Distribution of terpenes in heartwood and sapwood of loblolly pine

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Abstract

The purpose of this study was to investigate the distribution of terpenes in loblolly pine with respect to the potential impact of volatile organic compound emissions during drying. The total terpene content in the inside, middle, and outside of increment core sections from twelve 40-year-old loblolly pines was determined over a period of 14 months. A method for extracting and analyzing terpenes from increment core sections is described. The average terpene contents and standard deviations (in parentheses) in the heartwood, inner sapwood, and outer sapwood of the increment core samples were 2.3 (0.42), 0.77 (0.31), and 0.35 (0.16) percent, respectively. The distribution profile of terpenes in pines could be better defined by analyzing smaller increment core sections from locations throughout a large number of trees.

Pines and other softwood species contain a variety of monoterpenes and other compounds with boiling points in the range of 150° to 215°C. The monoterpenes have been observed to make up a substantial fraction of volatile organic compounds (VOCs) that are emitted during drying of southern pine lumber (Ingram et al. 2000b). This paper reports a portion of our efforts to gain a better understanding of the occurrence and distribution of terpenes in loblolly pine and the impact on VOC emissions during drying of lumber.

Drew and Pylant (1966) reported the composition and laboratory yields of turpentine from 28 pulpwoods commonly used in the United States and Canada. The turpentine yield from samples of loblolly pine was 0.970 gal/ton of wood on a dry weight basis (about 7 lb/dry ton). The major components were α-pinene, camphene, β-pinene, myrcene, limonene, β-phellandrene, transβ-terpineol, 4-allylanisole, and isoborneol. Samples for this study were representative of the species and yields were determined by condensing the volatile oil from simulated pulping conditions. The major components found in the exhaust from a laboratory scale kiln when drying samples of loblolly pine were α-pinene, camphene, β-pinene, myrcene, limonene, and 4-allylanisole (Ingram et al. 2000b).

In a study of VOC emissions from drying lumber samples with different frequency of knot occurrences, the concentrations of terpenes found in sapwood, heartwood, and knot samples by methylene chloride extraction were 0.31, 1.51, and 3.31 percent, respectively. Results from this study also indicated that an increase in the presence of heartwood and knots in lumber could result in an increase in VOC emissions during drying (Ingram et al. 2000a).

The distribution and composition of terpenes in 24- to 45-year-old radiata pine were previously reported (Kininmonth and Whitehouse 1991). The concentration of terpenes was found to be highest in samples of heartwood and decreased in samples nearer the outside of the tree bole. The average concentration of extractives was 1.8 to 2.3 percent on a dry weight basis and approximately one-third of the extractive content was assumed to be terpenes. The concentration of extractives also decreased toward the top of the stem.

The overall objective of this research project was to investigate the seasonal and climatic variation of terpenes in loblolly pines and the potential impact on VOC emissions. The results from that part of the research project were reported by Conners et al. (2001). The objective of the research reported in this paper was to determine the percent concentration of terpenes in different tissue types of loblolly pine and the potential impact on VOC emissions during the drying of lumber.

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Experimental

The trees used in this study were approximately 40 years old and were located on Mississippi State University's John Starr Memorial Forest, which is located 16 km south of Starkville, MS. These trees were naturally reseeded and were approximately the same height and size in diameter (39 cm). Increment cores were collected monthly from March 1997 to August 1997 from the selected trees. However, these trees were harvested as part of a logging equipment demonstration and samples from October 1997 to December of 1998 were collected monthly from trees of similar size, age, and assumed similar genetic makeup. No samples were collected in September of 1997.

Increment core samples were collected approximately 1.2 to 1.5 m above ground level from 12 loblolly pines using a 30.5-cm by 0.51-cm (12- by 0.200 in) increment core borer. Wood dowels were driven into the empty increment cavity to avoid resin exudation and exclude pathogens. Each successive sample was taken approximately 7.5 cm to 10 cm from the previous sample. The cores were measured, divided into three equal sections, and labeled heartwood, inner sapwood, and outer sapwood. Each increment core section was placed in a pre-weighed screw cap test tube, stored on ice, and returned to the laboratory for analysis.

