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Tropospheric layering of ozone in regions of urbanized complex and/or coastal terrain: a review

I.G. McKendry and J. Lundgren

Atmospheric Science Programme, Department of Geography, University of British Columbia, 251–1984 West Mall, Vancouver, BC, V6T 1Z2, Canada

Abstract: Exchange of pollutants between the atmospheric boundary layer and free troposphere is an important (yet often neglected) process that tends to produce distinct layers of pollution in the lower troposphere. These layers represent a potential sink for pollutants from the boundary layer, have the potential to be mixed to ground and likely influence tropospheric chemistry and the global climate system. Factors influencing the vertical distribution of ozone in the troposphere are outlined as a prelude to a more specific discussion of elevated layers and myriad meteorological processes responsible for their development. Evidence from a range of geographical settings suggests that these phenomena are ubiquitous. A rich data set from the Lower Fraser Valley, British Columbia, is used to provide an inventory of layer structures and to highlight their diverse origins and histories. Approaches used to assess the impact of downmixing of pollutants from elevated layers on ground-level concentrations of ozone are outlined and future research priorities recommended.

Key words: elevated layers, tropospheric ozone, urban pollution, vertical mixing, vertical profiles

I Introduction

Pollutant distributions across the surface of the earth have long been a primary focus of applied air quality research (e.g. Comrie's, 1990, review of the climatology of surface ozone (O_3)). In part, this is a consequence of the predominance of surface-based measurements and reflects a natural concern with surface-based receptors (notably humans). However, from the mid-1970s technology in the form of cheap, lightweight balloon-borne sondes, instrumented airborne platforms and remote sensors permitted probing of the vertical chemical structure of the troposphere. Much of this technology was orientated towards the measurement of O_3 and fine particulate matter, two

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pollutants deemed to have both global climatic consequence and to be deleterious to human health (both are currently the focii of regulatory efforts in urbanized areas worldwide). Three-dimensional views of the lower troposphere afforded by the new technology have revealed quite startling complexity in vertical pollutant profiles, particularly in regions of urbanized coastal or complex terrain where a significant proportion of the worlds's population reside (Steyn, 1996). Formerly, conventional wisdom suggested that anthropogenically produced pollutants with a surface origin such as O_3 and fine particulate matter were effectively constrained from entering the free troposphere (FT) by the inversion that caps the atmospheric boundary layer (ABL – lowest ~1 km of the troposphere that is influenced by surface friction and tends to be well mixed due to thermal and mechanical turbulence) (Stull, 1988). However, evidence from studies adopting a three-dimensional perspective in a wide range of geographic locations suggests that ABL–FT pollutant exchange is not only significant but also commonly produces a complex layered structure of pollutants in the FT. Understanding of such elevated layers of pollution is vital as they:

- represent a potential sink for pollutants from the ABL, thereby effectively ventilating the ABL;
- have the potential to be mixed to ground and thereby contribute to ground-level pollutant concentrations that influence human health;
- must be adequately resolved by air quality models if predictions are to be valid; and
- influence tropospheric chemistry and therefore possibly the global climate system (e.g., O_3 directly affects climate because it absorbs incoming UV radiation and outgoing long-wave radiation). It is also linked with the concentration of OH in the troposphere, a radical which ultimately controls the fate of other greenhouse gases in the atmosphere (Atherton *et al*., 1995).

Given the vital importance of such processes to urban air pollution meteorology and global climate studies, the primary objective of this review is to describe and categorize the myriad phenomena that contribute to exchange of pollutants between the lower troposphere and free troposphere (a process also referred to as 'handover'; Priestley, 1967). Invariably, elevated pollutant layer structures result. Evidence is drawn from recent studies in several geographic locations, all of which have in common urbanized complex and/or coastal terrain. Due to the urban focus of these studies, emphasis is placed on elevated layers of O_3, a secondary photochemical pollutant for which vertical profiling technologies are well developed. Where appropriate, elevated layers of fine particulate matter are also described. Fine particulate pollution is well suited to remote-sensing technologies (e.g., LIDAR – a radar-like system based on laser light; McKendry *et al*., 1997; Papayannis and Balis, 1998) and, like O_3, is a pollutant deemed to be deleterious to human health.

In describing the characteristics of elevated pollutant layer structures, new data are presented from the Lower Fraser Valley (LFV) of British Columbia, where a rich data set from several years of vertical profiling of ozone is now available. Finally, methods used to quantify the magnitude of ABL–FT pollutant exchange are described.

II Ozone and fine particulate matter

O_3 is a secondary photochemical pollutant produced from a variety of natural and anthropogenic precursors that include industrial and vehicular emissions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) (Comrie, 1990). It occurs naturally in the troposphere and also in the stratosphere where it acts to shield the earth from harmful ultraviolet radiation (the so-called 'O_3 layer'). With respect to possible global climatic impacts, the main concern is that tropospheric O_3 is increasing (with perhaps important chemical and radiative consequences) while stratospheric O_3 is decreasing (Ravishankara, 1995). At concentrations of the order of 80 ppb, O_3 is known to have detrimental effects on vegetation, human health and various natural materials (Guicherit *et al.*, 1987). Downwind of large urban centres, daytime ground-level concentrations of O_3 may reach ten times background concentrations due to photochemical activity in an urban plume rich in ozone precursor species (e.g., in Mexico City concentrations exceed 100 ppb on most days; Fast and Zhong, 1998). As a powerful oxidant, and the main indicator of photochemical smog, it is therefore not surprising that O_3 has long been the primary target of regulatory efforts throughout the world. It is important to note that the lifetime of tropospheric O_3 in a sufficiently aged photochemical air mass is dependent on proximity to the earth's surface (where deposition or chemical destruction by fresh injections of NO can occur), and on the distribution of water vapour and the amount of solar radiation available (Fishman *et al.*, 1991). Consequently, with distance from the earth's surface and increasing latitude (which reduces photochemical activity and the potential for chemical destruction mechanisms), the lifetime of tropospheric O_3 may extend to several months (Fishman *et al.*, 1991).

Fine particulate matter on the other hand is a component of 'aerosol' (a suspension of liquid and solid particles in air; Wilson and Suh, 1977) and is now widely acknowledged as a priority air pollutant in urbanized settings. This has arisen as a result of mounting evidence that particles of less than 10 μm in diameter (so called PM_{10}) may be ingested deep into the respiratory system, resulting in significant impacts on human morbidity and mortality (Vedal, 1997). Unlike tropospheric O_3, which has potential sources at both ground level and in the stratosphere, fine particulate matter mostly originates from a variety of natural and anthropogenic sources at the surface of the earth. Furthermore, fine particulate matter includes material that varies considerably in chemical composition, size and atmospheric lifetime. Coarse-mode particles ($PM_{2.5–10}$) are formed primarily by the disintegration of larger particles and include wind-blown material from soil surfaces and roadways, evaporation from salt spray and biological material. Fine-mode particles ($PM_{2.5}$) are usually formed from gases and include material emitted during combustion processes, and secondary particles formed by gas to particle conversion in the atmosphere (often during photochemical episodes). As the primary source of aerosols is the earth's surface, fine particulate matter concentrations are naturally highest in the ABL and decrease with height. Consequently, aerosols are an excellent tracer of ABL dynamics (Browell *et al.*, 1994).

More detailed descriptions of the chemistry of ozone and fine particulate matter is provided in Seinfeld (1989). However, for this review, it is sufficient to emphasize that both pollutants have significant health impacts, are associated with urbanized regions and due to their respective roles as active constituents of the troposphere (both

radiatively and chemically), they have the potential to affect the global climate system significantly.

