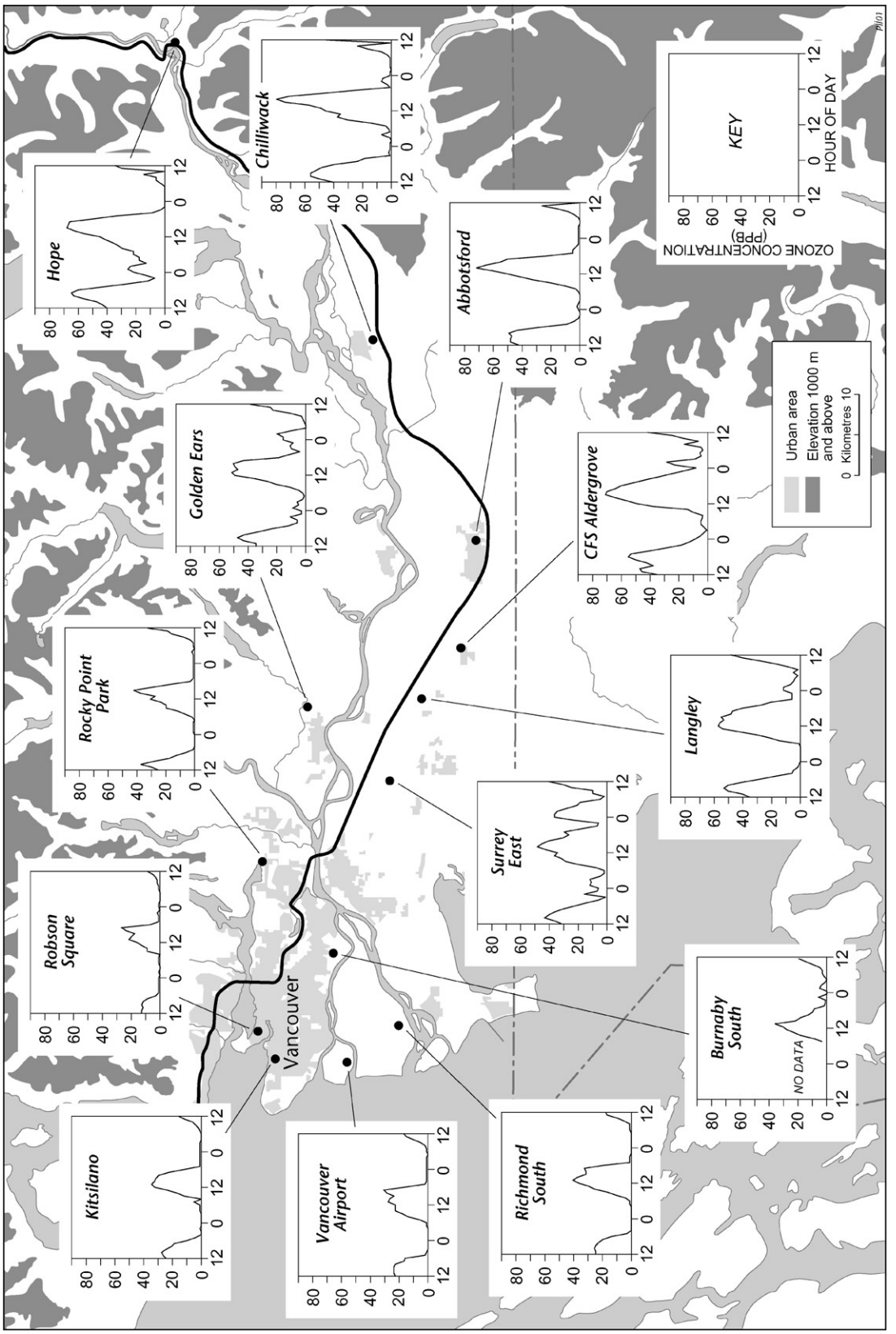

Fig. 1. Map to show the variations in O_3 concentration recorded at 12 of the Greater Vancouver Regional District O_3 monitoring sites and at CFS Aldergrove between 1200 PDT 30 August and 1200 PDT 1 September 1998.

Canadian Forces Station (CFS) Aldergrove located 100 km east of Vancouver (Fig. 1). This grassland site is situated in the middle of the valley away from the immediate influence of tributary valleys.

2.2. Methods

The field study was conducted between 1 July and 5 September 1998. Continuous measurements of O_3 (Monitor Labs 9811 with intake at 4 m, 5 min resolution), turbulence (Gill three-axis sonic anemometer exposed at 5.05 m on lattice tower) and ancillary meteorology were made during this period. These data were supplemented by additional measurements made during intensive observational periods (IOPs), including additional surface chemistry observations (NO and nitrogen dioxide (NO_2)) and vertical soundings of O_3 and meteorological variables. Routine hourly observations of O_3 and NO_x from surrounding Greater Vancouver Regional District (GVRD) network stations were used to assess horizontal advection. IOPs were undertaken throughout the field season and were chosen to coincide with periods when synoptic conditions supported the development of high O_3 concentrations. Observations commenced following several days of anticyclonic conditions, when forecasts predicted the continuance of the synoptic regime.