Ten mL of methylene chloride along with 1.00 mL of 1000 µg/mL 1,4-dichlorobenzene in methylene chloride were added to each sample and the caps were replaced to prevent vaporization of the methylene chloride. Samples were stored in a laboratory refrigerator prior to placing in an ultrasonic water bath for 30 minutes. For heartwood samples, 0.50 mL of a 1000 µg/mL solution of diphenylmethane in methylene chloride was added to each sample and the volume adjusted to 5.0 mL by evaporation using a water bath or addition of methylene chloride. For other sample types, 0.10 mL of internal standard solution was added and the volume adjusted to 1.00 mL. Approximately 1 mL of the sample extract was transferred to an auto sample vial for gas chromatography (GC) analysis. The caps were discarded and the residual methylene chloride was evaporated under a hood using a water bath. The samples were dried in an oven at 103°C and the dry weight of each sample was determined by reweighing the test tube containing the dried increment core section.

Extraction efficiency was evaluated on three different sets of core samples. Core samples from a tree in an adjacent plot were extracted twice and the total amount of terpenes was determined in each extract by GC analysis. The target compounds for GC analysis were α-pinene, camphene, β-pinene, myrcene, limonene, 4-allylanisole, methyleugenol, borneol, and fenchyl alcohol. Percent extraction efficiency was calculated by dividing the total amount of terpenes found in the first extract by the total amount of terpenes found in the first and second extract and multiplying by 100. This procedure was previously described by Thompson (2004).

Results

The results from the three recovery experiments indicated the average recovery from a single extraction was greater than 78.9 percent with standard deviations (SDs) in the range of 3.7 to 11 of the means (**Table 1**). All increment cores from the 12 loblolly pines were analyzed by the same procedure throughout this study. To monitor the overall efficiency of storage, extraction procedure, and GC analysis, 1,4-dichlorobenzene (surrogate standard) was added to each recovery sample. Recoveries of the surrogate standard ranged from 95.0 to 104.0 for all samples with SDs in the range of 7.2 to 19 (**Table 1**). The calculated amount of the internal standard ranged from 68.2 to 112.0 percent. Values in the range from 70 to 130 percent are considered acceptable.

Table 1. — Average percent recoveries of target compounds, internal standard and surrogate standard for southern pine core samples.[a]

	Percent recovery[b]			
	Experiment 1	Experiment 2	Experiment 3	Core samples[c]
Monoterpenes	79.4 (3.7)	83.3 (11)	78.9 (11)	N/A
1,4-Dichlorobenzene	96.5 (16)	97.2 (7.2)	95.0 (19)	104.0 (16)
Diphenylmethane	73.1 (22)	68.2 (21)	85.5 (20)	112.0 (21)

[a]GC conditions: J & W DB-5 capillary column, 30 m by 0.32 µm, oven temperature 60°C for 2 minutes and increased at 60°C/minute to 280°C.
[b]Each value represents the average percent recovery from three replicate core samples taken from trees in an area adjacent to the study trees. Percent recovery = (total terpenes found in first extraction × 100)/(total terpenes found in first extraction + total terpenes found in second extraction). Values in parentheses are standard deviations.
[c]Average recovery for surrogate and internal standard for all field samples in this study. Diphenylmethane was the internal standard and 1,4-dichlorobenzene was the surrogate standard.

Table 2. — Results of ANOVA analysis comparing average total terpenes in increment cores from heartwood, inner sapwood, and outer sapwood sections.[a]

Location	Average percent terpenes	t-grouping[b]
Heartwood	2.3 (0.42)	A
Inner sapwood	0.77 (0.31)	B
Outer sapwood	0.35 (0.16)	C

[a]n = 156 for each sample set. Values in parentheses are standard deviations.
[b]Different letters indicate different t-groupings at a 95 percent confidence interval.

