Cumulative Ozone Dose and its Variation with Height in an Herbaceous Canopy

Peter L. Finkelstein[1], Tilden P. Meyers[2], Donna B. Schwede[1], Alan W. Davison[3], Howard S. Neufeld[4], Seth Peoples[4], and Arthur H. Chappelka[5]

[1]Atmospheric Sciences Modeling Division, NOAA; in partnership with the U.S. EPA, Research Triangle Park, NC, 27711, USA

[2]Atmospheric Turbulence and Diffusion Division, NOAA, P. O. Box 2456, Oak Ridge, TN, 37830, USA

[3]School of Biology, University of Newcastle, Newcastle upon Tyne, NE1 7RU, England

[4]Department of Biology, Appalachian State University, Boone NC 28608, USA

[5]School of Forestry and Wildlife Sciences, 108 M. White-Smith Hall, Auburn University, Auburn AL 36849, USA

Corresponding Author: Donna B. Schwede, U.S. EPA, MD E-243-04, Research Triangle Park, NC, 27711 USA; schwede.donna@epa.gov Phone (919) 541-3255, fax (919) 541-1379

Abstract

Ozone profiles and sub-canopy turbulence were observed in a stand of cutleaf coneflower during a field study conducted in the Great Smoky Mountains National Park during the Summer of 2003. These observations were used to evaluate a higher-order sub-canopy diffusion and deposition model developed by Meyers and Paw U. The evaluation showed that the turbulence levels predicted by the model, and hence ozone, did not always agree with the observations, but also showed that turbulence levels measured at this forest-edge site were quite different from those expected for a normal well-developed boundary layer. As a proof-of-concept, the model was used to compute cumulative growing season dosage of ozone, on a leaf by leaf basis for the typical coneflower plant. The model predicted that the highest cumulative ozone dose would be in the lower to mid level leaves in the canopy, which is qualitatively consistent with observed patterns of visible injury.

Index terms: ozone, dose, exposure models, sub-canopy deposition

1. Introduction

Frequently, ozone concentrations are sufficiently high to cause visible injury to sensitive plant species. For example, in Great Smoky Mountains National Park (GSMP), a World Heritage site, about 25-30 species develop typical injury symptoms during most summers (Neufeld *et al*., 1992; Chappelka *et al*., 2003). Although there has been a great deal of research on ozone impact on crops, interest in its effects on native herbaceous species is relatively recent, and it is still not clear how ozone impacts their ecological fitness (Davison and Barnes, 1998). To understand pollutant impacts, it is helpful to know the ozone dose at the leaf level so that effects can be related to actual uptake. In this paper, we report on the second of two field studies conducted with the goal of better understanding the distribution, flux and dose of ozone in an herbaceous canopy. The results of the first, preliminary, study were presented in Finkelstein *et al* (2004; hereafter denoted as F-'04).

Cutleaf coneflower (*Rudbeckia laciniata* (L.)) is an edge plant that grows along the boundary between field and forest. It is abundant in the Purchase Knob area, Clingman's Dome, and other locations within the GSMP. Stands range in size from a meter to more than 20 meters across, and may run along a forest edge for hundreds of meters. The plant heights range from 1.5 to 2 meters. Flowering typically occurs in July and August. In this species, ozone injury symptoms start as patches of dull-red, mottled areas (stipples) between the veins of the upper surfaces of the lower leaves. The mottle may develop into tan or brown necrotic patches and the affected leaves senesce prematurely. As the season progresses, visible symptoms often spread

up the plant to the younger leaves and the floral bracts. In previous papers, we reported on the variation in symptom expression, genetic diversity within populations, stomatal conductance, and gradients in light and ozone within canopies (Chappelka *et al*., 2003; Davison *et al*., 2003, F-‘04). Data indicate that there is marked variation in the degree of injury exhibited by individual plants within and between populations that are relatively close to each other (Chappelka *et al*., 1997; Chappelka *et al*., 2003).

Observations of ozone concentration above a plant canopy, although easily measured, do not give a direct indication of ozone concentrations at the leaf surfaces or flux through the stomata. As plants develop from spring onwards and the canopy develops, the degree of ozone penetration into the canopy changes so that successive leaves are exposed over time to different combinations of ozone, light, temperature and humidity. Changes in the environment alter stomatal conductance resulting in a change in ozone flux. In addition, stomata respond to short-term environmental factors such as vapor pressure deficit and water stress; so conductance and flux may alter over time scales of hours to days independent of the ambient ozone above the canopy. The history of ozone flux and the cumulative ozone dose for any one leaf over its life span may be quite complex. Therefore, to try to understand the patterns of exposure symptom development and relate the physiological effects to ambient ozone at each leaf surface, it is necessary to determine the relationships between ozone above the canopy and ozone concentrations at each leaf surface. Our goal is to estimate the ozone dose to each leaf during its life and relate it to physiological effects.

Since the technology to measure flux to an individual leaf in the field has not been developed, we have to estimate the flux and dose with models of sub-canopy deposition. In an earlier study, (F-‘04) we reported on results from a brief field study conducted in 2002 in which we measured ozone profiles within and turbulence above the canopy, and compared those measurements with a sub-canopy deposition model. Here, we repeat that field program with an improved ozone profile system, an additional turbulence sensor located within the canopy, and extended field time that allowed for many more hours of observations.

This study extends the evaluation of the Meyers-Paw U (M-P) model as it applies to an herbaceous canopy that we initialized in F-‘04. (Meyers and Paw U, 1986; Meyers and Paw U, 1987; Paw U and Meyers, 1989) The model utilizes higher order closure theory to represent the wind and turbulence profiles. The M-P model also includes a radiation model to estimate the amount of light reaching each leaf, and a dry deposition model to estimate the flux of pollutant at multiple levels within the canopy. The model is evaluated by comparison to turbulence levels and ozone concentrations in the canopy. It is then used with inputs from a near-by air monitoring station to estimate the growing season cumulative dose of ozone at each leaf on an “average” plant.

2. Site Description

The study area was located within the Great Smoky Mountains National Park, an International Biosphere Reserve and World Heritage Site, which straddles the North Carolina-

Tennessee border, in the southeastern United States. The measurements were taken within the Park at the Purchase Knob - Appalachian Highlands Science Learning Center, (35.588 N, 83.074W), which is an area set aside for teaching and research in the south-eastern end of the Park. The Purchase Knob site consists of approximately 200 ha of high-elevation (1400 - 1500 m above MSL) forests and fields.

Measurements were taken in a stand of coneflower on the outside edge of a forest-field boundary, about 15 m from the well-defined edge of the forest. In the vicinity of the stand the terrain was quite level near the top of a ridge but sloped away steeply to the northeast within 100 meters. The forest was comprised of deciduous trees, approximately 30m high. The crown height of the forest was approximately 113± 3m (live crown ratio of 60%) (F-‘04) with a moderately dense understory so that wind flow through the forest was reduced, but not hindered completely.

The coneflower stand was very homogenous in composition and quite dense. The population had a mean height of 1.5 ± 0.3 m. Multiple observations of height and LAI were taken at five locations near our study area. The LAI of the stand at the time of the field study was 4.3 ±0.4. The mean LAI profile with height is shown in Figure 1. Further details on the site are given in F-‘04.

3 Instrumentation

3.1 Ozone

Ozone profiles were measured using a 2B Technologies, Inc. ozone monitor. This monitor works on the principal of UV absorption at 254 nm. The monitor was calibrated at the factory before the field program, and checked in our lab against a primary reference standard. Every four days in the field the instrument was checked for zero by putting a charcoal filter in the line, and adjusting the zero offset if needed. These adjustments were usually very small. The monitor was connected to a microprocessor controlled pump and valve system which sequentially sampled four inlet lines. All sample lines and valves were Teflon coated. Air was drawn continuously through the four lines to minimize lag time. To accommodate the response time of the instrument, which we measured to be approximately 35 seconds for a step change of 30 ppb, data from the first minute of sampling at each height were discarded. Each line was sampled for a total of three minutes, the last two minutes were considered valid data. Using this protocol, five profiles were collected each hour, and averaged.

In the field, our inlet lines (Teflon) of the same length were tied to a pole placed in a dense part of the stand. Inlets were set to four heights as shown in Table 1. Periodically the ends of the inlet lines were brought together to check for bias caused by any dirt or moisture in the lines. Any small differences were corrected numerically using level 3 as a reference.

3.2 Meteorological Instruments

Wind speed and turbulence measurements were made at two levels (Table 1). Above the canopy an R. M. Young model 81000 sonic anemometer was used. It was mounted in the coneflower stand, on a tripod tower 10 m from the ozone profile system. The manufacturer supplied internal shadow correction algorithm was used. An Applied Technologies Inc. (ATI) "V" style sonic anemometer was mounted about 0.3 m above the ground to measure flow and turbulence within the canopy. This is a special purpose sonic anemometer with a short path length (10 cm) designed for operation in these conditions. It is mounted on an 85 cm long horizontal tube so that it can be inserted into the spaces between the plants without damaging or disturbing the leaves.

Standard global, net, and Photosynthetically Active Radiation (PAR) measurements were made, along with temperature and relative humidity (in a non-aspirated shield). These instruments were also mounted on the tripod tower. The heights of the instruments are given in Table 1. While it would have been desirable to include additional instrumentation to obtain more detailed information about the surface gradients of temperature and humidity, the cost of additional instruments was beyond the scope of the project.

3.2.1 Transducer shadow correction

No published information was available for transducer shadow correction for the "V" style sonic. To develop an appropriate correction algorithm, the instrument was calibrated in the 3 meter square cross-section wind tunnel in EPA's Fluid Modeling Facility. Turbulence was

generated for calibration runs using a square lattice in the front of the test section. Turbulence levels were about 8% at the location of the sonic. The instrument was mounted on a large machinist's turntable so that its angle to the flow in the tunnel could be easily adjusted in 1° increments. Both horizontal and vertical shadowing were considered. Tests were conducted at 0.5, 1.0, and 2.0 m/s. Very low wind speeds of < 0.5 m/s, as were frequently observed within the canopy, could not be maintained in the wind tunnel. The transducer and support arm shadow correction algorithm developed from these tests is

$$U_T = U_{obs}\,[1.24 + 0.015(1 - 0.1\phi) - 0.08\cos(4\theta) + 0.053\cos(2\theta)] \qquad \textbf{(1)}$$

where U_T = Correct wind speed,

U_{obs} = observed horizontal speed = $(u^2 + v^2)^{0.5}$

θ = horizontal wind direction relative to the mount (0° = wind flow toward and parallel to the mount)

ϕ = vertical angle = $\tan^{-1}(w/U_{obs})$ in degrees. If $\phi > 10$ then $\phi = 10$, ie. ϕ must be between 0 and 10,

u, v, w = outputs from the three channels of the sonic.

Data from both sonics were collected at 10 Hz. in half-hour raw data files. The shadow correction was applied to the "V" style raw data files. After the experiment a 2-axis rotation algorithm (Wilczak *et al*., 2001) was applied to raw data files, then the first, second, and third moments and covariances of the wind vector were computed.

4. Data

Data were collected at the Purchase Knob site from July 30 - August 13, 2003. Ozone concentrations were measured continuously at four levels. Turbulence measurements were taken at two sonics and only during the day (due to the presence of feral pigs at night). This resulted in about 300 hourly average ozone concentration at each level and about 150 hourly averaged turbulence values for each sonic. Averaging methods and quality assurance procedures are described below.

4.1 Meteorological Data

To better understand the characteristics of flow and mixing above and within the coneflower canopy one may examine various measures of turbulence, the gradients between above and within the canopy, and relations between turbulence and ozone profiles.

4.1.1 Spectra

The nature of turbulence at the site is well illustrated by considering normalized power spectra. Rotated 10 Hz. data from the sonic anemometer mounted at 2.5 m were used for this analysis. Periods were selected when the stability was approximately neutral, as defined by $0.1 > z/L > -0.1$ where L is the Monin-Obukhov mixing length. Monin-Obukhov length and friction

velocity (u_*) were determined from measurements of heat and momentum flux using the upper sonic.

