Use of Bioindicators and Passive Sampling Devices to Evaluate Ambient Ozone Concentrations in North Central Pennsylvania

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Abstract

Ambient concentrations of tropospheric ozone, ozone-induced injury to black cherry (*Prunus serotina*), and ozone-induced injury to common milkweed (*Asclepias syriaca*) were determined in north central Pennsylvania from May 29 to September 5, 2000 and from May 28 to September 18, 2001. Ogawa passive ozone samplers were utilized at 15 rural, open-area sites, of which, six were co-located with TECO Model 49 continuous ozone monitors. A significant positive correlation was observed between the Ogawa passive samplers and the TECO continuous ozone monitors for both seasons (r = 0.959, p<0.0001 in 2000 and r = 0.979, p<0.0001 in 2001). In addition, a significant positive correlation existed between ozone concentration and elevation (r = 0.720, p<0.002 in 2000 and r=0.802, p<0.0001 in 2001). Classic ozone-induced symptoms were observed on black cherry and common milkweed leaves at monitoring sites. For the 2001 season, a significant positive relationship showed that injury to black cherry was a function of cumulative ozone concentrations and available soil moisture. Spatial analysis and modeling using GIS applications showed a distinct regional pattern of ozone exposure and trends in concentrations with elevation.
Chapter 1. Literature Review

Ozone Source and Formation

Tropospheric ozone emerged as a regional air pollution problem in the mid 1970s (Dimitriades and Altshuller, 1978). Ozone is a secondary air pollutant formed by photochemical reactions involving oxides of nitrogen (NOx) and volatile organic compounds (VOCs), mainly hydrocarbons (Crutzen, 1979). In the presence of solar radiation, nitrogen dioxide (NO<sub>2</sub>) dissociates to form nitric oxide (NO) and an oxygen atom (O). Ozone (O<sub>3</sub>) is then formed by molecular oxygen (O<sub>2</sub>) reacting with the oxygen atom (O). However, when hydrocarbons are present, NO is converted to NO<sub>2</sub>, thus leaving little NO to react with O<sub>3</sub>. This reaction leads to a build-up of O<sub>3</sub> in the atmosphere.

Sources of NOx and VOCs are primarily anthropogenic, generally produced during combustion processes from automobile emissions and industrial activities. However, VOCs may also be produced from natural sources such as certain types of conifers and deciduous trees.

Transport/Gradient of Ozone in Pennsylvania

Solar radiation is not the only factor affecting ozone production. Other meteorological variables also affect the formation and transport of ozone. In the Mid-Atlantic region of the United States, ozone concentrations are often highest in the summer months when physical factors such as solar zenith angle and length of day are optimal (Ryan, 2000). This leads to a diurnal cycle of ozone formation.
Concentrations peak in the mid – to late afternoon hours and are lowest at pre-dawn hours. Other meteorological phenomena that affect ozone concentrations near the earth’s surface are radiational or thermal inversions. Generally, ozone laden air parcels that remain above the inversion layer will not break down as rapidly as parcels contained under the inversion layer (Liu et al., 1987). Because of this occurrence it is then possible for ozone parcels above the inversion layer to be mixed back down to the surface within the following days or be transported over regional distances.

The regional transport of ozone is influenced by the passage of pressure cells. Slow moving anticyclonic pressure cells, known as high pressure cells, circulate ozone and its precursors from the front to the back of the cell as the system gradually moves from west to east (Vukovich, 1977). Ozone concentrations are broken down by the passage of cold fronts and are well-mixed under the influence of fast moving fronts. In Pennsylvania, the movement of tropospheric ozone air pollution may be explained by three rationales: 1) air parcels that travel greater distances tend to be associated with more well-mixed systems as opposed to parcels that travel over shorter distances. The well mixed systems tend to suppress photochemical activity that leads to accumulated ozone formation; 2) air parcels that travel over areas that are associated with high NOx emissions tend to produce higher ozone concentrations as opposed to areas with low NOx emissions; and 3) precipitation events tend to suppress ozone production by limiting the amount of solar radiation from reaching the surface thus inhibiting photolytic reactions (Jagodzinski, 2000).
One approach to determine the source region of ozone is through the use of modeling and Back Trajectory Analysis (BTA). Comrie, 1994, utilized BTA to determine regional transport of ozone in central Pennsylvania. The research showed that most transport flowed from the lower Ohio Valley in a southwesterly direction. Critical elevated concentrations of ozone originating from the Ohio Valley were associated with air masses that stagnated two to three days upwind followed by at least one day of southwesterly transport.

Similarly, Jagodzinski, 2000, also noted an ozone gradient across Pennsylvania. It was indicated that lower ozone concentrations dominated the central region of the state whereas higher ozone concentrations were observed in the Southeast and Southwest regions of the state. Back trajectory analysis of the air circulation patterns indicated that for the centrally located sites in Pennsylvania, air parcels move over longer distances and were associated with faster moving frontal systems. Southeastern sites in the state are affected by slower, short distance systems that originate or pass through more industrialized, high NOx emission regions. Skelly et al, 2001, also noted the trend of lower ozone concentration observations in the north central region of Pennsylvania surrounded by air parcels that have higher ozone concentrations.

**Bioindicators**

Since the detection of weather fleck on tobacco (Rich et al., 1969) and grape leaf stipple (Richards et al., 1958) over 40 years ago, many plant species have been studied and identified as being sensitive to ambient ozone concentrations. Symptoms exhibited
by sensitive plant species to ambient ozone exposure include interveinal chlorosis, 
adaxial stipple, and premature leaf drop with older leaves showing these characteristics 
first. Foliar stipple appears as a reddish-purple, black, purple-black, or brownish 
pigmentation between veins on the adaxial surface of the leaf (Skelly, 2000). Many 
known species of plants that are sensitive to ambient ozone serve as bioindicators. A 
good bioindicator, black cherry (*Prunus serotina* Ehrh.), is a hardwood tree species that 
has been studied extensively over the recent years. Simini et al., 1992, studied the effects 
of ozone on black cherry and three other eastern hardwood tree species in north central 
Pennsylvania. Using open-top chambers, seedlings were exposed to treatments of 
ambient air or charcoal-filtered air containing 95, 60, or 40% of ambient ozone. Of the 
species studied, black cherry and yellow poplar (*Liriodendron tulipifera* L.) exhibited 
foliar stipple and showed a high correlation to temporal and spatial differences in ozone 
concentrations. Results were similar to research performed by Davis and Skelly, 1992, in 
which black cherry exhibited foliar stipple as well as premature senescence and leaf 
abscission as a result of elevated ozone concentrations in controlled environmental 
chambers. Research conducted by Hildebrand et al., 1996, in the Shenandoah National 
Park, VA, further confirmed a symptomatic response of black cherry to ozone 
concentrations under ambient and forested conditions. Significant relationships were 
determined between cumulative ozone concentrations sum 60 ppb and foliar injury. In 
the Great Smoky Mountains National Park, Chappelka et al., 1997, evaluated ozone 
injury on foliage of native plant species including black cherry. Results indicated that 
47% of the black cherry surveyed exhibited foliar injury with average leaves per plant 
and average leaf area injured at 43 and 6%, respectively.
Aside from black cherry, common milkweed (*Asclepias syriaca, L.*) has been frequently studied as a native plant bioindicator that appears sensitive to ambient ozone exposures. Duchelle and Skelly (1981), fumigated milkweed with ozone under CSTR conditions in the Shenandoah National Park. The fumigation produced foliar symptoms that increased with elevated ozone concentrations, up to 0.15 ppm. Adaxial stippling and premature senescence was observed on plants with symptoms more severe on older leaves. They also demonstrated that milkweed grown in charcoal-filtered chambers were asymptomatic or showed slight stippling. Chappelka et al., 1997, as part of a survey conducted in the Great Smoky Mountain, reported ozone-induced injury to greater than 70% of tall milkweed (*A. exaltata L.*) thus indicating its sensitivity to ozone. Of those milkweed injured, it was noted that over 60% of the leaves per plant displayed symptoms. Additionally, Skelly et al., 2001, observed adaxial stippling on common milkweed in rural areas of central Pennsylvania. Research indicated that injury developed progressively toward the end of a summer-long observation period and symptom expression was significantly correlated with elevation.

