**Low VOC Drying of Lumber and Wood Panel Products
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Summary

- Hydrogen isotope exchange between water and hydroxyl groups in wood is promoted by microwave irradiation, indicating that irradiation (at least partially) overcomes hysteresis.
- Although RF-treatment induces pit aspiration, the drying rate is unaffected.
- A good mass balance was obtained in one of two trials between the VOCs present in green wood, and the sum of that retained in the dry wood, released during RF-treatment, and emitted during drying.
- One gram of steam removes 1 gram of pinene from the low-headspace RF reactor. Hence, condensation of the small amount of steam released during RF-treatment should allow full recovery of the VOCs.
- Delayed venting during lumber drying reduces VOC emissions.
- Preliminary correlations between VOC release and seasonal parameters have been identified.

Effect of microwaving on wood structure (IPST)

Green pine blocks (2"x1"x1") were dried to different moisture levels at 120°C. They were immersed in D₂O (>99% isotopic content) for different periods at room temperature, and were then cut in halves. One piece from each set was then wrapped in plastic, and microwaved at 110 W, for 30 minutes, with the field being cycled to keep the wood surface at 90-100°C. Fibers taken from just inside the wet surface from five regions along the length of the piece were then analyzed by mass spectrometry with a direct insertion probe. The *m/e* profiles of the three isotopic forms of water, namely H₂O, HOD, and D₂O, remained unchanged as the wood was heated inside the spectrometer, indicating that they were bound equally strongly to the wood.

The water released from the green wood had the same isotopic composition regardless of whether or not the wood was microwaved (Table 1), indicating that the exchangeable protons in wood were not affected by microwaving. However, as the wood progressively dried, the water released from the microwaved wood was of lower isotopic content, which means that microwaving increases access of the exchangeable protons in wood tissue to water. The only exchangeable protons in dried wood are those sited on hydroxyl groups, and the difference in isotopic exchange is the greatest for dried wood. This must mean that as wood dries, internal hydrogen bonding

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Table 1: Isotopic content of water released from wood			
MC (%) ¹	soaking pe- riod (days)	percent deuterium (σ) ²	
		control	microwaved
125	5	48 (15)	47 (8)
44	10	56 (16)	47 (5)
24	2	60 (4)	49 (7)
0	5	61 (7)	45 (3)
¹ dry basis; ² averaged from 5 samples			

restricts access of the D₂O to the hydroxyl protons. Presumably the energy transferred to water upon microwaving is sufficient to to at least partially overcome this barrier. The effect is akin to the hysteresis that occurs for moisture sorption to green and dried wood. Similar isotope exchange work with D₂O has been previously conducted¹⁻¹¹ to determine the accessibility of cellulose to water.

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Pit aspiration during RF-Treatment (IPST)

In order to determine the extent to which RF-treatment alters pit structure, control and RF-treated samples (2"x3.25"x22" pieces) were examined by SEM, after solvent-exchange with acetone, and air drying. The wood was irradiated for 30 minutes, with the field being cycled to keep the surface temperature at 90-100°C. SEM photographs of sapwood samples taken just below the surface are shown in Figures 1 and 2, respectively, and demonstrate that RF-treatment induces pit aspiration. Each board was cut in two, and each half was dried at 70°C and 90°C under an airflow of 4 lpm. The drying rate data shown in Tables 2 and 3 demonstrate that although the RF-treated wood reaches the fiber saturation point slightly earlier than does the control (because of its lower initial MC), the overall drying rate is not materially affected by irradiation.

Figure 1. SEM of the control sample

Figure 2. SEM of the irradiated sample

Table 2: Replicate drying rates of (2"x3.25"x11") wood at 70°C						
time (hr)	MC		MC		MC	
	control	RF	control	RF	control	RF
0	69.0	53.3	58.4	44.9	97.8	101.2
2	62.9	49.3	54.0	39.3	94.5	97.7
5	52.4	42.5	46.7	31.6	85.3	88.2
7	45.7	37.4	41.6	26.9	78.3	81.2
9	39.7	32.3	36.3	23.0	71.1	73.7
21	18.6	16.6	18.7	14.1	43.0	38.1
27	14.0	13.3	15.0	11.6	29.6	25.1
36.5	10.4	10.2	11.5	9.0	19.1	16.2
51.5	6.6	6.8	7.7	6.1	10.6	9.6
119	1.8	1.9	2.1	1.9	2.3	2.2

Table 3: Drying rates (MC) of (2"x3.25"x11") wood at 90°C						
time (hr)	MC		MC		MC	
	control	RF	control	RF	control	RF
0	71.1	56.1	56.1	44.3	105.0	101.0
3	55.2	44.7	45.4	29.5	93.1	90.7
7.5	34.3	25.7	30.3	16.5	68.8	64.3
10	26.8	19.4	25.1	13.5	58.6	51.6
11.5	22.6	16.6	22.1	11.8	52.5	43.9
18.75	11.7	9.8	12.7	7.0	31.8	19.4
21.5	9.5	8.1	10.5	5.7	25.8	15.3
24.5	7.5	6.6	8.5	4.5	20.1	12.0
29.5	5.1	4.7	6.1	3.1	13.1	8.3
34	3.6	3.4	4.4	2.2	9.1	6.0
43	1.6	1.6	2.2	1.4	4.0	2.6