During the IOPs an Atmospheric Instrumentation Research Inc. model 5 m^3 tethersonde balloon system, equipped with a radiosonde meteorological sensor and a KZ-ECC ozonesonde (EN-SCI Corporation) was used to document the vertical characteristics of the boundary layer. Flights were made approximately hourly between 1700 and 1100 Pacific Daylight Time (PDT) and typically lasted 45–60 min ascending to an altitude of between 500 and 800 m. An ascent rate of between 0.25 and 0.5 $m\,s^{-1}$ enabled a minimum vertical resolution of 5 m.

In order to objectively assess the presence of nocturnal increases in O_3 concentration the following criteria were developed to identify secondary maxima (or spikes). These criteria included the observation of a (temporarily localised) minimum increase in O_3 concentration of 5 ppb, sustained for at least 15 min and followed by a well-defined decrease of at least 5 ppb at the end of the episode. This was to ensure that the increases in concentration were both significant (given the sensitivity of the O_3 analyser) and temporally localised. This definition excluded from analysis increases that occurred during the morning and evening transition periods. These were difficult to isolate from the general trends in O_3 concentration. As the GVRD data were only available at an hourly resolution the time criteria for identifying spikes in concentration were modified from 15 min to 1 h with some loss of detail.

2.3. Meteorological context

Clear skies and strong subsidence associated with the prevailing anticyclonic synoptic conditions during the 11 nights of intensive observations facilitated the development of a very stable nocturnal boundary layer at CFS Aldergrove. This typically developed between 2100 and 2300 PDT and was comprised of a shallow, very stable layer typically 50–150 m in depth, marked by a strong temperature inversion. The depth of the stable boundary layer (SBL) oscillated with time, showing no consistent trends in growth through the latter parts of the night, similar to the definition of a type 1 SBL suggested by Beyrich (1994).

Surface winds were typically light (consistently $<2\,m\,s^{-1}$) and variable. The top of the stable layer was marked by a wind speed maximum, which frequently developed into a weak nocturnal LLJ. A nocturnal LLJ was observed at the site intermittently during every night of the IOPs (a LLJ was defined using the criteria of a $2\,m\,s^{-1}$ decrease in wind speed immediately above the localised wind speed maximum, Stull, 1988). However, the characteristics of the jet continually evolved with time and were variable between nights. The LLJ typically developed at the top of the SBL between 70 and 150 m, where Richardson numbers were high and conditions very stable (as predicted by Blackadar, 1957). A second jet (separated by a distinct wind speed minimum) was also periodically observed well above the stable layer between 300 and 500 m. Whilst wind speeds of up to 13 $m\,s^{-1}$ were recorded in the jet, more typical values ranged between 5 and 6 $m\,s^{-1}$. The prevailing direction of the LLJ was southerly, however jets from a range of directions between NE–S–NW were observed.

Although down-valley winds developed during 8 of the 11 IOP nights (with winds backing from a W–SW daytime direction to a SE–NE direction), they often developed at different heights and at different times throughout the residual layer. The profile was frequently layered, with isolated bands existing in directions often counter to the prevailing wind flows. A westerly band was commonly observed between 200 and 300 m for 1–2 h following wind reversal through the remainder of the profile. During the three nights when down-valley winds failed to develop, a prevailing southerly flow was observed.

3. Results

3.1. Spatial and temporal patterns in surface ozone concentration

Nineteen near-surface nocturnal O_3 maxima were identified during eight of the 11 nights at the Aldergrove

site. These spikes were superimposed upon a mean background concentration of 6 ppb. Although net increases in concentration of up to 32.5 ppb were recorded, the average increase was 12.7 ppb. Secondary nocturnal O_3 maxima were observed between 2320 and 0645 PDT with no obvious periodicity in occurrence. The average duration of a single event was 2 h.

Ozone data from 12 surface monitoring sites throughout the LFV operated by the Greater Vancouver Regional District were examined to provide a spatial context for these results during the IOPs. The results, summarised in Table 1, reveal 57 nocturnal spikes in O_3 concentration at stations within the LFV with at least one spike occurring in the LFV per night. Figs. 1 and 2 illustrate the diurnal changes in O_3 concentration at selected sites throughout the LFV between 1200 PDT 30 August and 1200 PDT 1 September. The increase in O_3 concentration associated with these events was typically of the order of 15–25 ppb, although values of more than 40 ppb were recorded at Surrey East (0000 PDT, 27 July 1998). The increase in concentration observed occasionally reflected values of more than half the maximum recorded the previous day at that site (Fig. 2). The decrease in frequency of nocturnal maxima at these sites compared to the Aldergrove site can be partially accounted for by the decreased temporal resolution (hourly compared to 5 min averaging periods) of the GVRD data sets.

