THE SEASONAL CHANGES IN THE LIPOPHILIC EXTRACTIVES CONTENT AND COMPOSITION OF BLACK SPRUCE (PICEA MARIANA), BALSAM FIR (ABIES BALSAMEA), AND THEIR ASSOCIATED TMP-MILL SAMPLES

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by

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Abstract

Wood cores were collected from living trees and already harvested trees on a monthly basis. During the same period, mill samples were collected monthly at six different locations in the production line at Corner Brook Pulp and Paper, a thermomechanical pulp mill in Newfoundland. Wood cores were divided into sapwood and heartwood portions and analyzed separately. The quantity and composition of the lipophilic extractives for each sample were determined. No consistent seasonal changes in total extractives were observed for the wood cores and mill samples. Gas chromatography analysis of the mill sample extracts showed changes in lipophilic extractive components during the papermaking process. Species-specific differences were also found in the chromatograms of fir and spruce samples.

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List of Abbreviations and Symbols

ASW . . . . . alcohols, sterols, waxes

°C . . . . . degrees Celsius

cm . . . . . centimetre

EFA . . . . . esterfied fatty acids

g . . . . . gram

GC . . . . . Gas chromatography

GC-FID . . . . . gas chromatography - flame ionization detector

GC/MS . . . . . gas chromatography/mass spectrometric

ISTD . . . . . internal standard

LC . . . . . liquid chromatography

mg . . . . . milligrams

min. . . . . minute

ml . . . . . millilitre

mm . . . . . millimetre

MTBE . . . . . methyl-tert-butyl ether

ppm . . . . . part per million

TMP . . . . . thermomechanical pulp

μl . . . . . microlitre

μm . . . . . micrometre

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1 Introduction

1.0 Overview

The pulp and paper industry constantly strives to improve product quality and consistency. Testing is carried out at pulp and paper mills and pulp and paper research institutions to monitor the paper making process at various stages. These tests can be divided into four main areas: the wood supply, the pulp, the paper, and the process waters associated with both the pulp and the paper. When problems such as pulp strength, refiner power consumption, pulp brightness, and paper strength occur seasonally each year during paper production, the wood supply is one obvious starting point for investigation. This thesis project was initiated in an attempt to see if there were seasonal changes in the quantity and composition of extractives in the wood supply used by a thermomechanical pulp mill which correlated with paper quality problems. A better understanding of the mechanisms associated with these problems may lead to a more consistent product and lower production costs.

1.1 Wood Extractives

1.1.1 Extractives in General

Extractives are those chemical components which can be removed from wood by organic solvents or water. Fengel and Wegener (1983) define extractives as the large number of different compounds which can be extracted from wood by means of polar and non-polar solvents. Water soluble carbohydrates and inorganic compounds are also considered extractable substances (Fengel and Wegener, 1983).

One class of extractives which receives considerable attention are the lipophilic extractives. These are commonly extracted from wood with neutral organic solvents such as alcohol-benzene (mixture), petroleum ether, acetone, or dichloromethane. Lipophilic extractives consist mainly of glycerol esters (monoglycerides, diglycerides, and triglycerides), fatty acids, resin acids, sterols, terpenes, steryl esters, waxes, fatty alcohols, and other semi-volatile compounds (Sjöström, 1993).

Ekman et al. (1990) separate the lipophilic extractives of softwoods into those mainly located in the resin ducts (canal resin) and those extractives located in parenchyma cells (parenchyma resin). The canal resin is composed primarily of resin acids and volatile terpenes, and parenchyma resin is composed of fatty acid esters such as triglycerides and steryl esters. Similarly, Sjöström (1993) classifies extractives by their function in the tree: pathological and physiological. Pathological extractives are those extractives located in resin canals and mainly composed of resin acids and monoterpenes which serve to protect the wood against biological degradation. In contrast, physiological extractives are located in the ray parenchyma cells, are rich in fats, and constitute a reserve supply of food. Extractives can also include items such as oils (from defoamers or lubricants), sizing agents, and other solvent soluble additives used in pulping and papermaking which do not originate from the wood (Sitholé, 1993).

1.1.2 Analysis of Extractives

Most methods for the analysis of extractives and the characterization of the chemical contents of the extractives involve two primary steps: 1) the extraction of wood

with a solvent and 2) the analysis of the extracts. Solvent extraction typically is carried out using a Soxhlet or Soxtec extraction unit. Both give similar results when used according to Sitholé et al. (1990). Compounds of the resulting extracts are typically identified through gas chromatography (GC) procedures, liquid chromatography (LC) procedures, or gas chromatography/mass spectrometric (GC/MS) procedures.

1.1.3 Seasonal Variation of Extractives

Several studies have looked at the seasonal variation of the quantity of extractives as well as changes in their composition (Ekman et al. 1979; Saranpaa and Nyberg, 1987; Ekman and Holmbom, 1989). Ekman et al. (1979) performed an extensive study of seasonal variation of extractives and extractive composition in Norway spruce (Picea abies (L.) Karst.). A slightly lower resin acid content is observed in the sapwood of Norway spruce during the summer months which is possibly indicative of some metabolic activity in the wood tissues involving these compounds (Ekman et al., 1979). Swan (1968) also saw a decrease in the resin acid content of spruce extractives in early summer. Later, Ekman and Holmbom (1989) found that there was no seasonal dependent variation of free fatty acid and stilbene concentrations in Norway spruce. This agrees with Swan (1968) who also found that the total amounts of fatty acids were constant throughout the year.

However, when the sapwood and heartwood are examined separately a different pattern is observed. Saranpaa and Nyberg (1987) found relatively large seasonal changes in the free fatty acid fraction of the sapwood of Scots pine (Pinus sylvestris L.). Free fatty

acid levels were greatest at the beginning and at the end of the growing season (end of April and middle of August). In contrast, no significant seasonal changes were observed in the amount of free fatty acids in the heartwood. Since the heartwood cells are believed, for the most part, to be dead then this is not surprising. Because the free fatty acid fraction reflects the metabolic activity of the plant, both in quantity and composition, the results of Saranpaa and Nyberg (1987) indicate the existence of a resting period in winter when the amount of free fatty acid fraction was observed to be very small. Ekman et al. (1979) also related changes in extractives content and composition to metabolic activities of the tree.

Esterified fatty acid quantities and compositions were found by Saranpaa and Nyberg (1987) to remain fairly stable throughout the year both in the sapwood and the heartwood. This indicates that the lipids are not readily subject to changes caused by environmental factors (Saranpaa and Nyberg, 1987). This is also in agreement with the results of Ekman et al. (1979) who found no yearly changes in the amount of triglycerides from studies of Norway spruce.

1.1.4 Radial Variation of Extractives

Studies which examine radial variation typically look at differences in the extractive content and composition between the heartwood and sapwood. In softwoods, heartwood is defined as the central portion of the stem where all the cells are dead (Tyrvainen, 1995). In contrast, sapwood or young xylem conducts sap (primarily water), strengthens the stem and to some extent serves as a storage reservoir for food. On

average, only about 10% of the cells in the sapwood are alive (Kramer and Kozlowski, 1979). During differentiation into water-conducting elements, sapwood cells die and reserve materials are consumed or withdrawn (Fischer and Holl, 1992). Heartwood differs from sapwood mainly due to its higher extractives content. Amounts as high as five times more extractives can be present in the heartwood in comparison to the sapwood (Tyrvainen, 1995). The boundary between the heartwood and sapwood in some trees is not always obvious but there is usually a difference in the moisture content of two regions. Tyrvainen (1995) states that the moisture content of spruce (Picea spp.) sapwood can be as high as 60% in comparison to the 30% moisture levels typical of spruce heartwood. The ratio of sapwood to heartwood as well as moisture content varies with species of tree of geographic location (Tyrvainen, 1995).

A study by Gao et al. (1995) on lodgepole pine (Pinus contorta Dougl.) found significant differences in extractive contents between the sapwood and heartwood. Gao, et al. (1995) found triglycerides decreased from the sapwood inwards toward the center of the heartwood. This agrees with Nugent et al. (1977) who reported the triglyceride content of the heartwood to be usually less than half that of the sapwood. Triglycerides were also found to be the largest single class of chemical compounds in the sapwood of black spruce (Picea mariana (Mill.) B.S.P.) and jack pine (Pinus banksiana Lamb.) trees (Nugent et al., 1977). This trend is opposite to that seen for sterol content which is higher in the heartwood than in the sapwood. Free fatty acids and resin acids were also found to increase sharply from the sapwood to the heartwood, 0.4% to 6.0% respectively (Nugent

et al., 1977). This fatty acid distribution was also noted by Fengel and Wegener (1983). Within the heartwood, the fatty acid content declined as the center of the tree was approached and older wood encountered (Ekman et al., 1979). In contrast, Gao et al. (1995) did not find differences within the sapwood area or the heartwood area of lodgepole pine.

1.1.5 Vertical Variation of Extractives

Some studies have been performed to examine the vertical variations of extractives in trees. Nugent et al. (1977) found larger amounts of extractives evident in the heartwood at the base and top of jack pine trees. They also observed that sterols in the spruce heartwood decreased with increasing height. Gao et al. (1995) found that extractives decreased with height in the four longitudinal sections along the logs of lodgepole pine however these differences were not statistically significant. Ekman et al. (1979) also reported little variation in the extractives vertically along the trunk of Norway spruce, however, they did report that the amount of resin acids and diterpene alcohols increased slightly in an upward direction in the sapwood of Norway spruce. Vertical variations appear to be dependent on which groups of compounds are observed as well as the region (sapwood versus heartwood) of the tree sampled.

1.1.6 Compounds Typically found in Spruce and Fir

As mentioned earlier, extraction of wood with non-polar solvents typically yields a mixture of compounds which includes fatty acids, terpenes, esterified fatty acids, alcohols, hydrocarbons, and other neutral compounds associated with these materials

(Mutton, 1962), however, specific studies on the extractives composition of black spruce and balsam fir are difficult to locate. Studies of other species of Picea and Abies are more readily available. The structures of the compounds discussed in this section can be found in Appendix A.

In fresh wood samples the bulk of the fatty acids is usually present as esters with glycerol (Mutton, 1962; Assarson and Åkerlund, 1966). Upon wood storage, however, these esters have been found to hydrolyze to their component fatty acids and glycerol backbone (Nugent et al., 1977; Hemingway et al., 1971; Assarsson et al., 1963; Mutton, 1958). Both saturated and unsaturated fatty acids exist in wood with common examples including palmitic acid (hexadecanoic acid), stearic acid, oleic acid, linoleic acid, linolenic acid, and eicosatrienic acid (Fengel and Wegener, 1983). Spruce extracts studied by Kahila (1957) showed that linoleic acid was the major component of fatty acids. Similarly, Quinde and Paszner (1991) reported palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid as the major fatty acids present in another conifer, slash pine (Pinus elliottii Engelm.)

Another group of compounds found in softwood extractives are the terpenes. These compounds are grouped according to the number of isoprene units they contain and are classed as follows: monterpenes (2 units), sesquiterpenes (3 units), diterpenes (4 units), sesterterpenes (5 units), and triterpenes (6 units) (Fengel and Wegener, 1983). Examples of common spruce and fir monoterpenes in softwood include α-pinene, β-pinene, Δ^3-carene, camphene, myrcene, limonene, β-phellandrene, and terpinolene (Drew

and Pylant, 1966; Zavarin and Snajberk, 1965). This is similar to the findings of Roshchin et al. (1986) who also found the above-listed terpenes as the most common found in spruce with the exception of β-phellandrene and terpinolene.

One specific group of terpenes characteristic of softwoods but extremely rare in hardwoods are the acidic diterpenes or resin acids (Fengel and Wegener, 1983). Quinde and Paszner (1991) reported the most abundant resin acids found in slash pine as pimaric acid, sandaracopimaric acid, isopimaric acid, palustric acid, dehydroabietic acid, abietic acid, and neoabietic acid. A more recent study by Cheung et al. (1994) extracted pimaric acid, levopimaric acid, palustric acid, neoabietic acid, abietic acid, dehydroabietic acid, 7-oxodehydroabietic acid, and 7α-hydroxydehydroabietic acid from the bark of Chinese red pine (Pinus massoniana Lamb.). Ekman et al. (1979) list levopimaric acid, palustric acid, abietic acid, neoabietic acid, dehydroabietic acid, isopimaric acid, sandaracopimaric acid, and pimaric acids as common resin acids in Norway spruce. A similar list of resin acids would be expected for fir based on the similarities of the monoterpene compositions reported by Drew and Pylant (1966) and the common softwood resin acids listed by Fengel and Wegener (1983). However, morphologically the resin canals present in black spruce are absent in balsam fir (Isenberg et al., 1980). Therefore, balsam fir is expected to contain a lower proportion of resin acids in its extractives.

Another important group of terpenes is the triterpenes. Most triterpenes have a stearane structure and can be grouped as steroids (Fengel and Wegener, 1983). Squalene is the precursor for the cyclic triterpenes and can be found in very small amounts in the

wood of conifers (Fengel and Wegener, 1983). Triterpenes and steroids occur mainly as fatty acid esters (waxes) and glycosides, but also in the free form (Sjöström, 1993). Common steroids found in the extractives of softwoods include β-sitosterol, β-sitosanol, campesterol, cycloarthenol, and citrostadienol (Ekman et al., 1979; Fengel and Wegener, 1983; Ekman and Holmbom, 1989). The most abundant steroid compound in Norway spruce is β-sitosterol (Ekman et al., 1979). A structurally-similar steroid to β-sitosterol, stigmasterol was used by Sitholé et al. (1992) as a reference compound for the sterols and triterpene alcohols group of aspen extractives. Unfortunately no specific references to the steroid composition of Abies were found.

Other components of the extractive mixture which have been documented include alcohols and waxes. Alcohols associated with extractives are saturated straight-chain compounds with 16-28 carbon atoms and are either free or combined in waxes (Fengel and Wegener, 1983). Waxes are esters of fatty acids with higher alcohols (C_{18} to C_{24}), terpene alcohols, or sterols (Sjöström, 1993). Other wax-like components are free alcohols such as arachinol (arachidic alcohol), behenol (behenyl alcohol), and lignocerol (lignoceric alcohol) (Sjöström, 1993). Holmbom and Ekman (1978) determined the main alcohols in Norway spruce and Scots pine as 1-docosanol (behenyl alcohol) and 1-tetracosanol (lignoceric alcohol). Ekman (1979) later determined that most waxes in Norway spruce are esterified with ferulic acid. Swan (1967) reported the presence of the abienol along with the labdane alcohol manool and its associated oxides (manoyl oxide and 13-epimanoyl oxide) in the extracts of various Abies spp. including Abies balsamea.

Bol'shakova et al. (1988) reported the presence of the primary alcohols pimarinol, dehydroabietinol, abietinol, neoabietinol, palustrol, levopimarinol, and the tertiary alcohols cis-abienol and isocembrol in Norway spruce.

No studies which referred to specific esterified fatty acids present in black spruce and balsam fir were found, however, a study by Sitholé et al. (1992) used monostearin, distearin, tristearin, tricaprin, and trinonadecanoin as reference standards in a method developed to characterize the acetone extractives of aspen (Populus tremuloides Michx.). Similarily, triolein, trilinolein, diolein, and monolein were used by Suckling et al. (1990) as reference compounds in their analysis of radiata pine (Pinus radiata D. Don) extracts. Among the esterified fatty acids, triglycerides are dominant compared to mono- and diglycerides (Fengel and Wegener, 1983; Assarsson and Åkerlund, 1966).

Other compound groups which have been studied in softwood resin include sesquiterpenes, hydrocarbons (thunbergene, pimaradiene, other saturated and unsaturated alkanes ranging from undecane to tritriacontane), oxides (manoyl oxide), and aldehydes (pimarinal, isopimarinal, dehydroabietinal, abietinal, neoabietinal, palustral, levopimarinal) (Bol'shakova et al., 1988; Roshchin et al., 1986; Fengel and Wegener, 1983; Assarsson and Åkerlund, 1966). The extractives of softwood also contain numerous phenolic compounds which fall outside the scope of this study; such as, lignans, stilbenes, flavonoids, and mono- and disaccharides. Further discussions of these compounds can be found in Sjöström (1993) and Fengel and Wegener (1983).

1.1.7 The importance of extractives to the production of paper

The ability of wood fibers to form bonds with each other is a fundamental property of the fibers and a necessary requirement for paper strength. Papers made from mechanical pulps are generally limited in strength by their fiber-to-fiber bonds (Rudie et al., 1995). In mechanical pulping the fiber structure is compressed repeatedly and finally disrupted, which promotes the liberation of resin and its deposition on the resultant surface of the fiber material (Brandal and Lindheim, 1966). Since mechanical pulps are normally not washed, most of these extractives are carried over to the paper machine (Ekman et al., 1990). In general, the main effects of lipophilic extractives, as they relate to papermaking, are "pitch" contamination and deposit formation on pulp and paper making equipment, occasional sheet breaks, paper dirt specks, loss of brightness potential, and mill effluent toxicity (Sundberg et al., 1996; Tyrvainen, 1995; Welkener et al., 1993).

When pitch is deposited on the fiber surface it inhibits bonding between the fibers (Brandal and Lindheim, 1966). The strength of such papers formed under these conditions is reduced. In contrast, when pulp is freed from pitch by extraction with an organic solvent, such as acetone, the strength of such sheets is increased (Brandal and Lindheim, 1966). Sierra et al. (1990) also reported that wood that had been previously extracted with solvent produced paper with greater strength and whiteness.

The free fatty acid component of wood resin has been found to affect paper strength. Relative changes in tensile strength are found to correlate most strongly against

free fatty acid concentration (Wearing et al., 1985). The strength potential of the sheet depends on the intrinsic fiber-to-fiber bond strength and the bonded area. Free fatty acids may affect both these factors by reducing surface tension and, in the absorbed state, reducing inter-fiber hydrogen bonding - thus resulting in decreased tensile strength (Wearing et al., 1985).

At the paper machine, contamination of newsprint white water (the water, fines, and additives which drain through the forming fabric as the sheet is formed on a paper machine) with excessive concentrations of dissolved and colloidal extractives from mechanical pulping processes also leads to impairment of product quality. Contaminating filtrates can result in a decreased attraction between paper fibers in early sheet formation (wet-web formation) at the paper machine by lowering surface tension (Wearing et al., 1985). A loss in tensile strength due to surface tension effects can be expected to reduce paper machine efficiency and speed.

As a result of reductions in mill effluents and increased water system closure, alternate forms of processing are required to control the levels of extractives in process waters and their negative effects on paper production. Measures such as the addition of pitch dispersion agents to the mill process waters are often necessary to ensure product consistency.

1.2 Wood Seasoning

Following harvest, logs are either chipped into piles at the mill or piled in roundwood form (bark intact) and allowed to stand for a period of time. During this seasoning period many biological processes occur. The extractives of seasoned wood have been found to be less accessible and extractable in the process waters of the mill (Ekman et al., 1990).

The storage of wood is a balancing act between reduction of extractives and retention of freshness. The longer the wood is seasoned the lower it is in terms of extractive quantity and composition, however, wood which has been stored and seasoned too long produces thermomechanical pulps of less desirable characteristics and results in unnecessary wood weight loss. At favorable temperatures most of the chemical changes in extractives composition occur during the first two months of storage (Nugent et al., 1977; Levitin, 1967).

1.2.1 Changes that Occur as a Result of Seasoning

It is an accepted fact that the storage of wood, as chips or in roundwood piles, alleviates pitch deposition problems in the subsequent production of sulphite and groundwood pulps (Nugent et al., 1977). There are four processes which are generally recognized to occur and affect the chemical composition of extractives during wood seasoning: 1) the hydrolysis of esterfied fatty acids catalyzed by the enzyme lipase, 2) oxidation of free fatty acids through many intermediate products to the end products of carbon dioxide and water, 3) the biological activities and utilization of materials by living

cells until their death following harvest (days to weeks later), 4) microbiological attack by both bacteria and fungi which are capable of producing hydrolyzing enzymes and of consuming certain components of resin (Ekman and Holmbom, 1989; Nugent et al., 1977; Assarsson et al., 1963; Bethge and Lindgren, 1962). Nugent et al. (1977) note an initial increase in free fatty acids followed by the eventual decrease of free fatty acid content during seasoning to be a result of two different mechanisms at work. The initial increase is generally attributed to the rapid hydrolysis of esterfied fatty acids, which takes place to completion during the first several months while the subsequent decrease is a result of the slower oxidation processes (Nugent et al., 1977; Assarsson and Åkerlund, 1967; Assarsson, 1966).

In a study on the effect of seasoning at different temperatures (-20 °C, 5 °C, and 21 °C) very little change in the amount of extractives was seen in 2 cm wide sections of roundwood seasoned at -20 °C and only small changes in the amount of extractives were seen for wood stored at 5 °C and 21 °C (Nugent et al., 1977). However in the same study the changes in the extractives composition were found to be significant. The largest change as a result of seasoning seems to occur in the sapwood.

Certain extractives found in fresh wood may also be responsible for the yellowing of pulp (Fengel and Wegener, 1989). Yellowing of pulp is thought to be a result of reactions with the phenolic group of extractives (Hu et al., 1997; Hon, 1979).

Seasoning also has been found to depend on the form of storage (chips vs. roundwood) and the relative moisture of the wood. Wood stored as chips is found to

undergo greater decreases in resin content and triglycerides content than logs stored in piles (Assarsson et al., 1963). Nugent et al. (1977) found in the very dry heartwood of black spruce that triglycerides were still present even after seven months of seasoning.

There has also been some examination of the physical changes (in contrast to chemical changes) to the wood during seasoning. There are indications that the pressure in parenchyma cells in the living tree is very high (Tyrvainen, 1995). This pressure may decrease with seasoning (reductions in extractives and moisture content of the wood) and the parenchyma cells may then be less apt to rupture during pulping and certain papermaking operations.

For the most part, the benefits of wood seasoning outweigh the negative points (such as decreases in cellulose content) and it is a common practice in the pulp and paper industry today.

1.3 Refiner-based Mechanical Pulping

Mechanically-produced pulps use wood chips and/or sawdust as their raw material and mechanical force is used to separate wood into its individual fibers. Refining involves the process of placing wood chips and water between radially-grooved steel disks which are rotating in very close proximity (Fig. 1.1). Material is introduced into the refiner at the center of the refining disks and as the wood moves towards the periphery of the disk it is progressively broken down into smaller particles and finally into fibers (Smook, 1982). Refiners use either a single stationary disc and a rotating disk, two counter-rotating discs, or a revolving double-sided disc between two stationary disks

(Smook, 1982). All types of refiners result is the separation of wood fibers based on mechanical force aided by the heat generated from the associated friction of the process.

1.3.1 Thermomechanical Pulping in General

Thermomechanical pulp (TMP) refers to a mechanical pulping process where wood chips are initially steamed (under pressures of 160 kPa - 200 kPa) at temperatures of 120 - 130°C, refined under pressure and at temperatures above 100°C (primary refiner), and further refined at atmospheric pressures and temperatures of 100°C (secondary refiner) (Tyrvainen, 1995; Smook, 1982) (Fig. 1.2). The steam serves to soften the wood chips prior to refining, thus producing a pulp that has a greater percentage of long fibers (increased paper strength) and less shives (small bundles of fibers that have not been separated completely in the pulping operations) (Smook, 1982). It is important that refining be carried out below temperatures of 140°C. When chips are refined at temperatures above 140°C, the fibers are easily separated at low energy consumption because the lignin has undergone a dramatic softening (Smook, 1982). Consequently, the fibers are released intact but are coated with soft lignin sealing the fiber and making it less permeable to later stages of processing, such as bleaching. Following secondary refining, the refined pulp is diluted to a low concentration and agitated at 85°C to 90°C for approximately 30 minutes in a latency chest (Tyrvainen, 1995). This allows the fibers to relax and straighten before they are screened to remove fiber bundles and shives.

The pulp yield from wood chips for mechanical pulping processes is always over

90% compared to that of chemical processes (usually under 50% yield) (Tyrvainen, 1995). Tyrvainen (1995) also indicated that since TMP is entirely a mechanical process that it is much more dependent on its wood supply to produce a consistent product in comparison to chemical pulping. Variation of important wood properties such as basic density, moisture content, tracheid dimensions, latewood content, proportion of heartwood, and extractives content will ultimately affect the pulp produced (Tyrvainen, 1995). Fiber morphology (shape and size) and fiber wall structure directly influence fiber flexibility, plasticity (deformability), and resistance to mechanical processing, and thereby indirectly influence the development of interfiber bonding and other physical properties of the end-product (Tyrvainen, 1995).

1.3.2 Thermomechanical Refining and Paper Strength

The extent of refining also significantly affects the strength of the final product. When the forces which hold the individual fibers together (hydrogen bonds) exceed the strength of the fiber itself, then the tensile strengths of the fibers are the limiting factors in the tensile strength of the paper. To avoid fiber strength losses in high yield pulping, it is important to consider fiber damage that occurs early in the process (Rudie et al., 1995). Fiber damage in chipping, chip handling, chip compression in the plug screw feeders, and the initial size reduction in the first stage refiner may increase the susceptibility of the fiber to cleavage later in the paper-making process (Rudie et al., 1995). Fiber length gives a clear indication of fiber damage in the refiners. Seasonally, the winter-harvested and spring-harvested wood have slightly longer average fiber lengths than the summer

samples. Rudie et al. (1995) found that the net fiber length retention from wood chips to the secondary refiner is 77% in spring, 65% in winter, and 63% in summer. The shorter fibers appear to contribute to paper strength negatively as greater paper strengths are associated with the longer fibers of the spring season. An analysis of wood chips for the three seasons in question (spring, summer, and winter) showed a slight increase in oversized chips during the winter and summer periods, and a decrease in the wood density of the winter and summer samples (Rudie et al., 1995). The observed change in wood density was thought to be sufficient to induce the changes in strength observed in the mill (Rudie et al., 1995). However a study of mill paper samples by Rudie et al. (1995) found that bond strength in contrast to fiber strength was the limiting factor in paper strength during the winter and summer months. Therefore, an alteration of refining conditions is likely required for the production of increased bond strengths and paper strengths.

1.4 Process Waters

The production of paper involves the usage of large quantities of water in log washing, chip washing, pulping, and at the paper machine itself. During mechanical refining, colloidal dispersions of extractives are generated when resins and fatty acids are released from the wood fibers into the process waters (Sundberg et al., 1996). Resin acids especially have been found to be acutely toxic to fish. To reduce the impact of effluents on the environment, mills have been forced to reduce the quantities of effluents which they dispose of into the environment. While this practice is beneficial to the

environment it has lead to increased pitch-related problems in the paper-making process (see also section 1.1.7).

1.4.1 The Effects of Water System Closure

Reduction of effluent volume is usually achieved by water system closure and the utilization of the same water several times at different locations throughout the mill. This results in increased concentrations of dissolved and dispersed substances in process streams. It can be calculated that a decrease in the fresh-water intake from 30 m^3/ton to 10 m^3/ton of water means an increase of 40% in the concentration of dissolved material (Lindstrom et al., 1977). These substances (pitch) can have a negative impact on paper machine efficiency and product quality (Holmbom, 1995; Ekman et al., 1990). Problems attributed to dissolved colloidal substances, as discussed earlier, include deposit formation, increased drainage time (important in sheet formation at the paper machine), decreased wet strength, interference with cationic process chemicals, impaired sheet brightness, and impaired paper strength in the final products (Sundberg et al., 1996). Other major dissolved (hydrophilic) components in the process waters include hemicelluloses, pectins, lignans, and lignin (Orsa and Holmbom, 1994; Ekman et al., 1990). Lignans and lignins have been suggested as affecting paper brightness and strength (Hu et al., 1997; Orsa and Holmbom, 1994).

Ekman et al. (1990) and Ekman and Holmbom (1989) found that there were no differences in the extractive chemical compositions of the pulp or the TMP water. These similarities indicate that canal resin (resin acids) and the parenchyma resin (fatty acids

and sterols) were about equally extractable in the pulp. This reinforces the idea that during refining extensive breakage of parenchyma cells occurs. Ekman et al. (1990) also found a decrease in the dissolution and dispersion of lipophilic extractives at increasing concentrations of total dissolved and dispersed substances in pulp filtrates. This phenomenon is likely due to the solubility limitations of the process water itself. However, with water system closure and reductions in mill effluent this equilibrium level is still sufficient to produce pitch and deposit problems.

1.4.2 Analysis of Process Waters

In the study of process waters there are general steps followed to determine the composition of the water sample. A typical sample manipulation in the modern literature initially involves the separation of the solid and liquid sample portions through centrifugation. The supernatant from centrifuged suspension (containing the colloidal suspension and the dissolved substances) is then extracted with solvent. Methyl-tert-butyl ether (MTBE) or petroleum ether are the two most commonly used extracting solvents and have been reported to give good reproducibility (Orsa and Holmbom, 1994; Holmbom, 1995). The organic solvent layer is then removed, evaporated to dryness, and prepared for analysis by gas chromatography (Holmbom, 1995).

1.4.3 The Effect of pH

The pH can have a profound effect on the composition of extractives dispersed or dissolved in the process waters. At increasing pH, free fatty acids and

especially resin acids will be dissolved in the process waters. Sundberg et al. (1996) found this higher dissolution point was noticable above a pH level of 6.5. At pH levels of 6.5 and below all component groups found in dispersed colloidal droplets are retained when the process water is filtered through a 0.1 μm filter (Sundberg et al.,1996). This agrees with a study by Ekman et al. (1990) who also found that resin and fatty acids are more easily liberated from fibers and colloidal resin at higher pH. In contrast to this, triglycerides and steryl esters were not affected by pH and remained primarily unhydrolyzed in the colloidal droplets (Ekman et al., 1990).

1.5 Study Aims

The aims of this study are to observe the quantity and composition of lipophilic extractives from a thermomechanical pulp mill and its wood supply over the period of one year. This will provide information that may help address and understand the issues of seasonal paper quality problems (pulp strength, refiner power consumption, pulp brightness, and paper strength) experienced by the mill studied in this thesis.

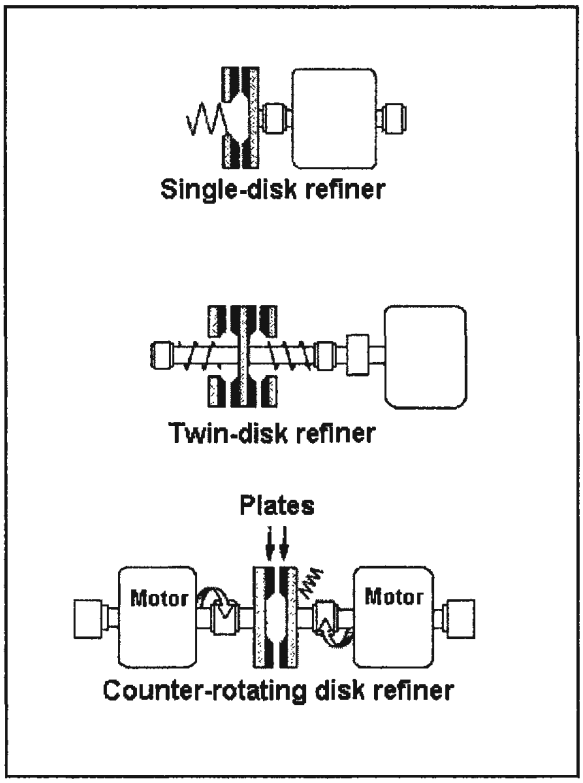


Figure 1.1. Common types of mechanical refiners (modified from Fengel and Wegener, 1984).

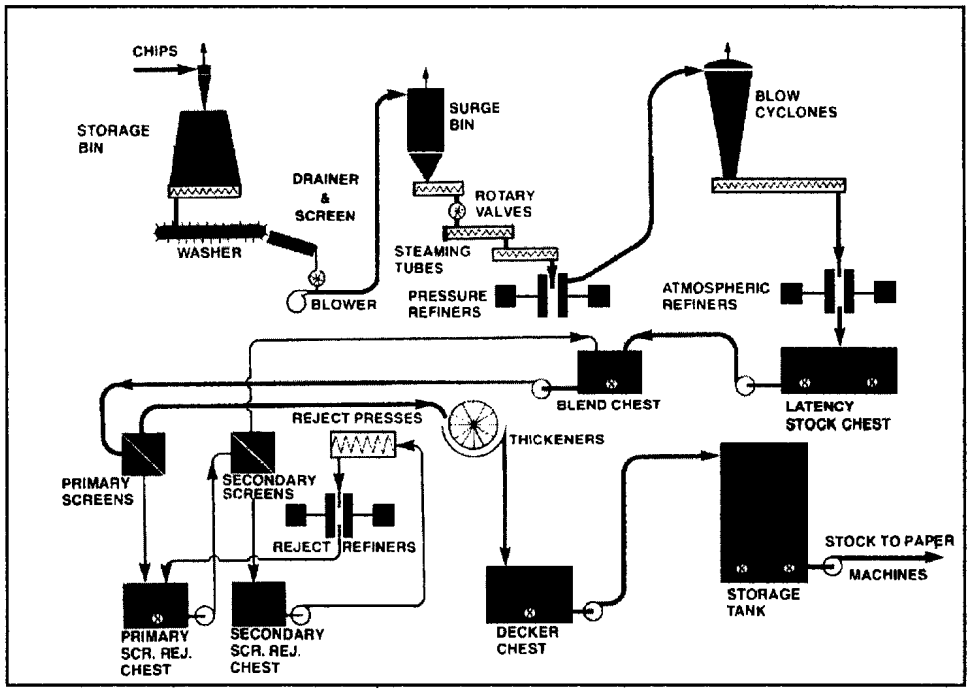


Figure 1.2. A typical TMP-mill layout (modified from Smook, 1982).