III Meteorology and idealized vertical distribution of O_3

Vertical pollutant distributions can be interpreted as a function of source strength and location, meteorological processes of transport and dispersion, deposition and chemical processes of production and destruction. In Figure 1(a), a schematic diagram is presented to illustrate the major vertical exchanges and processes that influence the distribution of O_3 in different sections of the troposphere. Diurnally evolving vertical temperature and O_3 profiles arising from such processes are shown in Figure 1(b) for the idealized case of a flat homogeneous plain downwind of an urban centre during conditions conducive to the build-up of photochemical smog (i.e., anticyclonic, summertime conditions).

In Figure 1(a) arrows are used to indicate the direction of major fluxes contributing to the overall tropospheric O_3 budget. Transport of O_3 and its precursors downward from the stratosphere represents a major source of tropospheric O_3 (for O_3 alone, estimated at about $3\sim8 \times 10^{10}$ molecules cm^{-2} s^{-1} for the Northern Hemisphere; Beck *et al*., 1997). Tropospheric/stratospheric exchange takes place primarily during tropospheric folding events that permit intrusion of stratospheric air to as low as 3000–5000 m above the earth's surface (see schematic in Comrie, 1990). This process is strongly developed in higher latitudes, has marked seasonality and is associated with cyclogenesis and upper tropospheric frontogenesis in the vicinity of the jet stream (Shapiro, 1980). Deposition at the surface represents the major net sink for O_3 ($\sim15 \times 10^{10}$ molecules cm^{-2} s^{-1}, Northern Hemisphere), while net chemical production in both the free troposphere and the atmospheric boundary layer is a source that appears to exceed significantly the downward flux from the stratosphere ($\sim10 \times 10^{10}$ molecules cm^{-2} s^{-1}, Northern Hemisphere; Beck *et al*., 1997). Significant exchange of O_3 and O_3 precursors is also known to take place between the ABL and the free troposphere (Beck *et al*., 1997) and is the focus of much of the remainder of this article. For example, over the continental USA, Jacob *et al*. (1993) estimated export of O_3 from the ABL to the free troposphere of 2×10^{10} molecules cm^{-2} s^{-1} and an equivalent amount of O_3 in the form of O_3 precursors. Neglecting diurnally variations in the ABL and urban effects, this budget gives rise to a mean vertical background distribution of O_3 in the mid-latitudes characterized by lowest concentrations at the surface (where wet and dry deposition represent a sink for O_3) and steadily increasing concentrations through the troposphere to the stratosphere (a major source of O_3 and precursors). The characteristic profile that results is described by Browell *et al*. (1994) and Doran *et al*. (1996) for northern Canada. It has low concentrations at the surface, free tropospheric background levels of 10–50 ppbv which increase with height at a rate of 5–7 ppb/km until the lower stratosphere is reached and concentrations exceed 100 ppbv.

Over land during anticyclonic conditions, the ABL has a well defined structure that follows the diurnal cycle of surface heating and cooling (lower portion of Figure 1(a)). Diurnal variations in the extent of both horizontal and vertical dispersion as well as the depth over which mixing occurs have a significant impact on pollutant concentrations near the ground (Figure 1(b)–(d)). During daytime, surface heating produces a

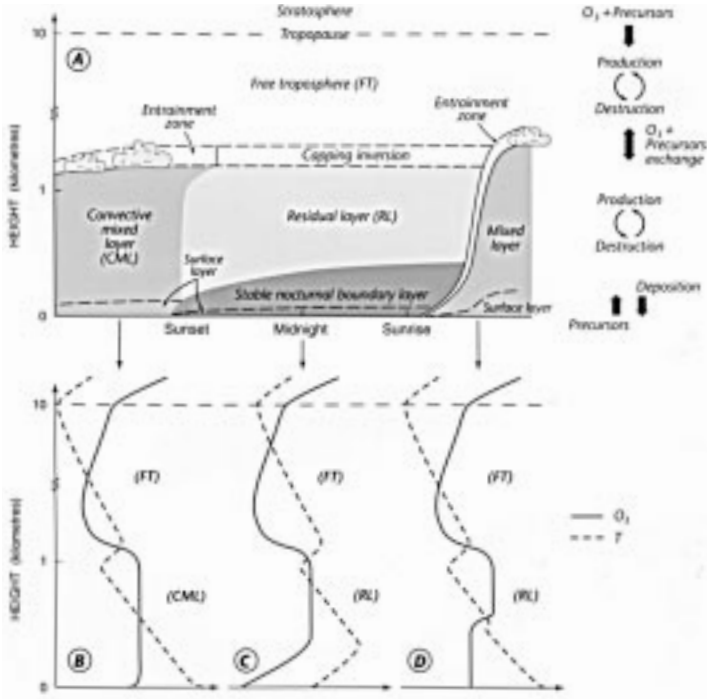

Figure 1 Conceptual model depicting the diurnally evolving boundary layer over land in anticyclonic conditions (top). At right, processes and exchange pathways affecting the tropospheric ozone budget are shown; below, characteristic profiles of ozone and temperature for: (b) mid-afternoon; (c) midnight; and (d) after sunrise
Source: Derived from Stull (1988); Beck *et al*. (1997)

turbulent convective mixed layer (CML) which grows to a late afternoon maximum height by entraining (mixing down into it) less turbulent air from aloft. Downwind of urban centres, strong mixing in this layer typically produces a vertical profile of pollutant concentrations (including O_3 and fine particulate matter) in which there is little variation with height (Figure 1(b)) and in which concentrations may significantly exceed background levels due to photochemical production below the effective lid provided by the capping inversion. Typically, concentrations drop to background tropospheric concentrations across the capping inversion layer.

Prior to sunset, generation of thermals at the ground ceases and turbulence in the CML begins to decay, leaving a residual mixed layer (RL). Pollutants incorporated in the RL may persist through the night (e.g., O_3) or may undergo further chemical reactions. As such, the RL can act as a 'reservoir' of pollutants that can be mixed to ground (Figure 1(d)) when the early morning CML begins to develop (Kleinman *et al*., 1994; Neu *et al*., 1994).

As nocturnal surface radiational cooling progresses through the night, a stable boundary layer (SBL) characterized by weak, sporadic turbulence develops at the earth's surface, effectively isolating the RL from the surface (and thereby isolating O_3 from its depositional and chemical sinks). Primary pollutants emitted into the shallow

stable layer (e.g., automobile emissions or smokestack effluent) may build to high concentrations due to poor dispersion. In contrast, O_3 within the SBL undergoes surface deposition and chemical destruction (by primary emissions of NO) resulting in a strong concentration gradient (Figure 1(c)) with height (Reiter, 1991; Hastie *et al*., 1993; Wanner *et al*., 1993; Neu *et al*., 1994; Gusten *et al*., 1998). Occasionally, mechanical turbulence generated in the SBL by strong wind shear associated with a nocturnal low-level jet results in bursts of down-mixing of pollutants from the RL. This frequently results in nocturnal 'spikes' in surface O_3 concentrations (Samson, 1978; Corsmeier, 1997).

Figure 2 shows a typical diurnal cycle of ground-level O_3 resulting from the processes described above. After sunrise, concentrations increase rapidly due to down-mixing of O_3 stored overnight in the RL. Photochemical production then dominates and produces an afternoon maximum in concentrations (depending on distance from the source of precursors). Concentrations fall off rapidly in the early evening as the SBL develops and deposition and chemical destruction mechanisms dominate. During night-time, occasional peaks in O_3 may be observed when sporadic turbulence in the SBL mixes O_3-rich air downward from the RL. At higher elevations over complex terrain, this strong diurnal variation in O_3 concentrations is not usually observed as a ready supply of O_3 is always available from the RL or FT (Zaveri *et al*., 1995).

