Assessment of Pollutant Exposure and Nitrogen Enrichment Experienced at the University of Michigan Biological Station in 2007

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Abstract

The chemical composition of the air is influenced by meteorological conditions, emissions, and climate change. Atmospheric composition can have detrimental impacts on tree physiology that can lower productivity, but can also have positive nutrient enriching impacts that can increase productivity. Hourly ambient values of SO_2, NO_2, and O_3 for Pellston, MI were used to calculate the number of times each pollutant separately and together would exceed critical levels set by the World Health Organization European Air Quality Guidelines (WHO Air Quality, 2000). Hourly ambient values of these pollutants were also converted to weekly and monthly (24 hour day and daylight day) to analyze whether the suite of pollutants of SO_2, NO_2, and O_3 would have a significant influence on the residual variance of NEE and GPP after the primary drivers of photosynthetic photon flux density (PPFD), vapor pressure deficit (VPD), soil moisture, air temperature, and humidity are taken into account. After running the data in the SPSS statistical package, it was found that the suite of pollutants did not cover the residual variability for either NEE or GPP, but that AT1.5(NO_2) (among all the pollutants) was found to be significant the greatest number of times out of the 24 trial runs. Out of all the trial runs tested, it was found that the pollutants were significant a greater number of times in monthly, daylight hours, for NEE.

Introduction

Atmospheric Composition Impacts Ecosystems

The chemical composition of the air can have positive and negative impacts on ecosystems. From increasing productivity through nutrient enrichment, to damaging leaf physiology and retarding growth, the composition of the air can have significant impacts on the growth of vegetation (e.g. Krupa, 2001). While certain pollutants such as ozone are known to be phytotoxic to plants, other chemical compounds such as NO_2 can have both growth enhancing and growth deterring effects (e.g. Felzer et al, 2007). The factors that determine the chemical composition of the air can ultimately have significant impacts on the environment.

The Type of Compounds Emitted Impacts Chemical Composition of the Air

The chemical composition of the air is determined by emissions, meteorological conditions, and chemical and physical loss processes. Chemical composition impacts air quality. Air quality is defined as a measure of air conditions determined by the needs of humans or biotic species (Johnson, 1997). Firstly, the chemical make-up of the air, while primarily composed of

molecular nitrogen (78.084%), molecular oxygen (20.95%), and argon (.93%), is changing due to increased human activities such as fossil fuel combustion (e.g. Gaston, 2006). Fossil fuel combustion has resulted in an increased concentration of compounds such as carbon monoxide (CO), nitrogen oxides ($NOx = NO + NO_2$), and volatile organic compounds (VOC) (alkanes, alkenes, aromatics, etc.) in the troposphere (e.g. Jacobs, 2004). With the increased emission of these compounds, the formation of O_3 (which is harmful to human health and vegetation) in the atmosphere is also increasing (e.g. Lin, 2007). Of greater importance to ozone formation is the emissions of VOCs. These hydrocarbons, primarily emitted through biogenic processes in forests and agricultural areas (e.g. Pierce, 1995), is one of the main precursors to O_3 formation (e.g. Jacobs, 2004).

Meteorology Impacts the Chemical Composition of the Air

Temperature, pressure, and water vapor pressure (parameters that describe meteorology) impact the chemical composition of the air. Wind (speed and direction), determined by pressure gradients, controls the transport of air masses (which contain chemical species) from one location to another. The path of the air parcel is important in determining the emissions that the air parcel may entrain. The conditions along the path are determined by frontal activity associated with the meeting of air masses. When air masses that have different properties (e.g. temperature, dew point) meet, this often results in cloud and/or fog formation and precipitation. Temperature changes and light intensity can affect the chemistry along the path. Higher temperatures can lead to higher rates of reaction. Certain reactive pollutants can form secondary pollutants via photochemistry.

Chemical Transformations and Physical Loss Processes Impact the Chemical Composition of the Air

After the industrial revolution, fossil fuel combustion and biomass burning increased NO_x and CO concentrations in the atmosphere by factors of 2-8 and 3-4, respectively, as indicated in Table 1 (e.g. Jacob, 2004), and because of this, ozone concentrations have increased by 63% since preindustrial times in the troposphere (e.g. Jacob and Wang, 1998). OH concentrations have been fairly constant for the past 20 years due to the fact that NO_X and O_3 increase OH production while CO and hydrocarbons eliminate it (e.g. Jacob, 2004).

The secondary pollutant and greenhouse gas, ozone, is formed from the precursors CO, NOx, and VOCs. Net accumulation of ozone occurs in the sequence of reactions below:

$CO + OH \rightarrow CO_2 + H$ (R1)

$H + OH + M \rightarrow HO_2 + M$ (R2)

$HO_2 + NO \rightarrow NO_2 + OH$ (R3)

$NO_2 + hv \rightarrow NO + O\ (3P)$ (R4)

$O(3P) + O_2 + M \rightarrow O_3 + M$ (R5)

The majority of CO and nitrogen oxides emitted are from anthropogenic emissions (e.g. Jacob, 2004

Table 1. Sources, Sinks, and Production Rates for Tropospheric Ozone (e.g. Jacob, 1998)

		Sensitivity Simulations Departing from the Preindustrial Atmosphere					
	Preindustrial	A 1.7 ppmv CH_4	B Present CO + NMHCs	C Present NO_x	D Present Fuel + Industry	E Present Biomass Burning	Present
Sources (Tmol yr^{-1})							
Chemical production	39	46	45	65	59	55	85
Transport from strato-sphere	8.4	8.4	8.4	8.4	8.4	8.4	8.4
Sinks (Tmol yr^{-1})							
Chemical loss	38	44	44	60	54	52	77
Dry deposition	8.7	9.8	9.6	13	13	11	17
O_3 burden (Tmol)	4.0	4.5	4.4	5.2	5.1	4.7	6.5
O_3 lifetime (days)	31	31	31	26	28	27	25
O_3 production efficiency α_N per of NO_x emitted (mol/mol)	60	71	70	22	28	39	28
O_3 yield α_C per unit of CO or hydrocarbon oxidized (mol/mol)	0.80	0.67	0.56	1.1	0.81	0.80	0.72

The budgets and production efficiencies are for odd oxygen ($O_x = O_3 + O + NO_2 + HNO_4 + 2 \times NO_3 + 3 \times N_2O_5$ + organic nitrates + HNO_3) in the model air column from the surface to 150 mbar (specified as the tropopause). Over 95% of O_x is O_3. Chemical production of O_x is by reactions of peroxy radicals with NO, and chemical loss is principally through the reactions O^1D+H_2O, O_3+HO_2, and O_3+OH. Sensitivity cases are the same as in Table 1.

