White Pine Emission Trends of Monoterpenes and Sesquiterpenes After Acute Ozone Exposure

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Abstract

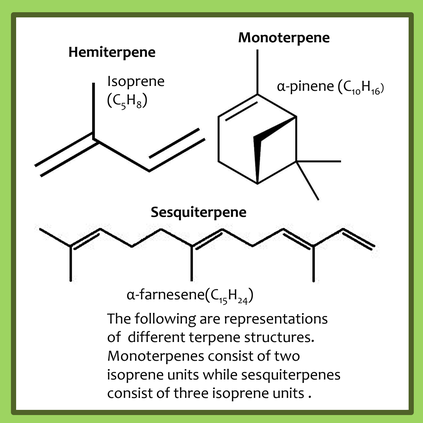
Volatile organic compounds (VOCs), such as terpenes, are consistently produced and stored on a large scale in forests. Monoterpene and sesquiterpene emissions from trees significantly contribute reactive carbon to the atmosphere and change as a response to various environmental stresses. Once in the atmosphere, these terpenes react and contribute to ozone and secondary aerosol formation. This project investigates the effect of an abiotic stress, specifically acute ozone exposure, on the terpene emissions of White Pine (*Pinus strobus*) specimens located at the University of Michigan Biological Station (UMBS). To measure terpene production, dynamic branch enclosures were simultaneously positioned on White Pine branches of a control tree with no treatment and another tree that was exposed to 200 ppb of ozone for two hours. Purge air was continuously fed through the branch enclosures, which maintained the health of the branch. To collect the VOC's emitted by the branch; sampling cartridges containing Tenax GR (an absorbent resin) were attached to a sampling line placed in the enclosure. These cartridges have been analyzed by thermally desorbing the captured VOCs and passing them to a GC/MS/FID system, which identifies compounds and measures the quantity of the respective compound in each sample. With this data the monoterpene and sesquiterpene emission rates are then calculated and normalized to the branch enclosure's dry biomass. Conclusions from this study will enable predictions for how total terpene emission rates may change from White Pine forests due to predicted future increases in tropospheric ozone.

Goals

- To better understand hydrocarbon release rates from plants to the atmosphere, specifically terpene emission rates due to acute ozone exposure on White Pine.
- To determine the relationship if any between an acute ozone exposure to White Pine and its quantifiable terpene emission rates.
- To analyze the specific speciation emission trends of monoterpenes and sesquiterpenes before and after ozone exposure.

Biogenic Terpenes

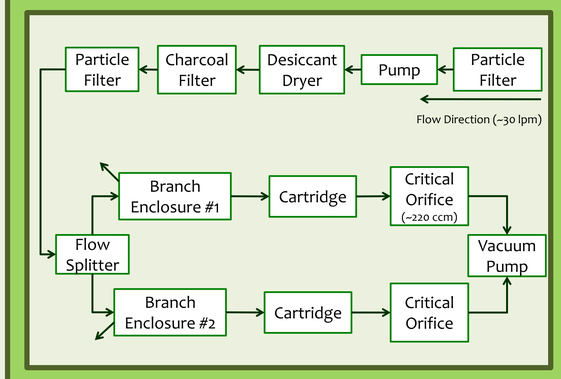
Terpenes are a large class of hydrocarbons which are produced primarily from plant species, particularly coniferous trees. All terpenes consist of a combination of isoprene structures(C_5H_8). Terpenes are responsible for the pine smell of a forest, the hop aroma in beer, and the scent of green apples. Plants emit a wide variety of terpenes in response to different stresses such as temperature, herbivory, and air pollution. These hydrocarbon emissions released into the atmosphere react with other compounds to create tropospheric ozone. Terpenes also react with ground-level ozone to produce secondary organic aerosols in the atmosphere which contribute to climate change. The importance of studying and understanding terpene emissions under stressed conditions arises because forested areas are exposed to tropospheric ozone due to airflow from urban environments.