2 Materials and Methods

2.0 Sample Collection

2.0.1 Overview

All samples were collected by staff of Corner Brook Pulp and Paper (Kruger Inc.), Corner Brook, Newfoundland, between November 1995 and October 1996. Samples were either collected at Corner Brook's TMP mill or at timber stands harvested by the mill. This produced two types of samples: 1) mill samples and 2) wood core samples. Corner Brook Pulp and Paper uses two tree species for the production of paper: black spruce (Picea mariana) and balsam fir (Abies balsamea), 40% and 60 % respectively. Mill samples reflect a mixture of these two species while wood core samples address the two species separately.

2.0.2 Wood Cores

Wood cores consisted of samples taken from both living trees and harvested/seasoned logs at the mill wood yard. In each case samples were taken from 6 trees or logs of both black spruce and balsam fir (total = 12 wood cores/species). Sampling occurred between the 13th day and 17th day of each month. Wood cores, equivalent in length to the radius of the tree, were taken using a 0.5 cm increment borer. Core samples were taken from only one side (selected at random) of the tree within a designated 1.5 meter vertical region (centered at breast height), and avoided compression wood associated with branches. With the bark removed, cores were inserted into plastic drinking straws (on which the sapwood end had been labeled) and wrapped in plastic

wrap. Each core was sealed in a labeled plastic bag and frozen within 12 hours. All holes in trees and logs produced by core removal were plugged with dowel stock.

For the forest samples, trees were selected from previously thinned stands of mature black spruce and balsam fir. Trees were required to have a live and healthy crown, no physical damage, be the dominant or co-dominant species in a stand, and have straight trunks of average breast-height diameter. Samples were taken from the same 6 trees of each species (6 fir and 6 spruce) for the entire sampling period.

For the wood yard logs, samples were obtained from 3 separate sets of 6 logs (1 wood core/log/month) harvested at 3 different times during the year (Table 2.1) . The first set of 6 logs was harvested in mid-October 1995 and were sampled monthly from November 1995 to February 1996. A second set of 6 logs was harvested in mid-March of 1996 and sampled from March 1996 to August 1996 with the exception of July 1996 (no sample provided). A third set of logs was harvested in mid-May 1996 and sampled from May 1996 to Oct 1996, again with the exception of July 1996. The months of May 1996 to August 1996 produced two separate sets of yard samples and were studied separately since these samples represented logs harvested at different dates.

2.0.3 Mill Samples

There were six different sampling locations in the mill: 1) the #4 refiner wood chip bin, 2) the #4 primary refiner blow line, 3) the #4 secondary refiner blow line, 4) the #4 screen accepts line, 5) finished paper from the #7 paper machine (supplied by #4 refiners), and 6) white water from the #7 paper machine wire pit. Sampling occurred

once daily on the 14th day, 15th day, and 16th day of each month. The 3 daily samples were then combined to give one sample per location per month (total = 6 samples/month) and frozen.

2.1 Preparation for Extraction

Prior to freeze-drying, most samples required processing to facilitate later grinding in a Wiley mill. The type of sample directly influenced its treatment before freeze-drying.

2.1.1 Wood Cores

Wood cores were separated into heartwood and sapwood portions. The six individual wood core sections for each sample were combined to create one sample large enough for extraction and analysis. Thus one heartwood and one sapwood sample for each location per month was produced. Prior to freeze-drying, wood cores were frozen in liquid nitrogen and ground in a Wiley mill (#20 mesh). Ground samples were placed in small plastic vials, covered with perforated Parafilm, and freeze-dried for 2-3 days.

2.1.2 Mill Samples

In preparation for freeze drying, a portion of the wood chips (~ 100 g) were broken along the grain into narrower pieces less than or equal to 1 cm in width. Refiner pulps were an exception and a portion of the sample (~ 100 g) was freeze-dried as sampled. Screen accepts samples (500 ml) were allowed to thaw and separated into solid and liquid portions by use of a centrifuge. The resulting supernatant was filtered through coarse filter paper (Reeve R22) under vacuum. The solid portion (pulp) of the sample

was combined with the fibers trapped by the filter paper and freeze-dried. The pH of the liquid portion was measured and the liquid sample was frozen for later extraction. Newsprint samples were also cut into strips 2-3 cm wide and 10 cm long prior to freeze drying. White water samples were treated similar to the screen accepts samples as fines were removed using a centrifuge and filtration. The pH of the liquid portion of the white water sample was measured and the filtered supernatant was frozen for later extraction. The fines portion of the white water sample was not analyzed.

Processed samples were freeze-dried for 2-3 days and then ground in a Wiley mill (#20 mesh for wood chips and wood cores, #10 mesh for all other samples). Following grinding, freeze-drying of samples was repeated.

2.1.3 Extraction Thimbles

All samples were extracted in 26 mm cellulose Soxtec extraction thimbles. Immediately following removal from the freeze-drier, an accurately weighed sample between 3 g and 4 g was placed into a fresh thimble and covered with dry glass wool which had been previously washed in chloroform. For each sample two thimbles were prepared for duplication purposes.

2.2 Extraction - Solid Samples

Prior to extraction, glass Soxtec extraction cups were washed with chromic acid, oven dried, cooled in a desiccator, and weighed. Samples were extracted on a 6 sample Soxtec HT extraction system (Tecator, Sweden). Dichloromethane (methylene chloride) was used as the extraction solvent (70 ml/sample). Sample thimbles were extracted in

boiling solvent for 1 hour, rinsed for 1 hour, and the extracts dried on the Soxtec under a stream of nitrogen. Dry extracts were removed to cool in a desiccator prior to weighing. A second set of clean previously weighed Soxtec extraction cups was filled with 70 ml of fresh dichloromethane and the same sample was extracted again following the protocol used for the first extraction. Following extraction, cups were weighed to measure the amount of extractables. The combined extracts were transferred to an already-weighed sample vial (20 ml) using hot dichloromethane and the solvent was evaporated with low heat under a flow of nitrogen. Samples in vials were freeze-dried overnight and weighed the following day. Weighed samples were capped under nitrogen and frozen until analysis.

2.3 Extraction - Liquid Samples

Samples were extracted with petroleum ether using a modification of the Saltsman Extraction (Saltsman and Kuiken, 1959). In a 1000 ml separatory funnel, 100 ml of sample and 100 ml of acetone were combined with 25 ml of methanol and 80 ml of petroleum ether. The mixture was agitated for 10 minutes and allowed to separate. The sample-acetone-methanol-washing-water layer was removed and the remaining petroleum ether layer was washed twice with 15 ml of washing water (mixture of acetone, methanol, and distilled water in a ratio of 2:1:1). The washing water was combined with the original sample-acetone-methanol layer while the petroleum ether-extracted sample was set aside for evaporation. The sample-acetone-methanol-washing-water layer was extracted again with 80 ml of fresh petroleum ether. The two petroleum ether layers were

combined and the solvent reduced on a rotary evaporator. The extracts were transferred, with a small amount of solvent, to an already-weighed 40 ml glass vial. The solvent was removed with low heat under a flow of nitrogen. Extracts were freeze-dried overnight, weighed the following day, capped under nitrogen, and frozen until analysis.

2.4 Data Analysis - Solid and Liquid Extractions

Results of the extractions were reported as percentage of dichloromethane extractives. This percentage was calculated by comparing the combined dry weight of the extractives in both Soxtec cups with the dry weight of the sample in the thimble. Dry weights of extracts in the 20 ml sample vials were also determined and used in calculations for gas chromatography analysis.

2.5 Gas Chromatography Analysis

2.5.1 Sample Preparation and Methylation

Dried extracts in 20 ml vials (mill sample and wood core extracts) and 40 ml vials (liquid sample extracts) were dissolved either with 5000 μl of solvent (4500 μl methyl tert-butyl-ether (MTBE) and 500 μl methanol) for mill samples or 1250 μl of solvent (1130 μl MTBE and 120 μl methanol) for wood core and liquid samples. A 1000 μl sample was removed from the extractive solution and placed into a 2 ml GC autosampler vial and evaporated under nitrogen. The dried sample was then dissolved either with 1000 μl of MTBE containing 250 ppm of lauric acid and 250 ppm of cholesterol (mill samples) or 1000 μl of MTBE containing 125 ppm of lauric acid and 125 ppm of cholesterol (wood core and liquid samples) . Samples were then methylated with

diazomethane using an apparatus and chemical mixture similar to that used by Levitt (1973). Methylated samples were again dried under nitrogen and dissolved either with 250 μl of chloroform (mill samples) or 125 μl of chloroform (wood core and liquid samples). A 100 μl sample was removed from the methylated extracts and placed in a 2 ml GC autosampler vial containing a 250 μl glass insert and capped. Processed samples were stored in a refrigerator until analysis.

2.5.2 Gas Chromatograph Configuration

Samples (1.0 μl) were analyzed on a Hewlett Packard 5890 Series II Plus gas chromatograph equipped with a HP 7673A autosampler and a flame ionization detector (FID). A DB-5ht column ((5% Phenyl) Methylpolysiloxane, 30 m x 0.32 mm I.D., 0.1 μm film, J&W Scientific) was used for sample analysis. An injector temperature of 360°C and a detector temperature of 390°C was used along with an oven temperature program starting at 100°C for 5 minutes. The oven was then heated to 200°C at 10°C/min., held for 3 min., then to 245°C at 2°C min., and then to 390°C at 10°C/min. and held for 7 minutes (total run = 62 min.). The carrier gas was helium at 1.0 ml/min and the split ratio was 50:1.

2.5.3 Analysis of Gas Chromatography Results

Analysis was based on the peak height measurement of 24 different compounds and the use of two internal standards (lauric acid and cholesterol). Internal standard reports were created using Hewlett Packard's GC support software - HP ChemStation. Prior to analysis, individual responses for each of the 24 compounds and 2 standards were

calculated at the 250 ppm, 500 ppm, and 1000 ppm levels and entered into the HP ChemStation software for use in the generation of internal standard reports. Internal standards were used by the software as references for the adjustment of retention time drift and response quantitation. The 24 compounds (structures in Appendix A) were grouped into 4 categories: fatty acids (palmitic acid, heptadecanoic acid, linoleic acid, linolenic acid, stearic acid, tricosanoic acid), resin acids (pimaric acid, levopimaric acid, palustric acid, dehydroabietic acid, abietic acid, neoabietic acid), alcohols sterols and waxes (ASW) (manool, behenyl alcohol, stigmasterol, stearic acid steryl ester), and esterified fatty acids (EFA) (monopalmitin, monostearin, 1,3-dipalmitin, 1,3-distearin, tricaprin, tripalmitin, triolein, tristearin). Concentrations (in ppm) for each of the 24 compounds were sorted accordingly and summed to produce a group concentration (fatty acids, resin acids, ASW, and EFA). Each group concentration was then converted to its weight in milligrams based on the sample in the 20 ml vial. This was achieved by dividing the group concentration by either 4 (mill samples) or 8 (wood core samples) to produce a concentration based on a 1 ml dilution (vs. 250 μl - mill samples or 125 μl - wood cores and liquid samples). This number was then converted to milligrams (divide by 1000) multiplied by either 5 (mill samples) or 1.25 (wood cores and liquid samples) to give the weight of each group present in the original 20 ml or 40 ml vial respectively. This amount was expressed as a percentage of the total extractives in the 20 ml vial as well as the number of milligrams it represented per gram of dry extracted sample (wood chips, pulps, paper, wood cores). The percentage each group represented based on the

total weight of all 24 compounds was also calculated. All calculations were made using the spreadsheet MS Excel 97 and graphs were produced using SigmaPlot 5.0.

Table 2.1 Summary of harvest dates and grouping for black spruce and balsam fir wood yard samples.

Month Sampled	Number of Wood Cores*	Date Harvested	Sample
November 1995	12	mid-October 1995	Yard Sample #1
December 1995	12		
January 1996	12		
February 1996	12		
March 1996	12	mid-March 1996	Yard Sample #2
April 1996	12		
May 1996	24	mid-March 1996 & mid-May 1996	
June 1996	24		
August 1996	24		
September 1996	12	mid-May 1996	Yard Sample #3
October 1996	12		

*12 wood cores = 6 black spruce and 6 balsam fir
24 wood cores = 12 black spruce and 12 balsam fir total

3 Results

3.0 Overview

For the purposes of this thesis, results of the sample analysis will be presented in a sequence which follows the conditions in living trees through to the changes that occur following harvest (yard samples) and then to the conditions at 6 different stages in the papermaking process at the mill. Results will first be discussed on the basis of total extractives (sapwood then heartwood - where applicable) and secondly on the basis of the composition of those extractives (sapwood then heartwood - where applicable). The chapter will be concluded with a presentation of balsam fir and black spruce and their associated mill samples.

3.1 Wood Cores - Total Extractives

3.1.1 Forest Fir

With the exception of April, there were only small differences in the monthly total sapwood extractives (Fig. 3.1).

The heartwood extractives in general were the same or greater in concentration than the sapwood extractives for the forest fir wood cores (Fig. 3.1). The heartwood portion of the forest fir sample showed an elevated level of extractives for December, May, and August (Fig. 3.1).

3.1.2 Yard Fir #1

There were no changes in the sapwood and heartwood total extracts for the yard fir #1 sample (Fig. 3.2). As seen in the forest fir sample, total extractives for heartwood

increased slightly for December but otherwise remained at roughly the same level (Fig. 3.1). The yard fir #1 profile resembled the Forest Fir profile from November to February (Figs. 3.1 and 3.2).

3.1.3 Yard Fir #2

Unlike the yard fir #1 sample, the yard fir #2 sample did not follow the trends observed for the forest fir sample (Fig. 3.3). Overall, there were no trends for the total extractives in the yard fir #2 sample. The sample variability was as large as the differences between the individual months (Fig. 3.3).

3.1.4 Yard Fir #3

Sapwood concentrations for the yard fir #3 sample showed a decreasing profile similar to the profile seen in the forest fir sample for May and June (Figs. 3.1 and 3.4). While sapwood concentrations were relatively constant in the forest fir profile, they were decreasing in the yard fir #3 sapwood sample between August and October (Figs. 3.1 and 3.4).

The increased concentration of heartwood total extractives seen for May and August in the forest sample were not seen in the yard fir #3 sample. Yard Fir #3 heartwood total extractives did not show any trends for May through October (Fig. 3.4).

3.1.5 Forest Spruce

The forest spruce sapwood extractive concentrations were found to be constant during the sampling period (Fig. 3.5). When the within sample variability was considered for the forest spruce heartwood profile there was very little seasonal variation in the

heartwood extractive concentrations (Fig 3.5).

3.1.6 Yard Spruce #1

There was no variation in the yard spruce #1 extractive concentrations between November and February for either the sapwood or heartwood total extractive profile (Fig. 3.6).

3.1.7 Yard Spruce #2

The yard spruce #2 sample showed very little change in wood core total extractive concentrations (Fig. 3.7). When the large within sample variability was taken into account for the May sapwood sample, it was not different from concentrations observed in the other months of the yard spruce #2 wood cores (Fig. 3.7). The yard spruce #2 profile was similar was similar to the profile seen for the forest spruce sample for the same sampling period (Figs. 3.5 and 3.7).

3.1.8 Yard Spruce #3

The yard spruce #3 sapwood concentrations were lower between August and October when compared to the forest spruce sample for the same time period (Figs. 3.5 and 3.8). The forest spruce sapwood total extractive concentrations remained relatively constant for the sampling period between August and October (Fig. 3.5). There was no difference in the heartwood total extractive concentrations between May and October for the yard spruce #3 samples (Fig. 3.8). This was similar to the trend observed for the total heartwood extractives in the forest spruce sample (Fig. 3.5).

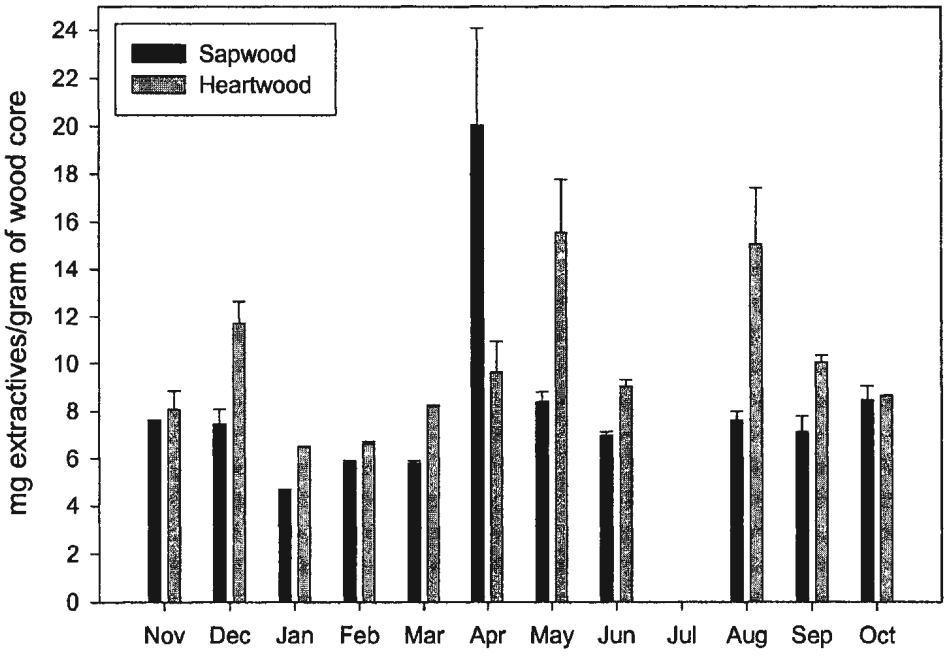


Figure 3.1. Total sapwood and heartwood dichloromethane extracts for forest fir wood cores collected monthly between November 1995 and October 1996. (Error bars represent the standard error of the mean and were calculated based on 2 extractions from a pooled sample of sapwood or heartwood wood core portions.)

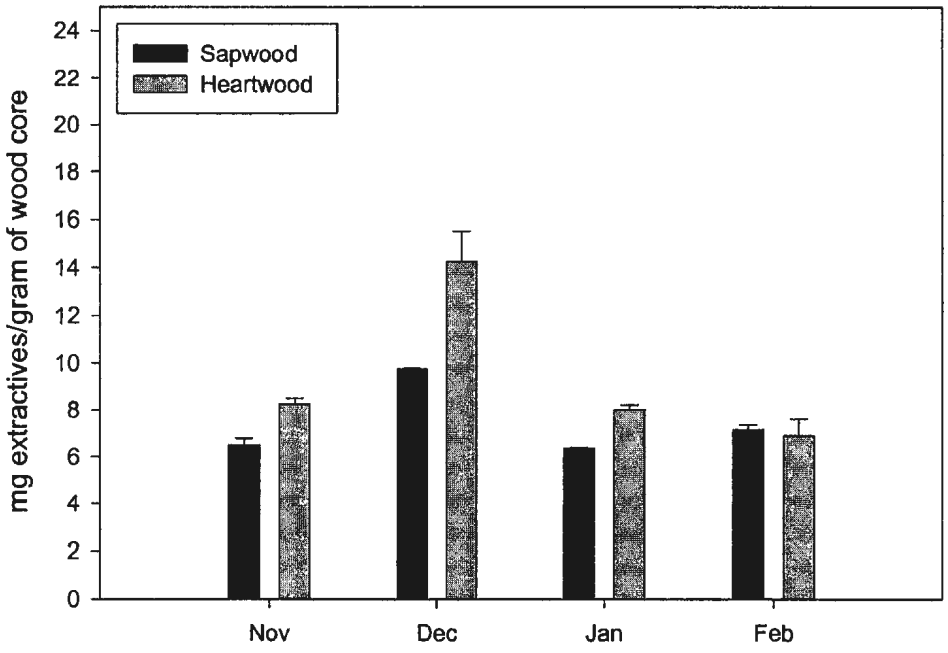


Figure 3.2. Total sapwood and heartwood dichloromethane extracts for yard fir #1 wood cores collected monthly between November 1995 and February 1996. (Error bars represent the standard error of the mean and were calculated based on 2 extractions from a pooled sample of sapwood or heartwood wood core portions.)

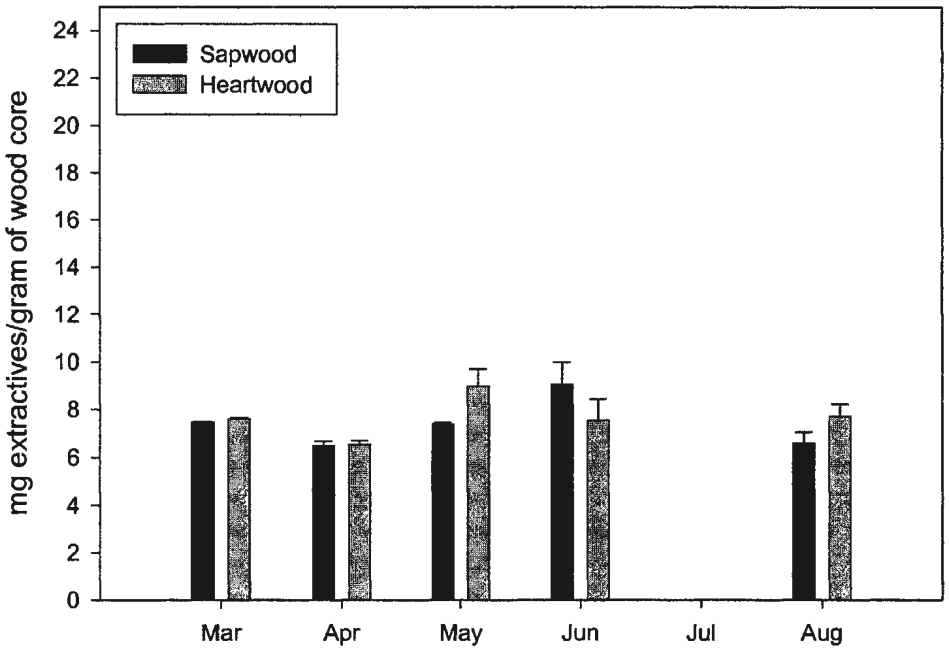


Figure 3.3. Total sapwood and heartwood dichloromethane extracts for yard fir #2 wood cores collected monthly between March 1996 and August 1996. (Error bars represent the standard error of the mean and were calculated based on 2 extractions from a pooled sample of sapwood or heartwood wood core portions.)

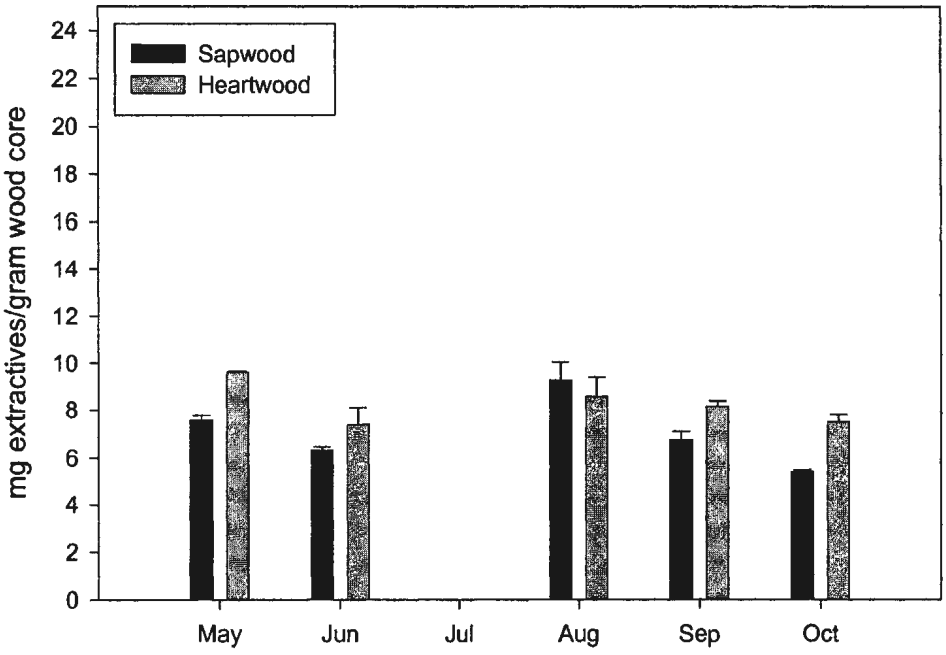


Figure 3.4. Total sapwood and heartwood dichloromethane extracts for yard fir #3 wood cores collected monthly between May 1996 and October 1996. (Error bars represent the standard error of the mean and were calculated based on 2 extractions from a pooled sample of sapwood or heartwood wood core portions.)

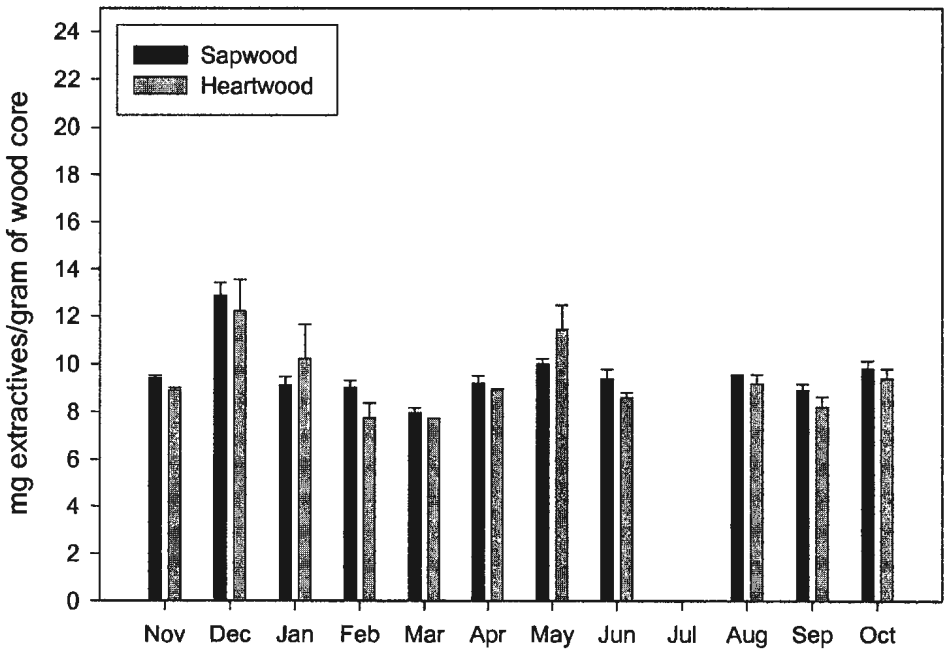


Figure 3.5. Total sapwood and heartwood dichloromethane extracts for forest spruce wood cores collected monthly between November 1995 and October 1996. (Error bars represent the standard error of the mean and were calculated based on 2 extractions from a pooled sample of sapwood or heartwood wood core portions.)

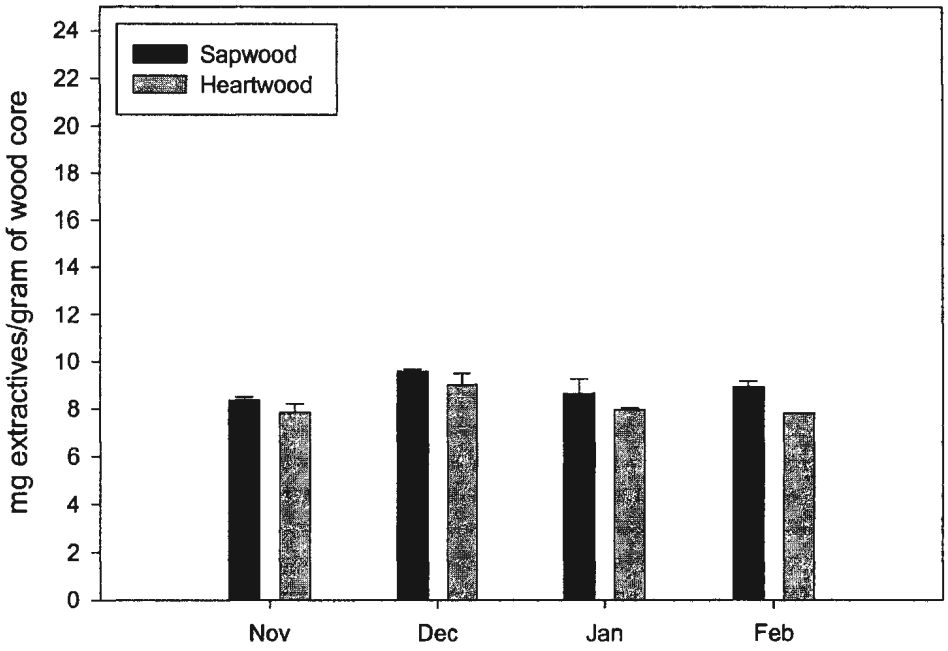


Figure 3.6. Total sapwood and heartwood dichloromethane extracts for yard spruce #1 wood cores collected monthly between November 1995 and February 1996. (Error bars represent the standard error of the mean and were calculated based on 2 extractions from a pooled sample of sapwood or heartwood wood core portions.)

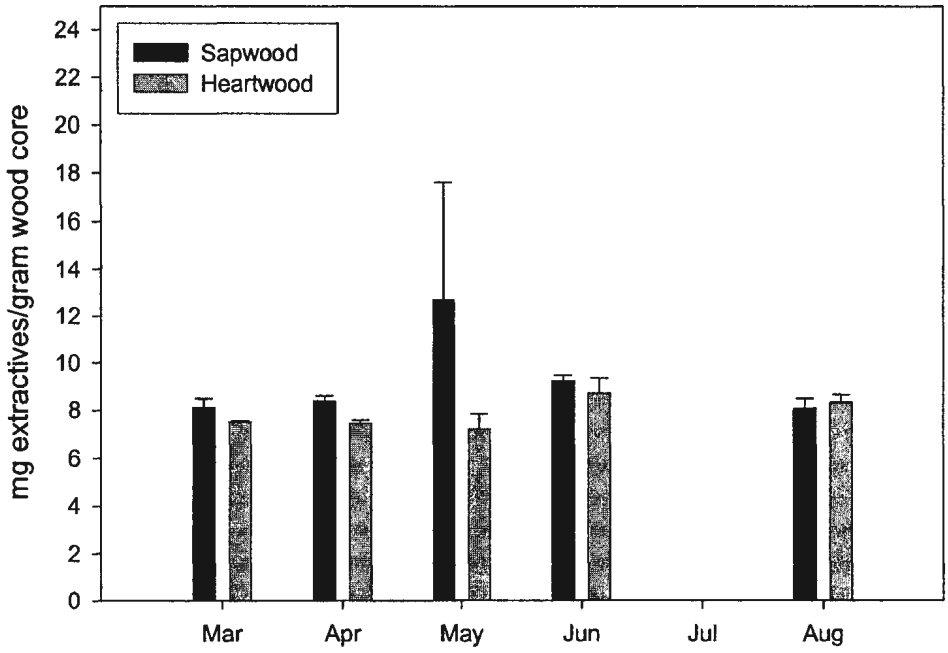


Figure 3.7. Total sapwood and heartwood dichloromethane extracts for yard spruce #2 wood cores collected monthly between March 1996 and August 1996. (Error bars represent the standard error of the mean and were calculated based on 2 extractions from a pooled sample of sapwood or heartwood wood core portions.)

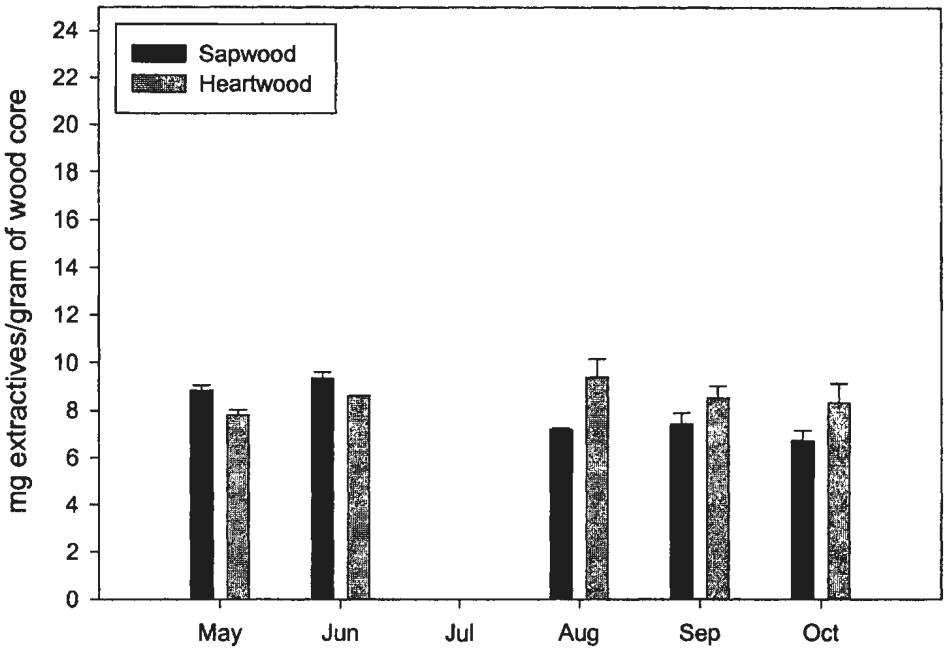


Figure 3.8. Total sapwood and heartwood dichloromethane extracts for yard spruce #3 wood cores collected monthly between May 1996 and October 1996. (Error bars represent the standard error of the mean and were calculated based on 2 extractions from a pooled sample of sapwood or heartwood wood core portions.)