Particulate matter is made up of organic and inorganic substances and is divided into two groups: coarse and fine (1.0 and 2.5 micrometers, respectively). One study found that ozone and particulate matter were positively correlated, primarily due to temperature (e.g. Adhikiri, 2005). A subdivision of particulate matter, called secondary particles, is formed primarily from the oxidation of sulfur and nitrogen oxides which are emitted from primarily anthropogenic sources. This chemical process transforms gaseous species into very small particles. The nitrate and ammonium ions components of certain particulate matter can also act as sources of nitrogen enrichment in ecosystems (Mellilo et al, 1983). Ultimately, NOx can be a precursor to sources of soil fertilizers (ammonium and nitrate ions) but can also be a precursor to particulate matter and acid rain (which can damage stomatal conductance) (Mansfield et al, 1993). At the University of Michigan Biological Station, the levels of particulate matter are much lower than levels that could be damaging to the vegetation.

Physical loss processes of these chemical compounds can also impact air quality. Large particles, sticky gases, or aerosols can be lost by dry deposition (gravitational settling or impaction), while water soluble gases and aerosols can be lost in fog or rain.

Climate Change Impacts Air Quality

With its strong dependence on weather, air quality is sensitive to climate change. In the future, the planet is predicted to experience weaker global circulation and a lower frequency of storms (e.g. Jacob and Winner, 2009). This is expected to lead to an increased frequency of stagnant conditions (e.g. Jacob and Winner, 2009). With increased stagnation in polluted areas, this could lead to higher frequency of acute pollution exposure. Chemical transport models have found that increased temperatures will increase ozone in polluted areas in the summer by 1-10 ppbv (e.g. Jacob and Winner, 2009). This is most significant in urban areas. While not as high as

the change in ozone, changes in temperature and precipitation frequency in future decades have been predicted to increase the PM concentration in urban areas (e.g. Jacob and Winner, 2009).

Air Quality Impacts Vegetation Productivity

Many air pollutants, including O_3, PM, NO_2, and SO_2 can damage foliage and decrease ecosystem productivity (e.g. Beckett et al, 1997, Wellburn et al, 1988). PM accumulation on leaves or bark forms a crust that can block stomata and disrupt the efficiency of gas and nutrient exchange (e.g. Beckett, 1997). PM can also increase leaf temperature, which can increase the leaf's susceptibility to drought (e.g. Beckett, 1997). It can damage leaf tissue, decreasing the efficiency of photosynthesis and increasing plant susceptibility to pests. PM can also inhibit bud breaks, pollination events, and impact the amount of light reflected or absorbed (e.g. Beckett et al, 1997). When the PM crust dissolves it releases CaOH into intercellular spaces and causes the cell to burst (e.g. Farmer, 1991). Similarly, when O_3 decomposes into organic radicals, the radicals damage the guard cells that control stomatal opening and the units in the chloroplast that harbor light (e.g. Krupa et al, 2001). This damage reduces photosynthetic efficiency and growth (e.g. Krupa, 2001). Additionally, the O_3 reaction with RUBISCO reduces photorespiration and suppresses the messenger RNA required for its synthesis (e.g. Pell and Eckhardt, 1992). SO_2 is highly toxic to the chloroplast because it also forms free radicals that damages plant cells and chloroplast components (e.g. Wellburn, 1988). Furthermore, while nitrogen can act as a nutrient for plant growth, certain levels of deposition through stomata can cause leaf tissue injury and lower the uptake of nitrogen in the roots (e.g. Ng et al., 2001).

Reactive nitrogen deposition, as a source of nutrient enrichment, can increase the productivity of vegetation in nitrogen limited ecosystems (Meinzer and Grantz, 1991). As additional nitrogen is inputted into an ecosystem, the net primary productivity of a forest (NPP, the total carbon fixed by photosynthesis minus autotrophic respiration) is predicted to increase. This nitrogen deposition principally results in an increase of ammonium and nitrate inputs primarily formed from NOx, HNO_3, PAN, and NH_3. In a study done by Emily Nave at UMBS in 2000-2004, she found that 13% of the nitrogen required for NPP came from atmospheric deposition (Nave, 2007). She found that 6.5kgN/ha/yr was 13% of the *net* amount of atmospheric nitrogen needed to meet the forest's NPP requirement (*after soil solution losses were taken into account*). Net atmospheric nitrogen deposition is found by adding wet nitrogen deposition, dry nitrogen deposition, and nitrogen canopy retention (taking into account soil solution losses). She found that on average, 2.2kgN/ha/yr was accounted for by nitrogen canopy retention (<4% of the 13%), 3.6kgN/ha/yr by wet deposition, and .7kgN/ha/yr by dry (Nave, 2007). She mentions however that these were underestimates because dry deposition was only measured for a 7 month period. In a separate study, it was also found that nitrogen can increase other nutrients inputs, such as the nutrient nitrate, by 8 percent (Hogg et al, 2005).

Assessing Pollutant Exposure at UMBS and Residual Variance in Net Ecosystem Exchange and Gross Primary Productivity

At UMBS, 74% of the forest is O3 sensitive, 83% is SO_2 sensitive, and 21% is NO_2 sensitive. 11% (made up of Eastern White Pine) was determined to be sensitive to NO_2+SO_2 based after a study done on Scotts Pine where Scotts Pine was shown to be sensitive to the combination of these two pollutants (Manninen and Huttunen, 1999). I assumed that Eastern White Pine behaved similarly to Scotts Pine.

