Multi-Season Monoterpene and Sesquiterpene Analysis of *Pinus taeda* Needle Tissue

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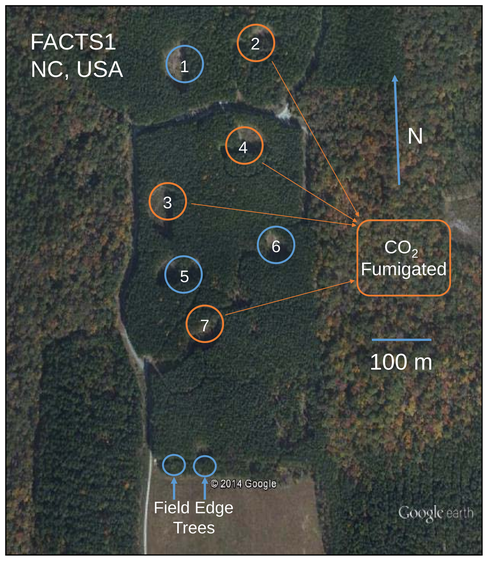

Figure 1: Google Earth view of the FACTS1 research site, Orange Country, NC. FACE CO_2 enrichment plots (orange) and control rings (large blue) and forest edge trees (small blue) are indicated.

Introduction:

Pinus taeda (Loblolly pine) is one of the worlds most important timber crop and accounts for a significant portion of the southeastern U.S. landcover. Biogenic voltile organic compound (BVOC) content was extracted from the tissue material of *P. taeda* needles and analyzed over a multi-year period from an experimental forest in North Carolina, USA. Seasonal patterns in needle monoterpene (MT), oxygenated MNT (MT_{oxy}), sesquiterpene (SQT), and oxygenated SQT (SQT_{oxy}) concentration and percent speciation by BVOC class are examined to increase our understanding of controls on the emission of these compounds into the atmosphere. Twenty six compounds were quantified. A possible CO_2 effect was detected for total SQT (suppression at elevated CO_2), and a difference in MT composition. This works seasonal MT and SQT concentration and composition data are compared with field emission studies conducted at the same site, including branch enclosure emission rate studies and REA Flux data.

Emission models such as the Model of Emissions of Gases and Aerosols from Nature (MEGAN) should include temporal production and storage effects of BVOC, in particular SQT, which interact with phenology and temperature. Only the latter is included in current emission models. CO2 effects and needle VOC production rate controlling factors, ie. exchange from needle tissue concentration to gas phase emission, should be further investigated with the goals of including these effects in emission models.

Figure 5: Aerial photograph of the FACTS1 research site, Orange Country, NC. FACE CO_2 enrichment and control plots are visible in the forest canopy.

Seasonal Factor:

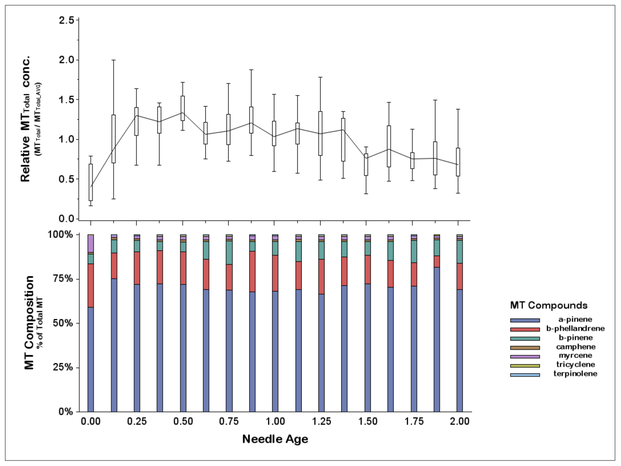

Figure 3 (Left):

Time series of study averaged Total MT concentration (top) and MT composition (bottom) over a two year needle life span.
MT concentrations quickly increase to maximum by early spring, tapering off slightly by the end of summer of the second year. Compound speciation remains constant throughout the needles lie span.

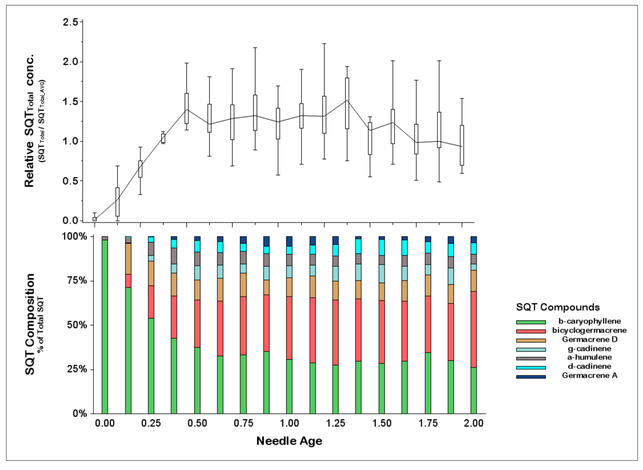

Figure 4 (Right):

Time series of study averaged Total SQT concentration (top) and SQT composition (bottom) over a two year *P. taeda* needle life span.
SQT concentration within the needle tissue increase slowly, reaching a maximum by Fall. SQT compound diversity begins with only b-caryophyllene, growing more complex with needle age.

