IDENTIFICATION AND ANALYSIS OF EXTRACTABLE ORGANIC COMPOUNDS PRESENT IN PULP AND PAPER MILL EFFLUENT

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In Loving memory of my Father,

who made

dreams come true

ABSTRACT

The extractable organic compounds present in the effluent streams of a New Zealand pulp and paper mill have been investigated. Nearly 200 compounds were detected, of which 170 were identified. Most of the compounds are released during mill operations. Some of the compounds detected in treatment system samples arise from the degradation of the released compounds.

The progress of black liquor spills through the treatment system can be monitored by measuring the levels of compounds such as 4-hydroxy-3-methoxybenzaldehyde and 4-hydroxy-3-methoxyacetophen- one. Similarly, α-terpineol can be used to assess turpentine losses through the treatment system.

Chlorinated pinenes and terpineols were detected in the No. 2 bleach plant along with significant quantities of chlorinated analogues of aromatic compounds such as guaiacol, 4-hydroxy-3-methoxyacetophen- one and 4-hydroxy-3-methoxybenzoic acid.

The ability of the biological treatment to degrade extractable organic substances was investigated with respect to 4-day and 8-day retention times. The 8-day system was found to be more effective than the 4-day system in removing aromatic compounds and 2-cyclopentenone derivatives. It also reduced the levels of resin acids and fatty acids. BOD_5 levels were found to decrease exponentially through the extended treatment system.

An anaerobic sludge lagoon which accepts solid waste from the clarifier and reject pulp was found to give rise to a series of resin

acids degradation products which were resistant to further degradation in the aerated treatment system.

The sediments of the aerated ponds were found to include a series of polychlorinated compounds ranging from C_2 to C_6 units. Many of these compounds, which may be degradation products of chlorinated lignin, were tentatively identified from their mass spectral fragmentations. The sediments also contained high levels of monoterpene hydrocarbons.

Compounds present in the final discharge from the treatment system to the Tarawera River were detected in down-stream water and sediments. The Tarawera River was found to have little assimilation capacity; resin acids together with some chlorinated compounds and fatty acids were found in river sediment samples taken six weeks after mill closure.

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Siva Panadam-Twigley

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Abbreviations

amu	- atomic mass unit
ASB	- Aerated stabilization basins
BLOX	- Black liquor oxidation
BOD	- Biological Oxygen Demand
BoPCC	- Bay of Plenty Catchment Commission
COD	- Chemical Oxygen Demand
FRI	- Forest Research Institute
FSOT	- Fused silica open tubular
GC	- Gas chromatography
GC-FID	- Gas chromatography-Flame ionization detector
GC-ITDS	- Gas chromatography-Ion trap detector system
GC-MSD	- Gas chromatography-Mass spectrometry detector
HBL	- Heavy black liquor
Ml	- Megalitre
NSSC	- Neutral Sulphite Semi Chemical
Pin	- Pond inlet
P1-2	- Pond 1 outlet
P2-3	- Pond 2 outlet
P3-4	- Pond 3 outlet
Pout	- Pond 4 outlet
RAME	- Resin acid methyl ester
RWB	- Regional Water Board
SBL	- Strong black liquor
SH2	- State Highway 2
SH30	- State Highway 30
Tasman	- Tasman Pulp and Paper Company Ltd.
µl	- microlitre
WBL	- Weak black liquor

PREFACE

Environmental awareness is rapidly growing both in the public and industrial sectors. Like the ripples that form when a stone is thrown into a lake, the consequences of environmental pollution will eventually affect every one of us.

This thesis investigates some aspects of the chemistry of the extractable organic substances present in the effluent streams and biological treatment system of the Tasman Pulp and Paper Company's pulp mill situated on the banks of the Tarawera River immediately below Kawerau.

CHAPTER ONE

INTRODUCTION

Over the last 10 years, the total New Zealand pulp production increased at an annual rate of 4 percent and the production of paper at 3 percent (New Zealand Official Yearbook, 1986). Pulp production increased from 455,000 tonnes in 1968-69 to 1,145,000 tonnes in 1984-85. For the year ended June 1985, the export of forest products was valued at $796 million. The Central North Island Planning Study (CNIPS) reports that future forestry development is of major national and regional importance. Forest planting programmes of the 1950's and 1960's make it necessary for the pulp and paper industry to undergo further expansion, and economic factors dictate that this expansion occurs at existing sites (Tarawera River Management Plan, 1985).

Pulp and paper mills utilize vast quantities of clean water and rivers are normally their main sources. It is also into these rivers that the effluent is usually discharged. These discharges place enormous stress on the aquatic life forms. Brownlee and Strachan (1976, 1977), Brownlee *et al* (1977), Leach and Thakore (1973, 1975), Oikari *et al* (1980, 1983), and Kinae *et al* (1981a, 1981b) have carried out extensive studies on water-soluble organic

compounds present in Kraft pulping effluent which are discharged into Canadian, Scandinavian and Japanese waterways. In most pulp and paper mill effluents, resin acids and chlorinated aromatic substances are the major organic toxicants. Besides these compounds, the effluents contain a great number of other organic compounds such as carbohydrates, sulphides, mercaptans, phenols, terpenes and their chlorinated analogues (Leach and Thakore, 1975; Lindström and Nordin, 1976; Walden and Howard, 1977; Lindström and Österberg, 1986).

Differences in the wood species utilized in the Northern Hemisphere means that the results of these studies are not directly applicable to New Zealand pulp and paper mill effluents. The species pulped overseas are predominantly *Douglas fir, Western Hemlock,* larch, spruce and various pines. *Pinus radiata,* a softwood, is extensively grown in New Zealand and is used for pulp production in New Zealand, Australia and Chile. This species takes only 25-30 years to grow from a seedling to a mature tree (saw-log size) under New Zealand conditions (New Zealand Official Yearbook, 1986). While overseas studies provide a valuable indication of the compounds to be expected, differences resulting from different tree species, growing conditions and process technologies are inevitable.

Virtually all previous studies on New Zealand pulp effluent have been concerned with colour, foaming or biological oxygen demand (BOD). Timperley (1975, 1985) had investigated the occurrence of discoloration and foam in Lake Maraetai and the Waikato River due to effluent discharge from the New Zealand Forest Products Limited, Kinleith Mill. This study assessed the sources of discoloration in the

Waikato River, the distribution and source of the polyphenolics, and the polysaccharide level in Lake Maraetai, as well as the foaming characteristics of the Waikato River. Procedures for decolorization of *P. radiata* pulping effluent were studied by Buisson and Grey (1978) while the Forest Research Institute (F.R.I.) had investigated BOD levels and the presence of dissolved and suspended solids in the effluent discharged from the thermomechanical pulp mill at Whirinaki (Corson and Lloyd, 1978a, 1978b). Cox (1981) examined the effluent produced by New Zealand pulp and paper mills, the treatments available and the effects of these discharges on the aquatic environment.

The Water and Soil Conservation Act (1967) requires that the various pulp and paper companies meet specific standards as determined by the water classifications with regard to BOD, pH, temperature, suspended solids and colour of their discharges, and also that the discharged effluent be non-toxic to aquatic organisms. Despite this, fish kills have occurred (Tarawera River Management Plan, 1985). At present there is no enforcement on colour, due to the lack of an economically viable method for colour removal.

The Chemistry Department of the University of Waikato, Hamilton, first became involved in pulp and paper mill effluent studies in 1983. Much of the initial work was concentrated on the New Zealand Forest Products Limited, Kinleith Mill. Williams (1986) studied the soil adsorption of resin acids and fatty acids using different soil types. Stuthridge (1987) investigated the low molecular weight extractable organic compounds present in bleach plant effluent. Continuing studies on extraction procedures, quantification,

microbiological degradation and absorption of water-soluble organic species are being carried out at the University of Waikato.

In the case of the Tarawera River, concern for water quality in the lower reaches has resulted in the Bay of Plenty Catchment Commission preparing the Tarawera River Management Plan (1985), which is intended to act as a guideline for the future allocation of water from the Tarawera River. The Tasman Pulp and Paper Company Limited is one of the major users of water from the Tarawera River and its effluent discharges have a major impact upon water quality.

The present study was designed as part of a programme to minimize this impact. Specific aims of this study are:

i) to assess the individual plant sources at Tasman's Kawerau mill and identify, and quantify the extractable organic compounds present.

ii) to document the low molecular weight organic compounds formed by the chemical and biological processes that occur during pulping, bleaching and in the effluent treatment system.

iii) to assess the behaviour and performance characteristics of Tasman's treatment system with respect to the removal of low molecular weight organic compounds.

iv) to investigate a possible correlation between extractable organic compounds and physical parameters, in particular BOD_5.

v) to investigate the Tarawera River's ability to assimilate Tasman's discharge loadings and its capacity to recover to a steady state.

The problems caused by industrial discharges to natural waters are complex and multi-faceted. The overall strategy that needs to be adopted is succinctly expressed by the National Academy of Sciences' report on Principles of Protocols for Evaluating Chemicals in the Environment (1975): "The need to know what chemicals may escape into the environment and at what levels they may be harmful leads rather quickly to a realization that until one can identify these compounds with certainty and measure their presence in selected compartments of the environment, effective control of these chemicals is essentially impossible."

CHAPTER TWO

PAPER AND PAPER-MAKING

2.1 INTRODUCTION

"Man's inspiration to record his contemporary world had its origins in his growing awareness of the mysterious forces of nature which governed his existence yet eluded his understanding" (Stacey, 1964). Man has progressed from nomad to villager to citizen of society governed by codes of conduct. These codes of conduct need to be preserved for later generations. Early civilized Man erected palaces and tombs which he decorated with chiselled and painted murals, and statuaries which he explained with cuneiform, hieroglyphic or alphabetic inscriptions. Prior to the invention of paper, ancient people recorded their thoughts on different materials such as bark, metal, clay tablet, bone, skin, and cloth. About 3,000 B.C. the Egyptians developed a system of writing using sheets of papyrus (from which the word paper is derived).

Paper making, as we know it today, is attributed to a Chinese scholar, Ts'ai Lun, who developed the method in about 105 A.D. (Casey, 1980). He formed a sheet of paper by macerating barks of trees, hemp waste and old rags, and poured a slurry of this onto a mould covered with a silk cloth. The paper mat was then dried. This

knowledge did not reach Europe until the twelfth century when it was passed on by the Moors. In 1839, Anselme Payen, a French chemist, opened the door for the production of wood pulp when he isolated a fibrous substance called cellulose by treating wood with nitric acid. Paper today is used not only for commerce, communication, literature and art, but also for wrapping, packaging and a variety of disposable products.

2.2 NATURE OF WOOD

The terms softwood and hardwood can be misleading as some softwoods are hard and many hardwoods are soft. Softwood is derived from coniferous trees *(Gymnosperms)* while hardwood is the product of broad-leaved species *(Angiosperms).* The chemical components of wood may be divided into macromolecular substances such as cellulose, hemicellulose and lignin, and low molecular weight organic compounds (often classified as extractives) and inorganic minerals (Figure 2.1).

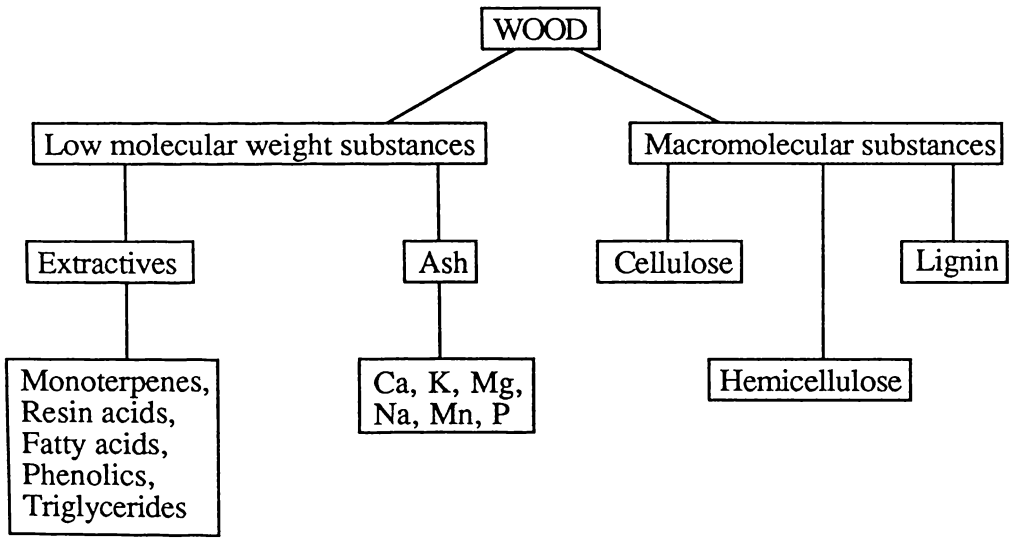


Figure 2.1. The main components of wood

The pulping industry in New Zealand uses predominantly *P. radiata* (softwood) and so this study deals mainly with softwood processing though comparison with hardwood is made. The cell is the basic building unit of wood. Wood is composed of fibres which are largely elongated cells that are long in relation to their diameter and have a definite cell wall and a cell cavity, or lumen (Uprichard, 1964; Sjöström, 1981).

The two cell types that contribute to wood tissue in softwoods are tracheids (90-95%) and ray cells (5-10%). The long axes of the fibres are vertically orientated in the tree. The softwood fibres (2-4 mm) are comparatively longer than the hardwood fibres (0.3-0.6 mm) and reputedly produce stronger paper. Pulp made from hardwood has excellent bonding properties but has a rather low tearing strength. Bonding strength is the force with which the fibres adhere to each other within a sheet, or with which a coating and/or film adheres to the surface of a sheet, or with which plies in a board or laminated sheets adhere to each other. Tearing strength is the force required to tear a specimen under standardized conditions.

The plant cell wall is made up of several layers, namely middle lamella (ML), primary wall (P), outer layer of the secondary wall (S1), middle layer of the secondary wall (S2), inner layer of the secondary wall (S3) and the warty layer (W) (Figure 2.2). Plant cell walls are composed of polysaccharides: cellulose, hemicellulose and lignin, which form the major structural material.

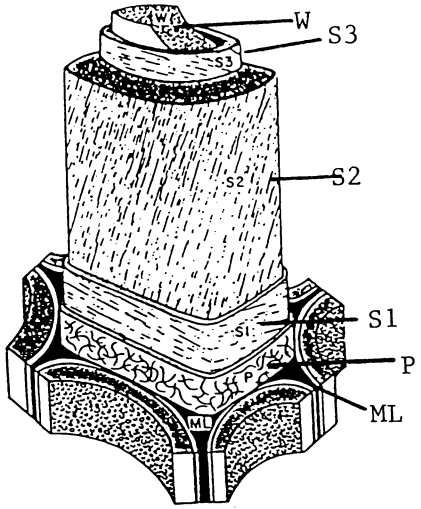


Figure 2.2. Plant Cell Wall (Sjöström, 1981).

Cellulose accounts for 40-45% of the dry weight in wood and is located predominantly in the secondary cell wall. It exists in the cell walls as long thread-like fibres called microfibrils. Cellulose is a homopolysaccharide composed of β-D-glucopyranose units which are linked together by 1,4-glycosidic bonds (Figure 2.3). These molecules are completely linear and have a strong tendency to form intra- and intermolecular hydrogen bonds. As a result of its fibrous structure and its strong hydrogen bonds, cellulose has high tensile strength and is insoluble in most solvents (Sjöström, 1981). Wood cellulose in its native state is composed of at least 10,000 anhydro-glucose units (Kringstad and Lindström, 1984). Cellulose and hemicellulose are bound together by lignin, an aromatic polymer derived from phenylpropanoid units.

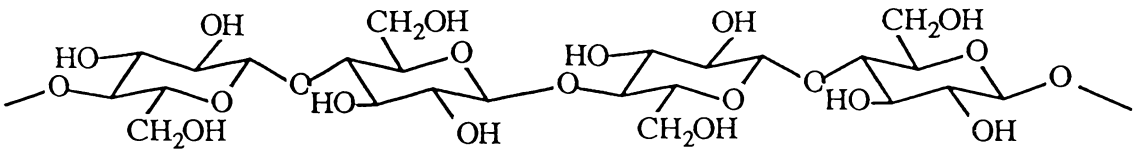


Figure 2.3. Structure of cellulose

Hemicelluloses form 20-30% of the dry weight of wood. In contrast to cellulose which is a homopolysaccharide, hemicelluloses are heteropolysaccharides. Hemicelluloses are made up of five neutral sugars in various combinations; the hexoses: glucose, mannose and galactose, and the pentoses: xylose and arabinose. Hemicelluloses differ from cellulose in that they are branched to various extents, with a degree of polymerization of approximately 200 units. Hardwoods contain more hemicelluloses than softwood and the sugar composition is different.

Next to cellulose, lignin is the most abundant and important polymeric organic substance in wood. Lignin is a three-dimensional polymer made up of substituted phenylpropanoid units (Figure 2.4).

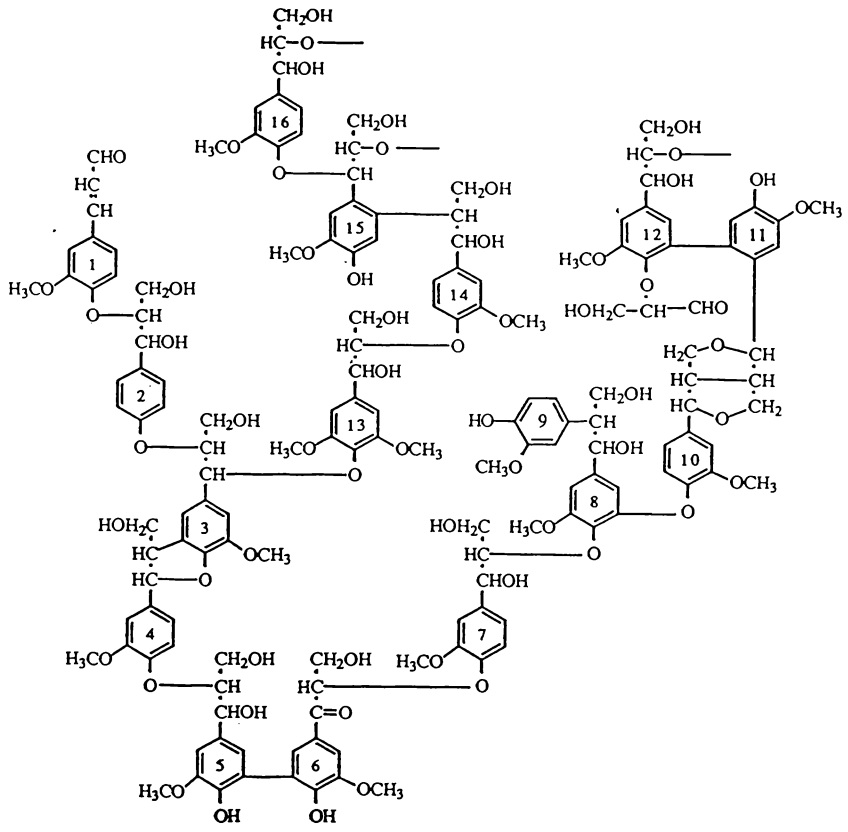
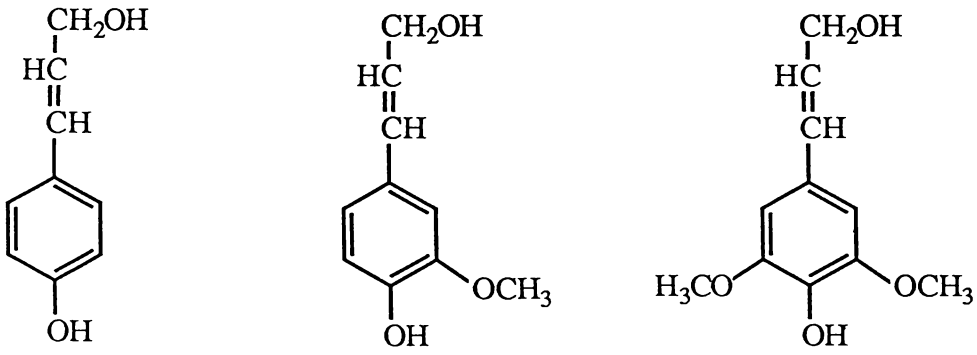


Figure 2.4 Structure of softwood lignin (Adler, 1977)

Lignin occurs mainly in the middle lamella and the primary wall. It is formed in wood by enzyme-initiated dehydrogenative polymerization of a mixture of three different 4-hydroxyarylpropenyl alcohols (Figure 2.5). Softwood lignin is largely a polymerization product of coniferyl alcohol and to a lesser extent, *p*-hydroxycinnamyl alcohol (coumaryl alcohol). In hardwoods, lignin is formed by co-polymerization of coniferyl and sinapyl alcohols.

Softwood has a higher lignin content (25-35%) than hardwood (18-25%). Softwood lignin consists of 85-90% guaiacyl aromatic units whereas hardwood lignin shares evenly in guaiacyl and syringyl units.



p-Coumaryl alcohol Coniferyl alcohol Sinapyl alcohol

Figure 2.5. Lignin precursors

The low molecular weight components of wood consist of organic compounds (extractives) and ash forming minerals. The extractives are those wood components that can be extracted using neutral organic solvents such as petroleum ether, benzene, diethyl ether, acetone, dichloromethane and chloroform. Major constituents of the extractives are fats and waxes; terpenoids, which includes mono-, sesqui-, and diterpenes; phenolic extractives such as tannins,

flavanoids, and stilbenes. The extractive content in pine species is between 4 and 14% (Sjöström, 1981). The amount of ash (the residue obtained after burning the organic matter) is between 0.2-0.5% in temperate zone woods, but much higher in tropical woods (0.2-3%) (Fengal and Wegner, 1984). These include calcium, potassium and magnesium as the major elements followed by manganese, sodium, phosphorous and chloride in smaller quantities.

2.3 WOOD PREPARATION

Before the wood is chipped, it needs to be debarked. The presence of bark causes lower digester efficiency, higher pulping and bleaching costs, and a reduction in pulp quality. The removed bark is burnt to provide a valuable energy source. There are three principal types of debarkers: drum, ring and hydraulic debarkers.

Drum debarkers remove the bark by abrasion. Short lengths of wood (1.2 - 2.4 m) are fed into large rotating drums where the bark is rubbed off by contact between the logs and the corrugated interior of the drums. Water showers are used to flush the loose pieces of bark through the perforated sides of the drum, into the disposal area.

Ring debarkers are used for large diameter logs where the bark is removed by mechanical abrasion. The log is passed through a rotating ring fitted with cutting knives to peel off the bark. Some damage to the surface of the log is caused.

Hydraulic debarkers are best suited for large diameter logs, 6-12 metres long. High pressure jets of water, 7,000-10,000 kPa

(1,000-1,500 psi), are used to blast the bark from the logs. Due to the high pressures utilized, the cost of this operation is high.

2.4 PULPING

Pulping is the process involving the separation of the fibres in wood. Pulp may be produced mechanically (stone groundwood and refiner mechanical pulp), chemically (alkaline and sulphite) or by a combination of the two (neutral sulphite semichemical). In mechanical pulping the fibres are separated by physical means, leaving the original chemical composition of wood intact (very little lignin is removed) except for the removal of the water soluble constituents. In chemical pulping, the wood is treated with chemicals to selectively remove the lignin that holds the fibres together.

2.4.1 Mechanical Pulping

The oldest form of mechanical pulping is stone groundwood pulping. More recent developments include the refiner mechanical pulping and the thermomechanical pulping. The fibres of mechanical pulp are shorter than those of chemical pulp and there is a greater proportion of fines (fibre fragments), giving rise to lower strength. Mechanical pulp retains practically all the lignin of the original wood, therefore pulp yields are high (90-95% of the original wood). It is lower in cost than chemical pulp and little or no bleaching is required since the lack of chemical treatment means that few chromophores are produced.

surface of a rotating grindstone while water is sprayed on the grinding surface to carry the pulp away and to absorb the heat generated. The heat generated in the grinding zone, which can be over 150°C, helps to soften the lignin. Fibre bundles and fibre fragments are torn out of the wood surface and transported to the grinder pit.

Refiner mechanical pulping involves the mechanical reduction of wood chips to pulp in a precision built attrition disk mill called a refiner. The disk mill consists of two grooved steel units set parallel to each other, rotating in opposite directions. The compressive and decompressive forces produced by these surfaces heat the wood fragments to temperatures of 100°-120°C at which the lignin is softened enough for the fragments to disintegrate into fibres. The pulp produced is stronger than that from the stone groundwood process.

Thermomechanical pulping is a modified refiner mechanical pulping process in which the chips are steamed for a short period at about 120°C to soften the lignin. The pretreated chips are then fed to the disk refiner for defibration. This process produces fewer damaged fibres compared with refiner pulping and consequently the pulp produced is of a higher strength though the yield is marginally lower due to the leaching of water soluble substances.

2.4.2 Chemical Pulping

The two principal forms of chemical pulping processes are sulphite pulping and alkaline pulping. Although sulphite processes give higher yields, cost less and produce brighter unbleached pulp

compared with the alkaline processes, their limitations are the restricted number of wood species that can be pulped and the weaker pulp produced. Due to these factors, production by this method has been greatly reduced. Also sulphite pulping causes extreme environmental problems because the effluent discharges have very high BOD levels. There is no chemical recovery.

There are two alkaline processes: soda and sulphate (or Kraft) processes. Sodium hydroxide is the main cooking chemical in both processes with sodium sulphide as an additional active pulping chemical in the latter. The Kraft process is the dominant alkaline pulping process with regard to the rate of pulping, pulp yield, pulp quality and cost, and is currently the main process used in New Zealand (Table 2.1).

Table 2.1
Production Capacity of New Zealand Pulp Mills in 1986[a]

Company	type of pulp	tonnes/year
Carter-Holt	thermomechanical	240,000
Caxton Paper Mill	refiner mechanical	50,000
NZFP (Kinleith)	Kraft and semi-mechanical	668,000[b]
NZFP (Whakatane)	neutral sulphite semi-chemical and stone groundwood	110,000
NZFP (Mataura)	imported speciality pulp and local Kraft	20,000
Tasman	Kraft, stone groundwood and refiner mechanical	500,000[c]
Winstone	chemical and thermochemical	85,000

[a] New Zealand Official Yearbook (1986)
[b] including 260,000 tonnes of paper
[c] including 335,000 tonnes of newsprint

2.4.2.1 Kraft Pulping

The lignin which binds the wood fibres is dissolved using a solution of sodium hydroxide and sodium sulphide (3:1 ratio), called white liquor. The chips are cooked either by the batch method or by continuous digestion under high temperature (~170^{o}C) and pressure (~800 kPa). The pressure is then lowered to atmospheric pressure which causes the chips to disintegrate into pulp. After digestion is completed, the pulp and spent liquors are discharged to a blow tank where the larger uncooked chips are screened and usually recycled to the digester for re-cooking. The spent liquor is separated from the pulp by countercurrent washing. The pulp is diluted to low consistency and small contaminants are removed by fine screens. The cleaned stock is thickened and stored. The screened spent liquor (black liquor) is then concentrated before being burnt in the recovery furnace (see Section 6.1). A schematic diagram of the Kraft process is given in Figure 2.6.

Sodium sulphate is added to the strong black liquor prior to incineration in the recovery furnace. The smelt, consisting mainly of sodium carbonate and sodium sulphide, is dissolved in a weak wash solution on leaving the furnace. The "green" liquor from the dissolving tank contains sodium carbonate, sodium sulphide and some caustic soda. It is clarified and transferred to the causticizers to react with calcium hydroxide (slake lime) to form sodium hydroxide. The precipitate, calcium carbonate (lime mud) is removed and burnt in the lime kiln to regenerate lime for use in the causticizing reaction.