It should be recalled that this site is on the side of a mountain, and 15 m from a forest edge with trees up to 30m high (F-‘04). Thus these measurements are clearly not in a well developed boundary layer or in the constant-flux layer, but in a roughness layer. (A roughness layer may be defined as a surface zone of the atmosphere in which individual roughness element’s contribution to the turbulent field may be important (Arya, 1988).) Sampling periods were divided into three groups based on wind direction: wind blowing into the site from the side of the mountain, wind coming through the trees, or wind blowing parallel to the forest edge. As an example of a spectra taken when the wind was blowing into the site, consider Figure 2A. The spectra look fairly “normal” with u and v components having about the same energy and the expected - ⅔ slope at higher frequencies. The w component has much less energy at the lower frequencies. The dominant energy containing eddies in u and v have a period of 1 to 5 minutes, while the vertical eddies have less energy at a peak period of 0.05 to 0.4 minutes. For winds coming through the trees, the spectra are quite different (Figure 2B). The spectra are more peaked at the low frequency end, and have the characteristic dip in energy at mid-frequency (n = 0.01 - 0.05, or a period of 0.2 to 0.05 minutes) caused by absorption of energy by the trees (Kaimal and Finnigan, 1994). The peak of the energy spectra for u and v are at a higher frequency than they were for the first group. For winds more or less parallel to the trees, the spectra are quite distinctive (Figure2C). The energy in v is much less than in u, sometimes by a factor of 10. The trees on the edge of the forest seem to be channeling the flow (the u direction)

and damping out the energy perpendicular to the flow (the v direction). There is also some suggestion in the spectra that the dip in energy that is seen in flow through the trees is also present. The w spectra has the same maximum energy as the other w spectra, but doesn't peak until n = 0.1 (0.05 min), just before the inertial subrange. The average slope of the u spectra in the inertial dissipation range for all 10 neutral cases (all wind directions) studied is -0.92. For these spectra, in which we are plotting $f\,S(f)/u_*^2$ vs. n, (where n=f z/u) the slope should be -.67 (Kaimal and Finnigan, 1994). It would appear that within the roughness layer with trees and shrubs nearby, the atmosphere is dissipating energy at a faster rate than would be expected in a more "ideal" setting. The results of the spectral analysis suggest that mixing and diffusion will not be similar to a "normal" mixing process, and that models may have to be adjusted to compensate in settings like this one. Since this is a "real-world" setting, this may be a large issue in many atmospheric models.

4.1.2 Integral length scales and Taylor's hypothesis

Another way to consider the nature of turbulence at our site is to look at the integral length scale, Λ, and its relationship to other measures of turbulence. By Taylor's hypothesis, Λ should relate to the integral time scale, $\mathscr{T}$, as $\Lambda = u\,\mathscr{T}$ (Kaimal and Finnigan, 1994 - eq. 2.2). The integral time scale is the time over which the turbulence remains correlated and may be calculated as the time it takes for the autocorrelation of the velocity to decrease from 1 to 1/e. As an example, from the spectra on day 220, 13:00 (Figure 2A), we estimated $\Lambda_u \simeq 200$m and $\Lambda_w \simeq 20$m using the method shown in Kaimal and Finnigan, Figure 2.1. On the other hand, using the

autocorrelation values from the 10 Hz data we estimate $\mathscr{T}_u$ = 11 seconds and $\mathscr{T}_w$ = 1 second. The average wind speed was 1.4 m/s. Thus, our estimates for $\Lambda_u = 15.4 \neq 200$, and $\Lambda_w = 1.4 \neq 20$, i.e. the two methods give very different results. Note that the ratio of the errors is the same for u and w. Therefore, Taylor's hypothesis is not supported in this very rough boundary layer, as Kaimal and Finnigan suggested would be the case. This shows that the turbulent structure at our site is much less organized than it would be in a typical boundary layer with a clear fetch.

4.1.3 Wind and turbulence above and within the canopy

Wind and turbulence within the canopy are driven by energy transferred from above the plants. For a rough, relatively inhomogeneous layer a question is whether this transfer is regular and predictable. Comparison of wind speed and turbulence above and within the canopy may help to answer that question. Figure 3A is a scatter plot of mean wind speeds as measured by the two sonic anemometers for all the valid half-hour measurement periods. The plot shows a strong relationship between winds above and within the canopy with a ratio of approximately 0.16, implying that there is strong coupling between the two layers. Figures 3B, C, and D show similar plots for the components of turbulent energy, u'^2, v'^2, and w'^2. The relationship is not quite as strong, possibly because of the difficulty of measuring such small second moment quantities at the in-canopy level, possibly because the transfer of energy isn't as predictable. The ratios of energy within to above the canopy are 0.04, 0.09, and 0.02 respectively. These ratios are plausibly consistent with that for wind speed ($.16^2$), but different among themselves by a factor of two to four. Whether or not these differences are significant and repeatable is an open

question.

4.2 Ozone

The ozone profiling system ran continuously during the experiment, except for maintenance and calibration periods, and problems associated with a lightning strike. Data were carefully quality controlled. An independent audit of the ozone sensor was performed before and after the three week experiment. The readings from the top level of the profile system were compared daily to the State of North Carolina's permanent ozone monitoring station that was 50 m away.

4.2.1 Diurnal Cycle.

The average diurnal cycles of ozone at each level are shown in Figure 4. This figure shows several unique features. The diurnal cycle from the top level, just above the canopy, is a mirror image of what one would normally expect from a ambient diurnal ozone cycle. In most locations, both urban and rural, ozone is high during the day, and low at night; a consequence of the photochemical production of ozone. In this study, measured concentrations at the highest 3 levels are high at night, and low during the day. We hypothesize that during the night stable flow brings air rich in ozone from distant urban areas that has not been in contact with the ground and has very low NO levels into the mountain-top site. The ozone in this airmass has not been subject to scavenging by other pollutants, or removal by the surface. In the morning, as

turbulence increases, the air coming to the sensor has had more and more contact with the ground, and the ozone has been removed by deposition and titration so the ozone concentration decreases to a minimum. During the afternoon the photolytically generated ozone, both local and transported up the side of the mountain, starts to replenish the ozone in the air, which increases until dark when stability increases, removal mechanisms are reduced in effectiveness, and the ozone levels remain high.

Contrast this profile with that from the lowest level, 0.24m, which is near the bottom of the coneflower canopy. In this case the profile looks more like the "typical" profile from low-elevation sites, but for completely different reasons. This profile, we speculate, is a consequence of the mixing rate within the canopy. At night the mixing from above is very slow, so that the ozone at the lowest levels, which is being depleted through contact with the plants and ground, is not replenished at a rate fast enough to keep up with the depletion. As a consequence, levels are low within the canopy and the difference between above and below canopy ozone is high. During the day the mixing is enhanced. Even though the ozone above the canopy has a lower concentration, and dry deposition is enhanced by fully open stomata, the mixing is great enough to support ozone at a higher equilibrium concentration and the vertical gradients are smaller. Note that the peak occurs near noon, when heating is a maximum. The second level, 0.86m, is just within the canopy, and during periods of maximum mixing its levels are almost the same as those above the canopy.

Unfortunately we were not able to run the sonic anemometers at night, so this hypothesis

must await better field studies before data can be gathered to support or refute it.

4.2.2 Ozone Profile

To better understand the effects of mixing and deposition on the ozone profile within the coneflower canopy, average normalized ozone profiles were constructed. The profiles were normalized by the concentration measured above the canopy. Three profiles were constructed, corresponding to three blocks of time, night (20:00 - 05:00), morning (08:00 - 12:00), and afternoon (14:00 - 18:00). These profiles are shown in Figure 5, along with curves that approximate the profile shape. These curves were generated by the equation $y = a + b \log(z/H_c) + c (\log(z/H_c))^2$. Parameters for the lines shown in the figure are given in Table 2 for the three time periods.

At $z/H_c = 0.5$ the ozone concentrations are still 80% to 90% of their above canopy ($z/H_c = 1.3$) value, while they don't reach 50% of the above canopy value until $z/H_c = 0.15$ to 0.2. Considering the effect of time-of-day, we can see again that the most mixing and steeper profiles take place in the morning, and the least mixing of the ozone in the stand at night. Thus the mixing - or lack of it - at night dominates over the lower deposition that is expected due to stomatal closure. The diurnal cycle of deposition to the soil and other surfaces is not known.

5. Model Evaluation

To model the flow and deposition within the canopy we used the M-P higher-order

closure model on which we had conducted a preliminary evaluation (F - ‘04). A number of changes were made to the model to make it more numerically stable. These changes did not impact the output values. Despite the changes, the model frequently experienced problems when the wind speed was less than 0.5 m/s. With that limitation, and the available input data, we had 43 one-hour periods to model. To challenge the model, we can look at wind in the canopy, turbulence above and within the canopy, and ozone profiles.

5.1 Wind and Turbulence

The M-P model predicts wind speed and turbulence profiles which can be compared to measurements. For wind speed, our measurements above the canopy are used as model input, so only the lower measurements can be used for model evaluation. The average values of the observed and modeled wind speeds at 0.34m., along with the 95% confidence limits, are shown in Figure 6. While there are some slight, and perhaps insignificant variations from hour to hour, it’s clear that the model consistently underpredicts the wind speed at this level. While the observed wind speeds are very light, averaging 0.15 to 0.2 m/s, the modeled wind speeds are closer to 0.1 to 0.13 m/s.

Turbulent energy is not a model input, so the model’s predicted values can be compared to observations both above (Figure 7A) and within (Figure 7B) the canopy. In Figure 7A, we see that the model underpredicts by a factor of two to three for each hour, with the largest error occurring during the mid-day period when the turbulent energies are measured to be the largest.

Within the canopy (Figure 7B) the model does much better, and only slightly underpredicts during the early afternoon hours. However, the gradients of turbulent energy between the two levels are too large, implying too much loss of energy in the upper canopy. A summary of model - observation comparisons for other second and selected third moments is given in Table 3. In general, the model is low for u and v components, and high for w components.

5.2 Ozone

Model input requires ozone at the top of the canopy. This value came from level 1, so only levels 2-4 are available for the evaluation. For this analysis, levels 2-4 were normalized by the concentration at level one, and expressed as a percentage. Figure 8 presents box plots summarizing all the model outputs and observations by level. There are three box plots for model output and three for observations. Modeled ozone values are lower than the observed values at levels 2 and 3 by significant amounts. Observed values at level 2 were 95% of the reference height, while the model had much more ozone depletion, and a mean prediction of 70%. At level 3 observed values had only dropped to about 87%, while the model assumed that they would be about 65%. At the lowest level (level 4), which is only 25 cm lower than level 3, the model and observations agree quite well, with predicted and observed values of about 60%.

Figure 9 presents the mean hourly observed and modeled ozone concentrations. Results from levels 2 and 3 are consistent with those discussed above, although the model does seem to be doing better late in the day. For level 4 however, the good agreement in the mean values

(seen in Figure 8) seems to be due to some over prediction in the morning and evening, when observed values were very low, and under prediction during the late morning when the model slightly under predicted.

In summary, the model seems to remove the majority of the ozone at upper levels of the canopy, while our observations suggest that most of the ozone remains until quite close to the ground. It is tempting to relate problems with ozone deposition to some of the issues we noted with the models ability to predict turbulence in the canopy, and that may indeed be the case. But there are many processes at work in the model, such as stomatal, plant surface, and soil resistance which may play as big a part as mixing. Unfortunately we don't have the observations needed to support model improvement in these areas. Since observations of the individual resistances are very difficult, this will require a dedicated research project.

6. Total O_3 Dose

We can now use the sub-canopy deposition model, ever mindful of its strengths and weaknesses, to estimate the total dose to each leaf of an average coneflower plant over the growing season, which lasts from May until mid August. To run the model for this period requires the growth history of the plants as well as model input for the period.