3.2 Mill Samples - Total Extractives

3.2.1 Wood Chips

When the total extractive data for the wood chip samples were considered, there were no consistent overall trends. However, there were some smaller trends during the season. Total extractive levels were relatively constant during November and December (Fig. 3.9). This was followed by a general increasing trend from January to May. Extractive levels fell sharply in June and then began an increase/decrease trend between June and October which peaked in August (Fig 3.9).

3.2.2 Primary Refiner

Primary refiner total extractives showed little variation over the sampling period. There were no differences in extractive levels between November and October (Fig. 3.10).

3.2.3 Secondary Refiner

The was very little variation in the secondary refiner total extractive profile throughout the sampling period (Figs. 3.11). By comparison the total extractive levels in the primary refiner samples and secondary refiner samples were roughly the same in concentration (Figs. 3.10 and 3.11).

3.2.4 Screen Accepts - Pulp

The screen accepts pulp samples showed only small changes in concentration between November and May (Fig. 3.12). Following December, screen accepts pulp extractive levels fluctuated slightly between January and May. Total extractive levels

began to decrease steadily between June and October (Fig. 3.12).

3.2.5 Screen Accepts - Liquid

The total extractive data for the screen accepts liquid sample was much more variable than the screen accepts pulp sample (Figs. 3.12 and 3.13). The pH values for the screen accepts liquid sample also did not show any seasonal trends (Table 3.1). There was no relationship between extractive levels and pH (Fig. 3.13 and Table 3.1).

3.2.6 Paper

The total extractives levels in the paper samples were in general lower than the total extractives levels observed for the wood chip and pulp samples (Figs 3.9-3.12 and 3.14). The paper sample did not show any obvious seasonal trends and only small month-to-month variations (Fig 3.14).

3.2.7 Paper Machine White Water

The extraction of the paper machine white water samples gave a total extractive profile with considerable variability (Fig. 3.15). There appeared to be an obvious decrease/increase trend between March and October for the paper machine white water total extractives (Fig. 3.15). However, large within sample variability limited the conclusions which could be made from the monthly samples. When the months which showed lower or higher levels of white water extractives were compared to the pH data in Table 3.1, there were no correlations between pH and concentration of extractives (Fig. 3.15). The white water pH data itself also did not show any seasonal trends (Table 3.1). In general, the total petroleum ether extractives for the white water were lower in

concentration than the petroleum ether extractives for the screen accepts sample (Figs. 3.13 and 3.15). There was also no correlation between the monthly pH values for the screen accepts and the monthly pH values for the white water (correlation value = 0.12).

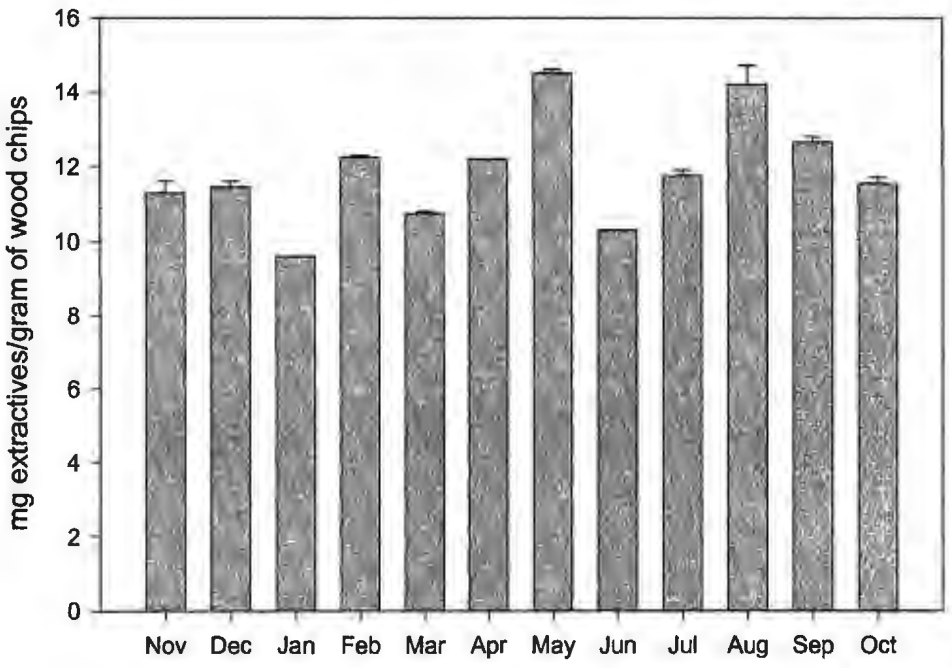


Figure 3.9. Total dichloromethane extractives per gram of dry wood for wood chip samples collected monthly between November 1995 and October 1996 from wood chip bin #4 at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated from the duplicate analysis of a single sample of wood chips.)

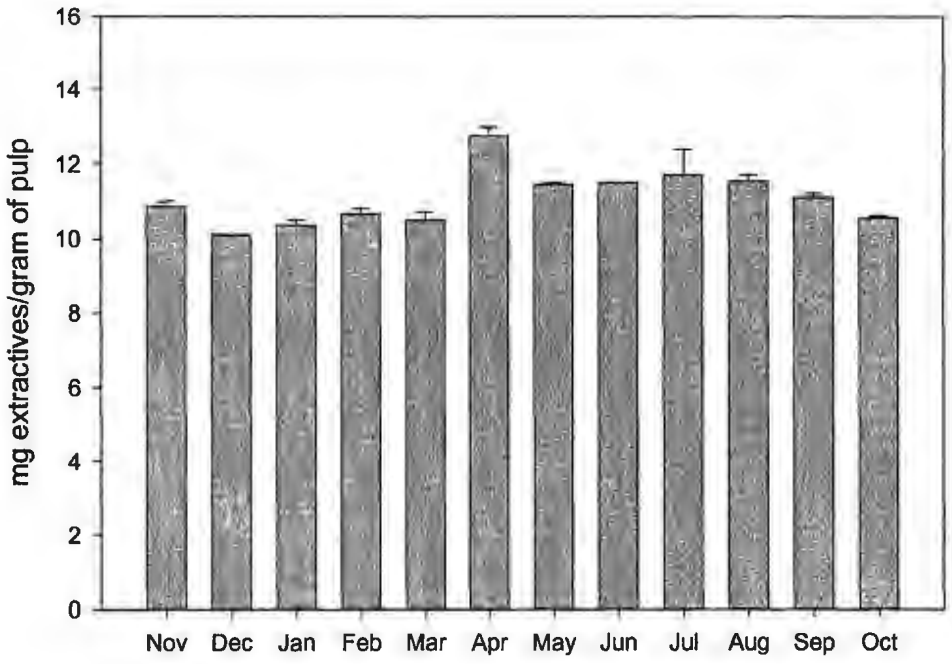


Figure 3.10. Total dichloromethane extractives per gram of dry pulp for samples collected monthly between November 1995 and October 1996 from primary refiner #4 blow line at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated from the duplicate analysis of a single sample of pulp.)

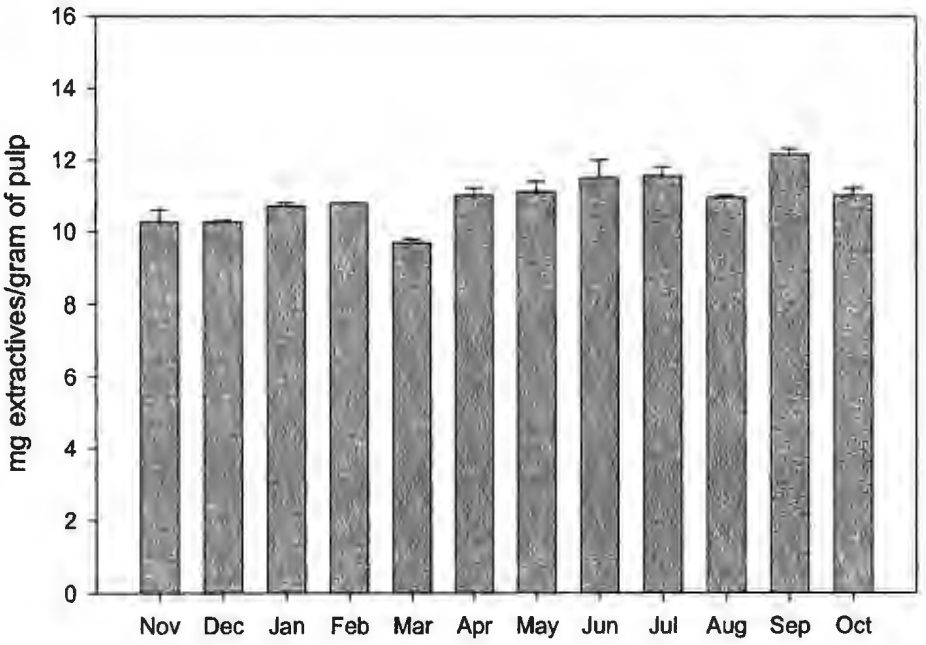


Figure 3.11. Total dichloromethane extractives per gram of dry pulp for samples collected monthly between November 1995 and October 1996 from secondary refiner #4 blow line at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated from the duplicate analysis of a single sample of pulp.)

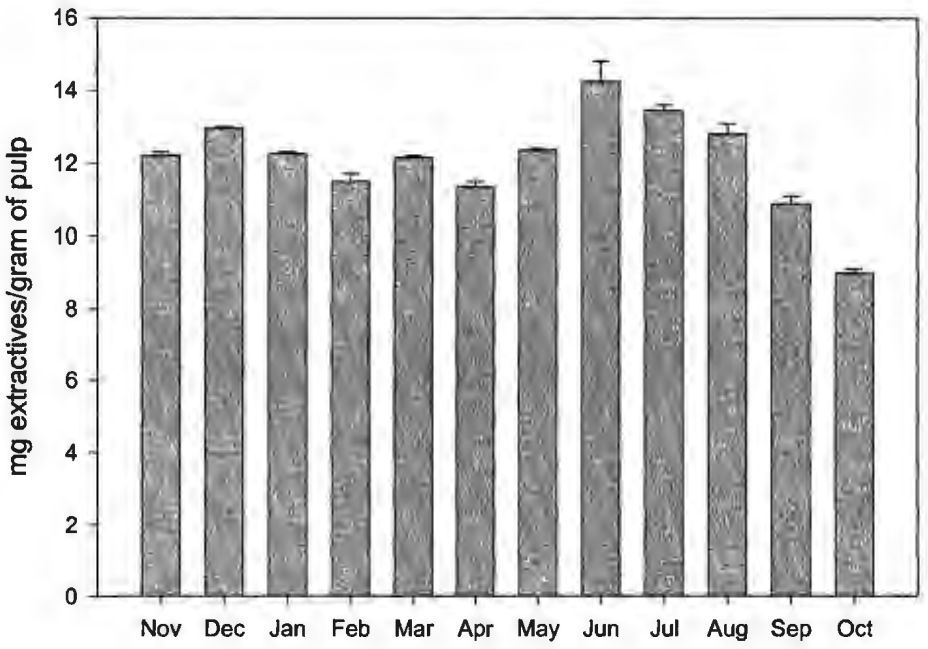


Figure 3.12. Total dichloromethane extractives per gram of dry pulp for screen accepts (pulp portion) samples collected monthly between November 1995 and October 1996 from screen accepts #4 line at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated from the duplicate analysis of a single sample of pulp.)

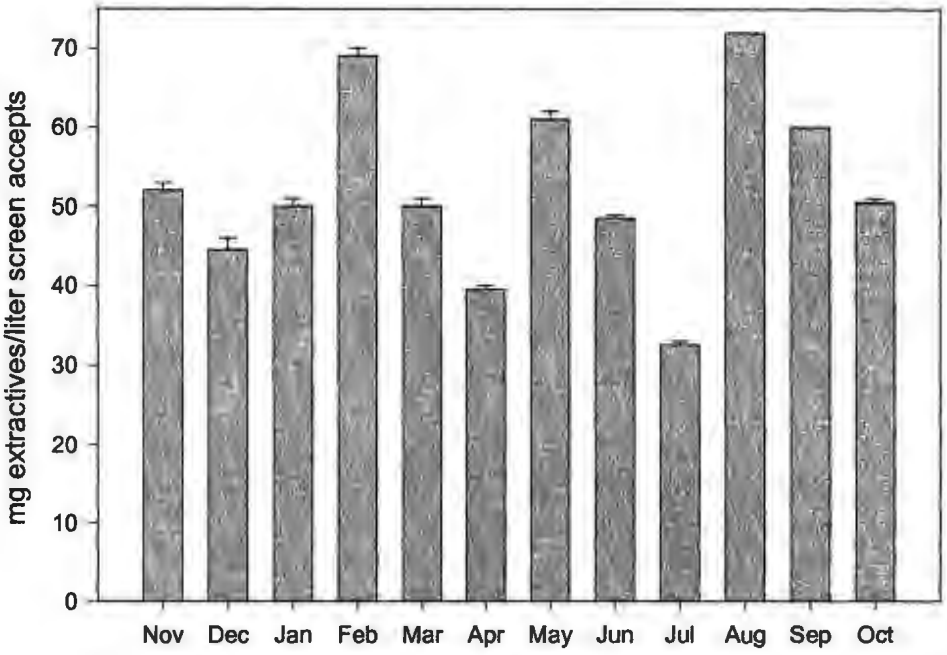


Figure 3.13. Total petroleum ether extractives per liter of screen accepts (liquid portion) samples collected monthly between November 1995 and October 1996 from screen accepts #4 line at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated from the duplicate analysis of a single sample of liquid.)

Table 3.1. pH values for the liquid portions of the #4 line screen accepts and #7 paper machine white water samples collected monthly between November 1995 and October 1996.

Month	Screen Accepts pH	White Water pH
November 1995	4.59	6.32
December 1995	4.70	5.76
January 1996	4.66	8.94
February 1996	4.53	9.09
March 1996	4.64	6.45
April 1996	4.58	6.68
May 1996	4.85	6.66
June 1996	5.07	7.30
July 1996	4.50	4.68
August 1996	4.58	5.73
September 1996	4.69	5.76
October 1996	4.82	6.53

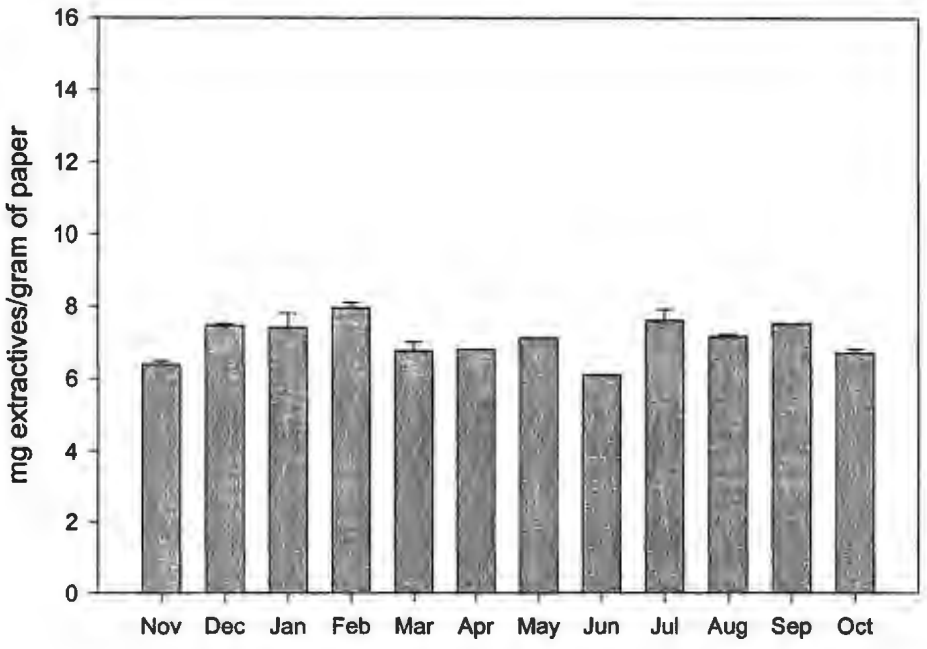


Figure 3.14. Total dichloromethane extractives per gram of dry paper for finished paper machine samples collected monthly between November 1995 and October 1996 from paper machine #7 at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated from the duplicate analysis of a single sample of paper.)

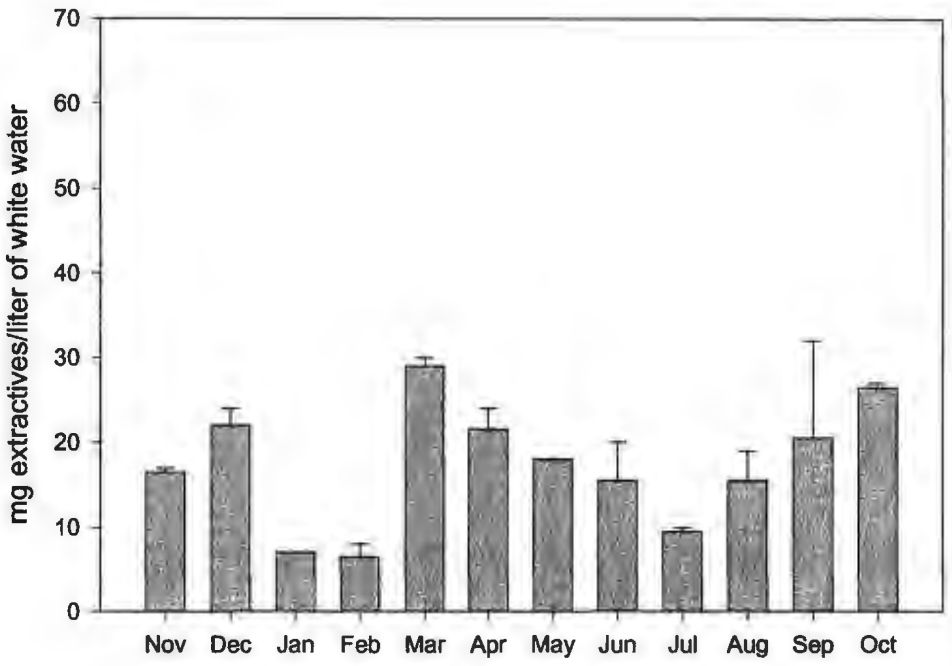


Figure 3.15. Total petroleum ether extractives per liter of white water (liquid portion) samples collected monthly between November 1995 and October 1996 from paper machine #7 wire pit at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated from the duplicate analysis of a single sample of liquid.)

3.3 Wood Cores - GC Analysis

3.3.1 Sapwood GC Analysis

3.3.1.1 Forest Fir Sapwood

When within sample variability was considered, it was difficult to show any differences in fatty acid concentrations from November to October in the forest fir sapwood sample (Fig. 3.16). However, slightly higher concentrations in fatty acid levels were observed for May and August.

The first noticeable point when considering the resin acid extractive composition of sapwood in living fir trees was the high concentration in resin acids for April (Fig. 3.16). On a seasonal basis, the lowest levels for resin acids were observed in the winter months of January, February, and March (Fig 3.16).

When the ASW group was considered, there was very little variation in concentration from November to October (Fig. 3.16).

When within sample variability was considered, there were only slight differences in EFA levels from November to May. For the observed sampling period, EFA levels were found to be at their highest levels between June and October (Fig. 3.16).

3.3.1.2 Yard Fir #1 Sapwood

When the yard fir #1 samples were compared in general to the living tree profile for the same sampling period, differences were seen for the resin acid group in November and December yard samples (Figs. 3.16 and 3.17).

Fatty acid levels, ASW levels, and EFA levels in the yard fir #1 samples remained constant and similar to the forest sample.

3.3.1.3 Yard Fir #2 Sapwood

When compared to the sapwood forest fir sample for the same sampling period, the yard fir #2 samples did not show a large peak in resin acid levels for April (Figs. 3.16 and 3.18).

Within the yard fir #2 sample, there was very little change in fatty acid levels from March to August. Resin acids also showed very little change over the sampling period when the sample variability was considered (Fig 3.18). The ASW group showed trends similar to those seen for the fatty acids with ASW concentrations only showing small changes during the sampling period (Fig. 3.18). EFA levels, in contrast, were higher in June and August when compared to levels observed for March, April, and May (Fig. 3.18). The increase in EFA levels observed for August in the forest fir sample was not seen in the yard fir #2 sample (Figs. 3.16 and 3.18).

3.3.1.4 Yard Fir #3 Sapwood

Overall, fatty acid concentrations seen for the yard fir #3 sample were relatively constant throughout the sampling period and similar to the forest fir sample (Figs. 3.16 and 3.19). The resin acid profile for the yard fir #3 sample decreased from May to October. The elevated levels observed for August and October in the forest fir sample were not observed in the yard fir #3 sample (Figs. 3.16 and 3.19).

The ASW levels showed little variation throughout the sampling period from May

to October (Fig 3.19).

In general, the EFA fraction represented the greatest proportion of both the forest fir and yard fir #3 sample for June to October (Figs. 3.16 and 3.19). However when the sample variability of the yard fir #3 sample was considered, there were only slight differences in EFA levels for the entire sampling period.

3.3.1.5 Forest Spruce Sapwood

The first noticeable trend seen in the forest spruce sapwood profile was the dominance of the resin acid component of the fraction. The resin acid component was found to represent the largest portion of the total extractives (Fig. 3.20). When compared to the forest fir sapwood sample, the overall forest spruce fatty acid profile was lower in concentration (Figs. 3.16 and 3.20).

Within the forest spruce sample, fatty acids were at low levels and showed no change during the months sampled (Fig. 3.20).

The resin acid group had considerable within sample variability on a monthly basis (Fig. 3.20). There were no obvious seasonal trends between November and October.

The ASW group showed very little variability throughout the sampling period and no obvious seasonal trends were observed for the forest spruce sapwood sample (Fig. 3.20).

The EFA group showed very little change between November and May (Fig. 3.20). Following May, forest spruce EFA levels increased sharply in June, before reaching seasonal high levels in August. After August, EFA levels decreased towards October.

3.3.1.6 Yard Spruce #1 Sapwood

There was little difference in the levels or distribution of any of the extractive groups in the yard spruce #1 sapwood sample (Fig. 3.21). When compared to the forest sample, the fatty acid and resin acid components were lower in concentration for the yard spruce #1 sapwood sample (Figs. 3.20 and 3.21).

3.3.1.7 Yard Spruce #2 Sapwood

The yard spruce #2 sapwood sample showed a fatty acid trend similar to the forest spruce sapwood sample from March to August (Figs. 3.20 and 3.22). The variability of the monthly samples resulted in a resin acid profile which did not exhibit any trends for the sampling period (Fig. 3.22). Similarly, ASW levels were found to remain roughly constant throughout the sampling period (Fig. 3.22). The considerable increase in EFA levels seen for June in the forest sample was also seen for the month of June in the yard samples (Figs. 3.20 and 3.22).

3.3.1.8 Yard Spruce #3 Sapwood

The yard spruce #3 sapwood profile was similar to the forest sample for the same time period (Figs. 3.20 and 3.23). The elevated fatty acids levels observed for August in the forest spruce sample were not seen in the yard sample until September (Figs. 3.20 and 3.23).

The yard spruce #3 fatty acid and resin acid profile were similar to the forest spruce sapwood profile (Figs. 3.20 and 3.23). The ASW group was found to show very little variation throughout the sampling period (Fig. 3.23). EFA levels in the yard spruce #3 sample also showed the sharp jump in levels between May and June which was observed for the forest spruce sapwood sample (Figs. 3.20 and 3.23).

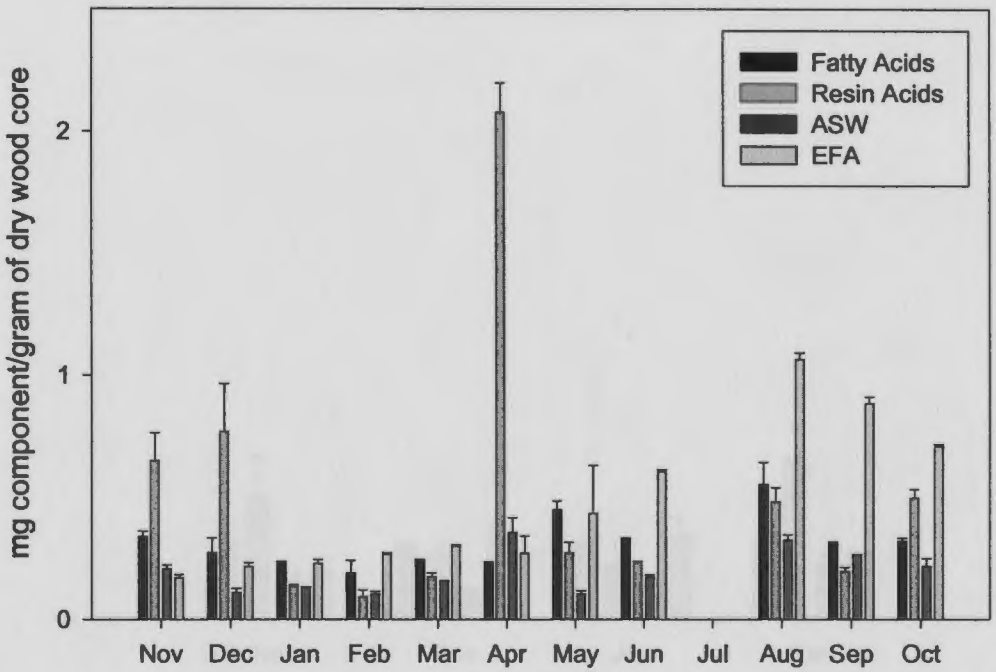


Figure 3.16. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for forest fir sapwood samples collected between November 1995 and October 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of sapwood wood core portions for each month.)

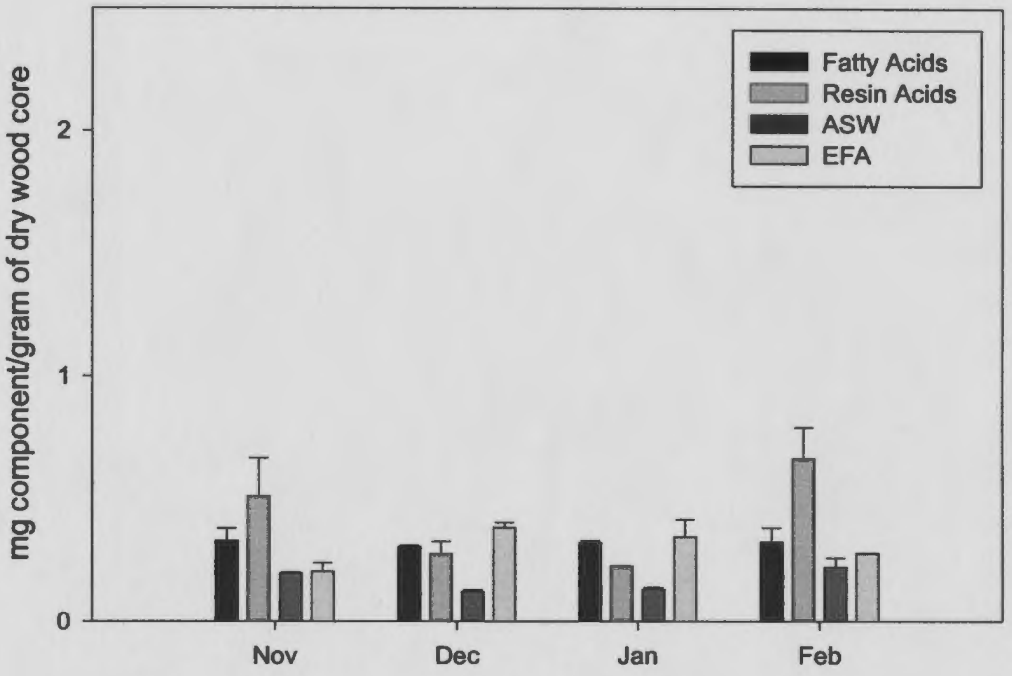


Figure 3.17. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard fir #1 sapwood samples collected between November 1995 and February 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of sapwood wood core portions for each month.)

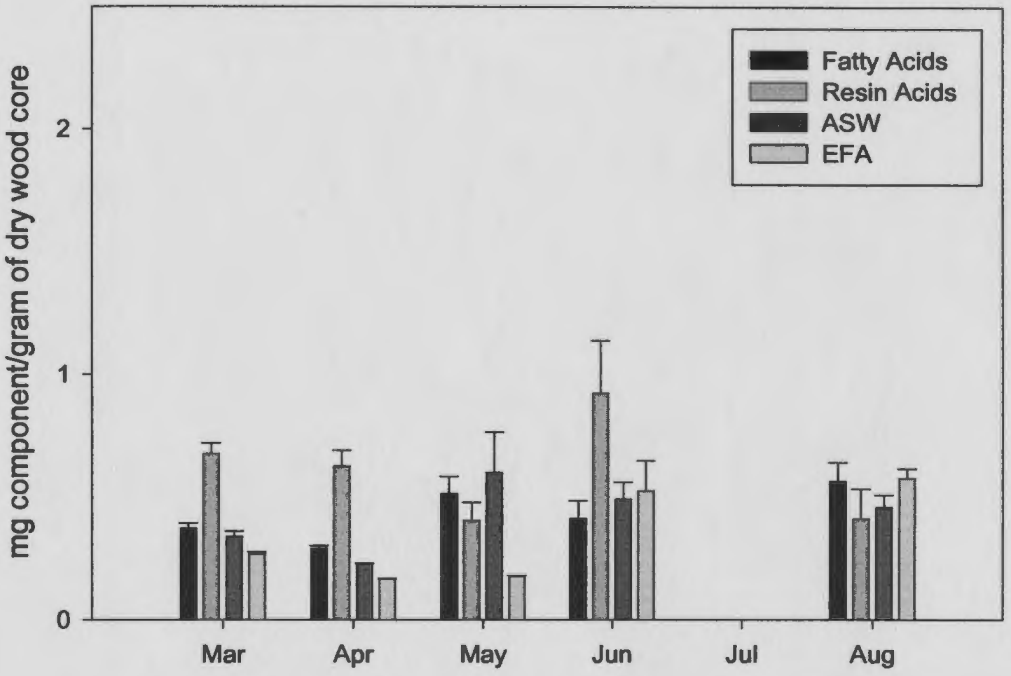


Figure 3.18. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard fir #2 sapwood samples collected between March 1996 and August 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of sapwood wood core portions for each month.)

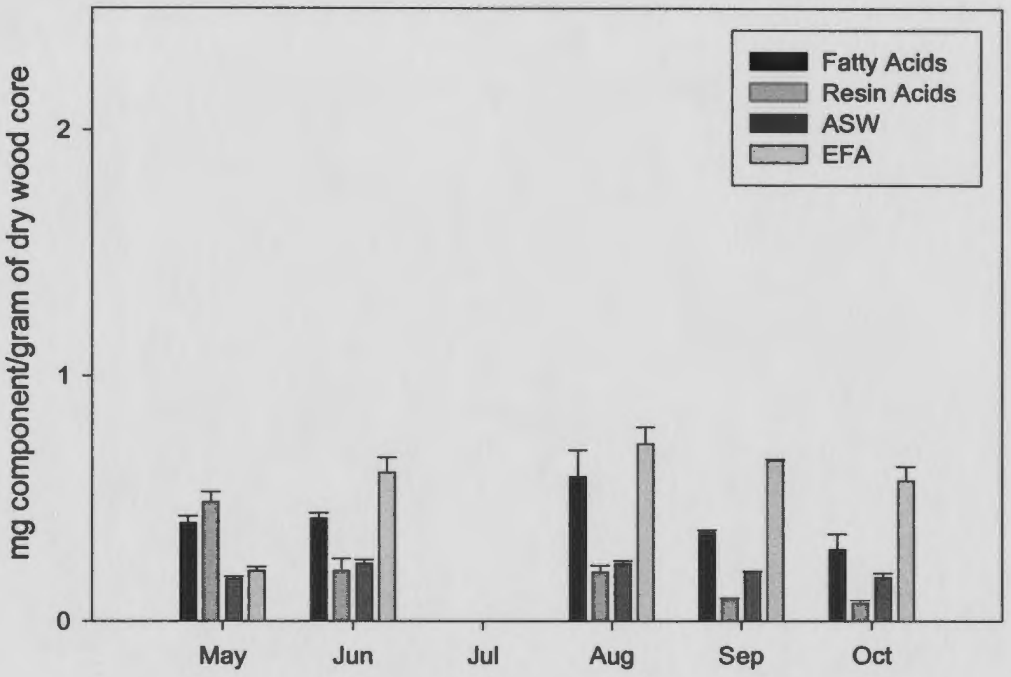


Figure 3.19. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard fir #3 sapwood samples collected between May 1996 and October 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of sapwood wood core portions for each month.)