The idealized representation of important meteorological and chemical processes and resultant vertical distribution of pollutants (notably O_3) presented in Figure 1(a)–(d) neglects several important meteorological processes responsible for the vertical redistribution of O_3 through the troposphere. These processes are summarized by Beck *et al*. (1997) and include:

- large-scale downward movements due to anticyclonic subsidence*
- convective growth of the boundary layer (entrainment)
- convective clouds*
- large-scale upward motion in cyclonic systems
- frontal systems
- stratus clouds

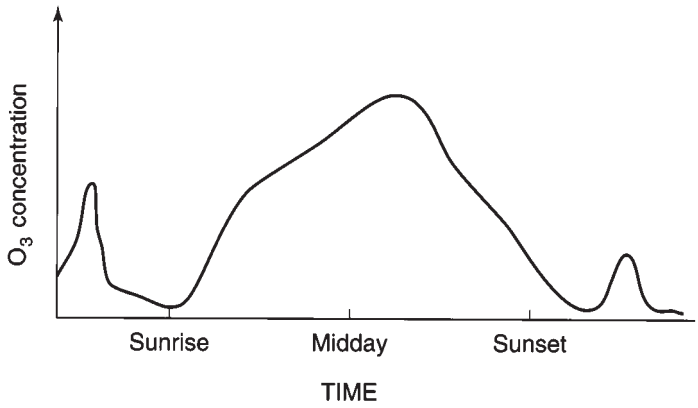

Figure 2 Typical diurnal cycle of ozone for a lowland site downwind of an urban centre

- rain scavenging
- downward flux from the stratosphere
- orographic effects*
- land–sea/lake breezes*
- heat island effects.*

Many of these processes contribute to ABL–FT pollutant exchange and are vital to understanding development of elevated pollutant layers. In the remainder of this review emphasis will be placed on the those meteorological processes (marked with asterisks above) associated with elevated polluted layer development during anticyclonic conditions conducive to the development of photochemical smog in urbanized regions.

IV Elevated pollutant layers

1 Layer identification

Despite a growing literature on elevated pollutant layers, definition of what exactly constitutes 'a pollutant layer' remains arbitrary at best. However, precise definition is essential in order to develop a systematic description/climatology of elevated layer structures. Such a definition should at least take account of:

- the range of vertical and horizontal scales that apply to layers (e.g., when does a plume become a layer?); and
- the magnitude of pollutant concentrations within layer structures (by what amount should measured concentrations in a layer exceed background concentrations?).

Even with precise definition, investigation of elevated pollutant layers is confounded by the one-dimensional nature of many observations (i.e., vertical profiles by balloon). Such measurements give no indication of the horizontal extent (or temporal persistence) of features observed. What might appear as a layer on a vertical profile may instead be a 'puff' of pollution (perhaps vented from a cumulus cloud). Multiple soundings, aircraft and/or remote-sensing information (from LIDAR) permit three-dimensional structure to be better resolved, although such rich information is rare. Some of the problems of elevated layer identification are well illustrated in the annotated ozonesonde profile shown in Figure 3. This early-afternoon sounding is characterized by multiple layers, some of which are clearly associated with advection of air masses of quite different origins (e.g., compare the moist, O_3-deficient layer 2500–4000 m with the dry O_3-rich layer from 4000 to 5500 m). Clearly, in identifying 'layers' within this context, ancillary meteorological information, including wind data, is required, while issues of signal versus instrumental noise, and assessment of the true magnitude of background concentrations at a particular location, altitude and season (as a basis for determining whether concentrations are 'elevated') are also of paramount importance.

In contrast to the static one-dimensional view provided by vertical balloon profiles, Figure 4 presents a two-dimensional lidar-derived view of aerosol (~1 μm diameter) layer structures in which the overall impression is one of dynamism and quite daunting complexity (especially from the perspective of pollution modellers). This morning

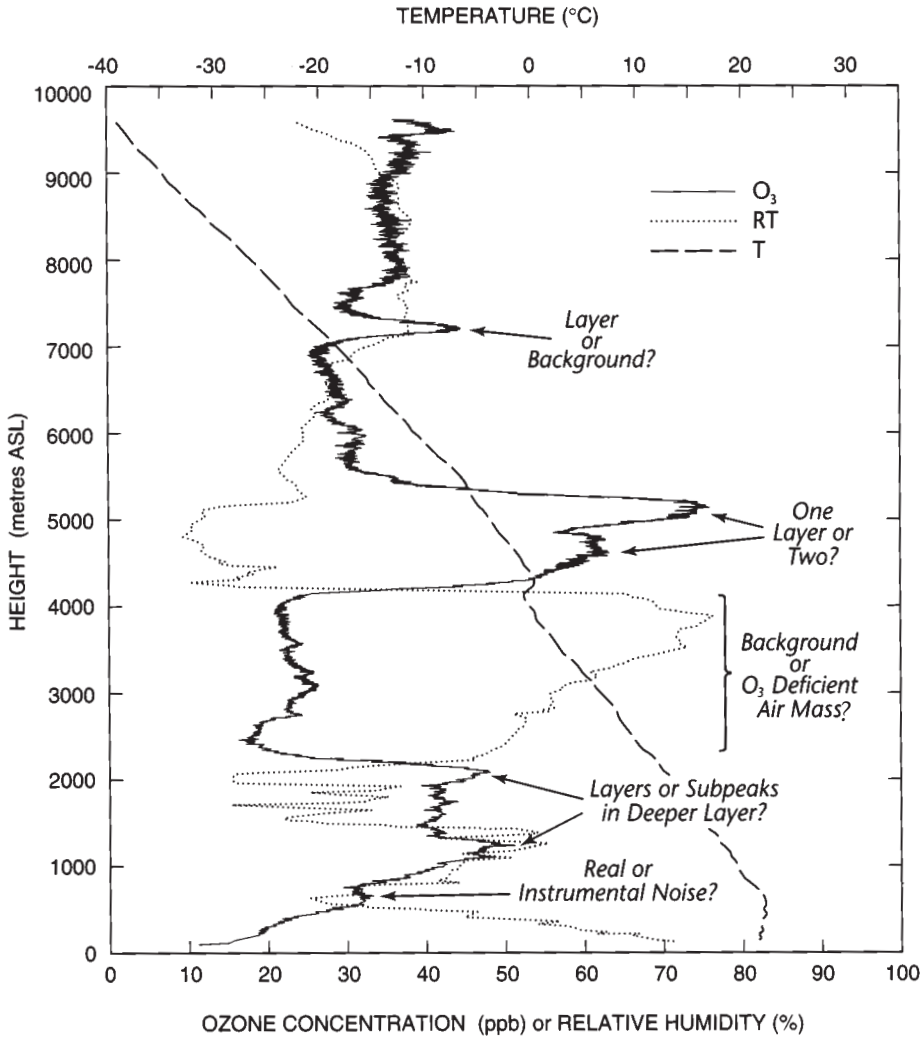

Figure 3 A tropospheric profile of ozone, temperature and humidity (Langley, British Columbia, 1300 PST, 1 August 1993) derived from balloon-borne sonde and showing complex layer structures

image over the LFV captures multiple layering, sloping layers, horizontal variability, discontinuities and wave activity. At the very least, it suggests that care should be taken in interpreting results/statistics derived from vertical soundings alone.

For the purpose of the inventory for the LFV described in section IV.3, an elevated O_3 layer was defined as: 'a band of finite vertical extent occurring above the ground and in which O_3 concentrations exceed 20 ppb above background and differ from those above and below by at least 20%'.

