Ozone Deposition on *Pinus Ponderosa* Surfaces

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Abstract Stratospheric ozone is a secondary compound defined by the EPA as one of six "primary pollutants." Recently, high ozone concentrations have damaged stands of *Pinus ponderosa* found in California's Sierra Nevada mountain range. While the flux of ozone entering these forest ecosystems is well quantified, the relative contribution of each ozone removal mechanism is poorly understood. Surface deposition is one such removal mechanism. Surface deposition rates of ozone onto *Pinus ponderosa* needle and bark surfaces were measured in a laboratory chamber under varied conditions of relative humidity, temperature, and ozone concentration. Statistically significant correlations could not be established between surface deposition rate and ozone concentration, surface deposition rate and temperature, and surface deposition rate and relative humidity. The measured rates, when compared to the amount of area these surfaces represent, indicate surface deposition does not play a significant role in removing ozone from the ecosystem.

Introduction

Tropospheric ozone is a compound produced by the reaction of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in the presence of sunlight (Haggen-Smit, 1952). Elevated tropospheric ozone concentrations can damage vegetation by oxidizing material in their stomates (Wesley et al., 1978). This leads to an eventual decrease in carbon accumulation (Arbaugh et al., 1998). Ozone has been defined by the Environmental Protection Agency as one of six criteria air pollutants (USEPA, 1996). Because forest ecosystems act as a removal mechanism for ozone-polluted air basins it is important to understand the removal mechanisms within the forest.

The Sierra Nevada mountain region is a forested ecosystem that has been defined by the EPA as "serious" non-attainment area for high ozone concentrations (USEPA, 1996). *Pinus ponderosa* (Ponderosa pine) forest accounts for 8% of the vegetated area in the Sierra Nevada region (SNEP, 1996). Ponderosa Pine forest is being studied for two reasons: (1) As a common plantation tree, damage from ozone carries substantial economic consequences and (2) Ponderosas are more sensitive to ozone damage than other species (Miller and McBride, 1988).

Prevailing winds blow ozone precursors from the Sacramento metropolitan area into the Sierra Nevadas, where they react and create ozone. This ozone is removed from the forest ecosystem through four major pathways, as illustrated in Figure 1: (1) by wind that carries some ozone away from the ecosystem, (2) by reactions where certain gases in the atmosphere are oxidized by ozone, (3) by ozone entering leaf stomata, and (4) by ozone deposition onto forest surfaces.

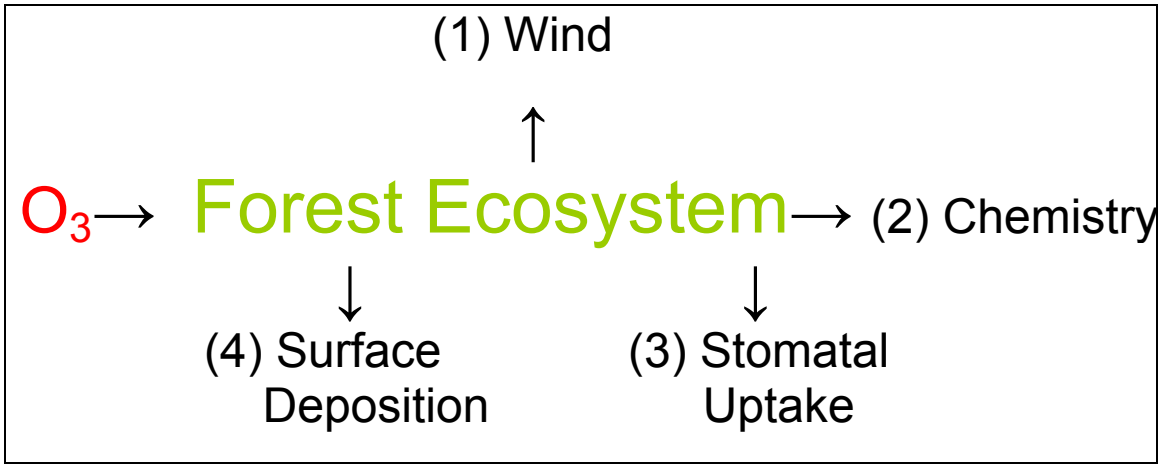

Figure 1. Forest ecosystem ozone removal pathways.