6.1 Model Inputs

Observations of coneflower growth were made by one of us (Peoples) every week or two from the middle of May to the middle of August when the flowers set and growth stopped. The date of emergence of each leaf, its height, the height of the canopy and the LAI profile were noted on each visit. Observations were made on 5 to 10 plants in each of 5 plots in the vicinity of the experiment. Leaves were numbered on each plant from bottom to top with a maximum of 15 leaves. Table 4 summarizes the observations, giving for each leaf number, the mean, maximum, and minimum date of observed leaf emergence and the mean, standard deviation, maximum and minimum heights of those leaves across the different plants. Note that many of the upper leaves came out, on average, at nearly the same time, within the resolution limits of the observations, but that the date they appeared varied quite a bit from plant to plant.

Ozone concentrations and meteorological variables were obtained from the North Carolina air monitoring station at Purchase Knob, which was very close (approximately 50 m) to our study area. The observations were taken at 10 m. To simplify computations and keep the timescale consistent with the timescale of the plant observations, weekly averages of the input variables were estimated. Two sets of input variables were estimated for each week, an average daytime value (6 am to 8 pm), and an average nighttime value. The inputs developed for this modeling exercise are given in Table 5.

6.2 Computation of Leaf Dose

The M-P model predicts the ozone concentration and flux at 20 levels between the top of

the canopy and the ground, basing its calculation on a smooth leaf density profile. The dose to an individual leaf was assumed to be the difference between the flux above the leaf and the flux below the leaf. So, for example, if on a given date the average plant had three leaves out, the canopy was divided into 4 layers, with the height of the top and bottom of each layer determined by the leaf height. The dose to the top layer would be the difference between the flux at the top of the canopy and the flux at a level below the first leaf and above the second leaf. The same process is used for each leaf. The flux below the lowest leaf is assumed to go into the soil and the understory. The computation is done twice for each week, once for daytime, and once for night. The model output units for fluxes is ppb m/s, which was converted into μg - mole / m^2-s. The final dose per leaf is ΔFlux * seconds/week (day or night) * m^2/stem (i.e. 1/stem density). From our observations in the field, we estimated a stem density of 80 to 100 stems/m^2, and used 100 for this calculation. The final conversion is

$$\Delta F(\mu g - mole/week - leaf) = \Delta F(ppb\ m/s) 4.46 * 10^{-8} \frac{p}{p_0} \frac{T_0}{T} * 3.53 * 10^5 \frac{s}{week} * 10^{-2} \frac{m^2}{stem} * 10^6 \frac{\mu g}{g} \qquad (2)$$

where an ambient pressure of 850 mb. was assumed. At night we used $2.5*10^5$ rather than $3.53*10^5$ s/week. Cumulative dose for the growing season was the sum of the weekly day and night doses for each week.

6.3 Results

Total ozone dose (μg-mole/leaf) over the growing season (May 2 - August 18) as a

function of height and leaf number for the “average” coneflower plant are shown in Figure 10. The model predicts that the lower leaves receive the highest dosage, with leaves in the middle of the stand getting the maximum dose. The leaves at the top of the plant receive considerably less ozone than the lower leaves. This is a consequence of the time available to them to absorb ozone, and the dose for that layer having to be distributed among more leaves that crowd the highest layers. Over the growing season, (Figure 11) the lowest two leaves have the highest cumulative dose until mid-summer, when the third and fourth leaves, even though later emerging, overtake them. The upper leaves on the plant seem never to accumulate a very high dosage, in part because of their late emergence, and in part because of their density in the upper layer of the canopy.

We observed that ozone injury to cutleaf coneflower seems to occur most often, and most severely, in the lower to middle leaves of the mature plant. Chappelka et al (2003) noted that earlier in the season the most damaged leaf was Leaf #1 (lowest leaf), which is consistent with our results in Figure 11. The observations of leaf injury lends credence, in a qualitative way, to the approach we have taken to modeling total ozone dose on the leaf level.

7. Summary

In this study we measured ozone profiles within a stand of cutleaf coneflower, and made coincident turbulence measurements deep within the canopy. Comparison of these measurements with modeling results using the M-P sub-canopy model suggests that the model

has room for selective improvement. Some turbulence measurements are enough different from modeling results that it would suggest that reformulating the higher-order turbulence treatment might improve the results. Differences in the sign of the bias between the horizontal and vertical turbulent energy is especially interesting. However, there are other processes in the model that we are not able to measure or verify experimentally, and these processes may also be contributing to the outcomes we observe. We also note that, as shown in Sections 4.1.1 and 4.1.2, the turbulence at our study site was not at all typical of a well developed boundary layer. This difference could easily have influenced the comparisons between model and observations. It may be that more detailed inputs that include characterizations of on-site turbulence may improve model performance.

Using the M-P model with on-site observations of meteorology and ozone over the growing season, along with bi-weekly observations of plant growth and LAI, we have been able to compute the cumulative ozone dose, leaf by leaf, over the growing season. These results suggest that the highest cumulative dose occurs in the low to mid-canopy leaves. These results are in qualitative agreement with our observations of ozone injury on the plants in the study area. However these calculations have used limited input data, we've made a number of simplifying assumptions, and we know that the model isn't perfect. In fact, the model's tendency to over predict depletion high in the canopy means that the true dose may be even smaller near the top of the canopy and larger in the lower layers. In addition to improved accuracy, improvements in the application of the model to dose estimates might include higher resolution output, so that individual vertical layers could be assigned to individual leaves, hour-by-hour input of

meteorology and ozone, observations of drought and other effects on the photosynthesis rates of the plants, and the use of growth data from a population of individual plants, rather than an "average" plant so that a range of outputs could be developed. That being said, we have demonstrated that calculations of this nature are feasible, and that the results, at least qualitatively are reasonable. With better inputs, an improved model, and more through modeling, quantitative relationships between plant injury and cumulative dose should be possible.

8. Acknowledgments

We would like to thank National Park Service personnel Susan Sachs, Paul Super, and Jim Renfro from the Great Smoky Mountains National Park for their hospitality and assistance with this research, David Heist for his guidance in the Fluid Modeling Facility and David Brown who helped with the calibration of the sonic. This research was funded in part by the National Geographic Society, the U.S. Environmental Protection Agency, the National Oceanic and Atmospheric Administration (NOAA), the National Park Service (PMIS#66941) and the Graduate School at Appalachian State University. This paper has been reviewed and approved for publication by both the Environmental Protection Agency and the National Oceanic and Atmospheric Administration. Mention of commercial products does not constitute an endorsement for use by either agency.

9. Disclaimer

The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. This work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

Instrument	Height (m)
O_3 - 1	1.97 ± 0.01
O_3 - 2	0.86 ± 0.01
O_3 - 3	0.48 ± 0.01
O_3 - 4	0.24 ± 0.01
Sonic - 1	2.5 ± 0.05
Sonic - 2	0.34 ± 0.02
Rad/T/RH	1.3 ± 0.05
Plant Canopy	1.5 ± 0.3

Table 1. Instrument and Canopy Heights

Time	a	b	c
8 - 12 (morning)	100.21	0.64	-13.06
14 - 18 (afternoon)	98.35	7.09	-11.90
20 - 5 (night)	97.16	11.32	-11.92

Table 2. Parameters for model of average ozone profile in the canopy. The model is $O_3/O_{3max} = a + b \cdot \ln(z/H_c) + c \cdot (\ln(z/H_c))^2$.

Var.	Level	Summary
$u'w'$	2.5	Model is high by 50%
	0.34	Model is high by a factor of 2, correlation is poor, but note that $u'w'$ can change sign in the center of a canopy, so prediction is very difficult.
u'^2	2.5	Model is low by a factor of 2
	0.34	Magnitude of model is OK, but correlation is poor.
v'^2	2.5	Model is low by a factor of 2
	0.34	Model is low by a factor of 2 to 3
w'^2	2.5	Model is high by 50%
	0.34	Model is high by an order of magnitude
$u'w'^2$	2.5	Model is low by a factor of 5
	0.34	Model is high by a factor of 2, correlation is poor
w'^3	2.5	Model is high by a factor of 5 to 10
	0.34	Model is high by a factor of 2 to 4

Table 3 Summary of Model performance in predicting turbulence.

Leaf#	Obs.	Avg.Date	First	Last	Height (cm)	σ Ht.	Min Ht. (cm)	Max Ht. (cm)
1	60	5/24/03	5/20/03	5/27/03	48	9	29	63
2	51	5/27/03	5/20/03	6/20/03	54	8	36	79
3	45	6/6/03	5/27/03	6/20/03	68	11	44	92
4	38	6/21/03	6/3/03	7/15/03	84	12	54	105
5	39	7/2/03	6/10/03	7/16/03	97	15	60	127
6	39	7/12/03	6/20/03	7/16/03	109	17	68	135
7	39	7/14/03	7/7/03	7/16/03	117	19	71	148
8	39	7/16/03	7/7/03	8/8/03	123	18	81	156
9	40	7/19/03	7/7/03	8/8/03	130	20	82	165
10	29	7/16/03	7/15/03	8/8/03	130	20	82	164
11	18	7/17/03	7/15/03	8/8/03	137	17	107	165
12	7	7/22/03	7/16/03	8/8/03	148	6	137	154
13	5	7/16/03	7/16/03	7/16/03	151	6	144	160
14	2	7/16/03	7/16/03	7/16/03	156	8	150	161
15	1	7/16/03	7/16/03	7/16/03	151	0	151	151

Table 4 Summary of observations on leaf emergence date and height

Date	Canopy Ht	LAI	Solar Rad.	WS day	WS night	T day	T night	RH day	RH Night	O_3 Day	O_3 Night
5/20/03	55	4.7	600	1.5	1	16	12	65	80	43	43
5/27/03	60	4.7	600	1.5	1	16	12	65	80	60	60
6/3/03	70	4.2	550	2.5	1	19	17	70	99	50	50
6/10/03	76	4.8	500	1.5	1	20	18	75	90	39	39
6/17/03	89	5	700	2.5	1	18	12	80	85	45	55
6/24/03	100	5	700	1.5	1	20	16	75	90	60	60
7/1/03	105	4.7	600	3	1	17	15	90	95	35	35
7/8/03	118	4.8	600	1.5	1	20	17	85	95	44	44
7/15/03	140	4.5	650	2	0.8	20	18	80	92	58	62
7/22/03	150	4.5	700	2	1	18	15	75	90	48	52
7/29/03	155	4.5	610	1.25	0.75	19	17	85	97	42	42
8/5/03	155	4.2	415	1.5	0.9	18	17	85	95	50	60
8/12/03	155	4.2	465	2	1.5	19	18	85	95	50	50

Table 5 Model Inputs for Seasonal Dosage Calculation

References

Arya, S. Pal, 1988: *Introduction to Micrometeorology*. Academic Press, San Diego, CA. 307pp.

Chappelka, A. H., Renfro, J. R., Somers, G. L., Nash, B., 1997. Evaluation of ozone injury on foliage of black cherry (*Prunus serotina*) and tall milkweed (*Asclepias exaltata*) in Great Smoky Mountains National Park. *Environmental Pollution*, **95**, 13-18.

Chappelka, A. H., Neufeld, H. S., Davison, A. W., Somers, G. L., Renfro, J. R., 2003. Ozone injury on cutleaf coneflower (*Rudbeckia laciniata*) and crown-beard (*Verbesina occidentalis*) in the Great Smoky Mountains National Park. *Environmental Pollution*, **125**, 53-59.

Davison, A. W., Neufeld, H. S., Chappelka, A. H., Wolff, K., Finkelstein, P. L., 2003. Interpreting spatial variation in ozone symptoms shown by cutleaf coneflower, *Rudbeckia laciniata L.* *Environmental Pollution*, **125**, 6170.

Davison, A. W., Barnes, J. D., 1998. Effects of ozone on wild plants. *New Phytologist*, **139**, 135-151.

Finkelstein, Peter L., Alan W. Davison, Howard S. Neufeld, Tilden P. Meyers, and Arthur H. Chappelka, 2004: Sub-canopy deposition of ozone in a stand of cutleaf coneflower. *Environmental Pollution*. **131**, 295-303.