Table 2. Tree Sensitivity at UMBS

Tree	% of Forest	Ozone Sensitive	SO_2 Sensitive	NO_2 Sensitive	NO_2+SO_2 Sensitive
Red Maple *Acer rubrum*	9%		X		
Red Oak *Quercus rubra*	17%				
Eastern White Pine *Pinus strobus*	11%	X	X	X	X*
Paper Birch *Betula papyrifera*	10%	X	X	X	
Big Tooth Aspen *Populus grandidentata*	53%	X	X		
Percent of Forest Sensitive/Tolerant	99%	74%	83%	21%	11%

Air Quality at UMBS

At UMBS air masses primarily come from the north/northwest, south/southwest, east/southeast, west (e.g. Ocko and Carroll, 2006). The northern air mass has been shown to be the dominant air mass that arrives at UMBS (44%), followed by the southern air mass (24%) (e.g. Cooper and Moody, 1998, Ocko, 2006). The northern air mass is primarily clean (lower levels of CO and ozone in the range of 20-30ppbv) and the southern air mass is dirty (high ozone and CO in the range 40-100ppbv) (e.g. Cooper and Moody, 1998). The south/southwest air mass has been shown to have the highest levels of NOx, CO, and VOC's, while the northern air mass had the lowest levels (e.g. Cooper and Moody, 1998). The east/southeast had the second highest levels of these pollutants (e.g. McNeal, 2008). PM2.5 arrives at UMBS at levels that are extremely low. To the north are cleaner areas of Canada and to the south/southwest are dirtier regions of Illinois, southern Michigan, Indiana, and Ohio. Between May and September, there

has been shown to be an increase in south/southwesterly flow and a decrease in north/northwesterly flow (e.g. Ocko, 2006). Ultimately, the typical air flow regimes at UMBS show that during the summer months there are higher levels of pollutants compared to the winter months.

As nitrogen inputs can increase productivity in N-limited forests, and phytotoxic pollutants can damage cell functioning, the effects of each are often difficult to detect in trees experiencing both pollutant exposure and N enrichment (Felzer et al, 2007)

Hypothesis

Since prior studies have shown that ambient O_3 alone and stomatal O_3 flux alone are not responsible for the residual variance in NEE (after considering the primary drivers), I expect the exposure to NO_2, SO_2, and O_3, *together as a suite*, to be a significant factor in UMBS forest NEE and GPP residual variance in the growing season (May 7-November 5) of 2007. To obtain a more accurate estimate of pollution exposure that simulates chemical reactions and physical loss processes along a path, output from the chemical model, CAMx, that simulates chemical transformations along a path with given meteorological conditions and emissions inputs, will be obtained from the Lake Area Directors Consortium (LADCO).

Materials and Methods

Site Description

The University of Michigan Biological Station (45°30'N, 84°42'W) located in northern Michigan consists of a mixed hardwood forest made up of 5 major tree species: bigtooth aspen (*Populus grandidentata*) (53% of forest), red maple (*Acer rubrum*) (9%), red oak (*Quercus rubra)*(17%), eastern white pine (*pinus strobus*)(11%), and paper birch (*Betula papyrifera*)(10%), primarily (e.g. Curtis, Gough, Vogel, Schmid, 2003, 2005, 2006). The forests primarily experience pollution from Chicago in the Southwest, Detroit in the Southeast, and Toronto in the east to southeast (e.g. Cooper and Moody, 1998).

Ambient Level Pollution Exposure

To obtain ambient levels for SO_2, NO_2, O_3, and PM2.5, output from the atmospheric chemical model CAMx was obtained from the Lake Area Directors Consortium (LADCO). LADCO provides technical assistance on air quality issues for the states of Michigan, Indiana, Wisconsin, Ohio, and Illinois. LADCO runs the model CAMx 4.5 for these states and creates outputs that contain hourly ambient levels of criteria pollutants. The CAMx4.5 atmospheric model is a three dimensional model that uses 36km and 12km grids for locations specified by latitude and longitude. The size of the grid determines the resolution or details of topography, lake breezes, and climactic conditions. It uses meteorology inputs from the NCAR/PENN state meteorology model (MM5), which obtains its data from the National Weather Service

(specifically, twice daily radiosondes and 3 hour surface observations). The meteorology input is formatted in a 3-dimensional grid, including horizontal wind components, temperature, pressure, water vapor, clouds, and precipitation. Emissions input data is from the National Oceanic and Atmospheric Association (NOAA) National Emissions Inventory dataset from 1991 and Continuous Emissions Modeling data from 2007 and 2008. The emissions data includes low-level point sources, mobile sources, area/non-road mobile sources, and biogenic sources. Air Quality data includes gridded initial concentrations and gridded boundary concentrations. The vertical distance that is assessed is 15km divided into 16 layers, with higher resolution in the lower layers. The model also predicts 1-hour O_3 concentrations. CAMx also incorporates photochemical and gas phase chemistry mechanisms in its model to calculate ambient levels of pollutants. The model treats species such as ozone, particulate matter, mercury, and reactive hydrocarbons, to name a few. It incorporates algorithms to determine dry and wet deposition and also horizontal advection and vertical diffusion. For this project, the local conditions of Pellston were processed in a 12km by 12 km grid.

The ambient data was used to create diurnal plots of the year and growing season to show the typical variability of each pollutant over a day. In addition, averages, minimums, maximums, and standard deviations were calculated for every month in the year 2007 using Microsoft Excel in order to characterize the levels of each pollutant seen over the year 2007.

Determining Critical Levels

In order to determine critical thresholds, a point at which an effect (such as a biomass reduction) occurs (e.g. Sanders et al, 1995), an extensive literature search was done to understand the best guidelines to use. Critical levels were first created in 1988 at the UNECE Workshop in Bad Harzburg, Germany (e.g. Sanders et al, 1995). Critical level is defined as the level above which adverse effects occur (e.g. Sanders et al, 1995) The threshold of 40ppb was set at the workshop because numerous studies had shown that at this level, damage occurs to vegetation (e.g. Sanders et al, 1995). The critical levels can be seen in Table 3. The critical level for ozone over a period of a 6 month growing season was determined to be 10ppmh*h, using daylight hours (WHO Air Quality Guidelines, 2000). Daylight hours were defined as the time period when radiation was above 50 W/m^2 (WHO Air Quality Guidelines, 2000). The daylight hours determined were: May: 6am-7pm, June: 5am-7pm, July: 6am-7pm, August: 6am-6pm, September: 7am-6pm, October: 8am-4pm, November: 9am-4pm. This level was calculated using the AOT40 index (Accumulated Exposure Over a Threshold of 40ppb). The AOT40 is a calculation primarily used in Europe and is calculated by subtracting 40ppb from hourly ambient values of ozone (Acid Deposition and Oxidant Research Center, 2006). The values that are negative are converted to a value of 0. The values that are positive are multiplied by the number of hours at that value and then summed together. This represents a dose, or a concentration over a given time. Not all countries have adopted the same guidelines. In the United States, the SUM60 index is used (e.g. Sanders et al, 1995). This index sums the hourly

ambient values over 60ppb over a given amount of time. In this study, the AOT40 index was used because known damage to vegetation had been reported to occur at 40ppb.