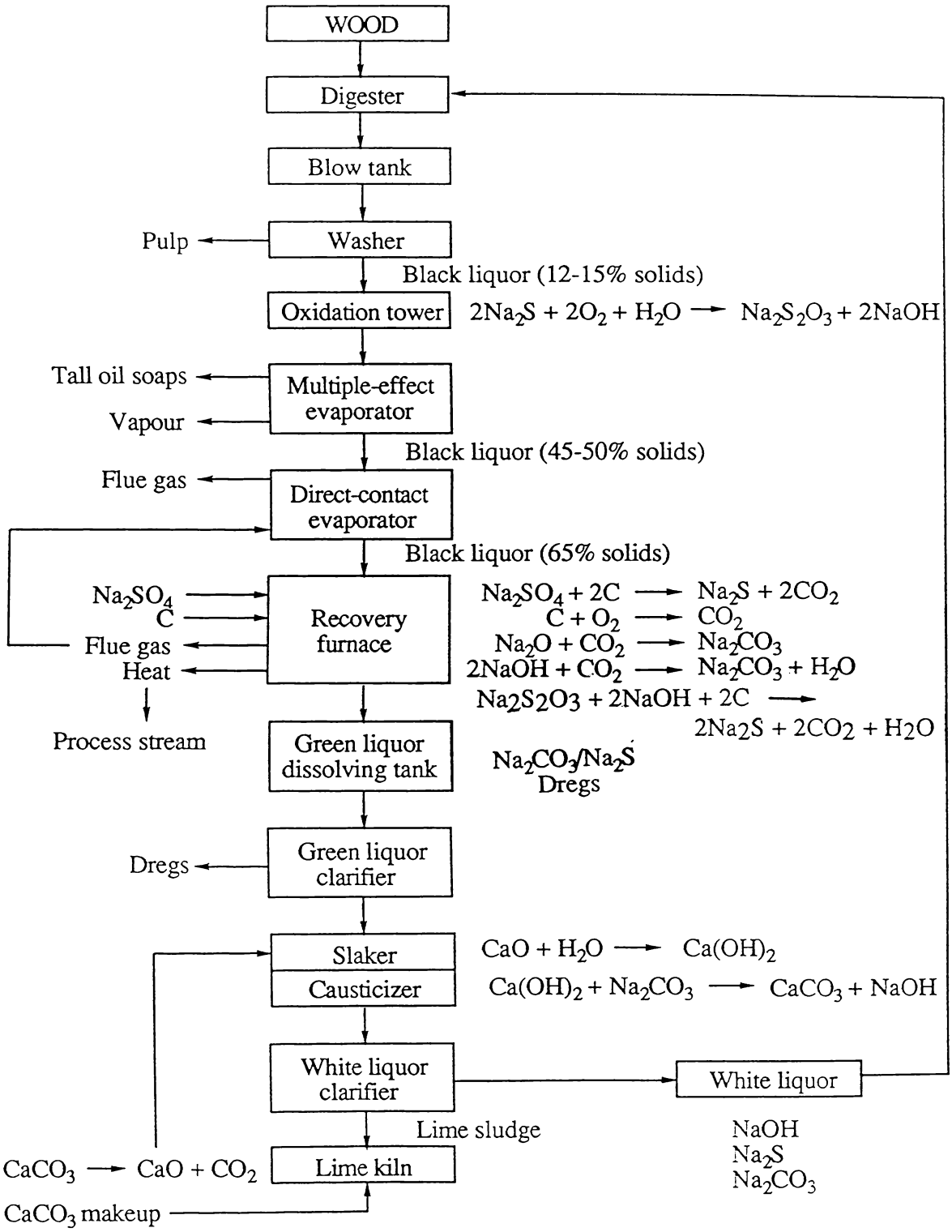


Figure 2.6 Schematic diagram of the Kraft pulping process (Casey, 1980)

Causticizing: $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$

Calcinating: $CaCO_3 \rightarrow CaO + CO_2$

Slaking: $CaO + H_2O \rightarrow Ca(OH)_2$

The recovery of these comparatively expensive chemicals is an integral part of the Kraft process. Besides reducing the cost of the pulping chemicals, the recovery system also reduces water pollution by burning the dissolved organic matter in the spent liquor, converts the sulphur in the black liquor into sodium sulphide and generates a substantial quantity of heat that is used in all areas of the mill.

The main advantages of the Kraft process over the sulphite process are (Casey, 1980; Fengal and Wegner, 1984):

1. wide flexibility of the wood supply, wood species and tolerance of high amount of extractives.
2. short cooking times.
3. less prevalent pitch problems.
4. excellent pulp strength.
5. well established recovery process of the spent liquor.
6. valuable by-products such as turpentine and tall oil are recovered.

The main drawbacks of this process are the odour problems (sulphurous compounds), lower pulp yields than in sulphite pulping, the dark colour of the pulp and the need to reclaim the cooking chemicals from the digester liquors.

Two important by-products are produced in the Kraft process,

namely turpentine and tall oil (see Chapter 9). Turpentine is obtained from the relief gases during decompression after digestion while tall oil separates as tall oil soap from the oxidation of the black liquor. The soap is skimmed off the spent liquor, acidified and refined to produce tall oil.

2.4.2.2 Delignification Reactions

Much of the understanding of delignification reactions occurring during alkaline pulping has been gained by studying the reactions of lignin model compounds. The sulphide ion (or more precisely, the hydrosulphide ion) acts as a catalyst, substituting in the lignin molecular structure and rendering it more readily soluble in alkali. This results in an increase in the rate of delignification, causing less damage to the cellulosic and hemicellulosic material in the wood. The attack on the lignin molecule involves the formation of groups that render the lignin more soluble in alkali. Fragmentation of lignin depends on the cleavage of ether linkages, whilst the carbon-carbon linkages are essentially stable. According to Gierer (1970), hydroxyl ions acting as nucleophilic agents, bring about the cleavage of certain types of ether linkages in alkaline pulping. In Kraft pulping sodium hydroxide in the presence of both the hydrosulphide and sulphide ions is less alkaline but more strongly nucleophilic than hydroxyl ions alone. The hydrosulphide ion is responsible for greater delignification efficiencies in Kraft pulping compared with soda pulping.

1. Cleavage of α-aryl ether bonds in phenolic units by way of quinonemethide intermediates. These phenolic groups increase

the solubility of lignin and make it more susceptible to other degradation reactions (Figure 2.7).

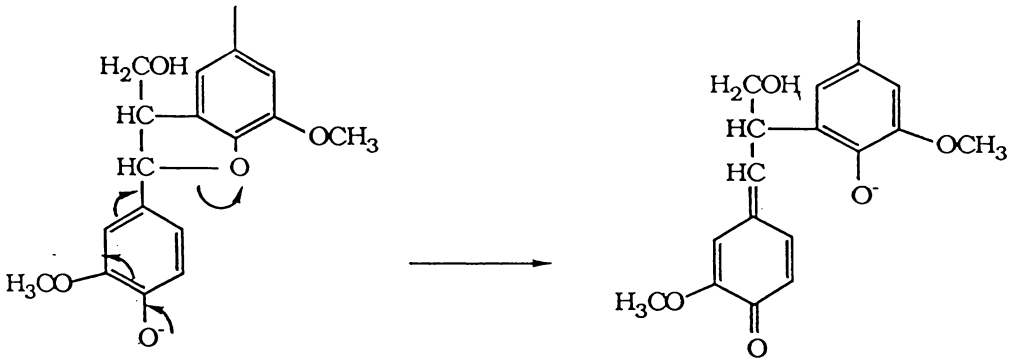


Figure 2.7 Formation of a quinonemethide by alkaline cleavage of an α-aryl ether bond of a phenolic lignin unit (Gierer, 1970).

2. Cleavage of β-aryl ether bonds in phenolic units by way of episulphide intermediates. The quinonemethide intermediate reacts more rapidly with sulphide ions than with hydroxyl ions (Figure 2.8).

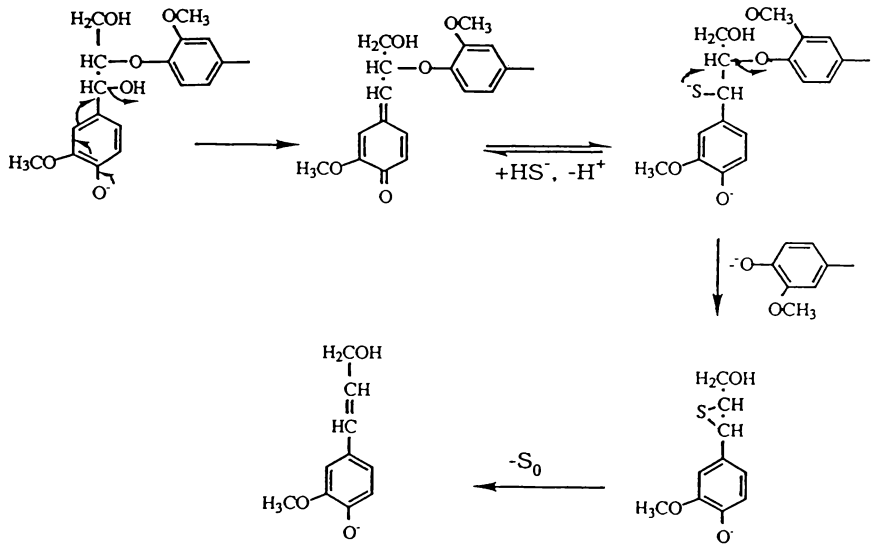


Figure 2.8 Sulphidolytic cleavage of β-aryl ether bonds in phenolic lignin units (Gierer, 1980)

3. Cleavage of β-aryl ether bonds in non-phenolic units by way of epoxide intermediates. This reaction liberates phenolic and glycolic groups, resulting in the complete separation of neighbouring units in the lignin structure and the formation of more soluble, lower molecular weight fragments (Figure 2.9).

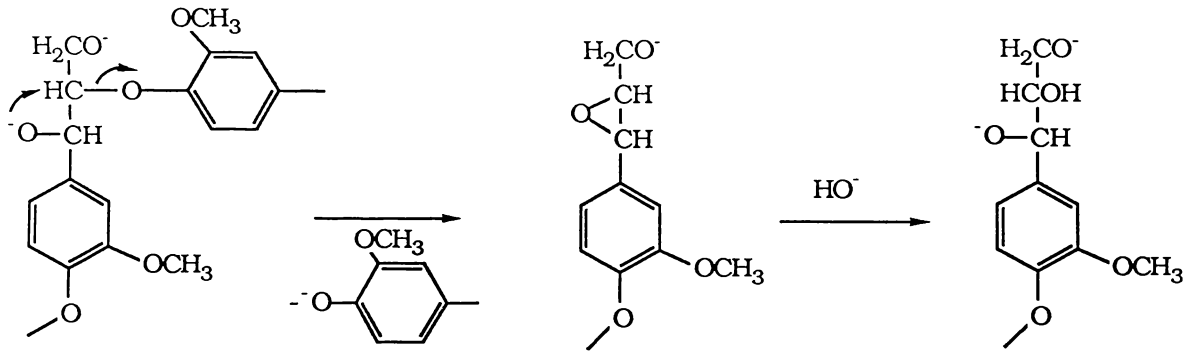


Figure 2.9 Cleavage of β-aryl ether bonds in non-phenolic lignin units (Gierer, 1980)

2.5 BLEACHING

The pulp from Kraft pulping is usually dark due to the presence of chromophoric groups in the residual lignin. The lignin cannot be removed by extending the cooking time as this results in a reduction of pulp yield and strength. The principal aim of bleaching is to obtain a brighter pulp. Bleaching can be achieved either by converting and stabilizing the chromophoric groups without the loss of lignin (lignin-preserving bleaching) or by removing the lignin (lignin-removing bleaching).

Due to its high lignin content and low chromophoric nature, mechanical pulp utilizes lignin-preserving bleaching to increase its brightness. In New Zealand, mechanical pulp bleaching is carried out

as a single-stage process either with peroxide or dithionite, or as a two-stage process with peroxide followed by the reductive dithionite step. Sodium dithionite has replaced zinc dithionite as zinc was found to be toxic to fish.

Chemical pulp bleaching in New Zealand utilizes lignin-removing bleaching and it is predominantly carried out in multi-stage sequences, using different combination of stages. These sequences are normally alternated between acid and alkaline stages. In the acid stage, an oxidizing agent is used; in the alkaline stage, the products formed in the oxidative stage are extracted from the pulp. Commonly used sequences include C_D-E-H-D-E-D, C_D-E-D-E-D, C-E-D-E-D, and C_D-E-H-D. The different stages in a sequence are denoted by the use of special symbols as represented in Table 2.2.

Table 2.2
Symbols of the different Bleaching sequences.

Stage	Symbol	Description
Chlorination	C	Chlorine gas or chlorine water
Alkaline extraction	E	Sodium hydroxide solution
Hypochlorite bleaching	H	Sodium or calcium hypochlorite
Chlorine dioxide bleaching	D	Aqueous chlorine dioxide
Chlorine/chlorine dioxide	C_D	Chlorination with addition of small amounts of ClO2
Sequential chlorine dioxide and chlorine	D/C	chlorine dioxide and subsequent chlorination without washing
Peroxide bleaching	P	Hydrogen peroxide (50% by weight solution)
Oxygen bleaching	O	Oxygen gas and alkali
Ozone bleaching	Z	Gaseous ozone (2% by weight in oxygen)

Table 2.2 cont.....

Oxidative extraction	E/H	Inclusion of sodium hypochlorite in E stage
Peroxide extraction	E/P	Inclusion of peroxide in E stage
Acid treatment	A	Sulphuric acid
Acid souring	S	Sulphur dioxide gas

2.5.1 Chlorination

Chlorination is the first bleaching step and is termed the prebleaching stage. Chlorine converts the lignin in the pulp to compounds that are soluble in water and alkali. Therefore, it is generally followed by an extraction step to remove these components. The bleach plant effluent from the chlorination process causes a large number of environmental problems (Lindström *et al*, 1981; McLeay *et al*, 1986).

Chlorine reacts with lignin primarily by substitution and by oxidation. Small amounts of chlorine are also introduced by addition to the double bonds present in the lignin. Since chlorine (Cl_2) reacts as an electrophile (polarized δ^+/δ^-), aromatic compounds are usually chlorine substituted. Hydroxyl and methoxy groups activate the *ortho-* and *para-* positions towards electrophilic reactions, hence in guaiacyl systems all of the ring positions are activated. On the other hand α-carbonyl groups deactivate *ortho-* and *para-* positions and are therefore *meta-* directing with respect to the α-carbonyl substituent (Figure 2.10).

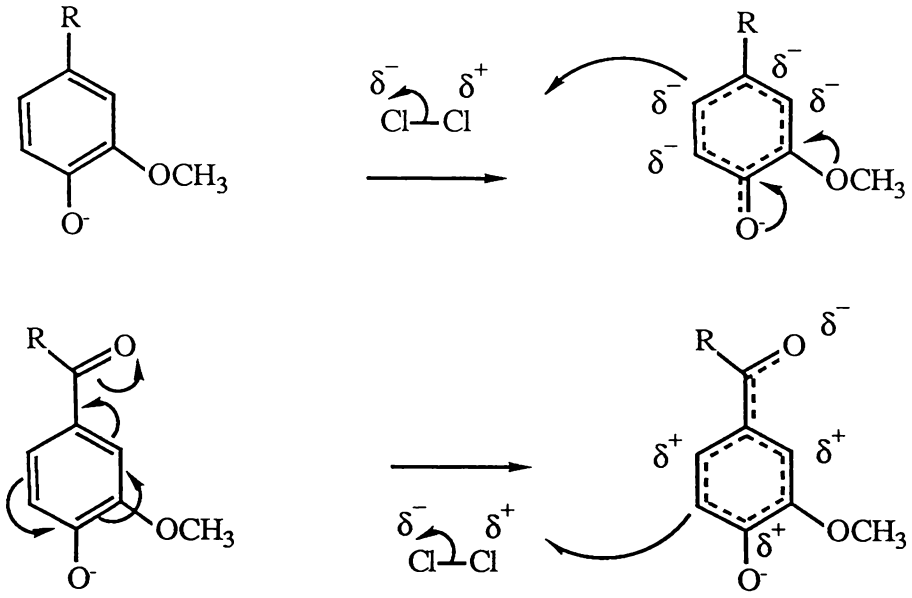


Figure 2.10 Directing effects of substituent groups

2.5.2 Extraction

Alkaline extraction is usually carried out after chlorination or chlorine/chlorine dioxide stage. This neutralizes the acids or acidic groups formed in the preceding stage. Many of the compounds formed by chlorination are insoluble in water but soluble in alkali. Chlorinated lignin contains a large number of acidic groups that are soluble in their anionic form. Some of these compounds are broken down by alkali to lower molecular weight substances. Sodium hydroxide is the commonly used alkali for pulp extraction.

2.5.3 Hypochlorite Bleaching

Hypochlorite reacts readily with cellulose as well as with the coloured impurities remaining in the pulp after alkaline extraction. It is therefore important that the conditions of the reaction are carefully controlled. These conditions are temperature, pH,

percentage of chemical added, consistency and time. pH has the most influence on the resultant pulp and is therefore maintained at pH 10.5 until the conclusion of the reaction.

Hypochlorite ion (ClO^-) is a nucleophile, hence it attacks positions carrying a positive charge, especially carbonyl carbon atoms and β- (and δ) carbons at double bonds conjugated with carbonyl or carboxyl groups. Therefore, lignin is fragmented to low molecular weight carboxylic acids (Sjöström, 1981).

2.5.4 Chlorine Dioxide

Chlorine dioxide is more specific in its oxidizing action than hypochlorite. It is able to remove residual lignin and other colouring matter without any effect on the remaining cellulose (Loe, 1964). Therefore a brighter pulp is produced. The pH of the reaction is controlled at pH 4 by the addition of a buffer. Chlorine dioxide oxidizes the free phenolic hydroxyl-groups, the non-phenolic phenylpropane units and the double bonds present in the pulp. After cleavage of the benzene ring, various dicarboxylic acids are formed including oxalic, muconic, maleic and fumaric acids. In addition, chlorine substituted products are also formed (Figure 2.11).

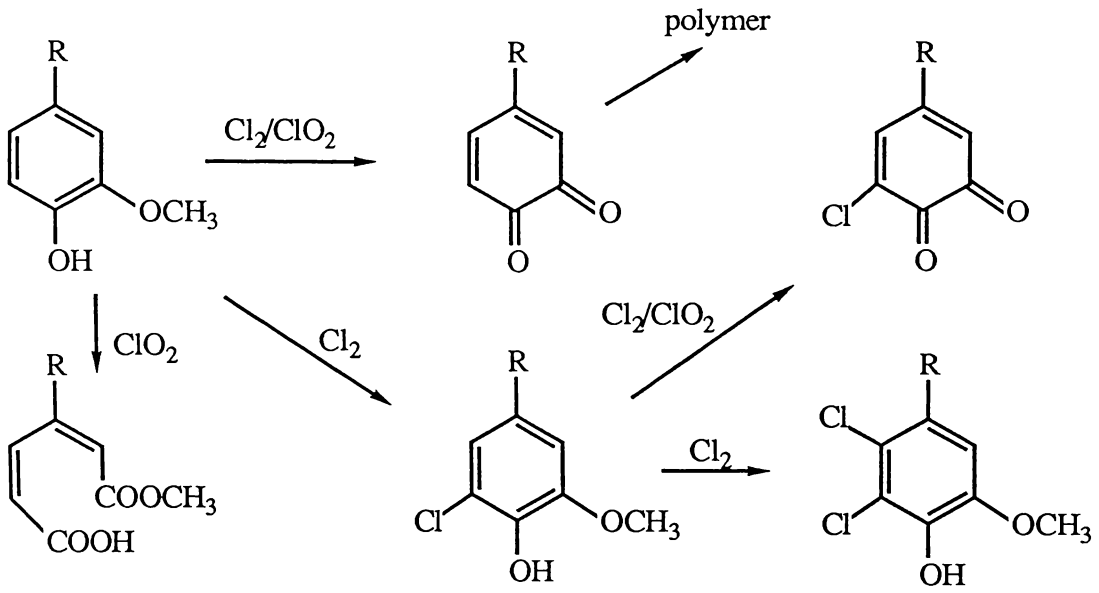


Figure 2.11 Reactions of a guaiacyl unit with chlorine and chlorine dioxide (Hardell and Lindgren, 1975)

2.6 ENVIRONMENTAL IMPACT

The early 1970's saw the beginning of a new phase of environmental chemistry, the identification and analysis of specific organic pollutants in water (Keith, 1976a). The wastewater discharges of pulp and paper mills have been known to affect the environment in a number of ways e.g. oxygen-depletion, suspended solids, foaming, colour and the release of toxic organic chemicals into natural waterways (Cox, 1981; Timperley, 1975, 1985).

2.6.1 Colour

The discharge of highly coloured effluent into the natural waterways is one of the more visible effects which the pulp and paper industry imposes on receiving waters. The main sources of these coloured effluents are the alkaline bleaching wastes, secondary Kraft pulp washing wastes and Kraft black liquor spills. The long term effects of high concentrations of colour on fish and smaller aquatic

life forms are unknown and have not been studied to date. The obstruction of transmitted light can be detrimental to aquatic life (Soniassy *et al*, 1977). It has been found that light acts as one of the stimuli affecting the grazing habits of zooplanktons, and assists fish and other marine organisms in discriminatory feeding. Hence, aquatic species relying on sight to locate food will have difficulty surviving in waters which are darkened by pulp mill effluent. This leads to shifts in aquatic populations and generally disrupts the aquatic eco-system.

It has also been noted that trout avoid heavy concentration of suspended solids and also coloured wastewaters. The reduction of light also interferes in the degradation of compounds that are broken down by photo isomerization.

Extensive work has been carried out on the removal of colour by flocculation (Davis, 1969; Gould, 1971), precipitation (Mittal and Mehrotra, 1981) and coagulation (Smith and Christman, 1969; Clarke and Davis, 1969; Tejera and Davis, 1970; Bebin *et al*, 1972; Olthof and Eckenfelder, 1973; Lang, 1981). As yet there is no one method that satisfactorily removes colour and is economically viable.

2.6.2 Biological Oxygen Demand

Biological oxygen demand (BOD) is a measure of the amount of oxygen used by organisms during aerobic decomposition of organic matter. It indirectly measures the amount of biodegradable organic matter in the water. BOD is commonly measured by the quantity of oxygen utilized by suitable aquatic micro-organisms during a five-day period and is denoted as BOD_5. Large amounts of lignin and

polysaccharides can deplete the dissolved oxygen level causing stress to aquatic organisms. The minimum acceptable levels of dissolved oxygen as given by Van Horn (1971) are 5 mg/l and 7 mg/l for warm and cold water biota respectively. While short term exposure to low levels of dissolved oxygen does not necessarily kill fish, it does place them under increased stress. In the case of freshwater trout one of the stress responses is inhibition of spawning.

2.6.3 Toxicity

The toxicity of pulp and paper mill effluent has been under extensive investigation particularly in Scandinavia, and more recently in Canada and North America. The effluent contains dissolved lignin and cellulose degradation products resulting from reactions between the pulp and pulping and bleaching chemicals (Leach and Thakore, 1975). Studies on the effects of pulp mill derived low molecular weight organic substances on several species of fish, including trout and salmon, have been carried out by Canadian (Rogers *et al*, 1972, 1975, 1979; McLeay *et al*, 1979; Kovacs *et al*, 1985, Kovacs, 1985; Leach *et al*, 1985; Kovacs and Voss, 1986), Scandinavian (Holmbom, 1980; Holmbom and Lehtinen, 1980; Oikari *et al*, 1980, 1983) and Japanese (Kinae *et al*, 1981a, 1981b) groups.

Toxicity can be expressed as the Median Survival Time of a fish population in a defined effluent concentration or as the lethal concentration (96-hour LC_{50}) which kills 50% of the fish population in 96 hours. Published LC_{50} (96-hour) values must however be interpreted with some caution since the quoted values invariably also depend on factors such as pH, water temperature, size of fish, water

replenishment rate and oxygen level. For example, McLeay *et al* (1979a, 1979b) demonstrated that the phenolic and acidic substances found in pulp mill effluents are less toxic at pH 9-10, than at pH 7, or between pH 3-5. This appears to reflect the extent of ionization of the phenolic and acidic hydroxyl groups.

The major toxicants in pulp mill effluent are resin acids and neutral diterpenes, unsaturated fatty acids, chlorinated phenols and chlorinated analogues of dehydroabietic acid (See Table 2.3).

Table 2.3
LC_{50} (96-hour) values of some pulp mill effluent substances

Toxicant	mg/l	ref.
3,4,5,6-Tetrachloroguaiacol	0.32	a
3,4,5-Trichloroguaiacol	0.75	a
Trichlorocatechol	0.30	b
Monochlorodehydroabietic acid	0.60	b
12,14-Dichlorodehydroabietic acid	0.60	a
Pimaric acid	0.80	c
Isopimaric acid	0.40	c
Palustric acid	0.50	c
Abietic acid	0.70	c
Dehydroabietic acid	1.1	d
Sodium linolenate	1.08	e
Sodium oleate	1.53	e
Sodium linoleate	3.7	e
Sodium stearate	>20	a
9,10-Epoxystearic acid	1.5	c

[a] Leach and Thakore, 1975; [b] Servizi *et al*, 1968; [c] Leach and Thakore, 1975; [d] Davis and Hoo, 1975; [e] Leach and Thakore, 1973.

The resin acids commonly found are secodehydroabietic acid, pimaric acid, sandaracopimaric acid, isopimaric acid, palustric acid,

abietic acid and dehydroabietic acid (Keith, 1969; Garrison *et al*, 1970; Rogers, 1973, Hrutfiord *et al*, 1967, 1975; Fox, 1977; Holmbom, 1980). Of these compounds dehydroabietic acid has been found to be the most persistent, presumably because its aromatic ring inhibits biological degradation. On the other hand the presence of an aromatic ring in dehydroabietic acid facilitates oxidation or chlorination during pulping operations to produce 7-oxodehydroabietic acid (Biellmann *et al*, 1973), 12- or 14-chlorodehydroabietic acid, and 12,14-dichlorodehydroabietic acid. The chlorinated analogues are *ca* 40% more toxic than the parent acid (See Table 2.3).

Unsaturated fatty acids have a higher toxicity level [smaller LC_{50} (96-hour) values] compared with the saturated analogues (Rogers *et al*, 1975; Leach and Thakore, 1976; Walden and Howard, 1977). For example, sodium stearate is about 20 times less toxic than sodium linoleate. It is also apparent that toxicity increases as the degree of unsaturation increases (See Table 2.3). Chlorination of oleic acid in aqueous medium can result in the formation of 9,10-dichlorostearic acid, or chlorohydroxystearic acid which can eliminate hydrochloric acid to form 9,10-epoxystearic acid, a substance that is an order of magnitude more toxic than the parent saturated acid (stearic acid).

Although chlorinated phenols are often present in much lesser quantities than resin acids, their impact is usually greater, due to their tendency to bioaccumulate (Lander *et al*, 1977). They are also mutagenic (Kringstad *et al*, 1983, 1984; Holmbom *et al*, 1984). Chlorinated phenols have been found to be quite resistant to

biodegradation; in general resistance increases with the degree of chlorination. A number of studies have been carried out to determine how the levels of chlorinated phenols and toxicity of bleach plant effluents are related to bleaching techniques (Voss *et al,* 1981a, 1981b; Kringstad and Lindström, 1984).

CHAPTER THREE

TASMAN PULP AND PAPER COMPANY

3.1 INTRODUCTION

The Tasman Pulp and Paper Company Limited has expanded considerably since producing 37,000 tonnes of Kraft pulp and 76,000 tonnes of newsprint in 1955. It now produces 170,000 tonnes of Kraft pulp and 330,000 tonnes of newsprint annually (Tasman Pulp and Paper Co. Ltd., 1985). Today Tasman is New Zealand's largest single exporter of manufactured goods, mainly Kraft pulp and newsprint. These are shipped mainly to Australia, South East Asia, the Pacific Islands, Middle East, Europe and China.