Stomatal uptake is a major removal pathway (Grantz et al. 1997), but other major removal pathways of ozone in this forest ecosystem are poorly understood (Bauer et al., 2000). Data provided by Goldstein and Kuripus in the ESPM department at UC Berkeley indicates that removal pathways other than stomatal uptake represent a non-negligible amount of ozone uptake. The data from Goldstein and Kuripus indicates that at certain times over 50% of ozone loss in ponderosa pine forest is due to chemical reactions between ozone, nitrogen oxide (NO), and several VOCs that occur in the air within the canopy rather than plant and soil surfaces. Additional removal of ozone may be occurring via deposition directly onto the ecosystem's surfaces.

The goal of my research is to identify and quantify the deposition of ozone on the predominant surfaces one would find in a Ponderosa Pine. Uncertainty in other data collection methods has failed to accurately address the magnitude of surface deposition, so it is unclear whether the effect is small or large. Care is taken to examine each of the variables that are known to affect ozone surface chemistry: concentration, temperature, relative humidity, and time. The ultimate goal is to create a model that accurately predicts ozone deposition behavior.

Methods

This study quantifies the flux of ozone onto the following surfaces: Ponderosa Pine needles and bark. Because only surface flux is being studied, all other removal pathways need to excluded. Therefore, the stomata need to be closed, and the samples need to not be producing volatile organic compounds (VOCs) that would influence ozone loss. Dead needles were tested in a proton transfer reaction-mass spectrometer (Ionicon Analytik PTR-MS) to evaluate their emissions of ozone-reactive mono- and sesquiterpenes. The needles are baked at 50˚C for 24 hours in order to remove these compounds.

The laboratory ozone chamber consists of a 6-liter ring of Pyrex capped on both sides by perforated Teflon film. A UVP Pen-Ray UV lamp in a separate Pyrex tube generates ozone, and air from a clean air generator (CAG) is metered to the lamp chamber by a MKS Mass-Flo controller. Thus $[O_3]$ is adjusted by changing the ratio between air flowing to the lamp chamber and total flow through the system. For the main system flow (3L/min), clean air passes through a bubbler that humidifies the air and through a bypass. The relative humidity (RH) of the air exiting the bubbler is nearly 100%. Thus adjusting the relative flows of the bubbler and bypass

controls humidity. For instance, if one needed 50% RH, flow between the bubbler and bypass would be split evenly. The humidified air and ozonated air are mixed just prior to chamber injection (see Figure 2). The chamber is designed in such a manner as to minimize turbulence: air injected into the chamber flows along the sides in a concentric circle pattern; air is drawn out near the center of the chamber and sent to the ozone analyzer (Dasibi-1020) at the rate of 0.5 L/min. The total system flow is always greater than the ozone analyzer's flow so as to create an overpressure inside the chamber, thus preventing outside air contamination. Air escapes from the chamber via the perforations, so the chamber remains at atmospheric pressure. A probe (Campbell Scientific model HMP45C) inside the chamber measures RH and T. The chamber is placed on top of a Pelletier cooler and surrounded by an insulated foam box. To lower T, the box is covered and the Pelletier turned on; to raise T, a 660W heat lamp suspended ~30cm above the chamber is turned on.

