Measurements of upward turbulent ozone fluxes above a subalpine spruce-fir forest

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Abstract. High rural concentrations of ozone (O₃) are thought to be either stratospheric in origin, advected from urban areas, or photochemically generated locally as a result of natural trace gas emissions. Ozone is known to be transported vertically downward from the above-canopy atmospheric surface layer and destroyed within stomata or on other biological and mineral surfaces. However, here we report winter-time eddy correlation measurements of vertical O₃ flux above a subalpine canopy of Picea engelmannii and Abies lasiocarpa in the Snowy Range Mountains of Wyoming that indicate anomalous upward O₃ fluxes. Upward fluxes of 0.5 μg m⁻² s⁻¹ (11 kg km⁻² day⁻¹) were routinely measured during the 1991-92 winter season. Decreasing O₃ concentration from several hours to several days that relate to increasing positive O₃ flux magnitudes and visa versa, suggest O₃ may be temporarily stored in the snow base.

Introduction

Forest ecosystems play a role in the uptake and destruction of tropospheric O₃. This role and the tropospheric O₃ budget in remote forested ecosystems is uncertain [Chameides and Lodge, 1992]. Ozone deposition, rapid during the growing season and slower during winter months [Wesely, 1983], is retarded further by surface snow cover [Stocker et al., 1995]. Our data show the unexpected effect of snow cover on O₃ fluxes above a subalpine spruce-fir forest. In the presence of below-canopy surface snow they reverse direction from negative (downward) to positive (upward) [Zeller and Hahn, 1994]. Positive O₃ fluxes attributed to vertical entrainment of clean air from aloft have been measured by aircraft [Lenschow et al., 1982] and modeled [Gao and Wesely, 1994] in the upper atmospheric boundary layer. Measurements of negative vertical O₃ profiles above forested canopies have lead to 'counter-gradient' O₃ flux claims assuming O₃ only deposits to the Earth's surface [Fontan et al., 1992; Enders, 1992; Denmead and Bradley, 1985]. Galbally and Allison [1972] reported wintertime upward ozone fluxes (1.6 μg m⁻² s⁻¹) over fresh snow based on gradient measurements at 1807m in SE Australia.

Snowy Range hourly O₃ concentrations average 45 to 60 ppb year round [Wooldridge et al., 1994], and are typical of clean high altitude rural sites [Wunderl and Gehrig, 1990]. The above-canopy diurnal O₃ concentration at this location does not exhibit the large day/night maximum/minimum pattern typical of urban, photochemically dominated air masses at any time during the year [Wooldridge et al., 1994]. However, below-canopy, 3 m, summertime O₃ concentrations have a predominant day/night pattern: minimum values can drop to 10 ppb at night. Ozone concentrations appear to be horizontally uniform in the surrounding area: simultaneously O₃ concentrations near Centennial, WY, 8 km southeast, during 1990 were within 1-2 ppb of those we measured at 3 m height and values measured at a U.S. EPA National Dry Deposition Site (NDDN) 10 m height, 400 m southwest of our Brooklyn Lake tower site during 1993 were within 1 ppb [Wooldridge et al., 1994].

These positive O₃ flux measurements are unusual and deserve a critical examination. Here we describe the experiment and present the results of measured O₃ fluxes, concentrations, and summarized meteorological data collected during five periods in 1992. These periods contrast the O₃ flux difference between winter (snow cover) and summer (no snow cover) and capture the spring and autumn O₃ flux directional transitions.

Methods

Site

Data were collected at the Brooklyn Lake tower site situated in an Engelmann Spruce - Subalpine Fir forest opening approximately 30 meters in diameter. The site is within the U.S.D.A. Forest Service’s Glacier Lakes Ecosystem Experiment Site (GLEES) area in the Snowy Range of the Medicine Bow National Forest, WY. The GLEES complex is described by Musselman [1994]. The 29 m Brooklyn Lake tower (base elevation 3,186 m, 41° 22'N, 106° 14.5'W) is approximately 3 km southeast of the Snowy Range ridge (3,460 m average elevation). The average forest stand height is 17 m with representative displacement height, d, 11.7 m and roughness length, z₀, 1.7 m. The terrain within 1 km of the tower slopes +2.5% from west to east and -9.7% from north to south. This site is relatively complex for eddy flux experiments, however concurrent measurements of momentum and sensible heat fluxes provided reasonable values. Fitzjarrald and Moore [1992] found scalar flux measurements in non-homogeneous regions were robust and representative of the upwind footprint. Upwind terrain in the predominant wind direction, west-northwest, is forested with a flat +2.2% slope for at least 1 km.