**Passive Sampling**

Recently, passive sampling devices (PSDs) have been widely used to determine cumulative concentrations of air pollutants. The benefits of passive sampling devices to detect ozone concentrations include low operational cost, high correlation results as compared to continuous ozone monitors, ease of use, and deployment in areas where no electricity is available (Krupa and Legge, 2000). In addition, research has shown that when using passive samplers to determine ozone concentrations, measurements are not
affected by temperature and humidity, and under ambient conditions, co-pollutant interference is negligible (Koutrakis et al., 1993).

Passive sampling devices work by chemical and/or physical sorption of air constituents across a medium contained inside the device. The medium is analyzed by optical methods to determine pollutant compounds. One such sampler, the Ogawa passive sampling device (Ogawa and Co. USA, Inc., Pompano Beach, FL.) is used to measure ozone concentrations. The device utilizes two nitrite-coated filters placed between diffusion screens inside a small, plastic cylinder. Upon exposure to ozone, nitrite ions are oxidized to nitrate ions. At the end of a defined exposure period, the two filters are removed and analyzed in a laboratory using ion chromatography to determine cumulative nitrate concentration. From this method, an average cumulative ozone concentration across a sampling period, such as average parts per billion (ppb)/ week, may then be determined (Manning et al., 1996).

The high correlation with continuous monitors allows the use of passive sampling devices in areas where no electricity is available or where budget constraints limit the use of expensive monitoring devices without sacrificing accuracy. Research conducted by Manning et al., 1996, in three Class I Wilderness Areas compared average ozone concentrations measured with the Ogawa passive sampling device versus the TECO Model 49 continuous ozone analyzer for a six week period. Results indicated a very good correlation ($R^2 = 0.759$, $p = 0.0003$) between the passive sampler and the continuous monitor for weekly average ozone concentrations. Additionally, Sather et al, 2000, demonstrated high correlations between the Ogawa PSDs and continuous monitors when measuring ambient ozone concentrations in urban and rural sites within the
Dallas/Fort Worth area over an eight week period of high ozone concentrations.
Comparisons of concentrations, over a 24 hour period, yielded excellent R values in the
range of .94 to .98. Similar results have been observed over summer-long study periods.
Skelly, et al, 2001, performed a 13 week comparison among passive ozone samplers and
continuous monitors in central Pennsylvania. Four out of eleven forested and
mountaintop sites were co-located with TECO Model 49 ozone analyzers. Results
showed a positive relationship between concentrations measured via passive sampling
devices and TECO Model 49 continuous monitors, noting a correlation coefficient of .96
(p<0.0001).

Additionally, the National Park Service (Flores et al., 1996) concluded that the
accuracy of passive samplers generally ranges within 15% of measurements recorded by
continuous monitors. Because of its high accuracy and repeatability and due to funding
limitations, as of 1996, the NPS has used PSDs in place of continuous monitors at 17
National Parks as baseline sites for measuring ozone. The NPS has cited the utility of
passive sampling devices for recording air quality data include canopy gradient
information, spatial concentration patterns, and assessment at biomonitoring sites.

Even though the utility of passive sampling is well documented, they are limited
to providing average concentrations as measured over time an extended period of time as
opposed to continuously monitored hourly concentrations. However, a recent study
conducted by Krupa et al., 2001, demonstrated the Weibull probability generator method
to replace unknown concentration values, normally measured by a continuous monitor,
that are not able to be measured by a PSD. By this method, a series of algorithms are
used to estimate parameters such as scale, shape, and distribution of continuously
monitored data; a cubic regression model was then formed using passive sampling data as
the predictor variable and synthetic ozone data using the Weibull generator was derived.
Results showed confidence levels $\geq 95\%$, when the Weibull method was analyzed
against actual recorded values generated by continuous monitors, thus supporting the
efficacy of this method to obtain hourly concentrations via a PSD. By deriving hourly
concentrations, this method may aid in the characterization between ozone and
bioindicators exposure-response relationships.

GIS Applications

Geographic Information Systems (GIS) serve as a tool for processing spatial data
into information related to some portion of the earth’s surface (Demers, 2000). Functions
of GIS include data management, manipulation, analysis, and output. Because of GIS
capabilities, many applicable uses can extend to disciplines such as environmental and
natural resource management, infrastructure planning and management, and urban/
regional management. The application for environmental purposes focuses primarily on
hazard and risk assessment where adverse effects result from exposure to a stressor.
Ecological risk can often be modeled and once that model of risk has been developed, it
may be applied in a spatial context through GIS. Hogsett et al., 1997, utilized GIS
capabilities to aggregate factors that characterize ozone exposure-response functions in
forested regions of the eastern United States. Exact usage of GIS for risk characterization
included the estimation of ozone exposures over the region, the measurement of ozone
effects on tree species, and the spatially distributed influences on species response to
ozone. The results may provide a visual record of spatial distribution of ozone- caused
effects as well as a tool for estimation of risk.
The capabilities of GIS to represent spatial characteristics are more significant and powerful when statistical methods are used in conjunction with current spatial analysis software. Such methods are often used to interpolate unsampled areas from a neighborhood of known point values. Utilizing the most powerful method is dependent upon point distribution factors such as the distance between sample points and the size of the area sampled. The most widely used statistical methods of interpolation include kriging, Inverse Distance Weighting (IDW), spline, and regression analysis.

Kriging is a method of local interpolation that is derived from a regionalized variable theory (Oliver et al., 1990). Kriging determines optimal weights for samples based on distance, relative position of samples to one another, and the area being estimated, thus reducing prediction error and bias. This estimation and interpolation method can be used for univariate or multivariate data. Because of its utility, kriging has been used to model air quality data. Reams et al., 1997, used point kriging to determine sulfate deposition at non-monitored sites utilizing direct and indirect estimation methods. The direct method consisted of only directly measured data at sampling locations whereas the indirect method additionally incorporated precipitation data from a spatially denser group of sites to be used as a co-variable. Results indicated that the direct method interpolated with more accuracy however the indirect method was better in representing sites that were unique or isolated from a cluster of sites, thus supporting the utility of kriging with strongly correlated variables. Similarly, Lefohn et al., 1997, utilized the kriging method to determine 7-hour seasonal mean ozone concentrations for major crop growing areas in the United States based on the U.S. EPA Storage and Retrieval of
Aerometric Data system (SAROAD) air quality data. The kriging method used did result in significant errors in predicted estimates even though the dataset was limited.