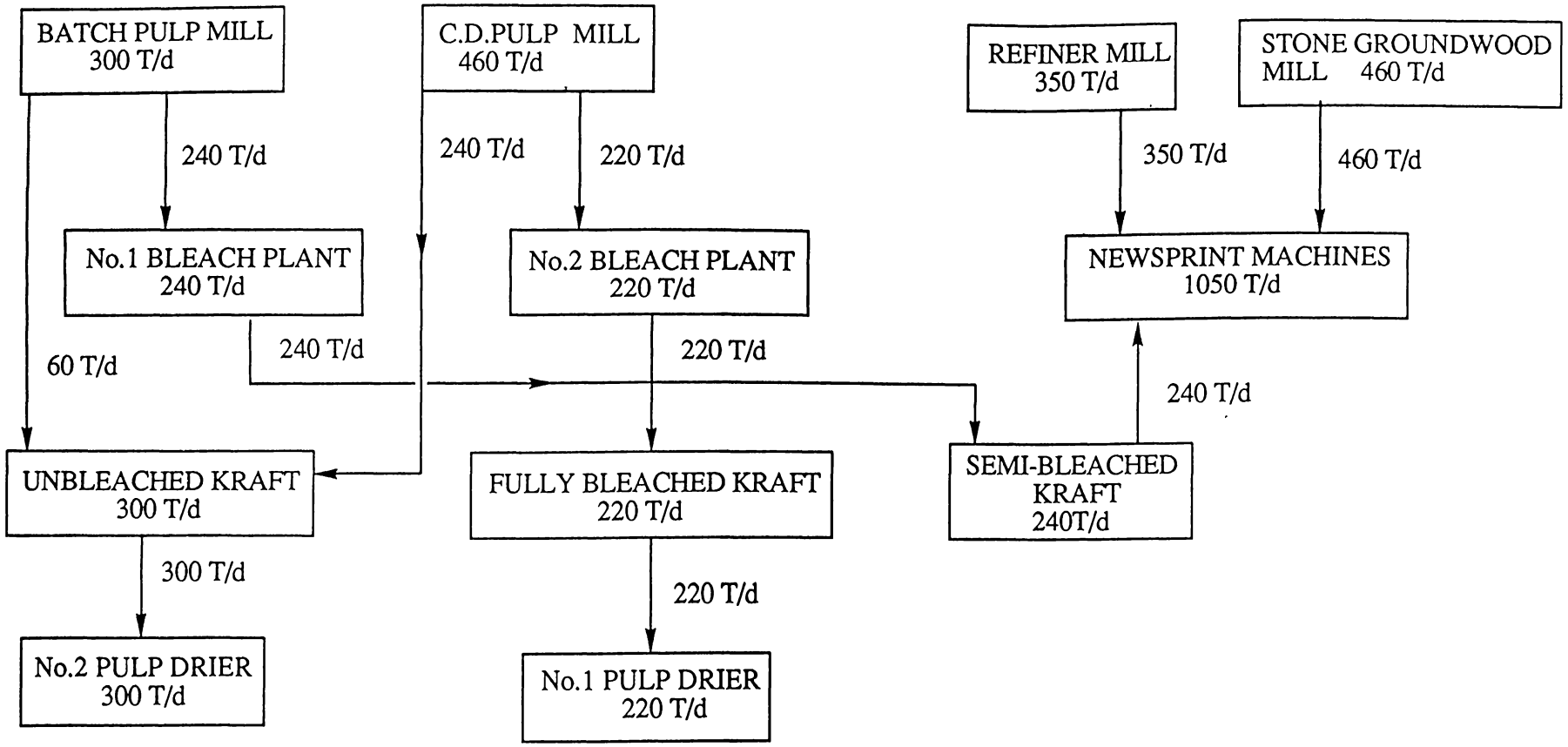
The mill is sited at Kawerau on the banks of the Tarawera River covering a total area of 93 hectares. It is an integrated pulp and paper mill with a sawmill and a chlor-alkali plant. The mill is strategically placed with a constant water supply from the Tarawera River, natural energy from a geothermal field and the relative proximity to an overseas port (Mount Maunganui). The Kawerau borefield is the largest of its kind in the world, and at one time, included one of the highest producing bores in the world; KA21 which was capable of producing enough steam to generate electricity for a town of 83,000 people (approximately 10 times that of the Kawerau township). This

together with the burning of pulp and sawmill wastes makes the Kawerau mill 90% self-sufficient in thermal energy. Tasman uses fuel oil and natural gas to make up the rest. The natural gas is used to fire the lime kilns. Tasman currently uses about 120 megawatts of electricity to drive the electric motors in the mechanical pulp mills. This is approximately twice the output of the Matahina dam on the adjacent Rangitaiki River.

3.2 HISTORICAL BACKGROUND

In 1898 the New Zealand Lands and Survey Department planted four experimental stands of exotic timber on the formerly unproductive pumice country of the central North Island plateau. Today the Kaingaroa State Forest spreading over 160,000 hectares is one of the world's largest man-made forests. Major development projects arose from this exotic pine forests: relief labour was used during the 1930's depression years (and later) to provide sawn timber, pulp and paper to overseas and local markets. In 1952, Tasman Pulp and Paper Company Limited was formed and it continued the utilization of this vast wood source. The Company is now fully owned by Fletcher Challenge Limited.

Tasman has three paper machines, two mechanical pulp mills, two chemical (Kraft) pulp mills, two bleach plants, and a chlor-alkali plant (the sawmill is operated by a separate subsidiary of Fletcher Challenge, Tasman Lumber Company Limited). The production capacity of the mill is given in Table 3.1, while Figure 3.1 depicts the production operations of Tasman's existing plant.



T/d - air dried tonne per day

Figure 3.1 Tasman's Production Operations

Source: Tasman Pulp and Paper Company Limited.

Table 3.1
Approximate Mill Capacity (1985).

	tonnes per year
Kraft pulp	
No. 1 mill (batch)	110,000
No. 2 mill (continuous)	150,000
Total Kraft pulp	260,000
Mechanical pulp	
Stone groundwood	180,000
Refiner groundwood	115,000
Total mechanical pulp	295,000
Kraft pulp bleaching	
No. 1 plant (C-E-H)	60,000
No. 2 plant (C_D-E-D-E-D)	70,000
Total bleaching capacity	130,000
Newsprint and wallpaper base	330,000

Source: Tasman Pulp and Paper Company Limited.

3.3. PULP MILLS

Tasman produces wood pulp by mechanical (groundwood) and chemical (Kraft) processes. The pulp used for Tasman's newsprint is a blend of 80% mechanical pulp and 20% Kraft pulp. All the mechanical pulp produced is used in the manufacture of newsprint while only 30% of the Kraft pulp goes to the paper machines, the rest being sold.

Mechanical pulping is carried out at the stone groundwood and refiner groundwood mills. Usually 460 tonnes/day of groundwood pulp is produced by 13 stones, each of which is driven by a 5,500 HP

motor. While 1.2 metre long logs are used to produce 500 tonnes/day of stone groundwood pulp, wood chips are used to produce 350 tonnes/day of refiner mill pulp. Mechanical pulp is bleached using sodium dithionite.

Kraft pulp is "cooked" in either batch or continuous digesters. Tasman has five batch digesters, each with a volume of 90 m^3 and can process 300 tonnes/day of pulp. The Kamyr continuous digester is a 70 metre high tower and produces pulp at the rate of 540 tonnes/day.

3.4 BLEACH PLANTS

The chlor-alkali plant produces all the chemicals used in the bleach plants except for chlorine dioxide which is manufactured in a separate plant called the SVP (Single Vessel Process). About 80% of the pulp from the batch digesters goes to the No. 1 bleach plant to produce semi-bleached Kraft pulp. This pulp is used in newsprint production. The No.1 bleach plant utilizes a C-E-H sequence and has a production capacity of 240 tonnes/day.

About half of the pulp from the continuous digester goes to the No. 2 bleach plant to produce fully bleached Kraft pulp, which is used in making stationery, fine printing papers and tissues. The No. 2 bleach plant utilized a C_D-E_1-D-E_2-D sequence prior to December 1985. This sequence was then modified to oxygen reinforced alkali extraction and the second alkali extraction was eliminated. The No. 2 bleach plant has a production capacity of 220 tonnes/day.

3.5 PAPER MACHINES

Tasman has three large Fourdrinier-type paper machines to produce mainly newsprint. These machines, which run at speeds of 625 to 1,000 metre/minute, are 100 metres long, 10 metres wide and 10 metres high; only 15 seconds is required to convert wet pulp to finished newsprint. The newsprint is wound onto steel spools in rolls 7.4 metres wide, 30 kilometres long and weighing about 9 tonnes. The blend of groundwood and Kraft pulps gives the finished newsprint good printing qualities and the strength required to run on high-speed printing presses.

3.6 EFFLUENT TREATMENT

In 1954, the Tasman Pulp and Paper Company Enabling Act was passed and provided for the discharge of the mill wastes into the Tarawera River (Tarawera River Management Plan, 1985). Under Section Four of this Act, mill effluent can only be discharged into the Tarawera River under the control of the Pollution Advisory Council. This Council was superseded by the Water Resources Council (Cox, 1981) and more recently by the National Water and Soil Conservation Authority (Slabber, *pers. comm.*). In 1986, the Tasman Enabling Amendment Act was passed by the Parliament. This puts full control of water rights and discharges with the Bay of Plenty Catchment Commission and the Regional Water Board.

In 1966, the lower reaches of the Tarawera River were given a Class D classification. Conditions of this classification are:

i) the natural water temperature shall not be changed by more than 3°C.

ii) the acidity or alkalinity of the waters should be within the range pH 6-9.

iii) the waters shall not be so tainted so as to make them unpalatable nor contain toxic substances to the extent that they are unsafe for consumption by farm animals, nor shall they emit objectionable odours.

iv) the natural colour and clarity of the water shall not be changed to a conspicuous extent.

v) the oxygen content in solution in the water should not be reduced to below 5 mg/l.

Wastewater in the mill originates from process wastewater, domestic, geothermal, stormwater, backwash from the treatment plant and supernatant solution from the solid waste lagoon. The process wastewater is derived from log washing and debarking, mechanical pulping, chemical pulping, bleaching of chemical pulp, paper-making, non-process discharges (spills) and geothermal steam condensate. This wastewater is directed to the treatment plant. Effluent from the bleach plants and the chemical pulping sections make up the bulk of the discharge to the wastewater treatment plant.

Stormwater from the main log storage area, roof areas, roads and other paved areas is discharged directly into the Tarawera River. Geothermal steam condensate is piped directly into the river without treatment. A project is now underway to use this as boiler feed water with very promising results (Slabber, *pers. comm.*). Hydraulic debarkers have been found to cause environmental problems as the

discharged effluent contains substantial amounts of suspended solids and dissolved sugars which give rise to high BOD_5. Hence, Tasman is replacing its existing hydraulic debarkers with a very large drum debarker. The large diameter logs will then be split or quartered to smaller sizes to go through the drum debarker.

3.6.1 Primary Treatment

The primary treatment comprises bar screens, a circular clarifier and a sludge lagoon. The bar screens remove large solids from the effluent prior to entering the clarifier. This is to prevent the clarifier rakes from being jammed. Most of the remaining suspended solids are settled out in an 84-metre diameter clarifier. The BOD_5 level of the clarified effluent (35 tonnes per day) is reduced by *ca* 10% by the removal of the suspended solids (Slabber, *pers comm.*). The suspended solids are composed of 70% fibres from the paper mill, pulp mill and wood preparation areas, while the remaining 30% is composed of lime-mud, fly ash (from the waste treatment boilers) and pumice. The solid waste from the clarifier is then pumped as a slurry to a sludge lagoon while the clarified effluent flows by gravity to the aeration ponds.

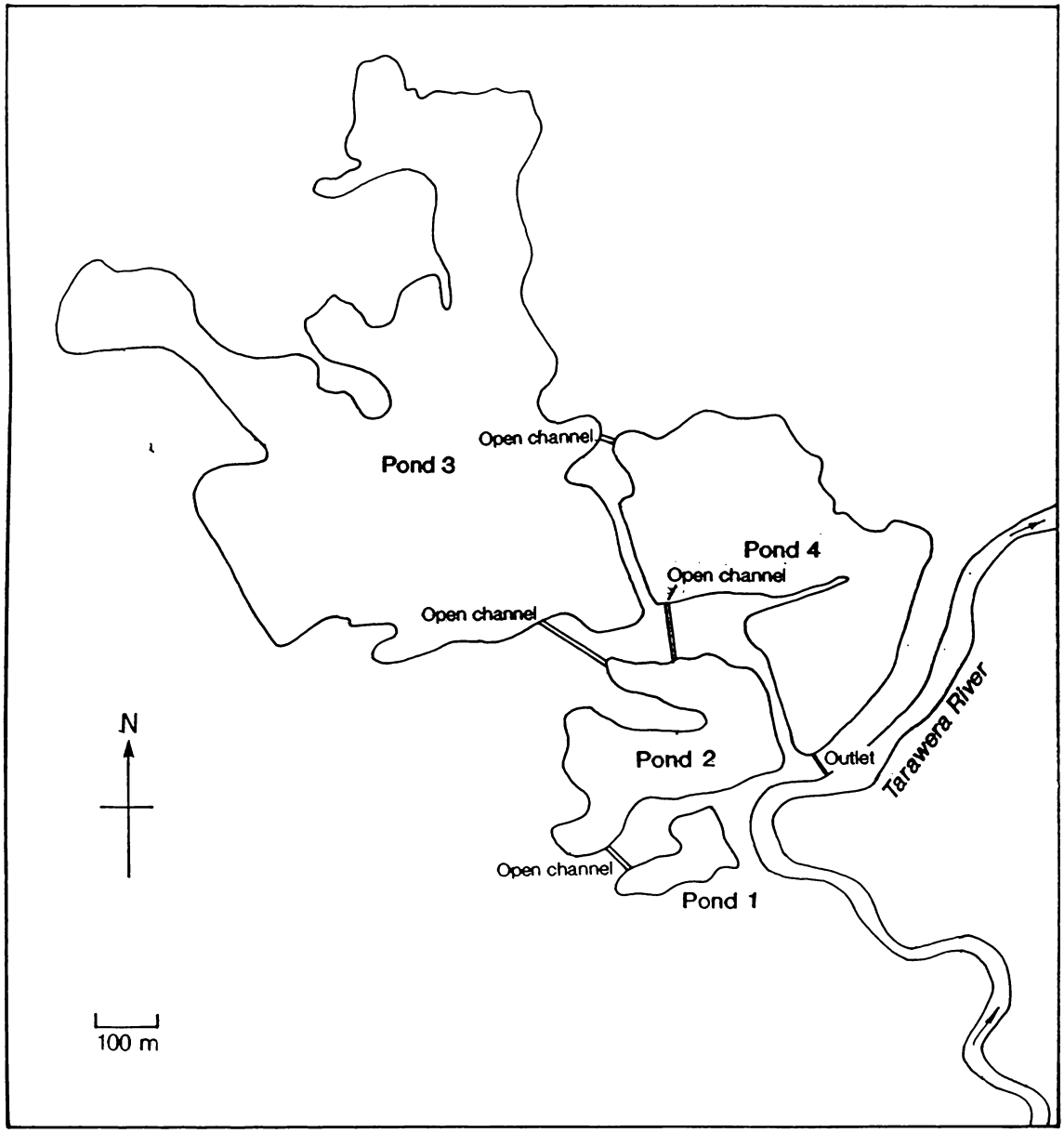
The sludge lagoon has a surface area of approximately 35 hectares (Tonkin and Taylor, 1985). It is located in a shallow valley adjacent to the Tarawera River and is enclosed by a 600 metre long earth-filled embankment. This valley originally contained a lake called Lake Rotoitipaku. Substantial flooding in 1904 resulted in large amounts of pumiceous sands being deposited on the low lying ground.

It has also been found that prior to 1904, the lagoon was covered with soft diatomaceous silt.

The incoming sludge which is predominantly wood fibre, is dispersed through the lagoon, where it settles out. The sludge lagoon seems to be a floating mass, between 3-5 metres thick at the centre. Tonkin and Taylor (1985) have stated that the incoming sludge, "is acted on by bacteria, producing a mass of floating sludge", although no evidence was given to support this statement. Indeed it is well-known that wood/cellulose is not degraded in anaerobic conditions. The underlying water zone varies from 0.1-0.6 metres in depth. The water stream which exits from the sludge lagoon is directed into the aeration ponds for treatment together with the effluent.

3.6.2 Secondary Treatment

Secondary treatment was introduced in 1973 to improve the quality of waste discharges. The secondary treatment at that time consisted of one holding pond and three aeration ponds (Figure 3.2). This covered a total area of 44.1 hectares. In 1976, the No.3 aeration pond was withdrawn (Slabber, 1984). This was due to insufficient aeration capacity to maintain the ponds in an aerobic condition; under anaerobic conditions odour problems occurred. The main problems were the irregularity in the shape of the pond due to two shallow arms which made effluent circulation difficult, and the shallowness of the pond which made it inappropriate for floating aerators. The treatment system was reduced to a three-pond system (one holding pond and two aeration ponds) having a four-day retention capacity with 1675 HP of aeration capacity. This resulted in



Prior to October 1986 - Treatment system consisted of Ponds 1, 2 and 4.
After October 1986 - Treatment system included Pond 3.

Source: Tasman Pulp and Paper Company Limited.

Figure 3.2 Tasman Pulp and Paper mill's Oxidation Ponds

the effluent discharges having a BOD_5 level of 10 tonnes per day. With a four-day aeration system, 80% of the BOD_5 was removed under normal mill operations (Slabber, *pers. comm.*). However, it was found that this was inadequate in cases of heavy BOD_5 loadings such as during a spill.

As a result of new guidelines set down in the Tarawera River Management Plan, it was necessary to be able to meet lower BOD_5 discharge limits. The No.3 pond was re-commissioned in October 1986 to meet these lower BOD_5 discharges (6-8 tonnes per day). This was achieved by cutting off the two arms and dredging the shallow areas to a depth of 4 metres. The system was then extended to an eight-day retention capacity with 2,500 H.P. of aerators. This expanded system has the capacity to remove 90% of the BOD_5; 40% being removed in the No.2 pond, 33% in the No.3 pond and 17% in the No.4 pond. The effluent typically, spends 1.5 days in the No.2 pond, 4 days in the No.3 pond and 2.5 days in the No.4 pond (Slabber, *pers. comm.*).

Table 3.2 gives a comparison of this system with those of 12 bleached Kraft mills in the U.S.A.

Table 3.2

Comparison of Tasman 's Aeration Ponds with 12 Kraft Mills in U.S.A.

Mill ID	Mill Production T/d	Effluent Flow Ml/d	Retention capacity days	Aeration capacity H.P.	Influent BOD5 T/d	Discharge BOD5 T/d	Removal Efficiency %	Influent BOD5 per H.P./kg	BOD5 removed per H.P./kg
001	1600	140	10.7	1300	36.3	7.4	80	27.9	22.2
107	520	64	6.5	750	12.0	6.2	48	16.0	7.7
203	330	51	9.0	2534	27.1	5.0	82	10.7	8.7
301	1300	218	5.9	2325	50.8	8.3	84	21.8	18.3
402	940	123	8.0	1620	27.2	4.7	83	16.8	13.9
409	1150	117	16.5	2700	37.9	4.9	70	14.0	12.2
606	400	86	13.2	1700	20.0	2.1	89	11.7	10.5
607	560	109	10.2	1700	57.9	11.5	80	34.0	27.3
719	1200	107	6.9	2700	35.1	10.4	70	13.0	9.1
907	1000	131	1.2	1425	30.1	9.3	70	21.1	14.6
4401	775	90	10.5	1725	20.1	1.8	90	11.6	10.6
Tasman[1]	1570	210	4.0	1625	36.0	9.0	75	21.5	16.1
Tasman[2]	1570	210	4.0	1925	36.0	7.0	est 80	18.2	14.6
Tasman[3]	1855	210	8.0	2725	36.0	3.6	est 90	13.2	11.0
Tasman[4]	2420	210	8.0	2725	48.0	7.2	est 85	17.6	15.0

1. 1984 situation
2. 1984 situation with 300 HP aerators added
3. Pulp mill modernized "Bleach" option
4. No. 4 Paper machine added

(Source: Tasman Pulp and Paper Company Limited)

CHAPTER FOUR

EXPERIMENTAL METHODS

4.1 INTRODUCTION

The nature of wastewaters is normally described in terms of BOD and chemical oxygen demand (COD). However these methods give little information as to the structures of organic species present in the wastewaters. The molecular weight range of organic compounds found in pulp and paper mill discharges typically ranges from 50,000 amu (e.g. lignins) to less than 50 amu (e.g. methanol). The classes of compounds present include carbohydrates, fatty acids, glycerides, aromatics, monoterpenes, resin acids, suphonated substances, chlorinated substances, and cyclopentenones. Hitherto considerable attention has been directed towards the characterization of low molecular weight substances (*i.e.* those having molecular weights less than 400 amu), largely because some of the low molecular weight substances have been found to have significant toxicity, and to be persistent in the environment.

The isolation of individual substances is a tedious and time consuming process, particularly in the case of water samples in which substances are present in concentrations of the order 1-1000 μg/l. However the state of development of combined capillary gas

chromatography-mass spectroscopy (GC-MS) systems is now such that, provided 10-100 nanograms of a complex mixture of extractives is available, individual substances can be routinely identified and quantified without the need for isolation. Analysis of low molecular weight compounds in the pulp and paper mill effluent involves four main procedures: (i) sampling, (ii) extraction, (iii) identification and (iv) quantification.

4.2 SAMPLING

Water samples were collected from various mill sites, including the bleach plants, black liquor oxidation plant, paper machine discharges, the treatment ponds and the Tarawera River. Samples from the mill sources were collected at the various sewer pipes directly into 2.5-litre glass winchesters, while surface water samples from the treatment ponds and river were collected by using a 5-litre pail. Surface sediment samples were obtained using a metal scoop (10 cm in diameter and 15 cm long) with a long handle (1 metre) unless otherwise stated. The sediment samples were stored in wide-necked glass containers.

Previous studies (Panadam *et al*, 1984) had indicated that samples collected in plastic containers were sometimes contaminated with plasticizers, chiefly phthalates. Therefore, glass containers were used instead, and where this was not possible, the plastic containers were washed with 2 M sodium hydroxide solution, rinsed thoroughly with water and dried. The extraction of distilled water that had been stored in these containers indicated that this procedure was adequate for the removal of phthalates and other

residues. Sample containers were stored in polystyrene boxes and on arrival at the University of Waikato, refrigerated at 4°C until required for extraction. This was generally performed within 48 hours. No stabilizers were added as it was found that no significant degradation occurred during this time. This was ascertained by dividing a sample into two portions and extracting one portion immediately on arrival at the laboratory while the other was extracted after being stored for 48 hours at 4°C.

BOD_5 measurements reported in this study were determined by the Environmental Laboratory, Tasman Pulp and Paper Mill on split samples.

4.3 EXTRACTION

Various techniques for the extraction of low molecular weight components from the aqueous phase of the pulp and paper mill effluent have been reported, namely the use of absorptive agents, solvent extraction with or without prior ultra-filtration, freeze drying and reverse osmosis.

4.3.1 Absorptive Methods

The removal of organics from aqueous media by using macro-reticular resins as sorptive agents has been widely used (Leach and Thakore, 1973; McKague, 1981; Voss, 1984). The use of XAD resins has been recommended for the qualitative analysis of large volumes of highly diluted effluents (Junk *et al*, 1974; Rogers and Mahood, 1977; Claeys and Owens, 1978; Van Rossum and Webb, 1978; Voss and Rapsomatiotis, 1985). While adsorption procedures have often proven

to be satisfactory for samples of low colour, local experience has indicated that highly coloured extracts (*i.e.* those with high lignin content) invariably give low recoveries (Letford, 1985). After several bed volumes of coloured effluent had been through the column, elution of coloured material was observed; evidence exists for the co-elution of appreciable quantities of low molecular weight organic substances, presumably because of hydrogen bonding interactions with the eluted lignin.

Other workers have found that extraction of resin acids using XAD resins varied with pH. For example, Claeys *et al* (1983) observed only 23% recovery efficiency for resin acids at adsorption pH values of 6.4-10 but obtained 90% recovery on acidification to pH 3. This was consistent with the results of Junk *et al* (1974) who found that lower recoveries were obtained at higher pH. Efficiency studies using Rohm and Haas XAD-2 and XAD-4 resins gave recoveries of 73-78% with pulp and paper mill effluent. Fox (1977) obtained 80-100% recoveries for monoterpenes, diterpene resin acids, phenols and fatty acids using XAD-2 columns. However studies at the University of Waikato (Letford, 1985) using XAD-2 resin, and local pulp mill effluents gave variable results.

The other sorptive methods include activated carbon, reversed-phase trace enrichment and the use of support-bonded silicones (Aue, 1972). The disadvantages in using activated carbon are its large variance in adsorption/desorption characteristics, its lack of cleanliness and its tendency to react with the adsorbed compounds

(Keith, 1976b).

4.3.2 Solvent Extraction Methods

The liquid-liquid extraction technique has proven to be a simple yet efficient method for organic extraction. This technique can be used with different quantities of samples; e.g. small scale vial extraction (Voss, 1983; Abrahamsson and Xie, 1983), separating funnel extraction (Kringstad and Lindström, 1984; Keith, 1976a; Holmbom, 1980; Voss and Rapsomatiotis, 1985) and continuous extraction (Keith, 1976a; Lindström and Nordin, 1976).

The vial and separating funnel procedures, besides being reproducible, have the advantages of short extraction times and low loss of volatile components. The major disadvantages of these methods are the precipitation of lignin on acidification prior to extraction and the formation of emulsion on agitation. Both of these problem were overcome by filtering the extract through glassfibre filter paper (Whatman GF/A).

Continuous liquid-liquid extraction typically requires an 18-hour extraction period to exhaustively recover extractable organic substances. However, refluxing of the extractive solution causes the loss of volatile substances and may promote the reaction/degradation of extracted substances. The loss of volatile substances can be monitored by the addition of a pair of inert internal standards, one of which is comparatively volatile, e.g. *n*-nonane (b.p. 154^{o}C) while the other is not, e.g. *n*-octadecane (m.p. 28^{o}C). The boiling point of *n*-nonane is in the range of that of the volatile components of interest such as α-pinene (b.p. 156^{o}C) and β-pinene (b.p. 164^{o}C). Hence the

assessment of the recovered nonane-octadecane ratio as opposed to that initially added allows an estimate of the losses of the relatively volatile monoterpene hydrocarbons. With care the ratio could be maintained in the region 0.6-0.7:1, however ratios in the region 0.2-0.5:1 were often obtained. It is apparent that during liquid-liquid extraction and concentration, appreciable loss of monoterpenes, especially the hydrocarbons, occurs. Therefore, the monoterpene concentrations given in the tables are considered indicative rather than definitive, and are likely to be lower than the actual quantity present.

Since liquid-liquid extraction procedures utilize acidified effluent solutions, significant quantities of acid will be carried over into the refluxing chloroform solution. This can lead to the acid-catalysed esterification of fatty acids (see Chapter 8), and mitigates against the use of a fatty acid as an internal standard. The principal advantage of the continuous liquid-liquid procedure is that extraction is repetitive, hence it leads to a high recovery of the organic substances, irrespective of their distribution coefficient. Also the presence of flocculated lignin in the extractor does not interfere with the extraction process.

The efficiency of extraction of phenolic and acidic substances is improved when they are present in their protonated (un-ionized) forms. Thus acidification of effluent samples to below the pKa values of the acids and phenols present in the sample is desirable. Initial studies (Panadam *et al*, 1984) revealed that acidification to pH 2 resulted in the precipitation of lignin, whereas acidification to pH 4 did not result in precipitation. Removal of the precipitated lignin by

vacuum filtration prior to extraction resulted in a substantial reduction in the recovery of extractable substances (see Table 4.1). Lindström (1986) has reported that for complete recoveries, a pH lower than 3 is necessary while Garrison *et al* (1981) reported that acidification to pH 2 or lower allowed the extraction of weak to moderately strong acids along with neutral compounds. Therefore the extractions were carried out at pH 2 and unfiltered.