Table 1
Table to illustrate the number of nocturnal ozone maxima, maximum recorded ozone concentration and mean time of occurrence during the IOPs in the Lower Fraser Valley, 1998

	Number of recorded ozone maxima during IOPs	Maximum nocturnal ozone concentration during IOPs (ppb)	Mean time of ozone maxima during IOPs (PDT)
Kitsilano	2	10.8	0030
Robson Square	0	—	—
Vancouver International Airport	8	28.6	0030
Rocky Point Park	0	—	—
Richmond South	6	18.7	0100
Burnaby South	8	32.5	0200
Surrey East	13	46.3	0000
Langley	1	11.8	0000
Abbottsford	0	—	—
Golden Ears Elementary School	12	25.6	0000
Hope Airport	4	25.6	0200
Chilliwack Airport	3	6.9	0130

Spikes in O_3 concentration show little similarity in magnitude or duration throughout the valley. However, Figs. 1 and 2 and Table 1 show that the secondary nocturnal maxima at different sites were typically observed within 2–3 h of each other suggesting that they may be initiated by a valley wide phenomenon. Distinct spatial patterns in the data set are discernable across the LFV. Few spikes occur at western edge of the valley at the Kitsilano, Richmond, Robson Square or Vancouver Airport sites, whilst there is an increased incidence of nocturnal maxima to the east of the Valley.

Previous studies have shown that O_3 concentrations were strongly affected by local titration with NO at sites located within close proximity to urban areas or major roads (Vecchi and Valli, 1999; Samson, 1978). It is interesting to note that nocturnal O_3 concentrations show a marked sensitivity to NO concentrations throughout the LFV. As expected, localised spikes in NO are shown to be out of phase with increased O_3 concentration (Fig. 3). At the Abbottsford and Robson sites, where high concentrations of NO are observed at night due to the downtown location of the monitors, ozone spikes do not occur. Although beyond the scope of this study, this observation warrants further investigation and modelling, as it is possible that NO concentrations may limit or obscure evidence for the vertical mixing of O_3, thus accounting for the spatial trends observed in this study.

3.2. Vertical distribution of ozone in the very stable nocturnal boundary layer

Ozone concentrations typically increased with height throughout stable layers at the Aldergrove site, revealing a marked depositional profile similar to that observed by Harrison et al. (1978). However, counter to the common assumption within the literature (Corsmeier et al., 1997), ozone concentrations where found to be highly variable with time and height in the residual layer. Generally, following the development of the down-valley wind regime, ozone concentrations in the lowest 100–300 m of the RL increased with height. This may be observed in the ozone contours for 30–31 August 1998 in Fig. 4a. Although concentrations increased at a slower rate in the lower layers of the RL compared to the SBL, this frequently blurred the expected boundary in the profiles between the top of the SBL and the RL. Banta et al. (1997) also observed reduced concentrations in the lowest 500 m of the boundary layer in their study of the LFV. This may be a consequence of the surrounding complex terrain. Depositional processes operating along the valley walls

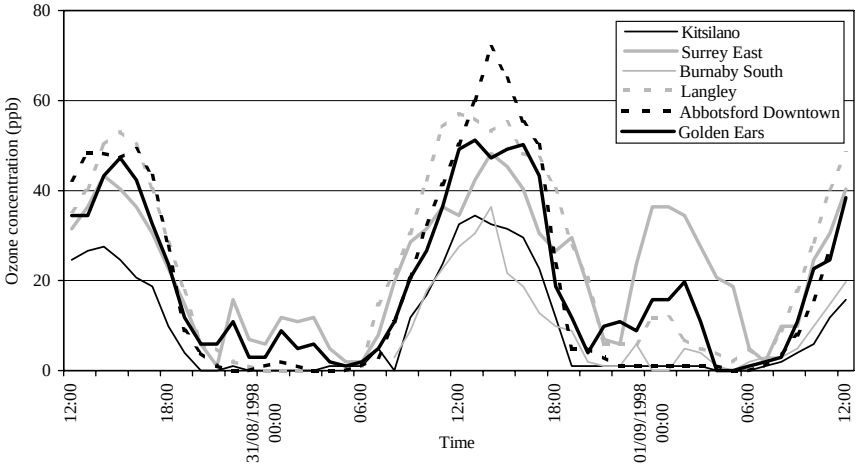

Fig. 2. Variations in O_3 concentration recorded at sites in the LFV 30 August–1 September 1998.