The thresholds that were set for SO_2 and NO_2 were determined based off of a study done on Scotts Pine with varying doses of sulfur and nitrogen (Manninen and Huttunen, 1999). It was found that when SO_2 and NO_2 were at 1.5ppb, damage occurred to the needles of Scotts Pine (Manninen and Huttunen). Assuming that the sensitivity of Eastern White Pine is the same as Scotts Pine, the critical threshold of 1.5ppb was set for NO_2 and SO_2 .

. To calculate the "Above Threshold" values for SO_2 and NO_2, the same method to calculate the AOT40 was employed using the threshold of 1.5ppb instead. These values were given the name AT(SO_2) and AT(NO_2). Groupings of AT(SO_2 and NO_2) and AT(SO_2+NO_2+ O_3) were also calculated using the separate "above threshold" values and then added together. After threshold values were determined using the ambient level data provided by LADCO, the frequency of these groupings exceeding the threshold was calculated and histograms were formed. In addition, the AOT40 value was calculated for the 2007 growing season and was compared to the critical level determined by the WHO European Air Quality Standards. Using their relationship that 10ppmh results in a 10% decrease in biomass, a weighted calculation was done to figure out the percent of trees that would be damaged at UMBS. Finally, AOT40 was also calculated for the years 1999-2005 (see Appendix E. Table 1.)

Table 3. W.H.O Europe Air Quality Tree Guideline Critical Levels and Thresholds

	WHO Europe Air Quality Tree Guidelines (daylight hours, growing season)	Thresholds	% > Threshold
SO_2	10 ppbv (annual avg) 35 ppbv (1 hr)	1.5ppb (as determined by Scotts Pine study)	**47%**
NO_2	16 ppbv (annual avg)	1.5ppb (as determined by Scotts Pine study)	**55%**
O_3	10 ppm*hour	40ppb	**47%**
SO_2 +NO_2	1.5ppbv each	NO_2>1.5 AND SO_2 >1.5	**86%**
SO_2 +NO_2 + O_3	1.5ppb for SO_2 1.5 ppb NO_2 40 ppb for O_3	NO_2>1.5 AND SO_2 >1.5 AND O_3 >40ppb	**88%**

Assumptions

After an extensive literature search was done on the CAMx model, on tree sensitivities to various pollutants, and on environmental factors that might affect productivities/sensitivities of trees, a list of assumptions were made. I assumed that the CAMx modeled produced output that was usable and accurate because research that had employed the model had found that the model and monitored ozone concentrations met the model performance guidelines (mean observation, mean prediction, bias, gross error, root mean square error, and index of agreement) (e.g. LADCO technical report, 2008, Baker and Scheff, 2007, Morris et al, 2003, Liang et al, 2000). It was also found that in general, the model underestimated ozone by 30% (LADCO technical report, 2008). When determining critical levels, I assumed that all trees within a species behaved in the same way. Although research has shown that many aspen trees are sensitive to ozone, some studies have shown that not all aspen clones are ozone-sensitive (e.g. Vahala et al, 2003). However, the clonal speciation of aspen trees in the UMBS forest is not known. Thus, for the purposes of this study, all aspen trees (53% of the forest) are assumed to be O_3-sensitive.

Inorganic Wet Nitrogen Deposition

Inorganic wet nitrogen deposition data for Pellston, MI was obtained from archives in the National Atmospheric Deposition Program website (http://nadp.sws.uiuc.edu). Annual total values from 1999-2007 were obtained from isopleths that provided the total value of wet inorganic nitrogen deposition in units of kg/ha/years. Weekly datasets were also obtained for the year 2007 and summed into monthly values. See Table 1. In Appendix F for the yearly total inorganic wet nitrogen deposition.

GPP, NEE, and Primary Drivers

Gross Primary Productivity (GPP) is the total amount of carbon that is fixed through photosynthesis. Net Primary Productivity (NPP) is Gross Primary Productivity minus autotrophic respiration. Net Ecosystem Productivity is Net Primary Productivity (NPP) minus heterotrophic respiration. Net Biome Productivity (NBP) is NEP minus lateral carbon fluxes. Finally, Net Ecosystem Exchange (NEE) is approximately equal to NEP over the course of a year.

- $NPP = GPP - R_A$
- $NEP = NPP - R_H$
- NBP= NEP-lateral fluxes
- **NEE≈ NEP (over course of year)**

NEE is determined by the net carbon uptake or loss by the ecosystem without including lateral carbon fluxes. Half hourly values for GPP and net NEE were calculated from measurements of CO_2 flux obtained at the 46 m AmeriFlux tower at UMBS. The convention adopted by AmeriFlux: fluxes into the forest are negative, fluxes out of the forest are positive; negative NEE indicates a greater flux of C into the forest than out of the forest. These data and PPFD, VPD, soil moisture, temperature, and humidity were obtained from the Ameriflux data archive (ww.fluxdata.org/).

SPSS Correlations/Multi-Regression Analysis

Three data sets were created. One data set had hourly values of model-generated ambient mixing ratios of O_3, SO_2, and NO_2. The second data set had weekly values of total inorganic nitrogen in wet deposition. The third data set had half hourly values of GPP and NEE, and half hourly values of PPFD, temperature, VPD, soil moisture, and humidity. I then calculated weekly, monthly, and growing season values of AOT40, AT(SO_2), AT(NO_2), and AOT40+ATNO_2+ATSO_2, cumulative monthly values for inorganic nitrogen deposition, and weekly and monthly cumulative values for NEE and GPP. The weekly and monthly values were also converted to weekly/monthly (24 hour) values and weekly/monthly (daylight hour) values, for a total of 4 separate time intervals. For each time interval, there were three main trials. Each trial had a different grouping of pollutants. Each trial was performed for GPP alone, and then NEE alone. The ambient pollutant data were converted into threshold values grouped into 3 main trials:

1st Trial: AOT40, AT1.5(SO_2), AT1.5NO_2

2nd Trial: AT(SO_2+NO_2), AOT40

3rd Trial: AT(SO_2+NO_2+O_3)

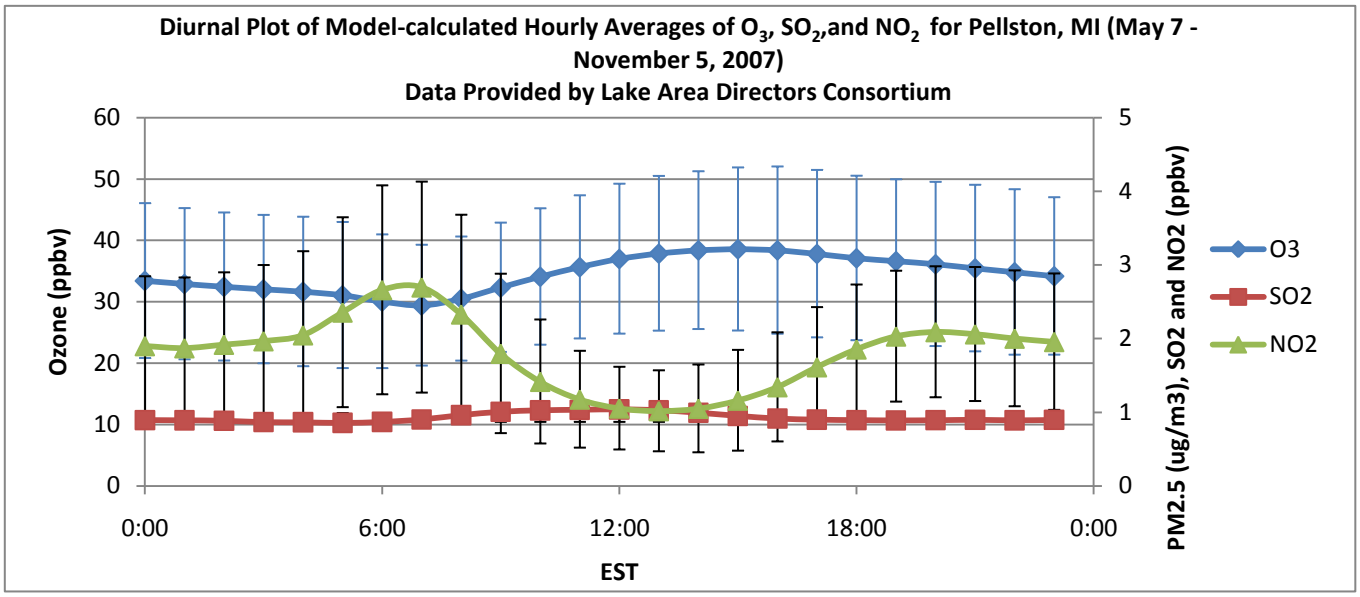
First, correlation analyses were run for each time interval with the specified grouping of pollutants. Then a step-wise regression was performed in which the primary drivers were considered before pollutant doses and insignificant variables were neglected..

Although the Croskey analysis required PPFD to be log transformed with NEE into a linear relationship for SPSS to accurately determine its significance and relationship (Croskey and Carroll, 2007), this study did not require any log transformations of any of the variables. Each variable was correlated with NEE and GPP, once as log transformed, and once in its original value. Each set of variables was compared for higher correlation and stronger significance. It was found that the log transformed variables showed a weaker correlation with NEE and GPP. In the cases where both log transformed and non log transformed were non-significant, the R value was analyzed.

Results

Diurnal plots were made for the growing season and year 2007. Graph 1 is the diurnal plot for the growing season. Ozone had an average value of 35.1ppb with standard deviation of 3.7ppb, and an average maximum of 40.0ppb. Sulfur dioxide had an average of .9ppb, with standard deviation less than .001, and maximum value of .9ppb . The average value of NO_2 was 1.4ppb with standard deviation of .5ppb. Its maximum value was 2.3ppb. SO_2 was the least variable and had the lowest average value while ozone was the most variable and had the highest average value. Ozone also had the greatest maximum value. See Appendix A for Diurnal Plot of year 2007 for O_3, SO_2, and NO_2.

Figure 4. Diurnal Plot of Hourly Averages of O_3, SO_2, and NO_2 May 5-November 7, 2007



The frequencies of exceeding the thresholds of 40ppb and 1.5ppb were calculated for ATO_3, $ATSO_2$, $ATNO_2$, $AT(NO_2+SO_2)$, and $AT(NO_2+SO_2+O_3)$ and placed in Table 3. SO_2 exceeded the threshold of 1.5ppb 47% of the time, NO_2 55%, O_3 47%, SO_2 and NO_2 together 86%, and the suite of pollutants exceeded the threshold 88% of the time. For the pollutants in groups, exceeding thresholds was determined by adding up the "Above Threshold" values together for each specified threshold for that pollutant. See Appendix G for histograms displaying hourly ambient levels and associated frequencies.

The total AOT40 was calculated for the growing season. The growing season total AOT40 was 8.3ppm•h. While this value is below the WHO European Air Quality Guidelines of 10ppm•h, it may still indicate a significant decrease in forest productivity. If (1) the linear relationship between AOT40 and crop damage (e.g. Mills et al, 2006) can be generalized to forests; (2) the finding that an annual O_3 exposure of 10 ppm•hr results in a 10% decrease in biomass can be generalized to the ozone-sensitive tree species that make up 74% of the UMBS

forest; and (3) the ozone mixing ratios generated by the CAMx model for Pellston Michigan suitably represent ambient ozone levels at UMBS and thus can be used to calculate AOT40 for the UMBS forest, a 6% loss in forest productivity is estimated.