Table 4.1
Methylated resin acids and fatty acids (mg/l) recovered from a black liquor sample at different extraction pH's.

Compound	pH 2 unfiltered	pH 2 filtered	pH 4 unfiltered
Methyl palmitate	6.8	0.2	11.0
Methyl anteisoheptadecanoate	1.1	0.1	1.6
Methyl oleate	12.3	0.4	1.6
Methyl linoleate	26.8	0.9	3.3
Methyl secodehydroabietate-1	4.5	0.1	1.0
Methyl secodehydroabietate-2	5.1	0.1	3.6
Methyl pimarate	4.2	0.2	8.7
Methyl sandaracopimarate	4.2	0.1	2.0
Methyl isopimarate	2.8	0.2	2.0
Methyl palustrate	6.2	-	7.0
Methyl dehydroabietate	15.8	0.7	13.0
Methyl abietate	22.0	0.5	17.0
Methyl neoabietate	12.9	0.2	1.3
Total fatty acid methyl esters	47.0	1.7	17.5
Total resin acid methyl esters	77.1	2.1	55.6

A variety of solvents have been used in the extraction of organic substances from pulp and paper mill effluents. Holmbom (1980) found that when dichloromethane was used to extract resin acids,

rapid acid-catalysed isomerization of levopimaric, palustric and neoabietic acids to abietic acid occurred. Solvent extraction studies by Webb (1978) have shown that chloroform is a more efficient extraction solvent. Chloroform was used in the present study, primarily because of its density, relatively low boiling point, non-flammability, its ability to extract both polar and non-polar compounds, and its limited tendency to promote resin acid isomerization.

4.3.3 Experimental Procedures for Solvent Extraction

Continuous liquid-liquid extraction was carried out in 100-ml, 250-ml, 1-litre or 2.5-litre extractors designed for the extraction of heavier-than-water solvents. Effluent samples were, unless otherwise stated, introduced into an extractor, and acidified to pH 2 in the extractor, using 2 M hydrochloric acid. The internal standards of 1 mg/ml concentration in chloroform were added to the effluent samples prior to acidification (see section 4.5). Acidified effluents were typically extracted for 16 hours (1- and 2.5-litre extractors) or 8 hours (100- and 250-ml extractors) using chloroform as the extracting solvent. Drum chloroform was distilled twice to remove stabilizers, phthalates and other industrial contaminants. Extractions of distilled water which was substituted for effluent afforded gas chromatograms devoid of any peaks after the solvent peak.

Using the derivatization and quantification procedures described in sections 4.3.4 and 4.5 respectively, recoveries of resin acids and fatty acids from a black liquor sample at pH 2 and 4 are given in Table 4.1. In the case of the filtered pH 2 extraction, the

black liquor sample was acidified in a beaker and the flocculated lignin removed by filtration. The filtrate was then introduced into the extractor. It is apparent that filtration of the acidified sample results in a dramatic reduction in the recovery of both fatty acids and resin acids. In accordance with the conclusions of other workers (Lindström, 1986; Garrison *et al*, 1981), recoveries at pH 2 are generally greater than at pH 4. Hence, samples were routinely acidified to pH 2 prior to liquid-liquid extractions.

Separating funnel extractions were performed in 1-litre glass separating funnels; typically a 500 ml effluent sample was extracted using two 40 ml aliquots of chloroform. The emulsion formed on agitation was clarified by vacuum filtration through a glassfibre filter paper (Whatman type GF/A). Table 4.2 compares the recoveries of resin acids by continuous liquid-liquid and separating funnel extractions of an effluent sample taken from the inlet of the treatment system on 6th October, 1986. Table 4.2 also compares the duplicate extraction of the same effluent sample with two portions of chloroform (also see section 4.5). It is apparent that the first portion of chloroform extracts the bulk of the extractives (typically greater than 80%), while a second chloroform extraction recovers most of the remaining material. Since extraction with a third portion of chloroform afforded a negligible quantity of extractives, separating funnel extractions were routinely performed using two portions of chloroform.

Table 4.2
Concentrations (µg/l) of methylated resin acids recovered from a treatment pond inlet sample of 6th October, 1986.

Compound	(1)	(2)	(3)	(4)	(5)	(6)
n-Octadecane (int. std.)	1000	1000	941	62	956	64
Methyl secodehydroabietate-1	22	32	21	4	27	6
Methyl secodehydroabietate-2	18	29	15	4	18	3
Methyl pimarate	283	225	216	36	220	41
Methyl sandaracopimarate	50	102	32	4	48	10
Methyl isopimarate	221	200	157	24	157	28
Methyl dehydroabietate	740	868	615	99	678	111
Methyl abietate	429	412	344	51	487	77
n-Hexadecane (ext. std.)[a]	-	-	1000	1000	1000	1000

[a] added as external standard after extraction, but prior to derivatization. (1) separating funnel extraction; (2) 16-hour continuous liquid-liquid extraction; (3) separating funnel extraction with added external standard (first portion of chloroform); (4) second extraction of (3) with added external standard; (5) duplicate of (3); (6) duplicate of (4).

Trial liquid-liquid extractions established (at least in the case of the 1-litre extractors) that the bulk of the extractives were recovered after 16 hours, hence a 16-hour extraction time was routinely used It is apparent that separating funnel recoveries are generally comparable to within *ca* ± 20% of those obtained by continuous

extraction. In general concentrated samples, such as black liquor samples were extracted by the separating funnel procedure, whereas more dilute samples (e.g. treatment pond and river samples) were extracted by continuous liquid-liquid extraction. Separating funnel extractions were also used when an immediate result was required; e.g. when following the progress of a black liquor or turpentine spill through the treatment system.

Sediment samples were dried at 130°C for 12 hours and extracted with redistilled chloroform for 12 hours in an all-glass Soxhlet apparatus. The chloroform extracts were then concentrated, derivatized and analysed as for the aqueous samples.

4.3.4 Concentration and Derivatization

Separating funnel and liquid-liquid extractive solutions were first concentrated under reduced pressure on the rotary evaporator to *ca* 1 ml and then dried by passage through a short column of anhydrous magnesium sulphate. Initially the extracts were evaporated to dryness and weighed to obtain the total extracted material, however GC profiles determined before and after complete evaporation established that this resulted in the loss of the more volatile components. To reduce this loss the temperature of the water bath of the rotary evaporator was maintained at 40°C and the extracts were concentrated *ca* 1 ml and not taken to dryness.

The acidic components of the samples were converted to their methylated derivatives by the addition of an ethereal solution of diazomethane. This was prepared by heating an ethereal solution of N-nitrosomethylurea over a 30% potassium hydroxide solution;

distillation of this mixture afforded an ethereal solution of diazomethane which was added to the concentrated chloroform extracts until a pale yellow colour persisted. The methylated extracts were then passed through a short florsil column. This generally afforded a colourless solution, presumably because of the removal of higher molecular weight (non-volatile) coloured components. The methylated extracts were further concentrated to *ca* 100 µl under a stream of dry nitrogen. GC analysis of the derivatized extracts before, and after, florsil filtration afforded essentially identical profiles.

Acetylation using, for example, acetic anhydride in the presence of pyridine, or sodium carbonate, has been employed in pulp and paper research as a means to distinguish between the presence of catechols (1,2-dihydroxybenzenes) and guaiacols (2-methoxyphenols) (see Section 6.3.1). However with respect to the present study, acetylation had several disadvantages, namely (i) acetyl group fragmentation ions tend to dominate the mass spectra of the derivatized compounds, making the recognition of other functional groups difficult; (ii) the majority of the compounds listed in the ITDS mass spectral library were methylated rather than acetylated derivatives; (iii) removal of pyridine (a relatively high boiling point solvent) can lead to the loss of volatile compounds; and (iv) incomplete neutralization of sodium carbonate can result in low recoveries of phenolic substances due to the presence of the corresponding non-GC volatile phenolate ions. After the bulk of the experimental work described in the present study had been completed, an efficient separating funnel procedure for the analysis of phenolic substances involving *in situ* acetate formation was

reported by Starck *et al* (1985). It appears the Starck procedure will become the method of choice since it is rapid and discriminates between catechols and guaiacols. Furthermore, an increasing amount of retention time and mass spectral data is becoming available for acetylated phenols.

4.4 IDENTIFICATION

Capillary column GC is a powerful separating system resembling fractional distillation, but having the capacity to separate more than 100 components in a 10-20 ng sample. Compounds present in the samples were identified by a combination of retention times, co-injection with authentic samples, and when combined with a mass spectrometer, by the matching of mass spectral fragmentation patterns.

4.4.1 Gas Chromatography

GC analyses were performed using the Varian 3700, the Pye Unicam PU4500 or the Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector (FID). The chromatograph was installed with a 12 m fused silica bonded-phase methyl silicone gum (BP-1) capillary column. Hydrogen was used as carrier gas, with a typical linear velocity of 35-40 cm/second; 1-3 µl injections were typically split 1 part to column and 150 parts to waste. when the Varian 3700 or the Pye Unicam PU4500 were used. In the case of the Hewlett-Packard 5890A, the Grob technique was used. Williams (1986) found that the split injection method gave rise to varying results and this was also observed in this study. While a splitless

injection would result in a higher precision, this was not possible with the instrument available during this study.

Analyses were temperature programmed from 40°C (2 minutes initial hold) to 240°C (20 minutes final hold) at 4°C/minute. The injector and detector temperatures were maintained at 220°C and 250°C respectively. Where only a fatty and resin acid analysis was required, the initial column temperature was increased to 150°C. Foster and Zinkel (1982) have reported the retention times of a large number of methylated resin acids, relative to the retention time of methyl pimarate, on Silar-10C, BDS, SP-2330, SP-1000, SE-54 and SE-30 capillary columns. Table 4.3 compares the retention times observed on a 12 m BP-1 (SGE, Australia) capillary column operated isothermally at 170°C and 190°C, using hydrogen as carrier gas (linear velocity of 40 cm/sec), with those reported for an SE-30 column using helium as carrier gas (linear velocity of 30.3 cm/sec). Both of these columns utilized non-polar methyl silicone gums as stationary phases. Despite the use of different carrier gases, there is a close correspondence between the relative retention times reported by Foster and Zinkel (1982), and those observed in the present study.

4.4.2 Combined GC-MS and GC-ITDS analysis

Initially, mass spectrometry work was performed on a Hewlett-Packard GC-MS system operated by the Forest Research Institute, Rotorua. However, early in 1986 the University of Waikato secured the use of a Finnigan MAT series 700 Ion Trap Detector System (ITDS). In this system sample molecules are ionized by electrons emitted from a heated filament in the ion trap detector. Unlike

conventional or quadrupole mass spectrometers, the ion trap detector operates at relatively high pressures (10^{-3} torr *cf* 10^{-6} torr).

Table 4.3
Relative retention times of methylated resin acids on a 12 m BP-1 fused silica capillary column operated isothermally at 170°C and190°C.

Compound	Observed[a] (170°C)	Reported[b] (170°C)	Observed[a] (190°C)	Reported[b] (190°C)
Methyl pimarate	1.000	1.000	1.000	1.000
Methyl sandaracopimarate	1.062	1.065	1.043	1.057
Methyl pimaran-18-oate	1.123	1.117	1.109	1.109
Methyl isopimarate	1.227	1.230	1.203	1.201
Methyl 13-abieten-18-oate	1.246	1.234	1.213	1.211
Methyl abietan-18-oate	1.370	1.373	1.327	1.319
Methyl dehydroabietate	1.444	1.439	1.364	1.362
Methyl abietate	1.704	1.703	1.608	1.603

[a] With hydrogen as carrier gas (40 cm/sec).
[b] With helium as carrier gas (30.3 cm/sec); Foster and Zinkel, 1982.

This can result in the formation of M+1 ion peaks, arising from the interaction of molecular ions and hydrogen, either from water, or another organic molecule. The formation of M+1 ions was much more pronounced from molecules which possessed carbonyl groups (e.g. fatty acid methyl esters), than was the case for hydrocarbons or phenolic substances. The subsequent development of a series 800 instrument with automatic gain control (AGC) software greatly

reduced this problem. The ITDS instrument was coupled to the Varian 3700 gas chromatograph via an open split interface. The operating conditions for the ITDS instrument are given in Table 4.4.

Table 4.4
Varian 3700-Finnigan MAT ITDS Operating Parameters

Column	12 m x 0.22 mm FSOT
Carrier gas	99.998 % Helium
Injector temperature	220°C
Injection mode	Grob (15 sec load time)
Injection volume	0.5-1.0 µl
Initial temperature	50°C
Temperature programme rate	6°C
Final temperature	240°C
Transfer line temperature	230°C
Mass range	50-420 amu
Scan rate	1 scan/sec
Multiplier	1600 volts
Detector pressure	1 x 10^{-6} torr
Ionization current	70 eV

The mass spectra obtained were identified either by fragmentation interpretation or by searching the National Bureau of Standards (NBS) mass spectral library data base. Selected ion profiles readily identified certain classes of compounds. For example, m/e 74 ($C_3H_6O_2$) and m/e 87 ($C_4H_7O_2$) ion plots (Figures 4.1 and 4.2) revealed the presence of saturated straight chain fatty acid methyl esters; m/e 57 ($C_4H_9^+$) and m/e 71 ($C_5H_{11}^+$) ion plots revealed

hydrocarbons, while a m/e 64 (S_2^+) ion profile located polysulphide compounds.

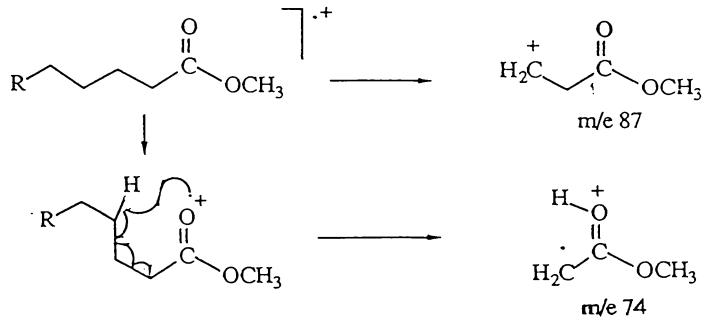


Figure 4.1 Straight chain fatty acid methyl ester fragmentation ions

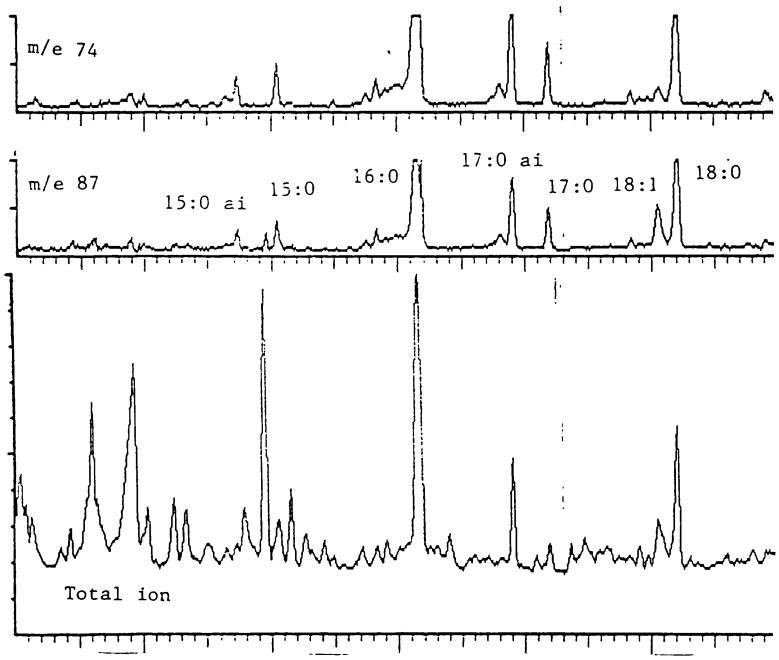


Figure 4.2 Selected ion profiles of m/e 74 and 87 for fatty acid methyl esters

Chlorinated compounds were identified initially by interpreting the observed fragmentation patterns. Chlorine occurs as ^{35}Cl and ^{37}Cl isotopes in the ratio 3:1. Thus a compound that has one chlorine atom will have an M+2 peak whose intensity is a third of that of the molecular ion. The presence of more than one chlorine atom gives rise to distinctive isotope patterns (see Figure 4.3).

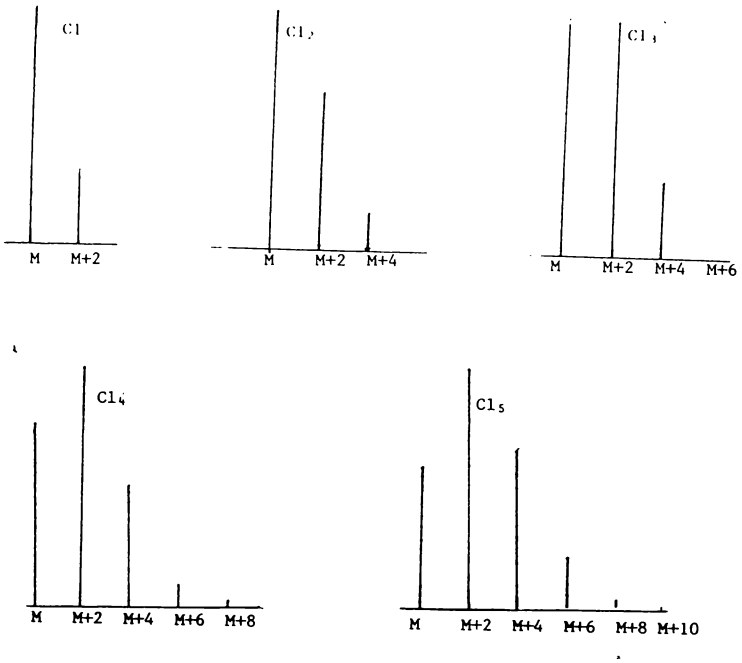


Figure 4.3 Chlorine isotope patterns

4.5 QUANTIFICATION

Internal standards were used for the quantification of the extracted organic compounds. This was in preference to the use of external standards which does not allow for variations in the extraction procedures. *n*-Octadecane was routinely used as the internal standard. It was chosen largely because of its retention time (non-overlap with extractive peaks), thermal stability (not decomposed by extended periods of refluxing) and chemical stability (does not react with alcohols or acids to give esters). Several groups (Holmbom, 1977; Chung *et al*, 1979; Oikari *et al*, 1980; Turoski *et al*, 1981) have used heptadecanoic acid as internal standard but significant quantities of this acid (in addition to the *anteiso* analogue) occur in New Zealand *P. radiata* extractives. Where monoterpene concentrations were required, either *n*-nonane, or *n*-dodecane were added as a second internal standard. *n*-Nonane, which eluted just

before α-pinene, was used to monitor the loss of relatively volatile monoterpene hydrocarbons, while *n*-dodecane, which elutes shortly after α-terpineol was used to monitor monoterpene alcohols and ketones.

The internal standards, of 1 mg/ml concentrations in redistilled chloroform, were added to the acidified samples prior to extraction. The dosage at which internal standard was added was dependent on the sample being extracted: 10 mg/l for black liquor samples; 1 mg/l for paper machines and effluent treatment system samples; and 0.1 mg/l for river and bleach plants samples.

As different compounds gave different FID responses, response factors (Rf) for the different classes of compounds were calculated. A standard chloroform solution containing 1 mg/ml of each of the compounds: α-pinene, guaiacol, camphor, *n*-dodecane, 1,4-dichlorobenzene, pentachlorophenol, *n*-octadecane, methyl palmitate and methyl dehydroabietate, was used to calculate response factors relative to the *n*-octadecane peak, as shown below:

$$\text{Response factor (Rf)} = \frac{(\text{Peak area})_s}{(\text{Peak area})_i} \cdot \frac{(\text{Conc.})_i}{(\text{Conc.})_s}$$

s = sample, i = internal standard (*n*-octadecane)

Studies by Stuthridge (1987) indicated that chlorine substitution lowers the GC-FID response factor of a compound. It was also found that the FID was less sensitive to chlorinated and sulphonated compounds than the GC-ITDS. Hence, some compounds that were detected on the GC-ITDS were not observed on the GC-FID.

These compounds were not quantified and denoted in the Tables with an asterisk (*).

Integration of the GC-FID peaks was performed using a Shimadzu CR3A reporting integrator. The concentration of the compounds present in a sample were calculated according to the following equation:

$$(\text{Conc.})_S = \frac{(\text{Peak area})_S}{(\text{Peak area})_i} \cdot \frac{(\text{Conc.})_i}{Rf}$$

s = sample, i = internal standard (n-octadecane)

Where a compound was not identified, it was quantified using the response factor for the region; e.g. if it was in the resin acid region, the response factor for dehydroabietic acid was used. Quantification results for the duplicate extraction and duplicate injection of a Tarawera River water sample are presented in Table 4.5. Since the agreement between duplicate analyses is of the order ±10-20% (see also Table 4.5) it can be concluded that similar precision limits apply to single analysis. Having regard to the manual injection technique used in this work, the *ca* ±15-25% variation in the data for compounds present in concentrations greater than 5 µg/l is considered reasonable, given that some of the peaks (*e.g.* those arising from methyl abietan-18-oate and methyl dehydroabietate) were not baseline resolved in all of the traces.

The main sources of errors can thus be identified as: sampling, storage, extraction, standard solutions, injection technique, signal to noise ratio (in the GC) and integration. Of these the greatest errors arise from the extraction, injection and integration. Therefore it can

be concluded that for concentrations below 10 µg/l the experimental errors involved can be up to ± 50%; 10-100 µg/l up to ± 30% and greater than 100 µg/l the error is ± 10-20%.

Table 4.5

Concentrations of methylated extractable organic substances (µg/l) recovered from a Tarawera River sample collected on 16 October, 1984.

Compound	(1a)[a]	(1b)[a]	(2a)[b]	(2b)[b]
Methyl palmitate	7	9	11	8
Fichtelite	1	1	2	1
Dehydroabietin	10	12	8	11
1,2,3,4-Tetrahydroretene	11	9	7	10
Methyl stearate	6	5	4	5
Methyl secodehydroabietate-1	4	4	3	5
Methyl secodehydroabietate-2	3	2	3	4
Retene	4	5	3	5
Methyl pimarate	12	16	13	17
Methyl sandaracopimarate	1	2	1	2
Methyl pimaran-18-oate	2	3	3	4
Methyl isopimarate[c]				
Methyl 13-abieten-18-oate[c]	11	16	10	17
Methyl abietan-18-oate	32	26	34	36
Methyl dehydroabietate	39	34	35	45
Methyl abietate	4	2	3	5

[a] Duplicate GC injection of the same sample

[b] Duplicate extraction and GC analysis of sample (1)

[c] Co-eluting peaks.

CHAPTER FIVE

INITIAL RIVER STUDY

5.1 INTRODUCTION

The Tarawera River is one of the most important water resources of the Bay of Plenty region. The upper reaches of the river are greatly valued for trout fishing and other water-based recreational activities while the lower reaches are used for whitebaiting, eeling and duck shooting. The plains associated with the lower reaches also provide sites for two major wood processing companies, as well as horticultural and dairy farming industries. However, over the past years, the quality of the water from the lower reaches of the river *i.e.* from Kawerau to the sea, has been substantially affected by treated waste from the Kawerau township, pulp and paper industries and geothermal bore discharges (Tarawera River Management Plan, 1985). This has aroused the attention of the local and national environmental groups (Clayton, 1983).

The Central North Island Planning Study (CNIPS) of Forest Processing and Transport Options reported that the future forestry development was a matter of major national and regional importance and that the best location strategy for the pulp and paper industry was to expand at existing sites. There has been substantial changes in public attitudes towards the environment and the use that is being made of the land adjoining the river. In view of the expected growth of the pulp and paper industry at Kawerau, it became necessary to

provide the Bay of Plenty Catchment Commission and the Regional Water Board with a framework for the future management of the water resource. The Tarawera River Management Plan was prepared by the Bay of Plenty Catchment Commission to establish water quality objectives and to present policies that protected social, cultural and environmental values even while allowing for the expansion of the pulp and paper industry at Kawerau (Tarawera River Management Plan, 1985). The Management plan provided the Bay of Plenty Catchment Commission and the Regional Water Board with the means to:

- Define the water resources of the Tarawera Catchment with emphasis on the Tarawera River;
- Assess the present and future demands for the use of the river;
- Outline policies proposed for the future management of water and particularly wastewater discharges;
- Allocate the resources in the river to appropriate uses.

The Chemistry Department of the University of Waikato was first approached by the Ministry of Works and Development, Water Quality Centre, Hamilton, to assist in technical studies of the river water quality submitted with the Tarawera River Management Plan (1985). The submission indicated that there was no information regarding the sources, identity, concentrations and toxicity of the dissolved extractable organic substances present in the effluent waters. The Tasman Pulp and Paper Company Limited is one of the major users of the river. The company discharges approximately 220,000 m^3 of effluent daily. This can represent 10% of the river flow at certain times of the year. The other two major users are

Caxton Paper Mill Limited (approximately 11,000 m^3/day) and the Kawerau Borough Council (approximately 2,100 m^3/day). The location of the mills with respect to the river is shown in Figure 5.1.

At the outset of the present investigation water samples were taken from the Tarawera River to ascertain the presence of extractable organic compounds. An array of substances, chiefly resin acids of pulp mill origin, was detected.

5.2 METHODS AND MATERIALS

Surface water samples were collected at two main points along the river: the State Highway 30 (SH30) and the State Highway 2 (SH2) bridges. The distances of these points from the Tasman discharge point to the sea are 3 km and 20.8 km respectively (Tarawera River Management Plan, 1985). The samples were collected from the middle of the river by throwing a pail attached with a length of rope over the side of the bridge. Samples were transferred to 2.5-litre alkali-rinsed glass winchesters and transported to the University of Waikato. Water samples were extracted and the extracts were dried, derivatized and analysed by GC, GC-MS and GC-ITDS as described in Chapter 4, and by Wilkins and Panadam (1987) (see Appendix B). Compounds were identified by a combination of retention indices (Foster and Zinkel, 1982), co-injection with authentic samples, and by their mass spectral fragmentation patterns. The mass spectra of selected compounds appear at the end of this chapter. Over a two-year period, more than a hundred water samples were taken from the river.