Mass balance of VOC released from and retained in wood during RF-treatment (IPST/MSU)

We have shown in previous work that a substantial amount of turpentine was released during low-headspace RF-treatment of wood. In order to establish a mass balance, 2"x4"x44" pieces of pine received from MSU on 12.12.97 were each cut into two 2"x3.25"x22" pieces, and RF-treated two weeks later. The power setting of the Strayfield RF unit was at 0.9A, and the dryer was cycled in order to keep the surface temperature of the wood between 90 and 100°C. The total treatment time was 30 minutes, including the period during which the RF power was turned off during processing. Pinene was collected in two instances in a 200 mL methanol trap attached to the low-headspace reactor described in report #4. Table 4 lists the weight changes and the VOCs emitted during both irradiation and the subsequent drying (conducted at MSU). Subsamples of the dried wood, EE and F, taken from the locations illustrated in Figure 3 were extracted by acetone and analyzed by GC; these results are provided in Table 5.

The differences in VOC released during drying between RF and control samples is least for the AA and B series in Table 4, which contain knots. For the other samples, RF-treatment reduced VOC emissions by an average of 56%. The VOC mass balance for samples EE and F where the VOCs were measured after each operation is provided in Table 6. The agreement is within 20%, indicating that the VOC removed during RF-treatment would otherwise be (principally) lost during drying, or retained in the dry wood.

A second set of measurements were run with larger (2"x4"x48") pieces of board. Wood obtained from MSU on 1.22.98 was cut into two pieces (2"x3.25"x22") for RF treatment four days after receipt. The middle 4" block left from each piece was extracted with acetone, which was then analyzed by gc for pinene and resin/fatty acids. The results are provided in Table 7. One of the two remaining pieces were RF-treated; the other was used as a control. Both pieces were then returned to MSU where they were dried, and the VOCs measured. The results are provided in Table 8. As noted earlier, the first VOC peak observed in the control sample was re-

Table 4: Release of water and pinene during irradiation

ID	wood weight (g.)			pinene released during RF ($\mu\text{g/g}$) ³	VOC ($\mu\text{g/g}$) released during drying ³
	green	post-RF	dried ¹		
AA-1 (control) ²	1882	-	867	-	253
AA-2 ²	1820	1580	859	-	469
B-1 (control) ²	2320	-	1311	-	885
B-2 ²	2266	2042	1031	-	727
C-1 (control)	1786	-	971	-	813
C-2	1792	1502	961	-	385
EE-1 (control)	2320	-	1311	-	690
EE-2	2372	1946	1284	717	279
F-1 (control)	2294	-	1048	-	804
F-2	2328	1988	1062	593	371

¹Dried at 125°C dry bulb temperature (82°C wet bulb) for 11.5 hr under an airflow of 12 lpm.

²These samples contained knots. ³dry basis

Figure 3. Location of subsamples taken for solvent extraction.

Table 5: Residual pinene in dried wood			
control		RF-treated	
ID	pinene (µg/g)	ID	pinene (µg/g)
F-1 I	192	F-2 I	75
F-1 II	249	F-2 II	129
F-1 III	224	F-2 III	33
F-1 IV	596	F-2 IV	34
average	315 (28%)¹	average	68 (15%)¹
EE-1 I	83	EE-2 I	13
EE-1 II	82	EE-2 II	25
EE-1 III	98	EE-2 III	209 ²
EE-1 IV	103	EE-2 IV	21
average	92 (12%)¹	average	67 (15%)¹
¹ percent of total pinene (residual and released during drying); ² the high result could be caused by a knot.			

Table 6: Mass balance of VOCs (µg/g)				
ID	VOC removed during		VOC remaining in wood	total VOC
	RF	drying		
EE (control)		690	92	782
EE (RF)	717	279	67	1063
F (control)		804	315	1119
F (RF)	593	371	67	1032

duced or eliminated for the RF-treated board.

Subsamples taken from two RF-treated pieces were analyzed for their pinene and resin/fatty acids content. The results are provided in Table 9. Note that the pinene is depleted along the edges, whereas resin acid levels are uniform across the board. The pinene remaining in wood after drying was extracted by acetone and analyzed by GC; the results are listed in Table 10. It is evident from Table 10 that the residual turpentine in dry wood and that released during drying is much less than that in green wood. It is possible that the difference is due to VOC loss from the hot wood during the cool down period, and during transportation to IPST. The reasons as to why a good mass balance was obtained in the preceding experiment and not in this one are unknown.