While not as powerful as kriging for some distribution data, Inverse Distance Weighting is another method that has been used for air quality modeling in GIS. The IDW method of interpolation, as the name implies, interpolates unsampled point values by calculating the inverse distance-squared weight of neighboring points. This method was applied in Dallas to show spatial distribution of ozone concentrations collected by passive sampling devices (Sather et al., 2000). The utility of the IDW method increases with the number of samples; however, it is limited by the areal extent of the interpolation region.

Further air quality modeling in GIS can be performed using a regression-based method of interpolation. This method was demonstrated on a local modeling level by Briggs et al., (2000). The regression model was used to interpolate traffic-related air pollution within a 300m buffer zone, which led to an analysis based on parameters that included altitude and NO\textsubscript{2} predictors. Final GIS spatial modeling was integrated with road traffic patterns, land use, and topography. Results showed interpolated estimates within 70-100% of actual recorded NO\textsubscript{2} concentrations with r\textsuperscript{2} values in the range 0.58 – 0.76, thus indicating the utility of this method.
Chapter 2. Objectives

1. To determine the exposure/response relationship among ambient ozone concentrations, foliar injury, elevation, and soil moisture.

2. To represent regional patterns of ozone concentrations and relationships to foliar injury through use of spatial analysis and mapping utilizing Geographic Information Systems (GIS).
Chapter 3. Materials and Methods

Research was conducted at fifteen sites in north central Pennsylvania from late May to mid-September in 2000 and 2001 to correspond with the high ozone season for that region (Comrie, 1994; Simini et al., 1992). The sites were chosen within large open areas and represented rural and higher elevations situated away from industrialized areas (Table 3.1). In 2000, field research was initiated on May 29th, with initial deployment of the passive sampling devices, and ended on September 5th, allowing a 14 week observation period. In 2001, the observation period lasted 16 weeks, which began May 28th with initial deployment of passive sampling devices and ended September 18th. Each site was visited weekly, within 24 hours of the previous week’s visit; foliar observation of bioindicators and deployment of a new passive sampling device took place during each visit (see Appendix A for schedule).

Ozone Monitoring

Within each site the Ogawa passive sampling device (PSD) was affixed to a pole, approximately 2m above the surface and shielded from wind and rain under a 7.6cm PVC cap. Six of the selected sites (State College, Moshannon State Forest, Tiadaghton Sportsman Club, Tioga County; Penn Nursery; and Williamsport) were co-located with TECO Model 49 continuous ozone analyzers.

The filter assemblies of the PSDs for the fifteen sites plus two control blanks were prepared in the laboratory each week on Sunday evening and kept frozen until being
Table 3.1: Description of 2000 and 2001 north central Pennsylvania monitoring sites.

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Site Name</th>
<th>County</th>
<th>Elevation (m, msl)</th>
<th>Latitude (dd)</th>
<th>Longitude (dd)</th>
<th>Landuse</th>
<th>TECO Model 49</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mid-State Airport</td>
<td>Centre</td>
<td>594</td>
<td>40.8875</td>
<td>-78.0864</td>
<td>Forested</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>Moshannon State Forest</td>
<td>Clearfield</td>
<td>653</td>
<td>41.1183</td>
<td>-78.5264</td>
<td>Forested</td>
<td>Yes</td>
</tr>
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<td>3</td>
<td>Piper</td>
<td>Clearfield</td>
<td>676</td>
<td>41.2164</td>
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<td>Forested</td>
<td>No</td>
</tr>
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<td>4</td>
<td>Sproul</td>
<td>Clinton</td>
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<td>5</td>
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<td>Lycoming</td>
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<td>Forested</td>
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<tr>
<td>6</td>
<td>Springer</td>
<td>Clinton</td>
<td>588</td>
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<td>Pasture</td>
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<td>7</td>
<td>Gleason</td>
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<td>8</td>
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<td>41.8103</td>
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<td>16</td>
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<td>Skyline</td>
<td>Lycoming</td>
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<td>41.1819</td>
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<td>Forested</td>
<td>No</td>
</tr>
</tbody>
</table>
transferred to an insulated ice chest the next morning for field travel. Upon arrival at each site, the previous week’s PSD was removed and replaced with a new PSD. Removed PSDs were stored in the ice chest until returned to the laboratory where they were placed back into a freezer. The control blanks were kept in the ice chest for the entire period of field travel, then placed back into the laboratory freezer with collected PSDs.

Filters were removed from the collected PSDs and corresponding control blanks on Wednesday mornings, placed in labeled vials, and shipped via express mail to the U.S. EPA, Exposure Methods and Monitoring Branch, Research Triangle Park, NC for analysis. Analysis for nitrate concentration was performed by ion chromatography. For each week, mean nitrate concentrations obtained from the blanks was subtracted from the exposed PSDs values to calculate net nitrate concentration. From that method, average weekly ozone concentrations (ppb) were obtained. Results were sent to Penn State periodically via facsimile; data were recorded for each site on a weekly basis.

TECO Model 49 continuous ozone analyzers were co-located at six sites (Table 3.1). Sensors were initially calibrated in early April at the beginning of the regional ozone season for north central Pennsylvania. A two-point check, autocalibration was performed nightly to each TECO. Calibration quality control measures were followed according to the standards documented by the Pennsylvania Department of Environmental Protection, Bureau of Air Quality.
Bioindicator Observations

Two species of bioindicators, black cherry and common milkweed, were located based on availability at each site within a 2km radius and 50m of elevation from the PSD. Size of black cherry trees ranged 1m to 20m in size. Fifteen representations of each bioindicator were selected and numbered for foliar observation at each site with only two exceptions: common milkweed was not located at the Mt. Pisgah County Park and Williamsport sites within the acceptable range of 2km from the PSD. Upon weekly arrival to the sites, each plant of the two species was evaluated for ozone-induced foliar injury, with recorded symptoms limited to the occurrence of adaxial stipple and reddening. A modified Horsfall-Barratt rating system based on the assignment of nominal values to represent broad injury classes was used to evaluate the injury amount and the injury severity. Symptom classes were: 0 = no injury; 1 = 1-6% injury; 2 = 7-25% injury; 3 = 26-50% injury; 4 = 51-75% injury; and 5 = 76-100% injury. A species injury index\(^1\) was calculated based on a formula created the U.S. Department of Agriculture Forest Service Forest Health Monitoring Program.

\[ \text{Species Index} = A \times B \]

Where (for each site):

\[ A = \frac{N_1}{N_2} \quad B = \text{Sum of } (\text{AMT} \times \text{SEV}) / N_1 \]

\[ N_1 = \text{the number of injured plants} \quad N_2 = \text{the number of evaluated plants} \]

\[ \text{AMT} = \text{injury amount per plant} \quad \text{SEV} = \text{injury severity per plant} \]

\(^1\)Species Index = A x B

Where (for each site):

\[ A = N_1 / N_2 \quad B = \text{Sum of } (\text{AMT} \times \text{SEV}) / N_1 \]

\[ N_1 = \text{the number of injured plants} \quad N_2 = \text{the number of evaluated plants} \]

\[ \text{AMT} = \text{injury amount per plant} \quad \text{SEV} = \text{injury severity per plant} \]
Soil Moisture

In the 2001 research season, available soil moisture was recorded at each site each week using a Delmhorst moisture measuring system. The system consisted of gypsum soil moisture blocks (sensors) and a Model KS-D1 Moisture Tester. Two soil blocks (one per species) were calibrated and deployed at each site three weeks prior to the observation period to equilibrate with natural soil conditions. The blocks were buried to a depth of 10-12cm amongst a group of bioindicator plants to represent the zone of water uptake. At sites where there were split groupings of a bioindicator, the soil moisture block was buried in the largest group to best represent that species of plant. In order to obtain the total potential reserve of moisture in the soil, potentiometer measurements were made weekly at each site. The moisture tester was calibrated weekly prior to field travel. A regression equation was used to calculate available soil moisture represented as percentage from the total potential reserve values measured via the potentiometer.