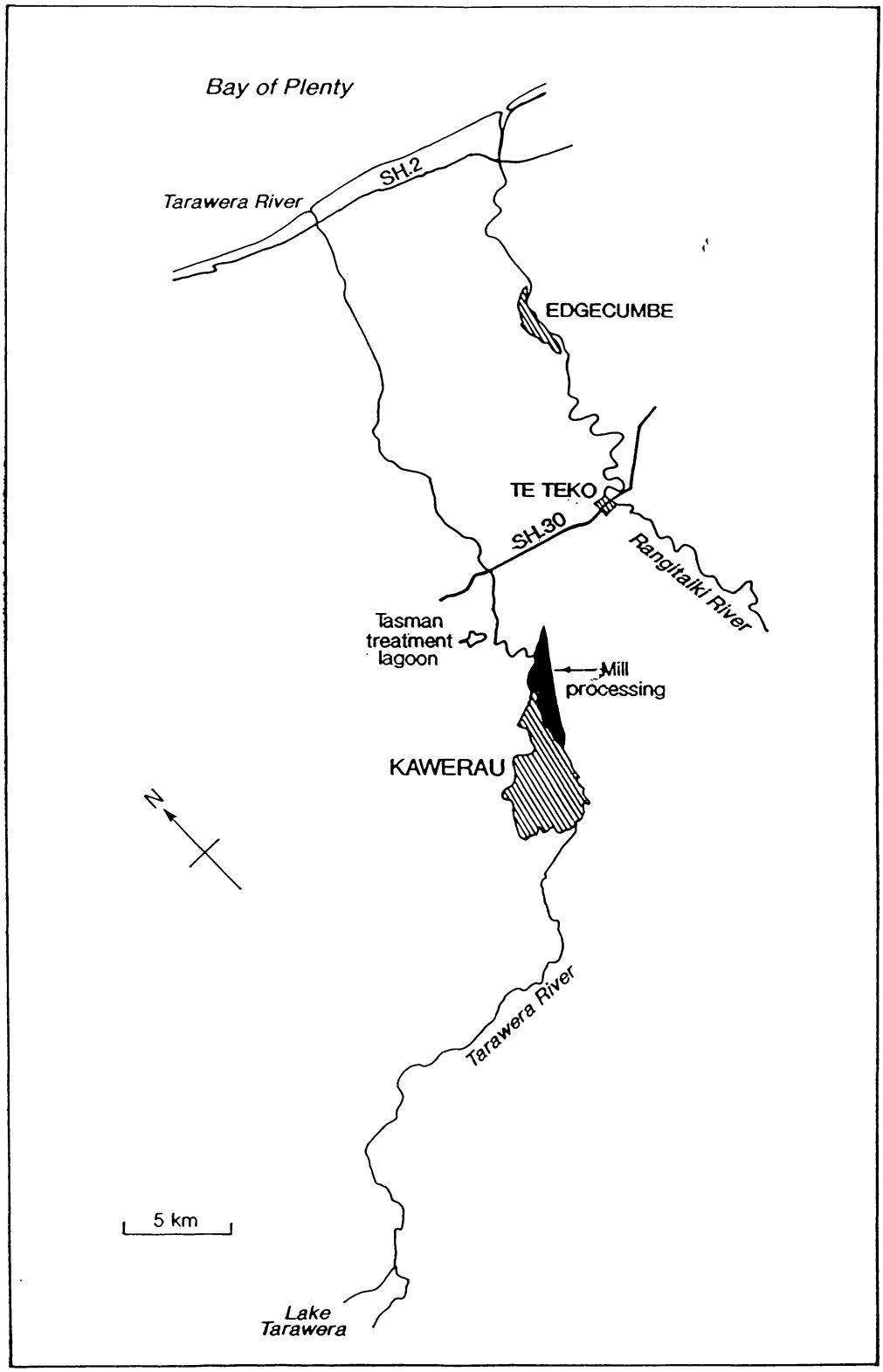


Figure 5.1 Location of the mill with respect to the Tarawera River (Source: Tarawera River Management Plan, 1985)

5.3 RESULTS

Figure 5.2 (page 71) shows a typical GC-FID profile of a derivatized extract of a sample from the Tarawera River at SH30.

GC-MS studies revealed the presence of resin acids (predominantly those possessing abietic, pimaric and isopimaric acid skeletons, Figure 5.3) as the major extractable substances with lesser amounts of fatty acids and phenolic substances. Also found on some occasions were lesser amounts (typically less than 2 µg/l) of cyclopentenones, monoterpenes, sulphonated and chlorinated compounds. While resin acids, fatty acids, monoterpenes, sulphonated compounds and chlorinated compounds have hitherto been frequently reported in the pulp and paper mill literature, 2-cyclopentenones have only recently been recognized (Turoski *et al*, 1983; Voss, 1984). The 2-cyclopentenones have been shown to arise from the alkaline degradation of the cellulose component of wood and to be comparatively resistant to degradation under aerobic conditions (Voss, 1984, 1987).

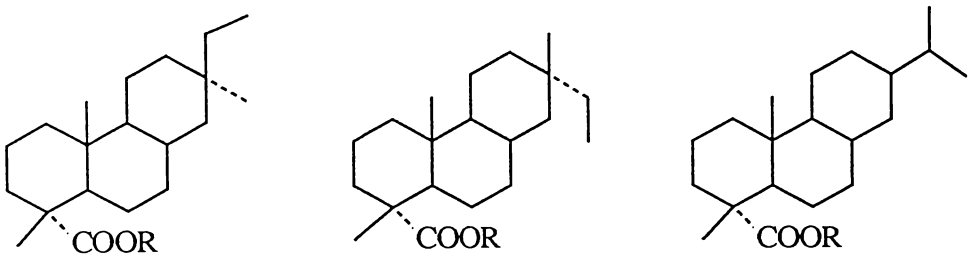


Figure 5.3 Pimarane, isopimarane and abietane acid skeletons

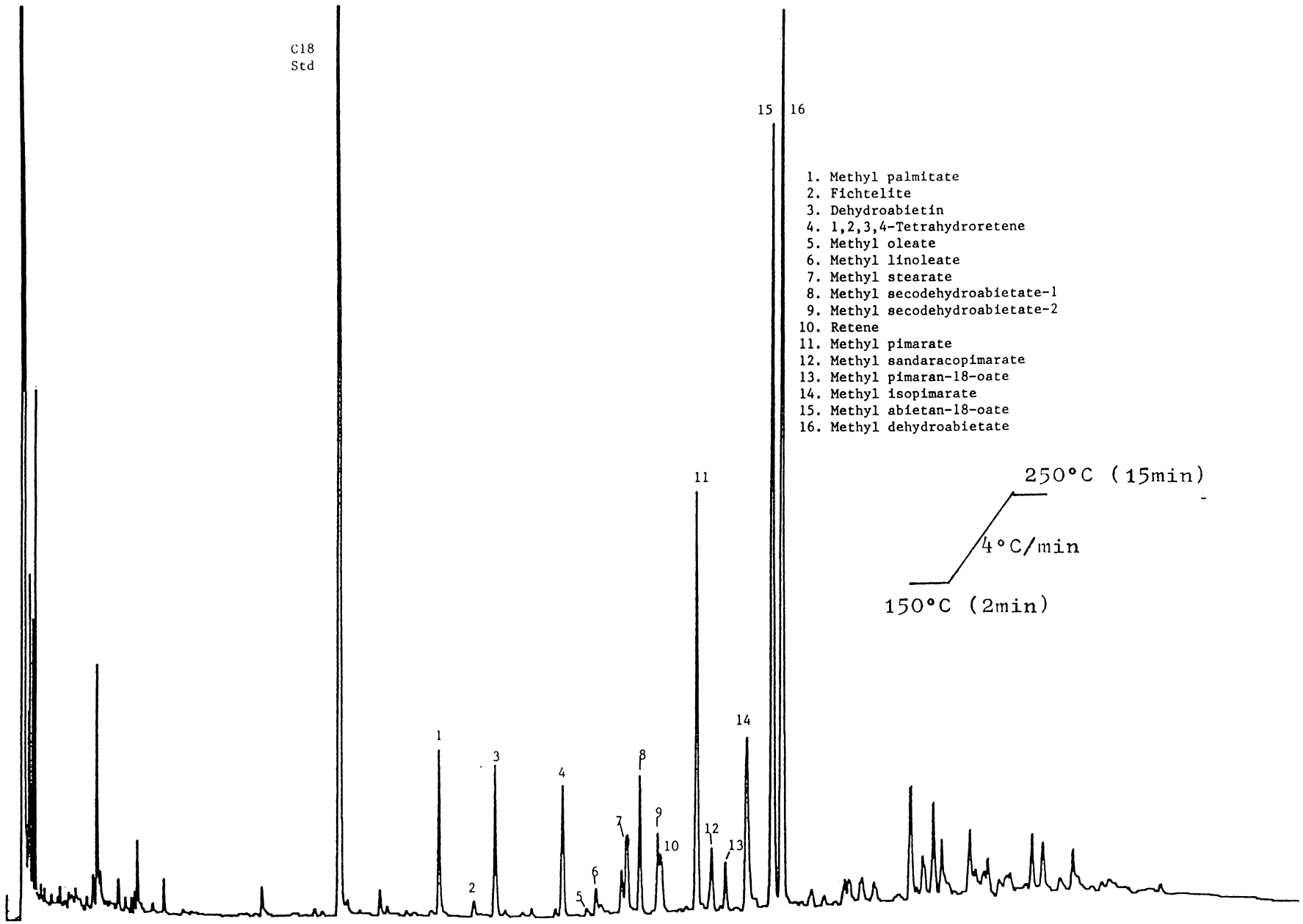


Figure 5.2 GC-FID profile of a derivatized extract of SH30.

5.3.1 Resin Acids

The structures of the typical resin acids found in the samples are given in Appendix A. From a combination of the relative retention time data for resin acid methyl esters reported by Foster and Zinkel (1982) (see chapter 4), and the mass spectral fragmentation patterns reported by Zinkel *et al* (1969, 1971), some of the peaks of Figure 5.2 were identified as methyl secodehydroabietates-1 (1b) and 2 (2b) (peaks 8 and 9 respectively), methyl pimarate (3b) (peak 11), methyl sandaracopimarate (4b) (peak 12), methyl isopimarate (5b) (peak 14) and methyl dehydroabietate (6b) (peak 16).

The major peak present in all the chromatographic traces was initially identified as methyl dehydroabietate (6b) and confirmed by co-injection with an authentic sample. However, it was found later that two components contributed to the major peak. If chromatographic conditions were selected such that methyl dehydroabietate eluted at a column temperature of *ca* 240-250°C, a single peak was observed, but at temperatures of 200-210°C, methyl dehydroabietate was base-line resolved from the second component (see Figure 5.2). The lower elution temperature was achieved by increasing the carrier gas linear velocity from 25 cm/sec to 40 cm/sec (see Appendix B). The second component was typically present in concentrations as high as methyl dehydroabietate. It was found by GC-MS analysis to have a molecular mass of 320 atomic mass units (amu). Major fragment ions occurred at m/e 277 (M^+-C_3H_7), 261 (M^+-$COOCH_3$), 245 (M^+-$HCOOCH_3$-CH_3) and 163 (base peak). These data suggested that this substance could be the methyl ester of

a saturated resin acid (Chang *et al*, 1971; Zinkel *et al*, 1971). The mass spectrum and relative retention time of the second component corresponded with that reported for methyl abietan-18-oate (8b) (Zinkel *et al*, 1971; Foster and Zinkel, 1982). This substance has also been detected by Mills and Stuthridge (*pers. comm.*) in related studies on the effluents and treatment pond sediments of a second New Zealand pulp and paper mill. A sufficient quantity of this substance was available from the second source for ^{1}H and ^{13}C NMR spectra to be determined. The ^{13}C NMR assignments presented in Table 5.1, follow directly from those made by Wenkert *et al* (1981) for structurally related resin acid methyl esters (Wilkins *et al*, 1987). The carbon numbering is given in Figure 5.3.

Table 5.1

^{13}C NMR signal assignments of methyl abietan-18-oate (8b) (δ ppm in $CDCl_3$).

C-1	38.2	C-12	29.9
C-2	18.1	C-13	43.7
C-3	37.3	C-14	38.5
C-4	47.7	C-15	32.8
C-5	50.0	C-16	19.8
C-6	24.5	C-17	19.8
C-7	35.3	C-18	179.4
C-8	36.6	C-19	14.5
C-9	56.1	C-20	16.9
C-10	36.3	$COO\mathbf{C}H_3$	51.8
C-11	24.8		

Another substance of molecular mass 320 amu was also detected (peak 13 of Figure 5.2). GC retention time and mass spectral data led to the conclusion that it was methyl pimaran-18-

oate (9b) (Chang *et al*, 1971; Zinkel *et al*, 1971). This compound was present in much smaller quantities than methyl abietan-18-oate (8b).

The mass spectra of methyl pimaran-18-oate (9b) and methyl abietan-18-oate (8b) were very similar. Both compounds exhibited base peaks at m/e 163, and the only other significant high mass ion occurred at m/e 261 ($C_{19}H_{33}$). This fragment corresponds to the loss of the carbomethoxyl radical (See Figure 5.4).

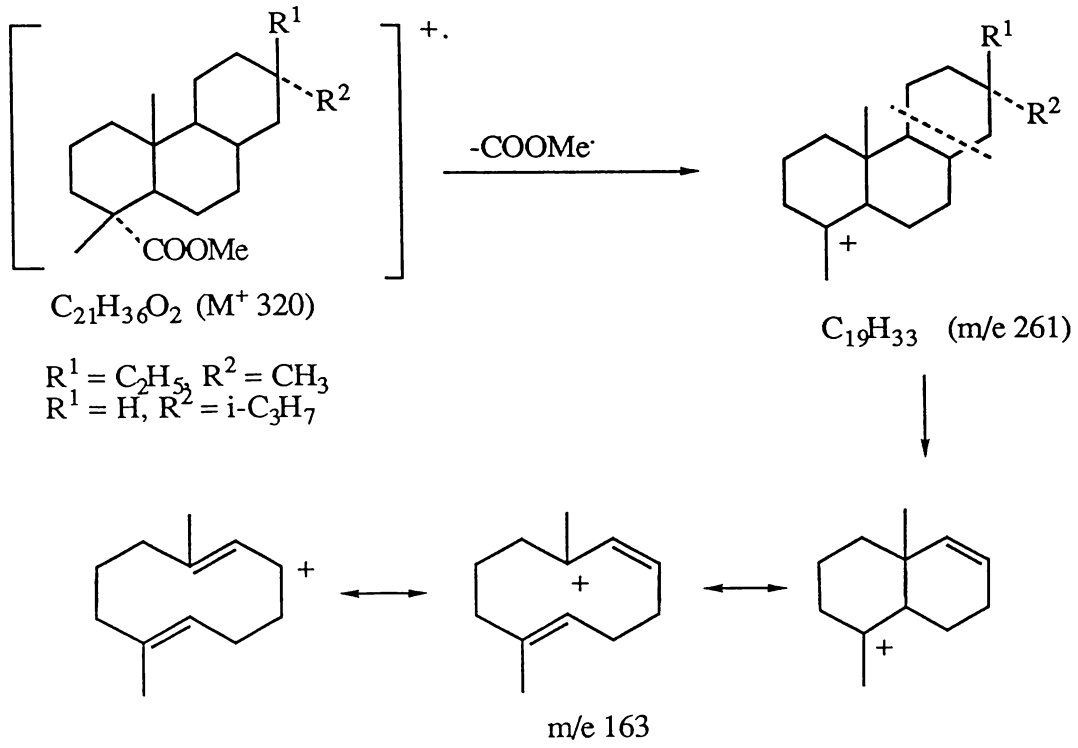


Figure 5.4 Mass spectral fragmentation of methyl abietan-18-oate and methyl pimaran-18-oate (Chang *et al*, 1971).

In addition, two components of molecular mass 318 amu were detected in some of the river samples. This is consistent with a single double bond within a methylated tricyclic resin acid skeleton. The mass spectrum of the earlier eluting of the two compounds exhibited a base peak of m/e 121; this ion is usually indicative (Zinkel

et al, 1971) of a pimaric acid type structure while a significant M^+-29 ion was reminiscent of the loss of an ethyl group allylic to a π-bond, such as that observed for methyl pimarate. The relative retention time (intermediate between methyl pimarate and methyl sandaracopimarate) and mass spectrum of this compound were in agreement with data reported for methyl 8(14)-pimaren-18-oate (10b) (Foster and Zinkel, 1982).

The second substance of molecular mass 318 amu (peak 14) co-eluted with methyl isopimarate (5b), however selected ion chromatogram profiles established that substances of molecular mass 316 and 318 amu were contributing to the peak. The GC retention time for the component of 318 amu appeared to correspond to that of methyl 13-abieten-18-oate (11b). This compound displayed a significant M^+-43 ion, arising from the loss of an isopropyl radical. This is typical of methylated resin acids which possess an abietic acid type skeleton (Zinkel *et al*, 1971). Methyl 13-abieten-18-oate (11b) has been observed by Keith (1969) and Fox (1977) in pulp and paper mill effluent streams.

Methyl 12-chlorodehydroabietate (12b), methyl 14-chloro-dehydroabietate (13b) and methyl 12,14-dichlorodehydroabietate (14b) were found on some occasions. These are products of bleaching and have been reported in the literature (Servizi *et al*, 1968; Leach and Thakore, 1975; Holmbom and Lehtinen, 1980). Methyl 7-oxodehydroabietate (15b) was also detected in most of the samples. Like dehydroabietic acid the parent keto- and chlorinated dehydroabietic acids (12a-15a) are comparatively resistant to biological degradation.

In all cases it was assumed that the parent acids were present in the water samples and that the methyl esters arose as a consequence of the reaction of the respective acids (1a-15a) with diazomethane. This conclusion was substantiated when GC-MS analysis of unmethylated extractive mixtures afforded peaks attributable only to the parent acids.

5.3.2 Fatty Acids

In a like manner the fatty acids (Figure 5.5) were characterized as the corresponding methyl esters. The fatty acids: palmitic acid, stearic acid, and oleic acid were identified by comparing their retention times with those of authentic samples. These were later confirmed by GC-MS analysis. The saturated straight chain fatty acids of molecular weight greater than 100 give very distinctive fragment ions of m/e 74 and m/e 87 (see Figure 4.1). The former ion arises by a McLafferty rearrangement involving the transfer of a proton from the γ-carbon to the ester carbonyl oxygen, while the latter ion arises from cleavage of the carbon-carbon bond β to the ester group. In addition, the fatty acid methyl esters display a series of less intense $[CH_3OCO\text{-}(CH_2)_n\text{-}]^+$ fragment ions formed by simple cleavages along the aliphatic chain. The concentrations of the principle fatty acids detected (palmitic acid, linoleic acid, oleic acid and stearic acid) are given in Table 5.2.

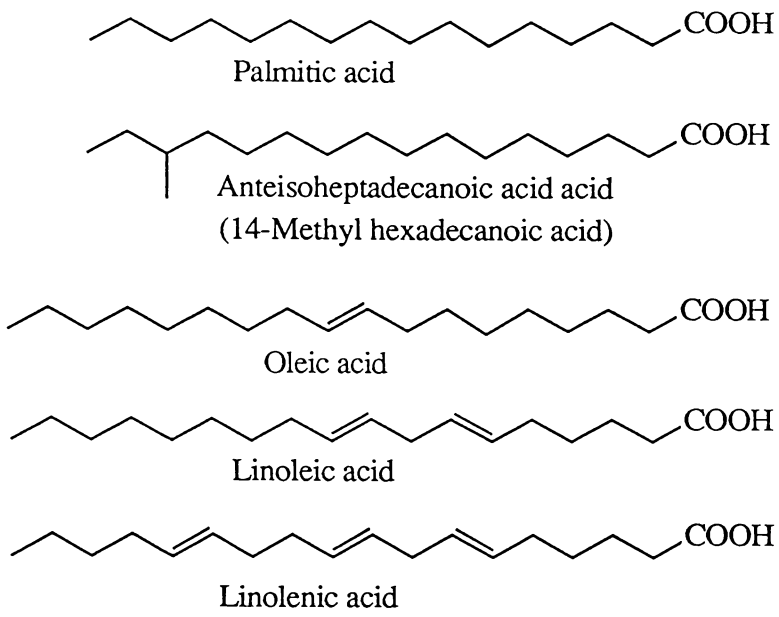


Figure 5.5 Structures of some common fatty acids.

5.3.3 Polycyclic Hydrocarbons

Significant quantities of four other compounds which did not appear to be methylated resins acids were detected. GC-MS analysis revealed their molecular masses to be 262, 256, 238 and 234 amu. Since compounds of these molecular masses have not been commonly reported in pulp and paper effluent, attempts were made to identify these substances.

The mass spectrum of the compound of molecular mass 234 amu was eventually found to correspond to that reported for retene (16) (Kinae *et al*, 1981). (see Figure 5.7). This identification was confirmed by a direct comparison of an authentic specimen supplied by the Forest Research Institute (F.R.I), Rotorua. Consequent upon the identification of retene, it became apparent that substances of molecular weight 262, 256, and 238 amu were analogues of retene which differed only in the number of double bonds present. Thus the compounds were identified as fichtelite (262 amu) (17),

dehydroabietin (256 amu) (18) and 1,2,3,4-tetrahydroretene (238 amu) (19). The mass spectra of these compounds appear in Figure 5.7. Dehydroabietin (18) and 1,2,3,4-tetrahydroretene (19) have been isolated by Mills and Wilkins *(pers. comm.)* from another pulp mill source in sufficient quantities to confirm their structures by ^{1}H and ^{13}C NMR analysis.

Dehydroabietin, 1,2,3,4-tetrahydroretene and retene have been reported by Wakeham *et al* (1980a, 1980b) who identified them in the sediment cores taken from Lake Zurich, Lake Washington and Lake Lucerne. Simoneit (1977) reported their presence in sediment samples taken from the north-east Pacific Ocean, Black Sea and North Atlantic Ocean. These diterpenoid derived hydrocarbons occur in significant amounts in higher plants and thus are potential terrigenous marker compounds. Fichtelite, on the other hand, is a well-known anaerobic decomposition product of decaying conifers (Burgstahler and Marx, 1969; Merck Index, 1983).

5.3.4 Quantification

The concentration levels found in the river samples taken at the State Highway 30 (SH30) and SH2 bridges are shown in Table 5.2. Concentrations found in an individual sample appear in the first column while the concentrations given in brackets indicate the range of concentrations found in random river samples collected over a 5 month period. On 8th July, 1984, the Eastern Bay of Plenty region experienced a small earthquake, the magnitude of which was such that a part of the embankment of the sludge lagoon collapsed and allowed sludge lagoon effluent to be discharged directly to the river.

Effluent from the sludge lagoon is normally directed into the aerated treatment system. Elevated levels of resin acids, fatty acids and diterpene derived polycyclic hydrocarbons (particularly dehydroabietin, 1,2,3,4-tetrahydroretene and retene) were found in the SH30 river sample collected on the afternoon of 8th July, 1984. This finding suggested that substantial levels of extractable organic substances were present in the sludge lagoon outflow. Later analysis of the sludge lagoon outflow (see Chapter 10) confirmed this observation.

Table 5.2
Concentrations (μg/l) of organic compounds (quantified as the corresponding methyl esters) detected in SH30 and SH2 river samples.

Compound	SH30[a]		SH2[a]		SH30[b]
Methyl palmitate	12	(2.0-12)	5	(1-8)	226
Fichtelite	2	(0.5-5)	-	(0-1)	13
Dehydroabietin	8	(2-12)	2	(0.5-5)	133
1,2,3,4-Tetrahydroretene	9	(2-14)	2	(0-5)	767
Methyl oleate	0.5	(0-3)	1	(0-2)	22
Methyl linoleate	0.5	(0-2)	1	(0-2)	31
Methyl stearate	2	(0.5-4)	2	(0.5-3)	55
Methyl secodehydroabietate-1	6	(1-10)	2	(1-7)	34
Methyl secodehydroabietate-2	6	(1-10)	1	(0.5-2)	25
Retene	5	(2-10)	0.5	(0.5-2)	72
Methyl pimarate	20	(6-24)	9	(5-10)	80
Methyl sandaracopimarate	5	(0.5-5)	1	(0-3)	16
Methyl pimaran-18-oate	2	(0.5-5)	-	(0-5)	88
Methyl 8(14)-pimaren-18-oate	2	(0-3)	1	(0-2)	-
Methyl isopimarate	19	(6-24)	7	(3-10)	-
Methyl 13-abieten-18-oate	3	(2-7)	1	(0.5-1)	189
Methyl abietan-18-oate	50	(15-80)	23	(9-40)	477
Methyl dehydroabietate	66	(11-83)	31	(10-35)	382
Methyl abietate	25	(0-30)	-	(0-5)	-

Table 5.2 cont.....

Methyl neoabietate	-	(0-18)	-	(0-11)	-
Methyl 7-oxodehydroabietate	0.5	(0-2)	-	(0-1)	17
Methyl 12-chlorodehydroabietate	1	(0-2)	-	(0-1)	-
Methyl 14-chlorodehydroabietate	1	(0-2)	-	(0-1)	-
Methyl 12,14-dichlorodehydroabietate	0.5	(0-2)	-	(0-1)	-

[a] Sample collected on 31st October, 1984.

[b] Sample collected on 8th July, 1984.

( ) Range of concentrations found in samples collected between August-December 1984.

5.4 DISCUSSION

The presence in the Tarawera River of compounds typical of anaerobic degradation of wood extractives was unexpected given that Tasman Pulp and Paper Mill's biological treatment system is extensively aerated. Three possibilities therefore appear to exist; (i) the characteristics of the aerated treatment system differ from those described in the literature, (ii) parts of the system are poorly aerated and become anaerobic, (iii) an independent (upstream) source is indicated e.g. anaerobic runoff from a tree-felling operation or other discharge into the river.

Water samples were taken from above the Kawerau town bridge, below the Kawerau Borough Council's discharge, below Caxton Paper Mill's discharge and from just below Tasman's final discharge. These compounds were found to be present only in the samples taken from below Tasman's discharge. Thus it was apparent that these compounds originated from the Tasman mill site. In accord with this conclusion it was noted that the concentration of these substances in the river dropped substantially when the mill was closed for a

prolonged period (June 1986-September 1986) due to industrial action. On the other hand elevated levels of these compounds were found in the river sample taken shortly after the collapse of the embankment of the sludge lagoon (8th July 1984).The presence of fichtelite, dehydroabietin, 1,2,3,4-tetrahydroretene, retene and the saturated analogues of the resin acids indicated anaerobic degradation of the resin acids in spite of the aerobic nature of the treatment system.

This combination of compounds found is indicative of two distinct anaerobic degradation pathways (Figure 5.6). One pathway appears to require that abietic acid is progressively saturated to give 13-abieten-18-oic acid and then abietan-18-oic acid which is subsequently decarboxylated to give fichtelite. The other pathway appears to require that abietic acid is dehydrogenated and aromatized to afford dehydroabietic acid which is in turn decarboxylated and progressively demethylated at C-10, and dehydrogenated in rings B and A to sequentially afford dehydroabietin, 1,2,3,4-tetrahydroretene and retene. Wakeham *et al* (1980b) have suggested a similar scheme for the conversion of abietic acid to yield dehydroabietic acid, dehydroabietin and retene.

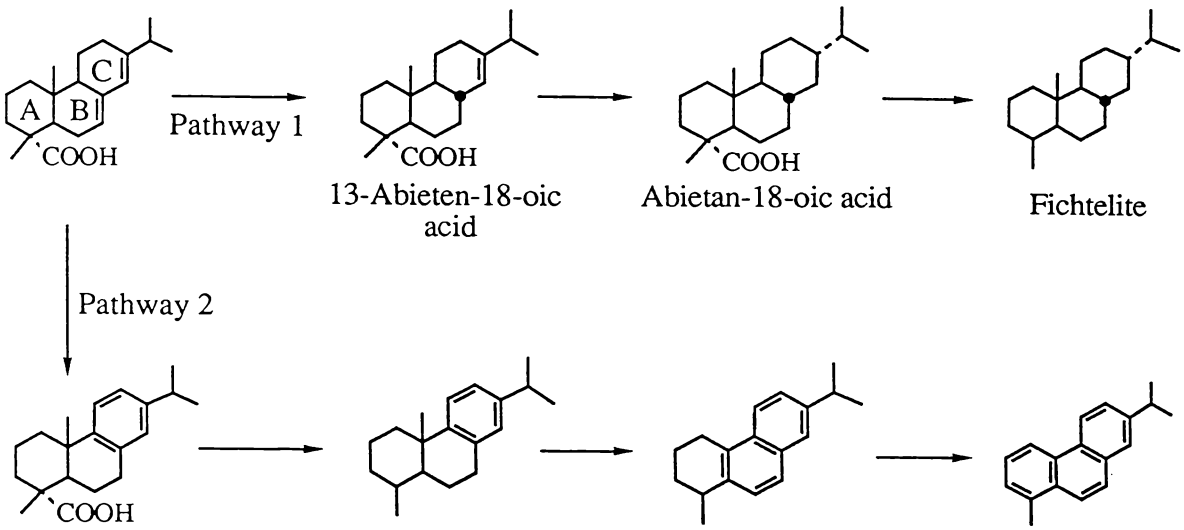
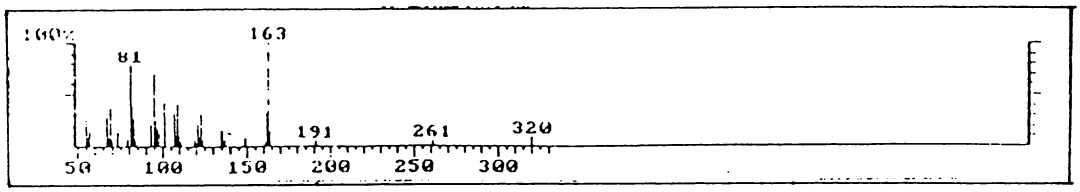


Figure 5.6 Possible pathways for the anaerobic degradation of abietic acid.