Kaimal, J. C. and J. J. Finnigan, 1994: *Atmospheric Boundary Layer Flows: Their Structure and Measurement*. Oxford University Press, New York, 289pp.

Meyers, T. P., Paw U, K. T., 1986. Testing of a higher-order closure model for modeling airflow within and above plant canopies. *Boundary-Layer Meteor*., **37**, 297-311.

Meyers, T. P., Paw U, K. T., 1987. Modeling the plant canopy micrometeorology with higher-order closure principles. *Ag. and Forest Meteor*., **41**, 143-163.

Neufeld, H. S., Renfro, J. R., Hacker, W. D., Silsbee, D., 1992. Ozone in the Great Smoky Mountains National Park: dynamics and effects on plants. In: Berglund, R. D. (Ed.), *Tropospheric Ozone and the Environment II.* Air and Waste Management Association, Pittsburgh, PA, pp 594-617.

Paw U, K. T., Meyers, T. P., 1989. Investigations with a higher-order canopy turbulence model into mean source-sink levels and bulk canopy resistances. *Ag. and Forest Meteor*., **47**, 259-271.

Wilczak, J. M., Oncley, S. P., Stage, S. A., 2001. Sonic anemometer tilt correction algorithms. *Boundary-Layer Meteor*., **99**, 127-150.

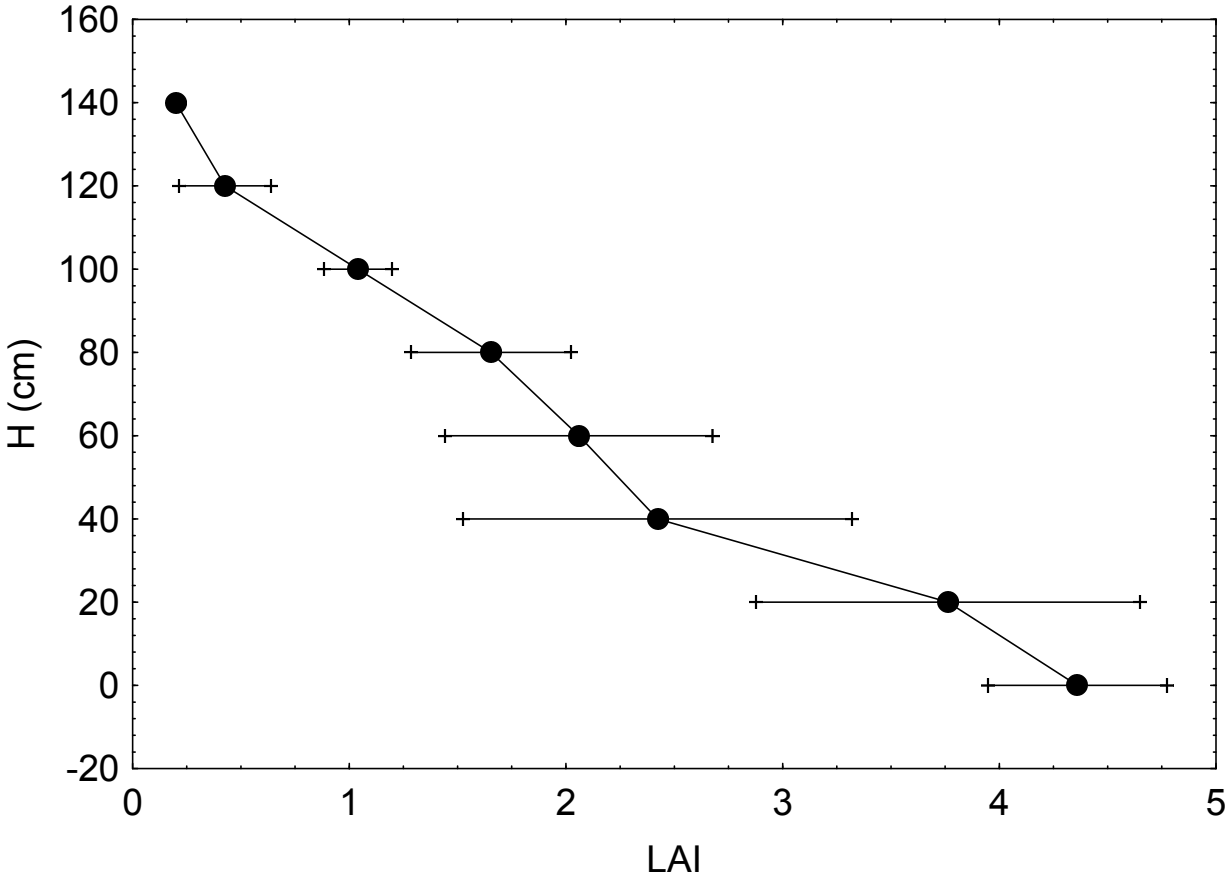

Figure 1. Mean LAI Profile for Coneflower Stand

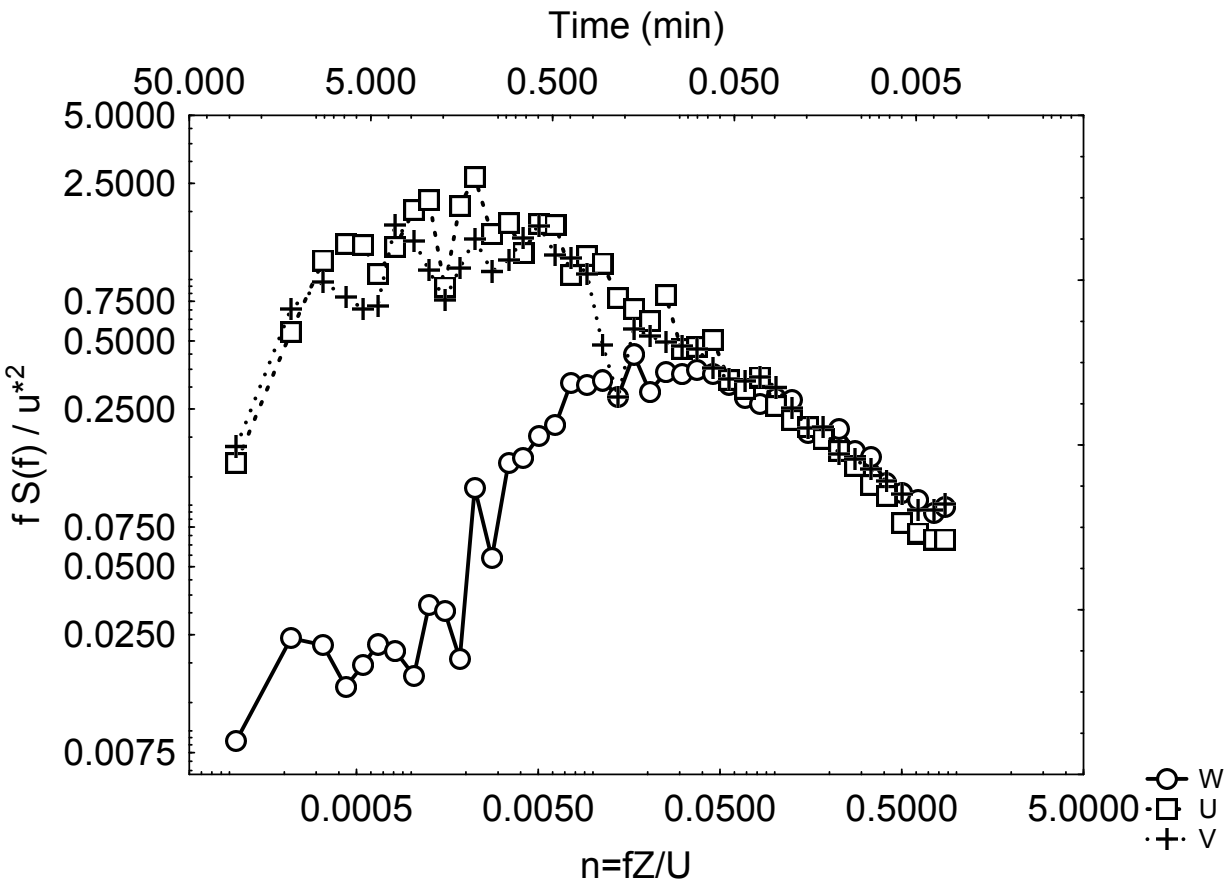

Figure 2A. Spectra with wind from the clear sector

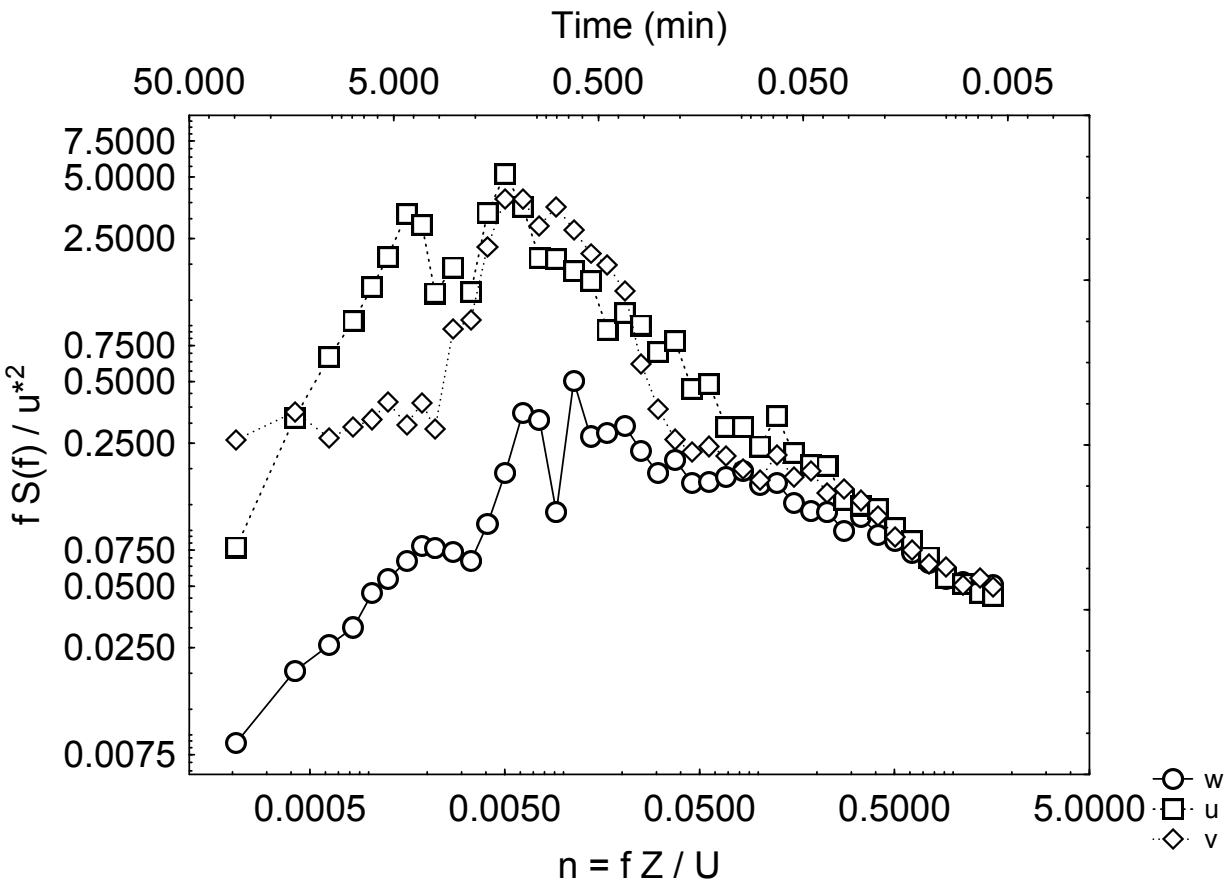

Figure 2B. Spectra with wind coming through the trees.