Data Analysis

Weekly and seasonal ozone concentrations measured via PSDs, plant injury values based on the species index, and soil moisture percentages were compared and ranked among sites by season. Comparison of seasonal means on a yearly basis for ozone and injury were performed using Paired T-tests.

Correlation and regression analyses were used to compare seasonal and weekly ozone concentrations measured via passive sampling devices to continuously monitored ozone concentrations and site elevation for each season. In addition, cumulative ozone averages were compared to elevation and plant injury by the same methods.
The progression of weekly plant injury and the interactions between ozone concentrations and soil moisture was performed using the Statistical Analysis System (SAS Institute Inc., 1985) PROC MIXED procedure. The PROC MIXED procedure was used due to the complexity of the dataset and the ability to measure random factors and repeated measures.

Spatial analysis and mapping was represented through GIS using ArcView 3.2 Spatial Analysis software (ESRI Inc., 1999). A regression interpolation projection was created based on the high correlation between ozone concentrations and elevation. In addition a spline interpolation surface was created to detail the trend in seasonal ozone across the study sites.

Plant injury and soil moisture were reclassified based on a quintile ranking system and represented as point data. The point data was overlayed on the regression interpolation map for each study season.
Chapter 4. Results

2000 Summer Season, 29 May to 5 September

Ozone

Ozone was monitored weekly at each site for a 14-week period in the summer of 2000. The deployment of passive sampling devices for the first 13 weeks were within a 1-hour window of the previous week's replacement time, however in the 14th week (last week of research), samplers were removed within a 2-hour window of the previous week. Ozone concentrations for the PSDs were calculated based on the device's exposure time in the field. Ozone concentrations measured via co-located TECO Model 49 continuous monitors were adjusted to correspond to the exposure period of the PSDs. The locations of the TECO monitors were situated across the research area to provide a feasible representation of local and regional ozone trends.

The relationship between seasonal ozone concentrations measured with passive sampling devices versus the TECO Model 49 continuous analyzer at the six co-located sites showed a highly significant positive correlation ($r = 0.959$, $p < 0.0001$). Mean ozone concentrations measured via PSDs at each of the six co-located sites were within a range of +/- 3.2 ppb of concentrations measured via continuous monitors (Figure 4.1). Mean PSD concentrations at Tiadaghton, Penn Nursery, and Williamsport were slightly overestimated while concentrations at Moshannon State Forest, Gleason, and State College were slightly underestimated. A comparison of combined means by week at the
Figure 4.1: Seasonal comparison of ozone concentrations measured via passive sampling devices versus concentrations measured via TECO Model 49 continuous ozone monitors at six co-located sites from May 29th to September 5th, 2000.

Six sites showed a closer fit between PSD and TECO Model 49 measured concentrations with values in the range of +/- 2.3 ppb (Figure 4.2). The slight overestimation of ozone concentrations by PSDs still accurately reflected the fluctuation of concentrations over the entire season that were detailed by the continuous monitors.

The correlation between seasonal ozone concentrations measured with passive sampling devices versus elevation was significant (r = 0.720, p = 0.002). Based on the correlation, most sites clearly defined the relationship that ozone concentrations increased with elevation (Figure 4.3). The high elevation sites, such as Mt. Pisgah County Park (760m msl), Gleason (758m msl), and Sproul (719m msl), generally had high ozone concentrations, while the lower elevations had lower ozone concentrations. Of note, the Williamsport site (202m msl) had the lowest seasonal ozone concentration of 23.2 ppb.
Figure 4.2: Comparison of weekly ozone concentrations measured via passive sampling devices versus concentrations measured via TECO Model 49 continuous monitors from May 29th to September 5th, 2000.

Figure 4.3 Seasonal ozone concentrations averages measured via passive sampling devices versus elevation for north central Pennsylvania monitoring sites from May 29th to September 5th, 2000.
However, two sites that did not accurately fit this trend were Skyline (580m msl) and Tiadaghton (562m msl). Skyline exhibited the highest seasonal ozone concentration (44.8 ppb) among all sites, even though it was classified as a mid-range elevation site out of those monitored (Figure 4.4). Tiadaghton showed the second lowest seasonal concentration at an elevation nearly as high as Skyline.

When seasonal ozone concentrations measured via the TECO monitors were compared to elevation, the same relationship was demonstrated as noted with PSDs (Figure 4.5). The highest elevation co-located site, Gleason (758m msl), showed a seasonal mean ozone concentration of greater than 40 ppb as compared to the lowest elevation co-located site, Williamsport (202m msl), with a seasonal mean concentration less than 25 ppb.

The pattern of ozone progression measured by continuous monitors on a weekly basis over the season showed an early peak during mid June (Week 2), with a seasonal high ozone average of 48.7 ppb (Figure 4.6). The mid-June peak was followed by a sharp decline in ozone that did not rise again until late June (Week 4). In the weeks that followed, ozone concentrations as a whole declined with the exception of small peaks in mid-July and late August, Weeks 7 and 13, respectively. The lowest week of recorded ozone concentrations was recorded in mid-August (Week 12), with an average ozone concentration of 24.4 ppb.
Figure 4.4: Seasonal ozone recorded at 15 sites in north central Pennsylvania using the Ogawa passive sampling device from May 29th to September 5th, 2000.

Figure 4.5: Seasonal ozone concentrations recorded at 6 co-located sites in north central Pennsylvania using TECO Model 49 continuous monitors from May 29th to September 5th, 2000.
Figure 4.6: Averaged ozone concentrations by week recorded at 6 co-located sites in north central Pennsylvania using TECO Model 49 continuous monitors from May 29th to September 5th, 2000.

**Foliar Injury**

Typical ozone-induced injury to black cherry and common milkweed was recorded at weekly intervals at each site over a 14-week period during the summer season of 2000. Two sites, Mt. Pisgah County Park and Williamsport, contained only black cherry; common milkweed was not located within the defined distance parameters.

Symptoms were first observed in mid-June (Week 3) at the Sproul Site (Clinton County, 719m msl) (Table 4.1). By early July, injury was present at five additional sites that included Moshannon State Forest (Clearfield County, 653m msl), Piper (Clearfield County, 676m msl), Mt. Pisgah County Park (Bradford County, 760m msl), Mt. Pisgah State Park (Bradford County, 429m msl), and Bald Eagle (Clinton County, 510m msl).
### Table 4.1: Injury start date and number of symptomatic black cherry and common milkweed recorded at 15 monitoring sites in north central Pennsylvania from May 29th to September 5th, 2000.