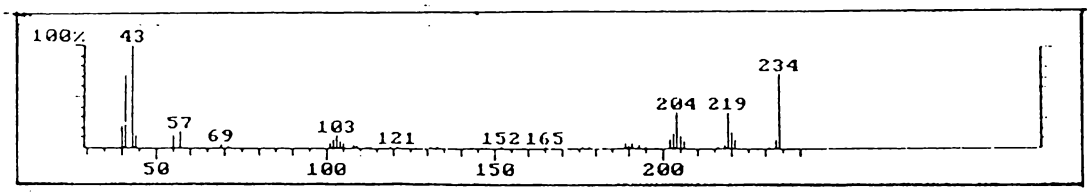
5.5 CONCLUSION

Having established Tasman's discharge as the source of a range of anaerobic and other mill derived compounds the need for an in-depth study of the plant to define their origin and modification by the treatment system was apparent In addition to the environmental aspects, a better understanding of the chemistry involved should allow better means of monitoring and optimizing the treatment system. This could have significant commercial implications.

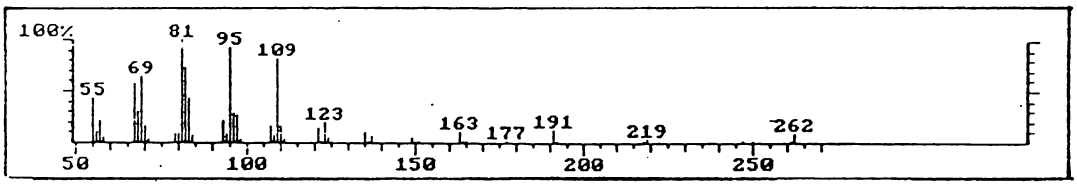
A part of the work described in this chapter was presented at the 40th Annual Appita Conference, (Auckland) 1986 and subsequently published in the Appita Journal (Wilkins and Panadam, 1987; see Appendix B).



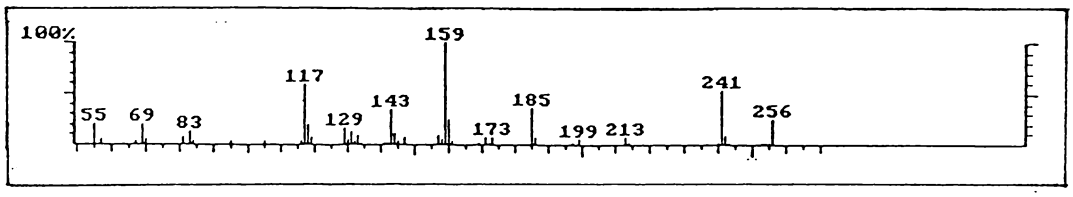
Peak 15 Methyl abietan-18-oate (8b)



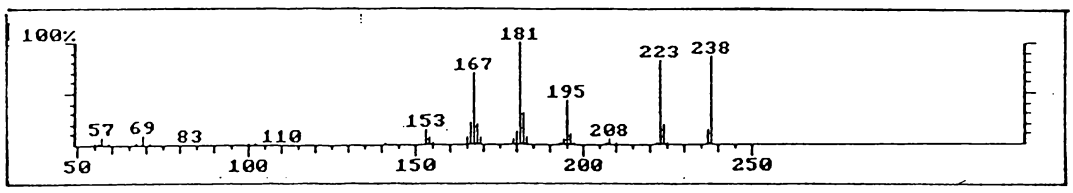
Peak 10 Retene (16)



Peak 2 Fichtelite (17)



Peak 3 Dehydroabietin (18)



Peak 4 1,2,3,4-Tetrahydroretene (19)

Figure 5.7 Mass spectra of the Anaerobic Degradation Products.

CHAPTER SIX

PLANT SOURCES I: BLACK LIQUOR

6.1 INTRODUCTION

Black liquor is the spent liquor from the batch and continuous digesters (see Section 2.4.1) and it is normally burnt to recover the cooking chemicals. A substantial portion of the sodium in the black liquor exists as sodium salts of the organic acids and phenols formed by degradation of lignin and carbohydrates under pulping conditions (Casey, 1980). Inorganic components include sodium carbonate, sodium sulphate, sodium thiosulphate and sodium hydrosulphide (if the weak black liquor was not oxidized). The weak black liquor leaving the pulp washers contains about 14-18% solids and this has to be concentrated to about 65% solids before it is incinerated in the recovery furnace. Weak black liquor is held in storage for several hours before going on to the evaporation and recovery stages. While in storage, it is passed through the black liquor oxidation (BLOX) plant where large blowers are used to sparge air into the liquor (Cooney and Dixon, 1982) (Figure 6.1). This oxidizes the residual sulphides into the more stable thiosulphates.

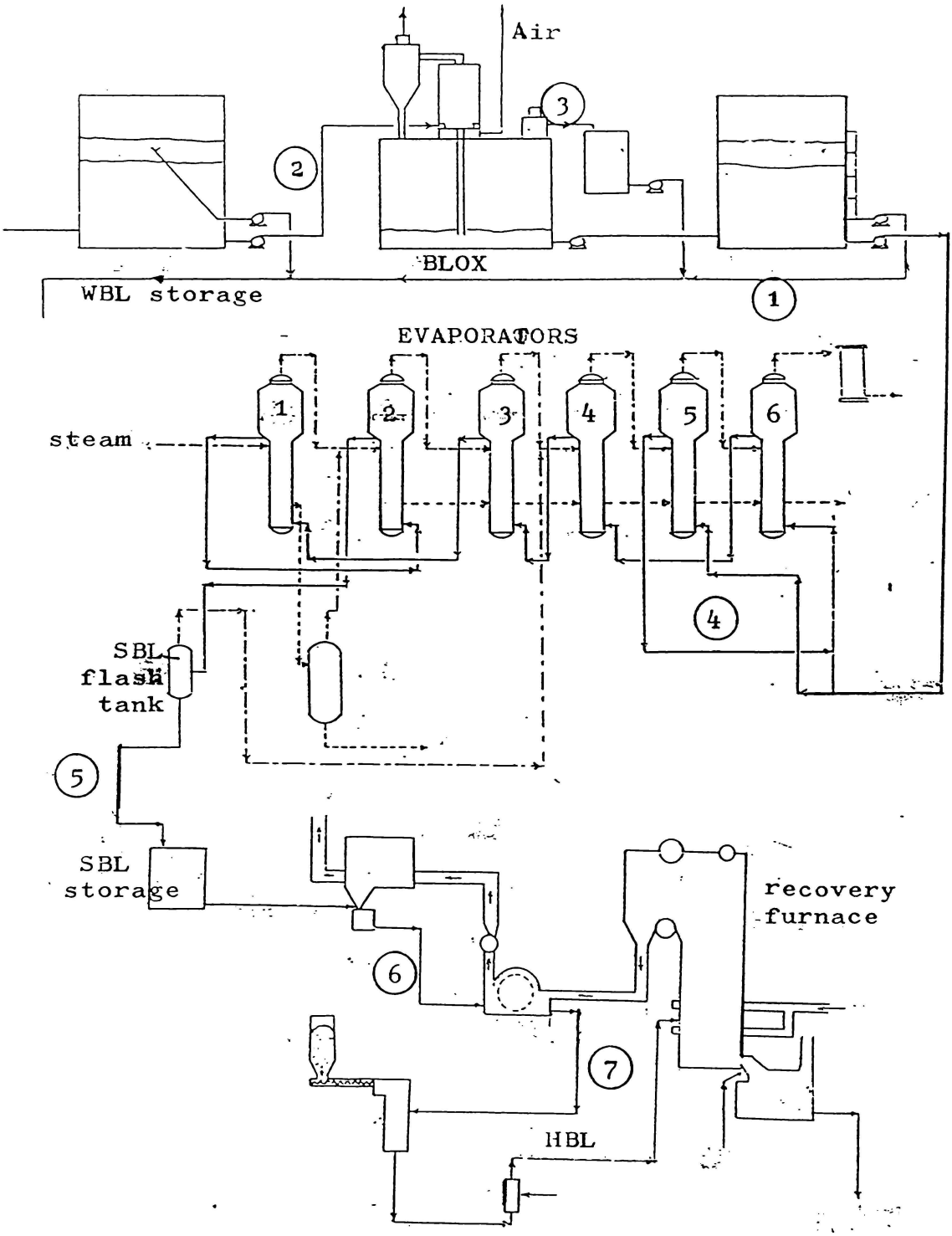


Figure 6.1 Black liquor oxidation
(Source: Tasman Pulp and Paper Company Limited)

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$$

By stabilizing the sulphide, sulphur loss is prevented and the odour, which is prevalent in most pulp mills, is largely reduced. The BLOX plant also separates the soap (sodium salts of the fatty and resin acids) from the liquor in the form of a foam which is broken down in cyclones. This is further concentrated before being pumped to the tall oil plant.

Multiple-effect long tube vertical evaporators are used to concentrate the solid content of the black liquor. Six stages are used and the vapour formed by boiling the liquor in one stage is used as the source of heat in another stage. The concentrated liquor from the evaporator unit is known as strong black liquor (50% solids). The strong black liquor is further concentrated to 65% solids and is referred to as heavy black liquor. Water is evaporated from the liquor in a direct contact cascade evaporator. The cascade evaporator consists of three-inch diameter steel tubes, arranged cylindrically around the circumference of a rotating wheel. The wheel is partially submerged in the strong black liquor and the boiler flue gas passes through the space above the vat of black liquor. The heat in the flue gas is then used to evaporate water from the liquor clinging to the rotating tubes. The liquor from the cascade evaporator is then passed into a small mixing tank where the required saltcake (sodium sulphate) make-up is dissolved in the liquor (see Section 2.4.2.1). It is then heated to about 125^{o}C and sprayed into the recovery furnace in the form of coarse droplets. These droplets are evaporated to dryness and then incinerated by the hot gas in the furnace.

Samples of black liquor were taken at the various recovery stages as it was concentrated from weak black liquor to heavy black liquor. Samples were taken at the following points: (1) weak black liquor (WBL), (2) black liquor oxidation inlet (BLOX in), (3) black liquor oxidation outlet (BLOX out), (4) strong black liquor inlet (SBL in), (5) strong black liquor outlet (SBL out), (6) heavy black liquor inlet (HBL in) and (7) heavy black liquor outlet (HBL out) (see Figure 6.1).

6.2. EXPERIMENTAL

The samples were extracted using the separating funnel method as described in Section 4.3.3. It was found that when using the continuous liquid-liquid extraction procedures to recover resin acids from highly concentrated liquors, significant isomerization of the more sensitive resin acids (especially levopimaric, palustric and neoabietic acids) occurred (Richardson and Bloom, 1982; Claeys *et al*, 1983). Separating funnel extraction minimized the extent of the isomerization and in general recoveries were comparable (see Section 4.3) to those found for the more prolonged continuous liquid-liquid extraction procedures. Given the reproducibility of the analytical GC system used in this study (± 20%), separating funnel recovery was considered satisfactory. However this may not be the case when using a highly reproducible automatic GC injector. The use of XAD-2 adsorption columns proved impractical due to the rapid overloading of the columns, presumably because of the high levels of lignin present in the black liquor samples.

Black liquor samples [100 ml for (1), (3), (4) and (6); 50 ml for (2) and (5); 10 g for (7)] were diluted ten-fold with distilled water and transferred into 1-litre separating funnels. After acidification to pH 2 with 2 M hydrochloric acid, 1 ml of a 1 mg/ml solution of *n*-octadecane in chloroform was added to each of the samples except (7). In the case of sample (7), 2 ml of the internal standard solution was added. The samples were then extracted with two 50 ml aliquots of chloroform. The chloroform extracts were dried over anhydrous magnesium sulphate and carefully concentrated to *ca* 1 ml on a rotary evaporator. The concentrated extracts were methylated with diazomethane and analysed by GC-FID and GC-ITDS. The lignin which flocculated in the course of the extraction was recovered by filtration, dried and weighed (Table 6.1).

Table 6.1
Flocculated lignin recoveries (gram/litre black liquor)

Weak black liquor (WBL)	69
Oxidation inlet (Blox In)	77
Oxidation outlet (Blox Out)	97
Strong black liquor inlet (SBL In)	100
Strong black liquor outlet (SBL out)	321
Heavy black liquor inlet (HBL In)	423
Heavy black liquor outlet (HBL. Out)*	199

* Determined as grams per 1000 grams

6.3 RESULTS AND DISCUSSION

A typical GC-FID profile of a weak black liquor sample is depicted in Figure 6.2. The GC-ITDS profile of the sulphonated and aromatic region of the same sample is given in Figure 6.3 as the FID response for these compounds was not very sensitive. The relative concentrations of the compounds are given in Table 6.2. The peak numbers in Table 6.2 refer to Figures 6.2 and 6.3. It was found that on the day of sampling, the soap layer had risen to the surface of the liquors undergoing treatment in the BLOX plant. Thus the concentrations of resin acids and fatty acids determined for the BLOX plant samples are probably lower than normal.

The major components of all the black liquor samples were found to be resin acids, fatty acids, aromatic compounds and sulphur containing compounds, together with lesser amount of unknown substances. Monoterpenes were generally absent. This is not unexpected given the likelihood that the monoterpenes will vapourize as the black liquor leaves the digesters and concentrated in the evaporators. Efficient removal and recovery of monoterpenes is desirable at these stages.

6.3.1 Aromatic Compounds

The black liquor extracts were found to contain appreciable amounts of degraded lignin products; *e.g.* guaiacol (20), 4-hydroxy-3-methoxybenzaldehyde (vanillin) (21), 4-hydroxy-3-methoxybenzoic acid (vanillic acid) (22), 4-hydroxy-3-methoxyacetophenone (vanillone) (23), cinnamic acid (24) and 4-hydroxy-3-methoxy

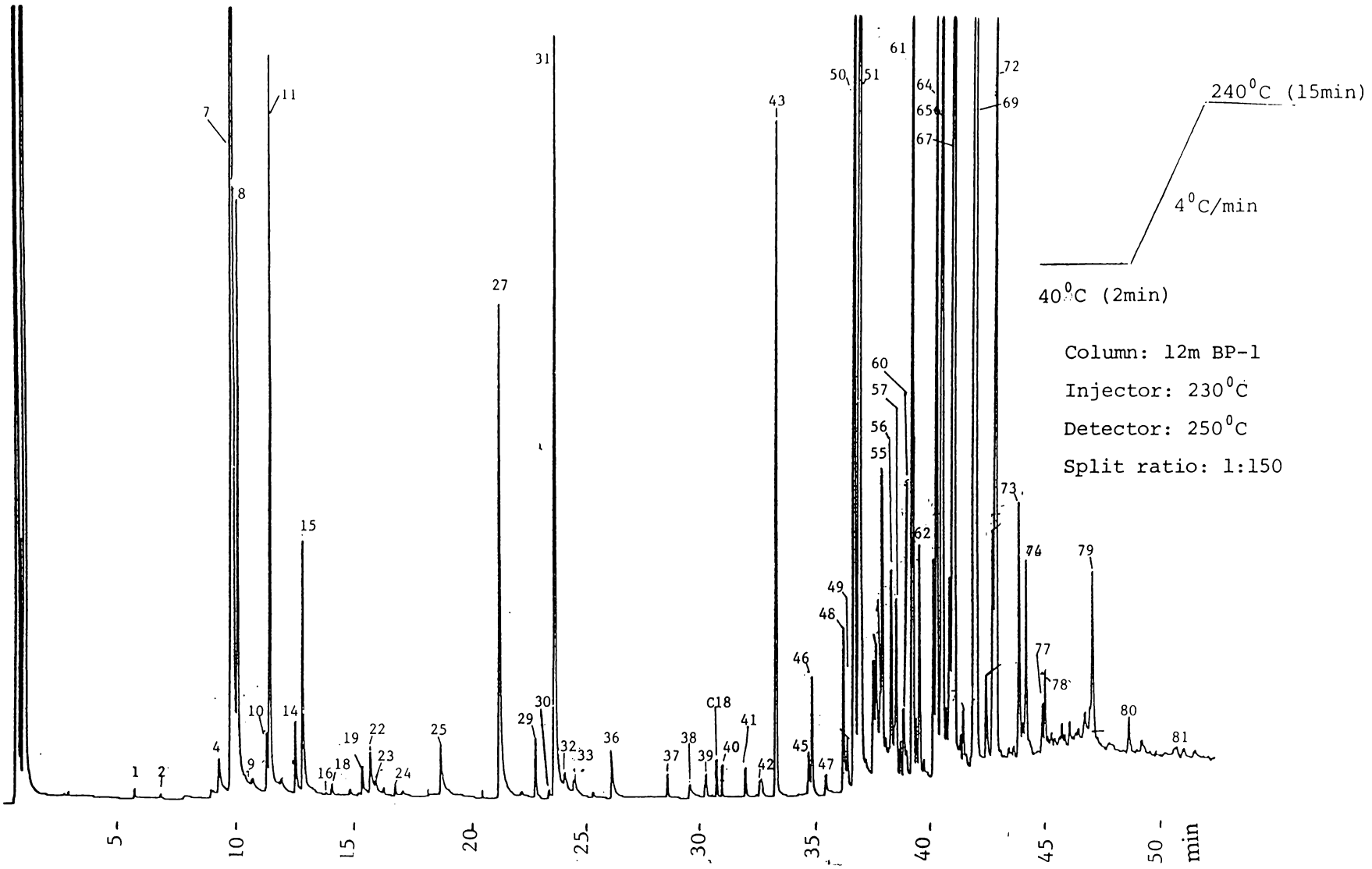


Figure 6.2 GC-FID profile of a derivatized extract of weak black liquor.

For peak identifications see Table 6.2.

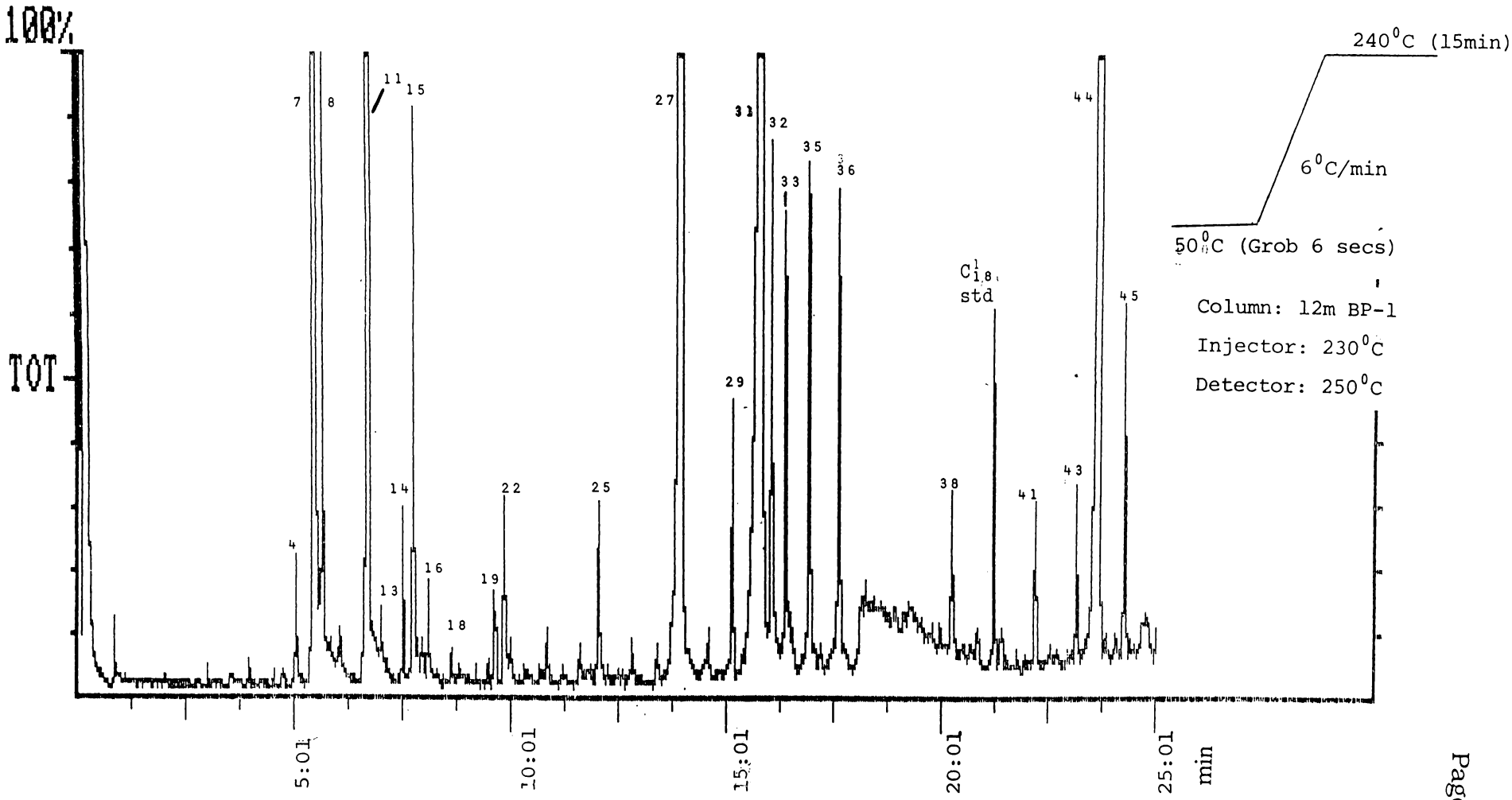


Figure 6.3 GC-ITDS profile of the aromatic region of a derivatized extract of weak black liquor. For peak identifications see Table 6.2.

Table 6.2

Concentrations (mg/l) of organic compounds, determined as the corresponding methylated derivatives, in black liquor samples [a] of 23rd January 1985.

Peak No	Compound	Blox In	WBL	Blox Out	SBL In	SBL Out	HBL In	HBL Out[b]
1	α-Pinene	-	-	3	-	2	-	-
2	β-Pinene	-	-	3	-	1	-	-
3	Dimethyl butenedioate	-	-	-	1	-	-	-
4	Dimethyl trisulphide	7	*	*	9	*	5	*
5	*p*- Cymene	-	*	-	-	-	-	-
6	Benzenetriol (M^+126)	*	*	*	2	*	34	*
7	Guaiacol	68	177	353	467	1621	2053	465
8	Methoxybenzenediol (M^+140)	10	61	87	22	*	176	93
9	Methoxybenzenediol (M^+140)	*	-	7	2	*	5	*
10	Dimethoxyphenol (M^+154)	1	4	*	3	-	36	*
11	Methyl guaiacol	47	109	156	31	141	406	135
12	Methoxybenzenediol (M^+140)	-	*	*	*	*	1	*
13	Methoxybenzenediol (M^+140)	-	5	*	*	*	7	*
14	Dimethoxyphenol (M^+154)	-	7	11	5	*	46	7
15	Dimethoxyphenol (M^+154)	*	2	38	*	*	150	30
16	Dimethyl tetrasulphide (M^+158)	*	*	-	*	-	8	*
17	α-Terpineol	-	15	-	8	-	-	-
18	Trimethoxybenzene (M^+168)	-	*	-	*	*	6	*
19	Trimethoxybenzene (M^+168)	-	*	-	*	*	18	*
20	Methyl phenylpropanoate	*	*	-	-	-	-	-
22	Ethyl guaiacol	*	*	9	8	*	35	*
23	Trimethoxybenzene (M^+168)	-	*	-	*	-	11	*
24	Unknown 196,139,107,94	-	-	-	-	-	3	-
24	Eugenol	*	*	-	*	*	3	*
25	Methyl cinnamate	2	3	*	35	*	39	*
26	Dimethyl pentasulphide (M^+158)	*	*	-	-	*	*	-
27	3,4-Dimethoxybenzaldehyde	35	96	155	129	272	387	261
28	Methyl eugenol	*	1	-	-	*	5	*
29	Unknown 206,174,132,119,91	2	9	13	51	34	18	15
30	Methyl laurate	*	2	-	-	-	4	-

Table 6.2 cont....

Peak No	Compound	Blox In	WBL	Blox Out	SBL In	SBL Out	HBL In	HBL Out[b]
31	3,4-Dimethoxyacetophenone	92	162	340	111	465	590	365
32	3,4-Dimethoxyphenylpropan-2-one	2	6	15	2	*	14	9
33	Methyl 3,4-dimethoxybenzoate	3	7	7	14	*	20	9
34	Methyl 4-hydroxy-3-methoxyphenylacetate	3	-	-	-	-	14	-
35	3,4-Dimethoxyphenylpropanal	*	1	3	*	*	4	-
36	3,4-Dimethoxyphenyl-propan-1-one	3	6	16	4	*	31	12
37	Methyl myristate	1	6	-	1	23	11	*
38	Methyl 3,4-dimethoxy-phenylthioate	*	*	-	*	-	12	-
39	Methyl *anteiso* pentadecanoate	*	8	-	2	-	7	4
40	Methyl pentadecanoate	1	4	*	1	-	15	*
41	Unknown 210,179,108	1	6	*	16	18	9	5
42	Methyl *anteiso* palmitate	*	9	-	2	-	11	*
43	Methyl palmitate	107	206	4	27	663	269	69
44	Sulphur, S_8	*	*	*	*	*	*	*
45	Juvabione	3	9	10	25	25	13	8
46	Methyl *anteiso* heptadecanoate	2	43	-	4	118	52	11
47	Methyl heptadecanoate	*	14	*	9	*	52	2
48	Methyl pinolenoate	7	81	4	8	173	76	20
49	Methyl linolenoate	1	2	-	62	29	29	6
50	Methyl oleate	44	779	7	74	1972	747	183
51	Methyl linoleate	66	1248	10	125	3343	1531	316
52	Methyl stearate	4	126	6	6	116	44	17
53	Methyl octadecenoate-1	*	3	3	-	-	-	-
54	Methyl octadecenoate-2	4	6	*	9	28	53	21
55	Methyl secodehydroabietate-1	7	57	5	11	120	104	19
56	Methyl secodehydroabietate-2	5	42	4	*	45	74	14
57	Methyl octadecenoate-3	1	18	*	2	183	4	3
58	Methyl octadecenoate-4	1	-	*	6	141	-	12
59	Unknown 240,225,165	3	26	8	*	-	14	11
60	Methyl 8,15-pimaradien-18-oate	-	26	-	1	*	13	-
61	Methyl pimarate	25	223	17	37	299	356	91

Table 6.2 cont....

Peak No	Compound	Blox In	WBL	Blox Out	SBL In	SBL Out	HBL In	HBL Out[b]
62	Methyl sandaracopimarate	5	44	3	7	57	72	17
63	Unknown 316,301,274,259	-	26	-	6	-	21	13
64	Methyl isopimarate	26	202	19	29	257	277	71
65	Methyl palustrate	38	50	20	67	494	574	94
66	Methyl 6,8,11,13-abietatetraen-18-oate	1	19	1	5	-	82	6
67	Methyl dehydroabietate	62	357	50	75	519	990	170
68	Methyl eicosanoate	1	20	2	1	28	22	4
69	Methyl abietate	85	815	46	114	1894	1228	315
70	Unknown 290, 230,121, 110	3	11	3	3	-	29	17
71	Methyl 8,11,13,15-abietatetraen-18-oate	2	*	1	5	20	90	11
72	Methyl neoabietate	24	317	7	35	326	399	62
73	Hydroxylated methyl abietate	6	21	7	4	5	77	18
74	Methyl 7,13,15-abietatrien-18-oate	2	66	8	7	28	94	11
75	Methyl 7-oxodehydroabietate	2	20	*	1	16	31	*
76	Hydroxylated methyl dehydroabietate	*	8	*	1	-	19	*
77	Hydroxylated resin acid methyl ester	*	3	*	1	-	16	2
78	Methyl behenoate	-	-	-	1	23	37	2
79	Unknown 286, 271	2	-	*	-	-	38	19
80	Unknown 300, 285	5	77	34	2	*	80	-
81	Methyl tetracosanoate	-	10	-	-	27	21	*

* detected on the GC-ITDS but not on the GC-FID system, hence not quantified.