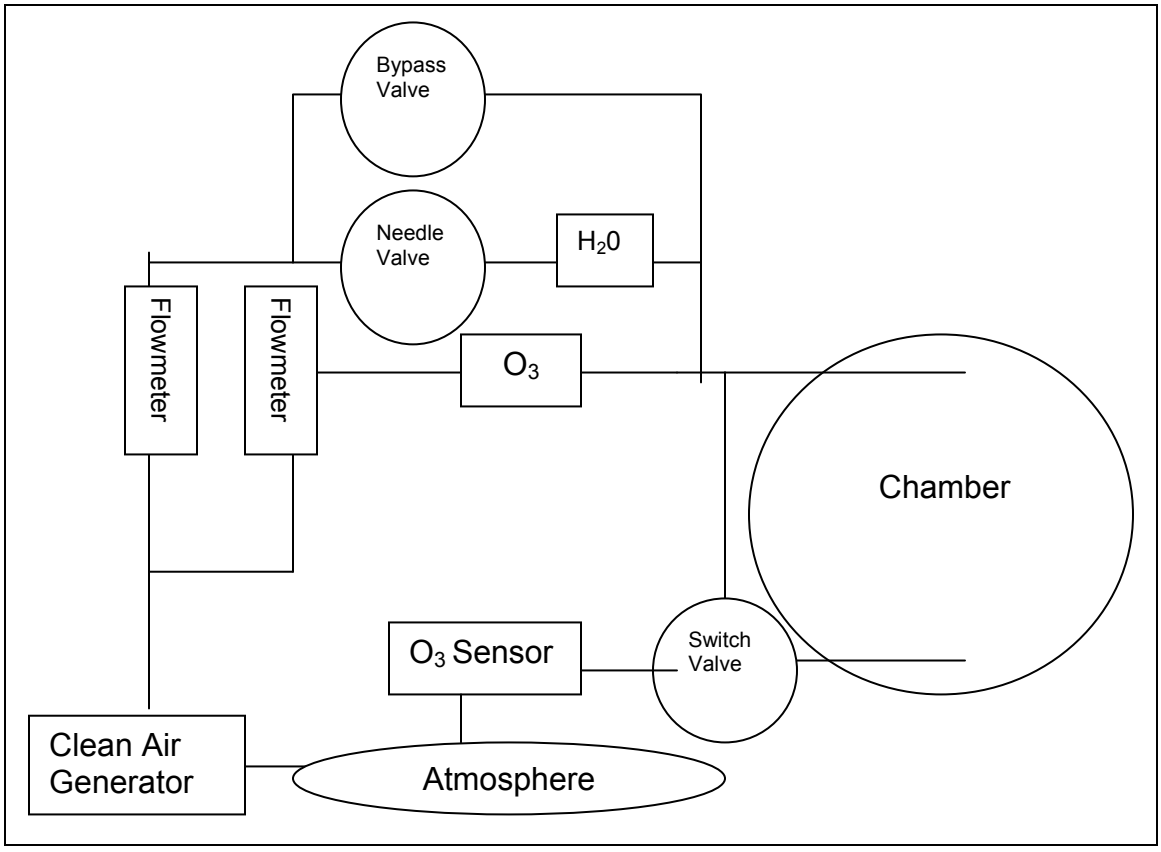

Figure 2. Ozone system layout.

Data from the instruments is collected by a Campbell Scientific CR10x data logger every ten seconds. These values are averaged every 5 minutes and placed in the final storage table. Because the ozone analyzer can only measure one input at a time, a switch is placed between the flow input and output lines which enables the ozone analyzer to spend 15 minutes establishing ozone concentration into the chamber ($[O_3]_{in}$) followed by 45 minutes measuring ozone concentration flowing out of the chamber ($[O_3]_{out}$). The difference between these averaged concentrations can then be used to calculate flux.

Surface area is calculated in the following manner:

- Ponderosa Pine needles come, with almost no exceptions (Wykoff, 2002), in bunches of three; together they form a cylinder of radius r and length l. Ideally represented, a cross section from the needle forms a wedge with two flat sides of equal length spaced 120° apart and backed by a semicircular arc. In other words, a needle is approximated as a cylinder equally cut lengthwise into thirds. Using this geometric model, surface area A of each needle can be approximated by Equation 1.

$$A=(2/3\pi r+2r)L \quad (1)$$

Needle bunches are measured by hand using a caliper and ruler.

- Bark surface area is calculated by measuring the length and width of the exposed face and multiplying. The sides and back of the bark are covered with cellulose tape, since these areas would not normally be exposed in the field. The tape is included in the chamber blank in order to calibrate unintended ozone removal.

Flux is defined as the flow of material per area per time (Grontoft, 2002). Surface flux is calculated by measuring the concentration of ozone prior to injection and comparing that to the concentration post injection. Flux is calculated using Equation 2,

$$J=\frac{([O_3]_{in}-[O_3]_{out})}{A}\frac{F_{in}}{RT}(pM_{O3}) \quad (2)$$

where J is the deposited flux (pg/cm^2/s), F_{in} is the flow into the chamber (cm^3/s), A is the sample's surface area (cm^2), M_{O3} is the molecular weight of O_3 (48 g/mol), R is the gas constant (8.314 J/K/mol) and T is temperature (in Kelvin).