<table>
<thead>
<tr>
<th>Site</th>
<th>Injury Start Date</th>
<th>Seasonal No. of BC Injured</th>
<th>Seasonal No. of MW Injured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mid-State Airport</td>
<td>July 7, 2000</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>Moshannon SF</td>
<td>July 3, 2000</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>Piper</td>
<td>July 3, 2000</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>Sproul</td>
<td>June 19, 2000</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>Tiadaghton</td>
<td>July 3, 2000</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>Springer</td>
<td>July 10, 2000</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Gleason</td>
<td>August 1, 2000</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Mt. Pisgah Co.</td>
<td>June 26, 2000</td>
<td>6</td>
<td>No MW</td>
</tr>
<tr>
<td>Mt. Pisgah St.</td>
<td>July 3, 2000</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Bald Eagle</td>
<td>July 3, 2000</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Penn Nursery</td>
<td>July 25, 2000</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>State College</td>
<td>August 21, 2000</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>World's End</td>
<td>July 18, 2000</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>Williamsport AQ</td>
<td>August 8, 2000</td>
<td>5</td>
<td>No MW</td>
</tr>
<tr>
<td>Skyline</td>
<td>July 18, 2000</td>
<td>5</td>
<td>8</td>
</tr>
</tbody>
</table>

The other nine sites had symptomatic plants within the following weeks. Injury to black cherry was observed at all sites, whereas injury to common milkweed was observed at only 12 of 15 sites.

Initial symptoms were first observed on black cherry. The site with the least number of black cherry injured was Mid State Airport (Centre County) having only 2 of 15 trees that showed symptoms. Conversely, the greatest number of black cherry injured was observed at sites that included Moshannon State Forest (Clearfield County), Springer (Clinton County), and World's End (Sullivan County) with 11 of 15 trees that were symptomatic. For common milkweed, State College (Centre County) showed no injury whereas at World's End 13 of 15 plants were symptomatic. A comparison of cumulative
injury between the two bioindicator species showed that common milkweed suffered
greater injury at 8 out of 15 sites.

For purpose of site analysis, field injury that was recorded using the modified
Horsfall-Barratt rating system was converted to a species index developed by the US
Department of Agricultural Forest Health Monitoring Program. Results of site
comparisons showed that the highest seasonal injury to both bioindicators was recorded
at the Moshannon State Forest site (Clearfield County, 653m msl) with a combined injury
index value of 9.13 (Figure 4.7). The lowest seasonal injury was recorded at the State
College site (Centre County, 425m msl) with a combined injury index value of 0.40. A
correlation analysis among all sites showed a significant positive relationship between
injury to black cherry and cumulative seasonal ozone concentrations (r = 0.614, p <
0.0001) with an injury progression rate of 0.030 by week. Similarly, the relationship
between common milkweed and cumulative seasonal ozone concentrations was also
highly significant (r = 0.658, p < 0.0001) with the weekly injury progression rate the
same as observed with black cherry.
Figure 4.7: Seasonal injury based on species index recorded at 15 sites in north central Pennsylvania from May 29th to September 5th, 2000.
Ozone

Ozone was monitored weekly at each site for a 16-week period during the summer 2001 with one exception: the passive sampler mounting system was vandalized at the Skyline at the end of Week 14, therefore no ozone measurements were recorded for the last 2 weeks of the season at that site. The correlation between ozone concentrations measured via PSDs versus TECO Model 49 as well as the correlation between ozone concentrations versus elevation were adjusted to reflect the same research period as in 2000 (from Memorial Day to Labor Day). The deployment of PSDs for the first 11 weeks were within a one-hour window of the previous week's replacement time, however in the last 4 weeks, samplers were replaced within a 24-hour window of the previous week. Ozone concentrations for the PSDs were calculated based on the device's exposure time in the field. Ozone concentrations measured via co-located TECO Model 49 continuous monitors were adjusted to correspond to the exposure period of the PSDs. The locations of the TECO monitors were situated across the research area to provide a feasible representation of local and regional ozone trends.

The relationship between seasonal ozone concentrations measured with passive sampling devices versus the TECO Model 49 continuous analyzer at the six co-located sites showed a high positive significant correlation ($r = 0.979$, $p < 0.0001$). Mean ozone concentrations measured via PSDs at each of the six co-located sites were within a range of -3.0 ppb of the concentrations measured via continuous monitors (Figure 4.8). Mean PSD concentrations at all co-located sites were slightly underestimated. A comparison of combined means by week at the six sites showed a looser fit between PSD and TECO
Model 49 measured concentrations with values in the range of -3.6 ppb (Figure 4.9). A slight underestimation of ozone concentrations by PSDs still accurately reflected the fluctuation of concentrations over the entire season that were detailed by the continuous monitors.

The correlation between seasonal ozone concentrations measured with passive sampling devices versus elevation was also significant ($r = 0.802$, $p < 0.0001$) (Figure 4.10). The high elevation sites, such as Mt. Pisgah County Park (760m msl), Gleason (758m msl), and Sproul (719m msl), generally had high ozone concentrations recorded for the season while the lower elevation sites showed lower ozone concentrations.

![Seasonal Ozone Trends by Site (TECO v. PSD)](image)

Figure 4.8: Seasonal comparison of ozone concentrations measured via passive sampling devices versus concentrations measured via TECO Model 49 continuous ozone monitors at six co-located sites from May 28th to September 18th, 2001
Similar to the 2000 season, the Williamsport site (202 m msl) once again showed the lowest seasonal ozone with a concentration of 26.1 ppb. Two sites that did not accurately fit this trend were Skyline (580 m msl) and Tiadaghton (562 m msl). Skyline exhibited the seasonal highest ozone concentrations (51.1 ppb) among all sites even though it was classified as a mid-range elevation site out of those monitored (Figure 4.11). Tiadaghton showed the second lowest seasonal concentration (30.2 ppb) at an elevation nearly as high as Skyline.
Figure 4.10: Seasonal ozone concentrations averages measured via passive sampling devices versus elevation for north central Pennsylvania monitoring sites from May 28th to September 18th, 2001.

Figure 4.11: Seasonal ozone recorded at 15 sites in north central Pennsylvania using the Ogawa passive sampling device from May 28th to September 4th, 2001.
When seasonal ozone concentrations as measured via the TECO monitors were compared to elevation, the same relationship as noted with PSDs was demonstrated (Figure 4.12). The highest elevation co-located site, Gleason (758m msl), showed a seasonal mean ozone concentration of greater than 45 ppb as compared to the lowest elevation co-located site, Williamsport (202m msl), with a seasonal mean concentration less than 30 ppb.

The pattern of ozone progression measured by continuous monitors on a weekly basis over the season showed a slight peak in early July (Week 5), followed by a sharp decline and did not peak again until late July (Week 8) (Figure 4.13). After rebounding from another steady decline, ozone reached its highest weekly average in mid-August (Week 11), with an average concentration of 44.83 ppb. The lowest week of recorded ozone concentrations occurred at the end of the study period in early September (Week 14), with an average ozone concentration of 25.5 ppb.
Figure 4.12: Seasonal ozone concentrations recorded at 6 co-located sites in north central Pennsylvania using TECO Model 49 continuous monitors from May 28th to September 18th, 2001.

Figure 4.13 Averaged ozone concentrations by week recorded at 6 co-located sites in north central Pennsylvania using TECO Model 49 continuous monitors from May 28th to September 18th, 2001.
Foliar Injury

Typical ozone-induced injury to black cherry and common milkweed was recorded at weekly intervals at each site over a 16-week period during the summer season of 2001. Two sites, Mt. Pisgah County Park and Williamsport, contained only black cherry; common milkweed was not located within the defined distance parameters.