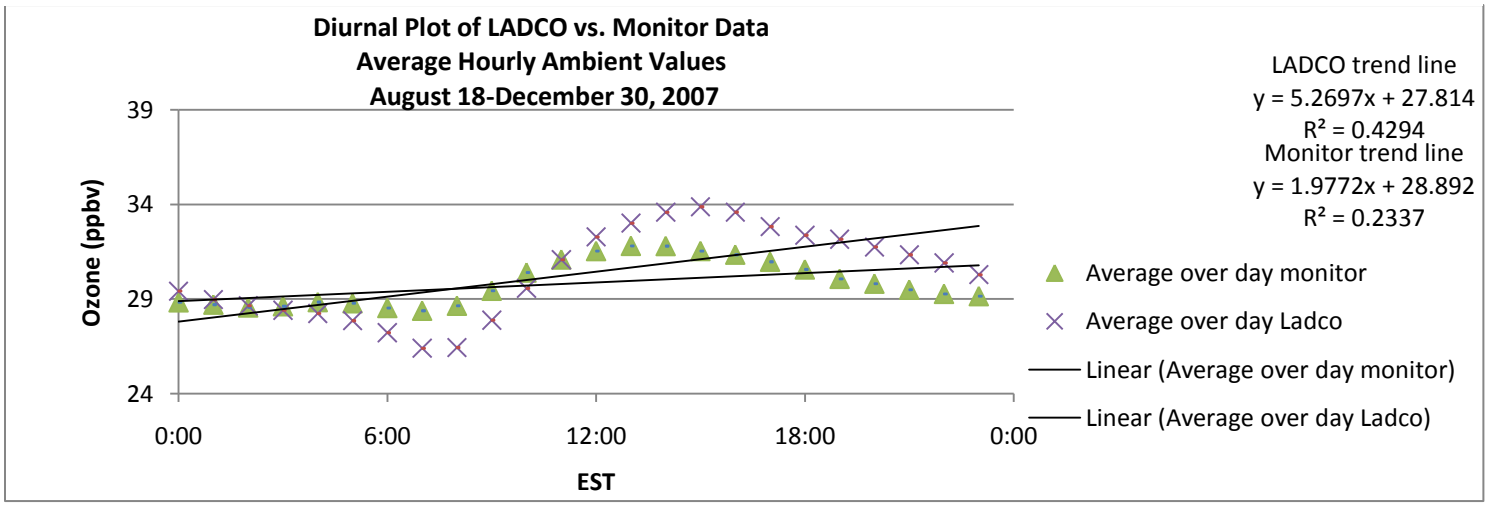
A summary table was made for the AOT40 values for each year from 1999-2005, and 2007. Hourly ambient values were used in the growing season months of May to November. It was found that for each five year average of AOT40 over the years 1999-2003, 2000-2004, 2001-2005, the average AOT40 was under the 10ppmh critical level. See Table 1. in Appendix E for table of yearly AOT40 values.

Paired T-Test and Correlation Analysis (LADCO and PROPHET monitor ozone data)

The data used for this analysis was hourly ambient values of ozone measured from the PROPHET tower at UMBS, and calculated hourly ambient values of ozone from LADCO. The months used were August 18th to November 30th as these were months that were in both datasets *and* in the growing season. The results of the Paired T-test in SPSS showed that there was a statistically significant difference between the LADCO and PROPHET ozone monitor data. It was found that overall, the LADCO dataset mean was 30.42ppb while the PROPHET monitor data mean was 29.001ppb. The difference between the means, -1.42 was reported to be significant ($p<.001$). The standard deviation of the differences was 14.6. See Appendix H for Paired T-test results and for Diurnal Plot between LADCO and Monitor data.

In addition, a diurnal plot was made between the LADCO and PROPHET data between August 18-December 30, 2007 (hourly ambient values averaged over each hour). When the two were compared, it was found that LADCO overestimated ozone ambient values 57% of the time (N=3216), and underestimated 43% of the time. It was also found that LADCO was overestimating, on average by 5.8ppb, and underestimating on average by 5.5ppb. The slope of the LADCO trend line was greater than the slope of the monitor trend line (5.3 vs. 2.0). Also, the y-intercept of the LADCO trend line was 27.8, while the monitor's was 29. LADCO underestimated ozone 10 days in August, 26 days in September, 24 days in October, 21 days in November, 21 days in December. LADCO overestimated 14 days in August, 29 days in September, 26 days in October, 27 days in November, and 17 days in December

Figure 5. Diurnal Plot of Hourly Ambient Ozone Values August 18-December 30, 2007 LADCO vs. PROPHET Monitor Data



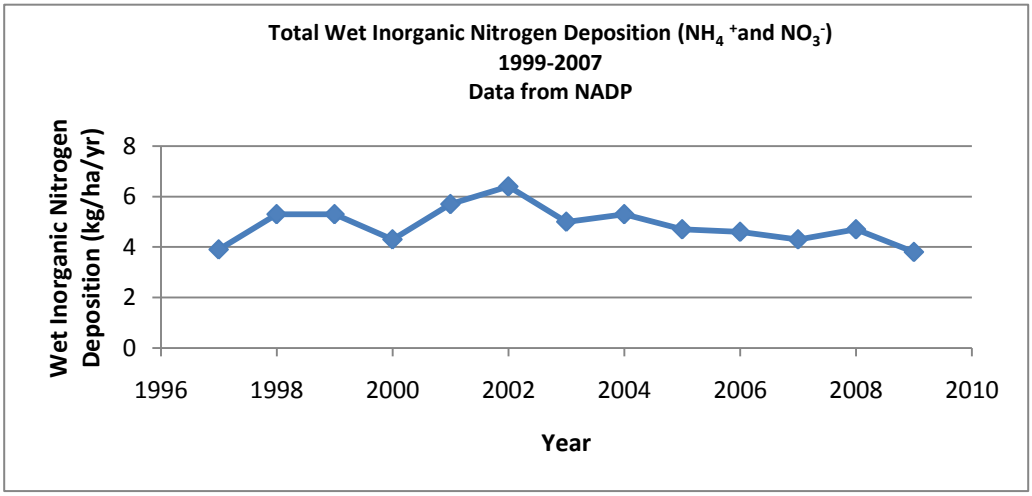
Another correlation analysis was performed between LADCO calculated hourly ozone data, and PROPHET monitor measured ozone data for the months August 18-December 31, 2007. In this analysis, it was found that the LADCO data had a significant correlation with $p<.001$ to the PROPHET data. The R value was .196 and the N=3216.

When a correlation analysis was run with the two data sets of hourly ambient values and GPP it was found that the PROPHET monitor data was significantly correlated ($p<.001$), however LADCO was not. The correlation matrix showed that the PROPHET monitor data was significantly ($p<.001$) correlated with both NEE and GPP, and that the LADCO ambient values were only significantly correlated to NEE ($p<.002$). See Appendix H. for correlation matrix results.