Flux Measurements

Ozone concentration and flux data presented were collected in 1992 during five distinct periods: April 16-26 with 1 m snow cover representing the subalpine winter environment; April 28 - May 4, beginning transition period with rapid snow melt; May 7-18, the transition period during the final days of spring snow melt; July 2-8, a subalpine summer scenario; and September 30 - October 7, during the autumn to winter transition.

The eddy correlation system [Zeller et al., 1989] used to measure O₃, sensible heat, and momentum fluxes, O₃ concentrations, temperature and wind speed was employed at 23 m (6 m above canopy) on the Brooklyn tower. Standard meteorological sensors are permanently mounted at 10 and 29 m for routine GLEES measurements [Musselman, 1994]. The essential sensors for O₃ flux measurements are the uvw Gill anemometer and the chemiluminescence ambient air monitor (CAAM1) [Ray et al., 1985]. The CAAM1 was continuously calibrated using a TECO49 commercial UV adsorption instrument. Ambient air was sampled from the 23 m height through a 25 m length, 1.6 cm diameter teflon tube. The intake system lag time, t₀, was typically 2.4 s. A Gill uvw anemometer was used in place of a sonic anemometer for its greater durability in harsh alpine weather. The 13 Hz O₃ eddy deviations, c' = c - <c> ( <c> : 3 minute recursive filter average
concentration) and turbulent wind components $u'$, $v'$ and $w'$, are multiplied then averaged over half-hour sampling periods [McMillen, 1986] to obtain the vertical flux, $F_c$ (mg m$^{-2}$ s$^{-1}$, equation 1) after a vector coordinate rotation for the $\bar{w} = 0$ streamline:

$$F_c = \bar{w}(t-t) c(t)$$  \hspace{1cm} (1)

Here, negative $F_c$ indicates downward flux. Sensible heat and 03 fluxes.

Results

The eddy correlation measurements show consistent upward daytime O$_3$ fluxes during two snow-covered winter periods and downward fluxes during the growing season with the absence of snow cover. Half-hour average upward O$_3$ fluxes exceeded 0.5 mg m$^{-2}$ s$^{-1}$ (11 kg km$^{-1}$ day$^{-1}$) during April 14-27, 1992. These values are the same magnitude as the downward fluxes measured during July 1992 at the same location. Sign-change shifts in daytime O$_3$ flux movement patterns occurred during the 13-day May 6-19, 1992 sampling period snow-melt was completed, and again during the 8-day period in autumn when snow returned. There are several examples when nighttime O$_3$ flux does not cease as might be expected. On these occasions, lapse rate and wind data indicate neutral stability which allows for continued turbulent transport. Figs. 1 through 3 show O$_3$ concentrations, O$_3$ fluxes.

Neutral stability micrometeorological statistics for wind, temperature and O$_3$ are fairly consistent from period to period and equivalent to results from other field studies. For example $\alpha_{u} u_{w}$ was consistently 1 $\pm$ 0.2 compared to 1.3 for flat terrain. Dimensionless wind shear, $\bar{u} = k z / u_{w}$ ($u_{w} / \bar{u}_{w}$), was consistently 1.1 $\pm$ 0.3 where $u_{w} = -\bar{w}'w'$ was calculated from the momentum flux. There are no aberrant values in Table 1 to indicate a sampling problem with either the sensors, the sampling system or the tower configuration.
fluxes and vertically integrated time rate of O₃ change for three of the five multi-day periods given in Table 1.

Table 1 summarizes the meteorological and O₃ data. Midday meteorological values are representative averages between 10:00 and 15:00 MST, the diurnal hours of greatest O₃ flux activity. Total O₃ flux was obtained by integrating half-hour values commencing midnight each day. The maximum daily deposition value, -23 mg m⁻², on Julian day (JD) 190 compares in magnitude to the maximum upward flux, 19 mg m⁻² on JD 113. In addition to the presence of snow, ambient temperature appears to affect O₃ flux direction. Between 5 to 10 °C, O₃ fluxes can be either up or down, below 5 °C they are mostly positive, and above 10 °C they are mostly negative. Ozone flux direction is neither effected by vertical wind speed or direction nor horizontal wind direction; both would indicate a terrain induced bias.