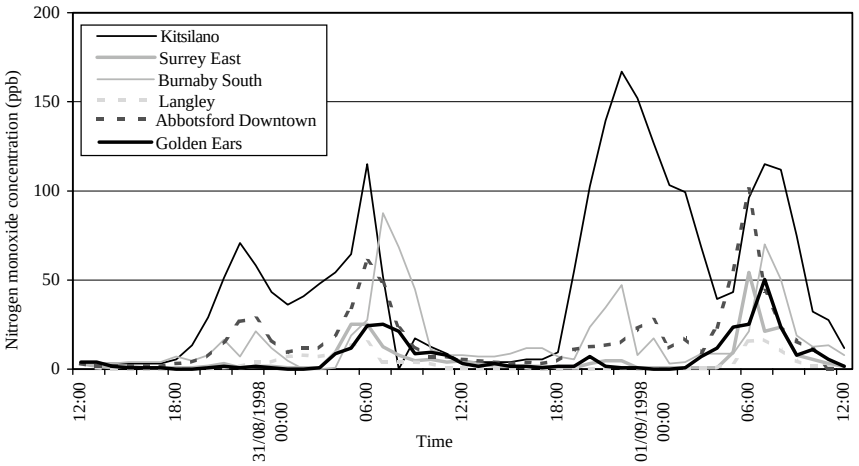

Fig. 3. Nitrogen monoxide concentrations at selected sites in the LFV during 30 August–1 September 1998.

may act to cleanse down-valley winds as they pass through tributary valleys prior to convergence in the LFV (Banta et al., 1997). Above 400 m ozone concentrations remained more stable with time and, more closely represented conditions observed during the previous afternoon, characteristics more akin to the conventional representation of the RL. This reflects the absence of depositional surfaces or primary sources of NO in the upper levels of the residual layer.

This simple scenario was rarely observed however. More commonly bands of high ozone concentration were observed such as those shown between 150 and 250 m in height observed between 0000 and 0500 PDT 27 July in Fig. 4b and between 100 and 200 m in height observed between 0000 and 0400 PDT 1 September in Fig. 4c. These data clearly demonstrate the sporadic advection of layers containing both high and low ozone concentrations across the site.

Due to the light winds and meandering motions (characteristic of flows in the residual layer) it was sometimes difficult to isolate the sources of these pockets effectively. Layers containing high concentrations of ozone were associated with winds from a variety of directions. For example three nights saw the advection of isolated layers with ozone concentrations in excess of 80 ppb (26–27 July, 27–28 July and 31 August–1 September). The band of high ozone concentrations was observed above the stable layer but below 300 m. During 31 August–1 September this band was associated with a SE flow. During the other two nights the pockets of high ozone concentration were associated with the late evening westerly band which remained following the