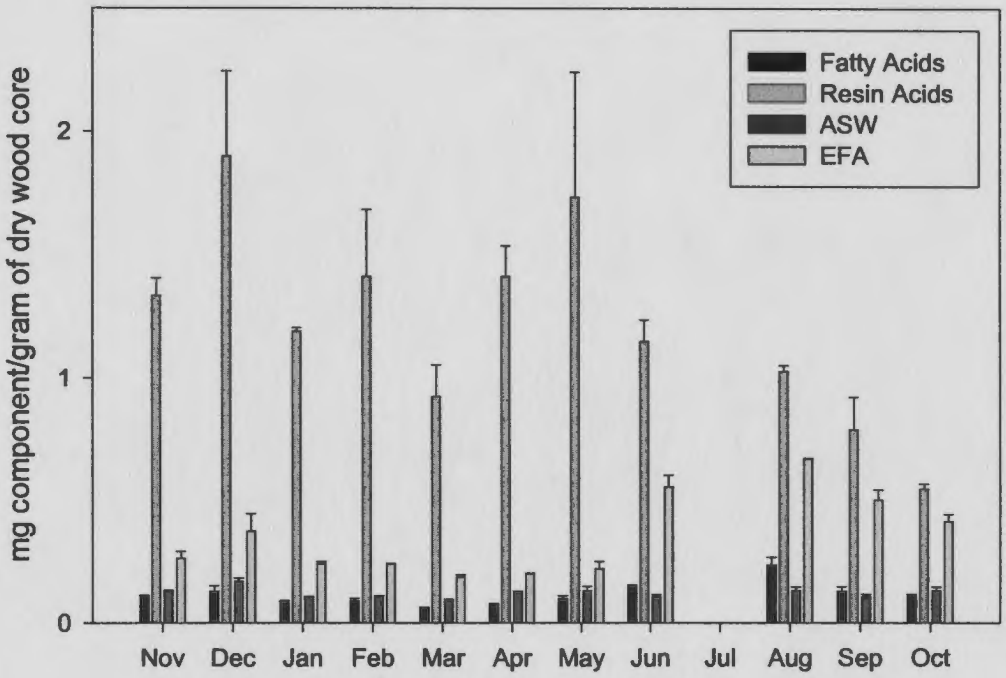


Figure 3.20. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for forest spruce sapwood samples collected between November 1995 and October 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of sapwood wood core portions for each month.)

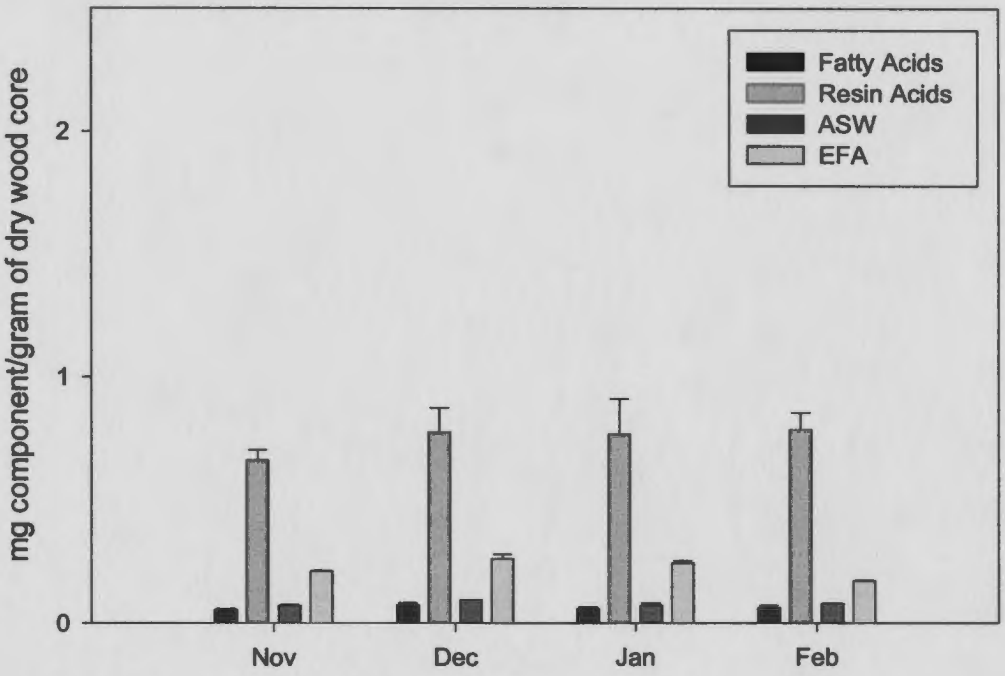


Figure 3.21. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard spruce #1 sapwood samples collected between November 1995 and February 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of sapwood wood core portions for each month.)

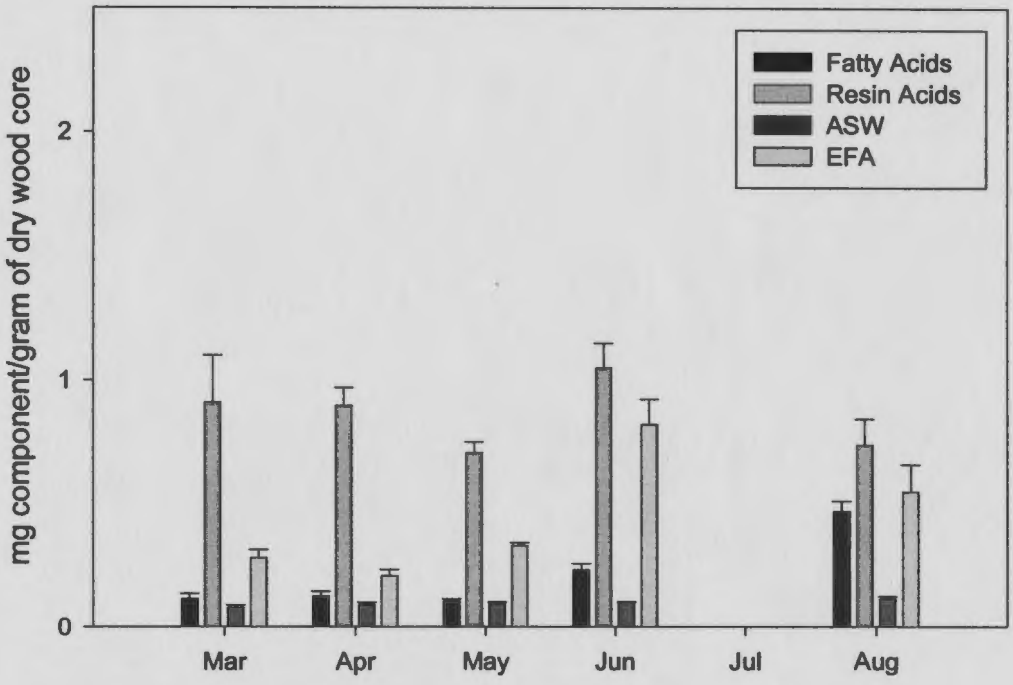


Figure 3.22. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard spruce #2 sapwood samples collected between March 1996 and August 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of sapwood wood core portions for each month.)

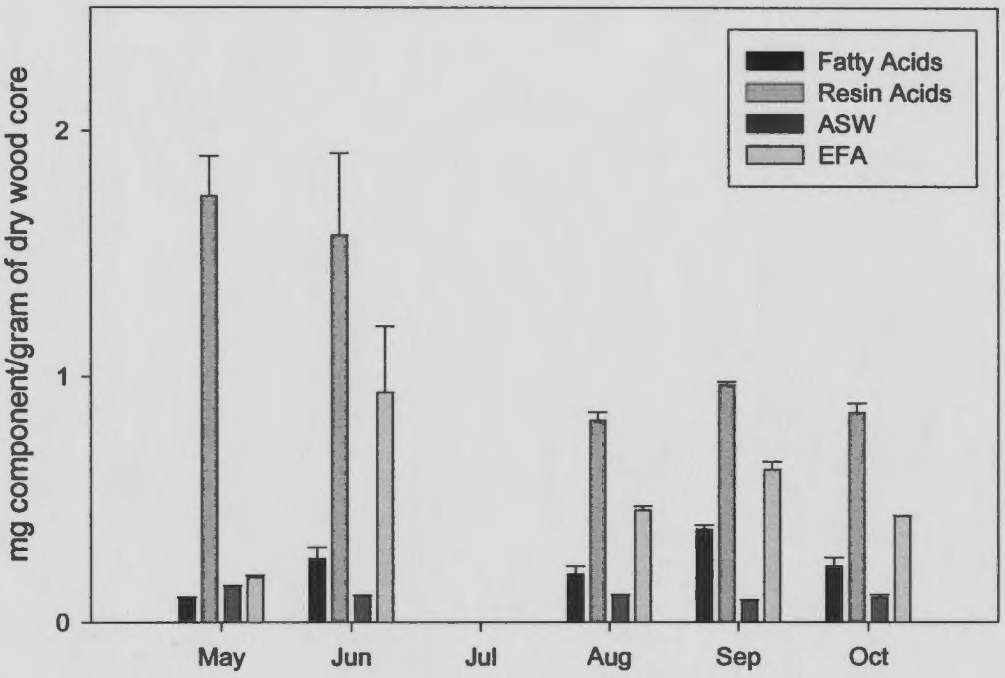


Figure 3.23. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard spruce #3 sapwood samples collected between May 1996 and October 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of sapwood wood core portions for each month.)

3.3.2 Heartwood GC Analysis

3.3.2.1 Forest Fir Heartwood

In general the observed fatty acid fraction of the forest fir extracts was shown to be the most dominant component while the resin acid component was found to be the least dominant component (Fig. 3.24). Fatty acids were at their highest levels in November, December, and May (Fig. 3.24). In contrast, resin acid levels were low for most of the sampling period with the exception of a sharp increase for April (Fig. 3.24). The ASW fraction was at higher levels than those observed in the sapwood but showed no seasonal trends during the period sampled (Figs 3.16 and 3.24). The EFA fraction was relatively constant with slightly elevated levels in March and September (Fig. 3.24).

3.3.2.2 Yard Fir #1 Heartwood

The overall profile of the yard fir #1 heartwood sample was found to resemble those trends seen in the forest fir heartwood for the same time period (Fig. 3.25). Within the yard fir heartwood sample, fatty acid levels were higher in December to February when compared to December to February of the forest fir heartwood (Figs. 3.24 and 3.25). Resin acid and EFA levels in the yard fir #1 sample showed very little variation throughout the sampling period (Fig. 3.25). ASW levels were found to decrease slightly from November and December to January and February (Fig. 3.25).

3.3.2.3 Yard Fir #2 Heartwood

With the exception of the March fatty acid levels, no differences could be seen between the yard fir #2 heartwood sample and the forest fir heartwood sample fatty acid

profiles (Figs. 3.24 and 3.26). Resin acid levels for the yard fir #2 heartwood sample showed no change between March and August (Fig. 3.26). The elevated levels of resin acids seen for April in the forest sample were not observed for the yard sample (Figs. 3.24 and 3.26). The ASW group did not show any obvious trends for the March to August sampling period and is roughly the same profile as the forest sample (Figs 3.24 and 3.26). The EFA trends were also similar to those seen in the forest sample with the only major difference being slightly lower levels of EFA when compared to the forest fir sample (Figs. 3.24 and 3.26).

3.3.2.4 Yard Fir #3 Heartwood

As seen in the yard fir #2 heartwood sample and the forest fir heartwood sample, May also showed elevated levels of fatty acids (Figs 3.24, 3.26 and 3.27). The yard fir #3 heartwood profile was also similar to the forest fir heartwood sample (Figs. 3.24 and 3.27). The resin acid profile closely resembled the heartwood forest fir sample for May and June but showed much lower levels for August and September with increased levels for October. The yard fir heartwood ASW profile showed a steady decrease in concentration from August through to October. This trend was less obvious in the forest sample when sample variability was considered (Fig. 3.24 and 3.27). The EFA fraction also resembled the forest sample profile for this same time period without any major seasonal trends (Figs. 3.24 and 3.27).

3.3.2.5 Forest Spruce Heartwood

In contrast to the forest fir heartwood samples where the fatty acid group was the dominant component, resin acids again were the dominant component in the forest spruce samples (Figs. 3.24 and 3.28). The fatty acid fraction of the forest spruce heartwood sample showed slightly higher levels in April, June, and August but these differences were small (Fig 3.28). Overall, there was very little difference in fatty acid levels observed between November and October (Fig. 3.28).

The resin acid fraction of the forest spruce heartwood showed elevated levels in December and October (Fig 3.28). However, once the variability of the sample was accounted for, there were no seasonal differences in resin acid concentrations

The ASW group was low in concentration and constant during the sampling period (Fig. 3.28). The EFA group also remained at roughly the same level throughout the sampling period.

3.3.2.6 Yard Spruce #1 Heartwood

With the exception of December resin acid levels, the yard spruce #1 heartwood sample followed a profile similar to that seen for the living trees in the forest spruce heartwood samples (Figs. 3.28 and 3.29). The extractive profile in general remained relatively constant throughout the sampling period (Fig. 3.29). As in the forest spruce samples, the resin acid component remains the dominant component for all months (Figs. 3.28 and 3.29).

3.3.2.7 Yard Spruce #2 Heartwood

The yard sample fatty acids were similar in concentration between March and June and consistent with fatty acid levels observed in the May forest spruce heartwood sample (Figs 3.28 and 3.30). The resin acid profile was roughly constant between March and May but slightly lower than the forest sample levels (Figs. 3.28 and 3.30). Resin acid levels were similar to those observed for June and August in the forest sample. The ASW and EFA groups for the yard spruce #2 heartwood sample remained constant during the sampling period and were similar to the forest spruce heartwood sample (Figs. 3.28 and 3.30)

3.3.2.8 Yard Spruce #3 Heartwood

When sampling variability was considered, the yard spruce #3 heartwood sample fatty acids closely resembled the profile observed for the forest spruce heartwood sample (Figs. 3.28 and 3.31). The resin acid group also showed a similar trend to the forest spruce heartwood sample for May and June but then resin acids decreased in the yard spruce #3 between August and October (Figs. 3.28 and 3.31). ASW levels were low in the yard spruce #3 heartwood sample and also showed very little change (Fig. 3.31). EFA levels were similar to the forest sample and did not show any strong seasonal variability (Figs. 3.28 and 3.31).

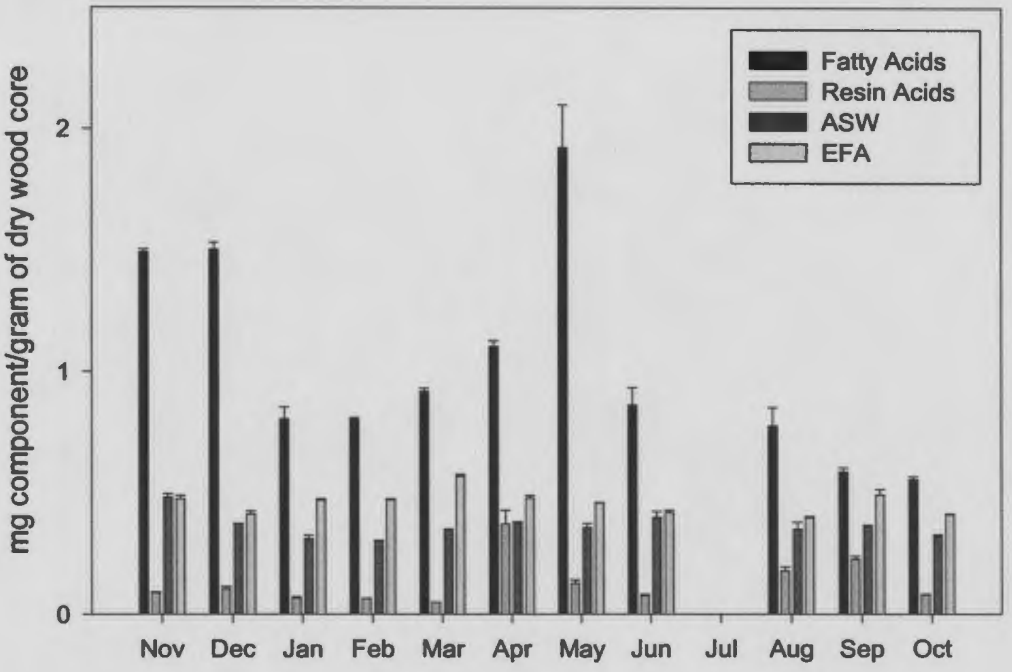


Figure 3.24. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for forest fir heartwood samples collected between November 1995 and October 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of heartwood wood core portions for each month.)

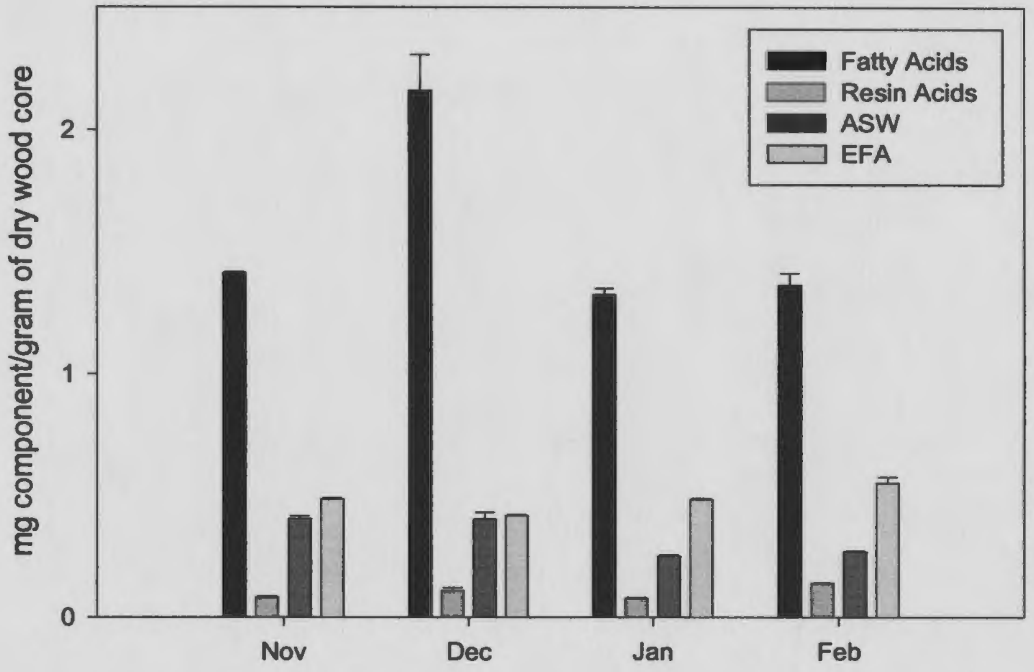


Figure 3.25. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard fir #1 heartwood samples collected between November 1995 and February 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of heartwood wood core portions for each month.)

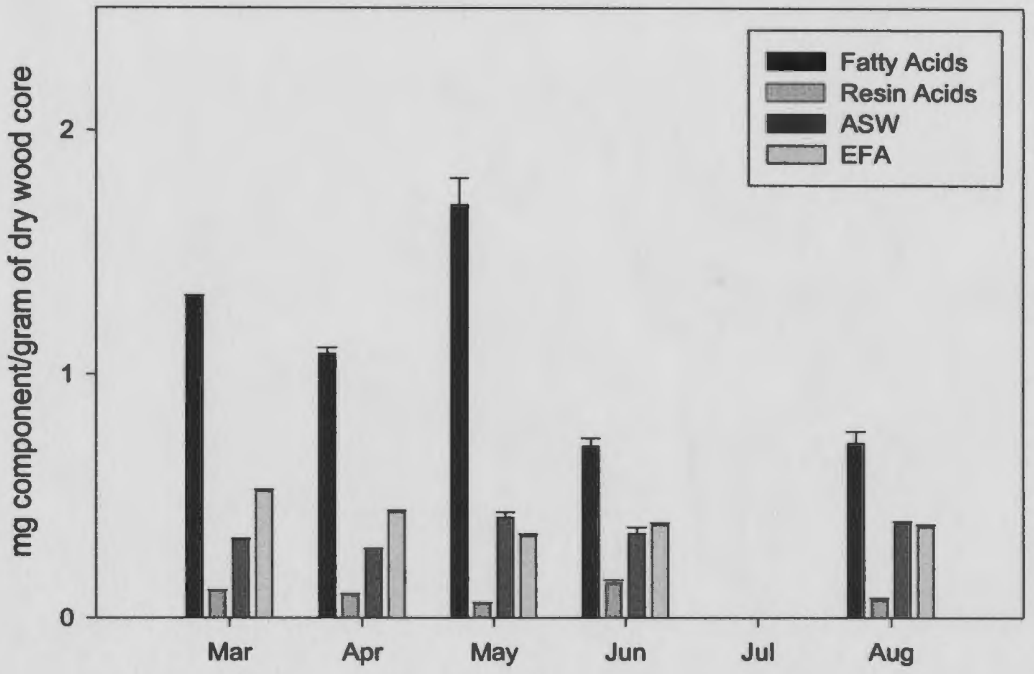


Figure 3.26. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard fir #2 heartwood samples collected between March 1996 and August 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of heartwood wood core portions for each month.)

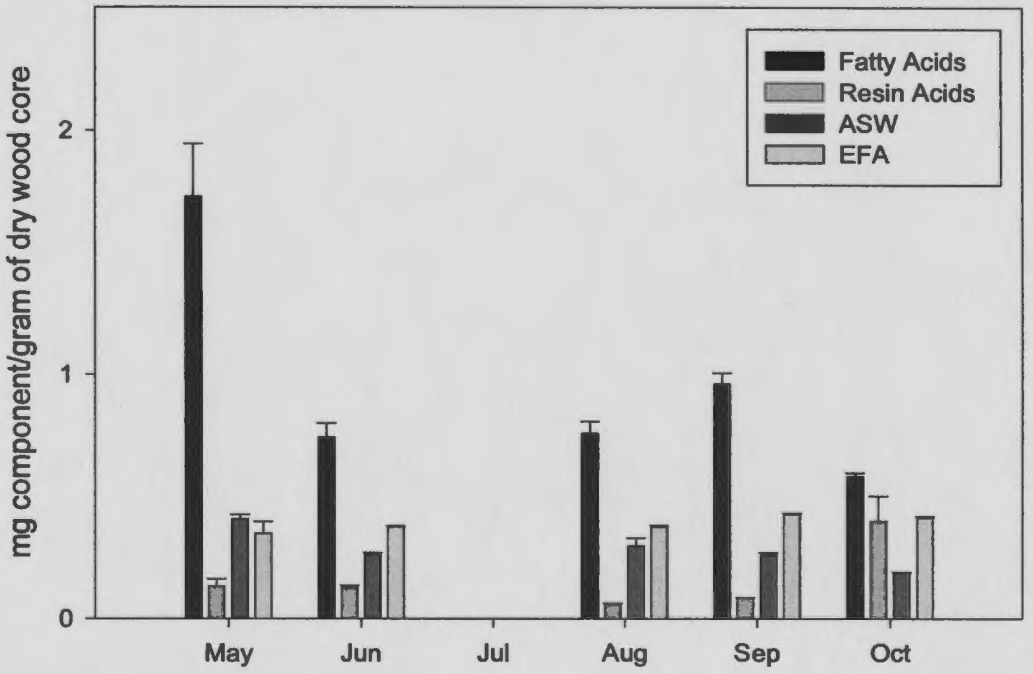


Figure 3.27. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard fir #3 heartwood samples collected between May 1996 and October 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of heartwood wood core portions for each month.)

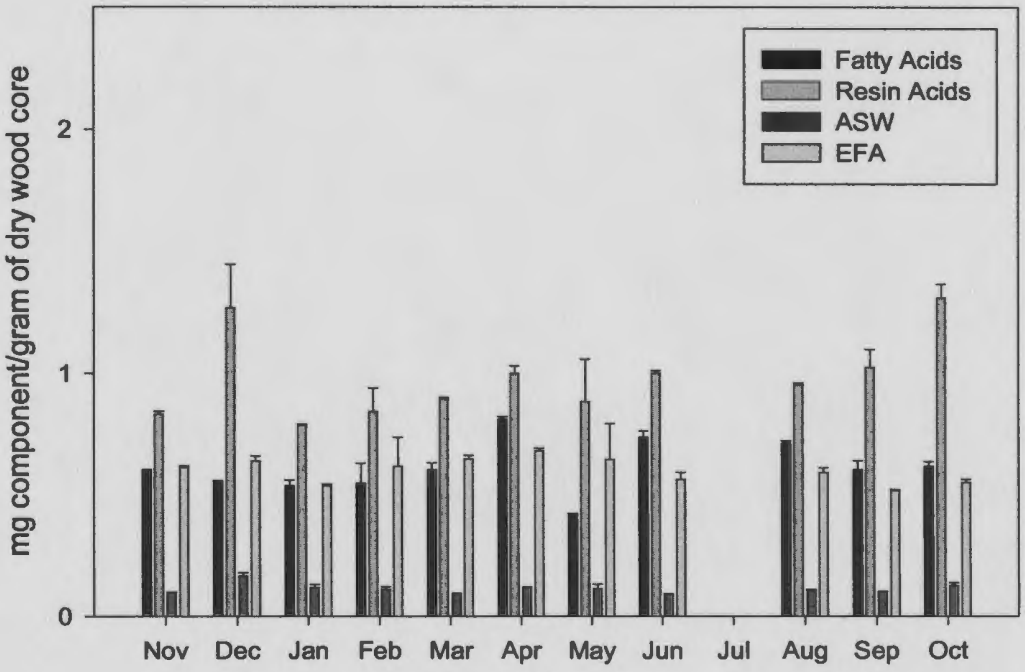


Figure 3.28. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for forest spruce heartwood samples collected between November 1995 and October 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of heartwood wood core portions for each month.)

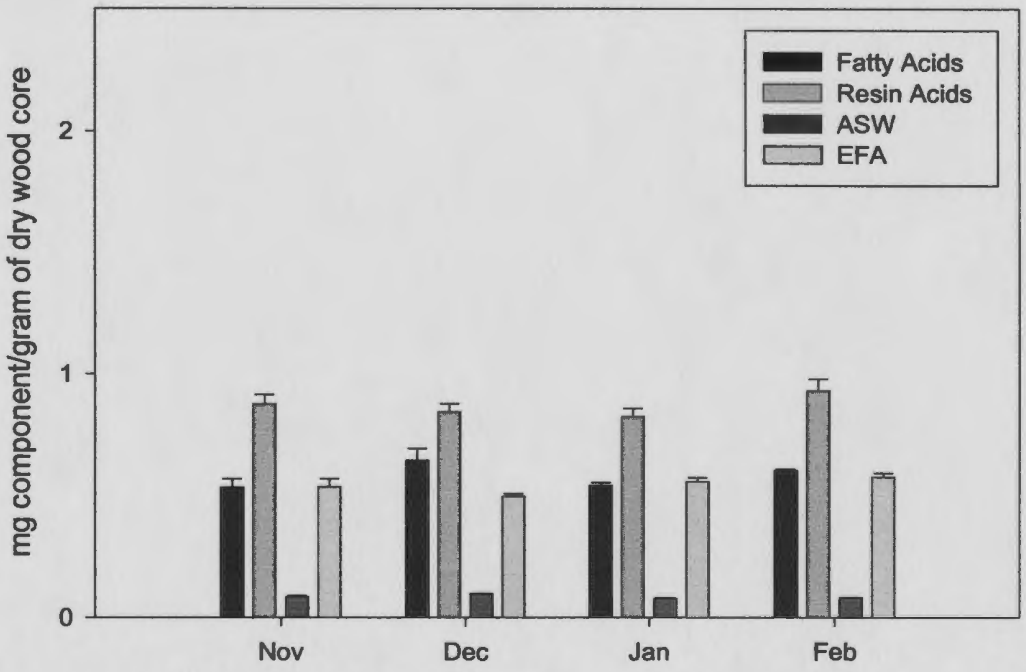


Figure 3.29. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard spruce #1 heartwood samples collected between November 1995 and February 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of heartwood wood core portions for each month.)

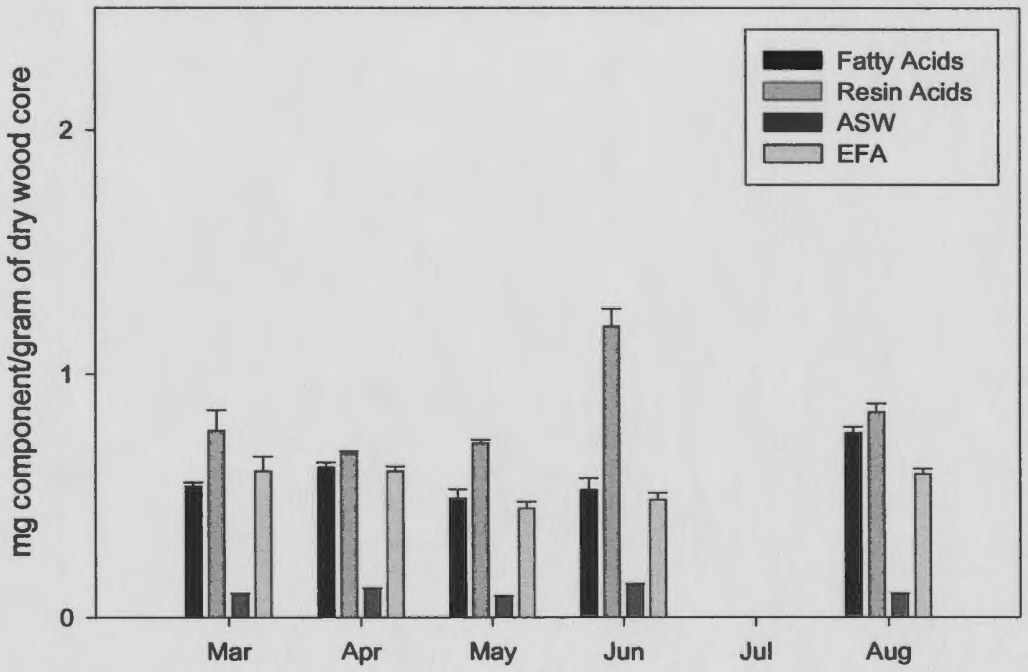


Figure 3.30. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard spruce #2 heartwood samples collected between March 1996 and August 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of heartwood wood core portions for each month.)

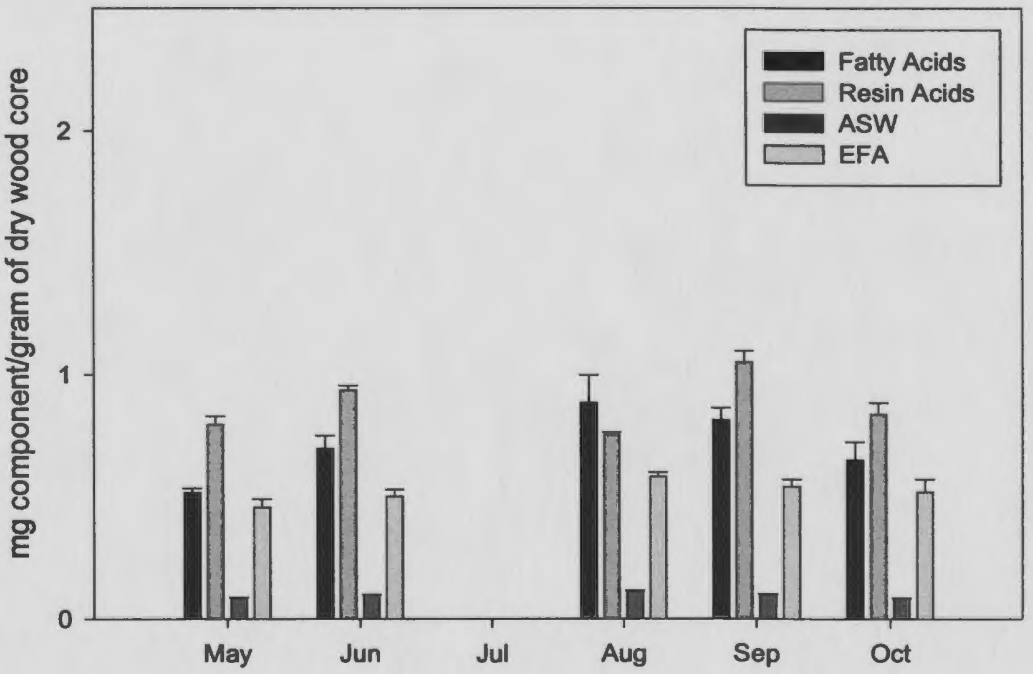


Figure 3.31. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for yard spruce #3 heartwood samples collected between May 1996 and October 1996. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of heartwood wood core portions for each month.)

3.4 Mill Samples - GC Analysis

3.4.1 Wood Chips

The wood chip sample was a mixture of both species studied and did not closely resemble the sapwood or heartwood wood core profile of either species. The fatty acid profile showed large month-to-month fluctuations and no overall trends (Fig. 3.32). Overall, the fatty acids group was higher in concentration (with the exception of the January sample) than the other three groups (resin acids, ASW, and EFA) with seasonal high levels in September (Fig. 3.32). The wood chip resin acid, ASW , and EFA profiles did not show any seasonal trends (Fig. 3.32).