The following are representations of different terpene structures. Monoterpenes consist of two isoprene units while sesquiterpenes consist of three isoprene units .

Field Experimental Setup

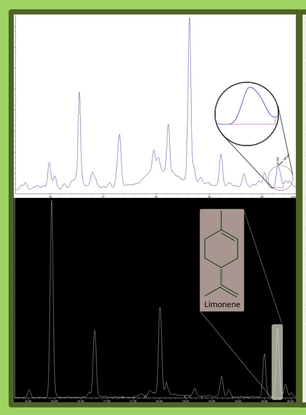
Field data was collected from UMBS which is located in an area substantially isolated from urban influence. A control tree and a tree that exposed to 200 ppb of ozone for 2 hours had dynamic enclosures placed around a single representative branch. The emissions from the ozone exposed tree were sampled periodically before treatment to set a baseline value and after treatment to analyze the effect on the terpene emissions from ozone exposure. VOC samples were collected from dynamic branch enclosures with sampling cartridges containing Tenax GR absorbent. A diagram of the branch enclosure sampling technique is shown below.



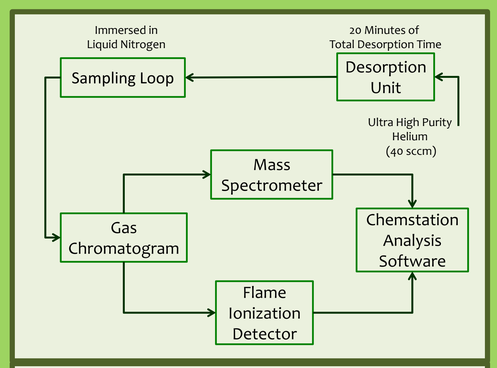
Dynamic Branch Enclosure

Lab Analysis

Samples were analyzed with a GC/MS/FID. Sample cartridges were individually attached to a sampling loop and purged with helium to remove oxygen from the sorbent bed. The VOCs were released from the Tenax GR absorbent with a thermal desorption unit. The sampling loop containing the released compounds was injected into the GC/MS/FID unit. The MS was used to identify the compounds within the sample, while the corresponding FID peaks were integrated and quantified with respect to a known 2,2-dimethylbutane standard.



These screenshots were taken from Chemstation software used in sample analysis. The FID analysis(top) shows what area of the peak is being quantified. The MS analysis(bottom) shows the respective peak and the detected compound in the selected area.



The diagram above shows a schematic of the laboratory analysis of a sample cartridge with a GC/MS/FID.

Emission Rate Calculations

Emission rate calculations are required to convert the measured concentration on the sampling cartridge to the more physically relevant parameter: the rate at which terpenes were produced by the White Pine branches at the time of sampling.

Air Sampled Onto Cartridge(V_s)

$$V_s(std\ cm^3) = F_s * t * P_{atm} * \frac{273}{(273+T)}$$

Emission Rate Temperature Correction(ER_T)

$$ER_T(\mu gC/g/hr) = ER/e^{(T-T_S)}$$

Flow Rate into Enclosure(F_{purge})

$$F_{purge}(mol\ air/hr) = F_e * P_{atm} * \frac{273}{(273+T)} * \frac{60}{22.4}$$

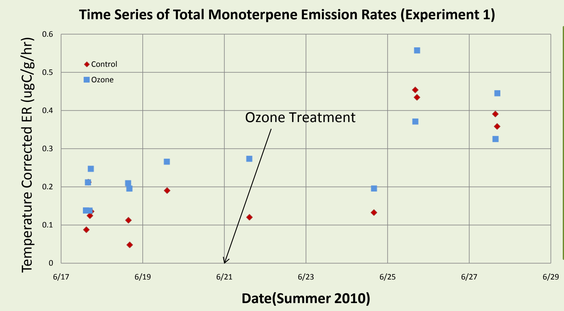
Emission Rate(ER)

$$ER(\mu gC/g/hr) = \frac{A}{(S*ECN)} * \frac{R*T}{(V_s*Patm)} * \frac{C\#*MMC}{1000} * \frac{F_e}{m}$$

