Low VOC Drying of Lumber and Wood Panel Products
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Summary

- Prolonged irradiation of wet heartwood under low-headspace conditions can occasionally lead to enhanced recovery of turpentine. The basis of the phenomenon is not understood.
- The RF field in our pilot unit was demonstrated to be homogeneous, so that the wood should be evenly heated.
- Continuing analyses of twelve trees in the MSU forest confirm that the absence of a significant seasonal influence on turpentine content.
- An apparatus for permeability testing has been constructed, and work is underway.

Apparent enhancement of terpene yield upon prolonged irradiation

Irradiation of wood blocks

This project is based on the finding that brief microwave or RF-treatment of wood under low-headspace conditions leads to the release of VOCs. On occasion we have found that prolonged irradiation increases turpentine yield much more than anticipated from a simple mass balance; i.e. more pinene appeared to be released than was present in the wood in the first place! If taken at face value, this suggests that *brief* low-headspace irradiation removes VOCs, while *prolonged* exposure creates it! While seemingly improbable, this could follow if dielectric heating exposed regions of wood that were otherwise inaccessible to the solvent used for extraction (unlikely), or if the irradiation induced depolymerization of terpene dimers or higher polymers. In this report we attempt to identify the conditions that lead to this apparent enhancement of terpene yield, by constructing relationships between yield and irradiation parameters. Our tentative conclusions are that this enhancement only occurs with relatively wet heartwood, and only under prolonged irradiation.

A 16 x 12 x 2 in piece of green pine (MC: 86.9%, dry basis) was cut into sections, and two adjoining 6.4 x 10.0 x 4.5 cm pieces were wrapped in plastic and microwaved for 30 minutes at 110W. The unit was shut off once the internal wood temperature reached 100°C, and the wood was allowed to cool for 15 minutes, whereupon the temperature dropped to 50-60°C. The unit was turned on again, until the temperature reached 100°C. The cycle was continued until the wood experienced a total of 30 minutes of irradiation; a weight loss of 3% was also incurred during this period. Shavings taken from the wood were extracted and analyzed for pinene. The

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differences in heartwood VOCs were too small to be statistically significant (Table 1). Importantly, the moisture content of the piece of wood was low at 86.9%, and as will be shown later, differences are only noted at higher moisture.

A second set of measurements were made with four 11 cm diameter x 3 cm samples cut from a piece of green loblolly pine (dry basis MC: 118 %). The heartwood content of the sample was about 30%. One of the pieces was wrapped in plastic and microwaved as above. Shavings taken from various regions were extracted, and the extracts analyzed for pinene. The results in Table 2 show that microwaving does not seem to induce any substantial change in pinene content. However, it should be noted that heartwood constitutes only 30% of the total quantity irradiated.

Table 1: Pinene recovered from wood (green basis, μg/g)

	α-pinene		β-pinene	
region	**control**	**microwaved**	**control**	**microwaved**
heartwood				
1	10,400	19,200	2,300	8,000
2	17,600	23,500	11,000	17,000
3	11,300	9,100	7,900	6,900
average	**13,100**	**17,300**	**7,100**	**10,600**
sapwood				
5	38	0	0	0
6	0	0	0	0

Table 2: Pinene recovered from wood (green basis, μg/g)

	α -pinene		β-pinene	
	control	**microwaved**	**control**	**microwaved**
heartwood	13,000	10,500	2,800	2,100
intermediate	1,700	2,600	700	1,000
sapwood	800	1000	300	400

Table 3: Pinene recovered from sapwood (green basis, μg/g)

	α-pinene		β-pinene	
region	**control**	**microwaved**	**control**	**microwaved**
MC: 48.69%, dry basis				
1	360	300	310	250
2	400	300	350	255
3	350	270	310	240
4	1120	490	975	415
average	**558**	**340**	**486**	**290**

In order to separately determine releases from sapwood and heartwood, pine sapwood was microwaved, and sub-samples were extracted. A weight loss of 1.5% was incurred during irradiation. Case hardening occurred for both samples. The results, shown in Table 3, again demonstrate no statistical difference in emissions between the control and microwaved samples.

One of two matched (5.5 x 5.5 x 4.4 cm) pieces comprising only heartwood (MC: 31.98 %, dry basis), was wrapped and microwaved. A corresponding run was made with a sapwood piece (MC: 96.36%, dry basis). The weight loss from the heartwood and sapwood pieces was 5.48, and 2.72%, respectively. Shavings taken from the wood were Soxhlet-extracted with acetone for 5.5 hours, and analyzed for α- and β-pinene. In contrast to the preceding findings, the results listed in Table 4 show that the pinene levels in heartwood increase substantially. There is a marginal decrease for sapwood. Hence these results indicate that pinene recovery increases from heartwood when it is irradiated independently.