[a] for abbreviations see Table 6.1

[b] mg/kg of solid sample.

(-) not detected on either the GC-FID or the GC-ITDS.

phenylacetic acid (25). Of these compounds, (21), (22), (23), (24) and (25) were present in the methylated extracts as the corresponding methylated analogues; *i.e.* 3,4-dimethoxybenzaldehyde (26), methyl 3,4-dimethoxybenzoate (27), 3,4-dimethoxy-acetophenone (28), methyl cinnamate (29) and 4-hydroxy-4-methoxyphenylacetate (30). Model compound studies established that where a carbon-carbon or carbon-oxygen (carbonyl) π-bond is conjugated with an aromatic ring, treatment with diazomethane resulted in the methylation of the phenolic hydroxyl group(s). This is presumably a consequence of the increased stabilization of the phenolate anions of the foregoing phenolic substances.

It therefore follows that the analytical procedure does not distinguish between 3,4-dihydroxybenzaldehyde (31) (a catechol aldehyde) and 4-hydroxy-3-methoxybenzaldehyde (21) (a guaiacyl aldehyde) since both react with diazomethane to give 3,4-dimethoxy-benzaldehyde (26). On the other hand 3,4-dihydroxytoluene (32) and 4-hydroxy-3-methoxytoluene (methyl guaiacol) (33) are distinguished since neither are methylated by diazomethane. Acetylation using acetic anhydride is one method of distinguishing between the guaiacyl and catechol analogues but this method has certain limitations (see Section 4.3.4).

Selected ion analysis proved to be a powerful procedure for the characterization of structurally related aromatic compounds. For example, an ion of m/e 137 is indicative of an α'-substituted methyl guaiacyl derivative while that of m/e 165 is indicative of a 3,4-dimethoxyphenylcarbonyl derivative (See Figure 6.4). Molecular ions

of 180 and 194 amu can be attributed to 3,4-dimethoxyacetophenone (28) and 1-(propan-1-one)-3,4-dimethoxybenzene (34), while that of 196 amu can be attributed to methyl 3,4-dimethoxybenzoate (27).

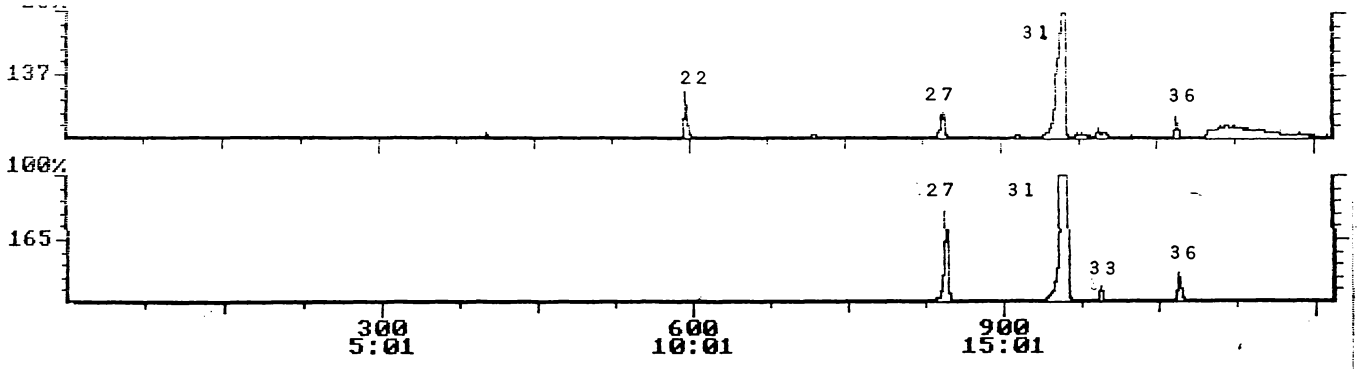


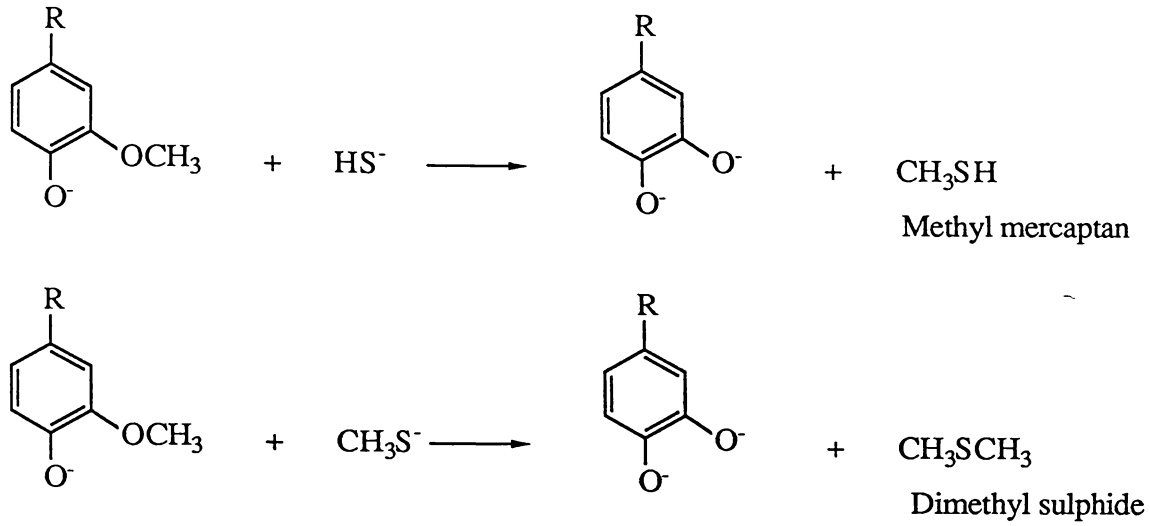
Figure 6.4 Selected ion plots of m/e 137 and 165

6.3.2 Sulphur Compounds

A compound of molecular weight 212 amu displayed a mass spectral fragmentation pattern similar to that observed for methyl 3,4-dimethoxybenzoate (27). Notably the loss of the methoxy group had been replaced by the loss of a fragment of 47 amu (methyl sulphide, SCH_3). Accordingly this substance was formulated as methyl 3,4-dimethoxyphenylthioate (35). Hence it can be concluded that the compound which occurs in the unmethylated extracts is 4-hydroxy-3-methoxyphenylthioic acid (36). Neither (35) or (36) appear to have been reported in the pulp and paper literature.

Methyl mercaptan (CH_3SH), dimethyl sulphide (CH_3SCH_3) and dimethyl disulphide (CH_3SSCH_3) have been frequently reported in pulp and paper research (Voss, 1984; Keith, 1976; Hrutfiord, 1975); however dimethyl trisulphide has only recently been reported (Voss,

1984). Methyl mercaptan and dimethyl sulphide are formed as a result of bimolecular nucleophilic substitution reactions with the methoxy group of lignin as shown below (Casey, 1980).



Dimethyl disulphide is formed on oxidation of methyl mercaptan.

$$4CH_3SH + O_2 \rightarrow 2CH_3SSCH_3 + 2H_2O$$

The mass spectrum of peak 4 of Figure 6.2 matched the NBS library spectra of dimethyl trisulphide (Mr 126 amu). This compound exhibited ions of m/e 64 and 79, attributable to S_2^+ and $CH_3S_2^+$ ions respectively. Since ^{34}S is 4.4% abundant relative to ^{32}S, it also displayed a significant M+2 ion (see Figure 6.7). Occasionally a substance of m/e 112 (M^+) was also detected; this compound can be formulated as methyl trisulphide, $HSSSCH_3$. In accord with this formulation fragment ions of m/e 79 and 64 appeared in the mass spectrum of this compound, together with an M+2 ion.

Two substances of Mr 158 amu (peaks 16 and 26) also displayed strong ions at m/e 79 and 64. Both of these compounds also displayed pronounced M+2 ions. The first of these substances

was considered to be dimethyl tetrasulphide ($H_3CSSSSCH_3$), while a plot of the GC retention times (as determined on the GC-ITDS system) led to the conclusion that the second substance was dimethyl pentasulphide ($H_3CSSSSSCH_3$) (Figure 6.5). In the case of the latter substance, the ion of m/e 158 can be envisaged as arising from the absent molecular ion by loss of a sulphur atom. The mass spectrum of the S_8 molecule exhibits a series of such losses (Figure 6.7). The pentasulphide can be envisaged as arising from the oxidative coupling of molecules of methyl disulphide and methyl trisulphide, as outlined in Section 6.3.2. for the oxidative coupling of methyl mercaptan.

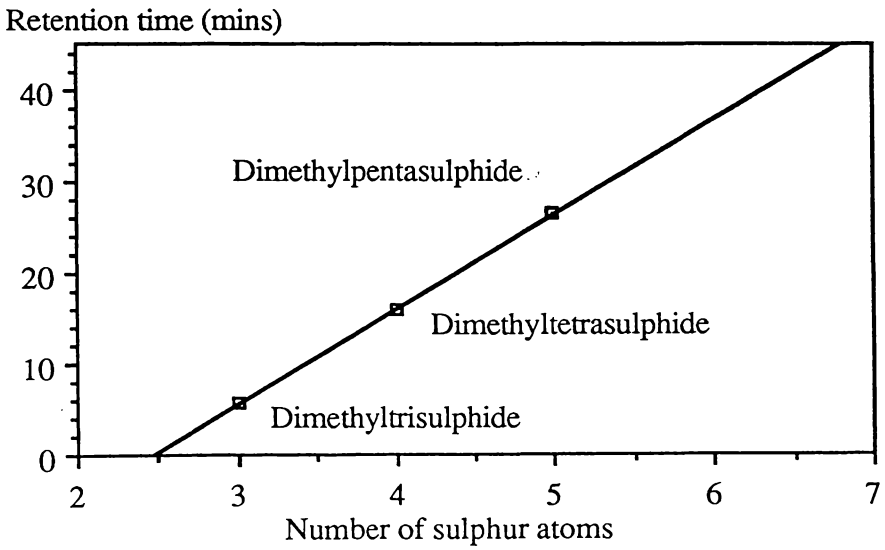


Figure 6.5 Plot of number of sulphur atoms in dimethylpolysulphides versus retention time.

GC-ITDS analysis also established the presence in the black liquor concentrates of significant quantities of elemental sulphur in the form of S_8 molecules (peak 44). This molecule, which eluted just after palmitic acid methyl ester displayed molecular ions at m/e 256 (M^+) and 258 (M+2) in the ratio *ca* 3:1 as required for S_8, together with daughter ions at m/e 224, 192, 160, 128, 96 and 64 (base

peak), each of which corresponded to the loss of sulphur atoms. This peak was less prominent in the GC-FID traces presumably because the FID response was small in comparison to the mass spectral ion current.

6.3.3 Juvabione

Juvabione (37) (peak 45) [the methyl ester of (+)-todomautic acid (38)] and its derivatives are major constituents in *Abies* species, particularly Balsam fir. Derivatives of juvabione are often referred to as insect juvenile hormone analogues (Ficini *et al*, 1974; Manville, 1976; Negishi *et al*, 1976; Manville and Kriz, 1977). This is because they exhibit activity for certain insects that resembles that of insect juvenile hormones, *i.e.* they are able to inhibit the maturation of the larval stages of such insects. Chung *et al* (1979) reported high concentrations of juvabione and juvabiol in the effluent of an ammonium-based mill pulping 75% Balsam fir.

Juvabione has also been reported in sediment samples derived from pulp and paper mill effluent by Kinae *et al* (1981a). Juvabione does not show a molecular ion at m/e 266, but has a base peak of m/e 134 (M^+-$C_8H_{13}O$), and prominent daughter ions of m/e 234 (M^+-CH_3OH) and 207 (M^+-$COOCH_3$) (Cerny *et al*, 1967; Kinae *et al*, 1981a). The mass spectrum of this compound is displayed in Figure 6.7.

About 10% of the wood pulped in the batch digesters by Tasman is Douglas fir. Since juvabione was absent from the black liquor concentrates of another New Zealand mill which like Tasman pulps mainly *P. radiata* but does not pulp Douglas fir, it can be

concluded that the latter species is the source of Tasman's juvabione. Studies carried out by Leach and Thakore (1976) indicated that while concentrations below 5 mg/l were not toxic, a 10 mg/l solution of juvabione killed juvenile rainbow trout in 27 minutes.

6.3.4 Fatty Acids

A total of twenty-three fatty acids were identified in the black liquor samples. Mass spectra of saturated straight chain fatty acid methyl esters have been discussed previously (see Section 5.3.2). The saturated fatty acids found ranged from C12 (lauric acid) to C24 (lignoceric acid).

The unsaturated fatty acids consisted mainly of octadecenoic (oleic), octadecadienoic (linoleic) isomers and octadecatrienoic (pinolenic) acids. The methyl esters of these compounds usually display significant M^+-CH_3OH ions. Selective ion plots of m/e 262 and 264 readily identified the methylated octadecenoic and octadecadienoic acid isomers. Six isomers of octadecadienoic acids were detected in most of the black liquor samples. Except for linolenic acid and linoleic acid, the other dienoic acid isomers were not distinguished. Holmbom *et al* (1974) reported the presence of a similar series of fatty acids in the effluent streams of a Scandinavian mill pulping *P. radiata*.

6.3.5 Resin Acids

Fifteen resin acids were identified in the black liquor extracts. These may be classified into three types: namely pimaric, isopimaric and abietic acid types, with the former two types characterized by

the presence of methyl and vinyl substituents at C-13, while the abietic acid analogues have an isopropyl group at this position (see Section 5.3). Typical concentrations of these resin acids are given in Table 6.2.

The dominant methylated resin acid was found to be methyl abietate (7b). This is consistent with overseas studies. Other methylated resin acid dienes detected were methyl pimarate (3b), methyl sandaracopimarate (4b), methyl isopimarate (5b), methyl palustrate (41b) and methyl neoabietate (42b). Three resin acid methyl esters displayed m/e 314 ions. Of these, methyl dehydroabietate (6b) (peak 67) (Holmbom *et al*, 1974; Keith, 1976a; Fox, 1977) was the major component. The other compounds eluted after methyl neoabietate. The relative retention time and mass spectral fragmentation of one of these compounds (peak 74) corresponded to that of methyl 7,13,15-abietatrien-18-oate (43b). The third compound (peak 77) also exhibited a weak ion of m/e 332, hence it can be reasoned that the ion of m/e 314 arises from that of m/e 332 by loss of a water molecule (M^+-18). The presence of a hydroxyl group was thus indicated, although the site at which the hydroxyl group has been introduced cannot be discerned. The mass spectral fragmentation pattern of the hydroxylated resin acid methyl ester corresponded closely with that of methyl abietate (7b) save for the displacement of the m/e 316 and 256 ions to m/e 314 and 254 in the hydroxylated derivative. Amongst the common methylated resin acids only methyl abietate displays a strong (M^+-60) loss (Zinkel *et al*, 1971).

Two isomers of secodehydroabietic acids were found to be present. These have been reported by Takeda *et al* (1968, 1969) as products of base-catalyzed thermal rearrangement of methyl levopimarate (44b) and sodium levopimarate. The mass spectral data corresponded with those of Zinkel *et al* (1969) and Takeda *et al* (1968). The first eluting isomer, methyl secodehydroabietate-1, (1b) has been widely reported in previous studies while the second eluting isomer (2b) has only been encountered occasionally (Zinkel *et al*, 1969; Mayr *et al*, 1982).

Two compounds displayed significant m/e 312 ions, typical of methylated resin acid tetraenes. One of the tetraenes eluted just before methyl dehydroabietate, while the other tetraene eluted between methyl abietate and methyl neoabietate. The mass spectral fragmentation patterns and retention times of these compounds corresponded with those reported by Zinkel *et al* (1969, 1971) for methyl abieta-6,8,11,13-tetraen-18-oate (45b) and methyl abieta-8,11,13,15-tetraen-18-oate (46b) respectively.

Methyl 7-oxodehydroabietate (15b) was detected in varying quantities in the samples. The mass spectral fragmentation displayed a strong molecular ion at m/e 328 ($C_{21}H_{28}O_3$) and a base peak at m/e 253. This is in agreement with the proposed scheme of Enzell and Wahlberg (1969) for methyl esters of dehydroabietic acid analogues.

6.3.6 Other Substances

A series of compounds of Mr 126 (peak 6), 140 amu (peaks 8, 9, 12, and 13), 154 amu (peaks 10, 14 and 15) and 168 amu (peaks

18, 19, and 23) were detected in most of the black liquor samples. The 14 amu difference (*i.e.* a CH_2 group) between these groups of compounds suggested them to be members of a homologous series. The mass spectra of these included strong M-15, M-28, M-28-15 and/or M-28-32 fragment ions. Library searching matched the mass spectra of two compunds of Mr 140 amu with those of 3-methoxy-benzene-1,4-diol (39) and 3-methoxybenzene-1,2-diol (40). This in turn suggests the substances of Mr 126, 154 and 168 amu may be benzenetriols, dimethoxyphenols and trimethoxybenzenes respectively. All of these substances are plausible lignin degradation products.

Besides the peaks discussed above a number of other unknown peaks were detected. For example, the highest ion observed for peak 41 occurred at m/e 210 with subsequent ions at m/e 179, 127, and 108 (base peak), while another substance (peak 59) exhibited strong ions at m/e 240, m/e 225 and 165. The latter two ions appear to arise by the consecutive loss of a methyl radical and a $HCOOCH_3$ molecule. In both cases the NBS library failed to find an appropriate match.

Peak 70 was present in most of the black liquor samples. This compound displayed a base peak at m/e 110 and lesser ions at m/e 235, and 121, however the NBS library was not able to find an appropriate match. Wilkins and Richardson *(pers. comm.)* also detected this compound in an Australian pulp mill effluent.

Two late eluting peaks (peaks 79 and 80) displayed strong ions at m/e 286 and 300 respectively. Each of these compounds also

displayed strong M-15 ions, arising from the loss of a methyl radical. The mass spectrum of the former compound matched that of the NBS library spectrum of dehydroabietol (47), however the retention time of peak 79 was substantially longer than that of dehydroabietol. The structures of these compounds remains uncertain.

6.4 THE USE OF EXTRACTABLE ORGANICS TO MONITOR BLACK LIQUOR SPILLS

It is apparent (see Table 6.2) that the dominant low molecular weight extractable organic substances present in black liquor are resin acids, fatty acids and aromatic substances together with some sulphonated compounds. The accidental discharge of black liquor to mill sewers leads to an increased level of these substances entering the effluent treatment system. While resin acids and fatty acids are also major constituents of tall oil and soap specimens (see Chapter Nine), aromatic substances are not. Thus elevated levels of aromatic substances, particularly 4-hydroxy-3-methoxybenzaldehyde (vanillin) (21) and 4-hydroxy-3-methoxyacetophenone (acetovanillone) (23) [detected as 3,4-dimethoxybenzaldehyde (26) and 3,4-dimethoxy-acetophenone (28)], are diagnostic of black liquor spills. It should be possible to use these compounds to monitor the black liquor contribution to mill sewers and the treatment system.

In order to demonstrate the feasibility of using aromatic compounds to monitor black liquor spills, an experiment was performed in which an effluent sample was spiked with black liquor. The recoveries of 3,4-dimethoxybenzaldehyde (26) and 3,4-dimethoxyacetophenone (28) from separating funnel extractions are

given in Table 6.3. Three 20-ml portions of chloroform were used to extract 200 ml treatment pond samples (pond inlet) spiked with increasing volumes of a strong black liquor sample (ex No 2 evaporator). The extracts were then methylated with diazomethane. While fatty acids and resin acids are rapidly methylated by diazomethane, 4-hydroxy-3-methoxybenzaldehyde (21) and 4-hydroxy-3-methoxyacetophenone (23) were found to react at a slower rate. On some occasions (particularly so in the case of samples having a high aromatic content) incomplete methylation of 4-hydroxy-3-methoxybenzaldehyde (21) and 4-hydroxy-3-methoxyacetophenone (23) was observed. Therefore in such cases, the areas of the methylated and unmethylated compounds were combined e.g. 4-hydroxy-3-methoxybenzaldehyde and 3,4-dimethoxybenzaldehyde peaks; 4-hydroxy-3-methoxyacetophenone and 3,4-dimethoxy-acetophenone peaks. Extension of the derivatization time from 30 minutes to 16 hours (*i.e.* overnight), using a large excess of diazomethane in a loosely stoppered vial, generally resulted in complete methylation.

The data of Table 6.3 is plotted in Figure 6.6. It is clear that for both the compounds studied, the analytical data increase linearly with the volume of strong black liquor added over at least three orders of magnitude.

Table 6.3

Recoveries of some aromatic compounds from a pond inlet sample (200 ml) of 4th July 1985, spiked with strong black liquor.

mls strong black liquor	0	10	20	30	40	50
3,4-Dimethoxybenzaldehyde (μg)	2	359	1011	1356	1725	2035
3,4-Dimethoxyacetophenone (μg)	2	350	670	958	1299	1704

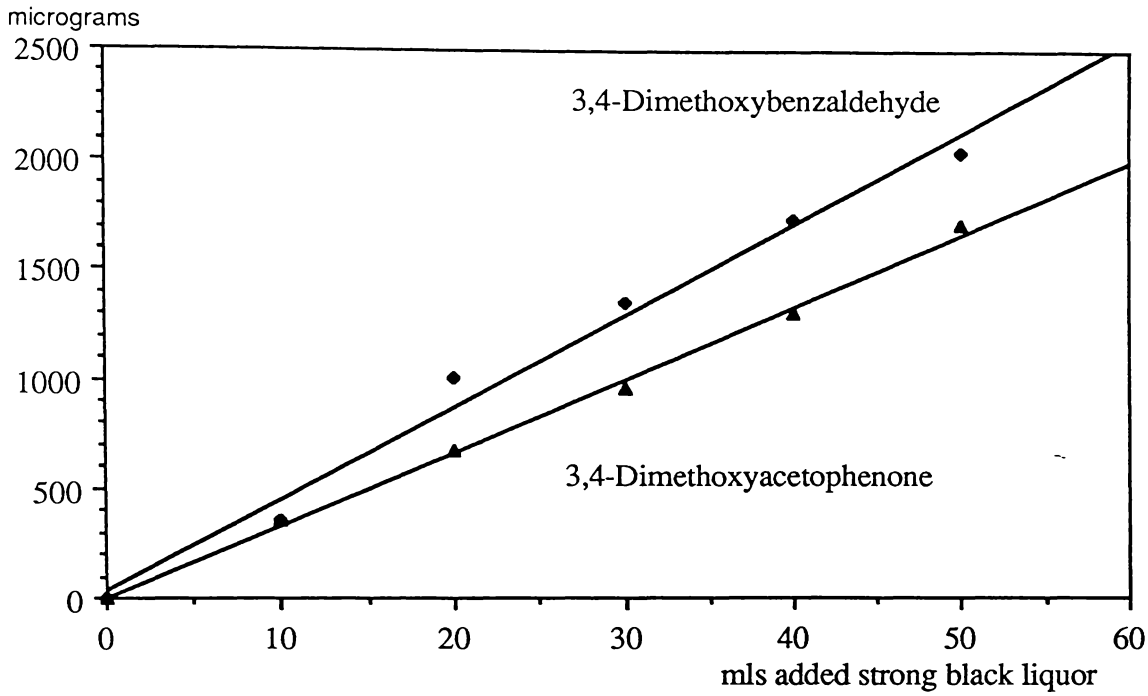
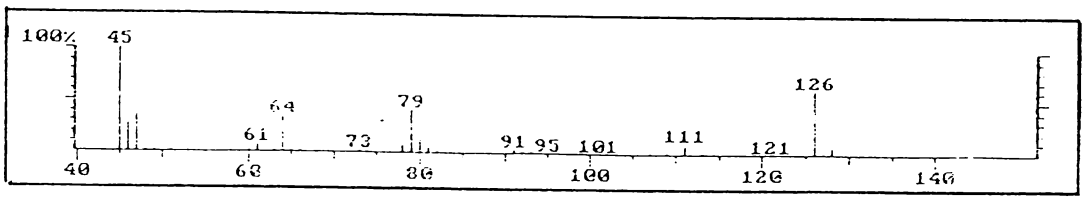


Figure 6.6 Recoveries of some aromatic substances from a treatment pond inlet sample (200 ml) of 4th July 1985 spiked with strong black liquor.

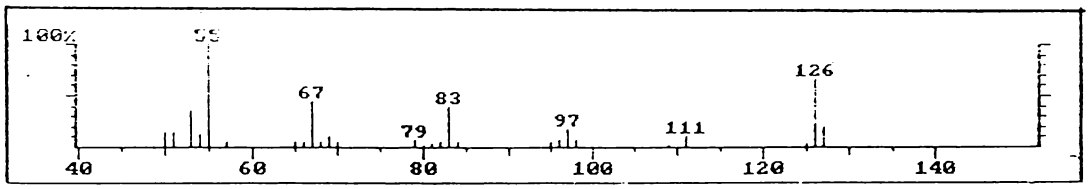
6.5 CONCLUSION

Tasman's black liquor can be characterized by its aromatic, fatty acid and resin acid content. Of these three classes of compounds, the aromatic compounds are the most distinctive source markers; resin acids and fatty acids are major constituents of soap and tall oil (Chapter Nine) whereas high levels of aromatic are found only in black liquor. While appreciably quantities of aromatic compounds are also found in bleaching discharges (Chapter Seven), these sources can be readily distinguished by the chlorination of the aromatic compounds. Monitoring of the levels of the aromatic compounds such as 4-hydroxy-3-methoxybenzaldehyde and 4-hydroxy-3-methoxy-

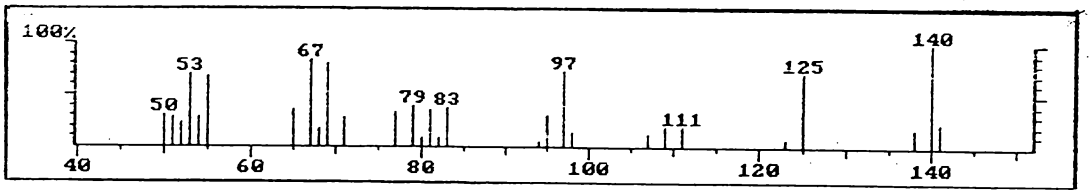
acetophenone has been shown to be a feasible procedure for determining the progress of black liquor spills through the treatment systems.