Needle Cohort Age:

P. Taeda needles remain intact on the branch for approximately two years before senescence. The composition and concentration of BVOC housed within the needle tissue was found to change over a needles lifetime, likely a mechanism of BVOC production and storage (Figure 3 and Figure 4):

- MNT accumulate quickly, reaching a maximum concentration and full compound composition within weeks of needle expansion.
- SQT concentrations are low in young expanding needles, reaching a maximum by late summer. Beginning with β-caryophyllene, SQT compound composition diversifies with needle age.
- MNT and SQT concentrations vary around a maximum value through the second growing season, showing a small decline near senescence.
- Oxygenated SQT (SQT_{oxy}) slowly accumulate with needle age, reaching a maximum by the second season of growth.

Experimental Methods:

Loblolly pine (*Pinus taeda*) needles were collected at the C–H_2O Free Atmosphere Carbon Transfer Scheme (FACTS1) Research Site in Orange County, North Carolina (35.98°N, 79.09°W).

The site is a *P. taeda* plantation, with an understory of sweetgum (*Liquidambar styraciflua*), red maple (*Acer rubrum*), yellow poplar (*Liriodendron tulipifera*), and oak (*Quercus*) species.

FACTS1 site was composed of seven free-air CO_2 enrichment rings:

- Four (4) CO_2 enhanced (ambient + 200ppmv CO_2) forest canopy plots
- Three (3) ambient CO_2 forest canopy control plots
- Two (2) ambient CO_2 ground level sites at the forest edge

Needles where collected monthly from the same branch per sample plot throughout the year. BVOC were partitioned from needle sample tissue by extraction with the non-polar solvent hexane, followed by liquid injection GC-FID/MS analysis.

This work compares BVOC available in *P. taeda* needle tissue with the following BVOC emission studies:

- Geron and Arnts (2010) ~ Branch enclosure emission rates
- Helmig et al (2007) ~ Branch enclosure emission rates
- Arnts et al. (2013) ~ Forest canopy REA flux

CO_2 Effect?

Needle extract samples were tested for possible CO_2 enrichment effects; fumigated (ambient + 200ppmv CO_2) vs. control (no CO_2 added).

- Total MNT concentration not significantly different between fumigated and control plots.
- The MNT β-phellandrene and myrcene concentrations were statistically higher from fumigated rings than control rings at the P<0.0001 level (Figure 6).
- Total SQT was 17% lower from CO_2 fumigated rings than control, significant at the P=0.015 level, suppression of β-caryophyllene and germacrene D.

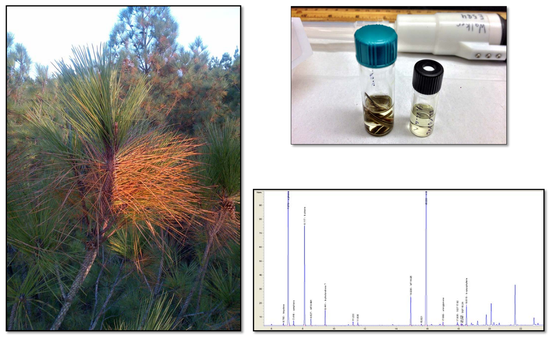

Figure 2: Clockwise from top left: a *P. taeda* branch displaying first and second year needles; solvent extraction process; GC-FID/MS analysis.