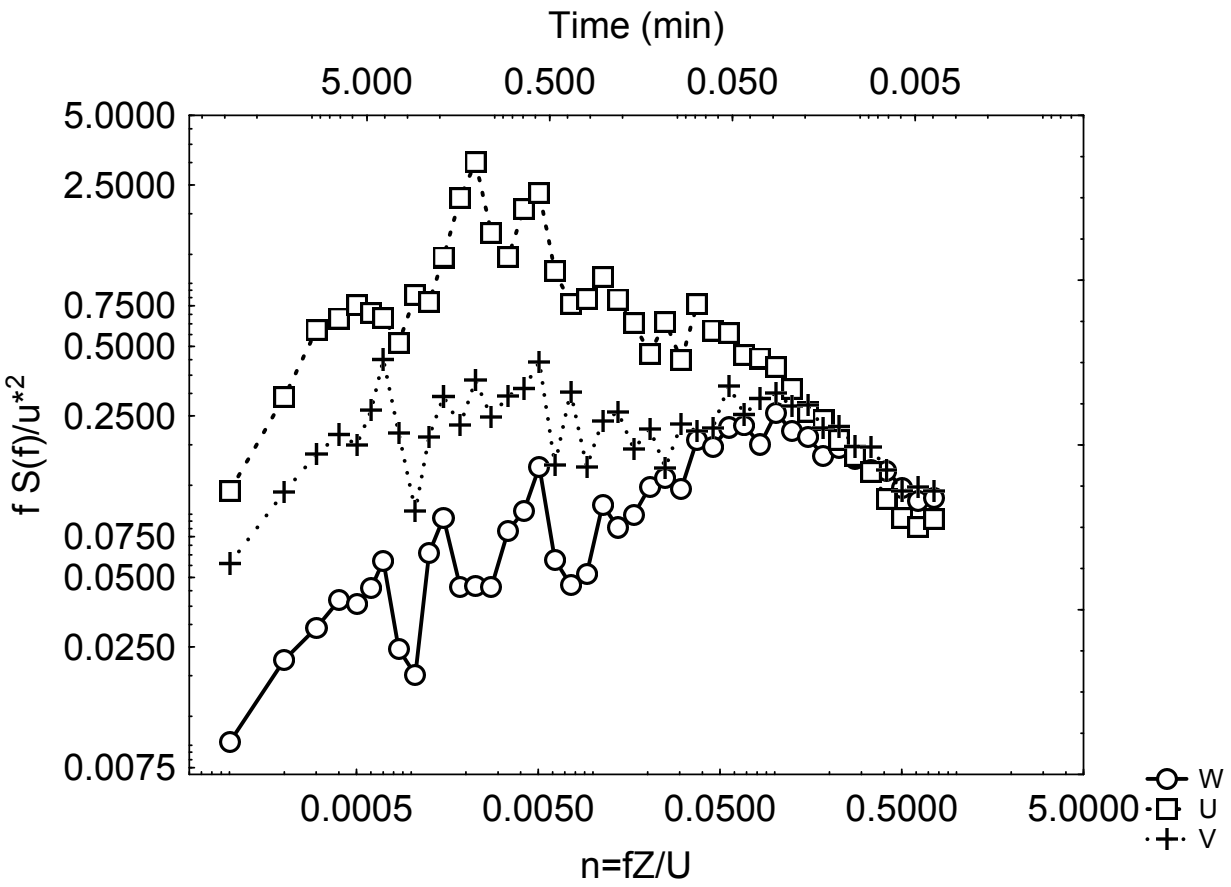

Figure 2C. Spectra with prevaling wind parallel to the tree line

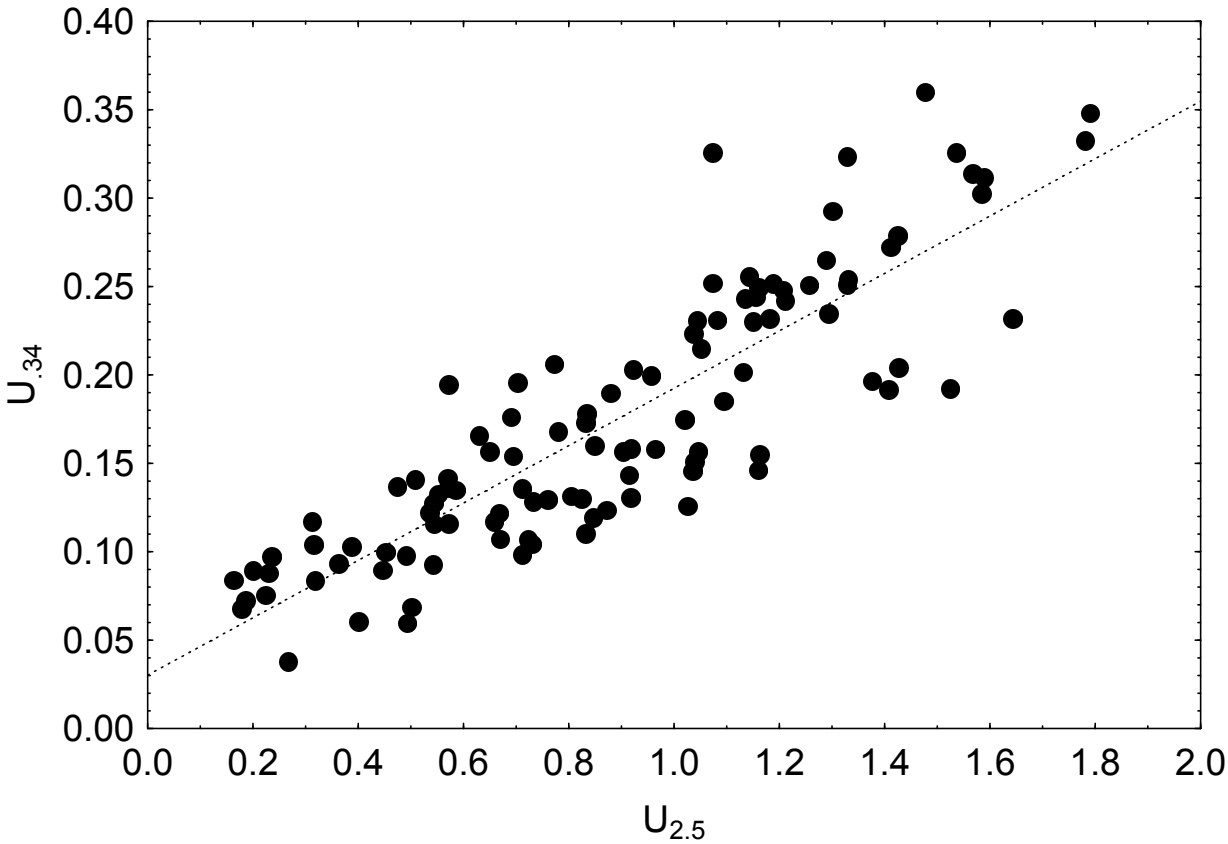

Figure 3A Wind speed above ($u_{2.5}$) and within ($u_{.34}$) the canopy. The RMS regression line is $u_{.34}=0.16u_{2.5}+0.03$

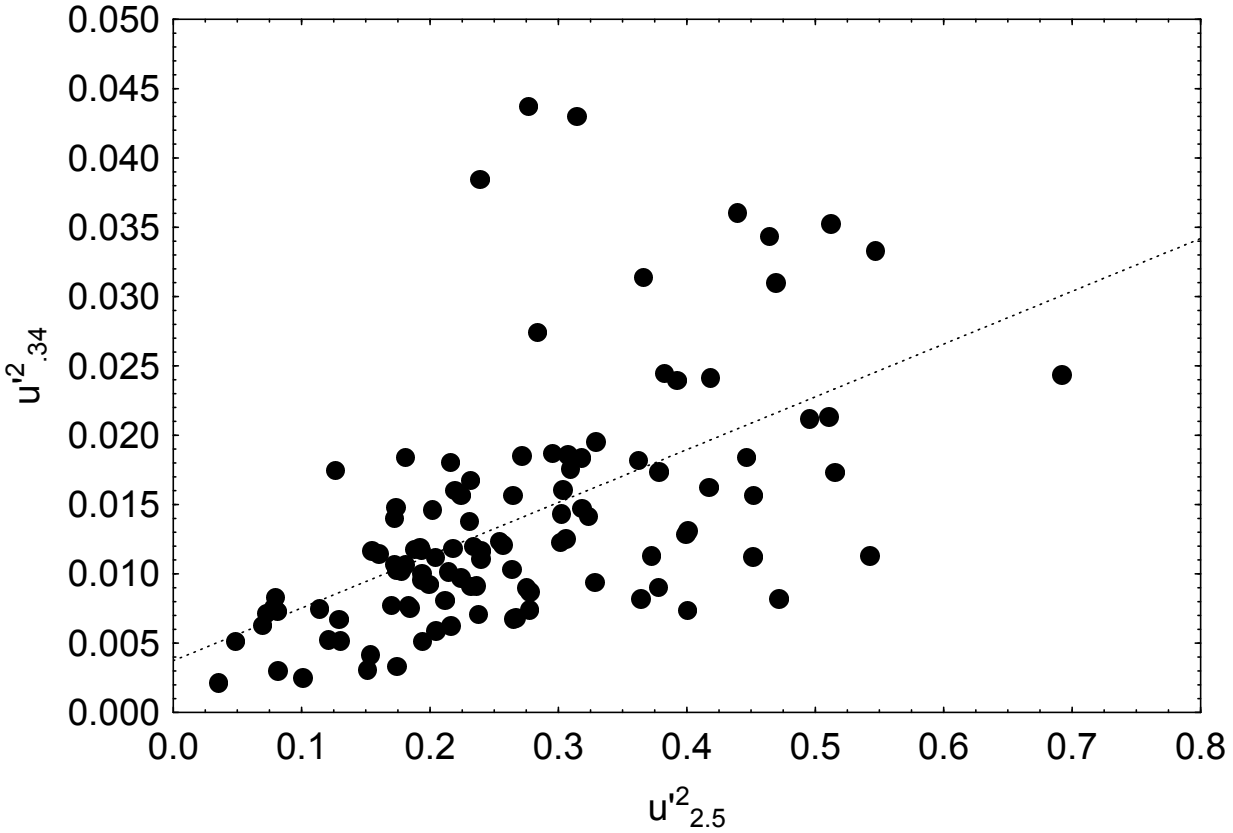

Figure 3B Turbulent energy parallel to the mean flow. $u'^2_{.34} = 0.04\ u'^2_{2.5} + 0.004$

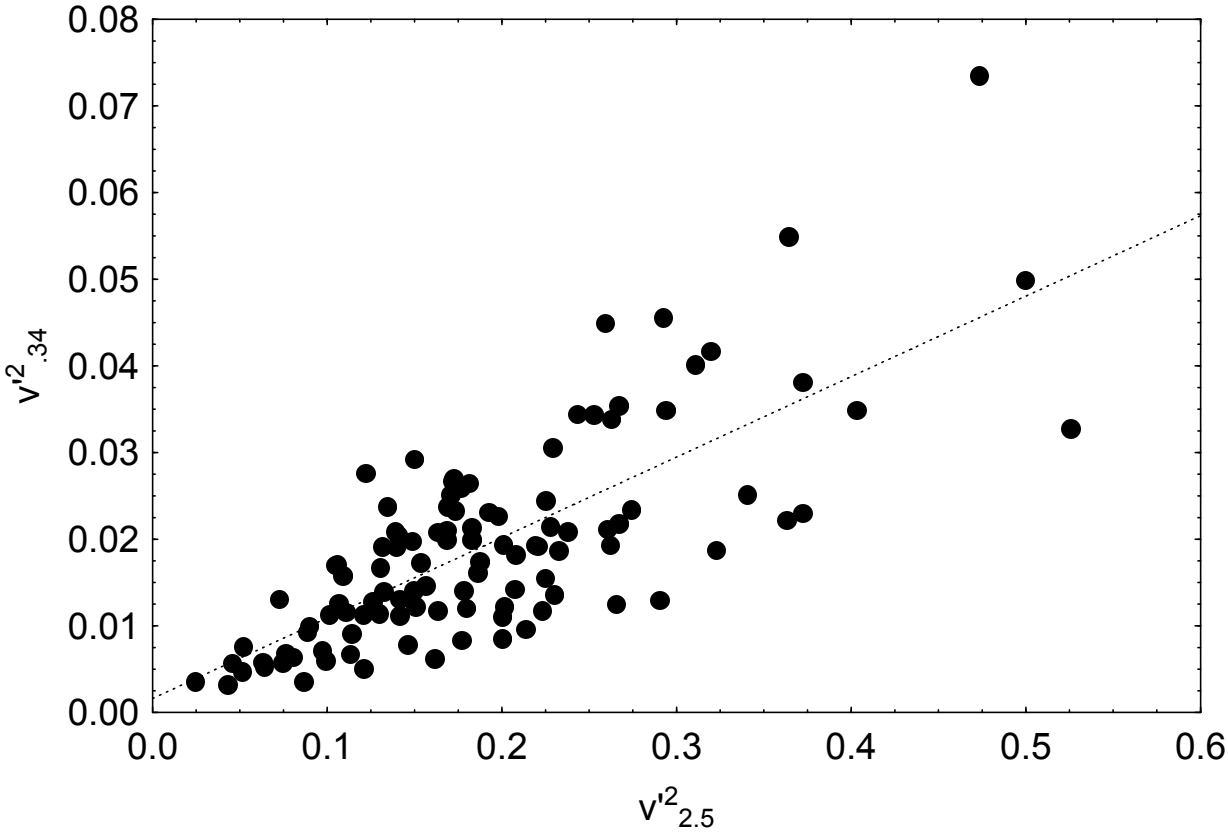

Figure 3C Turbulent energy perpendicular to the mean flow. $v'^2_{.34} = 0.09\ v'^2_{2.5} + 0.002$