Background concentrations were defined as 10 ppb up to 1000 m, increasing at 7 ppb/km up to the tropopause. This is consistent with summertime values in southern Canada observed by Browell *et al*. (1994). They also used a 20 ppb exceedance criterion

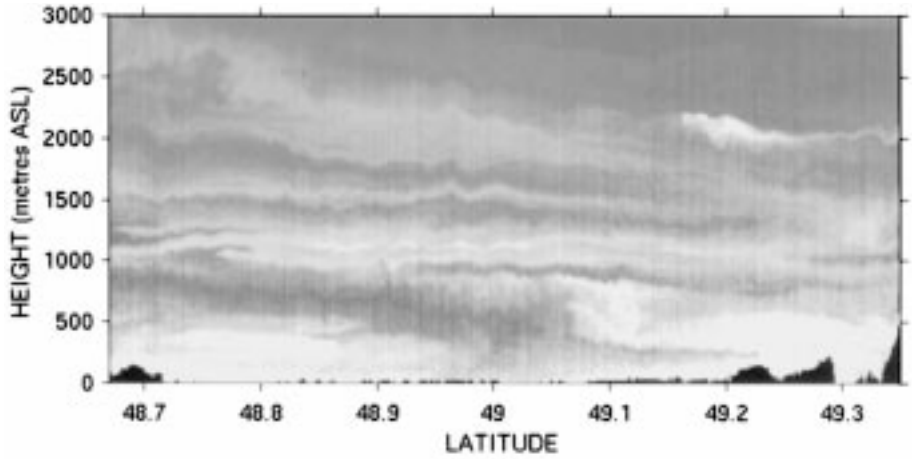

Figure 4 Airborne lidar north–south transect across the Lower Fraser Valley, British Columbia, showing aerosol backscatter at ~0700 LST, 5 August 1993. The grey scale represents the ratio of total backscatter to that of clear air (Rayleigh). Lighter shades represent higher aerosol concentrations. Terrain is shown in black

as a basis for discriminating between different mid-tropospheric layers over central Canada. In applying this definition in the LFV, it is assumed (despite evidence to the contrary in Figure 4) that the atmosphere is horizontally homogeneous (i.e., a concentration 'spike' in a vertical profile, in the absence of other data, is deemed to be part of a horizontal layer).

2 Meteorological processes responsible for elevated layer development

Photochemical smog is generally associated with anticyclonic conditions when light synoptic-scale winds, subsidence and clear skies promote not only reduced mixed-layer depths (and hence ventilation) but also strong horizontal thermal gradients responsible for convective activity and the development of thermally driven mesoscale circulations such as sea/lake breezes and slope/valley winds (Atkinson, 1981; Sturman, 1987). The latter phenomena all provide means by which vertical motion can inject pollutants from the ABL into elevated layers aloft.

a Coastal and orographic effects: Elevated layering of pollutants associated with the sea/lake breeze regime has long been recognized in quite diverse coastal environments (e.g., Chicago – Lyons and Olsson, 1973; Athens – Lalas *et al*., 1987; Los Angeles – Blumenthal *et al*., 1978; Tokyo – Wakamatsu *et al*., 1983). Often, such environments also possess coastal orography which creates complex interactions with the sea/lake breeze regime (e.g., Los Angeles, Athens, Tokyo, Sao Paulo, LFV). Elsewhere (e.g., Mexico City and central Europe) orographic effects alone may strongly influence the local air pollution meteorology. Recently, observational and modelling studies in such environments (e.g., Lu and Turco, 1994; 1995; McKendry *et al*., 1997; Millan *et al*., 1997; Kossmann *et al*., 1999) have revealed a range of mechanisms responsible for the creation

of elevated polluted layers. These are presented schematically in Figure 5(a and b) in the form of an idealized diurnal sequence for a coastal urbanized plain with inland mountains. Numbered descriptions below match the labelled processes depicted in Figure 5(a and b).

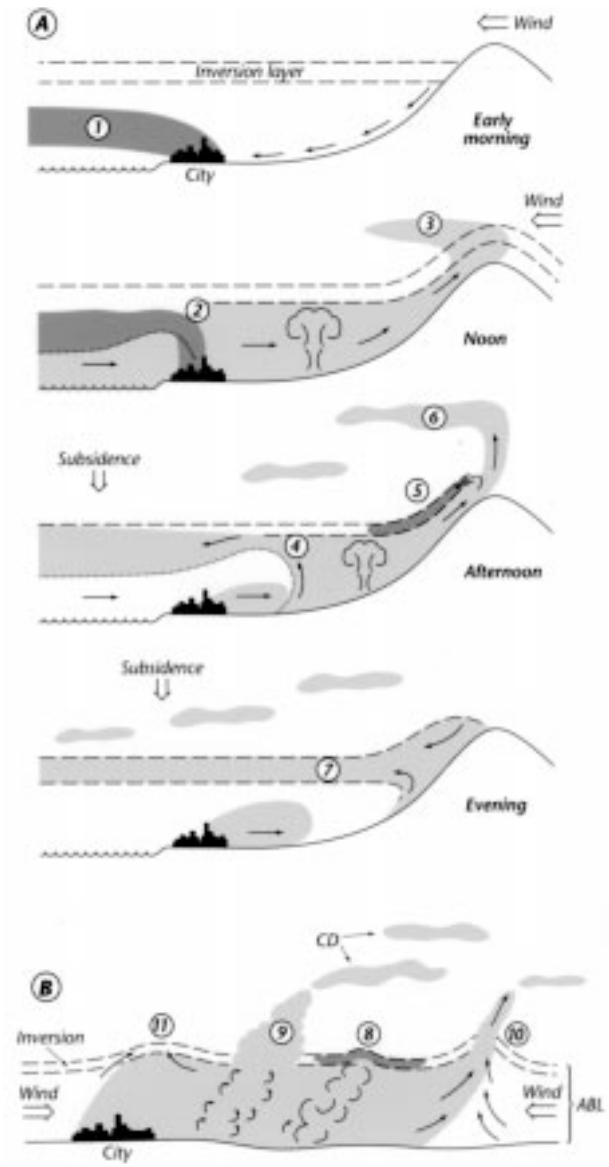

Figure 5 Schematic depiction of processes of elevated layer development and boundary layer venting over urbanized (a) complex coastal terrain; and (b) flat inland areas. Numbered processes are discussed in the text
Source: Derived from Lyons and Olsson (1973); Lu and Turco (1994); Millan *et al*. (1997); Kossman *et al*. (1999)

Process 1: offshore advection of pollutants: Observations (e.g., Lyons and Olsson, 1973; Lalas *et al*., 1987; Klemm *et al*., 1998) suggest that in early morning urban pollutants may be advected offshore by land breezes/downslope winds where they remain in a layer above the stable surface layer established over cold waters. These pollutants may then be advected across the city later in the morning when sea breezes become established. On a larger scale, Daum *et al*. (1996) have observed well defined pollutant layers between 0.3 and 2 km above the surface extending up to 1000 km offshore from source regions in the northeastern USA.

Process 2: lofting of pollutants in sea/lake breeze front and injection into inversion layer: By noon, surface heating over land is responsible for the development of upslope winds, growth of the convective mixed layer inland and the inland progression of the sea breeze circulation. At the sea breeze front, pollutants may be lofted and carried seaward in the light sea breeze return flow layer. Offshore subsidence may permit these pollutants to be recirculated in the sea breeze regime (Lyons and Olsson, 1973). In regions of complex coastal terrain, sea breezes and upslope flows often develop simultaneously and hence there may be no clearly defined sea breeze front at which lofting of pollutants may occur (e.g., Los Angeles Basin – Ulrickson and Mass, 1990; Lu and Turco, 1995; LFV – Steyn and McKendry, 1988).