To quantify the chamber surface loss term, chamber "blanks" are made in which the chamber is run empty under the same conditions and sub-conditions as each experiment. These blank averages are then subtracted from the sample averages to give a corrected experimental flux value.

When first exposed to ozone, materials uptake ozone at an increased rate, then reach a lower steady state flux after a period of time. Each fresh sample was exposed at 100ppb for 48 hours, with RH=50% and T=23˚C. Once steady state has been reached, the experiments begin. Each material experiences three different tests where two variables are held constant and a third variable is held at thee different values for at least four hours. The process is replicated at least three times, with each new replicate using a fresh sample. Table 1 explains the test procedures:

Test	**T**	**RH**	**$[O_3]_{in}$**
$[O_3]$	23˚C	50%	50, 100, 150ppb
RH	23˚C	25, 50, 85%	100ppb
T	16, 23, 35˚C	50%	100ppb

Table 1. Experiment procedure guide, T=Temperature, RH=Relative Humidity.

Each test attempts to establish a correlation between flux and the variable under question. My hypotheses state that $[O_3]$ and T have a positive correlation with flux, while RH has a negative correlation. Ideally, the temperature test would include a run at O˚C, but it is very difficult to achieve sub-ambient temperatures in the lab using only a Pelletier device.

Change in ecosystem ozone concentration due to surface deposition was estimated using Equation 3:

$$\Delta[O_3]_{chamber} I_{chamber} H_{chamber} = \Delta[O_3]_{forest} I_{forest} H_{mixing} \quad (3)$$

where $\Delta[O_3]$ is the change in ozone concentration (in ppb), I is an area index equaling the sample surface area divided by the floor area (in m^2/m^2), and H is the height above the floor where gases continue to be well mixed (in m). Using a mixing height for the forest ecosystem allows one to equate it as a finite column of air with a known volume. Multiplying I by H gives the surface area of the sample per volume of air. Forest leaf area index was based on 1998 data collected by Xu et. al 2001 from the Blodgett Forest Research Station (38º53'43''N, 120º37'58''W, 1315m) in the Sierra Nevada. Bark area index data for Blodgett was obtain from Laurent Misson in the ESPM department. The forest mixing height is 1000m, the low end of the range seen in the daytime at Blodgett (Lee 2003). $H_{chamber}$ was simply the internal height of the ozone chamber. Averaging the surface areas of the respective samples and dividing by the internal cross-sectional area of the chamber-established leaf and bark area indexes. $\Delta[O_3]_{chamber}$ was calculated by averaging the differences between $[O_3]_{in}$ and $[O_3]_{out}$ for runs where T=23˚C, RH=50%, and $[O_3]_{in}$=100ppb.

Results

After nearly all the experiments had been completed, an anomaly that caused a consistent under-estimation of ozone values was discovered in the ozone sensor. In order to minimize the change in flow to the chamber as the sensor cycled between measuring $[O_3]_{in}$ and $[O_3]_{out}$, the sensor was set to draw a flow of 0.5 L/min. The sensor actually needs a minimum of 1.5 L/min. to read correctly. This wrong setting meant that ozone concentrations (and therefore flux values) were on average 3.2 times higher than was originally thought. Fortunately it was possible to scale the data up to these higher actual concentrations and fluxes, although it must be emphasized that these concentrations are much higher than one would typically encounter in the Sierra Nevada.