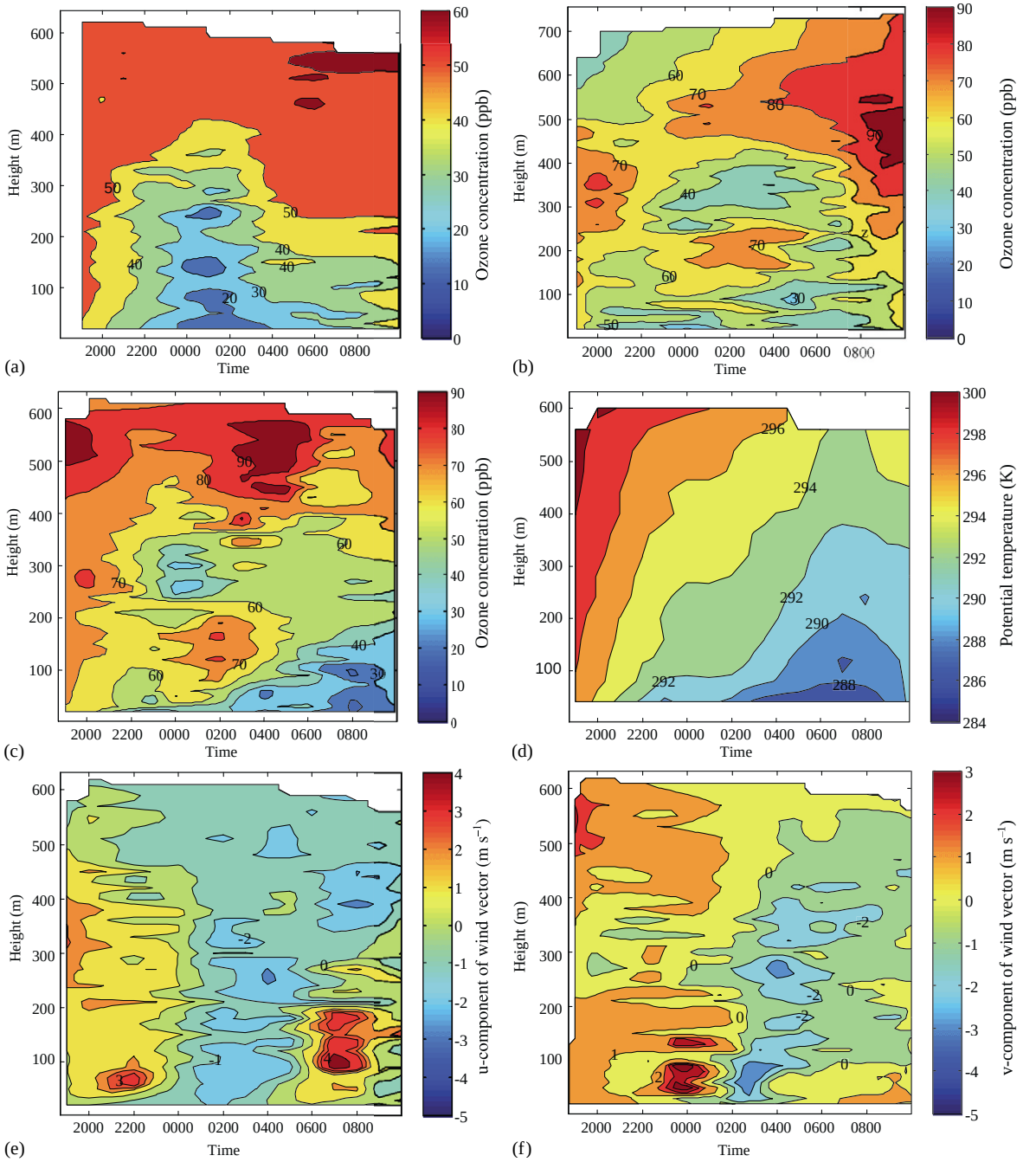

Fig. 4. Contour plots of ozone concentration for (a) 30–31 August, (b) 26–27 July, (c) 31 August–1 September and between 31 August–1 September 1998 for (d) potential temperature, (e) *u*-component and (f) *v*-component of wind vector.

development of the down-valley wind system as shown between 0000 and 0400 PDT on 27 July 1998. Clearly both the timing and trajectory of the mesoscale flows play a crucial role in determining the ozone concentrations in the residual layer.

3.3. Case study of vertical mixing: 31 August–1 September 1998

Detailed measurements of the characteristics of the residual layer and the stable boundary layer during the

11 nights of intensive measurement at CFS Aldergrove revealed some consistent trends during mixing events. These are illustrated here with reference to a specific case study for the night of 31 August–1 September. Fig. 5a illustrates the changes in O_3 and NO concentrations observed at the Aldergrove site between 2200 PDT 31 August and 0300 PDT 1 September 1998. This figure shows a clear nocturnal O_3 maximum between 2310 and 0230 PDT. A maximum increase in O_3 concentration of 32.5 ppb was recorded at the surface at 0130 PDT.

Fig. 5b demonstrates the weak, intermittent characteristics of the turbulence observed at this time in the very stable NBL. Fig. 5c illustrates the corresponding changes in surface temperature expected due to the down mixing of warmer air from aloft. It is interesting to note that the increase in temperature (and heat flux) is coincident with the onset of turbulence and occurs slightly before the corresponding increase in surface ozone concentration. This may be accounted for by the comparatively low concentrations of ozone in the lowest 50 m of the NBL at 2300 PDT (Fig. 4c). Concentrations of ozone at the surface may also be affected at this time by the slight increase in NO concentrations at the surface (Fig. 5a). The main burst of turbulence between 0000 and 0030 PDT is coincident with increased O_3 concentration aloft (Fig. 4c) and a corresponding increase in surface concentrations (Fig. 5a). During this time period no change in surface wind speed or direction was observed. Consequently, the evidence from surface variables strongly suggests that turbulent vertical mixing processes transported O_3 and warmer air from aloft to the surface.