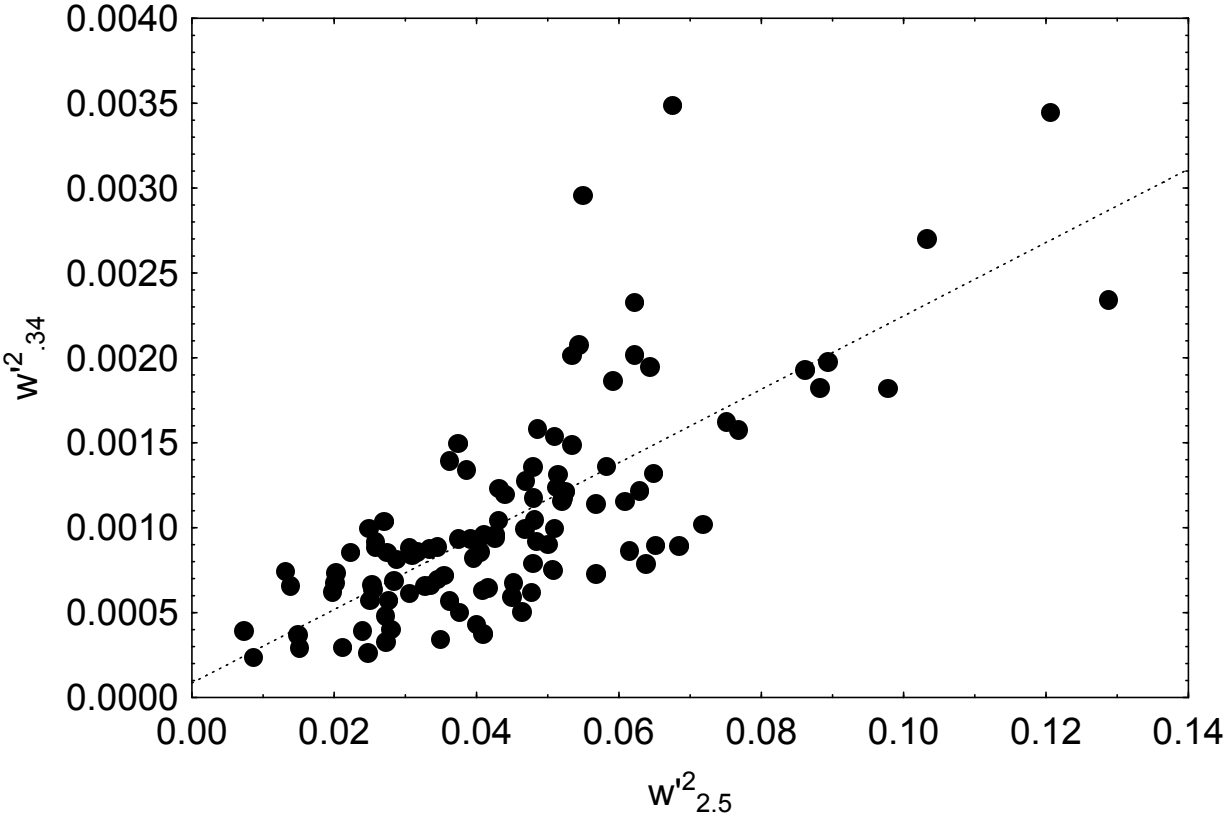

Figure 3D Turbulent energy in the vertical plane. $w'^2_{.34} = 0.02\ w'^2_{2.5}$

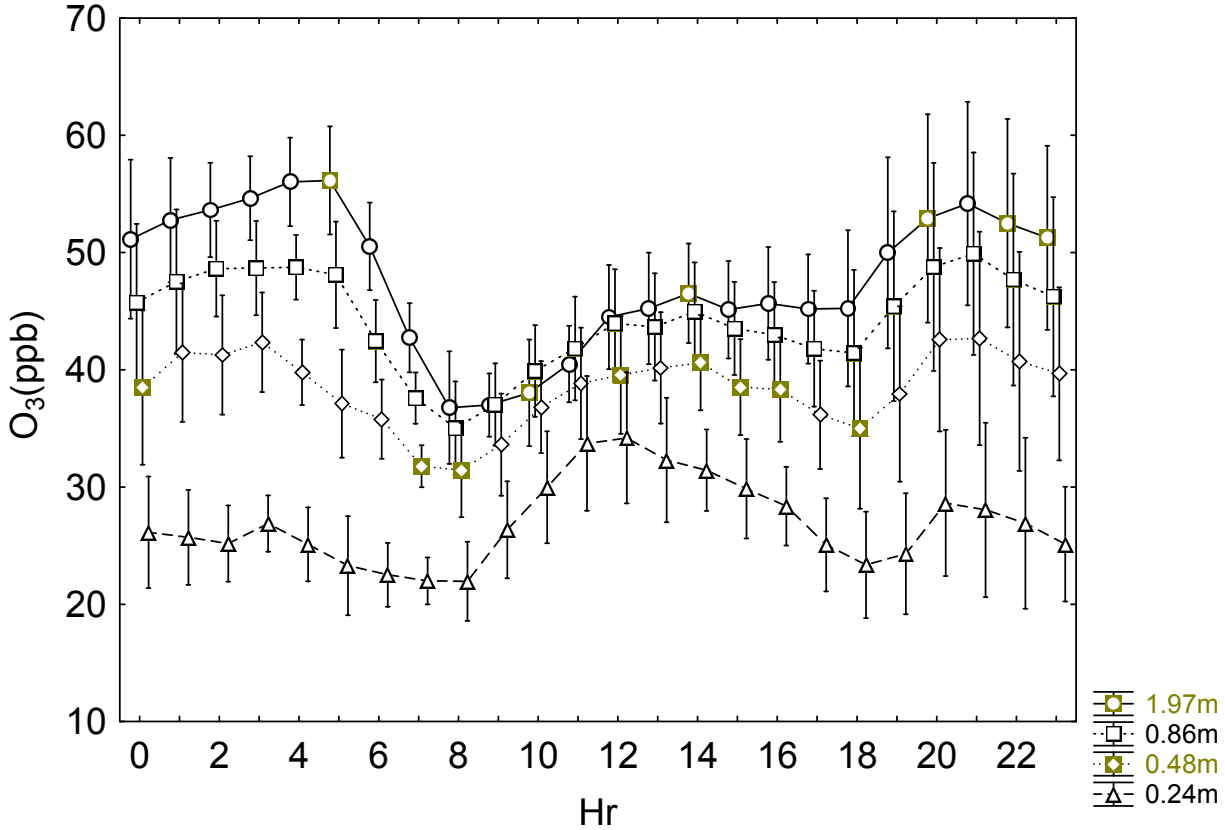

Figure 4 Average diurnal cycle of ozone during the study at each level, with 95% confidence limits

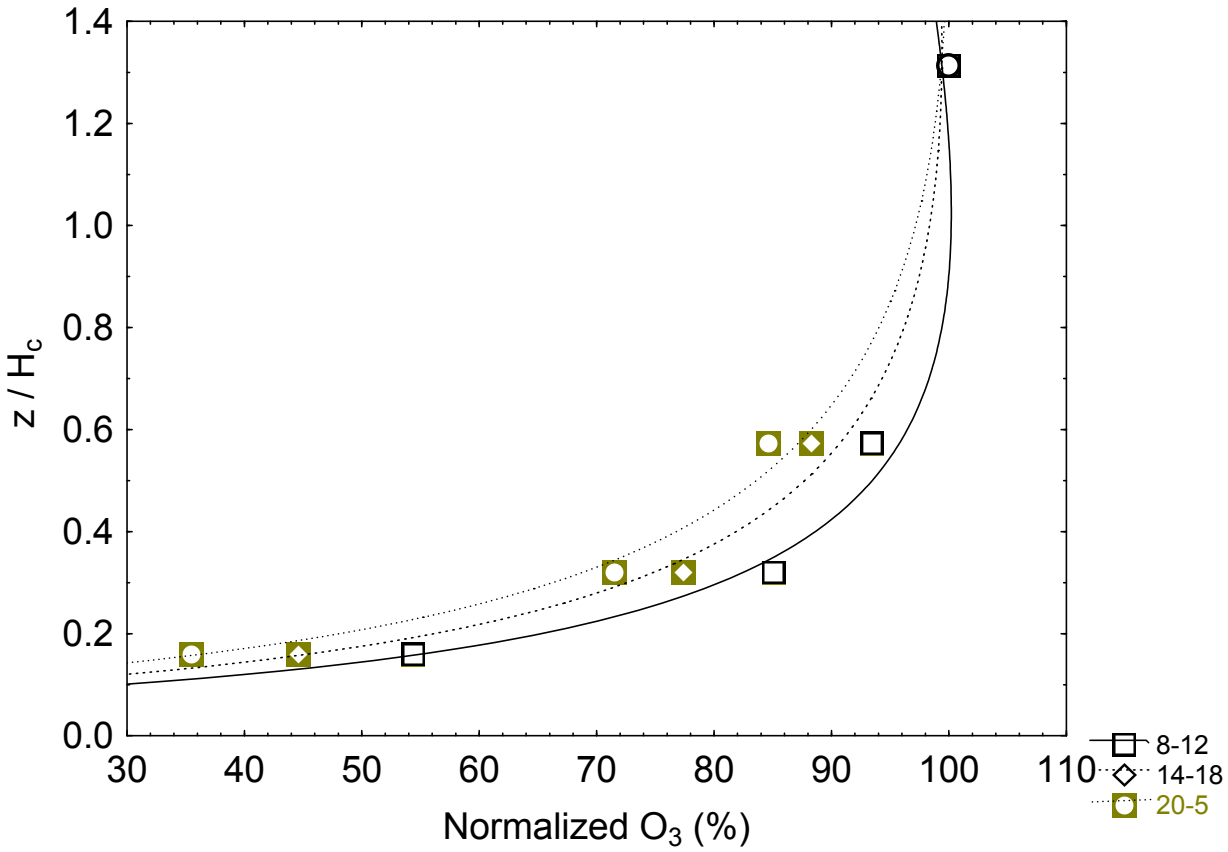

Figure 5 Average normalized ozone profiles for morning (8-12), afternoon (14-18) and night (20-5).