Table 7: Organics content (dry basis) of lumber before RF treatment¹			
ID	pinene (µg/g)	turpentine (µg/g)²	resin/fatty acids (µg/g)
1A	1900	2230	17000
1B	5860	6430	21700
1C	6660	7210	21400
1D	20100	26100	35500
1E	2640	4890	22900
1F	8680	13700	21300
1G	2730	3020	14100
1H	2780	4660	13500
¹ average of 2 determinations; ² includes other terpenes			

Table 8: Weight loss and VOC emissions of RF-treated wood				
ID	weight (g.)			VOC (µg/g, dry basis)¹
	green	post-RF	OD	
1A-1 (control)	1890	-	947	268
1A-2	1828	1680	885	145
1B-1 (control)	1920	-	-	-
1B-2	1962	1860	-	-
1C-1 (control)	2016	-	-	-
1C-2	2006	1892	-	-
1D-1 (control)	1882	-	1143	277
1D-2	1590	1380	1057	132
1E-1 (control)	2065	-	975	250
1E-2	2048	1900	992	132
1F-1 (control)	1701	-	991	1989
1F-2	1646	1472	930	608
1G-1 (control)	2207	-	1009	350
1G-2	2260	2118	999	154
1H-1 (control)	2216	-	1064	281
1H-2	2218	2078	994	154
¹ dried at 124°C for 11 hrs at MSU				

Table 9: Organics (µg/g, dry basis) in RF-treated wood (before drying)				
ID	location	pinene	turpentine¹	resin/fatty acids
1B2-E1	edge	1400	1590	21700
1B2-B	off-center	2030	2300	21900
1B2-M	center	2000	2250	20400
1B2-E2	edge	1460 ²	1700	21200
average		1810²	1960	21300
1C2-E1	edge	1930	2270	24500
1C2-B	off-center	2320	2700	23500
1C2-M	center	2480	2830	15100
average		2240	2600	21000
¹ includes other terpenes; ² not included in average				

Table 10: Organics in dried wood (µg/g, dry basis)					
ID	pinene	turpentine¹	turpentine in green wood	remaining turpentine (% of green wood)	VOC released during drying
1E1-E	123	251			
1E1-B	282	418			
1E1-M	89	286			
average	165	318	4890	6.5	250
1E2-E	10	87			
1E2-B	46	287			
1E2-M	93	287			
average	50	230	4890	4.7	132
1G1-E	24	170			
1G1-B	14	89			
1G1-M	763 ²	1113 ²			
average	19	130	3020	4.3	350
1G2-E	26	240			
1G2-B	12	192			
1G2-M	14	89			
average	17	174	3020	5.8	154
1H1-E	24	345			
1H1-B	25	420			
1H1-M	45	456			
average	31	407	4661	8.7	281
1H2-E	6	82			
1H2-B	5	199			
1H2-M	6	328			
average	6	203	4661	4.4	159
¹ includes other terpenes; ² excluded, due to the possible presence of a knot.					

Removal of turpentine from the low-headspace reactor with steam (IPST)

Water or pinene (30 g.) was placed in a $\phi 1.5 \times 4$ " Teflon cup fitted with a narrow bore vent tube and a tube which accommodated a fiber optic temperature sensor. The unit was run at a forward power setting of 350W, and the temperature rise is recorded in Figure 4. Finally, a mixture of 15 g each of water and pinene was microwaved under identical conditions. The quantity of condensate collected from the vent tube is listed in Table 11. The vapor pressure of α -pinene at 100°C is 0.14 atm, which means that 1.2 g. of pinene should be removed with every gram of steam. Although the experimental value of 1.0 from Table 11 is lower, possibly because the system was not at 100°C, it is clear that the bulk of the pinene can be carried out by a small amount of steam. Since even the small amount of steam evolved under low-headspace conditions will far exceed that of turpentine, most of the turpentine should be recovered in the condensed steam.

Figure 4. Temperature profiles for water and pinene.

Table 11: Condensate from irradiating a 1:1 water: pinene mixture			
time (sec)	temperature (°C)	condensed water (g.)	condensed pinene (g.)
0	31.2		
10	45		
20	56.2		
30	71.8		
50	94		
60	102.1		
210	107	5	4
360	108.2	6.5	6
420	109.4	7.54	7.61

Kiln modifications (MSU)

ADAM[®] analog/digital (A/D) and digital/analog (D/A) converters were interfaced to a PC through the serial input/output (I/O) port for monitoring temperatures and load cell readings. The additional temperature data acquisition capability allowed the monitoring and improved control of the wet-bulb/dry-bulb temperatures and rate of drying throughout the run. The wet-bulb temperature was computer-controlled by increasing or decreasing the air flow with a reference voltage applied with the D/A converter. A separate temperature controller was used to ramp the dry-bulb temperature at a rate that approximates the heating time of a full-size kiln. A shroud around the circulation fan was modified to increase the maximum flow rate through the stack of lumber samples. The fan is controlled by a variable speed DC motor and an air flow rate up to 1500 feet per minute can be achieved.