Process 3: advective venting: The ABL tends to follow surface terrain. Consequently, over steep terrain, the predominately horizontal wind 'may blow through' the ABL carrying pollutants with it. Advective venting in the upper Rhine Valley region creates elevated pollutant layers of ~400 m depth and has been associated with both slope winds (a process similar to (5)) and the basic large-scale flow (Kossmann *et al*., 1999). This process also appears to be significant in the transport of pollutants from the coast towards Sao Paulo and then coastward again in an elevated layer (Bischoff-Gauss *et al*., 1998).

Process 4: undercutting of mixed layer by advancing sea breeze: Intrusion of cool, dense marine air over a coastal plain can produce an elevated pollutant layer by undercutting the polluted mixed layer. This process has been observed in the Los Angeles Basin (Blumenthal *et al*., 1978; McElroy and Smith, 1993) and is thought to be responsible for inland ozone fumigation over inland Israel (Dayan and Koch, 1996). In the LFV, propagation of a shallow coastally trapped disturbance northward along the California and Oregon coasts into British Columbia has been shown to produce the same effect (McKendry *et al*., 1997).

Process 5: injection of pollutants into inversion layers by slope flows: Local thermotopographic circulations (sea breezes, slope flows, valley winds) are often characterized by light 'return flow' aloft in order to maintain continuity (Sturman, 1987). On slopes, this provides a mechanism for polluted air to be injected horizontally into inversion layers. Layers developed in this manner are thought to be important in the Los Angeles basin (Lu and Turco, 1994; 1995) and along the east coast of Spain (Millan *et al*., 1997).

Process 6: mountain venting: When strong mountain-induced updrafts are able to penetrate vertically through the capping inversion, pollutants may be injected high into

the free troposphere where elevated pollutant layers are formed. These layers may then be transported back across the basin in the large-scale flow. In the Los Angeles Basin context, this is called the 'chimney effect' and has been investigated in modelling studies (Ulrickson and Mass, 1990; Lu and Turco, 1994; 1995). It has also been observed over the Iberian peninsula (Millan *et al*., 1997), while a modelling study suggests that it is an important process affecting the air pollution meteorology of Mexico City (Fast and Zhong, 1998).

Process 7: evening stabilization: The final stage in the diurnal sequence shown in Figure 5(a) has been referred to as stabilization (Lu and Turco, 1994). In this process, rather than evolving into a classic stable surface layer with RL aloft (as shown in Figure 1(a)), stabilization of the ABL in the presence of blocking mountains may instead be a dynamical process whereby available potential energy in the afternoon mixed layer induces vertical motion along slopes and injection of polluted air into the inversion layer aloft (Lu and Turco, 1994; 1995). In two-dimensional model simulations, Lu and Turco (1994) demonstrate that for coastal blocking mountains, the afternoon horizontal pressure gradient force directed towards the mountains is approximately balanced by the convective turbulent friction. However, when surface heating diminishes in late afternoon, turbulent friction no longer balances the pressure gradient force and the warmer air in the mixed layer is free to move upslope and to be inserted into stable layers aloft. This process appears to explain the evening development of elevated aerosol layers observed over the eastern Los Angeles Basin by Wakimoto and McElroy (1986).

During anticyclonic conditions (and particularly in coastal regions), atmospheric subsidence in the free troposphere is an important ongoing process responsible for lower tropospheric warming and development of inversion layers. Within such an environment elevated layers of pollution become more stably stratified (Millan *et al*., 1997) and may be brought towards the surface where they have the potential to be intercepted by the growing mixed layer. In Figure 5(a) this process is represented by the progressively lower layers from inland to offshore. Subsidence is particularly important over the Iberian peninsula where strong convection in the thermal low over the central peninsula is compensated by strong coastal sinking motions (~10–15 cm s^{-1}) which bring elevated pollutant layers generated by mountain venting and slope flow/sea breeze effects towards the surface. Subsequently, they may be recirculated through the system on timescales of the order of 2–3 days (Millan *et al*., 1997).

b Convection: In the absence of coastal or orographic effects, convective activity in the ABL is also capable of venting pollutants either into or above the capping inversion layer to form elevated pollutant layers. A summary of these processes is presented schematically in Figure 5(b) and described below.

Process 8: convective debris in the capping inversion layer: Thermal updrafts (TU) in the convective mixed layer are regions of buoyant air of up to 1–2 km in diameter with vertical velocities that may reach 5 ms^{-1} or more (Stull, 1988). When the tops of thermals rise into the statically stable air of the entrainment zone they may become negatively buoyant and sink back down into the mixed layer, a process known as penetrative

convection (Stull, 1988) . During this process pollutants may be left trapped in the capping inversion layer giving rise to an elevated layer of pollutants. In the Los Angeles Basin this is referred to as the 'convective debris' mechanism (Edinger, 1963; McElroy and Smith, 1993).

Process 9: cloud venting: Stronger thermals may overshoot the entrainment layer and produce active clouds that permit venting of ABL air directly into the FT (Stull, 1988). Ching *et al*. (1988) demonstrated this process using an airborne UV-DIAL (Ultra-Violet Differential Absorption Lidar) to identify O_3 and aerosol structures over North Carolina. Their observations indicate that horizontal layers of pollutant develop by evening at heights of ~2000 m from the increasingly tilted remnants of clouds ('cloud debris' – CD). Clouds that develop over mountainous terrain may also be responsible for venting pollutants (Kossmann *et al*., 1999).

Process 10: low-level convergence of winds: Convergent (C) near-surface winds provide a second mechanism by which vertical motion can be initiated over noncomplex terrain. However, most observations of this process are derived from regions of complex or coastal terrain. For example, observations and modelling studies (Lu and Turco, 1995) in the Los Angeles Basin show the development of elevated pollutant layers within and above the capping inversion in the vicinity of the San Fernando and Elsinore convergence zones. In the Athens region, convergence between the sea breeze and opposing winds lofts pollutants up to 2000 m and represents an important venting process (Klemm *et al*., 1998; Svensson and Klemm, 1998). Similarly, over Mexico City, surface convergence near the centre of the basin produces strong vertical motion that effectively vents pollutants from the ABL (locally referred to as 'basin venting' or the 'stove-pipe effect' – Fast and Zhong, 1998). Perhaps most striking is the strong convection initiated over the Iberian pensinsula in summer by convergent flow over elevated terrain (see further discussion below). This flow is responsible for injecting aged pollutants from Madrid and the coast into the FT to heights of 5000 m where they form layers and contribute to long-range transport (Millan *et al*., 1997).

Process 11: urban heat island effect: It is possible that large cities themselves may induce vertical motion (by virtue of urban heat island-induced convection) that is capable of injecting pollutants into elevated layers (Lehning *et al*., 1998). To date there are few observations that document this process.

Processes 1–11 depicted in Figure 5(a and b) may occur alone or in a variety of combinations depending on a host of site-specific factors (e.g., the presence of water bodies, the height and distance from shoreline of orography, the prevailing synoptic environment). However, evidence from the studies presented here suggests that in urbanized regions of complex coastal terrain such processes are commonplace, and in conditions conducive to photochemical smog formation are responsible for the development of complex and dynamic multiple layers of pollutants.

c Synoptic-scale processes and long-range transport: Mechanisms of ABL–FT pollutant exchange depicted in Figure 5(a and b) generally give rise to layers of pollutants within or immediately above the inversion capping the ABL. When

convection is strong, or topography high, pollutants may also be injected into the middle troposphere. Once in the FT, pollutants then have the potential to be transported relatively long distances within synoptic-scale weather systems. Evidence from major field campaigns in a variety of contexts now supports the view that pollutants emanating from the boundary layer (including photochemical pollutants) may be transported relatively long distances while preserving distinct layer structures. Detailed investigation of the complex pathways that result is an important aspect of several ongoing European Commission-sponsored projects in the Mediterranean region (Millan *et al*., 1997). There, it appears that venting mechanisms are responsible for tropospheric O_3 anomalies detected over the region by satellite (Fishman *et al*., 1990) and possibly for elevated O_3 concentrations as far away as the Canary Islands (Millan *et al*., 1997).