Fig. 1, April 14 - 27, 1992 (JD 106-117), shows the day-to-day consistency of the upward O₃ fluxes. Temperatures ranged from 10 °C to -9 °C during this period. Ozone fluxes reached 0.6 µg m⁻² s⁻¹. The April 29 - May 4, 1992 (JD 119 - 126) period (Table 1) shows a decrease in O₃ flux after JD 123. This change was preceded by a sharp drop in O₃ concentration associated with a simultaneous jump in O₃ flux followed by sustained lower wind speeds. Temperatures ranged from -1 (occurred briefly midnight JD 123) to 13 °C. May 6-19, 1992 (JD 127-140), covers the period snowmelt ended and the daytime O₃ flux direction switched from upward to downward. Ozone fluxes remained positive to negative during this period but remain predominately negative after JD 138. Temperatures ranged from -5 to 16 °C (below zero values were brief nighttime excursions on JD 131-2) Fig. 2, July 2-9, 1992 (JD 184-191), shows the typical negative O₃ fluxes that occur during growing seasons. The downward diurnal flux pattern was briefly interrupted on JD 189 when it rained 0.3 mm. This is the only incident when positive O₃ flux was directly correlated with a precipitation event. Similar brief summertime events have been reported by Enders [1992] and Kelly and McTaggart-Cowen [1968].

Prior to JD 278 daytime temperatures ranged from positive to negative during this period but remain predominately negative after JD 138. Temperatures ranged from -5 to 16 °C (below zero values were brief nighttime excursions on JD 131-2) Fig. 2, July 2-9, 1992 (JD 184-191), shows the typical negative O₃ fluxes that occur during growing seasons. The downward diurnal flux pattern was briefly interrupted on JD 189 when it rained 0.3 mm. This is the only incident when positive O₃ flux was directly correlated with a precipitation event. Similar brief summertime events have been reported by Enders [1992] and Kelly and McTaggart-Cowen [1968].

Temperatures during this period ranged from 1 to 19 °C but remained below 7 °C on JD 189. Fig. 3, September 29 - October 8, 1992 (JD 274-281), shows the transition from negative daytime O₃ fluxes to positive fluxes. During this period, temperatures dropped below 0 °C and RH increased from 30 to 80% as O₃ fluxes turned positive. Based on meteorological data it is likely snow flurries started JD 278 with snow accumulating on the ground by JD 279. Prior to JD 278 daytime temperatures ranged from 3 to 17 °C.

Discussion

Upward fluxes suggest either surface or canopy emissions of O₃ and/or in the case of complex terrain, horizontal and/or vertical advection of O₃. The potential contributions of local O₃ production (or destruction), R, and advection below 23 m can be roughly estimated from the measured data by vertically integrating the equation for O₃ conservation from the surface to measurement height. Using the average wind streamline

\[ \frac{\partial c}{\partial t} + \nabla \cdot (w'c') = - \nabla \cdot (D \nabla c) + R + \nabla \cdot (c \nabla q) \]

(1)

where \( w'c' = 0 \), assuming \( w'c' = 0 \), and neglecting molecular diffusion gives equation 2.

\[ \frac{\partial c}{\partial t} = \frac{\partial (D \nabla c)}{\partial z} + \frac{\partial (c \nabla q)}{\partial z} \]

(2)

As seen in Figs. 1 - 3 the vertical flux (second term, equation 2) is at least an order of magnitude greater than the local time rate of change (first term) hence the local time rate of change does not significantly contribute to the vertical flux. If horizontal advection (third through fifth terms) were insignificant, the positive vertical fluxes would be due to either locally generated O₃ (last term) or vertical advection term which was canceled to obtain equation 2. Given the presumed lack of O₃ precursors in this wintertime scenario it is unlikely O₃ is generated locally and vertical advection does not seem a likely explanation given the lack of correlation between flux direction and \( \pm w' \). (Table 1). Horizontal advection is an unlikely contributor based on measurement comparisons between our site, the NDDN site and the Centennial, WY site, suggesting the horizontal gradient terms are also very small. This leaves R indicating either \( w'c' \) is not zero as assumed and/or the existence of a negative vertical O₃ profile at measurement height.