Total Wet Inorganic Nitrogen Deposition 1999-2009

After plotting the total wet inorganic nitrogen deposition annual values from the NADP data archives, nitrogen deposition reached a maximum of 6.4kg/ha/yr in the year 2002 and showed a decreasing trend till 2009 with a minimum of 3.8kg/ha/yr.

Figure 6. Wet Inorganic N Deposition '07



Correlations

After creating a correlation matrix in SPSS with all the primary drivers, each of the pollutant groupings, and the values for NEE and GPP for a specified time interval, it was found that for the weekly 24-hour day for GPP, the primary drivers that were most significantly correlated were: temperature and soil moisture. For NEE, the primary drivers most significantly correlated were: vapor pressure deficit. For weekly (daylight hour days), the primary drivers most significantly correlated with both NEE and GPP were: temperature, PPFD, VPD, and soil moisture. For monthly (24 hour day), PPFD, temperature, and soil moisture were all significantly correlated with GPP. For NEE, temperature and PPFD were the most significantly

correlated. For monthly (daylight hours), GPP was most significantly correlated with: temperature, and soil moisture. While for NEE, the same was true. See Appendix I for summary table of results of SPSS output including correlation analysis results and step-wise regression results.

As PPFD, temperature, VPD, and humidity increased the amount of carbon fixed by the forest increased. As soil moisture increased, less carbon was taken up by the forests.

Stepwise Regression

After running each time interval in SPSS with the different sets of pollutant groupings, it was found that the primary drivers accounted for the majority of the variability. For monthly (daylight hour days) GPP, 77% (R^2=.767) of the variability was covered by the primary drivers, while for NEE, 66% (R^2=.657) of the variability was covered. For weekly (daylight hours) GPP, 53% of the variability was covered by the primary drivers, while for NEE, 45% was covered. For weekly (24 hour days) GPP, 61% of the variability was covered by the primary drivers, while 47% was covered for NEE. For monthly (24 hour days), 90% was covered for GPP, and 70% was covered for NEE. See Table 4 for percent variability covered by primary drivers.

Table 4. Percent Variability Covered by Primary Drivers

	GPP	**NEE**
Weekly Daylight Hours	R^2=.532 53% of variability	R^2=.449 45% of variability
Monthly Daylight Hours	R^2=.767 77%	R^2=.657 66%
Weekly 24 hours	R^2=.613 61%	R^2=.467 47%
Monthly 24 Hours	R^2=.896 90%	R^2=.702 70%

The pollutants that were significantly correlated with NEE/GPP covered most of the residual variability in the monthly (daylight hour) time interval. For GPP, AT1.5 (SO_2) covered 2.6% of the 23% residual variability, and as it increased, more carbon was fixed by the forest. AT1.5 (NO_2) covered 20% of the 23% residual variability, and as is it increased, less carbon was fixed by the forests. For NEE, AT1.5 (SO_2) covered 3.5% of the 34% residual variability, and as it increased, more carbon was fixed by the forests. AT1.5 (NO_2) covered 30% of the 34%

residual variability, and as it increased, less carbon was fixed by the forest. AOT40 covered .8% and as it increased, less carbon was fixed by the forest.

For the weekly daylight hour, AT1.5NO_2 and AT (SO_2 + NO_2) significantly covered some of the 55% of the residual variability for NEE. No pollutant significantly covered any of the residual variability for GPP in this time frame. ATNO_2 covered 14% of the 55% (and had a positive effect), while AT (SO_2+NO_2) covered 12% of the 55% and had a positive effect. However, in the weekly 24 hour day, no pollutant significantly covered any of the residual variability for NEE, but AT1.5 (NO_2) covered 11% of the 23% residual variability for GPP. For monthly (24 hour day), AOT40 was the only pollutant that covered the 30% residual variability in NEE. AOT40 covered 83% and had a positive relationship. No pollutant significantly covered the residual variability in GPP in this time frame.

Table 5. SPSS Step-wise Regression Output

The convention adopted by AmeriFlux: fluxes into the forest are negative, fluxes out of the forest are positive; negative NEE indicates a greater flux of C into the forest than out of the forest

	GPP	NEE
	Weekly (daylight hours)	Weekly (daylight hours)
% Variability by PD	R^2=.532 53%	R^2=.449 45%
%Residual Variability	47%	55%
Pollutant Covering Residual Variability	0%	AT1.5(NO_2) Positive effect R^2 change = 14% AT(SO_2+NO_2) Positive effect R^2 change = 12%
	Weekly (24 hour)	Weekly (24 hour)
% Variability by PD	R^2=.767 61%	R^2=.657 47%
%Residual Variability	23% Residual Variability	34%
Pollutant Covering Residual Variability	AT1.5(NO_2) Positive effect R^2 change=11%	0%
	Monthly (daylight	Monthly (daylight hours)

	hours)	
% Variability by PD	R^2=.767 77%	R^2=.657 66%
%Residual Variability	23%	34%
Pollutant Covering Residual Variability	AT1.5(SO_2) Negative effect **R^2 change=2.6%** AT1.5(NO_2) Positive effect **R^2 change=20%**	AT1.5(SO_2) Negative effect **R^2 change = 3.5%** AT1.5(NO_2) Positive effect **R^2 change=30%** AOT40 Positive effect **R^2 change=.8%**
	Monthly (24 hour)	Monthly (24 hour)
% Variability by PD	R^2=.896 90%	R^2=.702 70%
%Residual Variability	10%	30%
Pollutant Covering Residual Variability	0%	AOT40 Negative effect **R^2 change=83%**

Pollutants were more significant a greater number of times in monthly trial runs versus weekly, daylight versus 24 hour day, and in NEE over GPP. The pollutant value that covered the residual variability the greatest number of times was AT (NO_2) with a total of 4 out of the 24 trials. NO_2 also appeared significantly once more, when in the group AT (SO_2+NO_2).

Discussion

The assumptions that were made about tree sensitivities led us to reach an estimate about the percent decrease in biomass at UMBS. However, since this calculation was based on the idea that all trees in a species behave the same way and that all trees that were marked as sensitive to a pollutant were sensitive in this forest, the value reached, is most likely an overestimate. Also, while the assumption that the relationship between pollutant exposure and productivity is linear allowed us to estimate that a value of AOT40 of 8.3 ppm•hr would result in a 6% decrease in biomass for the UMBS forest, the relationship between pollutant exposure and forest response has not been established for the mix of trees found at UMBS.