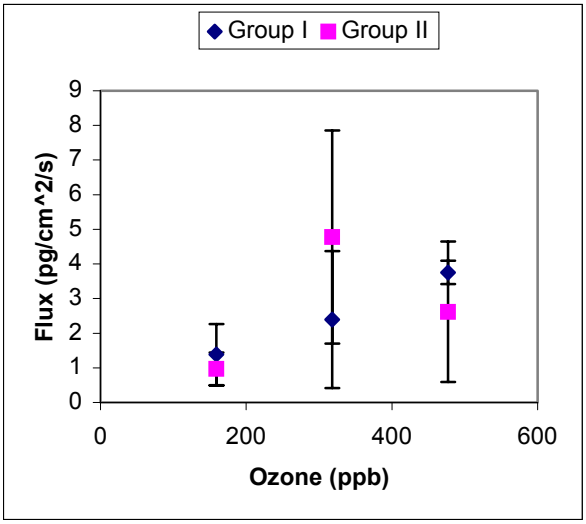

Figure 3. Needle flux vs. ozone concentration. R^2=0.40

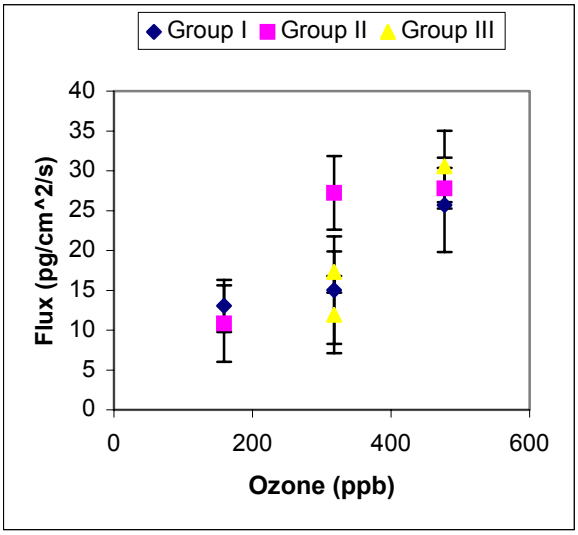

Figure 4. Bark flux vs. ozone concentration. R^2=0.68

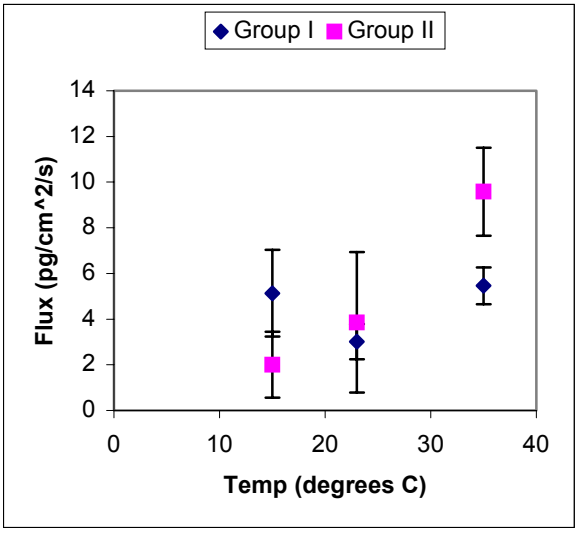

Figure 5. Needle flux vs. temperature. R^2=0.50

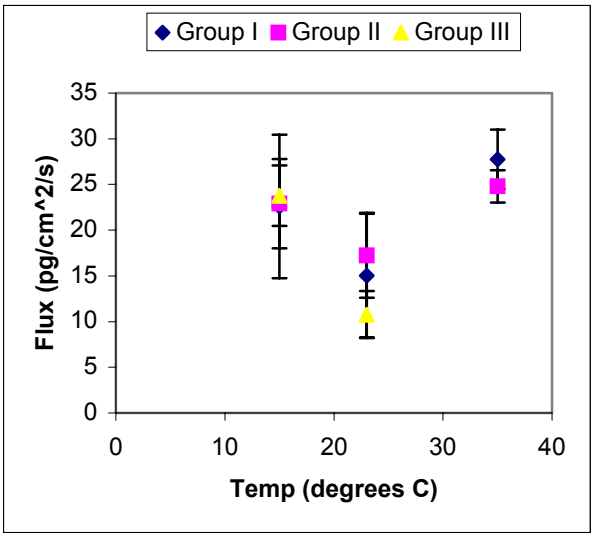

Figure 6. Bark flux vs. temperature. R^2=0.02

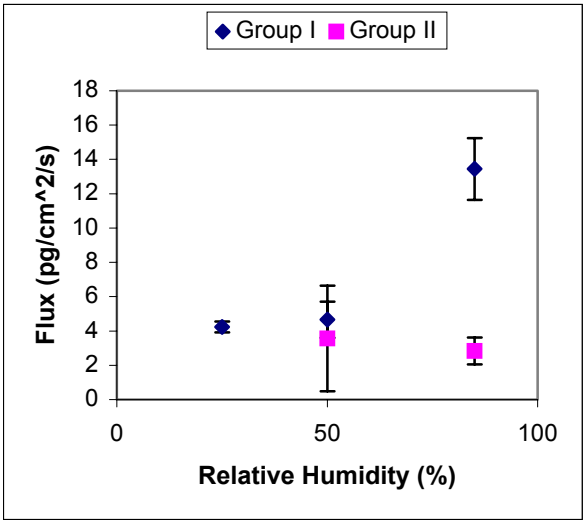

Figure 7. Needle flux vs. relative humidity. R^2=0.20

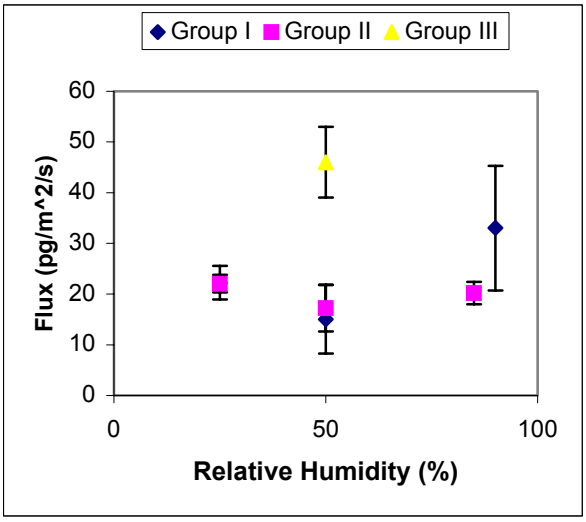

Figure 8. Bark flux vs. relative humidity. R^2=0.32

Discussion

It appears that bark and needle surfaces perform similarly under manipulation of concentration, temperature, and relative humidity. Bark flux is significantly higher under all conditions compared to needles, partly because the bark samples were still producing terpenes at the time of exposure. In all cases, linear regression analysis yielded inconclusive results in regards to establishing positive or negative correlations. This was due in part to the high

variability in the data and small numbers of replications. However, some general trends can be observed.

Although not statistically significant, Figures 3 and 4 indicate that both bark and needles share a somewhat positive relationship between $[O_3]$ and flux. The relationship between temperature and $[O_3]$ is less lucid. Figure 5 shows weak positive relationship exists for needles, but there is a curious dip in flux at 23˚C for bark in Figure 6. Further investigation and more replicates need to be made to establish whether the data is noisy or whether this phenomenon is real. A pattern for RH behavior is unclear for both materials. Figure 7 shows a large of amount of flux variation under high RH conditions, while the bark data in Figure 8 shows a dip in flux at 50% (with the exception of the outlier from sample Group III) similar to the pattern shown for the bark's temperature test.