Several studies have also detected pollutant plumes downwind of continents (e.g., Daum *et al*. 1996; Jonquieres *et al*. 1998; Tyson and D'Abreton, 1998). For example, during NARE (the North Atlantic Regional Experiment) plumes rich in urban pollutants (including O_3 and fine aerosol) were observed over the North Atlantic at distances up to 1000 km from source regions in the northeastern USA. Typically, these plumes were observed as broad well defined layers at altitudes between 0.3 and 2 km above the surface (Daum *et al*., 1996; Fast and Berkowitz, 1996). During the same observational programme Kleinman *et al*. (1996a; 1996b) found these layers to be markedly influenced by the temperature structure of the atmosphere and in particular the location of inversions. Most anthropogenically derived plumes were found to occur at an altitude of less than ~5000 m. This finding is consistent with observations of other surface-derived plumes, notably those from biomass burning. For example, in a study of summertime ozone and aerosol distributions over eastern Canada, Browell *et al*. (1994) noted numerous elevated layers of O_3 and aerosol at altitudes less than 4 km. These were linked to forest fires as far afield as Alaska.

Synoptic-scale processes also strongly influence development of continental-scale pollutant plumes in subtropical regions. Over southern Africa, a predominantly stable anticyclonic environment tends to inhibit vertical exchange processes and stratifies the atmosphere into persistant layers (Tyson *et al*., 1996). As a result, not only is layering of pollutants the norm, but also pollutants may be recirculated horizontally over considerable distances on timescales of days to tens of days. Within this regime a deep aerosol 'haze' (consisting of aeolian dust, industrial emissions and products of biomass burning) capped by a strong subsidence inversion at about 500 hPa (~mid-troposphere) may undergo complex recirculation patterns and ultimately contribute to continental plumes over the Atlantic and Indian Oceans (Tyson and D'Abreton, 1998). Over northern Africa quite different synoptic-scale effects have been observed. There, an O_3 and precursor-rich Harmattan layer resulting from biomass burning reaches elevations of 3–4 km where it interacts with the intertropical convergence zone and may be transported as far as South America (Jonquieres *et al*., 1998).

In summary, once vented into the FT, O_3 and other pollutants may be transported long distances by synoptic-scale systems, thereby influencing large-scale tropospheric chemistry and radiative properties and potentially contributing to ground-level concentrations at remote sites. Perhaps most interestingly, at considerable distances from the source, pollutant loadings tend still to be dominated by distinct layer structures, this time reflecting the larger-scale stratification of the atmosphere.

3 Inventory of layers

Despite a mounting literature on elevated pollutant layers, few statistics have been compiled on even their most basic characteristics (e.g., elevation, depth, frequency of occurrence, chemical signature). This largely reflects the short-term nature of field campaigns during conditions conducive to the formation of pollutant layers. Browell *et al*. (1994) have attempted to address at least some of these questions by assessing the contribution of particular air mass sources to the vertical profiles of O_3 and aerosol observed by airborne UV-DIAL over central and eastern Canada. On the basis of 22 aircraft missions (6 July–15 August 1990), the incidence of particular air mass types (characterized by combinations of enhanced or reduced ozone and aerosol concentrations) was identified for six tropospheric altitudes ranges (2 km intervals). For example, plumes from forest fires were most often observed below 4 km and represented only 10% of the tropospheric depth. Of the plumes observed 60% had elevated O_3 concentrations (> 20% above background). In contrast, stratospheric intrusions were observed on 68% of the missions flown and were found to be the major influence on the tropospheric O_3 budget over eastern Canada. Over 40% of the depth of the atmosphere between 4 and 8 km displayed enhanced O_3 and low aerosol scattering associated with intrusions.

Our own research in the LFV over several summers provides a rare opportunity to describe basic characteristics of elevated pollutant layers in a region of urbanized complex coastal terrain. In all, 105 vertical O_3 profiles were examined for the presence of elevated ozone layers (identified using the definition in section IV.1 above). Data sources and general results of the layer inventory are shown in Table 1. An important caveat is that results were strongly biased towards conditions conducive to the development of elevated pollutant structures (i.e., daytime, anticyclonic conditions) and towards the lower troposphere. Most profiles (79%) extended through only the lower troposphere (tethersonde and aircraft) while 50% incorporated only the ABL (i.e., tethersonde profiles). Not surprisingly, profiles extending through the entire troposphere (Atmospheric Environment Service (AES) observations) had a high incidence of the occurrence of at least one layer (95% profiles) and also multiple layers (81%). Of profiles associated with only the lower troposphere, 45% had elevated ozone layers present and few displayed multiple layering.

Table 1 An elevated layer inventory for the Lower Fraser Valley, British Columbia by data source

Data source	Year	Number of profiles	Number with layers	Multiple layers
AES	1993	22	21	18
Tethersonde	1993	38	18	2
	1994	13	6	1
Aircraft	1995	21	7	1
	1996	11	6	0
Total		**105**	**58**	**22**

Note:
AES refers to the Atmospheric Environment Service of Environment Canada.

Layers were classified into four basic types according to the height at which they were observed and an assessment of likely formation mechanisms. These types are summarized in Table 2 while basic statistics associated with layer structures are presented in Table 3. In summary, elevated O_3 layers were observed throughout the troposphere. Lower tropospheric layers tended to be shallow, confined to distinct inversions and exceeded background concentrations by the greatest amount. Middle and upper troposphere layers tended to be deeper, less likely to be associated with inversions and were less prominent in terms of exceedance of background O_3 concentrations. These results are broadly consistent with what might be expected from consideration of the major sources of pollutants and the mechanisms of layer development described in sections IV.2.a and IV.2.b. For example, in urban regions, elevated O_3 layers near the surface are associated with a rich surface source of precursors that can photochemically produce O_3 concentrations well above background values. When associated with processes (sea breezes, convective activity, slope winds) that drive pollutants into shallow inversions (e.g., capping inversion) very distinct layers which significantly exceed concentrations above and below may result. In contrast, pollutants driven higher into the lower troposphere (e.g., by mountain and cloud venting) are likely to be distributed more diffusely and give rise to deep layers (e.g., a 'deep haze') characterized by lower concentrations and perhaps capped by a mid-tropospheric subsidence inversion.

Chemistry of layer structures provides further important clues to their origin and history. However, little is known of the detailed chemistry of layers, nor even the systematic relationship between aerosol and O_3 concentrations within elevated layer structures. With respect to the latter, field studies suggest that when pollutants are associated with an anthropogenic ABL origin, concentrations of aerosol and O_3 both tend to exceed background values (e.g., Ching *et al*., 1988; McKendry *et al*. 1997). In contrast, layers associated with biomass burning typically show high aerosol concentrations but O_3 concentrations may vary markedly depending upon plume age and nature of the fire (Browell *et al*., 1994). Finally, stratospheric intrusion layers have a signature marked by very low aerosol concentrations and high ozone concentrations (Browell *et al*., 1994).

Results presented in this section suggest that layering of pollutants is a characteristic feature of the troposphere, particularly during anticyclonic conditions in regions of urbanized, complex or coastal terrain. The morphological and chemical attributes of these layers are also shown to differ considerably according to their origin and history. Understanding of such differences is essential to investigating the likely impact of elevated layers on tropospheric chemistry and radiative properties as well as the effects on ground-level concentrations of down-mixing from elevated layers.