Atmospheric boundary layer O₃ usually requires nitric oxide (NO), nonmethane hydrocarbons and ultraviolet energy to drive its photochemical production [Olszewski et al. 1994]. Forests are sources of natural nonmethane hydrocarbons, which are known precursors for O₃ production and a possible cause of higher rural O₃ concentrations. Concentrations of nitrous oxide (N₂O) above typical ambient levels have been measured under and above the snow cover at GLEES [Sommerfeld et al., 1993]. Since the same microorganisms which generate N₂O also generate NO [Hutchinson and Davidson, 1993], the possibility of an NO source during winter months exists, however the likely concentration is very low.

![Figure 1](image1.png)  
**Figure 1.** Half-hour average O₃ concentration (dashed) in parts per billion (ppb), O₃ flux (solid lines) and vertically integrated time rate of O₃ change (+) in µg m⁻² s⁻¹ for the period April 14 to 27, 1992.

![Figure 2](image2.png)  
**Figure 2.** Half-hour average O₃ concentration (dashed) in parts per billion (ppb), O₃ flux (solid lines) and vertically integrated time rate of O₃ change (+) in µg m⁻² s⁻¹ for the period July 2 to July 9, 1992.

![Figure 3](image3.png)  
**Figure 3.** Half-hour average O₃ concentration (dashed) in parts per billion (ppb), O₃ flux (solid lines) and vertically integrated time rate of O₃ change (+) in µg m⁻² s⁻¹ for the period September 30, 1992, to October 7, 1992.
Galbally and Allison [1972] speculated O₃ might absorb on fresh snow without total destruction, however we suggest adsorption is more likely. Laboratory experiments indicate O₃ adsorption to ice reaches saturation quickly (< 1 s) with no further uptake [Dlugokencky and Ravishankara, 1992]. Using 50 ppb O₃ (9 x 10¹⁰ molecules cm⁻²), an O₃ to ice sticking coefficient of 0.001 (range 0.01 - 0.0001) [Dlugokencky and Ravishankara, 1992] and 3 x 10⁸ cm⁻² s⁻¹ for O₂ molecular velocity, we estimate the rate of O₃ adsorption to snow to be 2.7 x 10¹⁶ molecules cm⁻² s⁻¹. Taking 9 x 10¹⁵ cm⁻³ as the specific surface for fresh snow [Sommerfeld and Rocchio, 1993] and accepting O₃ saturation within 1 s, there are potentially 2.4 x 10⁹ O₃ molecules m⁻³ in a 1 m snow base. It would take 4.5 days (range 0.5 - 45 days) to expel this O₃ assuming a constant flux of 0.5 µg m⁻² s⁻¹. Larger downward O₃ fluxes are typically associated with higher O₃ concentrations as seen in Fig. 2. Fig 1, however, shows O₃ concentrations decreasing with increasing positive flux for several days, then decreasing with increasing concentrations for the next few days. On JD 122, a sudden drop in O₃ is associated with a sharp increase in upward O₃ flux. Given an equilibrium between ambient O₃ concentrations and ice surface saturation, this inverse behavior adds credence to the possibility O₃ is temporarily stored in the snow field and released by turbulent air interactions through the porous snow interface. The delineating factor for upward versus downward O₃ fluxes appears to be snow cover (and to a lesser extent) ambient temperature. Both are environmental factors that potentially affect stomatal function. The measured fluxes are usually diurnal in nature reflecting daytime turbulent O₃ mass transfer. Some measurements show continued but weaker upward O₃ fluxes during nights with strong winds. Tree physiology also appears to play a role as the spring and autumn transition between positive and negative O₃ fluxes occurs around 5°C, a minimum ambient temperature for conifer growth [Prentice et al., 1992].

Conclusions

The O₃ flux data measured by eddy correlation at the GLEES Brooklyn tower, Snowy Range, Wy, show reasonable summer growing season deposition (0.5 µg m⁻² s⁻¹). During winter and non growing seasons, upward O₃ fluxes were measured. The late winter upward fluxes are the same magnitude as the summer downward fluxes. As O₃ does not readily deposit on snow, the measured rate of O₃ deposition is expected to decrease during the winter but not reverse direction. The flux directional transition is apparently seasonal. The explanation for the upward O₃ fluxes remains unknown but suggest either: (1) the possibility of O₃ stored in the surface snow base; or (2) negative O₃ profiles above the forest canopy.

References


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