	Summer								Winter							
	Needle Tissue concentration						Branch Enclosure ER	REA Flux	Needle Tissue concentration						Branch Enclosure ER	REA Flux
	CO_2 Enriched		CO_2 Control		Edge Trees				CO_2 Enriched		CO_2 Control		Edge Trees			
	(mgC g^{-1})		(mgC g^{-1})		(mgC g^{-1})		(μgC g^{-1} h^{-1})	(μgC m^{-2} h^{-1})	(mgC g^{-1})		(mgC g^{-1})		(mgC g^{-1})		(μgC g^{-1} h^{-1})	(μgC m^{-2} h^{-1})
	1st yr	2nd yr	1st yr	2nd yr	1st yr	2nd yr			1st yr	2nd yr	1st yr	2nd yr	1st yr	2nd yr		
Total MT	**189**	**172**	**184**	**165**	**89**	**85**	**2.9**	**1004**	**151**	**139**	**180**	**150**	**95**	**97**	**7.6**	**387**
α-pinene	59%	59%	81%	72%	87%	84%	48%	53%	57%	59%	73%	73%	82%	84%	48%	59%
β-phellandrene	25%	22%	2%	4%	3%	4%	9%	5%	33%	30%	4%	4%	5%	3%	7%	6%
β-pinene	12%	15%	14%	21%	7%	9%	22%	17%	5%	6%	20%	20%	9%	10%	27%	16%
camphene	1%	1%	1%	1%	1%	1%	2%	4%	1%	1%	1%	1%	1%	1%	2%	4%
myrcene	2%	2%	1%	1%	1%	1%	14%	7%	3%	2%	2%	1%	3%	1%	11%	5%
tricyclene	0%	0%	0%	0%	1%	1%	0%	1%	0%	0%	0%	0%	0%	1%	0%	1%
Total MT_{oxy}	**0.8**	**3.8**	**1.3**	**6.9**	**1.3**	**3.9**		**58.4**	**1.7**	**2.5**	**10.4**	**6.2**	**2.4**	**3.2**		**8.2**
Total SQT	**13.1**	**35.0**	**20.9**	**38.3**	**7.5**	**16.8**	**0.3**	**68.9**	**19.0**	**28.8**	**43.6**	**34.9**	**11.2**	**18.9**	**0.5**	**0.7**
β-caryophyllene	50%	27%	49%	31%	52%	30%	39%	48%	40%	30%	33%	33%	33%	28%	48%	157%
α-humulene	8%	6%	8%	6%	5%	6%	9%	8%	8%	7%	7%	6%	6%	6%	7%	171%
bicyclogermacrene	21%	40%	10%	29%	19%	36%			30%	37%	29%	29%	32%	34%		
α-cadinene	4%	7%	2%	6%	2%	6%	1%		6%	8%	5%	5%	7%	8%	0%	
γ-cadinene	4%	7%	2%	7%	2%	6%	5%	5%	5%	6%	6%	7%	4%	6%	9%	100%
germecrene A	12%	9%	27%	17%	20%	15%			7%	8%	18%	18%	15%	13%		
germecrene D	1%	4%	0%	3%	0%	1%			4%	5%	3%	2%	3%	4%		
α-bergamotene								19%								157%
Total SQT_{oxy}	**3.3**	**17.9**	**2.6**	**18.8**	**1.4**	**9.6**		**11.7**	**7.3**	**12.7**	**15.5**	**13.8**	**5.1**	**8.6**		**-6.9**

Table 1: A bi-seasonal comparison of *P.* taeda BVOC potential reported here using several kinds of measurement techniques: (1) Needle tissue concentration (mgC g^{-1}), (2) Branch Enclosure emission rate (μgC g^{-1} h^{-1}), and (3) Relaxed Eddy Correlation (REA) flux measurements above the forest canopy (μgC m^{-2} h^{-1}). Needle tissue samples are broken into plot type categories and further into 1st and 2nd year needles. BVOC class total's are listed in bold. Compound speciation (% of BVOC class total) are listed for each measurement technique.

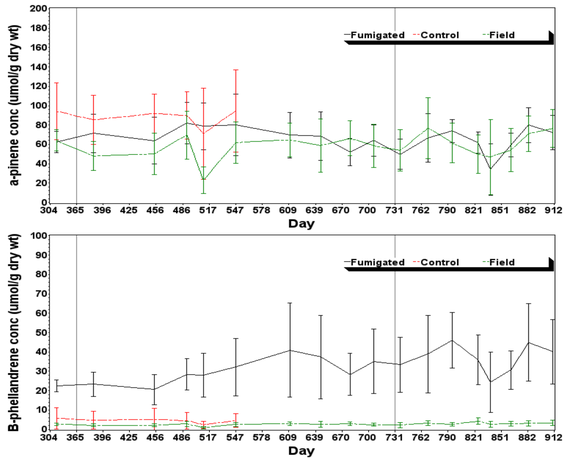

Figure 6: Averaged concentrations of MNT α-pinene and β-phellandrene from CO2 fumigated plots, control (no CO_2 added), and forest edge samples ('Field'). β-phellandrene was found to be significantly higher in fumigated plots (at P<0.0001 level) than control and forest edge samples. A possible CO_2 effect.

References:

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Acknowledgements:

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