The average percent terpenes for the 12 trees over the entire sampling period was 2.3 (SD = 0.42) percent for heartwood, 0.77 (SD = 0.31) percent for inner sapwood, and 0.35 (SD = 0.16) percent for outer sapwood (**Table 2**). Using analysis of variance (ANOVA) (SAS 3.2 1999-2001) with a 95 percent confidence interval, heartwood, inner sapwood, and outer sapwood were all significantly different. Terpene concentrations were highest in the heartwood and decreased outward. Previous research (Thompson 1996, Ingram et al. 2000b) also reported the highest concentration of terpenes in heartwood. However, these studies only contained data on a limited number of samples from a single loblolly pine log.

In order to determine if there was a difference in the terpene levels in the two groups of trees, additional statistical ANOVA tests were performed. Terpene concentrations from March of 1997 to August of 1997 were treated as one set of data and terpene concentrations from October of 1997 to April of 1998 were treated as a separate data set. The results from this comparison indicated that the season in which the increment cores were obtained had no influence on the percent terpene response due to the location within the tree stem.

The comparison of the two different data sets indicated that the terpene levels from the second group of trees were signifi-

cantly higher (45%) than the terpene levels from the first set of trees. This difference may have been due to the differences in tree characteristics or it may have been due to seasonal variation. However, the location of the sample within the tree had the greatest impact on terpene concentration for both groups of trees.

Drying lumber samples sawn mainly from heartwood gave higher VOC emissions than the drying of lumber samples sawn from sapwood (Thompson et al. 200_. For a single loblolly pine with age, size, and assumed genetic makeup as the trees used in this study, the VOC emissions from drying heartwood and sapwood lumber samples were 6.21 and 3.27 pounds of carbon/dry ton, respectively. These concentrations as percent terpenes in heartwood and sapwood are approximately 0.35 and 0.19 percent on a dry weight basis.

Conclusions

The results from these experiments indicated that higher concentrations of terpenes occur in heartwood than in sapwood of mature loblolly pine. The results of this study show significant quantitative differences in the amounts of terpenes found in loblolly pine heartwood and sapwood samples. The increment core zone between the center of the tree and outer sapwood was intermediate in concentration of terpenes. These results suggest that if the increment core is broken into smaller sections and analyzed for terpenes, then the concentration profile could be better defined. The difficulty in extracting and analyzing small increment core samples could be overcome by analyzing composite samples from a large number of trees. The higher concentrations of terpenes in heartwood contributed to higher levels of VOC emissions during drying of lumber containing heartwood. Results of VOC emissions from drying sapwood and heartwood samples of lumber will be reported in a separate publication (Thompson and Ingram 2005 in press). A quantitative relation between concentrations of terpenes in lumber and VOC emissions during drying has not yet been clearly established.

Literature cited

Conners, T., L. Ingram, W. Su, H. Yan, S. Banerjee, A. Dalton, M. Templeton, and S. Diehl. 2001. Seasonal variation of southern pine terpenes. Forest Prod. J. 51(6):89-94.

Drew, J. and G.D. Pylant, Jr. 1966. Turpentine from the pulpwoods of the United States and Canada. Tappi 10:430-438.

Ingram, L., M.C. Templeton, G.W. McGraw, and R.W. Hemingway. 2000a. Knot, heartwood, and sapwood extractives related to VOCs from drying southern pine lumber. J of Wood Chem. Tech. 20(4):415-439.

_____, R. Shmulsky, A. Dalton, F.W. Taylor, and M.C. Templeton. 2000b. The measurement of volatile organic emissions from drying southern pine lumber in a laboratory-scale kiln. Forest Prod. J. 50(4):91-94.

Kininmonth, J. and L. Whitehouse, eds. 1991 Properties and uses of New Zealand radiata pine. Vol. I. Forest Res. Inst., Rotorua, New Zealand. 216 pp.

Thompson, A. 1996 Volatile organic compounds emitted during the drying of southern pine lumber. MS thesis. Dept. of Forest Products, Mississippi State Univ., Mississippi State, MS.

_____. 2004 Effect of location within the tree and season on terpene distribution in loblolly pine and impact of volatile organic compound emissions from drying lumber. PhD diss. Dept. of Forest Products, Mississippi State Univ., Mississippi State, MS.

_____ and L.L. Ingram. 200_. Distribution of terpenes in loblolly pine and impact on VOC emissions from drying lumber. Forest Prod. J. (in press).