Additional experiments were run on sapwood, which was wrapped and microwaved. Sub-samples extracted from various zones were analyzed for pinene content. The dry-basis MC of samples A and B were 41.68 and 56.35 %, respectively. The weight loss from the two pieces, after microwaving was 0.73 and 1.24 %. Microwaving did not seem to significantly affect pinene recovery as shown in Table 5, supporting our earlier findings that terpene release from either sapwood is not affected by irradiation.

Table 4: Pinene recovered from wood (μg/g, green basis)

	α-pinene		β-pinene	
	control	**microwaved**	**control**	**microwaved**
heartwood	1,900	63,000	500	52,500
sapwood	1,800	1,100	1,600	900

Table 5: Pinene recovered from sapwood (μg/g, green basis)

	α -pinene		β - pinene	
	control	**microwaved**	**control**	**microwaved**
sample A				
1	500	500	400	400
2	500	500	400	400
3	500	400	400	350
4	500	300	400	300
average	**500**	**425**	**400**	**363**
sample B				
1	600	500	500	375
2	600	500	500	400
3	800	550	600	450
4	800	550	600	450
average	**700**	**525**	**550**	**419**

Dependence of pinene recovery on surface area during microwaving

In order to determine whether the size and shape of the furnish affected pinene recovery, three sets of heartwood and sapwood flakes (for OSB) were wrapped, irradiated at 110W, and then Soxhlet-extracted with acetone for 2.5 hours. The dry basis MC was 38%. The results shown in Table 6 illustrate that irradiation increases pinene recovery from heartwood, suggesting that microwave-enhanced release occurs from relatively moist wood.

Next, heartwood (MC: 24.5%, dry basis), and sapwood (MC: 81.1 %, dry basis) shavings taken from a block of wood were wrapped, microwaved for 30 minutes at 110W, Soxhlet-extracted with acetone for 5.5 hours, and analyzed for α- and β-pinene. The weight loss during microwaving the heartwood and sapwood samples was 4.15, and 7.86%, respectively. The results listed in Table 7 show that the pinene in heartwood and sapwood are unchanged. Note, however, that the wood was quite dry.

Another piece of green pine was cut separately into three 4.5 x 4.5 x 4.5 cm heartwood (MC 58.67%, dry basis) and sapwood (MC 78.62, dry basis) blocks. One of the pieces from each region was wrapped in plastic and microwaved for 30 minutes at 110 W. Shavings taken from the piece was then Soxhlet-extracted, and analyzed for α- and β-pinene. Finally, heartwood and sapwood shavings taken from the third piece were microwaved and extracted. The results summarized in Table 8 show that microwaving increases pinene recovery from heartwood, and that surface area does not seem to be a major factor in determining the amount recovered. In other words, a similar recovery is obtained whether a piece of pine or shavings therefrom are irradiated.

Summary

The results from Tables 1-8 are summarized in Table 9. Enhanced recovery was only observed when pure heartwood was irradiated, and then only when it had a dry-basis moisture content exceeding 30%. The mechanism for this phenomenon, and indeed, the phenomenon itself needs to be established more firmly before it is taken at face value. Our present position is that we have seemingly identified a novel situation, which needs to be examined further.

Table 6: Pinene recovery from flakes (μg/g, green basis)

			α-pinene		β - pinene	
	irrdn (min.)	**wt. loss (%)**	**control**	**microwaved**	**control**	**microwaved**
mostly sapwood	5	1.61	1,400	1,900	350	100
mostly heartwood	12	3.45	650	38,450	120	28,700
only sapwood	12	3.41	2,500	2,025	160	160

Table 7: Pinene recovery from shavings (μg/g, green basis)				
	α-pinene		β-pinene	
	control	microwaved	control	microwaved
heartwood	27,300	26,300	19,700	19,900
sapwood	650	685	600	600

Table 8: Pinene recovery from blocks and shavings(μg/g, green basis)				
block				
heartwood	9,500	18,200	630	1,350
sapwood	800	115	250	40
shavings				
heartwood	6,400	10,500	200	500
sapwood	600	240	200	80

Table 9: Summary of VOC recovery studies				
data from Table	heart-wood	sapwood	dry basis MC (%)	enhanced recovery
1	unknown		86.9	N
2	30%		118	N
3		100	48.7	N
4	100		31.98	Y
		100	96.36	N
5		100	41.68	N
		100	56.35	N
6	100		38	Y
7	100		24.5	N
		100	81.1	N
8	100		58.67	Y
		100	78.62	N