4 Down-mixing from elevated layers: assessing impacts

In complex or coastal terrain, distinct and persistent pollutant layers have been shown to develop preferentially in the lower troposphere, where they may be advected horizontally and lower further due to large-scale subsidence. This creates potential for layers to be intercepted by the growing mixed layer or be re-entrained into local circulations. Consequently, pollutants from the previous day may be mixed downward and

Table 2 A typology of elevated layers over the Lower Fraser Valley, British Columbia

Layer type	Description	Location	Formation	Occurrence	Characteristics
Type 1	Elevated layers within the PBL: 1) Nocturnal residual layer 2) Daytime decoupled layer	Above ground but below the height of the daytime mixed layer	Result of suppressed near-ground turbulence from surface-based inversion	Diurnal occurrence linked to solar forcings	Ability to transport boundary layer ozone with little loss Strong potential to affect ground-level concentrations
Type II	Inversion top layers or fumigating layers	From the base of the capping inversion to 200–300 m above May be as low as 300 m a.s.l. close to ocean or as high as 2000 m at ridge top	Interaction of convective debris, upslope venting and marine undercutting	Daily, may persist longer during episode conditions	Concentrations often exceed those within the mixed layer Potential to fumigate back down through the mixed layer
Type III	Deep haze layers	From above inversion top to the height of the 'closed' LFV circulation Approx 1000–4000 m a.s.l.	Upslope ridge-top venting trapped by elevated subsidence inversions	May persist for days Exist on same time scale as synoptic anticyclone that causes the elevated inversions	Haze of this depth often associated with highly polluted areas, i.e., Los Angeles Basin Not likely to affect ground-level ozone
Type IV	Free tropospheric layers 1) Stratospheric origin 2) Boundary layer origin	From above the height of the 'closed' LFV circulation up to the tropopause Approx. 4–10 km a.s.l.	Synoptic-scale advection of either boundary layer biomass burning plumes or stratospheric injections	Can last for weeks due to extended lifetime (up to 90 days) of free tropospheric ozone Possible seasonal dependence	Layers are indicative of widespread free tropospheric ozone pollution Very unlikely to impact surface ozone in the LFV

Table 3 Summary of layer characteristics by layer type for Lower Fraser Valley, British Columbia

Type	Number observed	Average height of ozone (max.) (m)	Average layer depth (m)	Average ozone above background (ppb)	Inversions
Type I	21	490	176	45	17 of 21, usually top and bottom of layer
Type II	34	830	173	59	32 of 34, usually bottom of layer, sometimes on top also
Type III	7	3440	860	24	2 of 7, inconclusive occurrence
Type IV	23	5640	630	30	13 of 23, usually bottom of layer

contribute to ground-level concentrations in perhaps unexpected locations. Understanding of processes of layer evolution and down-mixing is therefore essential to accurate prediction of ground-level O_3 concentrations.

In the Los Angeles region, McElroy and Smith (1993) used a combination of trajectory/isentropic analysis (showing when and where the mixed layer could intercept an elevated layer) and comparison of ozone diurnal cycles at surface monitors (identifying unusual peaks and the scale of down-mixing enhancement) to demonstrate that down-mixing from elevated layers enhanced ground-level concentrations by up to 30–40 ppb in the San Bernadino and Riverside areas.

A more sophistocated approach was adopted by Neu *et al*. (1994) to investigate the impact of early-morning down-mixing from the RL in Switzerland. A semi-empirical transilient turbulence model (Stull, 1993) was used to estimate that O_3 mixed down from the RL contributed 50–70% to the maximum concentration at the surface the next day. Transilient turbulence is a nonlocal form of turbulence closure well suited to applications in the convective mixed layer where the stability of individual air parcels is not dependent on local lapse rates. In this approach, unknown quantities at one point (i.e., mixing coefficients for, say, ozone) are parameterized using values of known quantities from many points in the vertical dimension (e.g., wind speed, temperature). The same method was used by McKendry *et al*. (1997) to investigate the impact of down-mixing from both the RL and an elevated layer created by undercutting associated with a coastally trapped disturbance. This elevated O_3 layer (highlighted in Figure 6(a)) was observed in late morning at an elevation of 600–1000 m and was associated with an inversion layer that was intercepted by the growing mixed layer at about midday (Figure 6(b)). The effect of down-mixing as predicted by the transilient turbulence model for two simulations beginning 0700 Pacific Standard Time and 1200 PST is shown in Figure 7(a and b). Predicted 1300 PST and 1500 PST ozone profiles based purely on vertical mixing processes and assuming no advection, deposition or photochemical production are denoted by the solid lines. Differences between the initial profiles and modelled profiles therefore represent the effects of vertical mixing. Both panels suggest that vertical down-mixing alone played an important role in contributing to ground-level concentrations observed in both the morning and early afternoon. Model results are consistent with the observed variations in ground-level concentrations (Figure 7(c)). These show a steep increase (9.55 ppb hr^{-1}) immediately after sunrise associated with down-mixing from the RL, followed by a second rapid increase in concentrations in late morning associated with down-mixing from the elevated pollutant layer.

Although clearly useful, both the isentropic (McElroy and Smith, 1993; McKendry *et al*., 1997) and simple transilient turbulence approaches (Neu *et al*., 1994; McKendry *et al*., 1997) are seriously limited by their dependence on availablility of frequent vertical profiles and, more importantly, their neglect of chemistry and advective effects. Both approaches treat O_3 as an inert pollutant and therefore ignore important chemistry that may occur during down-mixing. For example, O_3 mixed downward into an NO-rich mixed layer (e.g., from fresh morning emissions) may be rapidly destroyed and not contribute significantly to ground-level concentrations.

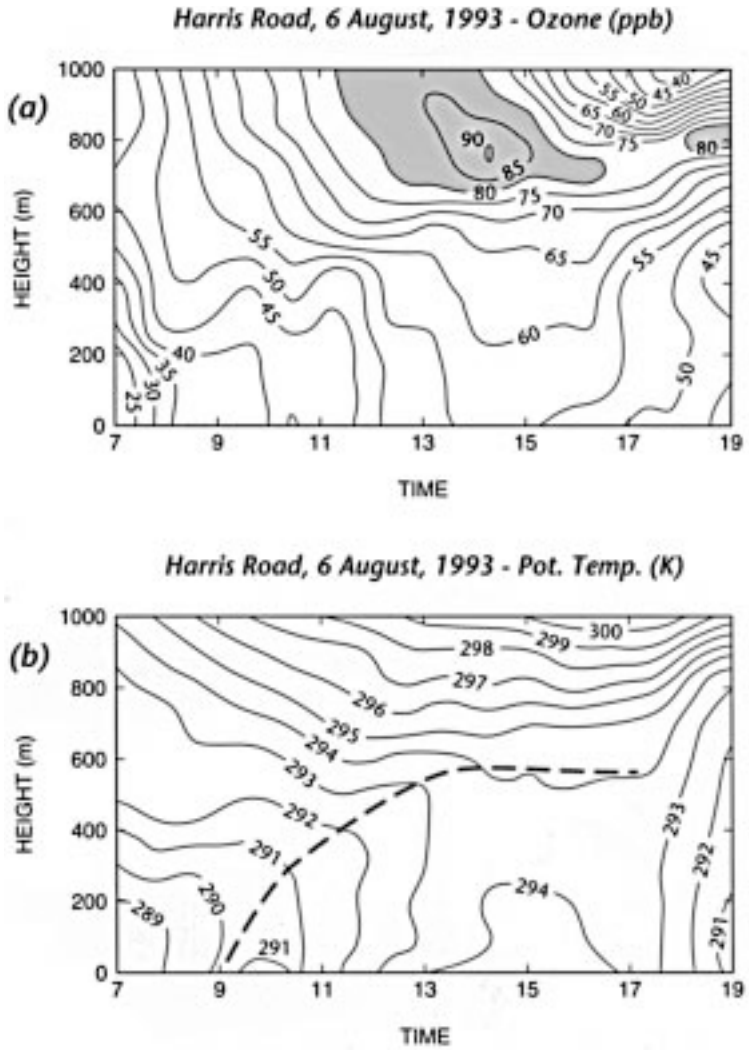

Figure 6 Time-height plots showing isopleths of: (a) ozone concentration; and (b) potential temperature based on tethersonde profiles from the Lower Fraser Valley, British Columbia. In (b) the growing mixed layer is denoted by a dashed line and appears to intercept the elevated ozone layer evident in (a) from 1100 to 1700 LST
Source: From McKendry *et al*. (1997) with permission of Elsevier Science