Ozone-induced symptoms were first observed in late June (Week 4) at Moshannon State Forest (Clearfield County, 653m msl), Piper (Clearfield County, 676m msl), Springer (Clinton County, 588m msl), Mt. Pisgah State Park (Bradford County, 429m msl), and Skyline (Lycoming County, 580m msl) (Table 4.2). By early July, injury was present at 9 of 15 sites. The other 6 sites started to show symptoms within the following weeks.

Table 4.2: Injury start date and number of symptomatic black cherry and common milkweed recorded at 15 monitoring sites in north central Pennsylvania from May 28th to September 18th, 2001.
Initial symptoms were first observed on black cherry on June 25 and on common milkweed by July 2. Injury to black cherry and common milkweed was observed at 12 of 15 sites, with all sites showing symptoms on at least one specie of bioindicator. Black cherry did not exhibit injury at Mid State Airport (Centre County), World's End (Sullivan County), or Bald Eagle (Clinton County). Conversely, the greatest number of black cherry injured was observed at Springer (Clinton County), with 8 of 15 trees that were symptomatic. For common milkweed, State College (Centre County) showed no injury whereas at the Mid State Airport, Moshannon State Forest (Clearfield County), and Tiadaghton (Lycoming County) sites, all 15 plants were symptomatic. A comparison of cumulative injury between the two bioindicator species showed that common milkweed suffered greater injury at 9 out of 15 sites.

For purpose of site analysis, field injury that was recorded using the modified Horsfall-Barratt rating system was converted to a species index developed by the US Department of Agriculture Forest Health Monitoring Program. The highest seasonal injury to both bioindicators was recorded at the Moshannon State Forest site (Clearfield County, 653m msl) with a combined injury index value of 12.8 (Figure 4.14). The lowest seasonal injury was recorded at the Williamsport site (Centre County, 425m msl) with a combined injury index value of 0.07. There was a significant relationship between black cherry and cumulative seasonal ozone concentrations ($r = 0.436, p < 0.0001$) and, after initial symptoms occurred, injury progressed at a rate 0.06 by week. Similarly, the relationship between common milkweed and cumulative seasonal ozone concentrations was also highly significant ($r = 0.450, p < 0.0001$) with weekly injury progression lower than black cherry at a rate 0.02.
Figure 4.14: Seasonal injury based on species index recorded at 15 sites in north central Pennsylvania from May 28th to September 18th, 2001

**Soil Moisture**

Soil moisture was measured at weekly intervals at each site for the 16-week 2001 season. A comparison of soil moisture averages among sites showed the wettest site to be World’s End (Sullivan County, 662m msl) with an average moisture content of 81%. Conversely, the driest site was State College (Centre County, 425m msl) with an average soil moisture content of 58% (Figure 4.15). Weekly soil moisture averages for all sites combined were calculated and graphed to illustrate a trend of wet and dry weeks (Figure 4.16). Steady soil moisture percentages, 80% or greater, occurred from the end of May to early July (Week 1 - Week 6). By mid-July (Week 7), soil moisture averages plummeted to 21% (Week 10) then rose sharply to 83% by the end of August (Week 12). A steady decline in early September led to the final recorded available soil moisture average of 68% (Week 16).
An analysis of weekly available soil moisture combined with cumulative ozone as a function of plant injury yielded a significant positive relationship, $p < 0.0001$ for black cherry only. The model of this relationship showed that plant injury progressed as cumulative ozone and soil moisture increased. Injury to common milkweed did not exhibit a significant response to the ozone and soil moisture variables.

Injury Model for Black Cherry:

$$
\text{Injury} = -0.0737 - (0.3135 \times \text{black cherry}) + (0.0027 \times \text{cumulative ozone}) + (0.6325 \times \text{soil moisture})
$$

![2001 Seasonal Available Soil Moisture](image)

Figure 4.15: Seasonal soil moisture averages recorded at 15 monitoring sites in north central Pennsylvania from May 28th to September 18th, 2001.
Figure 4.16: Average soil moisture by week recorded at 15 monitoring sites in north central Pennsylvania from May 28th to September 18th, 2001

Seasonal Comparisons

Seasonal ozone averages and species injury among all sites were compared from May 28th to September 5th for 2000 and 2001. Ozone averages measured via PSDs in the 2001 season were significantly greater ($p < 0.0001$) than during the 2000 season with mean concentrations of 37.65 ppb and 34.04 ppb, respectively (Figure 4.17). All sites showed an increase in concentrations from 2000 to 2001 with the exception of Mt. Pisgah State Park that showed a decrease in ozone of 2.74 ppb. The greatest increase was observed at the Gleason site that had a difference of 7.23 ppb between the two study seasons.
Figure 4.17: Comparison of ozone concentrations measured by passive sampling devices during the 2000 and 2001 seasons recorded at 15 monitoring sites in north central Pennsylvania from May 28th to September 5th.

The seasonal comparison of ozone measured via continuous monitors showed an increase from a combined site average of 31.8 ppb in 2000 to 36.4 ppb in 2001 ($p = 0.003$) (Figure 4.18). The greatest increase among the six sites was Williamsport with a measured difference of 6.5 ppb. Conversely, the lowest increase of ozone was seen at Moshannon State Forest with a difference of only 1 ppb.

A comparison of seasonal injury showed, on average, that the more severe injury was observed for both bioindicator species in the year 2000 (Figure 4.19). Only one site, Tiadaghton (Lycoming County, 562m msl) showed higher average injury among the two bioindicators combined in the 2001 season. Seasonal averages based on the species index among all sites for black cherry in 2000 and 2001 were 1.58 and 0.66, respectively. Common milkweed seasonal species index averages for 2000 and 2001 were 1.85 and
Figure 4.18: Comparison of ozone concentrations measured by TECO Model 49 continuous monitors during the 2000 and 2001 seasons recorded at 6 co-located sites in north central Pennsylvania from May 28th to September 5th.

Figure 4.19: Comparison of seasonal injury based on species index values recorded at 15 monitoring sites in north central Pennsylvania for the 2000 and 2001 seasons.
1.72, respectively. Over both seasons, injury to milkweed was greater (8% in 2000 and 44% in 2001) than injury to black cherry.

An individual comparison of species by year for black cherry showed that in 2001, no injury was found at Bald Eagle (Clinton County) and World's End (Sullivan County) as compared to 2000 when species injury index values were greater than 1.0 at both sites (Figure 4.20). The yearly comparison of the common milkweed bioindicator showed a large difference at Moshannon State Forest (Clearfield County) and Tiadaghton (Lycoming County) with injury index values in 2001 greater than twice the value in 2000 (Figure 4.21).

![Seasonal Injury Comparison - Black Cherry](image)

Figure 4.20: Comparison of black cherry injury based on the species index recorded at 15 monitoring sites in north central Pennsylvania for the 2000 and 2001 seasons
Figure 4.21: Comparison of common milkweed injury based on the species index recorded at 15 monitoring sites in north central Pennsylvania for the 2000 and 2001 seasons.