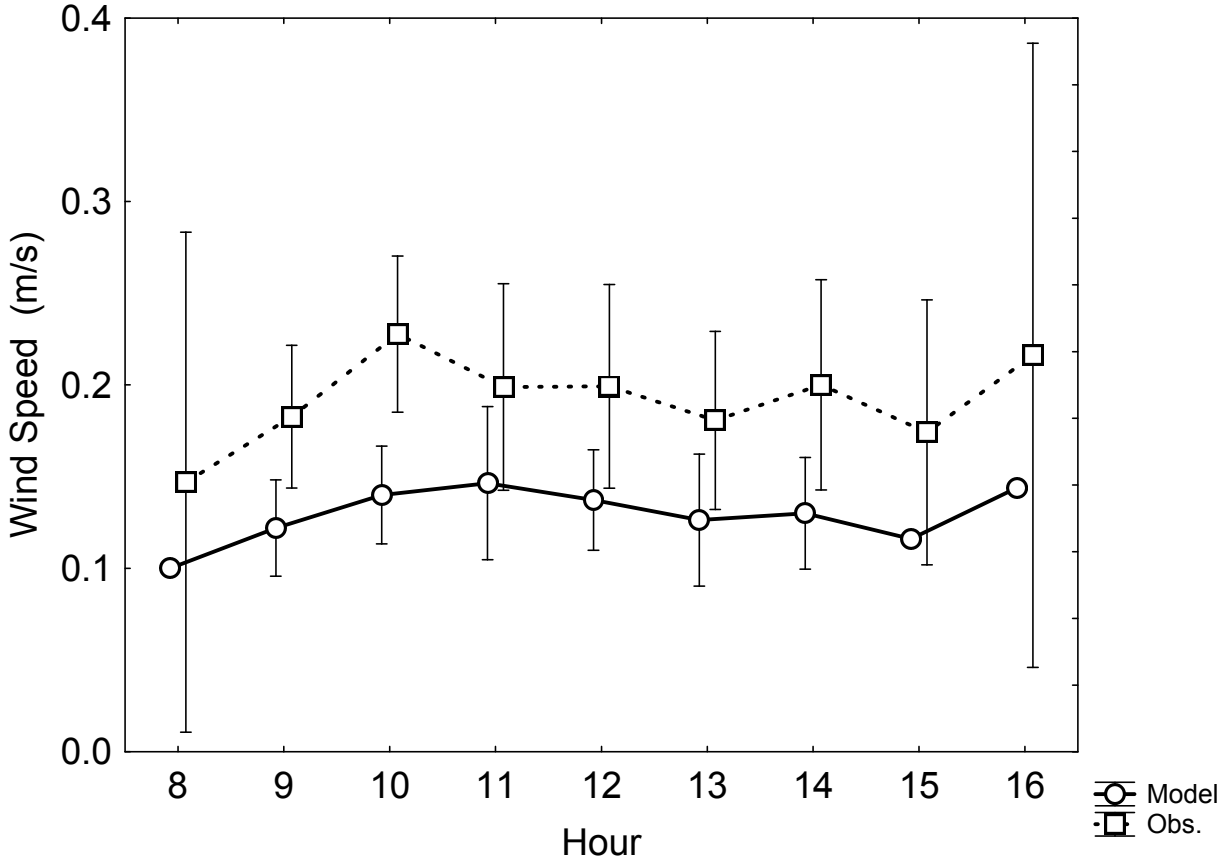

Figure 6 Observed and Modeled wind speed in the canopy at 0.34 m.

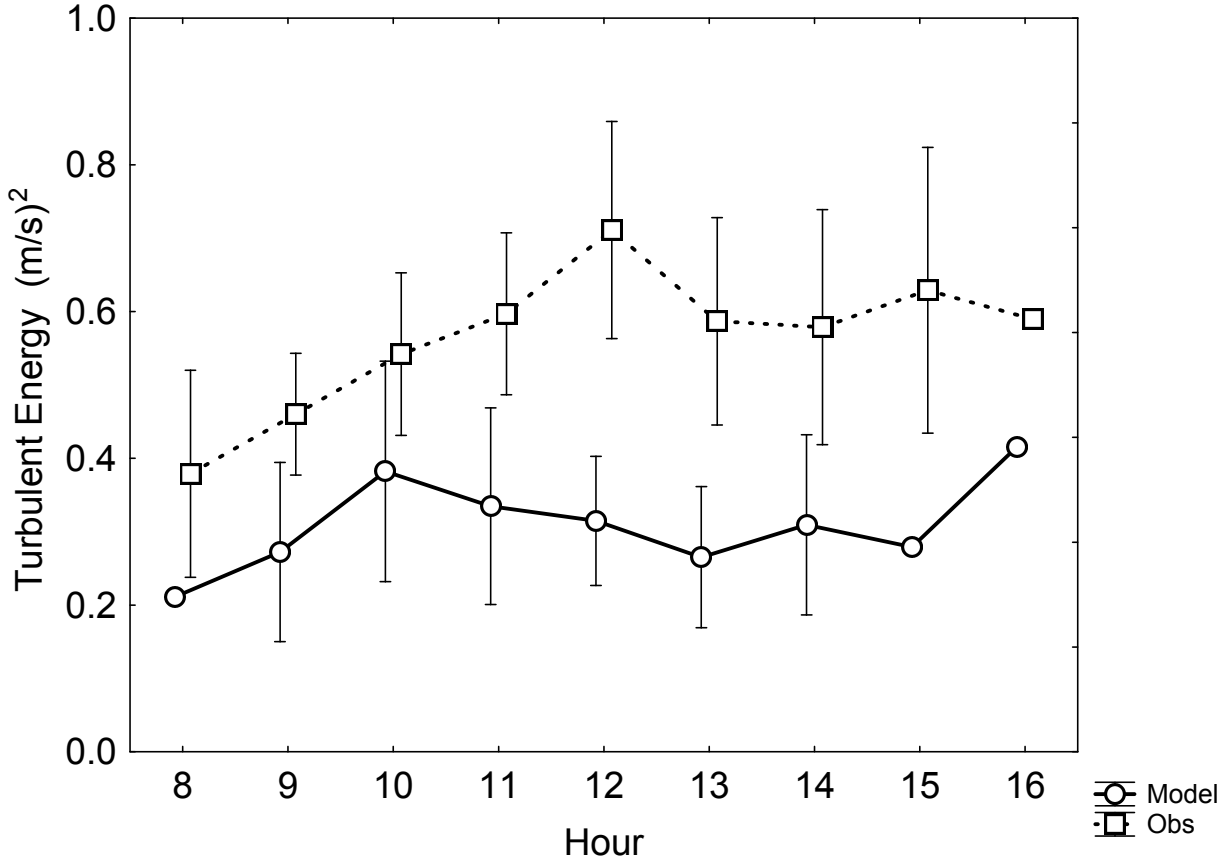

Figure 7A Observed and Modeled Turbulent Energy at 2.5m.

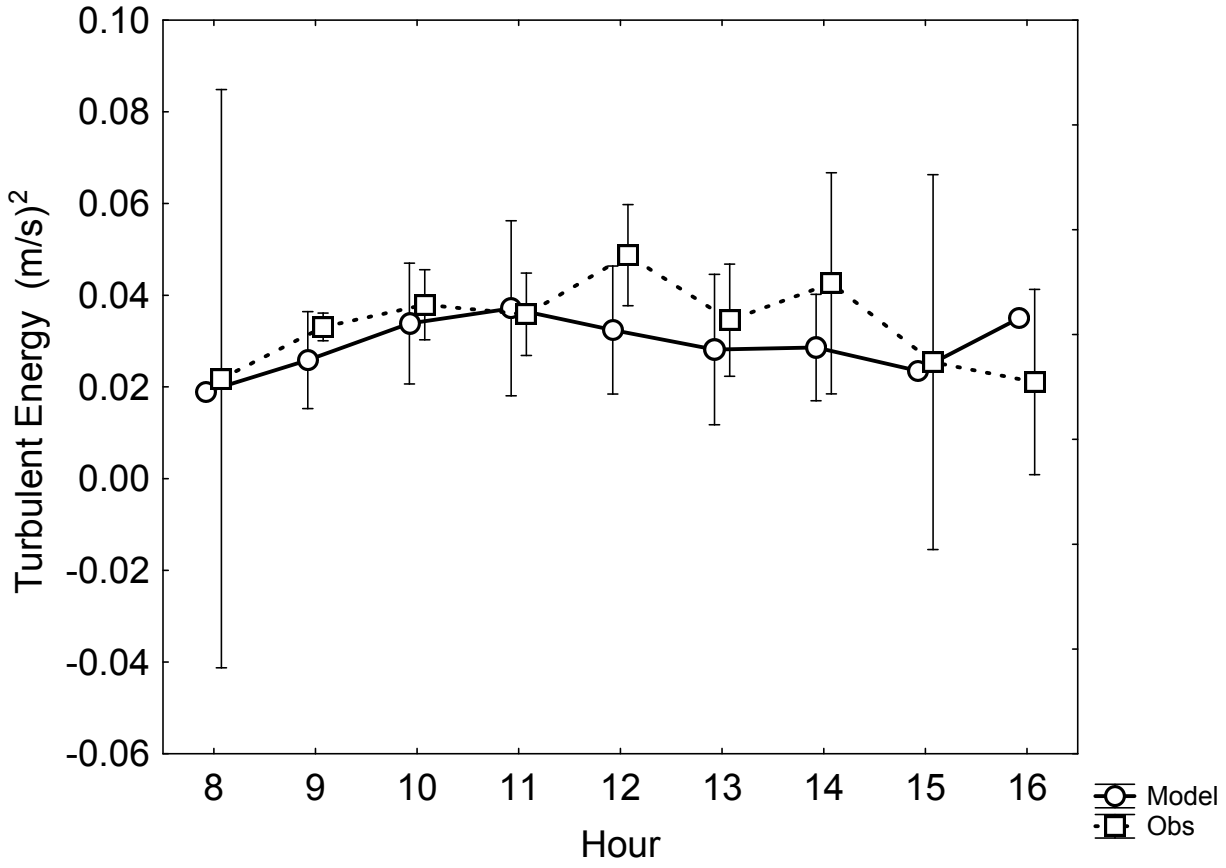

Figure 7B Observed and Modeled Turbulent Energy at 0.34m.

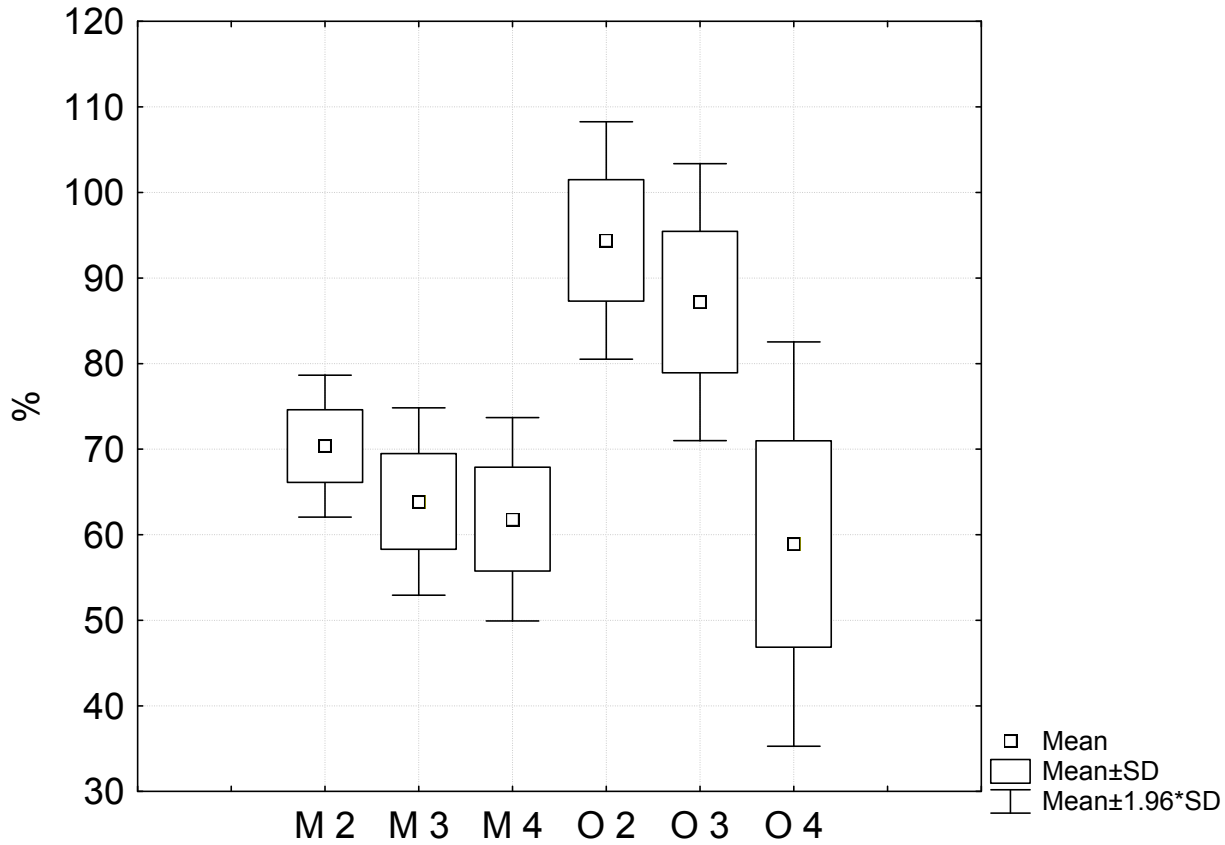

Figure 8 Box Plot of modeled (M) and observed (O) O_3 at each level (normalized by level 1) . Level 2=0.86m, 3=0.48m, 4=0.24m