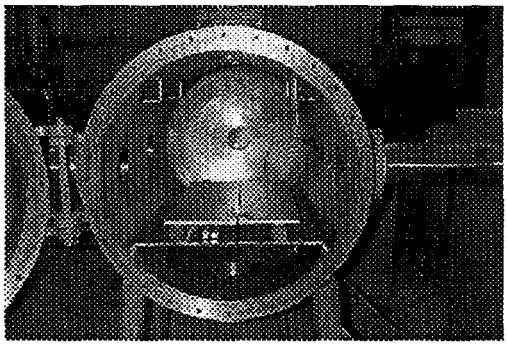

Figure 1: Photograph of the pilot RF unit

Determination of field homogeneity in the pilot RF unit

Two pilot units are presently being used. The first is the Strayfield dryer located at Georgia Power's Technology Application Center. The second is the unit illustrated in Figure 1, which is on loan to us from American Kiln. Ensuring field homogeneity is important for the wood to be irradiated evenly. In order to determine homogeneity, three (10 x 6 x 2 in.) pieces of green pine were wrapped in plastic, placed on top of each other, and irradiated at 0.95A. Thermocouples were positioned 1 and 5 inches, respectively, below the top surface at two peripheral locations. The wood temperature was not allowed to exceed 100°C. The same pieces of wood were then cooled, reshuffled and re-irradiated, and the temperature was measured as above. No significant differences in the time-temperature profile was noted between the upper and lower thermocouples, indicating that the radiation was not attenuated through its passage through the wood. Analogous experiments conducted with thermocouples positioned at the surface also showed no differences with wood position. Hence, we conclude that the oven uniformly heats the wood within.

Collection and analysis of increment core VOC data

This report describes a continuation of an experiment begun in March, 1997, to determine if there are seasonally-related variations in volatile organic emissions from wood harvested from southern pine trees. The same twelve loblolly pines (*Pinus taeda*) standing in the Mississippi State University Starr Memorial Forest have been sampled *via* increment core collection of samples since last October, and twelve trees in close proximity to this stand were sampled for the six months previous. All the trees are about 40-45 years old and have an approximate diameter of 14+ inches (35 cm). The increment cores were collected at a height of approximately 42 inches using a 12-inch long increment borer with a core diameter of 0.2 inches. Following each removal of an increment core, wooden dowels have been placed in the resulting cavity to decrease tree damage during the projected twelve months of sampling. After removal from the tree the cores are always divided into three sections, with the innermost section (closest to the pith) being designated as the "inside" sample, the second as the "middle" sample and the outermost (adjacent to the bark) being designated as the "outside" sample. Samples are placed in pre-weighed test tubes and returned to the laboratory for monoterpene analysis using gas chromatography.

Core samples for gas chromatographic analysis are prepared by adding 10 mL of methylene chloride and 1 mL of 1000 g/mL of 1,4-dichlorobenzene to each sample in a closed test tube. Samples are then sonically agitated for 1 hour, the appropriate amount of diphenylmethane (internal standard) added, and concentrated in a hot water bath to 5 mL for inside samples and 1 mL

for middle and outside samples. A 1 mL sample is taken from each concentrate for analysis and 0.1 mL of ether diazomethane is added to derivatize the sample for analysis on a Varian 3600 gas chromatograph equipped with a J&W DB-5 30 meter capillary column and flame ionization detector. Target monoterpene compounds are α-pinene, camphene, β-pinene, limonene, fenchyl alcohol, borneol, 4-allylanisole, and methyl eugenol; the gas chromatograph also analyzes the sonicated extract for the non-volatile diterpene compounds (*i.e.*, resin acids) pimaric acid, isopimaric acid, levopimaric acid, dehydroabietic acid, abietic acid, and neoabietic acid. Increment cores are dried in an analytical oven overnight to obtain the dry weight of the wood. The dry increment core weight (grams) and the amount of each individual compound (expressed as grams of compound) are used to calculate the percentage of each compound using this equation:

$$\frac{\text{Amount of Individual Compound}}{\text{Dry Weight of Sample}} x\ 100\% = \text{Total Percentage of Compound}$$

Samples have been collected for September and October, 1998, but the results could not be included in this report due to a computer I/O problem that could not be remedied by the report deadline. This completes the tree sampling regimen for this project. To finalize this portion of the work, a tree will be cut in November for direct examination of the sampling areas.

The results obtained to data are illustrated in Figures 2-4. There is little evidence for variation in α-pinene content based upon the analysis of the March 1997-August 1998 increment cores, although α-pinene of the outer samples may be lower during summer.