3.4.2 Primary Refiner

In general when compared with the wood chip profile, the primary refiner seasonal profile was less variable and had a smoother overall profile (Figs 3.32 and 3.33). The fatty acid profile for the primary refiner sample appeared to show a general trend of increase from a seasonal low concentration in November to a seasonal high concentration in July (Fig. 3.33). However when the within sample variability was considered, it was difficult to state differences between fatty acid concentrations for April, June, July, or August (Fig. 3.33). Again, the primary refiner resin acid, ASW, and EFA groups did not show any consistent seasonal trends (Fig. 3.33).

3.4.3 Secondary Refiner

One of the first general trends that became apparent when looking at the secondary refiner data was the overall reduction in the dominance of the fatty acids group

when compared to wood chip and primary refiner data (Figs. 3.32-3.34). In contrast the resin acid profile did not show any consistent seasonal trends (Fig. 3.34). The ASW and EFA groups were both found to be at low concentrations and constant during the sampling period (Fig. 3.34).

3.4.4 Screen Accepts - Pulp

With the exception of the first 3 months (November to January), the fatty acid group was again found to be the most dominant group in the sample (Fig. 3.35). There appeared to be an overall increase in fatty acid concentrations between November and July for the screen accepts pulp sample (Fig. 3.35). The resin acids group showed no seasonal trends during the sampling period (Fig. 3.35). The ASW group was roughly the same during the sampling period and was consistent with the wood chip and refiner samples (Figs 3.32-3.35). The EFA group also remained roughly the same during the sampling period. Overall EFA concentrations were similar to those observed for the primary refiner and wood chip samples (Figs. 3.32-3.35).

3.4.5 Screen Accepts - Liquid

Although the GC components for the screen accepts liquid sample were expressed in different units than the other mill samples, the trends within the sample could still be compared. The fatty acid group showed a decreasing trend between January and April and an increasing trend between April and August (Fig. 3.36). However, sample variability was considerable for the fatty acids group and restricted the conclusions which could be made on that data. The resin acid group also showed no consistent seasonal

trends (Fig. 3.36). The ASW group remained roughly the same during the sampling period but jumped to seasonal high levels in October (Fig. 3.36). The EFA group was often the second most dominant group in the screen accepts liquid sample. EFA concentrations in several cases were found to be higher than the resin acid and ASW groups (Fig. 3.36). The EFA group had large month-to-month fluctuations in its concentrations (Fig. 3.36).

3.4.6 Paper

In general, the fatty acid group was the dominant component in the paper sample (Fig. 3.37). Fatty acid concentrations remained at roughly the same level for most months but dropped sharply in May, June, and August (Fig. 3.37). The resin acid group in general was found to be at lower overall concentrations when compared to the other mill samples between November and June (Figs. 3.32-3.37). Resin acid concentrations jumped to higher levels from July to October (Fig. 3.37). In general the ASW group was lowest in overall concentration when compared to the other mill samples (Figs. 3.32-3.37). The ASW and EFA groups did not show any seasonal trends for the paper samples (Fig. 3.37).

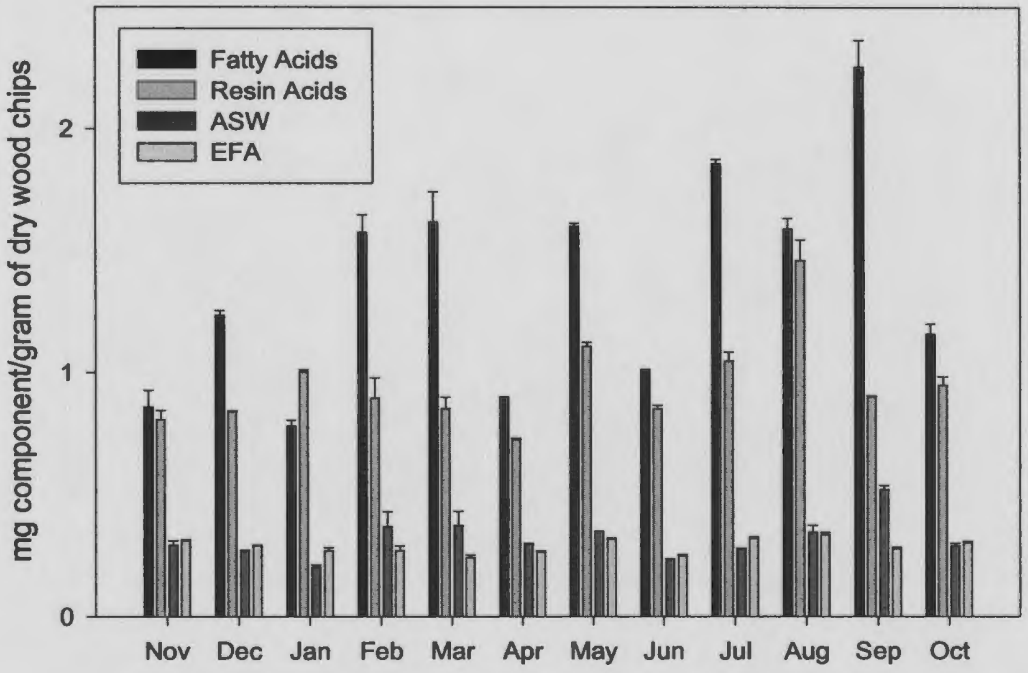


Figure 3.32. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for wood chip samples collected between November 1995 and October 1996 from wood chip bin #4 at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of wood chips for each month.)

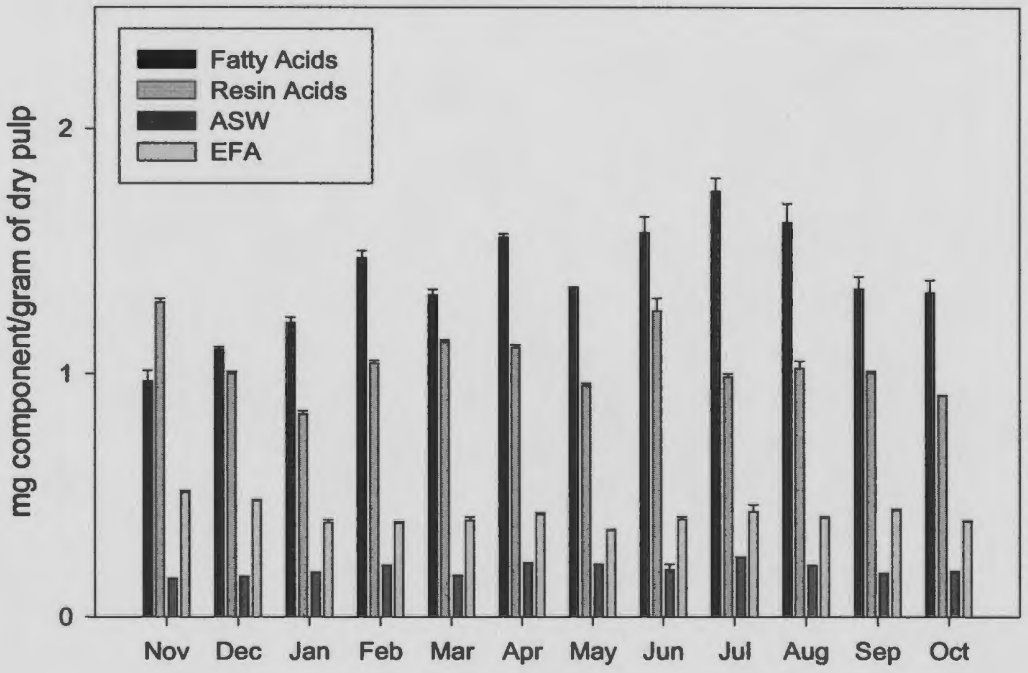


Figure 3.33. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for pulp samples collected between November 1995 and October 1996 from primary refiner #4 blow line at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of pulp for each month.)

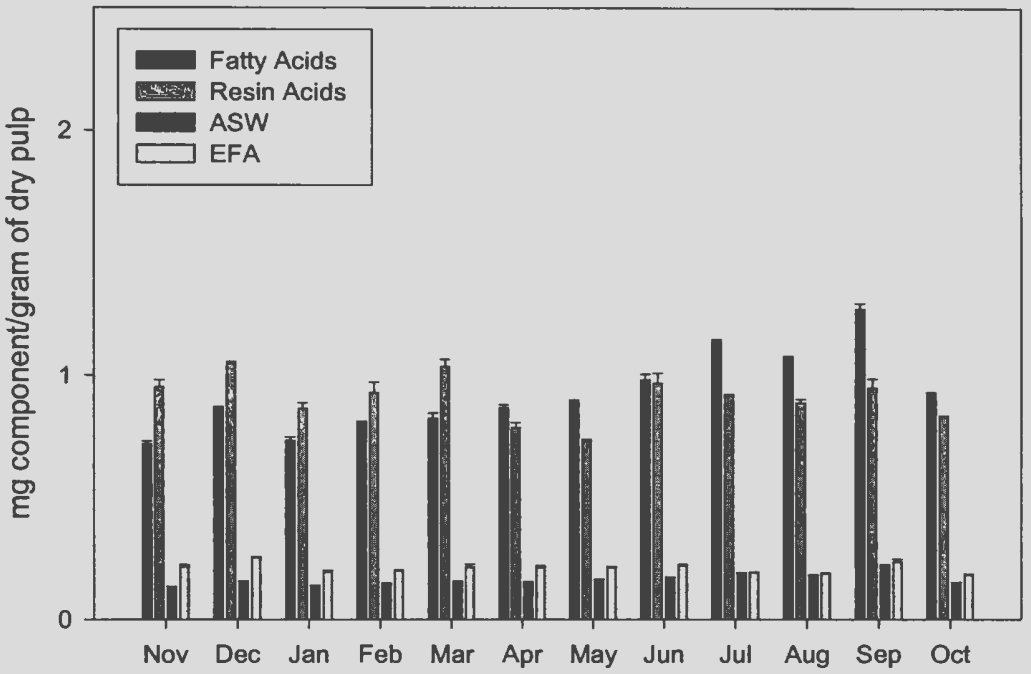


Figure 3.34. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for pulp samples collected between November 1995 and October 1996 from secondary refiner #4 blow line at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a pooled sample of pulp for each month.)

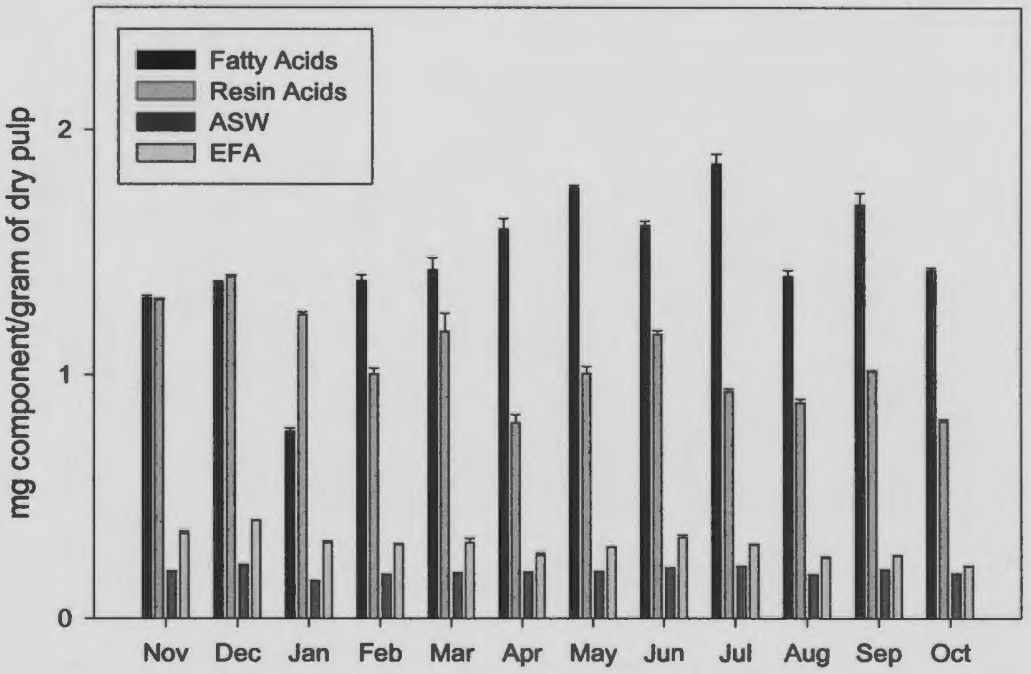


Figure 3.35. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for pulp samples collected between November 1995 and October 1996 from screen accepts (pulp portion) #4 line at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from the pulp sample portion of the screen accepts sample for each month.)

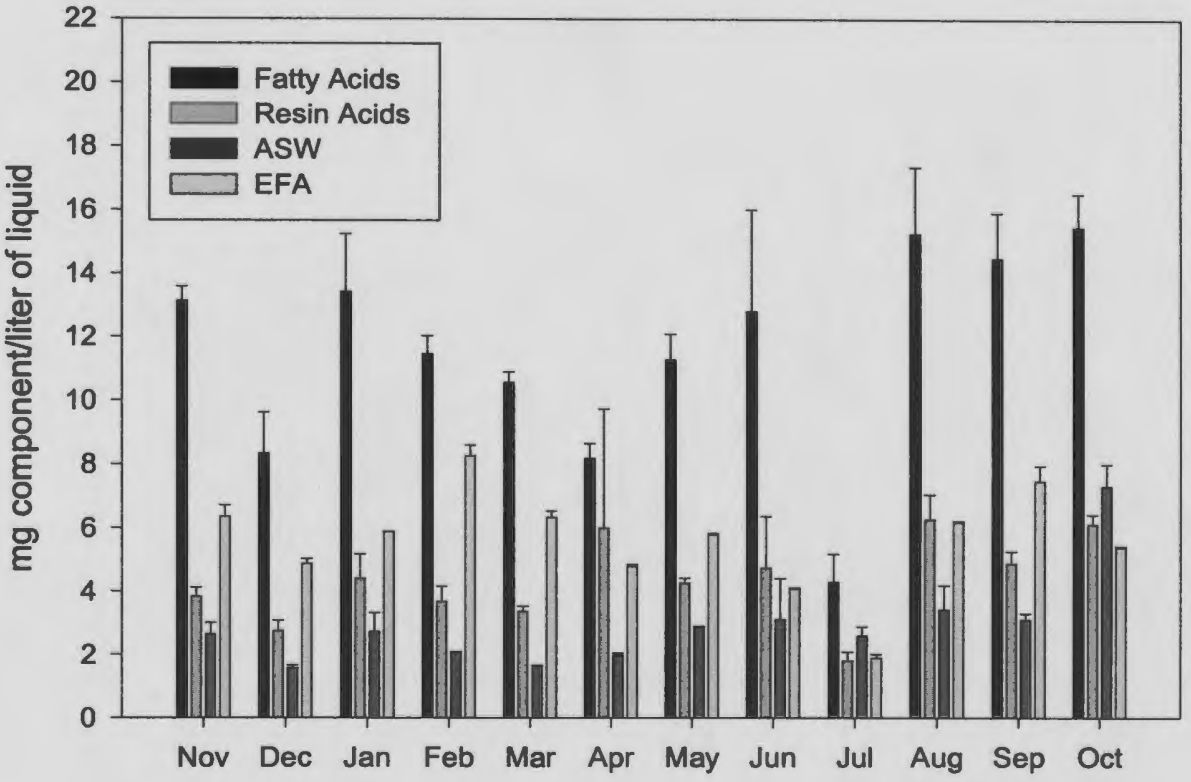


Figure 3.36. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for liquid samples collected between November 1995 and October 1996 from screen accepts (liquid portion) #4 line at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated based on the GC analysis of 2 extract samples (2 injections total) from the liquid sample portion of the screen accepts sample for each month.)

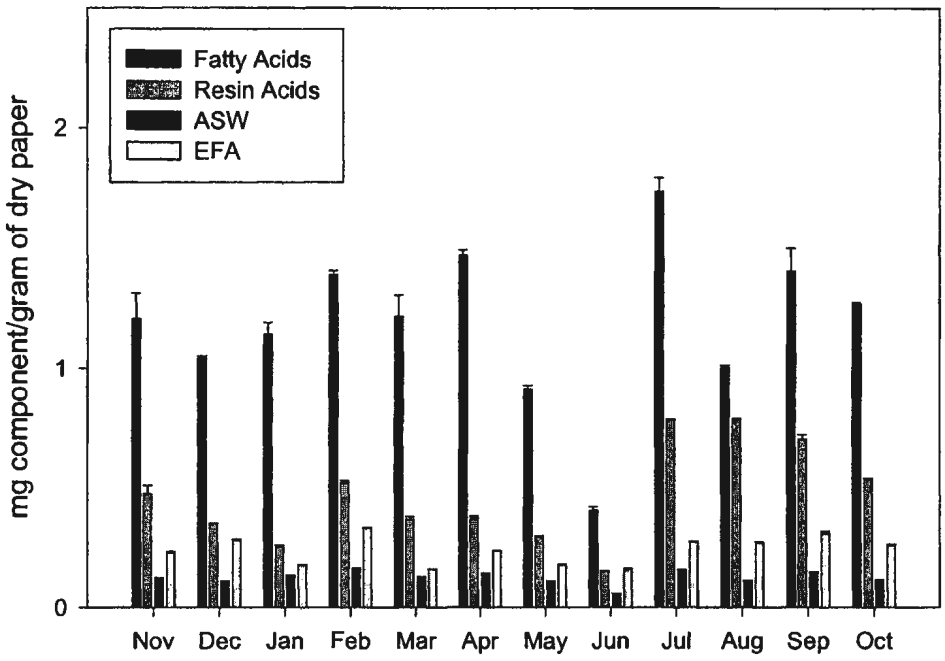


Figure 3.37. GC Component (fatty acids, resin acids, ASW, EFA - left to right) distribution for paper samples collected between November 1995 and October 1996 from paper machine #7 at Corner Brook Pulp and Paper Mill. (Error bars represent the standard error of the mean and were calculated based on the duplicate GC analysis of 2 extract samples (4 injections total) from a sample of paper for each month.)

3.5 GC Analysis Chromatograms

The major chromatographic groups (fatty acids, resin acids, ASW, and EFA) were labelled in each of the wood core and mill sample chromatograms for the month of August 1996. August was selected since the yard samples for this month were from logs harvested 5 months earlier and had the greatest potential to show changes as a result of seasoning.

3.5.1 Forest Wood Core Chromatograms

The GC profile for the forest wood cores (sapwood and heartwood) showed obvious differences between the fir and spruce. There was a greater proportion of fatty acids in both the sapwood and heartwood forest fir samples when compared to the forest spruce samples (Figs. 3.38 and 3.39). The forest spruce samples showed a lower concentration of fatty acids but some large peaks in the resin acids group (Figs. 3.38 and 3.39). There were also obvious differences between the sapwood and heartwood profiles for both fir and spruce samples. The forest fir heartwood showed a greater abundance of fatty acids when compared to the forest fir sapwood profile (Figs. 3.38 and 3.39). There were also more fatty acid peaks in the forest spruce heartwood profile when compared to the forest spruce sapwood profile (Figs. 3.38 and 3.39).

3.5.2 Yard Wood Core Chromatograms

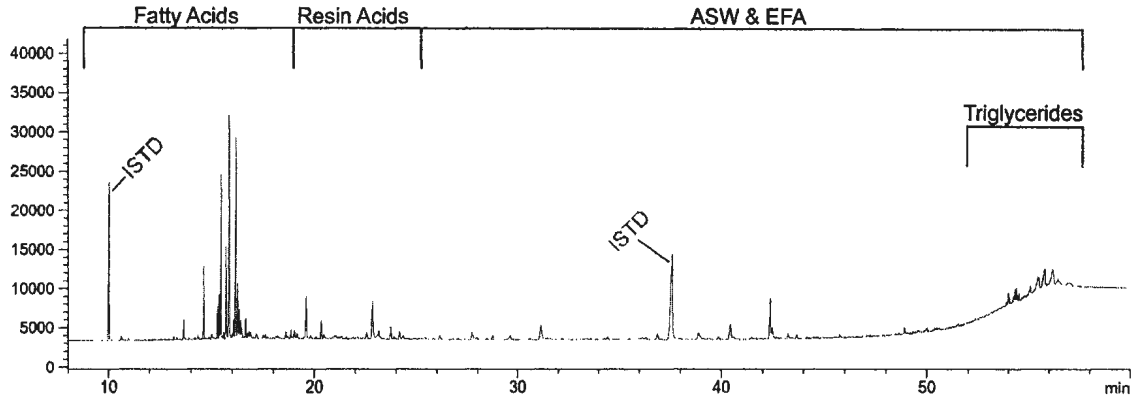
The GC profile for the yard wood cores showed similar species specific-differences between the fir and spruce samples as seen in the forest samples (Figs. 3.38-3.41). There was a greater proportion of peaks in the fatty acid area of the chromatogram

for the fir samples and a greater proportion of peaks in the resin acid group for the spruce samples (Figs. 3.40 and 3.41). There were increased levels observed in the fatty acids group of the yard fir and yard spruce sapwood samples when compared to the forest fir and spruce sapwood samples (Figs. 3.38 and 3.40).

3.5.3 Mill Sample Chromatograms

The wood chip and refiner sample chromatograms showed a profile which was a combination of the fir and spruce wood core samples (Figs. 3.38-3.42). The fatty acids group and resin acids group showed a decrease in levels from the wood chips stage to the primary and secondary refiner samples (Fig. 3.42). The primary refiner, secondary refiner, and screen accepts-pulp chromatograms were similar in their overall profile (Fig. 3.42). The screen accepts-liquid chromatogram showed an elevated level of fatty acids and triglycerides when compared to the other mill sample chromatograms (Figs. 3.42 and 3.43). In contrast the paper sample chromatogram showed a reduced amount of fatty acids when compared to the other mill chromatograms (Figs. 3.42 and 3.43). With the exception of the screen accepts-liquid chromatogram the ASW and EFA profile was similar for the wood chips, refiner, screen accepts-pulp, and paper chromatograms (Figs. 3.42 and 3.43).

Sapwood-Forest Fir 92



Sapwood-Forest Spruce

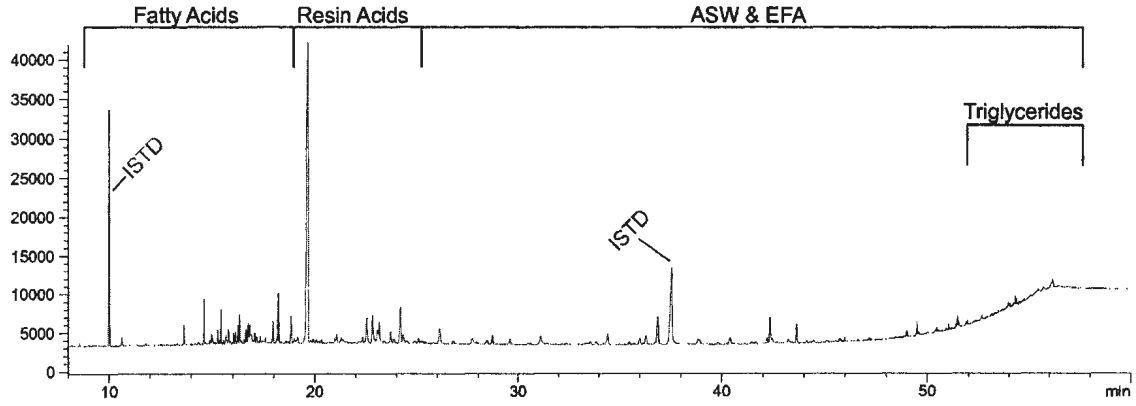
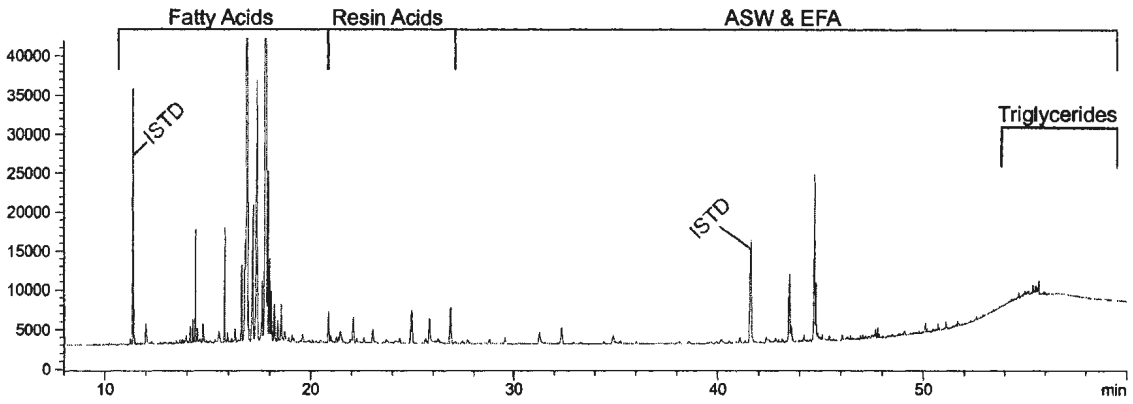


Figure 3.38. Typical observed GC chromatograms for forest sapwood samples (wood cores) collected in August 1996.

Heartwood-Forest Fir



Heartwood-Forest Spruce

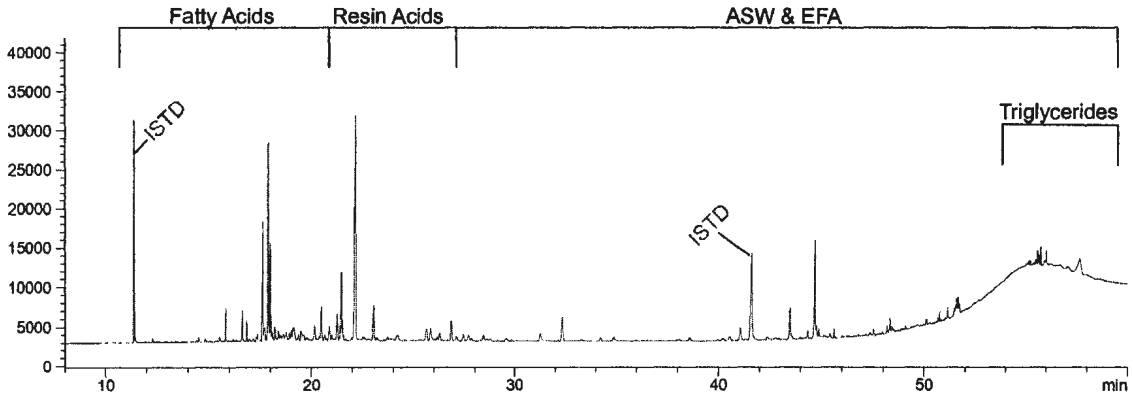
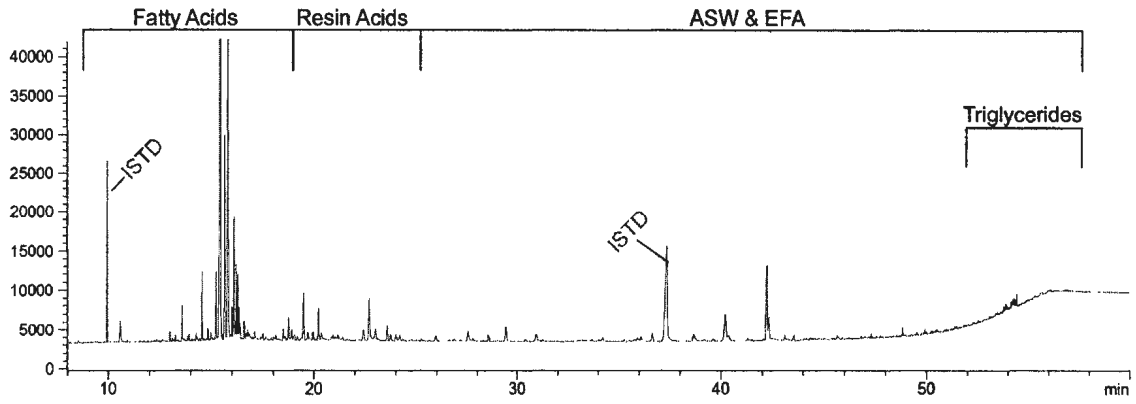


Figure 3.39. Typical observed GC chromatograms for forest heartwood samples (wood cores) collected in August 1996.

Sapwood-Yard Fir 94



Sapwood-Yard Spruce

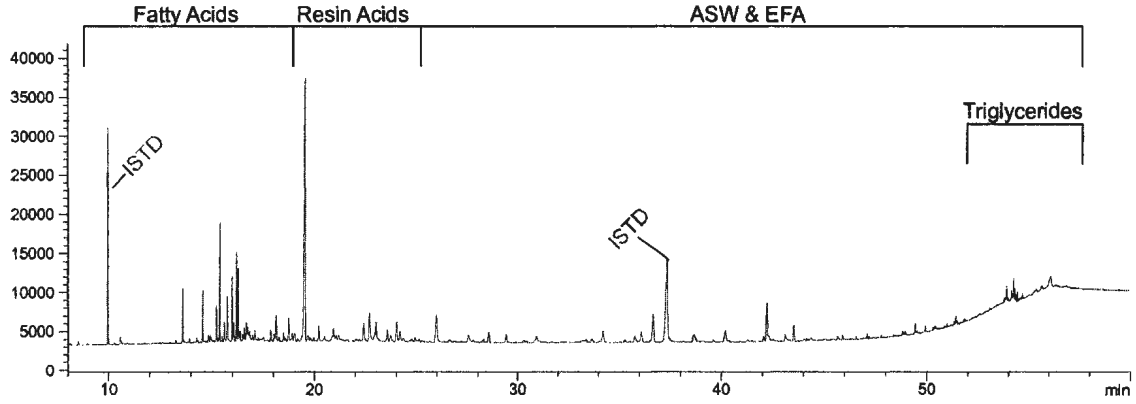
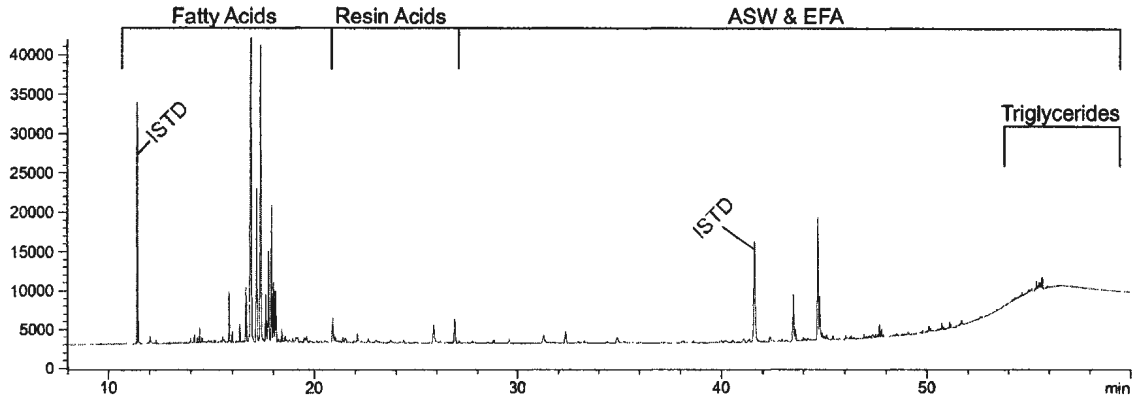


Figure 3.40. Typical observed GC chromatograms for yard sapwood samples (wood cores) collected in August 1996 from logs harvested in mid-March.