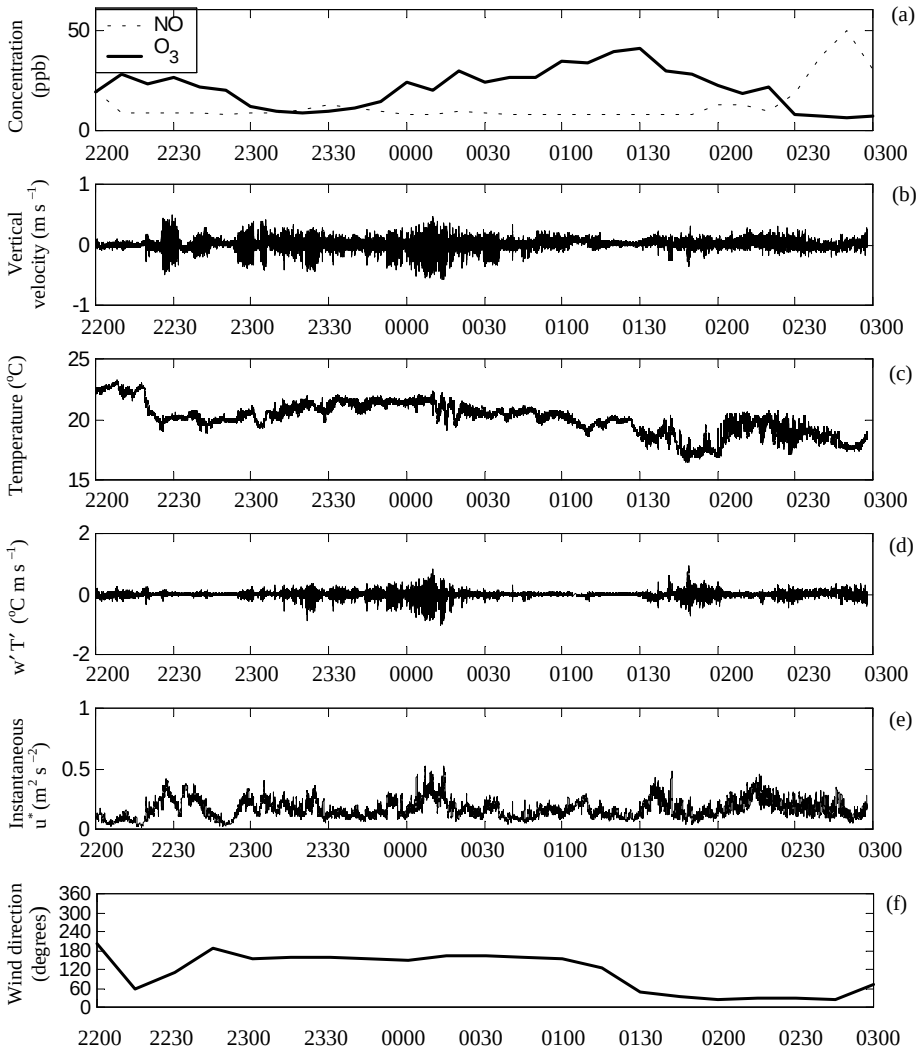

Fig. 5. Time series of (a) ozone and nitrogen monoxide concentration (b) vertical velocity, (c) temperature, (d) instantaneous surface heat flux (e) instantaneous ustar and (f) wind direction observed between 2200 PDT 31 August and 0300 PDT 1 September 1998.

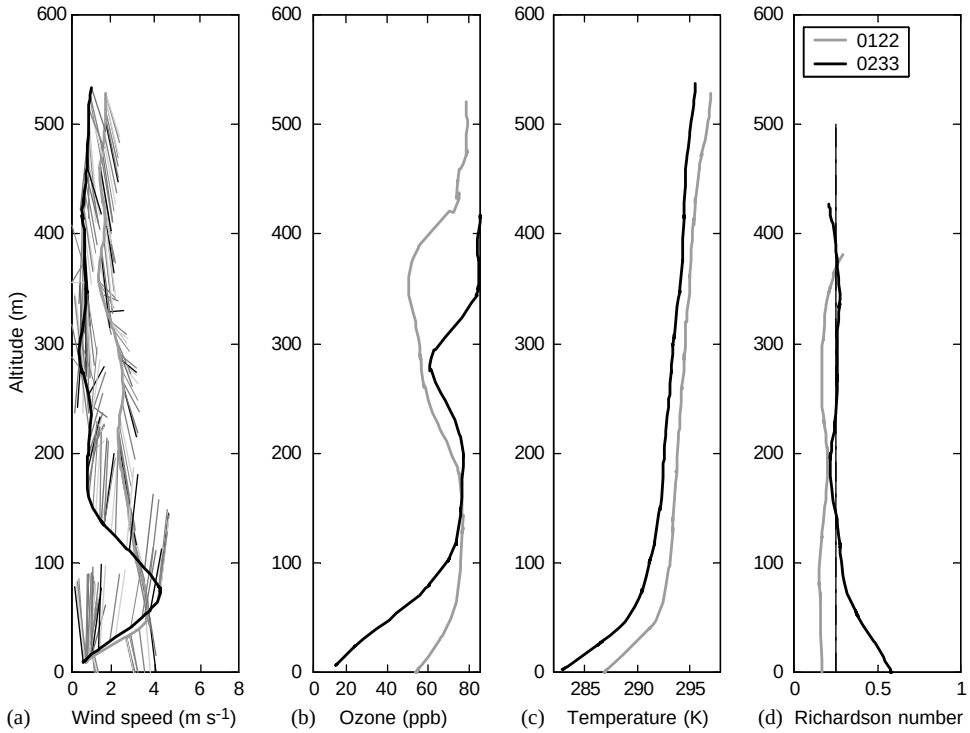

Fig. 6. Variation in (a) wind speed, (b) O_3 concentration, (c) potential temperature and (d) Richardson number with height observed during (0122 PDT) and immediately following (0233 PDT) a spike in O_3 concentrations observed at the surface on 1 September 1998.