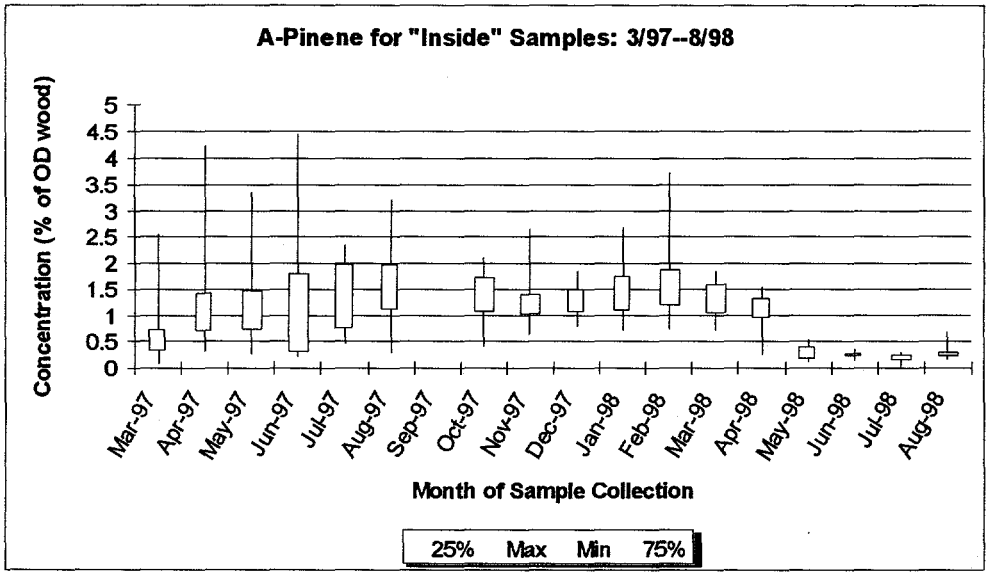

Figure 2: α-Pinene profiles for "inside" samples

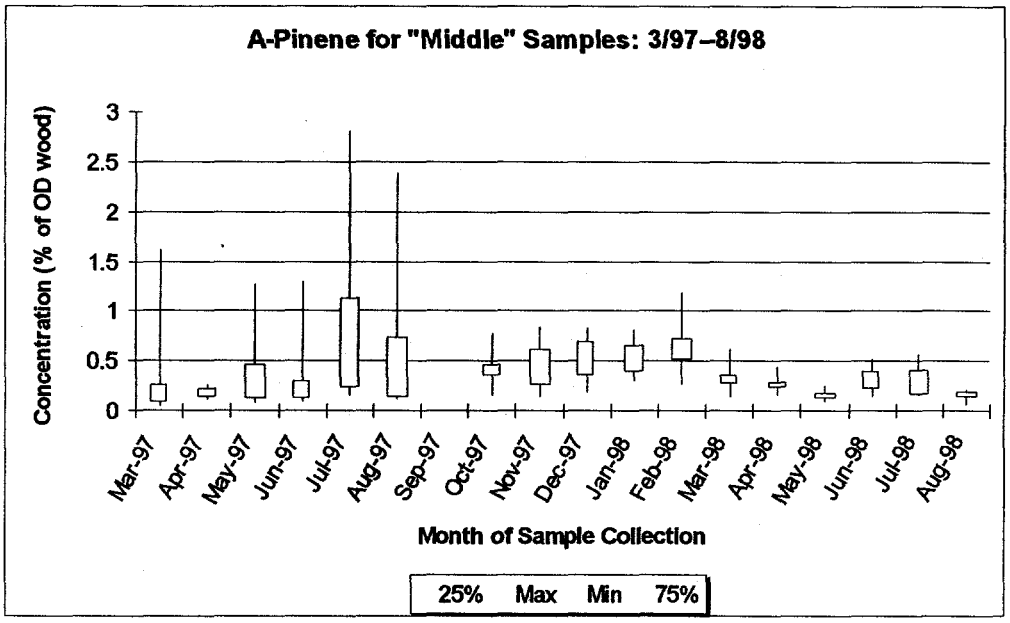

Figure 3: α-Pinene profiles for "middle" samples

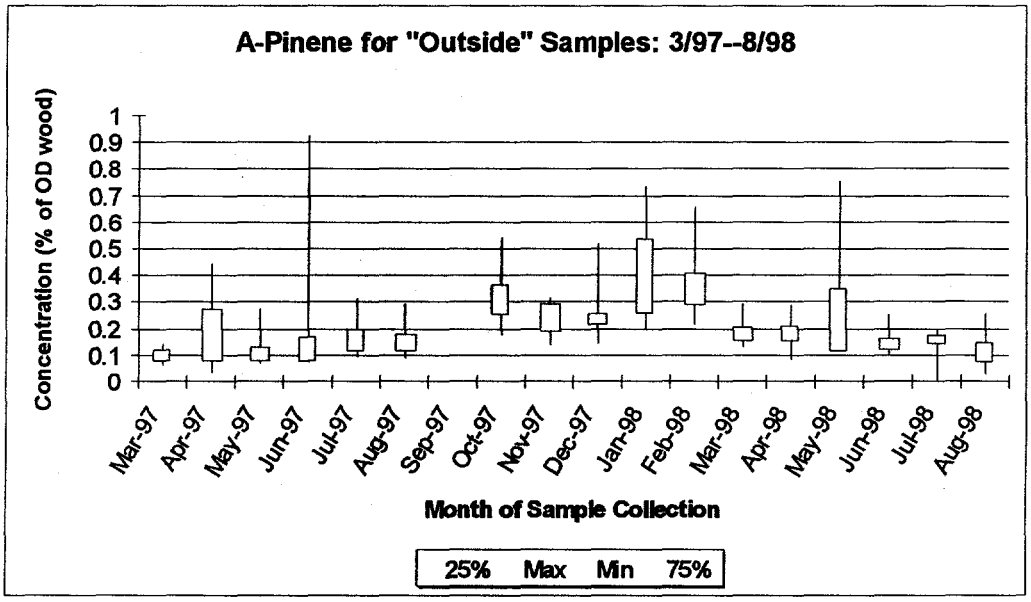

Figure 4: α-Pinene profiles for "outside" samples

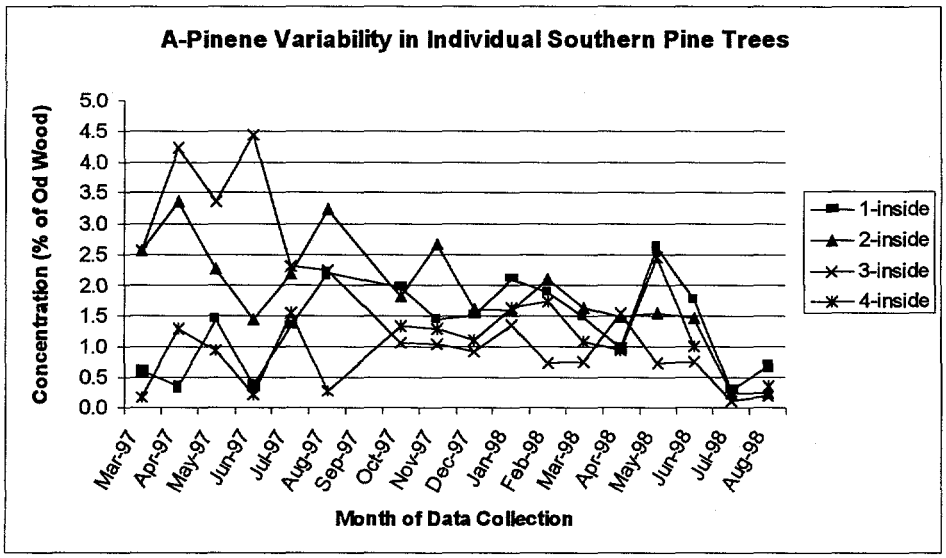

Figure 5: α-Pinene profiles for "inside" samples of individual trees

As this is a longitudinal study, the variation of α-pinene can also be charted by month to see if individual trees follow the identical trends. Figure 5 represents data from the *innermost* cores for four out of the possible twelve samples, indicates that some trees follow the same pattern of concentration changes as their brethren, while other trees act in exactly the opposite fashion. For example, note how tree #3 acts contrary to the others during the summer months of 1997 and 1998. It is difficult to determine from this sampling whether there are seasonal trends for inside core samples. There does appear to be less variability in the population of trees sampled after September 1997.

Figure 6 charts data for the *outside* core data; due to missing data in May of 1998, some different trees were included to represent the data trends. Tree #4, while missing data for May, was included purposely because of its wide-ranging concentration values. Once again some contrariness is noted (e.g., tree #1 during certain months), but all-in-all there appear to be similar trends for the different trees plotted here. In spite of the fact that the trends are similar, though, by comparing tree #9 with trees #4 and #12 it is apparent that there are great differences in the degree to which α-pinene concentrations vary with seasonal factors. As these trees are all maintained in the same sample plot in one plantation, it seems appropriate to conclude that there may be a genetically-based response to seasonal stimuli. There is considerable variability to consider, but perhaps there is a seasonal component to the variation found in these specimens; lower summer values seem possible in the outermost samples.

Total VOC emission data

The total VOC data collected are plotted as for the α-pinene data above in Figures 7-9. As was concluded on the basis of the α-pinene measurements, no particularly strong seasonal variation is apparent, although it is possible that there is a pattern in the decreased monoterpenes for the outermost core samples during summer months. It is possible, but not proven, that the diminished VOC contents of trees during the summer of 1998 are associated with the unusually dry weather.