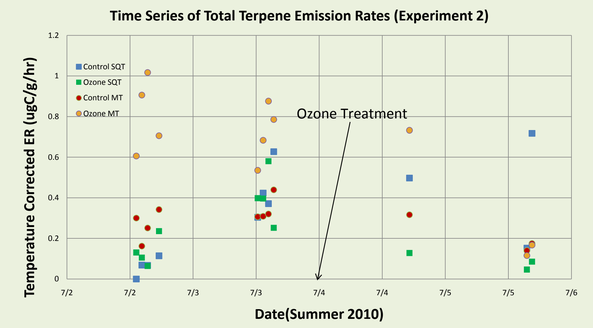
F_s=Flow Rate on Sampling Line(ccm)
t=Sampling Time(min)
P_{atm}=Atmospheric Pressure(atm)
T=Ambient Temperature(°C)
F_e=Flow Rate Into Enclosure(lpm)
A=Peak Area
S=FID Sensitivity(area/nmol C)

ECN=Effective Carbon Number
V_s=Air Sampled onto Cartridge(std cm3)
R=Gas Constant=82.05746(cm3*atm/(K*mol)
C#=Number of Carbons for selected terpene
MMC=Molecular Mass of Carbon (12ng/nmol)
1000=Conversion factor of ng to µg
M=Dried Biomass in Enclosure (g)
T_s=Leaf Temperature at a Standard Condition(303K)

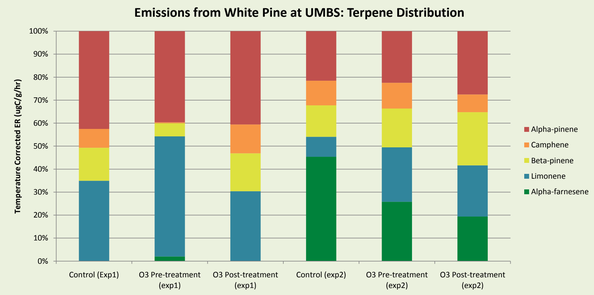
Results



Time series of monoterpene emissions for experiment 1. Ozone treatment occurred on June 21st. Emissions for both control and ozone specimens are highly variable. Note that monoterpene emissions from the ozone treatment trees constantly surpass the control tree samples until after stress is applied to the branch enclosure.



Time series of total terpene emissions for experiment 2. Ozone treatment occurs on July 4th. Emissions from both control and ozone specimens show variable emission rates. The ozone treatment tree shows a decline in sesquiterpene emission rates after stress is applied.



Speciation distribution of terpenes representing separate experimental conditions. Distribution of terpenes remains relatively constant in both experiments. α-farnesene contributes to a very large percentage of terpene emissions in experiment 2.

Summary

The data presented represents a limited sub-set of terpenes found in the samples collected from each experiment. Because of this, emission trends may not yet be recognizable with the terpenes that were identified in this analysis. The elevated presence of α-farnesene in the second experiment relative to the first experiment could be the result of unobserved environmental stressors such as herbivory stress, biogenic emissions from neighboring trees, and exposure to different meteorological conditions.

Future Work

- Further analysis of the emissions samples collected at UMBS during Summer 2010 will occur in the coming months.
- Four additional experiments will be completed this summer and will be added to the current analysis to gain a broader understanding of the relationship between monoterpene and sesquiterpene emissions and stressors applied to White Pine.
- Additional experiments were conducted looking at the impacts of simulated herbivory stress to White Pine. These will be analyzed comparatively with the ozone and control tree samples to better understand emission rates of terpenes.

Citations

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J. Ortega, D. Helmig (2008), Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques-Part A, *Chemosphere*, 72, 343-364.

A. C. Heiden (1999), Emission of volatile organic compounds from ozone exposed plants, *Ecological Applications*, 9(4),1160-1167.

Acknowledgements

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