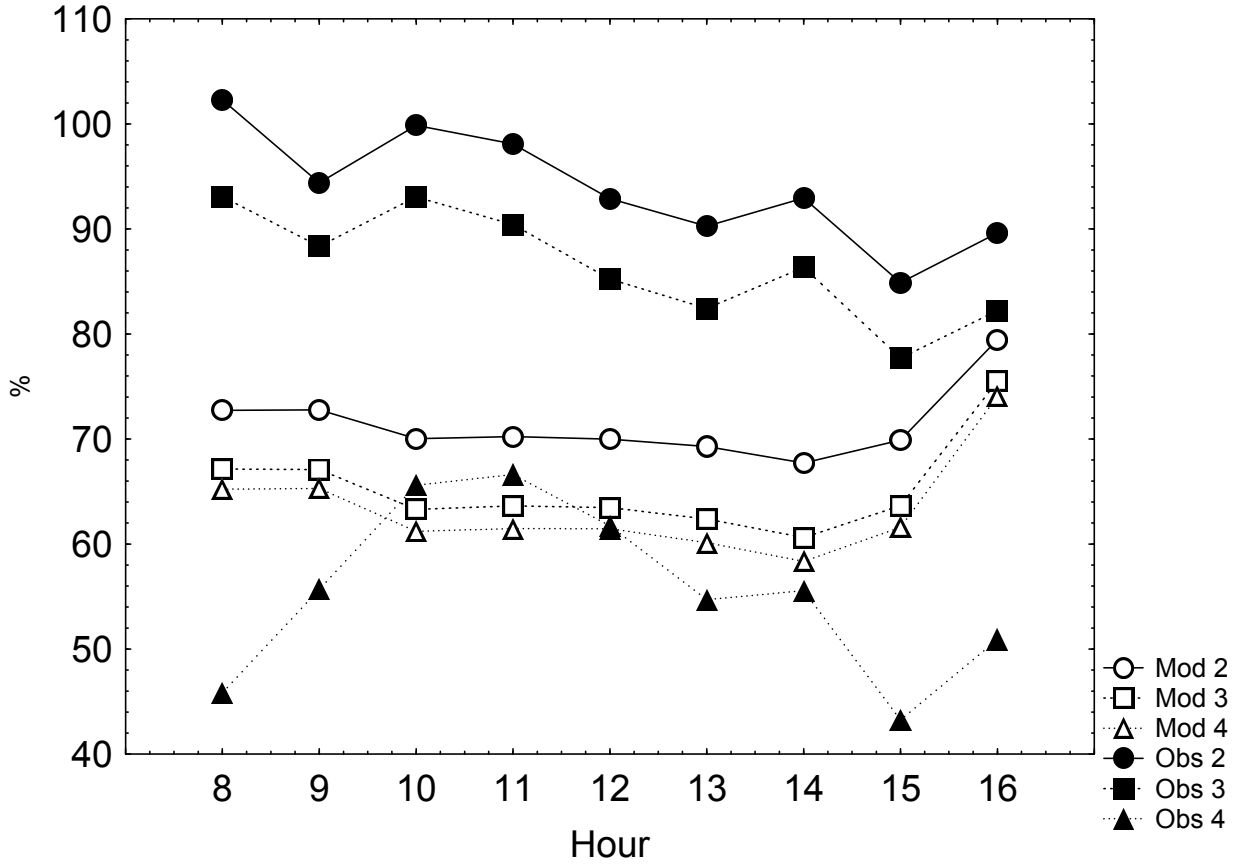

Figure 9 Average Model and Observed Normalized (by Level 1) O_3 by Hour

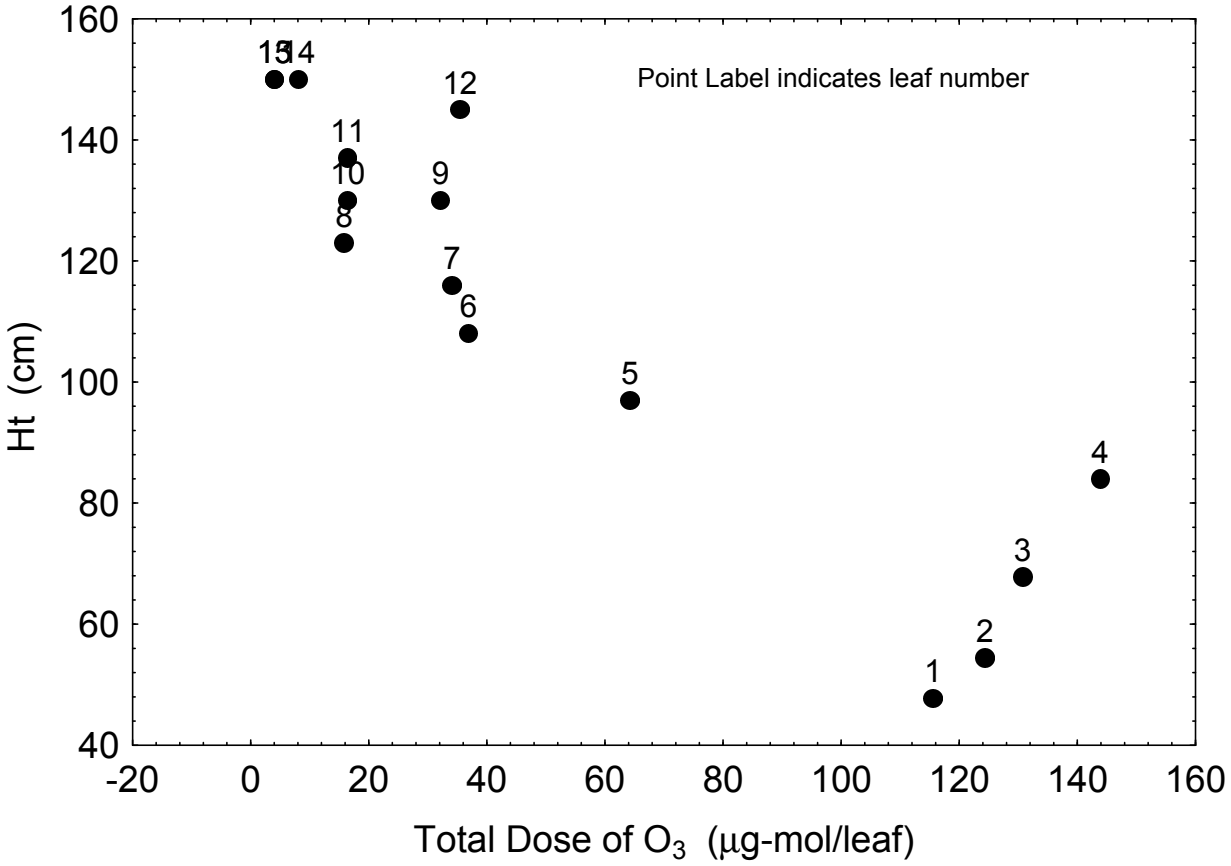

Figure 10 Total O_3 dosage of the average leaf, by leaf, for the period 5/20 - 8/18.

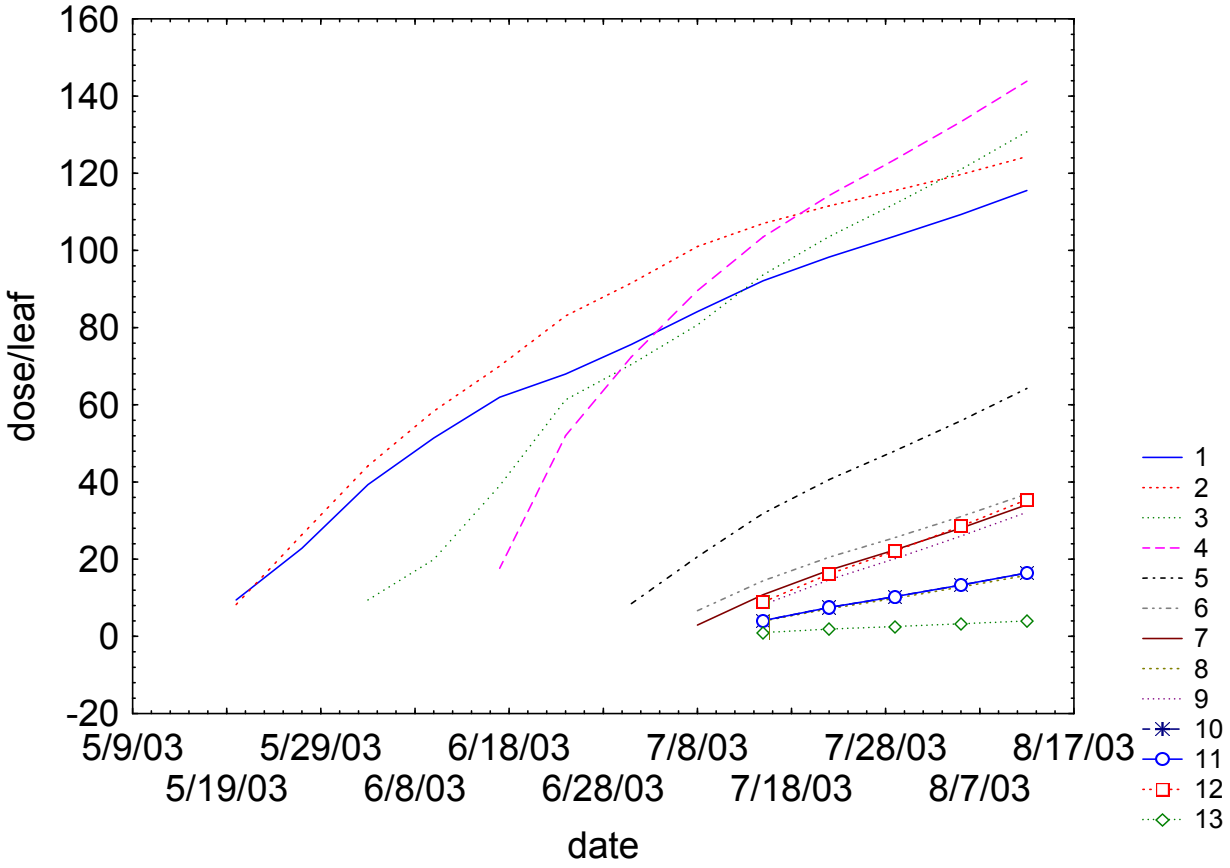

Figure 11 Cumulative Dosage (µg mol/leaf) by leaf during the growing season.