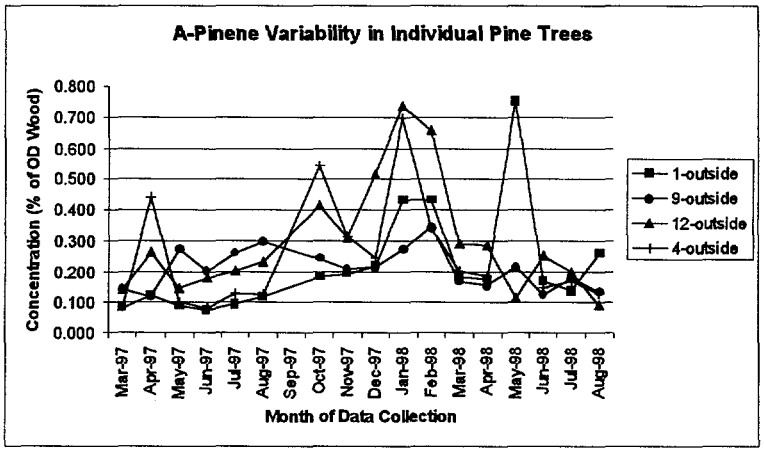

Figure 6: α-Pinene profiles for "outside" samples of individual trees

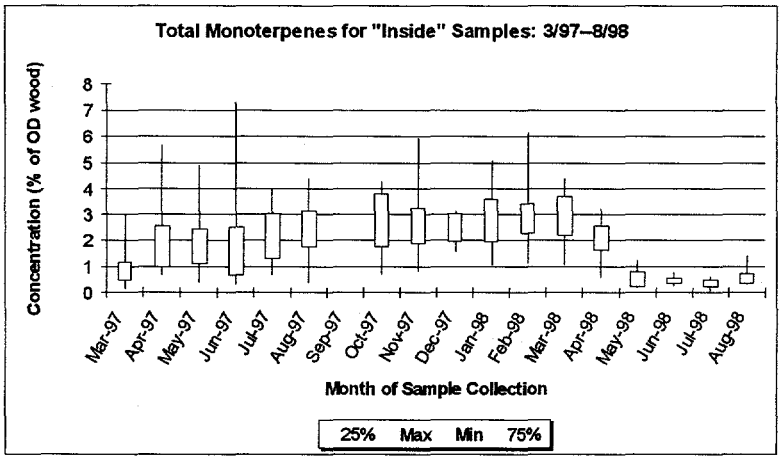

Figure 7: Total monoterpenes for "inside" samples

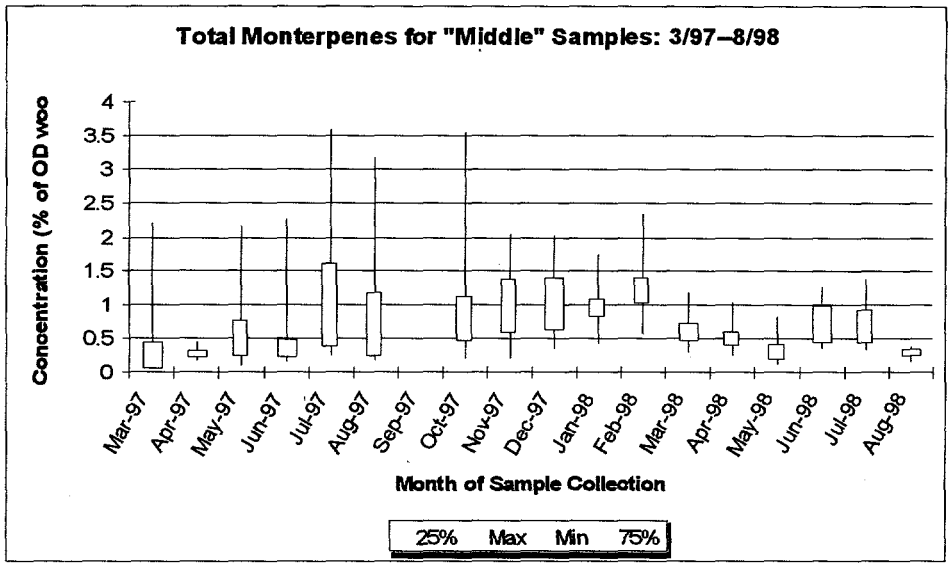

Figure 8: Total monoterpenes for "middle" samples

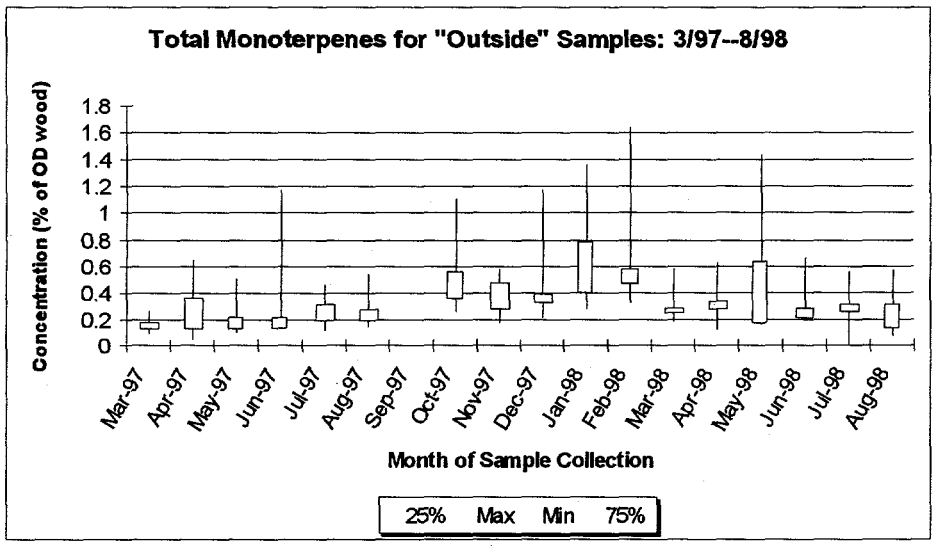

Figure 9: Total monoterpenes for "outside" samples

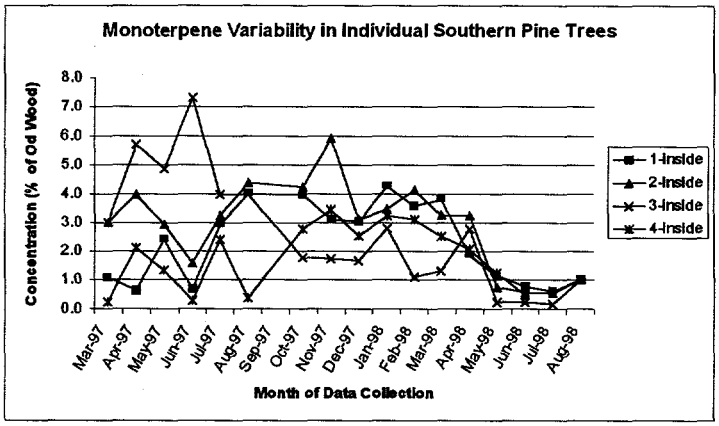

Figure 10: Total monoterpene profiles for "inside" samples of individual trees

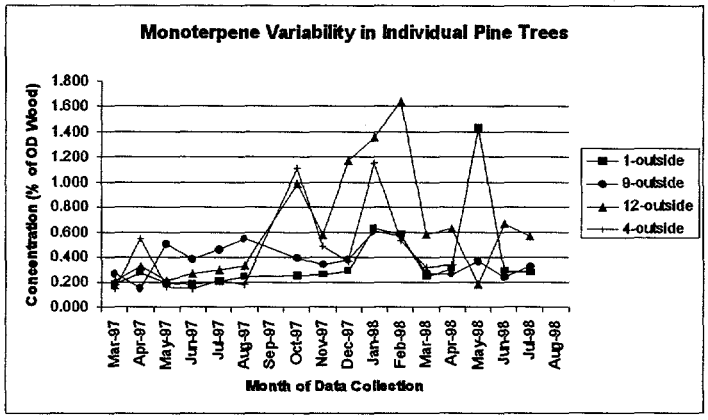

Figure 11: Total monoterpene profiles for outside" samples of individual trees

Trend data for some individual trees (the same as were used in the α-pinene diagrams in the earlier section) are illustrated in Figures 10 and 11. These data seem to reinforce the possibility that there are decreased monoterpene concentrations in the wood during summer months, and perhaps not exclusively within the outermost sections.

Permeability Testing

Because it is desirable to determine whether wood permeability is affected by the RF treatment, an apparatus for testing permeability has been constructed as shown by the illustration in Figure 12. The flow diagram of the essential elements contained in this apparatus, copied from the literature (Rice, R.W. and M. D'Onofrio Wood and Fiber Science 28(3): 301-308, 1996) is shown in Figure 13.