Figs. 6a–d illustrate the changes in wind speed, O_3 concentration, potential temperature and Richardson Number with height during (0122 PDT) and immediately after (0233 PDT) this nocturnal maximum. Fig. 6b clearly shows that during the O_3 spike, O_3 concentrations are more homogeneous throughout the stable boundary layer compared to the marked gradient in concentrations apparent at 0233 PDT. The potential temperature data (Fig. 6c) also show evidence of active vertical mixing processes in the lowest 100 m at 0122 PDT as, although cooling is apparent throughout the profile between 0233 PDT indicative of advection, a steeper gradient in temperature in the lowest layers of the boundary layer at 0233 PDT indicates increased cooling of the surface layers after the mixing event.

The existence of turbulence in the boundary layer can be determined using the Richardson number (Ri). However, the use of this parameter in the NBL has limitations. For example there is considerable scatter in the relationship between Richardson number and turbulent fluxes (Neu et al., 1994), especially under the non-stationary and non-equilibrium conditions typical of the very stable NBL (Mahrt, 1985). Further, the concept of a single critical Richardson number of $Ri_c = 0.25$ has been contested within the context of vertical profiles through the stable boundary layer (Derbyshire, 1994; Kunkel and Walters, 1982).

However, here we take the view (in agreement with Finnigan, 1999 and Mahrt et al., 1979) that in the absence of detailed micrometeorological measurements with height, the technique provides a good starting point for comparing the stability between layers. To minimise the depth of the layer for the calculation of the gradient Richardson from the tethersonde data, a linear interpolation scheme was applied to achieve a 0.5 m resolution. Thus the critical number should be close to $Ri = 0.25$.

Fig. 6d illustrates the variations in Ri with height calculated from the tethersonde data for 0122 and 0233 PDT on 1 September 1998. At 0122 PDT the results indicate that turbulent mixing may have occurred throughout the profile, whilst at 0233 PDT the lowest 150 m are stable. Thus at 0122 PDT the RL and SBL are coupled together by turbulence and there is evidence of mixing of ozone down to the surface. However, by 0233 PDT there is a clear stable layer close to the surface inhibiting the transport of O_3 from aloft. The Ri number indicates that turbulent conditions may still exist in the RL, however given how close the Richardson number is to the critical value this may indicate turbulent footprints rather than active turbulence.

Figs. 4c–f show time–height contour plots of O_3, temperature and up–down and cross valley wind components from 1900 PDT 31 August to 1000 PDT 1 September 1998. Figs. 4e and f illustrate that a shift in the mesoscale wind regime to nocturnal down valley flows occur between 2300 and 0100 PDT. This change occurs throughout the NBL and a coincident increase in potential temperatures at all levels is observed. This occurs during the same time period as the observed near-surface nocturnal O_3 maximum and observed increases in surface turbulence, strongly suggesting that the changes in the mesoscale wind regime result in active vertical mixing processes throughout the NBL.

On this occasion the timing of the wind flow reversal coincides with a band of high O_3 concentrations observed at 100–200 m between 0100 and 0200 PDT. The advection of this band of increased concentrations aloft may account for the apparent delay between the peak in surface-based turbulence shortly after midnight (Fig. 5b) and the maximum increase in O_3 concentrations that occurs at 0130 PDT (Fig. 5a). Clearly the temporal and spatial patterns of O_3 advection aloft and the depth and timing of the turbulence in the NBL have a strong influence on the resulting increase in near-surface O_3 concentrations.

3.4. Down-mixing mechanisms

Turbulence data reveal that intermittent turbulence is a key characteristic of the surface layer of the very stable NBL. Results from throughout the field season demonstrate that wind shear generated by mesoscale wind systems is an important source of turbulence at this site. For example, of the eight nights when a down valley wind regime developed at the Aldergrove site, simultaneous secondary nocturnal O_3 maxima were observed on seven occasions. This combined with the coincident timing of spikes observed throughout the LFV strongly suggests that changes in the mesoscale wind regime can result in the vertical mixing of O_3 to the surface.