Temperature dependence of the drying profile (MSU)

One kiln charge was dried to determine if the first and second peaks in VOC emissions were associated with either a change in drying rate or a change in the internal or surface temperature of the lumber samples. Load cells were used to monitor the weight loss, or the rate of drying. One thermocouple was positioned at the center of one lumber sample and a second thermocouple was positioned 2 mm below the surface. Target dry-bulb and wet-bulb temperatures were 240 and 180°F, respectively.

The maximum VOC emission rate occurred at approximately 1 hour into the drying cycle with a sample surface temperature in the range of 60 to 70°C (140 to 158°F). As drying continued and moisture content approached 30%, the surface temperature increased. At this point the VOC emission rate also increased. The increase in wood temperature at the lower moisture probably accounts for the second increase in VOC emissions that has been observed in previous drying experiments with lumber and also with OSB and particle (IPST results). Actual measurements for this experiment are shown in Table 12.

VOC reduction through delayed venting (MSU)

Three kiln charges of lumber samples were dried to determine if delayed venting would reduce VOC emissions. Each kiln charge consisted of fifteen matched 2"x6" rough sawn green southern pine lumber samples 23" in length. The temperature was ramped from ambient to 240°F over a two-hour time period. Venting and wet bulb controls were initiated after 2, 3, and 5 hours for the three different kiln charges.

During heating with no initial venting for 2, 3 and 5 hours the VOC emissions (Table 13) were 3.05, 2.47, and 1.89 lbs/dry ton, respectively. A small amount of steam was observed at the sample outlet of the kiln after about 3 hours. The amount of VOC emissions that occurred during this time period was not measurable and the weight loss indicated that the volume of water vapor was extremely small. Since the air flow was kept at zero, the wet-bulb and dry-bulb temperatures remained the same and no appreciable drying occurred during this time.

After the initial heating period the wet bulb was controlled at 180°F with the D/A signal to the Hastings airflow controller. Each charge was dried for a total of 18 hours to give a final moisture content of approximately 6 percent. This procedure substantially reduced VOC emissions. Similar results have been observed at IPST for smaller pieces of wood. Additional experiments are planned to verify these observations.

Table 12: VOC emissions, surface temperature and weight of wood for one kiln charge of Southern pine lumber samples. (3.3.98)

time (hours)	VOC ppm 10E-1	wood surface temperature, °C	MC %	weight (lbs.)
0.0	2.07	10.7	71.5	82.5
0.5	23.90	43.5	71.0	82.2
1.0	58.40	63.1	68.8	81.2
1.5	33.30	72.1	66.1	79.9
2.0	20.80	76.4	62.8	78.3
2.5	5.80	78.8	61.1	77.5
3.0	11.80	79.8	85.4	76.2
3.5	9.40	80.6	56.8	75.4
4.0	7.80	80.9	54.1	74.1
4.5	6.70	81.1	52.4	73.3
5.0	6.00	81.2	49.7	72.0
5.5	5.60	81.3	47.0	70.7
6.0	5.40	81.9	44.2	69.4
6.5	5.50	82.1	42.0	68.3
7.0	5.00	82.1	38.2	66.5
7.5	5.10	83.2	35.5	65.2
8.0	5.40	82.7	32.8	63.9
8.5	5.90	83.0	29.5	62.3
9.0	6.70	83.5	25.7	60.5
9.5	7.50	84.1	22.4	58.9
10.0	7.70	85.0	19.7	57.6
10.5	8.50	86.3	16.4	56.0
11.0	9.30	87.9	14.6	55.1
11.5	9.60	89.6	12.3	54.0

Table 13: Effect of delayed venting on VOC release

charge #	green weight (lbs)	dry weight (lbs)	VOCs (lbs/dry ton)
1 (no vent 2 hrs)	128	63	3.05
2 (no vent 3 hrs)	131	65	2.47
3 (no vent 5 hrs)	129	64	1.89

Table 14: Diameter of set 1 and set 2 selected loblolly pines approximately 40 years old.		
tree	set 1 (Feb-97)	set 2 (Oct-97)
	diameter (inches)	
1	16.7	17.2
2	15.9	17.2
3	18.2	17.2
4	13.7	16.2
5	15.9	15.9
6	14.6	17.8
7	14.0	15.9
8	14.6	17.8
9	14.0	15.9
10	16.2	15.3
11	14.3	13.7
12	15.3	16.6

Variation of monoterpenes and resin acids in loblolly pine (MSU)

Samples were collected monthly from 12 loblolly pines (~40 years average age, 16 inches average diameter) from March 1997 to March 1998. Samples were not collected in September due to inadvertent harvesting of all trees in the study. Twelve other trees of approximately the same age, diameter, and geographic location were selected for the October 1997 to March 1998 samples. Samples from March 1998 have not yet been analyzed. A 12-inch increment bore with a core diameter of 0.200 inches was used to collect cores at a height of approximately 42 inches. Each core was divided into outside, middle and inside sections approximately 4 inches in length. Each sample was then extracted with methylene chloride and the extract was analyzed for monoterpenes and resin acids by gas chromatography. Target compounds were α -pinene, camphene, β -pinene, limonene, fenchyl alcohol borneol, 4-allylanisole, methyl eugenol, pimaric acid, isopimaric acid, levopimaric acid, dehydroabietic acid, abietic acid and neoabietic acid. The extracted sample core was dried at 105°C, and the percentage of each compound was calculated on an extractive-free dry weight basis. Table 14 contains the measured diameter of the first and second set of trees used in this study. The use of a form that specifies the exact location of test sites were initiated after the first set of trees were harvested. The form has been completed and forwarded to John Starr Forest management personnel in order to prevent harvesting of the trees currently being sampled. Both sets of trees are in the same geographical area and the new set of trees is of approximately the same age as the trees that were cut.