V Discussion and conclusions

Elevated tropospheric layers of O_3 (and other pollutants) have been demonstrated to be a characteristic feature of the air pollution meteorology of virtually all regions of urbanized complex and/or coastal terrain in which studies of the vertical structure of the lower troposphere have been conducted. The propensity for pollutants to form into distinct layers appears to be a consequence of the nature of ABL–FT exchange processes

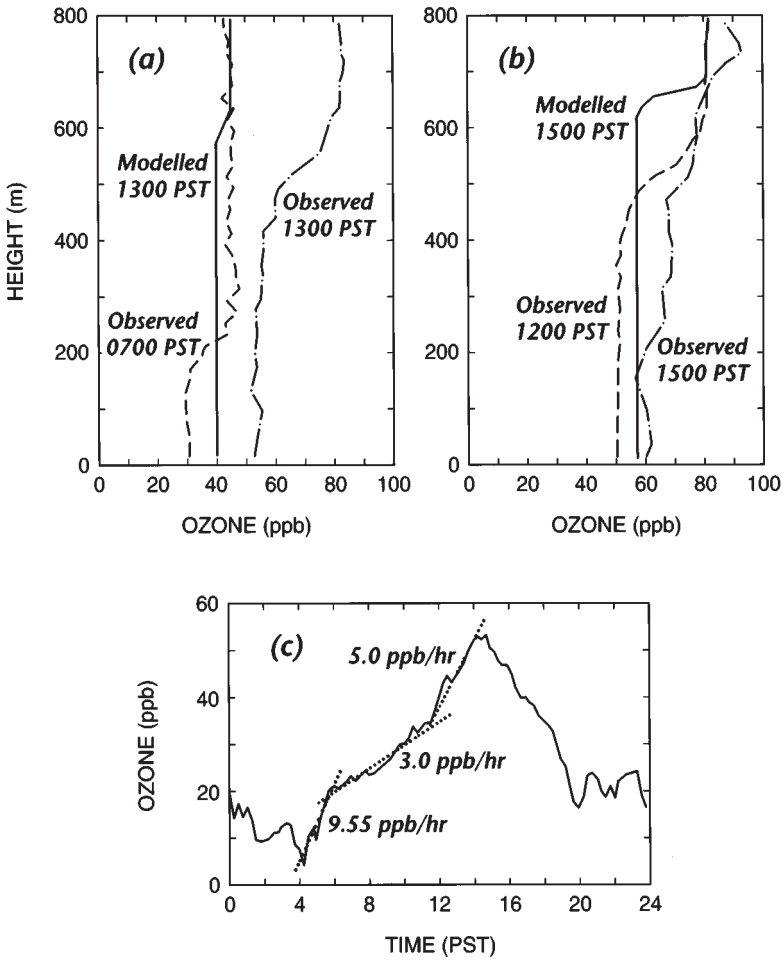

Figure 7 The modelled effect of vertical down-mixing on boundary layer ozone concentrations for the case shown in Figure 6. The transilient turbulence modelled is initialized at (a) 0700 LST and (b) 1200 LST to simulate the rapid down-mixing and resulting steep rises in ground-level concentrations observed 0400–0700 LST and 1200–1400 LST in (c). In (a) and (b) the differences in modelled and observed profiles at 1300 PST and 1500 PST respectively can be attributed to the effects of advection and chemical production. The differences between modelled and initial profiles can be attributed to vertical mixing
Source: From McKendry *et al*. (1997) with permission of Elsevier Science

(many of which inject pollutants into inversion layers) and the natural tendency for tropospheric stratification. Once in the FT, pollutants may contribute to long-range transport and influence tropospheric chemistry and radiative properties. Lower tropospheric layers may also be intercepted by growth of the daytime mixed layer and thereby contribute to ground-level concentrations. These processes of ABL–FT exchange are accentuated in regions of coastal or complex terrain where local thermo-

topographic circulations such as the sea breeze and slope winds, and other orographic effects, enable pollutants to be vented from the ABL.

Although much has been learnt from observational and modelling studies about the structure of elevated pollutant layers and the mechanisms responsible for their development, considerable scope for further research remains. Of most urgent need are studies addressing the following:

1) *Budgets*: ABL–FT exchange processes provide an important yet ill-defined sink for ABL pollutants (thereby venting the ABL of pollutants detrimental to human health) and provide a source of radiatively and chemically active constituents for the free troposphere. Although attempts have been made to quantify these exchanges (Lehning *et al*., 1998) considerable effort is needed to define more precisely the magnitude of the various exchange processes outlined in section IV.2 in a variety of physical settings.
2) *Chemistry*: Available technology has created a focus on elevated layers of O_3 and, to a lesser degree, aerosol. However, in order to determine the age and history of layers, as well as their potential impact if mixed to the ground, measurements of the detailed chemical composition (especially the nitrogen chemistry) of layers are necessary. This implies an urgent need for cheap, efficient instruments for vertical sounding of the lower troposphere (e.g., the NO_2 sensor developed by Pisano *et al*., 1997).
3) *Vertical mixing*: Down-mixing of pollutants from elevated layers enable aged pollutants to contribute to mixed-layer concentrations on subsequent days. Detailed understanding of this process is crucial to development of parameterizations that might be included in air quality models. Attempts to develop parameterizations for nocturnal depletion of O_3 from the RL provide a useful starting point (Neu, 1995).
4) *Climatology*: To date, observations have tended to be *ad hoc* (i.e., short-term field campaigns focused on conditions conducive to photochemical smog development). Detailed analysis of routine vertical soundings of pollutants is required in order to develop an unbiased climatology of layer structures for a variety of physical settings.
5) *Modelling*: Approaches that are time dependent, three-dimensional and incorporate complex chemistry hold the greatest promise for accurate prediction and improved understanding of the impact of elevated layers on ground-level concentrations. Three-dimensional mesoscale models such as those applied by Lu and Turco (1995), de Wekker *et al*. (1998) and Fast and Zhong (1998) are capable of resolving complex layer structures. However, rather than using passive tracers in a Lagrangian particle dispersion model (LPDM) to track pollutant pathways, such models urgently require detailed photochemistry. Although mesoscale models that incorporate photochemistry are available (e.g., Svensson and Klemm, 1998) considerable scope remains for their application to the problem of elevated layer structures.

Myriad processes have been identified that give rise to a quite dauntingly complex vertical structure of pollutants in regions of urbanized complex, coastal terrain. This complexity is at odds with widely held views about the distribution of pollutants near the ground and poses a challenge for observationalists, theoreticians and modellers alike. However, understanding of ABL–FT exchange processes and their accurate rep-

resentation in models is essential to the improvement of regional air quality models (and, consequently, the policy decisions derived from them). Recognition of the three-dimensionality of pollutant distributions is an important first step, while considerable progress in the research areas defined above is possible with innovative application and extension of existing techniques.

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