Heartwood-Yard Fir



Heartwood-Yard Spruce

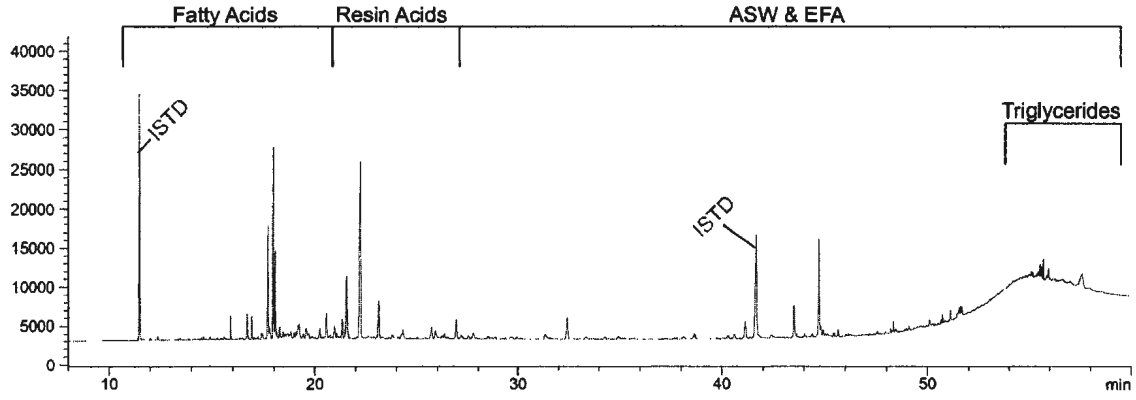
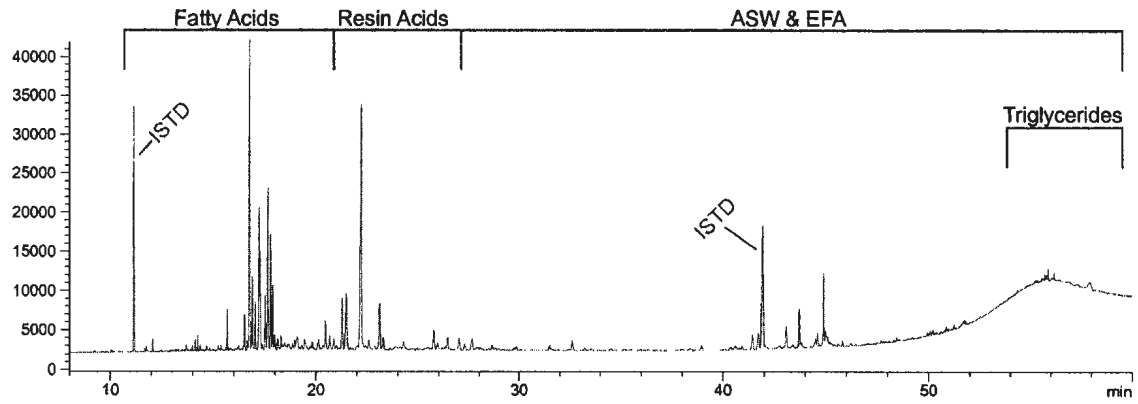
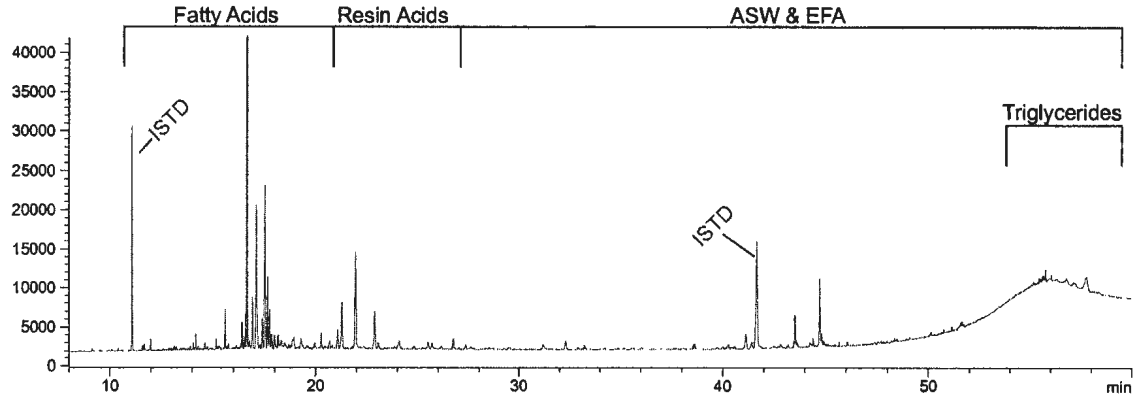


Figure 3.41. Typical observed GC chromatograms for yard heartwood samples (wood cores) collected in August 1996 from logs harvested in mid_March.

Wood Chips 96



Primary Refiner



Secondary Refiner

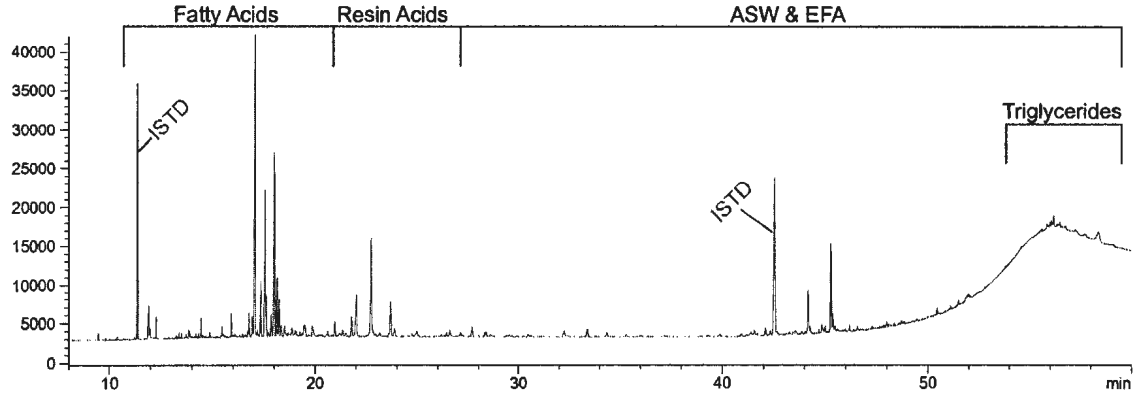
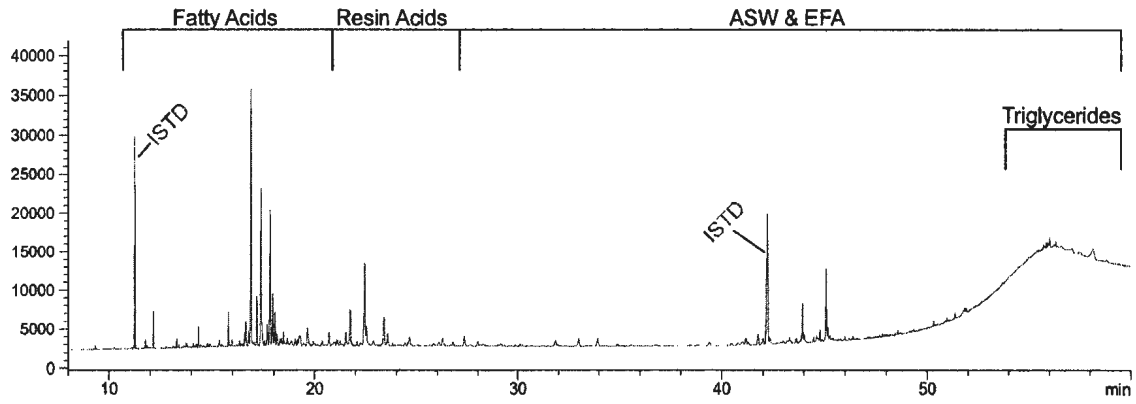
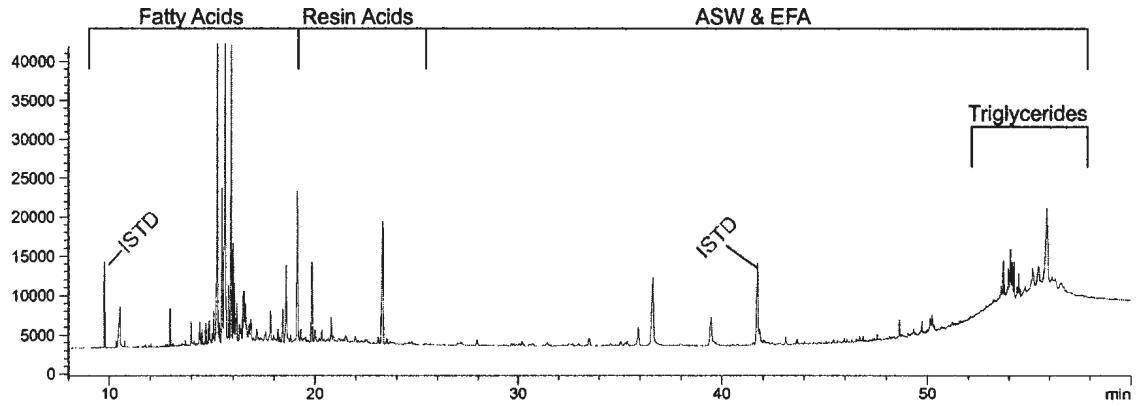


Figure 3.42. Typical observed GC chromatograms for mill samples (wood chips, primary refiner, and secondary refiner) collected in August 1996.

Screen Accepts - Pulp 97



Screen Accepts - Liquid



Paper

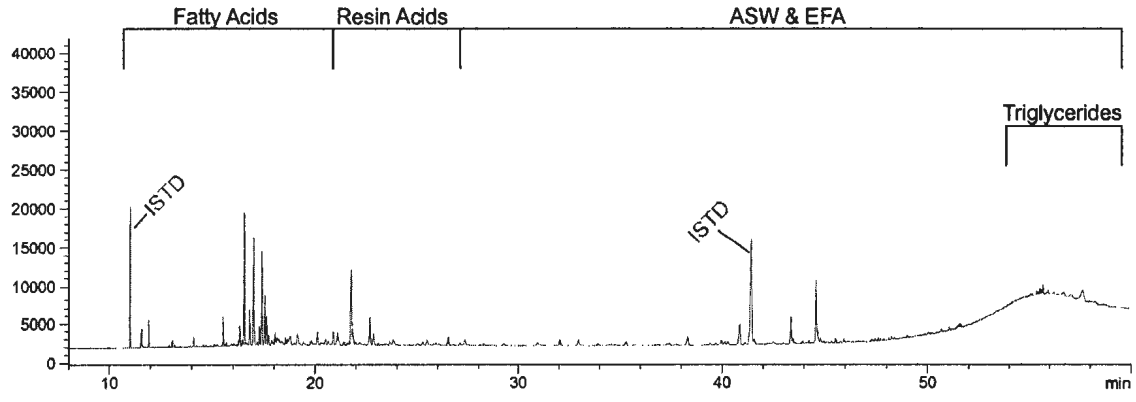


Figure 3.43. Typical observed GC chromatograms for mill samples (screen accepts - pulp, screen accepts - liquid, and paper) collected in August 1996.

4 Discussion

4.1 Wood Cores - Total Extractives

4.1.1 Fir - Total Extractives

The forest fir sapwood total extractives showed a decrease in total extractives between the months of January and March and a sharp increase in extractives for the month of April (Fig. 3.1). The increased sapwood total extractives may partially be explained by the work of Saranpaa and Nyberg (1987), who found significant seasonal changes in the sapwood of Scots pine. Saranpaa and Nyberg found that the free fatty acid portion sapwood had the highest levels around the end of April and middle of August. Researchers (Saranpaa and Nyberg, 1987 and Ekman et al., 1979) have attributed seasonal changes in the extractives content of wood to the metabolic activities of trees. The sharp increase in sapwood extractives for the forest fir sample for the month of April may indicate the change in the metabolic activities of the tree related to the growing season (Fig. 3.1). Since the wood core sample was a composite of 6 different trees, it is likely to confirm an elevated level of extractives for April. However more samples would be required throughout the month to confirm is something physiologically is occurring in April.

There were also visible differences in the total extractives portion of the heartwood forest fir sample. These were highlighted by the elevated levels of total extractives in December, May, and August (Fig. 3.1). This indicated that there was at least some month-to-month variations in the concentration of total heartwood extractives

in the forest fir sample.

When the yard fir #1 sample was compared to the forest fir sample, the total extractive profile was roughly the same (Figs. 3.1 and 3.2). The elevated levels of heartwood total extractives observed for December in the forest fir sample were also seen in the yard fir #1 sample. These similarities were felt to arise from the fact that the yard sample was harvested in October and allowed to season during the colder winter months of the year stored in roundwood form. This observation was not surprising since Nugent et al. (1977) found little change in the extractive content of wood seasoned at -20°C and only small changes in wood seasoned at 5°C and 21°C. Assarsson et al. (1963) also noted that wood stored as chips versus logs undergoes greater extractive changes (especially compositional) as a result of seasoning.

The yard fir #2 sample showed sapwood and heartwood total extractive concentrations which were also roughly the same for the sampling period between March and August (Fig. 3.3). There were no changes with total concentration of sapwood or heartwood extractives even at 5 months post-harvest. Although seasoning began during colder spring months, the wood was also allowed to season during the warmer summer months. This may also be attributed to roundwood storage practices of the mill. Although Nugent et al. (1977) highlight the fact that there were very small changes in the total extractive concentrations. They also detail that there were significant changes in the composition of those extractives as a result of temperature-controlled seasoning. The increased levels of total extractives observed in the forest fir sample in April, May, and

August were absent in the yard fir #2 sample (Figs. 3.1 and 3.3). This may indicate that the peaks observed in the forest sample were related to sampling variations and not physiological growth processes. More samples would be required to explain the peaks observed in the forest fir sample.

The yard fir #3 sample showed a total extractive profile (both sapwood and heartwood) which began to differ from the forest fir profile (Figs. 3.1 and 3.4). While the forest fir sample concentrations remained constant (in the sapwood) or increased slightly (in the heartwood) between August and October they began to decrease (in the sapwood) or remain roughly the same (in the heartwood) in the yard fir #3 sample (Figs. 3.1 and 3.4). This may be an indication of some seasoning action in the logs during this time period of 3 to 5 months post-harvest and a potential reduction in total extractives. The seasoning for the yard fir #3 sample occurred during the period which was likely to have the highest average temperature of all three yard samples. This possible seasoning action may be explained by the fact that the physiological processes related to seasoning would be expected to occur at a faster rate at elevated temperatures.

4.1.2 Spruce - Total Extractives

When the within sample variability for the forest spruce total extractives sample was considered, there were only minor changes in the total extractives concentration during the sampling period. This agreed with earlier work by Ekman et al. (1979) who also found only small seasonal variations in the lipophilic extractives content of Norway spruce from wood cores taken from living trees on a monthly basis.

There was very little difference between the yard spruce #1 sample and the forest spruce sample (Figs. 3.5 and 3.6). This was also felt to be related to the fact that the seasoning for this sample occurred primarily during the colder winter months of the year. The elevated levels of total extractives for the December forest spruce sapwood total extractives were not observed in the yard spruce #1 sample (Figs 3.5 and 3.6). The differences in the December sapwood total extractives levels were thought to be related to inconsistencies in the wood core sample itself.

The yard spruce #2 sample also showed very little difference between it and the forest spruce total extractives sample (Figs. 3.5 and 3.7). When the large within sample variability was taken into account for the May sapwood, there was no difference in the total extractive profile for forest spruce sample versus the yard spruce #2 sample for the same sampling period.

The yard spruce #3 sapwood sample showed a slight drop in total extractive concentrations when compared to the forest spruce sapwood sample between August and October (Figs. 3.5 and 3.8). This occurred in the period between 3 and 5 months post-harvest (Table 2.1). This type of decrease was also observed in the yard fir #3 sapwood sample when compared to the forest fir total extractives profile in the 3 to 5 month post-harvest period. There was no evidence of seasoning-related changes in the yard spruce #3 heartwood sample. Less obvious changes in the heartwood were expected since this is an area where the cells were considered to be dead, as earlier quoted by Tyrvainen (1995). Other sources such as Ekman et al (1979) and Gao et al. (1995) have reported gradients

(towards the centre of the tree) within the heartwood with decreasing or increasing concentrations of specific components of the extractives found in the heartwood. The heartwood sections of wood cores in this study were not processed in a manner which addressed radial variations within the heartwood sample.

4.1.3 Conclusions - Wood Cores - Total Extractives

The total extractive data for the forest-collected wood cores of fir and spruce and did not show any major seasonal changes. The fir samples were more variable than the spruce samples but neither species showed any trends which lasted more than a month. The sporadic monthly changes were thought to be related to sampling variability.

Initially, there was little change in the yard sample total extractive levels when compared to the forest samples. Physiological processes were thought to continue in the wood cells for days or weeks following harvest (depending on time of year harvested). It would be expected that during the winter months there would be limited cellular activity in logs which remained frozen and this would slow the seasoning processes in the wood. This was evident in the first sets of yard wood cores which continued to resemble the forest total extractives profile following harvest. The only yard samples which showed any potential for variation from the forest samples total extractive profiles were the yard fir #3 and yard spruce #3 samples. These samples showed some variation from the forest sample trends in the areas of 3 to 5 months post-harvest and this was attributed to the fact that the logs were allowed to season during the warmest months of the year.

The lack of seasonal trends in the total lipophilic extractives content of the

sapwood and heartwood of forest and yard samples of fir and spruce was not a surprise. Ekman et al. (1979) indicated that they found only small seasonal-dependent changes in the total extractives of in Norway spruce. The lack of seasonal changes in the total extractives content of fir and spruce heartwood may be explained by Tyrvainen (1997). He stated that extractives are relatively stable on a seasonal basis in the dead heartwood tissue.

4.2 Mill Samples - Total Extractives

4.2.1 Wood Chips - Total Extractives

There were no consistent trends in the total extractive data which spanned the entire sampling period. Sampling was felt to be the biggest factor causing the inconsistent total extractives trends in the wood chips sample. A sample collected from a chip bin, although pooled from three different samples, would be difficult to repeat and keep consistent to the 40% spruce and 60% fir recipe used by the mill to produce its paper. The volume that the sample represented in relation to the chip bin and the 100 grams which was sub-sampled, dried, ground, and again sub-sampled and extracted (3 grams) could have easily been altered by the chip composition from the area sampled in the chip bin. Factors such as chip species (fir versus spruce) and chip age could ultimately affect the total extractive composition of the sample.

4.2.2 Primary Refiner and Secondary Refiner - Total Extractives

The inconsistent trends observed in the wood chip total extractives sample were reduced to no trends in the primary refiner sample. Primary refiner total extractive levels remained at the same concentration for the sampling period (Fig. 3.10). The constant total extractive levels observed for the primary refiner sample were thought to be an indication of a more consistent sample. This was not surprising since the wood chip sample was now reduced to pulp and had undergone more sample mixing at the chip washers and in the refiner itself. The secondary refiner sample showed a similar profile to the primary refiner. In both samples the total extractives level remained at 10-12 mg of

total extractives per gram of dry refiner pulp (Figs. 3.10 and 3.11). The concentrations of these total extractives could be reduced by the utilization of a pulp washing system. Lloyd et al. (1990) found that the total dichloromethane extractives in thermomechanical pulps of radiata pine could be reduced by washing the pulp with water. A similar reduction in extractives would be expected for a fir/spruce system. Lloyd et al. (1990) also indicated that, although the resin content of the pulp would be reduced, the washing would load extra resin into the mill effluent system and require more treatment before the effluent could be discharged.

4.2.3 Screen Accepts Pulp and Liquid - Total Extractives

Between April and October there was a possible cyclical trend present which peaked in June (Fig. 3.12). Continued sampling of the screen accepts pulp would help to confirm if seasonal trends exist in this sample.

Based on the total extractives data, it was felt that the screen accepts pulp sample had the best potential to display seasonal changes in the mill system related to the wood supply. This was felt to true because the screen accepts pulp would have been one of the most consistently mixed samples as it went through a number of stages in the papermaking process that would have promoted sample mixing and homogeneity. However, the GC analysis of these samples indicates that the screen accepts pulp chemical composition varies considerably from month-to-month.

The liquid sample was less promising for displaying seasonal trends. There was no relationship between the total extractives present in the liquid portion of the screen

accepts and the total extractives present in the pulp portion of the screen accepts (Figs. 3.12 and 3.13). There appeared to be decreasing trends within the sampling period which was repeated every three months: February - April, May - July, and August-October (Fig. 3.13), however these trends could not be explained. The accumulation and release of extractives into the process waters and mill effluent does not necessarily follow the seasonal variations in the extractives arriving at the paper mill (Tyrvainen, 1997).

It was surprising that the total extractive concentrations of the liquid screen accepts sample did not follow the total extractive concentrations for the pulp screen accepts sample since it was felt that the extractives present in the pulp were in equilibrium with the extractives present in the water. The sample preparation process may have influenced the total extractives present in the liquid portion of the screen accepts. The filtering step after the centrifugation of the samples may have separated some of the colloidal resin from the liquid sample and left it will the pulp portion of the sample. The liquid sample may be a reflection of the dissolved extractives rather than both dissolved and colloidal extractives. A large pore grade of filter was used to help prevent the retention of the colloidal resin particles but some colloidal resin droplets may have been retained. Sundberg et al., (1996) were able to filter out colloidal droplets from process waters using a 0.1 μm filter. Another possible reason for the differences between the screen accepts solid and liquid samples may be related to the fact that the pulp portions were extracted with dichloromethane and the liquid samples were extracted with petroleum ether. Both are lipophilic solvents but there may be slight differences in their

selectivity towards certain extractives. Petroleum ether was used for screen accepts liquid samples because it separated better into phase during the liquid-liquid extraction. There were emulsion problems encountered when extraction with dichloromethane was attempted. These emulsion problems were not easily eliminated, even when centrifugation was used to help facilitate separation. The use of petroleum ether as an extracting solvent only allowed conclusions to be made about screen accepts liquid sample itself. Other groups have also had trouble analyzing mill process waters. Alvarado et al. (1992) state that the complexity and diversity of the hydrophobic substances in combination with their interactions with the dissolved and dispersed organic matter in the process stream make it difficult to determine the different species present in the process.

There was no relationship between the screen accepts total extractives and the pH of the sample. The pH levels of all screen accepts samples were in a small range of pH 4.50 to pH 5.07 (Table 3.1). Orsa and Holmbom (1994) found fatty acids and resin acids in mill process waters were almost equally extracted at pH 3.5, pH 6.5, and pH 8 using methyl tert-butyl ether. Thus there should have been limited or no differences in the total amounts of extractives related to differences in sample pH (Fig. 3.13 and Table 3.1). Extracting the screen accepts samples at unadjusted pH levels should have produced similar results to a procedure which adjusted the sample pH to same level for all samples.

If future extractions were to be done on the screen accepts liquid portion, a larger sample size would be recommended to facilitate easier liquid-liquid extractions. A 100

ml sample only yielded 4-7 mg of extractives. A larger sample or some form of concentration prior to extraction might help to increase the accuracy of these extractions. The method using methyl tert-butyl ether by Orsa and Holmbom (1994) could be investigated.

4.2.4 Paper and Paper Machine White Water - Total Extractives

There was very little difference in the total extractive levels for all the paper samples collected (Fig. 3.14). The major difference with the paper samples was that they had lower total extractive levels when compared to the wood chip and pulp samples (Figs 3.9-3.12 and 3.14). A large portion of the total extractives leaves the mill in the end-product, however, these extractives now also include the contribution of the recycled furnish used in production. The contribution of the recycled furnish to the end-product total extractives was not examined in this study.

There were limited conclusions which could be made based on the paper machine white water total extractives. There appeared to be a trend between March and October but large within sample variability did not allow conclusions to be made about the paper machine white water samples (Fig. 3.15).

Similar to the screen accepts liquid sample and its pH values, there were no consistent trends between sample pH and total white water extractives (Figs. 3.13, 3.15, and Table 3.1). The pH values of the white water varied from a pH of 5.73 to a pH of 9.09. Tyrvainen (1997) attributed the white water pH fluctuations to the amount and composition of the recycled material purchased and pulped into the papermaking process.

The changes in pH were felt to be partly attributed to the calcium carbonate content of the secondary fiber entering the production line (Tyrvainen, 1997).

A larger sample or different filtering process used for separating the fines from the white water liquid may have reduced the within sample variability seen for the petroleum ether white water total extractives. Again the total amount of extractives from a 100 ml sample was small - only 3 mg or less. The filtering step of the sample preparation may also have removed some of the larger colloidal resin particles from the sample and thus possibly reduced the amount of extractives present in the liquid sample.

4.2.5 Conclusions - Mill Samples - Total Extractives

Due to the nature of the wood chips sample, it was difficult to obtain a representative sample although every effort was made to obtain a random representative sample. Under controlled conditions, perhaps on a pilot scale, a sample with the appropriate ratio of fir to spruce could be produced but in an industrial setting it may not be realistic. There were only minor differences in the total extractives levels for both the primary and secondary refiner blow line samples. Both refiner samples only showed small month-to-month variations with no overall seasonal trends. The screen accepts pulp sample appeared to have a cyclical nature between April and October. It appeared to be a good sample for monitoring the total extractives in the production line at the mill. The screen accepts liquid sample, in contrast, did not show the same seasonal patterns as the screen accepts pulp. There was also no link found between the screen accepts liquid pH and the total extractives present in the pulp or the liquid portions of the sample. The

paper sample from the mill showed a reduction in total extractives when compared to the wood chip and mill samples. The paper sample did not show any seasonal trends for its total extractives.

4.3 Wood Cores - GC Analysis

As a result of the limited information available on the seasonal changes in the extractive composition of balsam fir and black spruce, examples of other conifer studies (Norway spruce and pine) were used in the discussion of the results of this study.

4.3.1 Sapwood Analysis

4.3.1.1 Fir Sapwood - GC Analysis

When within sample variability was factored in, there were only two months which were different from the others in terms of fatty acid concentrations. Fatty acid concentrations in the forest fir sapwood were higher for May and August (Fig. 3.16). The other months sampled showed very little difference in fatty acid concentrations for the forest fir sapwood sample (Fig. 3.16). This agreed with the work conducted by Saranpaa and Nyberg (1987) on Pinus sylvestris in Helsinki, Finland, who also found that there was increased levels of fatty acids in the sapwood at the beginning and end of the growing period (end of April and middle of August, respectively). Saranpaa and Nyberg (1987) noted that there was a fairly large variation of free fatty acids in the different trees studied. Since the forest fir sample in this study was a composite of cores from six different trees, then tree-to-tree variations should have been reduced. However Ekman et al. (1979) sampled Norway spruce for a period of one year and found very little seasonal variation in the fatty acids studied (palmitic, oleic, linoleic, and pinolenic).

The first major observation of resin acid concentrations for the forest fir sapwood sample was the elevated levels of resin acids in April (Fig. 3.16). Resin acid

concentrations remained low for the other months sampled (Fig. 3.16). Ekman et al. (1979) found there was very little seasonal difference in the resin acid composition of sapwood extractives with only slightly lower resin acid contents in the sapwood during the summer months for Norway spruce. The large resin acid peak in April may be indicative of some physiological change in the tree, possibly related to the initiation of the growing season. However, more samples would be required around this time period to determine if this large resin acid peak was related to physiological processes or sampling location (i.e. sampled an area containing a high concentration of resin).

There were only minor changes in the components which were grouped into the alcohols, sterols, and waxes (ASW) group during the sampling period for the forest fir sample. Similarly, Ekman et al. (1979) found no seasonal differences in the levels of alcohols and sterols in Norway spruce.

The EFA profile for the forest fir sapwood samples showed constant levels (when variability was considered) between November and May (Fig 3.16). EFA levels were at their highest levels during the sampling period between June and October. Kramer and Kozloski (1979) state that trees such as pines have higher fat content in the winter months while other tree species have high fat content in winter but lower fat content in summer. The EFA fraction of the forest fir sapwood sample appeared to have increased EFA levels during the late summer and fall months but low levels during the winter months of December to March.

When the yard fir #1 sapwood samples were compared to the forest fir samples for the same time period, the fatty acid levels were similar and constant. Resin acid levels were slightly lower for the yard sample in November and December. However, when the large within sample variability was accounted for in the resin acids group of the forest fir sapwood sample, the differences between the forest fir sapwood and yard fir #1 sapwood were only minor. The yard fir #1 ASW levels and EFA levels were low and only showed small variations between November and February and again were similar to the forest fir sapwood sample (Figs. 3.16 and 3.17). It was not surprising that the GC analysis results for the yard fir #1 sample were similar to the forest fir sapwood sample. It was felt that since the trees for the first yard sample were harvested late in the fall and seasoned during the colder winter months that they would resemble the profile of extractives in the living system sampled in the forest fir stand. Nugent et al. (1977) found only small changes in the extractive composition at sub-zero temperatures. The similarities between the two samples may partly be explained by the fact that physiological processes continue after the tree is harvested and the chemical extractive profile would continue to resemble the living tree for a period of time. When a tree is harvested, all its metabolic processes are not abruptly terminated nor are they suspended (Cohen, 1962). Thus the extractive profile at the time of harvesting is not preserved but is dynamic.

The yard fir #2 sapwood sample did not display the large resin acid peak observed in the forest fir sapwood sample for April (Figs. 3.16 and 3.18). Since these logs were

only harvested in mid-March, the large peak observed in the forest sample may have been related to sampling as opposed to physiology. There were higher levels of fatty acids observed in the yard fir #2 sapwood sample from May to August, however this was also observed in the forest spruce sample. It was possible that these increases were for different reasons. In the forest fir sapwood sample the increases could be related to tree physiology while in the yard samples they could be related to seasoning and the hydrolysis of EFAs. Nugent et al. (1977) found that there was an increase in fatty acids levels in the period following 2 months post-harvest. Two months post harvest for the yard fir #2 sample would correspond with the month of May in the sample. This presented the question of which changes in extractive chemical composition were related to seasoning and which were related to continued physiological processes occurring in the wood. The ASW group in the yard fir #2 sapwood sample showed increased levels in May, June, and August (Fig 3.18). These increased levels in May and June were not observed in the forest fir sapwood sample and may be related to seasoning. Nugent et al. (1977) also observed an increased level of sterols that began two months post-harvest in black spruce. The increases in EFA levels observed for the forest fir sapwood sample in August were not observed in the yard fir #2 sapwood sample (Figs. 3.16 and 3.18). This may be an indication of the changes in the EFA content of the yard fir #2 sample as a result of seasoning. Several references point to a decrease in EFA content as a result of seasoning (Cohen, 1962; Assarsson and Akerlund, 1966; Nugent et al., 1977). Cooler initial temperatures at the time of harvest may have delayed visible changes in the EFA

content of the yard sample as a result of seasoning until 5 months post harvest.

The yard fir #3 sapwood sample had a fatty acid profile which was similar to the forest fir sapwood sample (Figs. 3.16 and 3.19). The elevated levels of fatty acids in the August forest fir sapwood sample was also observed in yard fir #3 sample at 3 months post harvest. It was again unclear whether this was a physiological or seasoning process at work. In contrast, the resin acid profile for the yard fir #3 sample showed a decreasing trend for the entire sampling period while the forest fir sample showed elevated resin acid levels in August and October. This may point to possible seasoning mechanisms at work on the resin acids in the yard fir #3 sample. The ASW group showed very little variation throughout the sampling period for the yard fir #3 sample while the forest fir sample showed slightly elevated ASW levels in August, September, and October (Figs. 3.16 and 3.19). Although EFAs were still at increased levels in August, September, and October in the yard fir #3 sample they were not as high as the levels observed in the forest fir sapwood sample for the same months (Figs. 3.16 and 3.18). This may indicate that there were some seasoning mechanisms reducing the amount of EFA components in the yard fir #3 sample in the period 3-to-5 months post harvest.

4.3.1.2 Spruce Sapwood - GC Analysis

The first major difference between the forest spruce and the forest fir sapwood profiles was the fact that the resin acids group were the dominant component in forest spruce sapwood samples and the fatty acid component was less of a contributor to the extractive profile (Figs 3.16 and 3.20). This was obvious in the chromatograms produced

from the fir and spruce samples and will be highlighted later in the chromatogram discussion section. The fact that black spruce wood contains resin canals (absent in balsam fir) is one explanation as to why resin acids are the dominant component in spruce extracts. Even at their highest levels the forest spruce sapwood fatty acids were only present in small amounts and did not display any major seasonal fluctuations. This observation was similar to those made by Ekman et al. (1979) who found no variations in the sapwood fatty acids in Norway spruce.

There was considerable within sample variability for the forest spruce sapwood resin acids between November and June and no conclusions could be drawn (Fig. 3.20). There was an obvious decrease in resin acid levels between August and October for the forest spruce sapwood samples. In contrast, Ekman et al. (1979) found slightly lower resin acid levels in the sapwood of Norway spruce during the summer months. This could not be confirmed in the forest spruce sapwood sample due to large within sample variability during the summer months.

The forest fir sapwood ASW levels were constant during the sampling period (Fig. 3.20). This was in agreement with the findings of Ekman et al. (1979) for alcohols and sterols.

There was very little change in the EFA levels for the forest spruce sapwood sample between November and May. Following May, EFA levels jumped sharply in June and remained elevated but decreased slightly between August and October (Fig. 3.20). The jump in EFA levels in June, although small, may be related to the initiation of the

growing season or some processes related to the growing period of the tree. A jump in the EFA levels was also observed for the forest fir sapwood sample around the period between May and June.

The yard spruce #1 sapwood sample showed little change during the sampling period. Resin acids were still the dominant component but much lower in concentration than observed in the forest spruce sapwood sample for the same period (Figs. 3.20 and 3.21). The lack of change in the overall profile of the yard spruce #1 sample may have been related again to the fact that the reactions associated with seasoning occurred at slower rates during the colder winter months of the year. As mentioned earlier, Nugent et al. (1977) found negligible changes in the extractives of black spruce stored at sub-zero temperatures.

The yard spruce #2 sapwood sample showed a fatty acid profile similar to that observed for the forest spruce sapwood sample for the same sampling period. There were no apparent trends in the resin acid profile for the yard spruce #2 sample and resin acid levels were constant during the sampling period (Fig. 3.22). Quinde and Paszner (1991) found very little change in the total resin acids even after 24 weeks of seasoning of slash pine. However, there were significant changes in the composition of the resin acids group of slash pine after 24 weeks of seasoning (Quinde and Paszner, 1991). The ASW levels for the yard spruce #2 sample remained constant during the sampling period (Fig. 3.22). The forest fir sapwood for the same time period also remained constant. The sharp jump in EFA levels observed in the forest spruce sapwood sample for August was

also observed in the yard spruce #2 sample in August. This may indicate that something physiologically is occurring in the tree during August and, as indicated earlier, could be related to the growing season. It appeared as though the EFA levels increased slightly in the forest spruce sapwood sample between June and August while they decreased in the yard spruce #2 sample. Variability within the yard spruce #2 sample did not allow any conclusions to be made related to this or a potential seasoning effect (Figs. 3.20 and 3.22).