A further nine out of the total 19 nocturnal spikes in O_3 concentration coincided with the presence of a LLJ above the site. A relationship could not be identified between any specific characteristics of the LLJ (such as height or speed) and the magnitude, frequency or duration of O_3 spikes observed at the surface. This may be in part a consequence of the temporal resolution of the tethersonde data (flights were $\sim$1 h apart and lasted 45–60 min.). It also reflects the variability of O_3 concentrations in the residual layer, as the presence of vertical mixing mechanisms in the absence of O_3 aloft cannot generate increased levels at the surface.

Previous studies have shown that the low-level jet is an effective transport mechanism introducing higher O_3 concentrations to rural areas (Kalthoff et al., 2000; Corsmeier et al., 1997; Beyrich, 1994). There was little evidence to support this mechanism in the data collected from the Aldergrove site. The average O_3 concentration in the LLJ band was 46 ppb. This typically corresponded to only 70–80% of the value of the maximum O_3 concentration recorded in each vertical profile.

The largest increases in surface O_3 concentration occurred during periods when the turbulence was associated with reversals in the mesoscale wind regime. This may be a result of mixing through a deeper section of the boundary layer (compared to turbulence generated by a shallow LLJ). For example three nights saw the advection of isolated layers with O_3 concentrations in excess of 80 ppb. It is unlikely to be a coincidence that these three nights, which recorded the highest concentrations in the residual layer, were also the three nights with the largest spikes in O_3 concentration observed at the surface.

Three spikes in O_3 concentration could not be linked either to the LLJ or to changes in the mesoscale wind flow regimes. A possible further source of turbulence in regions of complex terrain is the breaking of gravity waves (Finnigan, 1999). This mechanism may generate sufficient turbulence to disrupt the formation of the LLJ (Coulter, 1990). Evidence from micro-barographs did not conclusively support the existence of gravity waves at the site. Thus, although gravity waves may prove important to our understanding of turbulence in the NBL, it was not possible to objectively identify them from the data analysed here. Thus the cause of turbulence for these three O_3 spikes could not be identified.

4. Conclusions

Despite the overall dominance of chemical titration and depositional processes in the NBL, significant increases in O_3 concentration were observed in the LFV during every night of the IOPs. These periods were characterised by rapid increases in concentration of up to 31.1 ppb. The increases were typically sustained for at least 2 h and followed by a rapid decrease in concentrations. The occurrence of nocturnal O_3 maxima was highly variable in time and space. However, analysis of data from the GVRD monitoring network showed a consistent sensitivity of increased O_3 concentrations to NO concentrations. These results highlight the potential significance of surface NO concentrations in a comprehensive understanding of the presence and characteristics of secondary ozone maxima.

O_3 concentrations were shown to be highly variable in the residual layer and the timing and trajectory of mesoscale flows had an important impact on O_3 concentrations. This variability strongly refutes the common assumption that concentrations of O_3 remain constant in the residual layer. This has significant

implications, not only for nocturnal surface O_3 concentration, but also for the temporal auto-correlation of O_3 concentrations at a daily scale. For example, advection may account for the mixed results of semi-empirical models designed to estimate the contribution of O_3 stored in the residual layer to the maximum O_3 concentration the following day (Teichmann et al., 1997; Neu, 1995). Understanding the interaction between advection and pollutant storage in the residual layer with turbulent mixing processes is therefore critical to understanding secondary nocturnal O_3 maxima and identifying the importance of these processes on diurnal pollutant cycles.

Vertical profiles through the NBL during individual O_3 spikes supported the hypothesis that these events were the result of vertical mixing processes. Richardson numbers calculated from tethersonde data revealed isolated patches of instability, which occasionally extended through to the surface layers. These results concur with the increasing number of studies that identify temporally localised nocturnal increases in surface O_3 concentration in regions of complex terrain (Kalthoff et al., 2000; Corsmeier et al., 1997; Löffler-Mang et al., 1997). As in their studies, surface O_3 concentrations during O_3 spikes rarely exceed 50 ppb, well below the Maximum Acceptable NAAQO hourly average of 82 ppb. Thus vertical mixing processes are unlikely to pose a significant health threat to local populations. However, given that O_3 concentrations in the residual layer occasionally exceeded the NAAQO, it is possible that in remote areas where NO concentrations are reduced, vertical mixing processes may have a greater impact on local air quality.

Despite the complexity introduced by the variability in O_3 concentrations aloft and localised increases in NO concentration at the surface, seven out of the 19 O_3 spikes observed at CFS Aldergrove occurred during periods occurred during the development of the down-valley wind system. A further nine spikes occurred during periods when a LLJ was present aloft. This highlights the heterogeneity of different turbulent processes operating in the NBL, and emphasises the need for future studies to consider changes in mesoscale wind regimes and breaking gravity waves, as well as the LLJ, as potential causes of vertical mixing.

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