Table 15: Percent extractives in January 1998 samples

	1-inside	1-middle	1-outside	2-inside	2-middle	2-outside	3-inside	3-middle	3-outside	4-inside	4-middle	4-outside
A-Pinene	2.110	0.3195	0.4318	1.5764	0.7922	0.59878	1.3611	0.79221	0.50661	1.6215	0.4160	0.6942
Camphene	0.081	0.0050	0.0077	0.0657	0.0332	0.00893	0.0447	0.03326	0.00814	0.0695	0.0193	0.0123
B-Pinene	1.448	0.0718	0.1407	1.1286	0.6229	0.12384	0.8581	0.62299	0.14826	0.5688	0.2856	0.3550
Myrcene	0.096	0.0058	0.0087	0.0784	0.0358	0.00932	0.0438	0.03582	0.00962	0.0584	0.0219	0.0147
Limonene	0.438	0.0092	0.0231	0.5028	0.2445	0.01701	0.4094	0.24459	0.05478	0.6893	0.1272	0.0398
Fenchyl Alcohol	0.020	0.0000	0.0000	0.0036	0.0015	0.00000	0.0032	0.00153	0.00000	0.0732	0.0016	0.0000
Borneol	0.021	0.0000	0.0000	0.0478	0.0042	0.00000	0.0311	0.00421	0.00000	0.0706	0.0102	0.0000
4-Allylanisole	0.043	0.0080	0.0159	0.0713	0.0019	0.02295	0.0608	0.00191	0.02253	0.0917	0.0480	0.0331
Methyl Eugenol	0.001	0.0003	0.0000	0.0008	0.0008	0.00083	0.0000	0.00083	0.00000	0.0000	0.0001	0.0009
Pimaric Acid	0.079	0.0214	0.0264	0.0886	0.0411	0.02541	0.0527	0.04118	0.02367	0.0606	0.0156	0.0254
Iso-Levo Pimaric Acid	0.092	0.1078	0.1641	0.3996	0.1334	0.16087	0.1802	0.13344	0.09445	0.2931	0.0681	0.1456
Dehydroabietic Acid	0.054	0.0083	0.0161	0.0588	0.0313	0.01272	0.0342	0.03134	0.02621	0.0393	0.0201	0.0200
Abietic Acid	0.132	0.0189	0.0295	0.1062	0.0500	0.03010	0.0906	0.05009	0.02602	0.1421	0.0469	0.0340
Neobietic Acid	0.110	0.0435	0.0512	0.1011	0.0465	0.05419	0.0810	0.04655	0.03301	0.1121	0.0251	0.0520
	5-inside	5-middle	5-outside	6-inside	6-middle	6-outside	7-inside	7-middle	7-outside	8-inside	8-middle	8-outside
A-Pinene	1.0574	0.5012	0.4209	0.7011	0.4302	0.5122	1.1532	0.6232	0.2026	1.4746	0.64660	0.3417
Camphene	0.0308	0.0122	0.0078	0.0141	0.0073	0.0084	0.0522	0.0201	0.0037	0.0553	0.03007	0.0051
B-Pinene	0.4735	0.4132	0.2729	0.1456	0.1333	0.1333	0.0526	0.0482	0.0182	0.3395	0.10648	0.0318
Myrcene	0.0276	0.0154	0.0114	0.0110	0.0114	0.0124	0.0387	0.0232	0.0051	0.0351	0.01678	0.0056
Limonene	0.2713	0.1020	0.0301	0.1355	0.1036	0.0967	0.4919	0.3197	0.0633	0.2192	0.08979	0.0207
Fenchyl Alcohol	0.0513	0.0002	0.0000	0.0049	0.0000	0.0000	0.0263	0.0048	0.0000	0.0464	0.00109	0.0000