The fatty acid profile observed for the yard spruce #3 sapwood sample was similar to the profile observed for the forest spruce sapwood sample (Figs. 3.20 and 3.23). In both cases the levels of fatty acids were very low and the differences between months were small. The yard spruce #3 sapwood resin acid profile showed elevated levels of resin acids in May and June and a sharp drop in resin acids in August which persisted until October (Fig. 3.23). This drop was also present in the forest spruce sapwood sample but was more gradual (Fig. 3.20). The decrease in resin acids at the 3-to-5 month post-harvest stage may indicate a reduction in resin acids; at least in the compounds which were used to quantify the resin acids group. The ASW group showed very little variation in both the yard spruce #3 sample and the forest spruce sapwood sample between May and October (Figs. 3.20 and 3.23). The EFA group for the yard spruce #3 sample showed the same jump in EFA levels in May and June that was observed for the forest spruce sapwood sample (Figs. 3.20 and 3.23). While EFA levels showed a steady decrease between August and October in the forest spruce sapwood sample, they were found to

fluctuate between August and October in the yard spruce #3 sapwood sample and no conclusions could be made related to the EFA group for the yard spruce #3 sample.

4.3.1.3 Conclusions - Sapwood - GC Analysis

In the forest sapwood samples there appeared to be some indications of increased levels of fatty acids, resin acids, and EFAs around the beginning and end of the growing season (April to August). The forest fir sapwood sample had a large jump in resin acids during April and increased levels of fatty acids and EFAs in August. Similarly, the forest spruce sapwood sample had increased levels of EFAs in June and increased levels of fatty acids in August.

When some yard sapwood samples were compared to the forest sapwood samples, they appeared to show seasoning effects. These effects were not consistent among all samples. In the first months following harvest, the yard samples appeared to follow similar trends to the forest samples. This was especially true for the yard fir #1 and yard spruce #1 samples which were left to season during the colder winter months. There appeared to be a delay of seasoning associated with the cold temperatures encountered during storage of the yard #1 samples. The second and third yard samples appeared to show more potential for seasoning especially when the profiles for 3-to-5 months post harvest were compared to the forest samples. There was a reduction in the EFA levels and resin acid levels observed for some of the yard samples (yard fir #2, yard fir #3, and yard spruce #3). In contrast, there were small increases observed in the ASW group and fatty acid groups in some of the yard samples (yard fir #2 and yard fir #3). These

increases may also be an indication of seasoning occurring in the yard samples, especially in the 3-to-5 month post-harvest samples as the hydrolysis of EFAs to fatty acids. However, it was difficult to separate changes in the extractives composition of the yard samples that resulted from physiological processes which continued in the tree following harvest and the mechanisms of seasoning at work on the wood such as the oxidation and reduction of compounds and degradation of extractives by microbes. The profile produced in the yard samples was likely a combination of both. The storage of logs in roundwood form as opposed to chips is also known to decrease the rate of seasoning in wood.

In some cases changes were observed which differed from those observed in the current literature. Some of the observed changes in this study may have been a result of changes in ratios of the different compounds which were used to quantify a group of compounds. Some compounds may have been converted into compounds which were not quantified in the grouping used in this study. The same could also hold true for groups which may have unexplainably increased in concentration as a previously unquantified compound was converted or degraded into a quantified compound.

In some samples the biggest contributor to inconclusive findings was sample variability. The amount of material used for the extraction of the wood core samples was small and may have introduced error into the quantitation process. Future work should use larger cores or more cores each month to help increase the accuracy and precision of the analysis of the extractives.

4.3.2 Heartwood Analysis

4.3.2.1 Fir Heartwood - GC Analysis

The fatty acids group was found to be the most dominant group in the forest fir heartwood sample and the resin acid group was found to be the least dominant. The dominance of the fatty acid group in the fir sample allowed for quick differentiation from the spruce samples which were dominant in resin acids (Figs. 3.24 and 3.28). The fatty acid levels in the forest fir sapwood were lower in concentration than those levels observed for the forest fir heartwood. Ekman (1979) also found that, when comparing the sapwood and heartwood fatty acids of Norway spruce, they were much higher in the heartwood. The forest fir heartwood fatty acids were found to be at increased levels of concentration in November and December and at seasonal high levels in August (Fig. 3.24). These seasonal high levels of fatty acids in the heartwood in August may correspond to the growing season in the fir tree. Saranpaa and Nyberg (1987) found increased levels of fatty acids in the sapwood of pine trees at the beginning and end of the growing season. In contrast, Ekman et al. (1979) found no significant seasonal variations in the fatty acids for Norway spruce.

Resin acid levels in the forest fir heartwood sample increased sharply in April but were still in low concentrations (Fig. 3.24). These increased levels were likely related to elevated levels of resin acids in the forest fir sapwood sample for April (Fig. 3.16). As mentioned earlier, this increase may have been related to physiological processes in the tree or a sampling-related issue.

The ASW group was in greater concentration in the forest fir heartwood sample than the forest fir sapwood sample (Figs. 3.16 and 3.24). In contrast, Ekman (1979) found minimal differences in sapwood and heartwood concentrations of alcohols and sterols. Overall, the ASW group for the forest fir heartwood sample showed slightly higher levels in November and June than for the other months sampled. However, these differences were not sufficient to qualify as a trend.

The EFA group showed slightly higher levels in March and September in the forest fir heartwood sample but, for the most part, EFA levels remained constant during the sampling period (Fig. 3.24). Tyrvainen (1997) stated that extractives are usually stable in the heartwood of a tree since the heartwood is dead tissue. This may explain the small seasonal differences observed for the heartwood extractives of this study.

For the most part, the extractive profile of the yard fir #1 heartwood sample mirrored the profile in the forest fir heartwood sample. This was felt to result from the cooler temperatures encountered during the winter seasoning period for the first yard samples.

The yard fir #2 heartwood sample had a similar profile to the corresponding months in the forest fir heartwood sample with respect to fatty acid levels but with the exception of slightly higher fatty acid levels in March (Figs. 3.24 and 3.26). There was no evidence of the largely elevated resin acid levels for April observed in the forest fir sapwood sample when compared to yard fir #2 sapwood and yard fir #2 heartwood samples (Figs. 3.18 and 3.26). This further reinforced that the large peak in resin acids

observed for the forest fir sapwood sample was likely related to sampling. Both the ASW and EFA groups showed only small variations in concentrations during the yard fir #2 heartwood sampling period (Fig. 3.26). The profiles observed for the ASW and EFA groups were similar to those observed in forest fir heartwood sample (Figs. 3.24 and 3.26). This was expected since there is no metabolic activity in the dead heartwood cells of a tree. Tyrvainen (1995) states that the sapwood moisture can be as high as 60% while heartwood moisture ranges around 30% moisture in spruce. The decreased levels of moisture present in the heartwood may also help to preserve the heartwood composition even during storage. Nugent et al. (1977) found that some of the components in the dry heartwood of black spruce were resistant to seasoning and showed only small changes even after 7 months of seasoning.

The yard fir #3 heartwood sample showed slightly elevated levels of fatty acids for May (Fig. 3.27). These elevated levels were also seen in the forest fir heartwood sample and the yard fir #2 heartwood sample (Figs. 3.24 and 3.26). Since these elevated levels were present in three different heartwood samples it was felt that something physiologically is occurring in fir trees in May. These increased fatty acid levels may have been related to the initiation of the growing season. There were increased levels of fatty acids in the yard fir #3 heartwood sample in September (4 months post–harvest). Also in September there was a small decrease in the EFA fraction of the yard fir #3 heartwood sample (Fig. 3.27). This may indicate a hydrolysis of the esterfied fatty acids causing an increase in the free fatty acids present in the tissue. The resin acid profile for

the yard fir #3 sample showed low levels in August and September and increased levels in October when compared to the forest fir heartwood sample (Figs. 3.24 and 3.27). The decreased levels of resin acids seen for August and September may indicate some seasoning mechanisms at work in the yard sample and an unexplained increase in October may be related to sampling. The ASW portion of the yard fir #3 heartwood sample showed a small decrease between August and October while the ASW group in the forest fir heartwood sample remained almost the same (Figs. 3.24 and 3.27). Overall, the differences in the ASW group between the forest fir heartwood sample and the yard fir #3 sample were very small. The EFA group for the yard fir #3 heartwood sample was similar (a slight drop in September) to the forest fir heartwood sample and remained constant throughout the sampling period. As highlighted by Nugent et al. (1977) some compositional changes were slow to occur in the heartwood of black spruce. This may explain the similarities found between the forest fir heartwood samples and the yard fir heartwood samples.

4.3.2.2 Spruce Heartwood - GC Analysis

Like the forest spruce sapwood sample, the forest spruce heartwood sample had a greater proportion of resin acids in its profile than any other group (Figs. 3.20 and 3.28). As mentioned earlier there is a morphological reason for this in that spruce wood contains resin canals. Fatty acids were found to drop in May and no explanations could be made for this other than sampling problems. These increased levels of fatty acids in April, June, and August may have been associated with the growing period in the tree.

The forest spruce heartwood sample showed elevated levels of resin acids for December and October (Fig. 3.28). However, variability within the monthly samples restricted the conclusions which could be made (Fig. 3.28). The increasing resin acids in the heartwood late in the sampling period may be a result of resin movements associated with previous bore holes from sampling. Ekman et al. (1979) found in monthly-sampled trees that there was a vertical movement of resin from previous bore holes into the surrounding tissue. Ekman et al. (1979) discarded samples from smaller trees after 5 months of sampling because of converging bore holes in the trees contaminating later samples of Norway spruce wood cores. In the same study, there were no movements of resin associated with sampling in the sapwood (Ekman et al., 1979).

The ASW and EFA groups remained constant during the sampling period for the forest spruce heartwood sample when sample variability was considered.

The yard spruce #1 heartwood sample had a profile similar to that of the forest spruce heartwood sample. Absent from the yard spruce #1 heartwood sample was the increased level of resin acids in December (Figs. 3.28 and 3.29). The absence of the resin acid peak for December in the yard spruce #1 heartwood sample may indicate that the elevated levels observed in the forest spruce heartwood were related to sampling variability as opposed to physiological processes. Otherwise, the extractive profile for all groups remained constant throughout the sampling period. As seen in the other yard #1 samples, there were only small changes in the extractive compositions during the cooler winter months.

The yard spruce #2 heartwood fatty acids concentrations were roughly the same between March and June (Fig. 3.30). These levels were lower than those observed in the forest spruce heartwood sample for the period between March and June. The levels of fatty acids observed for August in the yard spruce #2 sample were similar to those observed in forest spruce heartwood sample. There was no explanation for the decrease in March through June fatty acid levels observed for the yard spruce #2 heartwood samples. Like the fatty acids, the resin acids were constant between March and May but lower than those levels observed for the forest spruce heartwood sample. The resin acid levels for the yard spruce #2 heartwood sample for June and August were similar to those observed in the forest spruce heartwood sample but the August yard spruce #2 resin acids were slightly lower than the forest sample (Figs. 3.28 and 3.30). Again, this variation in the forest spruce heartwood sample could not be explained. The ASW and EFA groups for the yard spruce #2 heartwood sample were similar to the forest sample for the same sampling period and showed no variation (Figs. 3.28 and 3.30). The constant levels of ASW and EFA groups in the yard spruce #2 sample were also seen in the yard fir #2 and #3 heartwood samples and the yard spruce #1 heartwood sample.

The yard spruce #3 heartwood sample fatty acids showed a similar profile to the forest spruce heartwood sample for the same time period (Figs. 3.28 and 3.31). The similarities between the two samples, especially in the later months where the logs had been seasoned for 3-to-5 months, indicated that there was limited change in the fatty acid composition in the spruce heartwood as a result of seasoning. The resin acid group for

the yard spruce #3 heartwood sample began to differ from the forest spruce heartwood sample between August and October. Resin acids in the yard spruce #3 sample were found to decrease in the period of 3-to-5 months post-harvest (Fig. 3.31). This decrease in resin acids trend was also seen for the yard spruce #2 heartwood August sample and may have been an indication of a change in the composition the resin acids group after 3-to-5 months of seasoning (Fig. 3.30). There were significant changes in the resin acid composition of slash pine observed by Quinde and Paszner (1991) during seasoning. Again, both ASW and EFA levels of the yard spruce #3 heartwood sample were similar to the forest spruce heartwood sample for the same time period and did not show any major changes (Fig. 3.28 and 3.31). This was in accordance with the other yard spruce and fir heartwood samples which showed only small changes in their extractive composition during seasoning.

4.3.2.3 Conclusions - Heartwood - GC Analysis

Fatty acids were the most dominant group of extractives in the fir heartwood samples while resin acids were the most dominant group of extractives for the spruce heartwood samples. On average, fatty acids were higher in concentration in fir and spruce heartwood samples when compared to fir and spruce sapwood samples. Small increases in the concentrations of fatty acids were observed in the forest fir heartwood and the forest spruce heartwood during the growing season (April to August). Overall, the ASW and EFA levels do not show any trends in all the sapwood and heartwood (both forest and yard) fir and spruce samples observed. The first sets of fir and spruce yard

heartwood samples did not show notable changes in composition during the sampling period and in most cases followed the profile of the forest heartwood samples for the same time period. The yard fir #2 heartwood sample showed no change in its extractive composition and mirrored the forest fir heartwood sample. In contrast, the yard spruce #2 heartwood sample had unexplained decreases in fatty acids and resin acids when compared to the forest spruce heartwood sample during the first four months of sampling. The yard fir #3 and yard spruce #3 heartwood samples showed decreases in the resin acid levels following 3-to-5 months of seasoning.

The heartwood region of fir and spruce trees showed only small changes during the sampling period. These changes did not give any evidence of seasonal related changes in the lipophilic extractive composition of fir and spruce heartwood.

4.4 Mill Samples - GC Analysis

4.4.1 Wood Chips

The GC analysis of the wood chip extractives produced a profile which was a mixture of both fir and spruce sapwood and heartwood and contained considerable amounts of both fatty acids and resin acids. The fatty acid group was the most dominant group in the wood chips sample (with the exception of January). However, the wood chip sample was highly variable and showed no consistent fatty acid trends (Fig. 3.32). The large variability in the wood chips sample was expected since there was also variability in the wood chips total extractives. The resin acid and ASW group showed no consistent seasonal changes in the extractives composition (Fig. 3.32). EFA group of extractives in the wood chips sample remained constant during the sampling period (Fig. 3.32). Sampling variability was felt to be the key contributor to composition changes observed for the wood chips sample.

4.4.2 Primary Refiner

The primary refiner samples had less month-to-month variability between samples when compared to wood chips sample (Figs. 3.32 and 3.33). The primary refiner sample was felt to be a more consistent sample that better reflected the proportions of fir and spruce used by the mill. The fatty acids group in the primary refiner sample showed an increasing trend from low levels in November to seasonal high levels in July. These elevated fatty acid levels in the spring and summer months may be a result of the fact that the mill uses freshly harvested wood during this period and these elevated levels of fatty

acids were seen around this same time period in the forest wood cores. Unfortunately these changes are small and more regular mill samples would be required to determine if a trend exists. Tyrvainen (1997) states that most of the wood used by the mill during the summer has been harvested between one week and one month prior to use. Many of the metabolic process occurring in the tree would be expected to continue up to the time of pulping since, following the first two months of harvest, the extractive profile for yard samples is similar to the living trees. Resin acids levels remained similar during the sampling period with slightly higher levels observed for November and June (Fig. 3.33). These small variations in the resin acid profile were felt to be a result of variations in the wood supply not a seasonal trend. Both the ASW and the EFA groups remained stable during the sampling period. EFA levels were inexplicably higher in the primary refiner sample than in the wood chips sample.

4.4.3 Secondary Refiner

The secondary refiner samples showed a drop in fatty acids and EFAs when compared to the primary refiner and wood chip samples. These components were likely extracted by the water and/or steam used or generated during refining. Fatty acid levels for the secondary refiner samples showed small seasonal changes with fatty acid levels being slightly higher in July, August, and September (Fig. 3.34). This may be related to the fresh wood supply also showing a tendency towards increased fatty acids in the summer months. The resin acid, ASW, and EFA groups did not show any seasonal trends during the sampling period for the secondary refiner samples. The

EFA group, overall, was lower in concentration when compared to the primary refiner samples.

4.4.4 Screen Accepts - Pulp

The fatty acid portion of screen accepts pulp lipophilic extractives was the dominant component for most of the months sampled. With the exception of January, there was a general increasing trend for fatty acids between November and July (Fig. 3.35). A similar trend was observed for the primary refiner sample fatty acids group. The resin acids group was found to be too variable during the sampling period for conclusions to be made (Fig. 3.35). The overall trends for the fatty acids and resin acids were more variable than expected and may be related to the fact that the process waters are now contributing to the extractives present in the pulp. There were no changes in the ASW and EFA groups of the screen accepts pulp during the sampling period. Levels for the ASW and EFA groups were similar to those observed in the wood chip and primary refiner samples. These components may be less soluble in the pulp and paper process or the process waters may already be saturated with these components. Ekman et al. (1990) found that, as the concentration of dissolved substances increases in the pulp process waters, the capacity to dissolve additional lipophilic extractives decreases.

4.4.5 Screen Accepts - Liquid

The within sample variability was much higher in the screen accepts liquid sample when compared to the other mill samples. The fatty acids group almost showed a decreasing trend between January and April and an increasing trend between April and

August (Fig. 3.36), however, the fatty acid samples were highly variable and as a result no conclusions could be drawn. The resin acids group did not show any seasonal trends and also had large month-to-month fluctuations (Fig. 3.36). The ASW group showed minor and inconsistent monthly changes. The EFA group also had large monthly fluctuations which did not allow for conclusions to be made on seasonal trends. Despite this, the EFA group was often the second most dominant group, next to fatty acids, in the screen accepts liquid sample (Fig. 3.36). This was thought to be the result of the gradual accumulation of EFAs extractives in the process waters at the mill. Accumulations of extractives in the process waters of a mill have been found to cause deposit formations on paper machines and paper, decreased wet strength (important in sheet formation), interferences with process chemical, and impaired paper strength and brightness (Sundberg et al., 1996).

4.4.6 Paper

It was difficult to determine which portions of the paper sample profile came from the wood supply and which came from the recycled furnish. Since the recycled furnish was not sampled at the same time or monitored by this study the statements which can be made about paper sample in relation to the wood supply are limited. The fatty acids group still remained the dominant component in the paper sample although they were at lower levels than the initial wood chips samples. Fatty acid levels were inexplainably lower in May, June, and August (Fig. 3.37). Resin acid concentrations were generally low and stable in the paper sample but jumped sharply in July and remained at elevated

levels for the rest of the sampling period. This jump could not be explained and was not present in any of the wood core samples or other mill samples. The ASW and EFA groups were in low concentrations and stable in the paper sample.

4.4.7 Conclusions - Mill Samples - GC Analysis

Finding seasonal trends in a production system based on monthly samples was difficult and most groups remained constant within each sampling period during the study. There was only one potential seasonal trend for the mill samples. This was the slightly increased levels of fatty acids in the summer months for the primary and secondary refiner samples but they were not statistically significant. There were also changes in overall sample compositions that occurred at the sequential stages of the pulp and paper process.

The wood chips sample was too variable to draw conclusions about the seasonal trends occurring in the sample but it gave an idea of the proportions of the different components in the sample. The primary and secondary refiner samples were less variable and felt to be the most consistent samples. The refiner samples were thought to be the best mixed samples and a good reflection of the wood supply. Initially the screen accepts pulp sample was thought to be a good sample to use for monitoring the wood supply (based on total extractive data), however the GC analysis of the screen accepts pulp and liquid samples showed that they were too variable to serve this purpose. It was suspected that additional variability was introduced into the screen accepts pulp and liquid samples from the recycled process waters of the mill that were already rich in dissolved and

colloidal extractives.

Fatty acids were consistently the most dominant portion of the mill samples. The second most dominant component was usually the resin acids group. An exception to this was the liquid screen accepts sample which usually had the EFA group as the second most dominant group in its samples. The ASW and EFA groups remained consistent within samples but sometimes changed concentrations between samples. There was an overall drop in fatty acid and EFA concentrations between the primary refiner and secondary refiner samples. It was thought that some of these components were released and lost from the pulp during refining.

The contribution of the recycled furnish was felt to limit the conclusions made about the paper sample with respect to the wood supply. Fatty acids were still the dominant component in the extractive compounds that were quantified. Most of the components in the paper samples were at their lowest levels in comparison to the other mill samples, however, resin acids increased sharply in July, August, September, and October, and this could not be explained as there was no evidence of this in the other mill samples. The paper machine white water extractive analysis was not included in the GC analysis section because problems were encountered during the GC analysis of these samples. It was suspected that there were problems introduced by the pitch-controlling additives used by the mill in the white water system which interfered with the GC sample preparation.

4.5 GC Analysis Chromatograms

Although all the peaks in each chromatogram were not quantitated, general conclusions were made about the chromatograms. There were regions of the chromatogram which were predominantly one type of compound. Some compounds crossed over into other groups but this was not often observed. The fatty acids group had the shortest retention times and eluted early in the chromatogram. The resin acids group followed the fatty acids group with slightly longer retention times. The ASW and EFA groups eluted in the latter part of the GC run. Triglycerides were found to elute at the very end of the GC run. There was some retention time shifting of compounds but standards were run on a regular basis to correct for these shifts.

4.5.1 Forest Wood Core Chromatograms

The fir and spruce samples showed obvious differences in their chromatograms with fatty acids being the dominant group in the fir samples and resin acids being the dominant group in the spruce samples (Figs. 3.38 and 3.39). When wood core samples were compared radially, there was a greater abundance of fatty acids in the heartwood of the both the fir and spruce samples. Ekman (1979) also found increased levels of fatty acids in the heartwood of Norway spruce. Chromatography has been used in other instances to differentiate between different species of wood. Sundberg et al. (1997) found that they could differentiate between pine and spruce by the ratios of two resin acids (pimaric acid and sandaracopimaric acid) in their wood.

4.5.2. Yard Wood Core Chromatograms

The species-specific differences between fir and spruce remained even after five months of seasoning (Figs. 3.40 and 3.41). Fatty acids remained the dominant group in the fir samples and resin acids remained the dominant group in the spruce samples. The persistence of these groups would allow for fast differentiation of wood samples based on their chemical compositions. One of the known changes which occurs as a result of seasoning is the reduction of EFAs, especially triglycerides, to fatty acids. This has already been determined in seasoning studies such as Nugent et al. (1977). These changes in EFA and fatty acid composition were apparent when the forest sapwood and yard sapwood samples were compared. There was an increase in size and quantity of peaks in the fatty acids group of the yard fir and spruce sapwood samples when compared to the forest fir and spruce sapwood samples (Figs. 3.38 and 3.40). The fir heartwood samples showed a small reduction in fatty acids between the forest fir heartwood sample and the yard fir heartwood (Figs. 3.39 and 3.41). This may have resulted from the fatty acid oxidation mechanisms associated with seasoning and was not observed in the spruce heartwood samples. It should be noted that although differences in the fatty acids profile between the forest fir heartwood and yard fir heartwood were observed, they are only raw GC data files that do not reflect the differences in quantity of initial extracted sample. The graphical figures of the GC analysis work took into account the original sample sizes and applied the appropriate correction factors (Figs. 3.16-3.37).

4.5.3 Mill Sample Chromatograms

The utilization of both fir and spruce species in the manufacturing of paper was evident in the mill samples. There were fatty acid and resin acid peaks present in all the mill samples. The wood chip sample was naturally a reflection of the combination of the fir and spruce wood core chromatograms (Figs. 3.38-3.42). There was a reduction in the fatty acids and resin acids present in the wood chip samples following refining. This was obvious by the decrease in the number and size of fatty acid and resin acid peaks for the primary refiner, secondary refiner, and screen accepts pulp sample (Fig. 3.42). Earlier, it was reported that there was a reduction in the fatty acids and EFAs between the primary refiner and the secondary refiner. This was not apparent in the chromatograms but did occur in the compounds used to represent the fatty acids and EFA groups. The secondary refiner sample was slightly more concentrated than the primary refiner sample (as seen by the peak heights of the internal standards). As mentioned above, the original sample concentrations were taken into account for the calculations associated with the data but were not obvious in the chromatograms. The screen accepts liquid chromatogram was notably different from the other mill samples and demonstrated an accumulation of fatty acids and EFAs in the process waters of the mill (Fig. 3.43). It also should be considered that petroleum ether was used as the extracting solvent in the liquid samples. The chromatogram of the paper sample showed a large reduction in extractives, especially fatty acids. This reduction was also obvious in the August fatty acid peak of the GC analysis graph (Fig. 3.37) for the paper sample. The lack of change observed for the

ASW and EFA groups in the graphical GC analysis data of the mill samples (Figs. 3.32-3.37) was confirmed by the mill sample chromatograms (Figs. 3.42 and 3.43). There were only small changes to these corresponding ASW and EFA areas of the mill chromatograms (with the exception of the liquid samples) and visually demonstrated the constant levels of these types of compounds in the mill process line.

4.5.4 Conclusions - GC Analysis Chromatograms

Species- specific differences were obvious even through visual examination of the GC analysis chromatograms. Fir samples showed a dominance of peaks in the fatty acid area of the chromatograms with fewer and smaller peaks in the resin acid area of the chromatograms. In contrast, spruce samples showed fewer and smaller peaks in the fatty acids area of the chromatograms and a greater number of larger peaks in the resin acids area of the chromatogram. There was an obvious increase in the number and size of fatty acid peaks in the heartwood of the fir and spruce samples. Seasoning was evident in the yard samples when compared with the forest samples, especially in the sapwood portions, as there were an increased number and size of fatty acid peaks present in the seasoned logs.

The mill sample chromatograms showed fatty acid peaks and resin acid peaks characteristic of both fir and spruce samples. There were reductions in fatty acids as a result of refining. Some of the peaks in the resin acid group were also observed to decrease between the wood chips and the primary refiner. The primary refiner, secondary refiner, and screen accepts pulp samples produced visually similar chromatograms. The

screen accepts liquid sample was considerably different from the other mill samples and showed an accumulation of fatty acids and esterfied fatty acids. The paper sample chromatogram showed a reduction in extractives, especially for the fatty acids group.

5.0 Study Conclusions

There were limited conclusions which could be made based on the total extractive data found in this study. Forest sampled wood cores showed no trends and had inconsistent monthly jumps in the sapwood and heartwood total extractives profiles. These jumps were thought to be related to sampling variability between different trees as opposed to physiological events. Ekman et al. (1979) also found only small season-dependent changes in the total extractives content of Norway Spruce. In contrast, small changes in total extractives amounts were observed for the harvested logs. These changes required a period of 3-to-5 months to appear if the harvested logs that were stored in warm conditions. When the harvested logs were stored during colder months of the year, these changes were slower to appear.

Lipophilic extractives have been found to contribute to "pitch" contamination, paper sheet breaks, paper dirt specks, loss of brightness potential, and mill effluent toxicity (Sundberg et al., 1996; Tyrvainen, 1995; Welkener et al., 1993). When the total extractives data for the mill samples were examined, the wood chip sample was too variable to show any trends. In contrast, the refiner samplers were found to show a more stable total extractives profile. This was probably an indication of a more homogenous sample. On the basis of total extractives, the screen accepts pulp sample appeared to be the best sample for monitoring total extractives at the mill. However the GC analysis of this sample revealed that it was too inconsistent to use for this purpose and that one of the refiner samples might be a better choice for monitoring mill extracties. The liquid

portion of the screen accepts pulp sample showed no seasonal trends and was not affected by pH. The paper sample showed considerably lower levels of extractives but was without seasonal trends. The paper machine white water sample was too variable to make conclusions and may require a different extraction procedure to realize its full potential as sample for monitoring extractives levels in the process waters of the mill.

The gas chromatography analysis of the wood cores and mill samples produced some interesting results. GC analysis showed that in fir samples, both sapwood and heartwood, fatty acids were the dominant component when analyzed using the methods employed in this study. In contrast, resin acids were the dominant component in the spruces samples, both sapwood and heartwood. The sapwood analysis of the wood cores pointed towards events during the summer months of the year, usually between April and August. However, more samples would be required to confirm this. In many cases these trends were repeated in the yard samples confirming the existence of elevated levels especially when the month in question was only harvested 1-to-2 months prior. The wood core samples in this study showed higher levels of fatty acids in the heartwood areas of both fir and spruce when compared to the sapwood. As mentioned above, the time of year in which a log was seasoned was found to effect the composition of the harvested log. This study showed that, following harvest, physiological processes continue for some time in the tree, especially when left in log form. This was deduced from the fact that the composition profiles of the harvested logs resembled the living trees for at least 1-to-2 months following harvest. This was observed to continue for up to 4

months if the logs were seasoned during the winter months. Following 3-to-5 months of seasoning in warm summer temperatures, increases in fatty acids and decreases in EFAs and resin acids were observed for sapwood samples. In heartwood samples these changes were slower and smaller and only small reductions were observed for fatty acids. The ASW and EFA groups were stable in the heartwood samples observed in this study.

GC analysis of the different mill samples showed that the wood chip sample was too variable to draw conclusions from. The refiner samples were decided to be the best indicator of mill wood supply composition. These samples were felt to be most homogenous and have a limited contribution from the mill process waters. There were slight increases in fatty acids in the refiner samples during the summer months. This coincided with the increased levels of fatty acids in the living trees and seemed logical since most of the wood used during the summer at the mill had only been seasoned between 1 week and 1 month. An overall decrease in fatty acids and EFAs was observed for the secondary refiner sample when compared to the primary refiner. The refining process appeared to cause a reduction in these components. The analysis of the paper samples showed a reduction in the extractives present in the paper but could not account for the inputs from the recycled furnish used at the mill.

Sample chromatograms were included as figures in this study because they gave quick visual indications of the changes in composition of the wood samples and mill samples. The fir sample chromatograms had a greater number and size of peaks in the fatty acids region of the chromatogram while the spruce sample chromatograms had a

greater number of peaks in the resin acids region of the chromatogram. These two main differences in the samples gave quick visual differentiations between the two samples. The increased level of fatty acids in the heartwood of the fir and spruce trees was also easily recognizable by the increased number and size of peaks in the fatty acids region of the chromatogram. The changes in sample composition as a result of seasoning were also easily observed by an increase in fatty acids, especially in the sapwood portions of the yard samples. When the mill sample chromatograms were observed it was obvious that the wood chip sample was a combination of fir and spruce as it was rich in both fatty acids and resin acids. The decreases in fatty acids and EFAs was also apparent in the refiner chromatograms. The screen accepts liquid showed that process water accumulates fatty acids and EFAs. In contrast, the paper sample chromatogram showed that there was a considerable reduction in extractives in the paper sample, especially in the fatty acids region of the chromatogram. Signature profiles of fir fatty acids and spruce resin acids compounds were present in all mill samples at all stages, including the final finished paper product.

The GC analysis work in this study only looked at one quarter to one third of the total lipophilic extractives observed in this study. If the total monthly GC components (fatty acids, resin acids, ASW, and EFA) are summed they only add to about one-quarter to one-third of the total extractives collected for that same month. Many of the compounds present in the total extractives were not quantitated. Some of these components may not have been volatile using the GC configuration employed in this

study while other were not included in the grouping system employed in this study. However when stacked bar graphs of the GC components were made and compared to the total extractive graphs, they resembled the profiles observed for the total extractives.

There were certain limitations with the GC analysis work of this study. All GC work was related to retention times and comparison to known standards. A more complete study would require the use of more specific detectors such as mass-spectrometry. Although the compounds quantified may have been slightly different than the standards, they had similar retention times. Every attempt was made to ensure that same peaks were quantitated in each of the chromatograms and the software integrations and peak selections were confirmed manually for each sample analyzed. This allowed for confident comparisons to be made within samples. However the limitations of non-specific detection in GC-FID were still present. Alternate methods may be required to fully explore the compounds present in the lipophilic extractives of fir and spruce. An alternate method which may work well in a study such as this would be that used by Sithole et al. (1992) which grouped different areas of a chromatogram into groups such as fatty acids and resin acids and then summed all the peaks within that range and applied a group response factor to give concentrations of different component groups.

Due to the lack of specific research on seasonal changes in the extractives content and composition of balsam fir and black spruce, examples from studies of other conifer species were used in the discussion of the results. To obtain a more accurate account of the levels and composition of extractives for the two species of wood used in this study,

more samples would be required.

A complete discussion of seasonal changes in pulp strength, refiner power consumption, pulp brightness, and paper strength at Corner Brook Pulp and Paper during the same period of this study can be found in Tyrvainen (1997). Tyrvainen (1997) examined the production line at the mill and highlighted the need for improved capabilities in the areas of log de-icing, log chipping, wood chip screening, refiner temperature and consistency control, bleaching control, paper machine monitoring, and paper machine process water monitoring.

This study was unable to find any consistent seasonal trends for extractives content or composition in balsam fir or black spruce during the period sampled. However, this study was able to give some indications of the changes, or lack change in some cases, for yard stored wood which was harvested at different times of the year. This study also provided information on the extractives content and composition of mill samples collected at different stages in the paper making process. Analysis of more samples would be required before making recommendations as far as harvesting practices and seasoning practices are concerned

Researchers have found that pulp at certain times of the year produces better quality paper than other times yet there has been difficulty finding chemical differences in these pulps. The methods using in this study were unable to show any differences in the lipophilic extractive content or composition of the refiner pulps produced using the

seasoning practices employed by the mill. The link between tree physiology and seasonal pulp strength, refiner power consumption, pulp brightness, and paper strength problems still requires continued investigation to confirm if a link exists. Initial objectives in looking for correlations between seasonal changes in wood extractives and paper quality problems could not be addressed. This problem is likely a combination of many factors including the wood supply, but there are likely other factors, some may not yet be discovered.