**Spatial Analysis**

Spatial analysis of sites based on elevation, ozone concentrations measured via PSDs, plant injury and soil moisture were created by utilizing ArcView 3.2 (GIS) Spatial Analyst software (ESRI). Based on the high correlation between ozone concentrations and elevation, a regression-based interpolation was created for the 2000 and 2001 research seasons (Figures 4.22 and 4.23). The regression models for each year were:

2000: \[19.4 + 0.0254(\text{Elevation}); \text{R-Sq.} = 51.8\%, \ p = 0.002\]

2001: \[17.61 + 0.033(\text{Elevation}); \text{R-Sq.} = 64.4\%, \ p < 0.0001\]

The interpolation detailed ozone concentrations per meters of elevation for areas over the seven counties where monitoring sites were not located. Factors such as plant injury, soil moisture, and meteorological data were not included in the regression formula.
Figure 4.22: Regression interpolation of ozone concentrations measured via passive sampling devices versus elevation for 15 monitoring sites in north central Pennsylvania from May 29th to September 5th, 2000.
Figure 4.23: Regression interpolation of ozone concentrations measured via passive sampling devices versus elevation for 15 monitoring sites in north central Pennsylvania from May 28th to September 18th, 2001.
Seasonal ozone concentrations for 2000 and 2001 were also represented by the spline method of interpolation (Figures 4.24 and 4.25). The spline method detailed a more contoured representation of ozone across non-monitored areas between sites. However, meteorological data and elevation were represented in the projections. Seasonal injury based on the calculated species index for both seasons was reclassified to a quintile scale and overlayed as points onto the ozone concentration versus elevation interpolation projection (Figures 4.26 and 4.27). In addition, seasonal available soil moisture, for 2001 only, was overlayed onto the ozone concentration versus elevation interpolation in the same manner as plant injury (Figure 4.28).
Figure 4.24: Spline interpolation of ozone concentrations measured via passive sampling devices at 15 monitoring sites in north central Pennsylvania from May 29th to September 5th, 2000.
Figure 4.25: Spline interpolation of ozone concentrations measured via passive sampling devices recorded at 15 monitoring sites in north central Pennsylvania from May 28th to September 18th, 2001.
Figure 4.26: Reclassification of plant injury data based on the species index recorded at 15 monitoring site in north central Pennsylvania overlayed on the ozone versus elevation interpolation for the 2000 research season.
Figure 4.27: Reclassification of plant injury data based on the species index recorded at 15 monitoring site in north central Pennsylvania overlayed on the ozone versus elevation interpolation for the 2001 research season.
Figure 4.28: Reclassification of available soil moisture recorded at 15 monitoring site in north central Pennsylvania overlayed on the ozone versus elevation interpolation for the 2001 research season.
Chapter 5. Discussion

Ozone

Ambient ozone concentrations were successfully measured for both the 2000 and 2001 research seasons. The location of monitoring sites represented a large areal extent of north central Pennsylvania. While most of the sites were considered to be in a mid to high elevation range, a clear gradient of over 500 meters difference in elevation among sites added to the spatial variability of the research area. In addition, the accessibility of the monitoring sites and a well planned travel route enabled observations at all sites to be recorded within a strict 24-hour time frame. Due to these factors, spatial and temporal comparisons within respective sites and between sites were considered to be more defendable and scientifically sound.

Highly significant correlations (\(r = 0.959, p < 0.0001\) in 2000 and \(r = 0.979, p < 0.0001\)) between ambient ozone concentrations measured with passive sampling devices compared to concentrations measured with TECO Model 49 continuous monitors demonstrated that the Ogawa passive sampling device was a cost effective and accurate means of measuring ozone (Skelly et al., 2001). The slight over- and under-estimation of ozone concentrations measured via PSDs compared to TECOs was to be expected because PSDs measured pollutant concentration averages over time whereas continuous monitors have the ability to measure exact concentrations at short periods of programmed time intervals. Continuous monitors can also record fluctuations in pollutant concentrations, such as hourly highs and lows, unlike the capability of PSDs that require longer periods of exposures. Current research has focused on determining these fluctuations with PSDs; a widely used formula has not been developed (Krupa
et al., 2001). For the 2000 research season, the weekly comparison of ozone concentrations measured by PSDs showed a tighter fit to average concentrations recorded by continuous monitors than in 2001. It is suspected that the high weekly fluctuations of ozone in 2001 as compared to the more gradual weekly change in ozone in 2000 led to this result. It must also be noted that the 2% increase in correlation between the PSDs and TECOs in 2001 was most likely the result of the added 2 weeks of study.

The significant correlation between ozone and elevation (r = 0.720, p = 0.002 in 2000 and r = 0.802, p < 0.0001 in 2001) showed that concentrations increased with elevation, similar to results obtained by Winner et al. (1989) and Skelly et al. (2001). The three highest elevation sites, Mt. Pisgah County Park (760 m msl), Gleason (758 m msl), and Sproul (719 m msl) supported this correlation by exhibiting high seasonal ozone concentrations near 40 ppb in 2000 and greater than 40 ppb in 2001. As expected, the lowest elevation sites, Williamsport (202 m msl), State College (425 m msl), and Mt. Pisgah State Park (429 m msl) exhibited seasonally low ozone concentrations of 30 ppb or less in 2000 and 35 ppb or less in 2001. Outliers for this general correlation were observed at Skyline and Tiadaghton. When the ozone concentration results were adjusted in 2001 to coincide with the same observation period as 2000, Skyline (580 m msl) exhibited the highest ozone even though it was situated at an elevation nearly 200 meters less than the highest elevation site monitored (Mt. Pisgah County Park). It was suspected that the close proximity to the city of Williamsport was one of the primary factors influencing this result. Williamsport and its surrounding suburbs was the largest population center in north central Pennsylvania where monitoring sites were located, thus there was high probability that the regional transport of ozone coupled with an abundance of ozone-forming precursors in and
around the city led to the elevated concentrations recorded at the Skyline site. It was suspected that the Williamsport site did not experience the same elevated ozone effects even though it was situated within the city center due to NOx scavenging. NOx scavenging is the result of chemical processes where nitrogen oxides tend to dissociate ozone into O and O$_2$. Due to low elevation and location (less than 40 meters from a busy highway), ozone concentrations at the Williamsport site were broken down by the excess NOx emitted from high automobile traffic (Wishinski and Poirot, 1995).

The other site of special interest, Tiadaghton (562m msl), located approximately 20 miles northwest of the city of Williamsport, continually exhibited low seasonal ozone concentrations even though it was not categorized as a low elevation site. To understand why this occurred, air circulation patterns over north central Pennsylvania must be addressed. The dominant air mass trajectory for this geographic area originates from the northwest region of Pennsylvania, including Lake Erie and the Great Lakes airshed, which is usually characterized with much lower ozone air pollution (Jagodzinski, 2000; Skelly et al., 2001). Tiadaghtont was located directly in the path of this air transport pattern, just upwind from the Williamsport site where ozone concentrations were observed to be the lowest over both seasons. These observations provided evidence that many factors, not solely elevation, were involved in the formation, destruction, and transport of ozone and its pollutant precursors.

The seasonal comparison from May 28th to September 5th showed that ozone concentrations were greater for the 2001 season. The formation of ozone is caused by precursors such as NOx and hydrocarbons intermingled with photochemical processes. In general, hot, sunny days along with regional air circulation patterns add to the buildup of ozone-laden air
parcels. To provide an explanation as to why ozone was higher in 2001, meteorological data across the region of study was analyzed (Appendix B). The data from four co-located sites (Gleason, Moshannon State Forest, Tiadaghton, and Penn Nursery) showed that average seasonal temperatures were higher and average relative humidity percentages were lower in 2001 as compared to 2000. Based on that information, levels of ozone buildup were probably accelerated in 2001.