The average deposition flux for needles at T=23˚C, RH=50%, and $[O_3]_{in}$=160 ppb was around 1 pg/cm^2/s and around 10 pg/cm^2/s for bark. By comparison, Grontoft 2002 measured a flux of 6-3 pg/cm^2/s for concrete flooring and 8 pg/cm^2/s for activated carbon cloth, both at T=23˚C, RH=50%, and $[O_3]_{in}$=40 ppb.

In terms of the big picture, magnitude estimates indicate that surface deposition plays a negligible role in removing ozone from the forest ecosystem. Using Equation 3 as outlined in the methods section, needle and bark deposition each create a drop in $[O_3]$ of only 10^{-3} ppb at T=23˚C, RH=50%, and $[O_3]$=100 ppb.

There were several potential sources of error that could not be quantified. Because the flows and concentrations through the system were so low, small disturbances created significant fluctuations in values. The ozone sensor could be running stable for hours and then suddenly report a drop of 15ppb. Also, it is unknown whether baked dead, old needles have a different surface composition, and thus uptake ozone differently, than live, fresh surfaces. That particular question may be answered this summer 2003 when bark, needle, and litter ozone fluxes and VOC emissions will be measured in the field.

The behavior of ozone deposition on *Pinus ponderosa* surfaces is still not clearly understood. More replications are needed to solidify the roles temperature, relative humidity, and ozone concentration in determining deposition rates. However, it is fairly certain that these surfaces play a relatively minor role in removing ozone from the forest ecosystem.

Acknowledgments

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