Literature Cited

Alvarado, F., Lindstrom, K., Nordin, J., and Osterberg, F. 1992. Extractives in the process waters from paper making (TMP). Part 1. Determination by size exclusion chromatography-tandem mass spectrometry (SEC-MS-MS). Nordic Pulp and Paper Research Journal 5: 37-41.

Assarson, A. 1966. Studies on wood resin, especially the change in chemical composition during seasoning of the wood: Part 3. The chemical reactions of spruce wood resin during chip seasoning. Svensk Papperstidning 69: 291-299.

Assarson, A., and Åkerlund, G. 1966. Studies on wood resin, especially the change in chemical composition during seasoning of the wood: Part 4. The composition of the petroleum ether soluble nonvolatile extractives from fresh spruce, pine, birch, and aspen wood. Svensk Papperstidning 69: 517-525.

Assarson, A., and Åkerlund, G. 1967. Studies on wood resin, especially the change in chemical composition during seasoning of the wood: Part 5. Changes in composition of nonvolatile extractives during water seasoning of unbarked spruce, pine, birch, and aspen logs. Svensk Papperstidning 70: 205-212.

Assarsson, A., Croon, I., and Donetzhuber, A. 1963. Studies on wood resin, especially the change in chemical composition during seasoning of the wood: Part 2. A comparison of chip seasoning of spruce wood (Picea abies Karst.) with log seasoning. Svensk Papperstidning 66: 940-948.

Bol'skakova, V.I., Demenkova, L.I., and Shmidt, É.N. 1988. Neutral diterpenoids of oleoresins of five species of conifers of Transcarpathia. Chemistry of Natural Compounds 24: 691-694.

Brandal, J., and Lindheim, A. 1966. The influence of extractives in groundwood pulp on fiber bonding. Pulp and Paper Magazine of Canada 67: T431-T435.

Cheung, H.T.A., Fu, S.-L., and Smal, M.A. 1994. Inhibition of platelet aggregation by diterpene acids from Pinus massoniana resin. Arzneimittel-Forschung/Drug Research 44: 17-25.

Cohen, W.E. 1962. The Influence of Resins on Paper Manufacture. pg 421-450 from Wood extractives and their significance to the pulp and paper industries., ed. W.E. Hillis, Academic Press, New York.

Drew, J., and Pylant, G.D. 1966. Turpentine from the pulpwoods of the United States and Canada. Tappi 49: 430-438.

Ekman, R. 1979. Analysis of the nonvolatile extractives in Norway spruce sapwood and heartwood. Abo Academiae Aboensis, Ser. B 39(4): 1-20.

Ekman, R., Eckerman, C., and Holmbom, B.1990. Studies on the behavior of extractives in mechanical pulp suspensions. Nordic Pulp and Paper Research Journal 5: 96-102.

Ekman, R., and Holmbom, B. 1989. Analysis by gas chromatography of the wood extractives in pulp and water samples from mechanical pulping of spruce. Nordic Pulp and Paper Research Journal 4: 16-24.

Ekman, R., Peltonen, C., Hirvonen, P., Pensar, G., and von Weissenberg, K. 1979. Distribution and seasonal variation of extractives in Norway spruce. Abo Academiae Aboensis, Ser. B 39(8): 1-26.

Fengel, D., and Wegener, G. 1983. Wood: Chemistry, ultrastructure, reactions. Walter de Gruyter, New York.

Fischer, C., and Holl, W. 1992. Food reserves of scots pine (Pinus sylvestris L.) II. Seasonal changes and radial distribution of carbohydrate and fat reserves in pine wood. Trees 6: 147-155.

Gao, Y., Chen, T., and Breuil, C. 1995. Identification and quantification of nonvolatile lipophilic substances in fresh sapwood and heartwood of lodgepole pine (Pinus contorta Dougl.). Holzforschung 49: 20-28.

Hemingway, R.W., Nelson, P.J., and Hillis, W.E. 1971. Rapid oxidation of the fats and resins in Pinus radiata chips for pitch control. Tappi 54: 95-98.

Holmbom, B. 1995. Methods for analysis of dissolved and colloidal wood components in papermaking process waters and effluents. Proc. 7th Intl. Symp. Wood Pulping Chemistry (2): 810-817.

Holmbom, B., and Ekman, R. 1978. Tall oil precursors of Scots pine and common spruce and their change during sulphate pulping. Abo Academiae Aboensis, Ser. B 38(3): 1-11.

Hon, D.N.S. 1979. Discoloration and bleaching of thermomechanical pulps. Southern Pulp and Paper Manufacturer 42(3): 23-25.

Hu, T., James, B., and Wang, Y. 1997. Towards inhibition of yellowing of mechanical pulps: Part II: Water -soluble catalysts for the hydrogenation of lignin model compounds. Journal of Pulp and Paper Science 23(5): J200-J204.

Isenberg, I.H., Harder, M.L., and Louden, L. 1980. Pulpwoods of the United States and Canada. Volume I - Conifers. 3rd Ed. The Institute of Paper Chemistry, Wisconsin.

Kahila, S. 1957. Investigations on extract of wood and sulphite pulp made from Picea excelsa. Paperi ja Puu 39: 35-44.

Kramer, P.J., and Kozlowski, T.T. 1979. Physiology of Woody Plants. Academic Press, New York.

Levitin, N. 1967. Review of effect of chip storage on wood resins and pulps. Pulp and Paper Magazine of Canada 68: T454-T460.

Lloyd, J.A., Deacon, N.A., and Horne, C.W. 1990. The influence of pulping and washing conditions on the resin content of radiata pine mechanical pulps. Appita 43(6): 429-434.

Lindstrom, T., Sormark, C., and Westman, L. 1977. The influence on paper strength of dissolved and colloidal substances in the white water. Svensk Papperstidning 80: 341-345.

Levitt, M.J. 1973. Rapid methylation of micro amounts of nonvolatile acids. Analytical Chemistry 45: 618-620.

Mutton, D.B. 1958. Hardwood Resin. Tappi 41: 632-643.

Mutton, D.B. 1962. Wood Resins. pg 331-363 from Wood extractives and their significance to the pulp and paper industries., ed. W.E. Hillis, Academic Press, New York.

Nugent, H.M., Allen, L.H., and Bolker, H.I. 1977. Effect of seasoning on the acetone extractives composition of the wood from black spruce, jack pine and trembling aspen. Pulp and Paper Canada 78: TR103-TR109.

Orsa, F., and Holmbom, B. 1994. A convenient method for the determination of wood extractives in papermaking process waters and effluents. Journal of Pulp and Paper Science 20(12): J361-J365.

Quinde, A.A., and Paszner, L. 1991. Isomerization of slash pine resin acids during seasoning. Appita 44: 379-384.

Roshchin, V.I., Baranova, R.A., and Solov'ev, V.A. 1986. Terpenoids of the needles of Picea abies. Chemistry of Natural Compounds 22: 156-163.

Rudie, A., Shakhet, A., Carter, B., and Griffey, J. 1995. A chlorite holopulping method to evaluate strength changes in TMP. 1995 International Mechanical Pulping Conference: 227-232.

Saltsman, W., and Kuiken, K.A. 1959. Estimation of tall oil in sulphate black liquor. Tappi 42: 873-874.

Saranpaa, P., and Nyberg, H. 1987. Seasonal variation of neutral lipids in Pinus sylvestris L. sapwood and heartwood. Trees 1: 139-144.

Sierra, A.C., Salvador, A.R., and Soria, F.G. 1990. Extraction of wood with solvents. Tappi 73: 221-224.

Sitholé, B.B. 1993. A rapid spectrophotometric procedure for the determination of total resin and fatty acids in pulp and paper matrices. Tappi 76: 123-127.

Sitholé, B.B., Vollstaedt, P., and Allen, L.H. 1990. Comparison of soxtec versus soxhlet for the determination of extractives. Pulp and Paper Research Institute of Canada: Pulp and Paper Report #826.

Sitholé, B.B., Sullivan, and J.L., Allen, L.H. 1992. Identification and quantitation of acetone extractives of wood and bark by ion exchange and capillary GC with a spreadsheet program. Holzforschung 46: 409-416.

Smook, G.A. 1982. Handbook for pulp and paper technologists. 2nd ed. Angus Wilde Publications, Vancouver.

Sjöström, E. 1993. Wood Chemistry: Fundamentals and Applications. 2nd ed. Academic Press, Toronto.

Suckling, I.D., Gallagher, S.S., and Ede, R.M. 1990. A new method for softwood extractives analysis using high performance liquid chromatography. Holzforschung 44: 339-345.

Sundberg, K., Orsa, F., Wikstrom, B., Holmbom, B., and Ekman, R. 1997. Assessment of pine and spruce wood portions in pulp production by the analysis of resin acids. Paperi ja Puu 79: 327-329.

Sundberg, K., Pettersson, C., Eckerman, C., and Holmbom, B. 1996. Preparation and properties of a model dispersion of colloidal wood resin from Norway spruce. Journal of Pulp and Paper Science 22: J248-J251.

Swan, B. 1968. Seasonal variations in the extractives of spruce wood and sulphite pulps. Svensk Papperstidning 71: 436-440.

Swan, E.P. 1967. Higher terpenes in the heartwood extractives of several Canadian firs (Abies spp.). Canadian Journal of Chemistry 45: 1588-1590.

Tyrvainen, J. 1995. Wood and fiber properties of Norway spruce and its suitability for thermomechanical pulping. Ph.D. Thesis. Acta Forestalia Fennica #249.

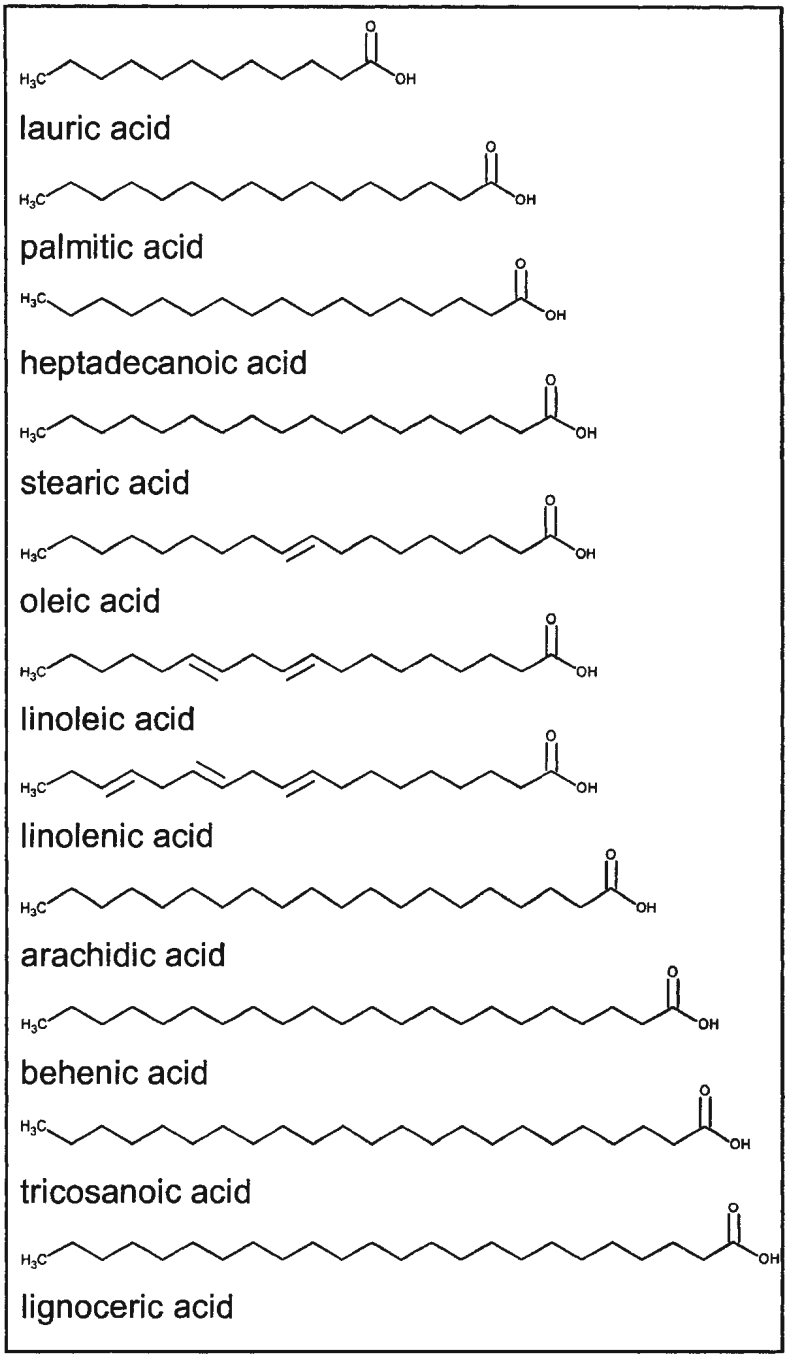
Tyrvainen, J. 1997. Influence of Seasonal Wood Variation on TMP properties, bleach consumption and newsprint runnability. Proc. 1997 International Mechanical Pulping Conference, June 9-13: 213-225.

Wearing, J.T., Barbe, M.C., and Ouchi, M.D. 1985. The effect of white-water contamination on newsprint properties. Journal of Pulp and Paper Science 11: J113-J121.

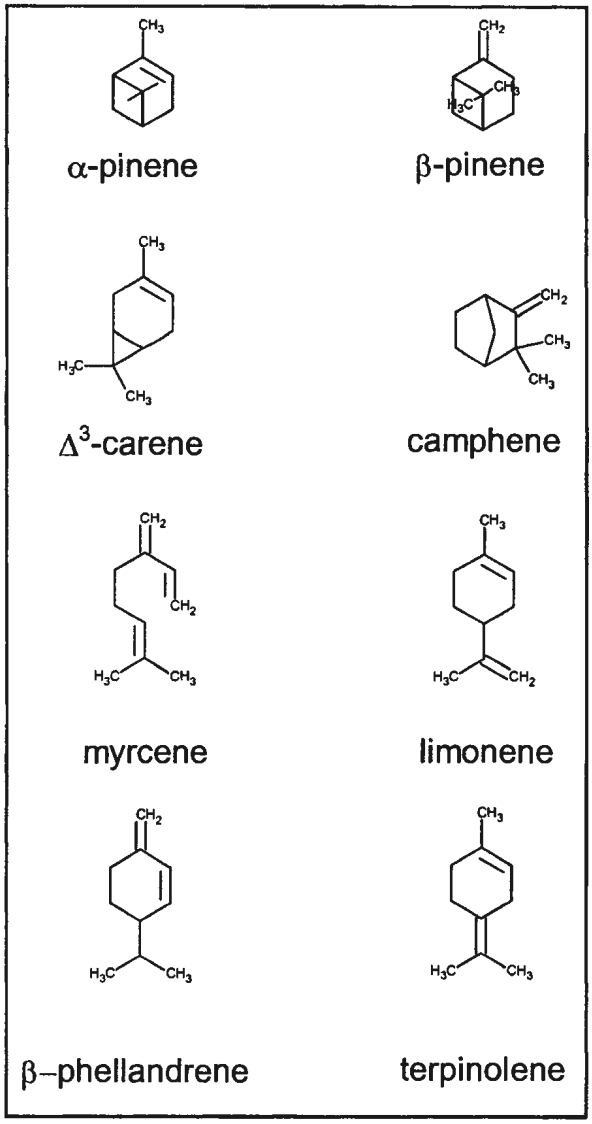
Welkener, U., Hassler, T., and McDermott, M. 1993. The effect of furnish components on depositability of pitch and stickies. Nordic Pulp and Paper Research Journal 8: 223-225.

Zavarin, E., and Snajberk, K. 1965. Chemotaxonomy of the genus Abies-I.: Survey of the terpenes present in the Abies balsams. Phytochemistry 4: 141-148.

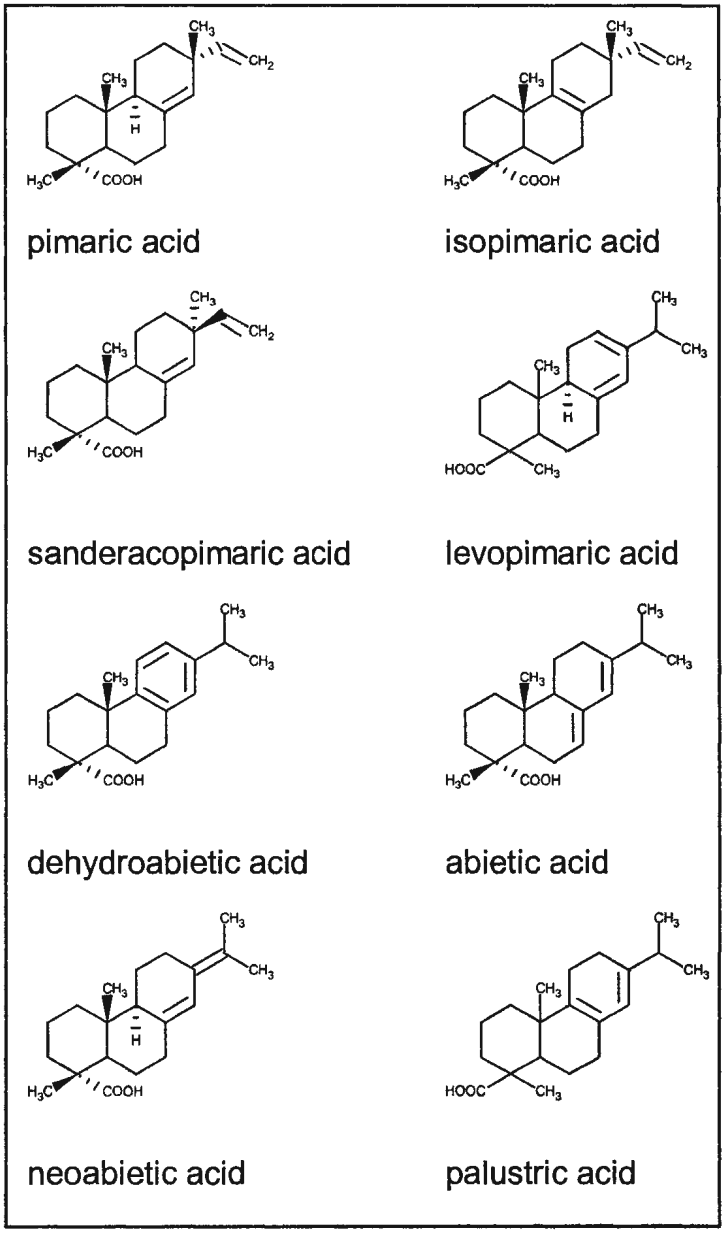
Appendix A - Structures of typical compounds found in wood extractives.



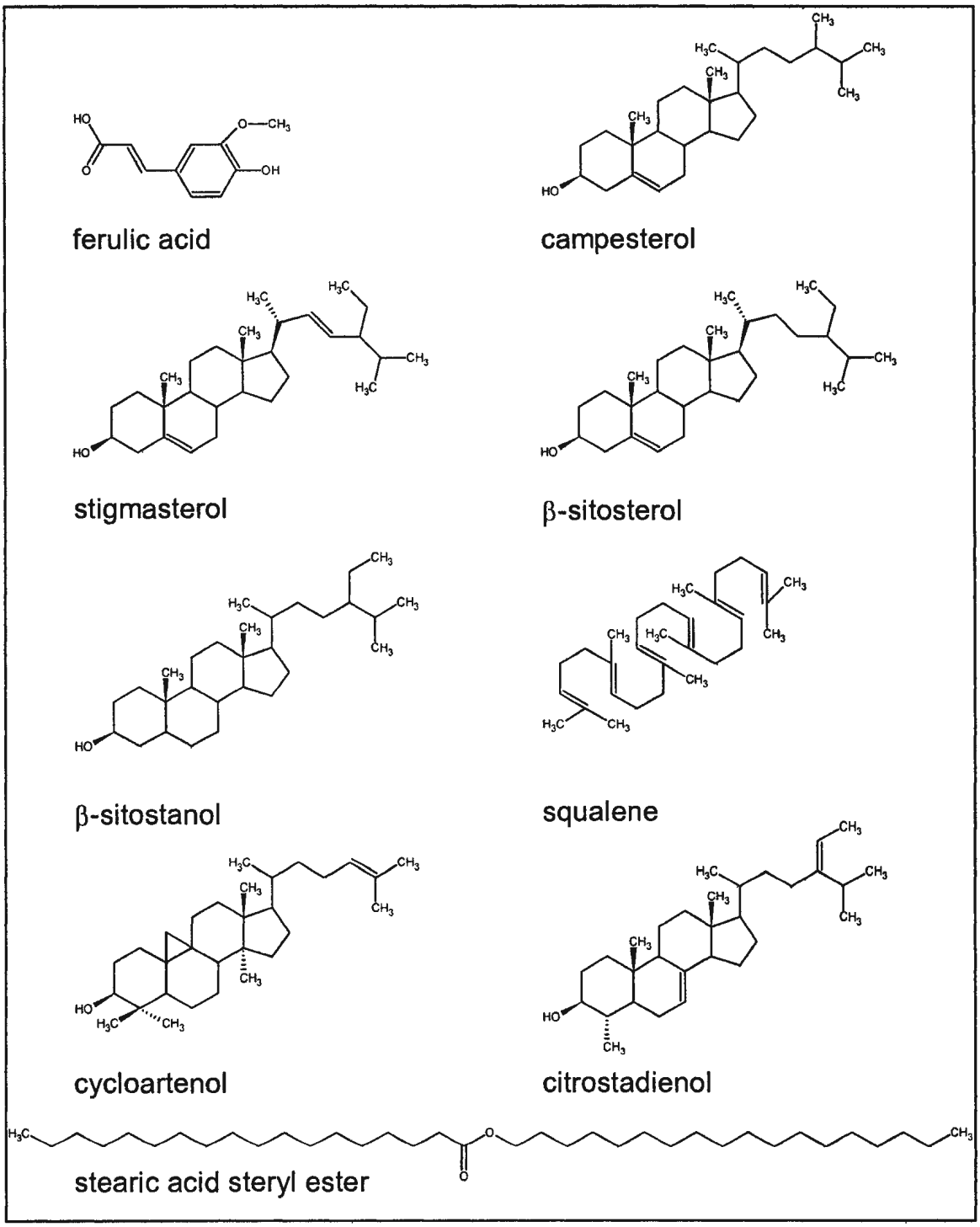
Fatty acids found in wood extractives.



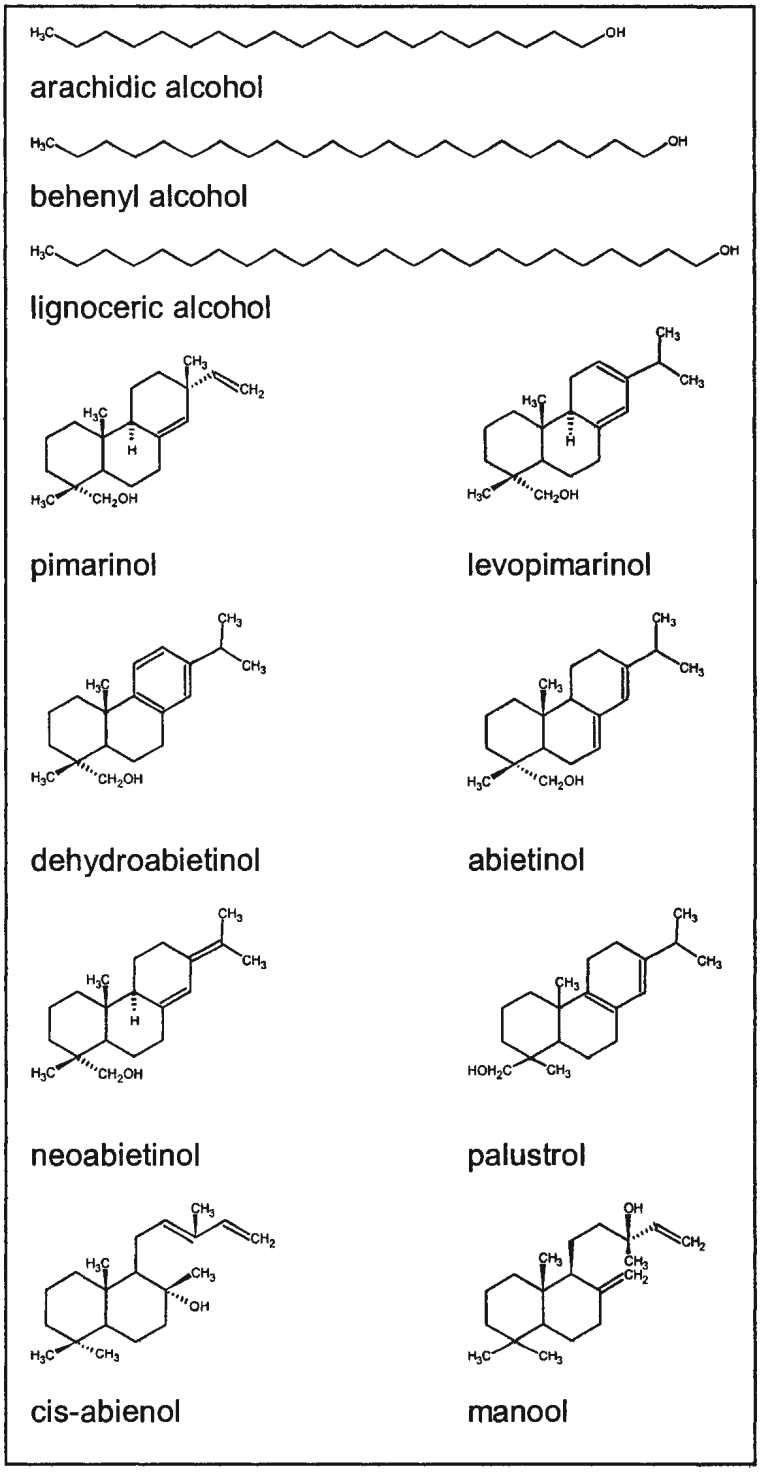
Monoterpenes found in wood extractives.



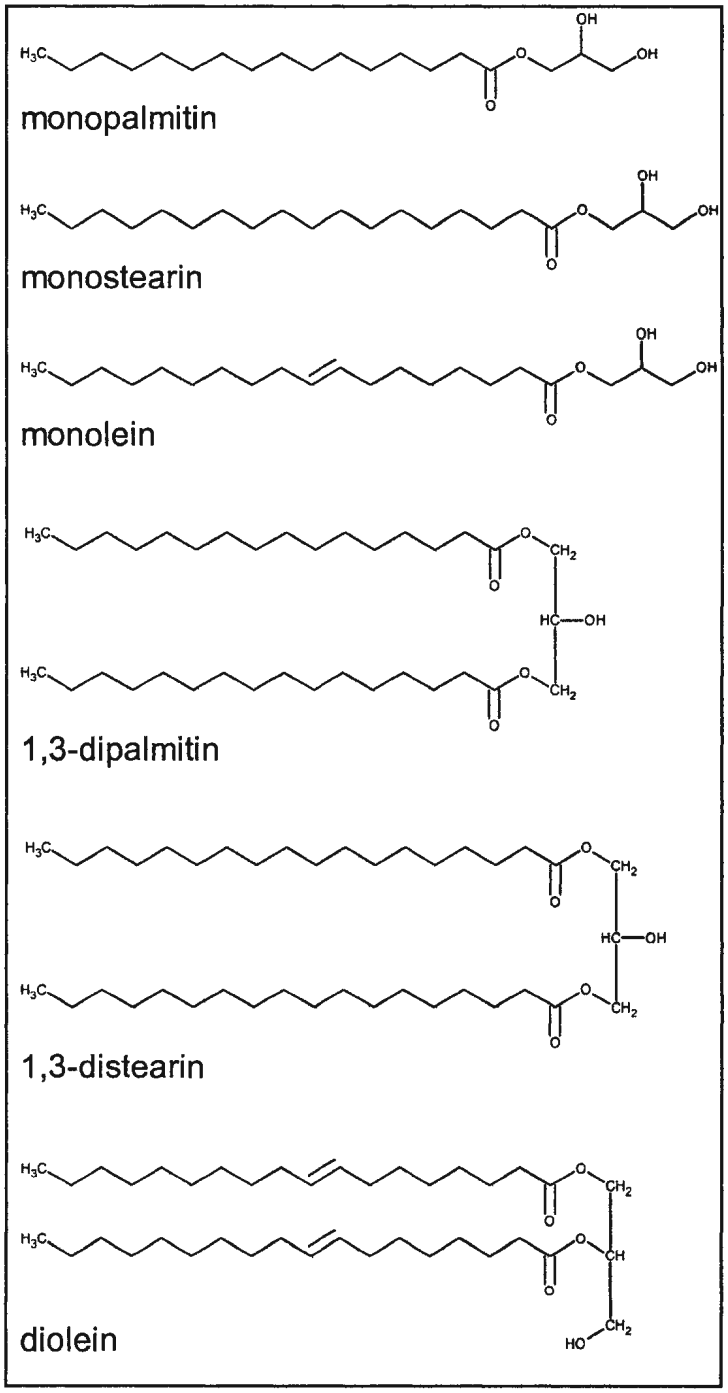
Resin acids (acidic diterpenes) found in softwood extractives.



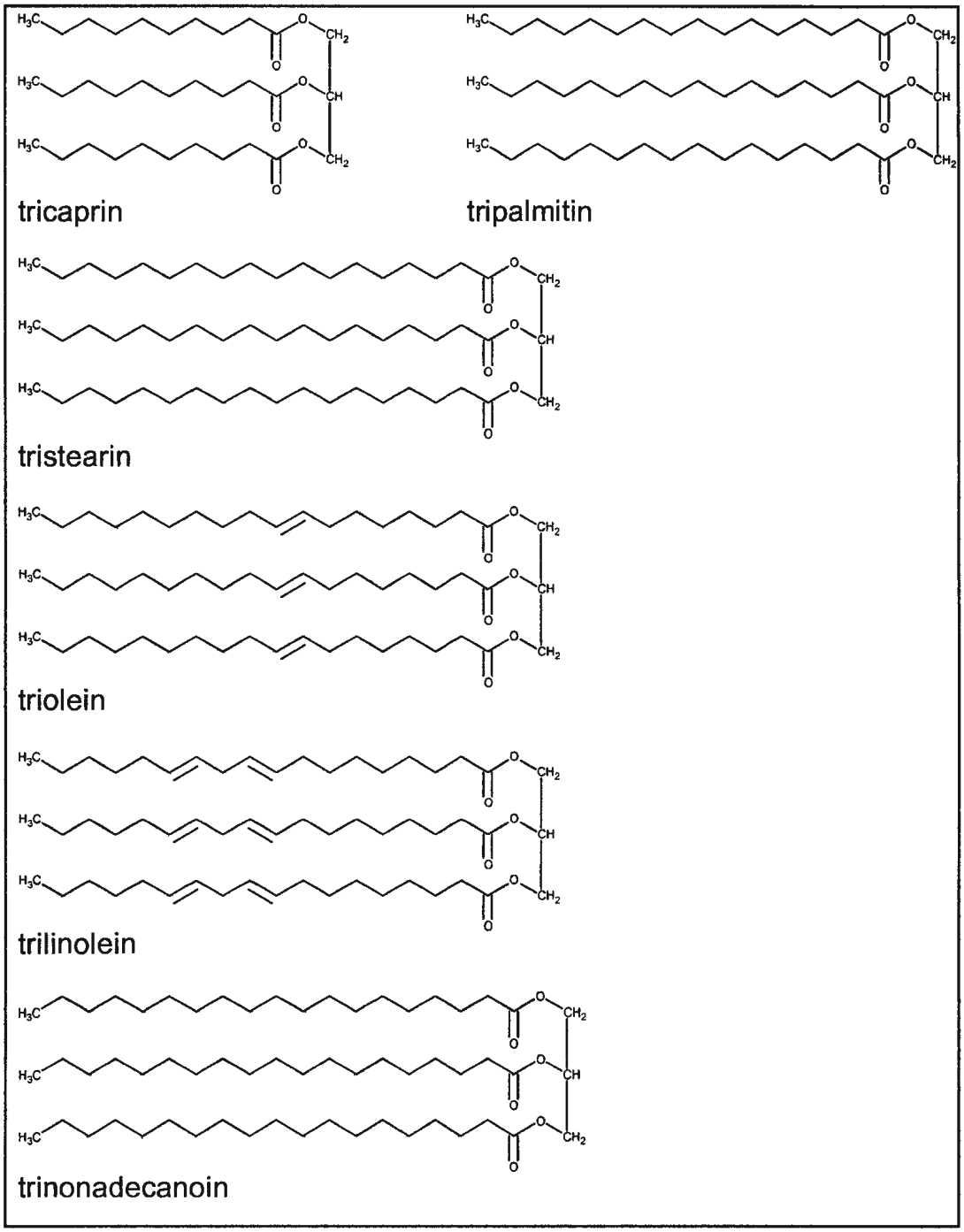
Waxes, sterols, triterpenes and some of their precursor compounds from wood extractives.



Alcohols found in wood extractives.



Monoglycerides and diglycerides found in wood extractives.



Triglycerides found in wood extractives.