**Foliar Injury**

Native populations of black cherry and common milkweed were found at all sites within a reasonable distance to the Ogawa passive sampling device with the exception of Mt. Pisgah County Park and Williamsport. Common milkweed was not located within the 3 kilometer distance or the 100 meter of elevation ranges at these sites. Since bioindicators were located within a 200 meter distance from the PSD at most sites, accurate relationships between ozone exposure and injury were able to be developed.

The species injury index calculation, used in the National Forest Health Monitoring Program, proved to be an efficient way to statistically rank and compare sites. Among the benefits of the index was the ability to apply nominal data, as measured in the field, to a formulation that reflected individual plant response by species as well as species response by plot.

Typical ozone-induced symptoms were observed at all sites over the study periods and thus supported the efficacy of using black cherry and common milkweed as suitable ozone bioindicator species. Over the two seasons, the highest amount of injury to both species was observed at the Moshannon State Forest site while the lowest injury was observed at sites that
included State College and Williamsport. Cumulative ozone concentrations were significantly correlated with cumulative plant injury as well as elevation. However, at the high elevation Mt. Pisgah County Park site, plant injury was consistently among the lowest recorded over the research periods whereas ozone concentrations were among the highest. These results suggest that there were other significant factors, such as genetics or soil moisture, which determined injury amount and severity on the black cherry trees at this site.

Soil moisture measurements, recorded for the 2001 season only, were analyzed to determine any significant interactions with plant injury development and the progress of symptoms. A relationship between the two variables showed that available soil moisture along with cumulative ozone concentrations were significant factors involved in determining the progression of black cherry injury on a weekly basis. This relationship between available soil moisture, ozone concentrations, and plant injury was consistent with previous research conducted by Showman, 1991. One of the sites that clearly demonstrated this relationship was Mt. Pisgah County Park. As a high elevation site, Mt. Pisgah County Park exhibited high seasonal ozone concentrations, however, since seasonal soil moisture percentages were among the lowest recorded for all sites, the injury index value for black cherry was also low. Additional examples of the soil moisture versus injury relationship were observed at Moshannon State Forest and Tiadaghton. Common milkweed at Moshannon was located in continually wet soil. Average height of the plants (4-6 feet), deep green color, and number of leaves present suggested healthy growth. It was speculated that this milkweed population was actively transpiring (though no formal measurements were made) and thus, with open stomata, there was most likely increased ozone uptake. Similar results were observed at the World's End site. At Tiadaghton,
even though ozone concentrations were relatively low, available soil moisture for the bioindicator populations averaged greater than 70% for the season. Making the same assumption as with Moshannon, the milkweed had active transpiration and therefore increased ozone uptake.

Combined black cherry and common milkweed injury data showed that greater cumulative injury occurred in 2000 than in 2001, except at the Tiadaghton site. Based on the strong relationship between injury and soil moisture, seasonal rainfall data collected from the co-located sites were analyzed in order to make a comparison between the two years. Rainfall data was used because soil moisture is a function of precipitation and evapotranspiration (Fetter, 1994) and available soil moisture was not directly measured in the 2000 season. In addition, soil composition (surveyed prior to when research was conducted) indicated sandy loam as the primary soil type at all of the monitoring sites. Analysis showed that average rainfall was greater at 3 of 4 co-located monitoring sites in 2001, suggesting that there was more available soil moisture in the low injury year and thus does not support the relationship between injury and soil moisture based on the yearly comparison. However, most of Pennsylvania has experienced low water tables typical of drought conditions due to a decrease in annual rainfall since 1999 (Figure 5.1). National Weather Service data for the state showed a decrease of 6.6 inches of rain from
Figure 5.1: Average rainfall data from 1990 to 2001 for the State of Pennsylvania. Source: National Oceanographic Atmospheric Administration, National Weather Service 2002.
2000 to 2001. Even though meteorological data from the co-located sites denote more rainfall in 2001, hydrogeologic principles suggest precipitation in drought seasons to go directly to infiltration processes to recharge the water table (Fetter, 1994). Therefore, even though soil moisture percentages of 70% were recorded in 2001 it was possible that this result was localized to specific sites (i.e. wetland areas) or, inferred from the statewide meteorological data gathered, soil moisture percentages in 2000 were assumed greater than in 2001.

**GIS Applications**

The use of GIS capabilities was an effective tool to visually project spatial trends among research variables across the study region. The availability and accuracy of digitalized geographic datasets for Pennsylvania allowed for interpolation models to be developed. GIS modeling was dependent upon the significance of statistical methods and errors in spatial variability within and between samples (Oliver et al., 1990). Since the research conducted in this study was observational with a limited number of variables, more advanced interpolation models, such as co-kriging, were unable to be used. In addition, the lack of significant correlations between plant injury and soil moisture with elevation limited the modeling to ozone alone.

The regression interpolation method used for projecting the ozone versus elevation correlation accurately interpreted concentrations within 3 ppb at all locations. Because of the accuracy of this method, the over- and under-estimation of ozone concentrations measured via PSDs were smoothed to fit monitored points more realistically to those concentrations measured via continuous monitors. The utility of the regression-based method of interpolation has also been proven in other air quality based
research with results comparable to those achieved by more sophisticated models (Briggs et al., 2000). To further improve the usefulness of the model, more monitoring sites might have been used across the seven county area.

The spline method of interpolation, while not as accurate as the regression method, detailed a regional ozone pattern based on site specific concentrations. The purpose of using this method was to illustrate a gradient of ozone trends from west to east across the monitoring region. The ozone pattern represented by the interpolation showed a consistent pattern from year to year of less ozone-laden air encompassing the Tiadaghton to Williamsport corridor. As with the regression method, more sample points would have increased the accuracy of the spline. However, surface tension was adjusted (based on ozone gradients with site elevations) to represent a significant fit of the interpolation surface at all points.

Plant injury and soil moisture were represented as reclassified points based on a quintile ranking. Since both variables did not correlate significantly with elevation, they were overlayed on the regression surface and not interpolated. If data on co-variables (temperature, light, weather events) were collected, or if these variables were statistically correlated, other methods of modeling could have been applied, further utilizing the capabilities of GIS.

Conclusion

The high correlation between passive sampling devices versus TECO Model 49 continuous monitors showed the utility of passive samplers as being cost effective and accurate. Trends in ozone concentrations versus elevation and geographic region illustrated a gradient of ozone across north central Pennsylvania. The ability to assess
and predict ozone concentrations throughout the region of study was dependent upon many factors that included primary precursor source region, air transport patterns, and geographic site location.

Typical ozone-induced injury on black cherry and milkweed bioindicators was observed in north central Pennsylvania following exposures to ambient air that contained ozone concentrations ranging from 23 to 51 ppb. The important interaction between soil moisture and plant injury provided evidence that symptom expression and progression is dependent upon many variables, not solely fluctuations in ozone concentrations. Finally, future research of ozone-induced foliar injury may need to incorporate more variables that include plant genetics and more detailed monitoring of controlling environmental parameters such as soil moisture, air temperature, and light to more fully understand the processes by which symptoms are expressed.
References


Appendix A: Passive Sampler Deployment Data

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Table A2. Passive sampling device deployment data for 15 monitoring sites in north central Pennsylvania recorded from May 28th to September 18th, 2001.

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Appendix B: Meteorological Data
Table B1. Meteorological data recorded from four co-located sites in north central Pennsylvania for the 2000 and 2001 research seasons.

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<th>Site</th>
<th>Rainfall (in.)</th>
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