Borneol	0.0470	0.0123	0.0000	0.0049	0.0000	0.0000	0.0301	0.0043	0.0000	0.0454	0.00476	0.0000
4-Allylanisole	0.0287	0.0176	0.0239	0.0117	0.0217	0.0585	0.0563	0.0025	0.0176	0.0636	0.00040	0.0212
Methyl Eugenol	0.0000	0.0000	0.0007	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00089	0.0000
Pimaric Acid	0.0355	0.0225	0.0235	0.0344	0.0082	0.0293	0.0403	0.0283	0.0103	0.0393	0.02237	0.0281
Iso-Levo Pimaric Acid	0.1565	0.1117	0.1435	0.1300	0.0294	0.1429	0.1754	0.1207	0.0571	0.0489	0.20719	0.1332
Dehydroabietic Acid	0.0415	0.0286	0.0230	0.0469	0.0075	0.0195	0.0430	0.0276	0.0047	0.0359	0.02181	0.0251
Abietic Acid	0.1114	0.0516	0.0407	0.0427	0.0056	0.0288	0.0862	0.0411	0.0106	0.0961	0.03966	0.0317
Neobietic Acid	0.0803		0.0496	0.0420	0.0076	0.0467	0.0644	0.0379	0.0153	0.0705	0.03079	0.0473
	9-inside	9-middle	9-outside	10-inside	10-middle	10-outside	11-inside	11-middle	11-outside	12-inside	12-middle	12-outside
A-Pinene	1.7497	0.29643	0.2738	1.7601	0.3891	0.19174	0.9352	0.6479	0.2146	2.6835	0.8123	0.73687
Camphene	0.0793	0.00503	0.0044	0.0706	0.0187	0.00315	0.0285	0.0250	0.0040	0.1824	0.0376	0.02303
B-Pinene	1.2584	0.17417	0.2781	0.8985	0.2432	0.04196	0.2145	0.4303	0.1074	1.2966	0.5325	0.52759
Myrcene	0.0811	0.00708	0.0056	0.0580	0.0177	0.00323	0.0273	0.0028	0.0067	0.6739	0.0213	0.02470
Limonene	0.6318	0.03414	0.0206	0.3703	0.0956	0.01939	0.1959	0.0000	0.0000	0.0014	0.0011	0.00084
Fenchyl Alcohol	0.0047	0.00000	0.0000	0.0011	0.0162	0.00000	0.0384	0.0009	0.0000	0.0014	0.0182	0.00929
Borneol	0.0602	0.00000	0.0000	0.0662	0.0161	0.00012	0.0379	0.0135	0.0007	0.0882	0.0188	0.00360
4-Allylanisole	0.0012	0.01304	0.0229	0.2246	0.0479	0.01456	0.0263	0.0063	0.0193	0.1328	0.0031	0.03718
Methyl Eugenol	0.0000	0.00000	0.0000	0.0000	0.0001	0.00391	0.0000	0.0080	0.0073	0.0033	0.0009	0.00434
Pimaric Acid	0.0925	0.01646	0.0180	0.0611	0.0176	0.01960	0.0273	0.0322	0.0312	0.1221	0.0181	0.02858
Iso-Levo Pimaric Acid	0.4612	0.07634	0.0914	0.0512	0.1138	0.11995	0.1092	0.2133	0.1971	0.6502	0.0427	0.13561
Dehydroabietic Acid	0.0645	0.01239	0.0083	0.0557	0.0304	0.01257	0.0271	0.0229	0.0258	0.0998	0.0877	0.01252
Abietic Acid	0.1416	0.01559	0.0164	0.1317	0.1012	0.03582	0.1028	0.1134	0.0862	0.1645	0.0575	0.07216
Neobietic Acid	0.1205	0.02720	0.0306	0.1080	0.0426	0.03709	0.0858	0.0680	0.0859	0.1470	0.0223	0.06633