Different tree species also have varying dose response relationships. One study had shown that for aspen trees, it took 75ppbv of ozone for 8 hours to produce visible damage to the tree (Vahala et al, 2003). However, in the ambient level data, it was not possible to determine levels based on both time and concentration. However, knowing that exposure to lower levels of pollutants for longer periods of time could result in chronic damage to photosynthetic activities and productivity, the time intervals of weeks and months were established when running the multi-regression.

Using these time intervals could have reduced some of the variability in the primary drivers and in GPP/NEE. This is because for most of the drivers, most of the variability occurs within a day. Using an average over a longer period of time could have washed out a lot of the variability that actually was influencing GPP/NEE. Thus, it was not surprising that when running the data using an hourly time frame, PPFD proved significant as was shown in Jennifer Croskey's study (Croskey and Carroll, 2007), but when running the data using weekly/monthly time frame, PPFD lost its significance. Instead of PPFD, temperature was found to be significant in 23 out of the 24 trials

Comparing Croskey's results to this analysis, she found that in the growing season, ozone stomatal conductance had a significant positive correlation with NEE after taking the primary drivers into account on an hourly time frame. In comparison, this study's focus was on determining whether the suite of pollutants significantly covered any of the residual variability after the primary drivers were taken into account. It was surprising that AOT40 did not prove to be significant in most of the trials , because while studies had shown that ambient ozone did not significantly cover residual variability, it was predicted that accumulated ozone would have somewhat of an effect, especially over a longer period of time. However, based on Croskey's study, ozone stomatal conductance is predicted to have more of an effect on GPP/NEE than ambient ozone or even accumulated ozone. This is because while pollutant levels can remain high, the amount of stomatal conductance will ultimately determine how much ozone is taken up into the plant. Similar to Croskey's study, however, AOT40 only proved to have an influence on NEE. AOT40 covered most of the residual variability (83% of 30%) one time in the monthly time interval, which is not surprising because exposure to accumulations of lower concentrations has been shown to reduce productivity more than over a shorter time interval (UNECE, 1995) .However, the most surprising result, was that the suite of pollutants did not prove to be significant at all, in any of the trial runs, as predicted.

Both AT1.5 (SO_2) and soil moisture effected NEE/GPP in the opposite way that was expected. AT1.5 (SO_2) had a negative effect, meaning that as SO_2 increased, GPP/NEE decreased (greater carbon storage). This could be because while some types of trees in this forest are sensitive to SO_2, there might be other types of vegetation that are more sensitive, thus reducing the impact that SO_2 has on the trees involved in NEE/GPP.

Soil moisture showed a positive relationship, meaning that as it increased, less carbon was being stored. One explanation could be, in general, in the summer months, less rain events occur than in the autumn. Thus, when productivity is at its highest in the middle of the summer, there is very little soil moisture. However, when the autumn months come around and productivity starts to decline, there is greater precipitation, and thus the effects are confounded by time. Also, because the soils at UMBS are sandy, the sand is not able to retain as much moisture for long periods of time. Thus, the trees use this moisture very quickly. This variability is seen over shorter time intervals than a week or a month; therefore, the results could have been due to the reduction of variability.

The pollutants were significant a greater number of times for monthly and daylight hours, for NEE. It was not surprising that daylight hours showed a greater amount of significant pollutants because studied have shown that in daylight hours, trees tend to be most sensitive to pollution because their stomata are open and the pollutants are typically at their peak levels (Sanders et al, 1995). However, some studies have shown that some trees keep their stomata open at night (e.g. Grulke et al, 2004). Even so, this might not be the case for the tree species in our forest, and because there are lower levels of pollutants at night, the effect did not prove significant possibly for this reason.

Compared to the values found by Nave in her study for inorganic wet nitrogen deposition at UMBS, the average value between the years 1997 to 2009 of 4.8kg/ha/yr was higher than what she found, 3.6kgN/ha/yr (Nave, 2007). However, she mentions that her study accounted for soil nitrogen losses, which were not accounted for in this project. Assuming her study is accurate, she states that a total of 51.kgN/ha/yr is needed to meet the forests NPP requirement, and 3.6kgN/ha/yr is the amount of inorganic wet nitrogen deposition needed. The total amount of net atmospheric nitrogen deposition amounts to 6.5kg N/ha/yr, which is made up of wet, dry, and net canopy retention. This net amount is 13% of the NPP nitrogen requirement. Thus, if dry nitrogen deposition and nitrogen canopy retention met the rest of the requirement, there *was* enough nitrogen enrichment for productivity to increase or stay stable within the time interval.

Conclusions

All pollutants studied exceeded their threshold values greater than 50% of the time. However, when comparing AOT40 summations, the UMBS total of 8.3ppmh was under the critical level of 10ppmh for the growing season. If this relationship was linear and if 74% of the UMBS forest is sensitive to ozone, then it can be speculated that there was a 6% decrease in biomass. In addition, the suite of pollutants together did not significantly cover the residual variability of NEE or GPP. However, of the conditions analyzed, pollutant groupings were significant more of the time in monthly, daylight hours in relationship to NEE. Of the pollutant groupings tested, AT1.5 (NO_2) was significant more times than the rest. Finally, the effects of the suite of pollutants on NEE could have been masked by the nitrogen deposition at UMBS.

These negative and positive effects of pollutants and nitrogen on NEE and GPP are hard to quantify because as one hinders productivity the other increases it.

Recommendations for Future Work

It would be useful to characterize the forest in terms of what types of clones within each species reside at UMBS and whether those clones are tolerant or intolerant to the pollutants listed. This would provide a better background for estimation of percent biomass lost. In addition, this study did not account for the influence of leaf area index on the productivity of the forests. Thus it would be interesting to observe how the results would change if only the time interval with maximum leaf area was used, thus eliminating any confounding that leaf area would have on NEE/GPP. This would decrease the number of months evaluated in the growing season to the peak growing season. Additionally, since PPFD does influence NEE because light drives photosynthesis, a study could also be conducted where PPFD is filtered to greater than 500 umol/m2/s photons. This would narrow the dataset to times when light was not a limiting factor for photosynthesis, but could significantly decrease the sample size. Another study could be done assessing the effects of only ozone levels on NEE/GPP above 60ppb using the SUM60 index.

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