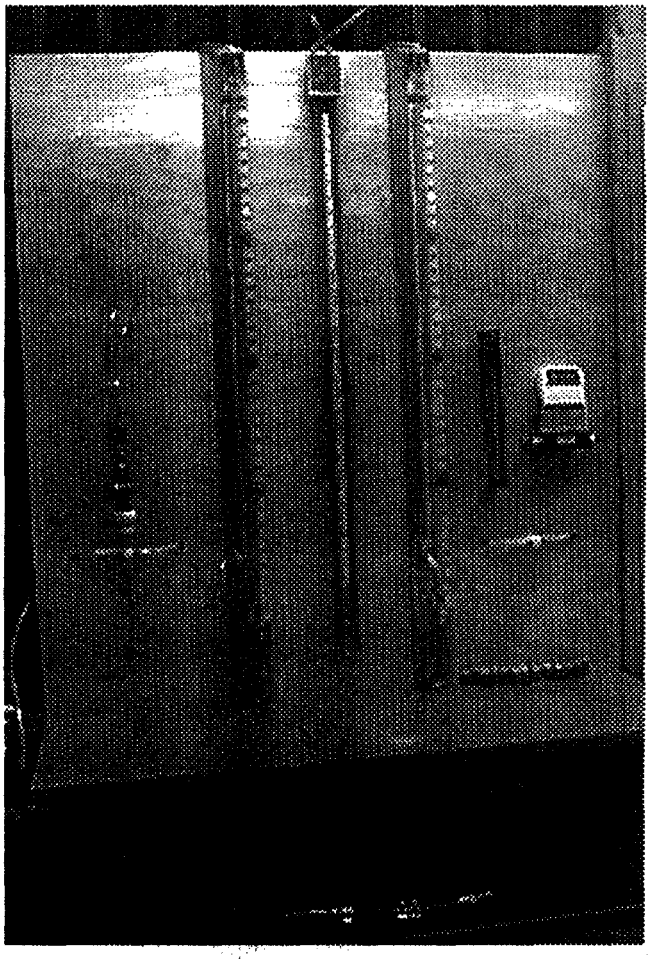

Figure 12: Illustration of the permeability apparatus

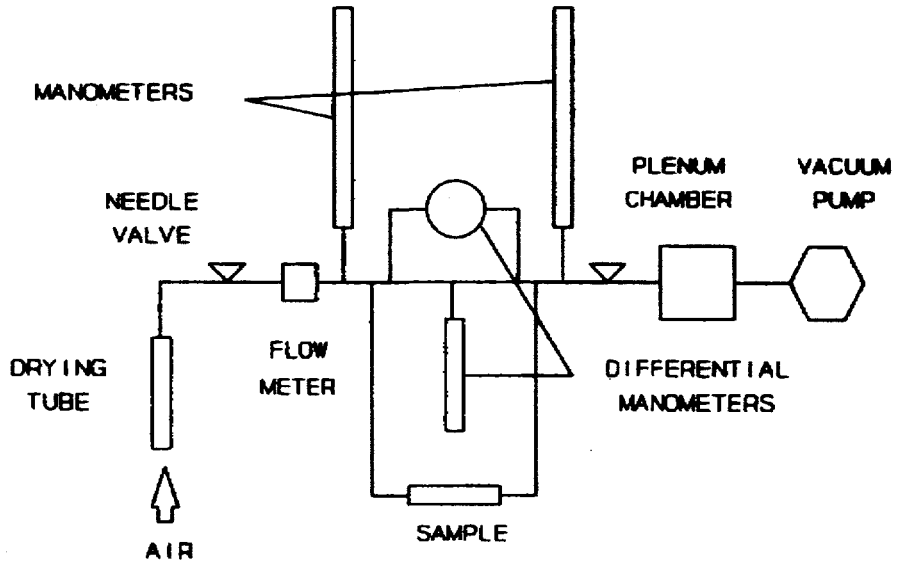

Figure 13: Illustration of the Rice and D'Onofrio set-up

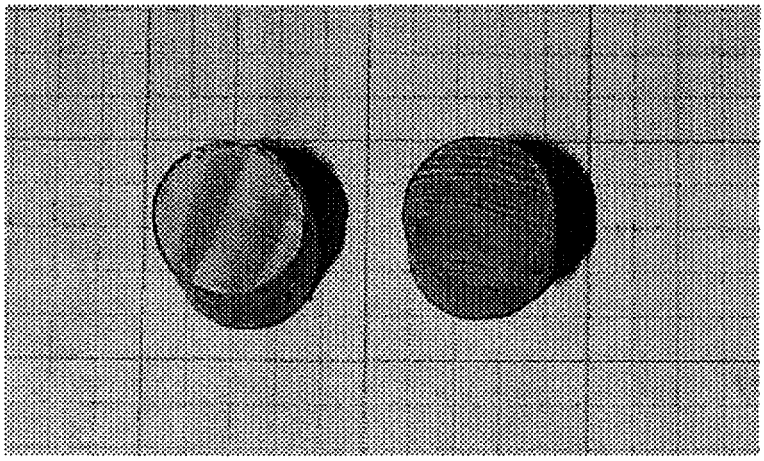

Figure 14: Illustration of specimens for permeability testing

We are currently testing the dry air permeability of dry pine cylinders with dimensions of 0.625" diameter by approximately 0.75" length. The specimens are coated on their circumference with a rubberized coating to ensure that gas passage is entirely through the length of the specimen, with no gas leaks due to cross-grain or small checks. We are making an effort to include both fast-grown and slow-grown specimens among our specimens to be tested. Notice the small crack in the cross-section of the specimen on the left in Figure 14. This has been typical of many of the specimens dried according to conventional kiln schedules, and only preliminary specimens have been tested thus far because these checks affect the permeability test results. We are presently attempting to dry our samples according to a gentler schedule to eliminate these checks.

Drying Schedule

We have dried two different batches of lumber as short pieces (6" lengths), but the commercial kiln schedules used (*e.g.*, 240°F dry bulb, 180°F wet bulb) have proven to be too severe for these short specimens and checks developed which affected the accuracy of our measurements. The checking was similar for both untreated and RF-treated specimens. A modified kiln schedule that ramps the temperature up over three days is being tested with somewhat longer pieces of wood, but although it will take three days instead of 18 hours to dry the wood it is anticipated that this will permit accurate test results to be obtained. Checking must be eliminated or minimized before the permeability tests and the mechanical tests can be conducted.

Summary

VOC data collected from tree increment cores during this period are consistent with those collected during the previous quarter. Data collected and analyzed as lumped data for VOC content since March of 1997 appear to show that the VOC content of loblolly pine trees does not significantly vary with the season, although some data may indicate that monoterpene concentrations decrease in standing trees during the dry Mississippi summer months. This method of analysis may obscure real trends due to contrary behavior of a portion of the sample population, and it is possible that there is a genetically-based response that has not been accounted for.

An apparatus has been constructed to test the dry air permeability of wood specimens. Permeability testing and mechanical testing will be underway shortly after delays caused by checking during kiln drying.