Table 16: Percent extractives in February 1998 samples

	1-inside	1-middle	1-outside	2-inside	2-middle	2-outside	3-inside	3-middle	3-outside	4-inside	4-middle	4-outside
A-Pinene	1.8675	0.7112	0.4299	2.103	1.1810	0.63432	0.7334	0.6966	0.39685	1.726	0.4153	0.34050
Camphene	0.1003	0.0262	0.0071	0.083	0.0652	0.00957	0.0289	0.0393	0.00707	0.075	0.0341	0.00672
B-Pinene	1.1074	0.4428	0.1078	1.311	0.7769	0.12898	0.1247	0.3913	0.11007	0.462	0.2560	0.12689
Myrcene	0.0891	0.0321	0.0080	0.080	0.0807	0.00997	0.0112	0.0234	0.00837	0.050	0.0292	0.00745
Limonene	0.3248	0.0902	0.0125	0.379	0.1593	0.01806	0.1416	0.1914	0.04251	0.582	0.2726	0.02306
Fenchyl Alcohol	0.0208	0.0080	0.0000	0.029	0.0007	0.00000	0.0215	0.0289	0.00000	0.063	0.0332	0.00000
Borneol	0.0227	0.0085	0.0000	0.028	0.0021	0.00000	0.0220	0.0283	0.00000	0.061	0.0329	0.00000
4-Allylanisole	0.0489	0.0256	0.0163	0.118	0.0758	0.01858	0.0226	0.0400	0.02055	0.076	0.0577	0.02179
Methyl Eugenol	0.0008	0.0006	0.0003	0.000	0.0000	0.00000	0.0000	0.0024	0.00000	0.000	0.0001	0.00000
Pimaric Acid	0.1778	0.0446	0.0180	0.129	0.0852	0.01298	0.0218	0.0330	0.01626	0.099	0.0287	0.01094
Iso-Levo Pimaric Acid	0.8009	0.2568	0.0670	0.388	0.2546	0.04397	0.1186	0.1315	0.04299	0.463	0.1576	0.03389
Dehydroabietic Acid	0.3024	0.0571	0.0056	0.159	0.0870	0.00168	0.0177	0.0368	0.01014	0.147	0.0363	0.00969
Abietic Acid	0.7936	0.1398	0.0325	0.337	0.0852	0.03073	0.1592	0.1365	0.02832	0.762	0.1060	0.03225
Neobietic Acid	0.3063	0.0623	0.0421	0.167	0.7153	0.02712	0.0582	0.0496	0.02655	0.246	0.0676	0.02388
	5-inside	5-middle	5-outside	6-inside	6-middle	6-outside	7-inside	7-middle	7-outside	8-inside	8-middle	8-outside
A-Pinene	1.1419	0.2589	0.2282	1.061	0.4590	0.27680	1.4849	0.5421	0.3929	1.948	0.6683	0.3432
Camphene	0.0503	0.0049	0.0037	0.019	0.0091	0.00480	0.0669	0.0336	0.0069	0.085	0.0435	0.0053
B-Pinene	0.5285	0.2364	0.1345	0.292	0.1579	0.08181	0.1166	0.0879	0.0240	0.562	0.0985	0.0343
Myrcene	0.0298	0.0078	0.0055	0.022	0.0132	0.00722	0.0573	0.0368	0.0100	0.067	0.0202	0.0065
Limonene	0.2708	0.0340	0.0119	0.233	0.1214	0.05759	0.7930	0.4335	0.1174	0.414	0.1012	0.0240
Fenchyl Alcohol	0.0483	0.0006	0.0000	0.002	0.0000	0.00000	0.0269	0.0094	0.0000	0.087	0.0328	0.0000
Borneol	0.0456	0.0004	0.0000	0.002	0.0000	0.00000	0.0301	0.0107	0.0000	0.085	0.0333	0.0000
4-Allylanisole	0.0327	0.0138	0.0180	0.023	0.0261	0.02756	0.0876	0.0550	0.0263	0.087	0.0472	0.0166
Methyl Eugenol	0.0000	0.0000	0.0010	0.000	0.0000	0.00000	0.0000	0.0003	0.0007	0.000	0.0012	0.0009
Pimaric Acid	0.0709	0.0183	0.0117	0.042	0.0252	0.00782	0.0778	0.0421	0.0228	0.062	0.0343	0.0200
Iso-Levo Pimaric Acid	0.3567	0.0645	0.0357	0.153	0.0846	0.02364	0.2441	0.2377	0.0560	0.269	0.3279	0.0731
Dehydroabietic Acid	0.1109	0.0291	0.0105	0.077	0.0584	0.00917	0.0970	0.0780	0.0163	0.077	0.0477	0.0274
Abietic Acid	0.4396	0.0593	0.0173	0.049	0.0570	0.00980	0.2713	0.0523	0.0473	0.163	0.1421	0.0567
Neobietic Acid	0.1430	0.0304	0.0223	0.061	0.0423	0.01306	0.0962	0.0458	0.0349	0.120	0.0566	0.0405
	9-inside	9-middle	9-outside	10-inside	10-middle	10-outside	11-inside	11-middle	11-outside	12-inside	12-middle	12-outside
A-Pinene	1.5942	0.6696	0.3415	1.396	0.4947	0.2128	1.2625	0.7406	0.2726	3.710	0.7291	0.6550
Camphene	0.0652	0.0311	0.0052	0.066	0.0254	0.0031	0.0401	0.0386	0.0046	0.232	0.0276	0.0404
B-Pinene	1.0137	0.4992	0.1393	0.621	0.1778	0.0596	0.6037	0.6429	0.1516	0.979	0.2693	0.6352
Myrcene	0.0524	0.0276	0.0071	0.042	0.0155	0.0038	0.0305	0.0299	0.0094	0.165	0.0176	0.0533
Limonene	0.2812	0.0957	0.0264	0.258	0.0856	0.0127	0.1701	0.1386	0.0424	0.678	0.0703	0.1623
Fenchyl Alcohol	0.0294	0.0082	0.0000	0.043	0.0190	0.0000	0.0311	0.0277	0.0000	0.083	0.0222	0.0148
Borneol	0.0340	0.0095	0.0000	0.043	0.0188	0.0000	0.0309	0.0277	0.0000	0.088	0.0248	0.0150
4-Allylanisole	0.0981	0.0456	0.0470	0.173	0.0692	0.0257	0.0431	0.0424	0.0217	0.158	0.0193	0.0650
Methyl Eugenol	0.0000	0.0000	0.0000	0.000	0.0002	0.0003	0.0000	0.0000	0.0000	0.000	0.0024	0.0082
Pimaric Acid	0.0984	0.0432	0.0172	0.044	0.0137	0.0118	0.0443	0.0192	0.0181	0.039	0.0359	0.0337
Iso-Levo Pimaric Acid	0.5478	0.1898	0.0511	0.142	0.1016	0.0331	0.1960	0.1742	0.0723	0.273	0.2059	0.2224
Dehydroabietic Acid	0.1407	0.0587	0.0108	0.060	0.0223	0.0087	0.0418	0.0487	0.0181	0.044	0.1165	0.0171
Abietic Acid	0.4105	0.1118	0.0168	0.201	0.0761	0.0131	0.1986	0.0985	0.0536	0.272	0.1099	0.0675

The additional data acquired during the reporting period are provided in Tables 15 and 16. The average concentration of α -pinene, and resin acids are illustrated in Figures 5 and 6, respectively. The variability of α -pinene across samples taken from the twelve trees is shown in Figure 7. The amounts of extractive components were higher in the inside samples than in both the middle and outside samples and the trend continued throughout the March 1997 to February 1998 sampling period. The average total percent concentration of resin acids plus monoterpenes ranged from 2.2 to 4.0 percent in inside samples while the highest average concentration in middle and outside samples was just over 1.5 percent. The average concentration of total extractives in the outside portion of samples was approximately 0.4 to 0.9 percent.

The average concentration of total monoterpenes ranged from 1.1 to 3.0 percent in outside samples while the average concentration of monoterpenes from the inside and middle samples was in the range of 0.2 to 1.2 percent. The concentrations of resin acids were more varied and the trends were not clear from graphical presentation of the data, although the "inside" analyses may exhibit a cyclical response (lowest in December, highest in March, then slowly decreasing).

The average concentrations of both α -pinene and β -pinene reflected the trends observed in the graphs of the total concentrations of monoterpenes. This result is not surprising since the concentration of α -pinene and β -pinene comprise a major portion of the total monoterpene fraction. The analysis of variance within the mean at the 95% confidence interval indicated that there was not a statistical difference between the middle and outside sample concentrations of resin acids plus monoterpenes. The mean concentration of the inside samples were different at the 95 confidence interval from the mean concentrations in outside and middle samples. Monthly differences in the mean were not significant.

The graphical presentation of the concentrations of individual compounds indicates that there was considerable variation in the results for the inside samples compared to the data for outside and middle samples. In some cases the changes in variability from month to month are more striking than changes in the mean extractive concentration (e.g., graph of total monoterpenes). Observed differences in some cases (e.g., limonene) appear to be the result of a change in the sample group after October 1997. It is possible that meteorological conditions influence VOC concentrations in trees. Preliminary correlation analyses have been conducted for the innermost samples, and in many cases there are significant relationships with the average day length. About half as many extractive components have statistically significant correlations with average temperature or average rainfall. Alpha-pinene concentration appears to be related to both the average rainfall and the average day length.

Statistical correlations of VOC data collected from 3.97-2.98 (MSU)

Data on the seasonal dependence of VOC emissions were analyzed by the SAS statistical package. While interpretation of the data is incomplete, some of the trends identified are as follows. The analysis was restricted to linear effects, and only correlations significant at 90% or better are reported. For example, the first item in the data indicates that the only coefficient of variance, CoV, (and not the absolute amount of dehydrobiotic acid) correlated with the average temperature.

Correlative Associations with the Average Temperature

Dehydroabietic Acid: CoV

Abietic Acid: CoV

Neoabietic Acid: Std. Deviation, Variance, Range, CoV

Total Resins: CoV

Correlative Associations with the Total Rainfall/Average Rainfall

Alpha-Pinene: Std. Deviation, Range

Dehydroabietic Acid: Range, Mean, Std. Deviation (Total rain only)

Abietic Acid: Mean, Std. Deviation, Variance, Range

Neoabietic Acid: Mean

Total Monoterpenes: Mean, Variance, Range

Total Resin Acids: Mean, Variance, Range

Combined Monoterpenes and Resin Acids: Mean, Range

Correlative Associations with the Total Sunlight/Average Sunlight

Alpha-Pinene: Std. Deviation, Variance, Range

Camphene: Negative Mean, CoV

Beta-Pinene: Negative Mean, CoV

Limonene: Negative Mean, Negative Std. Deviation, Negative Range

Fenchyl Alcohol: Negative Mean, Negative Std. Deviation, Negative Variance, Negative Range

Borneol: Negative Mean, Negative Std. Deviation, Negative Range, CoV

Dehydroabietic Acid: Mean, Std. Deviation, Variance, Range

Abietic Acid: Std. Deviation, Range

Neoabietic Acid: Std. Deviation, Variance, Range, CoV

Total Monoterpenes: Negative Monoterpene Totals, CoV

Total Resin Acids: Mean, Variance, Range, CoV

Combined Monoterpenes and Resin Acids: Mean, Variance, CoV

Figure 5: Average α -pinene concentrations in 12 loblolly pines between 2.97 and 2.98

Figure 6: Average resin acid concentrations in 12 loblolly pines between 3.97 and 12.97

Figure 7: α -Pinene distribution across individual trees