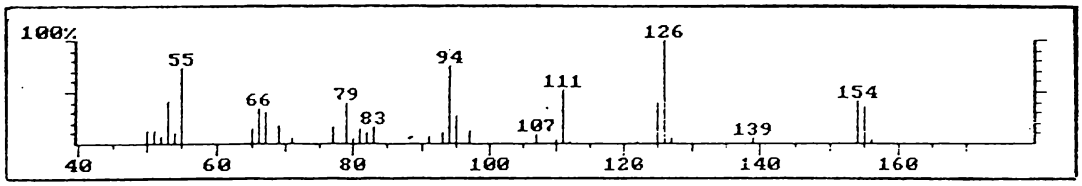
Peak 4 Dimethyl trisulphide



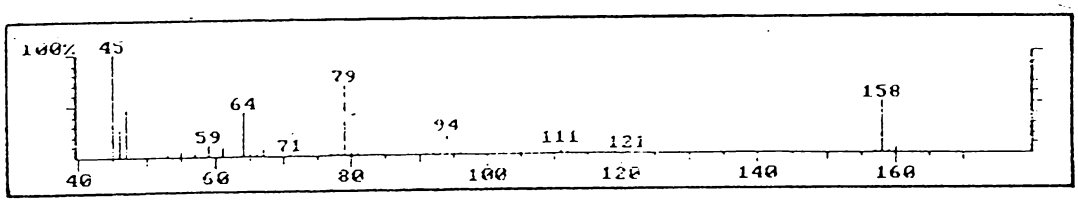
Peak 6 Benzenetriol



Peak 8 Methoxybenzenediol (39)



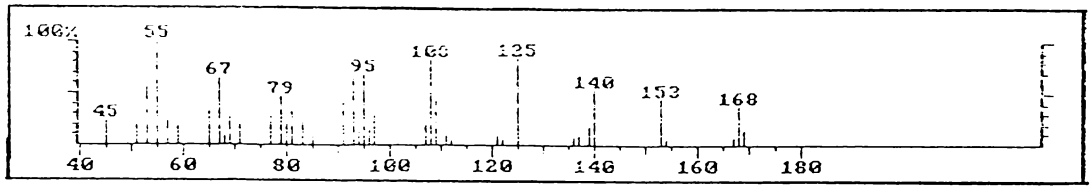
Peak 10 Dimethoxyphenol



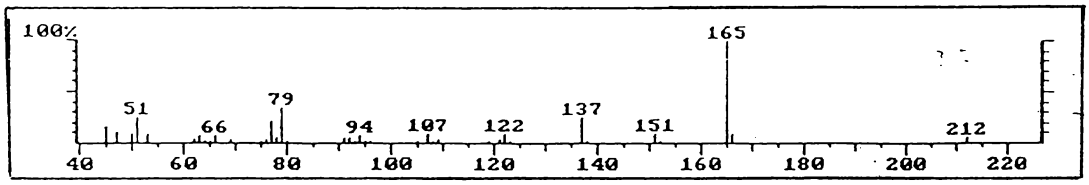
Peak 16 Dimethyl tetrasulphide

Figure 6.7 Mass spectra of some black liquor compounds

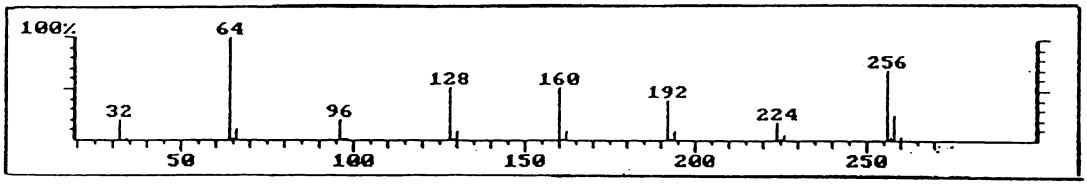
Figure 6.7 cont....



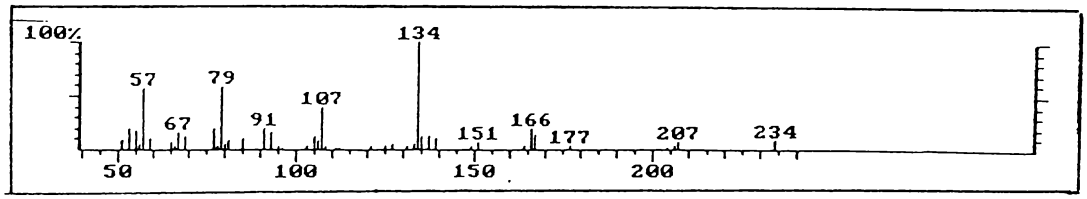
Peak 18 Trimethoxybenzene



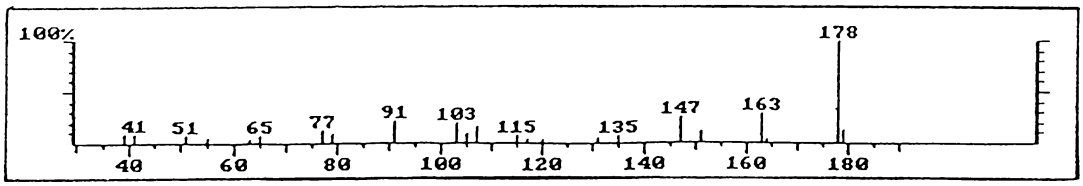
Peak 38 Methyl 3,4-dimethoxyphenylthioate (35)



Peak 44 Sulphur, S_8



Peak 45 Juvabione (37)



Peak 24 Eugenol

CHAPTER SEVEN

PLANT SOURCES II: BLEACH PLANTS

7.1 INTRODUCTION

Neither the Kraft nor the sulphite process can remove all the lignin in wood without seriously degrading the polysaccharide fraction. Hence, the remaining 5-10% of lignin is removed by multi-stage bleaching (oxidation), often with chlorination (C) as the first stage. This is usually followed by alkali extraction (E) using sodium hydroxide, to remove the residual oxidized, degraded and/or chlorinated organic products. A typical six-stage bleaching sequence is C-E-H-D-E-D, although a variety of modifications exist. The pre-bleaching stage constitutes the C-stage and 1st E-stage. These stages contribute about 70% of the total organic material in the spent bleaching liquors. The composition of spent bleaching liquors is very complex (Pfister, 1978). They contain a large array of chlorinated compounds of both high and low molecular weight.

7.2 CHEMISTRY OF PRE-BLEACHING

Chlorine may react either as a molecular species (with lignin) or via a radical mechanism (with carbohydrates) (Kringstad and

Lindström, 1984). Both oxidation and substitution reactions occur between the residual lignin in the pulp and chlorine. These reactions lead to substantial depolymerization of the lignin and make it more hydrophilic by the introduction of various acidic groups. Typical reactions of residual lignin during chlorination are summarized in Figure 7.1. About 10% of the chlorine charge applied to the pulp appears as organically bound chlorine in the spent liquors.

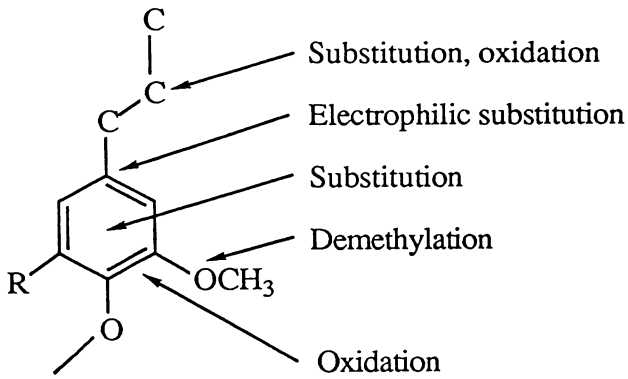


Figure 7.1 Reactions of residual lignin with chlorine

The acidic groups formed during the C-stage are ionized in the alkali extraction stage which facilitates the solution of the chlorinated lignin. About 70% of the substituted chlorine is subsequently removed as chloride ions; *i.e.* replacement of any chlorine atom by phenolic hydroxyl groups (Sjöström, 1980). Carbon dioxide is generated as decarbonylation of the degraded lignin occurs. Lindström *et al* (1981) reported that 70% of the organically bound chlorine in spent chlorination liquor is present as high molecular mass material (Mr > 1000) while in alkali extraction liquor about 95% of the spent liquor belongs to this class (Hardell, 1977).

7.3 LOW MOLECULAR MASS MATERIALS

More than 150 chlorinated compounds have been identified in bleaching spent liquors and more than half of these correspond to chlorinated neutral organic compounds (Kringstad and Lindström, 1984). These compounds can be classified under carboxylic acids, phenolics and neutrals. Many of the halogenated organic compounds are toxic and may show considerable resistance to biological and chemical degradation.

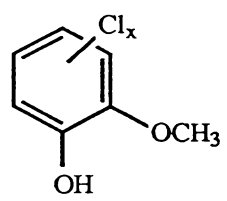
7.3.1 Acidic Compounds

This group comprises of fatty acids, hydroxyacids, dibasic acids, aromatic acids and resin acids. Chlorinated acetic acids are most abundant in both the C- and E-stage spent liquors (Lindström and Österberg, 1986). Ota *et al* (1973) identified several low molecular weight constituents of Kraft spent chlorination liquor, some of which were chlorinated aliphatic compounds. The hydroxyacids are considered to be chiefly oxidation products of carbohydrates. Dibasic acids such as oxalic, malonic, succinic and malic acids are present in considerable quantities in both spent liquors. Aromatic acids are formed from residual lignin by oxidation of the α-, β- or γ-carbons of the phenylpropane units.

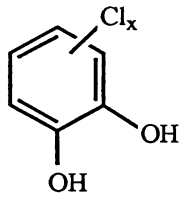
7.3.2 Phenolic Compounds

Voss *et al* (1981) reported an overall removal efficiency of about 30% for chlorinated phenolics in an aerated treated lagoon with an average 5-day retention time. However, Kringstad *et al* (1984a) found that the corresponding concentrations of these compounds were

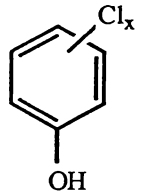
similar in the untreated and the treated effluent. Thus, the discharge of these materials into the environment is of great concern. Although the chlorinated phenolics may be present in the environment in sub-microgram levels, they are lipophilic in character and can accumulate in the fat of aquatic organisms. The three principal classes of chlorinated phenolic substances in bleaching effluents are chloroguaiacols, chlorocatechols and chlorophenols.



Chloroguaiacol



Chlorocatechol



Chlorophenol

Figure 7.2 Structures of chlorinated guaiacols, catechols and phenols. (x is the number of chlorine atoms)

Chlorocatechols are formed by the cleavage of the methylaryl ether bonds by nucleophilic components in the cooking liquor (Lindström and Nordin, 1976). The concentrations of chlorocatechols are usually greater in the C-stage while chloroguaiacols are dominant in the E-stage. This is believed to be due to the higher water solubility of catechols at low pH, than is the case for the more lipophilic guaiacols which require alkaline conditions to form the corresponding water-soluble phenolate salts (Lindström and Nordin, 1976; Lindström *et al*, 1981; Voss, 1981). Much of the work previously reported had been centred on the isolation and characterization of chlorinated phenolic compounds as they were found to be toxic and resistant to biodegradation. It was also found that the introduction of chlorine atoms into the structure of the phenolic compounds typically increased their toxicity (96-hour

LC_{50}) by an order of magnitude [*e.g.* phenol, 43.3 mg/l; 4-chlorophenol, 9.5 mg/l; 2,4-dichlorophenol, 5.5 mg/l; 2,4,5-trichlorophenol, 1.2 mg/l; 2,3,4,6-tetrachlorophenol, 0.6 mg/l; and pentachlorophenol, 0.4 mg/l (Salkinoja-Salonen *et al*, 1981)].

7.3.3 Neutral Compounds

Chlorinated neutrals are present in relatively small quantities but consist of a wide range of compounds, ranging from chlorinated saturated and unsaturated hydrocarbons, aldehydes, ketones and esters to various chlorinated benzene derivatives and chlorinated sulphur-containing compounds. Methanol is the dominant neutral compound and it is chiefly derived from the methoxy groups in lignin. When a hypochlorite stage is involved, the total quantity of chloroform and dichloromethane formed will be much higher. Kringstad and Lindström (1984) have speculated that the chlorinated dimethyl sulphones found in Kraft bleaching effluents may be formed by oxidation and chlorination of dimethyl sulphide which is produced during the Kraft cooking process (see Section 6.3.2) and carried over to the bleach plant along with the brown stock pulp. Chlorinated neutral organic compounds have been identified principally in the C-stage. There is increasing attention being paid to these compounds because the non-polar, lipid character of some of them suggests a propensity to bioaccumulate in living tissue. The discovery by Kringstad *et al* (1977, 1979) that spent chlorination (C) liquor exhibited a strong Ames mutagenic effect has heightened the concern.

Studies by Voss *et al* (1981a) have indicated that the major variables in bleaching are chlorine dosage, chlorine dioxide substitution, chlorination temperature and final chlorination pH. These can affect the types and quantities of chlorinated phenolics in bleaching effluents. When chlorine was completely replaced by chlorine dioxide, the only phenolic compound found in the spent bleaching liquor was 6-chlorovanillin (6-chloro-4-hydroxy-3-methoxybenzaldehyde).

Howard and Walden (1971) found that caustic extraction effluent was the most toxic of the major Kraft process streams in a survey of seven British Columbia mills. On the other hand, Sameshima *et al* (1979) reported chlorination liquor to be six times more toxic than caustic extraction liquor, though this was due to the relatively large volume of spent chlorination liquor compared with that of the caustic extraction. Chlorinated catechols have been found to contribute significantly to toxicity (McKague, 1981; Voss *et al*, 1981). In an early study, Leach and Thakore (1975) isolated five toxic components present in the caustic extraction effluent. They were 3,4,5-trichloroguaiacol, 3,4,5,6-tetrachloroguaiacol, 12- or 14-chlorodehydroabietic acid, 12,14-dichlorodehydroabietic acid and 9,10-epoxystearic acid. Of these, 3,4,5,6-tetrachloroguaiacol was found to be most toxic with a 96-hour LC_{50} of 0.32 mg/litre. 9,10-Epoxystearic acid is formed by hypochlorination of oleic acid in the first stage of bleaching followed by dehydrochlorination to give the epoxide in the E-stage.

7.4 BLEACH PLANTS

Bleaching at the Tasman mill is carried out in towers, while washing is carried out over drum rollers. Figure 7.3 shows the schematic diagram of the No. 1 and No. 2 bleach plants at Tasman. The No. 1 bleach plant produces semi-bleached pulp which is used for the manufacture of newsprint while the No. 2 bleach plant produces fully bleached pulp for the manufacture of high quality writing paper.

The bleach plants at the Tasman mill were sampled on two different occasions. The first sampling was in December 1984, when samples of the C, E- and H-stage effluents were collected from the No. 1 plant. Samples of the combined acid stages and combined alkali stages from the No. 2 plant were also taken. At this time, the No. 2 bleaching sequence was C_D-E_1-D_1-E_2-D_2. On this occasion the ITDS system was not available (*i.e.* mass spectral identification of the components was not possible), hence many of the compounds present in the foregoing extracts could not be identified. It was however apparent that in addition to the expected chlorinated guaiacols and catechols, the Tasman discharges also included an extensive array of other aromatic substances and lesser amount of some neutral compounds, most of which appeared to be chlorinated.

On the second occasion, April 1986, individual samples of the C-, E- and H-stages of the No. 1 plant were taken. The No. 2 plant was sampled in June 1986. By this time, the bleaching sequence of the No. 2 plant had been changed: the first alkali extraction was oxygen reinforced and the second extraction stage was eliminated. Samples

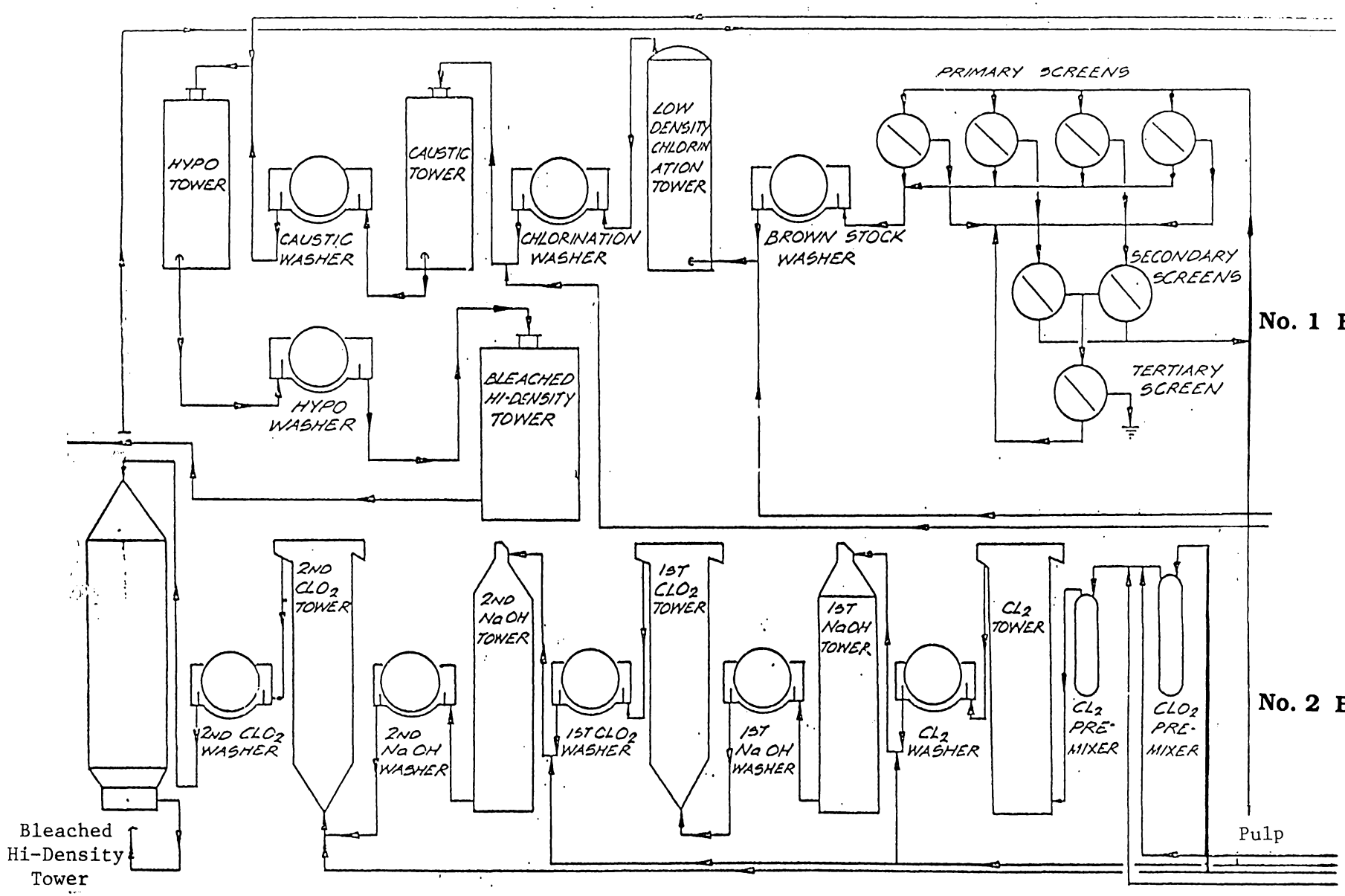


Figure 7.3 Tasman's No. 1 and No. 2 bleach plants (1985)
(Source: Tasman Pulp and Paper Company Limited)

of the C_D-, and E-stage effluents were investigated. Since the flow of the water is counter current to that of the pulp flow, the effluent discharged at C_D is the combined discharges of the C_D-, D_1- and D_2-stages.

7.5 EXPERIMENTAL

The E- and H-stage samples were acidified to pH 2 and extracted with chloroform by continuous liquid-liquid extraction. The C- and C_D- stages did not require acidification as the initial pH was 2. *n*-Octadecane (internal standard) was added at the rate of 1000 µg/l for the No. 1 bleach plant samples and 100 µg/l for the No. 2 bleach plant samples. The extracts were concentrated, dried and methylated with diazomethane as described in Chapter Four.

The presence of two or more chlorine substituents on the aromatic ring, or conjugation with a carbonyl-group usually leads to the methylation of phenolic hydroxyl-groups. Complete methylation of the phenolic hydroxyl-groups in compounds possessing one or no chlorine atoms was found to require a reaction time of *ca* 6-12 hours. The E- and C- stage extracts of the No. 2 bleach plant were additionally analysed in August 1988 using the Hewlett Packard-MSD system; the original samples having been stored in a cold room at 4°C since 1986. In the initial analysis of the extracts, methylation had not been completed. The extracts were re-methylated by adding further diazomethane and storing in the refrigerator overnight. The acceptability of this approach was established by comparing the levels of compounds that had been completely methylated in the original FID analysis with those subsequently found by MSD analysis after re-

methylation. In the case of the chlorinated aromatic compounds the sum of the methylated and unmethylated values were comparable with the value obtained for the fully methylated compound.

7.6 RESULTS AND DISCUSSION

GC analysis of the bleach plant extracts revealed them to be complex mixtures. Comparison of their GC and GC-MS profiles demonstrated that many of the peaks appearing in the GC profiles (as determined using a 12 m BP-1 column with hydrogen as carrier gas), were in fact mixtures of two or more components. In general a greater number of components were detected using the 20 m DB-1 column (helium as carrier gas) installed in the Hewlett Packard-MSD instrument. The differing retention times and resolution characteristics for the two systems prevented the reliable identification of the minor peaks which appeared in the GC profiles. The identification and quantification data for fatty acids, resin acids and aromatic compounds given in Table 7.1 were therefore derived from the corresponding GC-MSD profiles. The class response factors used for fatty acids, resin acids and aromatic compounds (0.59, 0.25 and 0.33 respectively), were determined in the manner previously described (see Section 4.5). The compounds in Table 7.1 are listed according to increasing retention times.

The organic compounds identified in the bleach plant samples were identified, where possible, using the NBS mass spectral library and by comparing mass spectral fragmentations with those that had been reported in the literature (Knuutinen and Korhonen, 1984; Knuutinen *et al*, 1982; Lindström and Nordin, 1976; Leach and

Thakore, 1973). In other cases compounds were identified on the basis of their molecular ions and the similarities that existed between the fragmentation patterns of chlorinated and non-chlorinated analogues. Many of the compounds detected were present in modest quantities, and were not quantified.

Figures 7.4, 7.5 and 7.6 are the expansions of the aromatic and fatty acid region of the GC-MSD profiles of the C-, E- and H-stage effluents from the No. 1 bleach plant.

TABLE 7.1
Methylated components of bleach plant sewer extracts (μg/l)

	Compounds	No.1 Plant			No. 2 Plant	
		E	C	H	E	C_D
1	Methyl benzoate	-	-	-	27*	-
2	Methyl naphthalene	-	-	-	12	50
3	2,4-Dichloromethoxybenzene	-	-	-	39	-
4	4-Chloro-1,2-dimethoxybenzene	-	-	-	14	-
5	Chlorinated monoterpene	-	-	-	-	278
6	2,4,6-Trichloromethoxybenzene	-	-	-	32	-
7	Unknown	-	-	-	33	120
8	Methyl 3-phenyl-3-hydroxypropanoate	-	-	-	30	-
9	Unknown	-	-	-	-	132
10	Chlorinated monoterpene	-	-	-	14	36
11	Chlorinated monoterpene	-	-	-	-	21
12	Chlorinated monoterpene	-	-	-	-	65
13	*3,4*-Dichloro-1,2-dimethoxybenzene	30	46	-	41	112
14	*3,5*-Dichloro-1,2-dimethoxybenzene	-	121	-	10	230
15	Chlorinated monoterpene	-	-	-	42	-
16	3,4-Dimethoxybenzaldehyde	42	-	5	62	-
17	*3,6*-Dichloro-1,2-dimethoxybenzene	35	-	-	86	23
18	Dichloro-1,2-dimethoxybenzene	772	80	22	613	230
19	Dichlorotrimethoxybenzene	-	-	-	-	20
20	3,4,6-Trichloro-1,2-dimethoxybenzene	12	-	-	38	43

Table 7.1 cont....

	Compounds	No. 1 Plant			No. 2 Plant	
		E	C	H	E	C_D
21	5-Chlorobenzaldehyde	-	-	-	48	-
22	Chlorinated monoterpene	-	-	-	-	68
23	Methyl laurate	14	10	-	13	-
24	Dimethyl nonanedioate	25	-	15	20	-
25	3,4-Dimethoxyacetophenone	63	-	-	39	-
26	Methyl dichloro-4-methoxybenzoate	37	-	-	62	-
27	Methyl chloro-4-methoxybenzoate	-	-	-	124	-
28	Dichloro-4-methoxyacetophenone	-	-	-	39	-
29	Methyl 2-chloro-4-methoxybenzoate	48	-	10	-	-
30	Unknown	-	27	-	-	44
31	Unknown	-	-	-	-	56
32	Methyl 3,4-dimethoxybenzoate	191	-	12	110	-
33	2-Chloro-3,4-dimethoxybenzaldehyde	-	-	-	81	-
34	Methyl 2,6-dichloro-4-methoxybenzoate	171	-	-	190	-
35	6-Chloro-3,4-dimethoxybenzaldehyde	189	-	18	362	-
36	Chloro-3,4-dimethoxyphenylethanal	18	-	-	-	-
37	Chloro-3,4-dimethoxyacetophenone	88	-	-	63	-
38	3,4,5-Trichloro-1,2-dimethoxybenzene	223	54	-	566	788
39	1-(Chloro-3,4-dimethoxyphenyl)-propan-1-one	206	-	-	-	38
40	1-(Chloro-3,4-dimethoxyphenyl)-propan-2-one	204	-	21	141	-
41	Methyl 2-chloro-3,4-dimethoxybenzoate	284	-	6	78	-
42	Chlorinated monoterpene	-	-	-	-	202
43	Dichloro unknown (M^+ 244)	-	30	-	-	-
44	Dichloro-3,4-dimethoxyacetophenone	14	-	-	-	-
45	1-(Chloro-3,4-dimethoxyphenyl)-propan-2-one	26	-	-	26	-
46	Dichloro-3,4-dimethoxybenzaldehyde	27	-	-	-	-
47	Dichloro-3,4-dimethoxybenzaldehyde	37	-	-	-	-
48	Trichlorotrimethoxybenzene	-	76	-	-	143
49	Methyl 5-chloro-3,4-dimethoxybenzoate	-	-	-	38	-
50	1-(Chloro-3,4-dimethoxyphenyl)-propan-2-one	476	-	10	142	-
51	Trichlorotrimethoxybenzene	-	26	-	-	232
52	3,4,5,6-Tetrachloro-1,2-dimethoxybenzene	52	-	-	186	304
53	1-(Dichloro-4-hydroxy-3-methoxyphenyl)-propan-2-one	23	-	-	-	

Table 7.1 cont....

	Compounds	No.1 Plant E	No.1 Plant C	No.1 Plant H	No. 2 Plant E	No. 2 Plant C_D
54	Methyl 6-chloro-3,4-dimethoxybenzoate	334	-	-	382	-
55	Methyl dichloro-3,4-dimethoxybenzoate	31	-	-	28	-
56	Methyl dichloro-3,4-dimethoxybenzoate	-	-	-	13	-
57	Methyl tetradecanoate	-	-	30	-	63
58	1-(Dichloro-4-hydroxy-3-methoxyphenyl)-propan-2one	26	-	-	-	-
59	Chlorinated monoterpene	-	-	-	-	98
60	1-(Chloro-3,4-dimethoxyphenyl)-propan-2-one	135	-	-	-	-
61	Dichloro-3,4-dimethoxyacetophenone	191	-	-	-	137
62	Dichloro-3,4-dimethoxybenzaldehyde	-	-	-	43	-
63	Dichloro-3,4-dimethoxyacetophenone	121	-	-	-	-
64	2,5,6-Trichloro-3,4-dimethoxyacetophenone	-	-	-	42	-
65	Methyl dichloro-3,4-dimethoxybenzoate	103	-	-	-	-
66	Methyl 2,5,6-trichloro-3,4-dimethoxybenzoate	-	-	-	78	129
67	Dichloro-3,4-dimethoxyacetophenone	-	-	-	83	34
68	Methyl palmitoleate	50	-	-	10	47
69	Methyl palmitate	674	66	114	152	220
70	Methyl *anteiso* heptadecanoate	43	-	5	-	-
71	Methyl heptadecanoate	98	-	13	-	-
72	Methyl oleate	423	-	-	14	-
73	Methyl stearate	411	19	48	33	46
74	Methyl 6,8,11,13-abietatetraen-18-oate	244	72	44	5	-
75	Methyl dehydroabietate	384	360	160	28	65
76	Methyl 9,10-dihydroxystearate	86	-	31	23	4
77	Methyl 12-chlorodehydroabietate	210	10	45	10	-
78	Methyl 14-chlorodehydroabietate	98	19	85	13	-
79	Methyl 7-oxodehydroabietate	304	-	75	8	12
80	Methyl 12,14-dichlorodehydroabietate	10	-	5	-	-

* Quantified on GC-FID on July 1986.

Tentative structural assignment are give in italics.

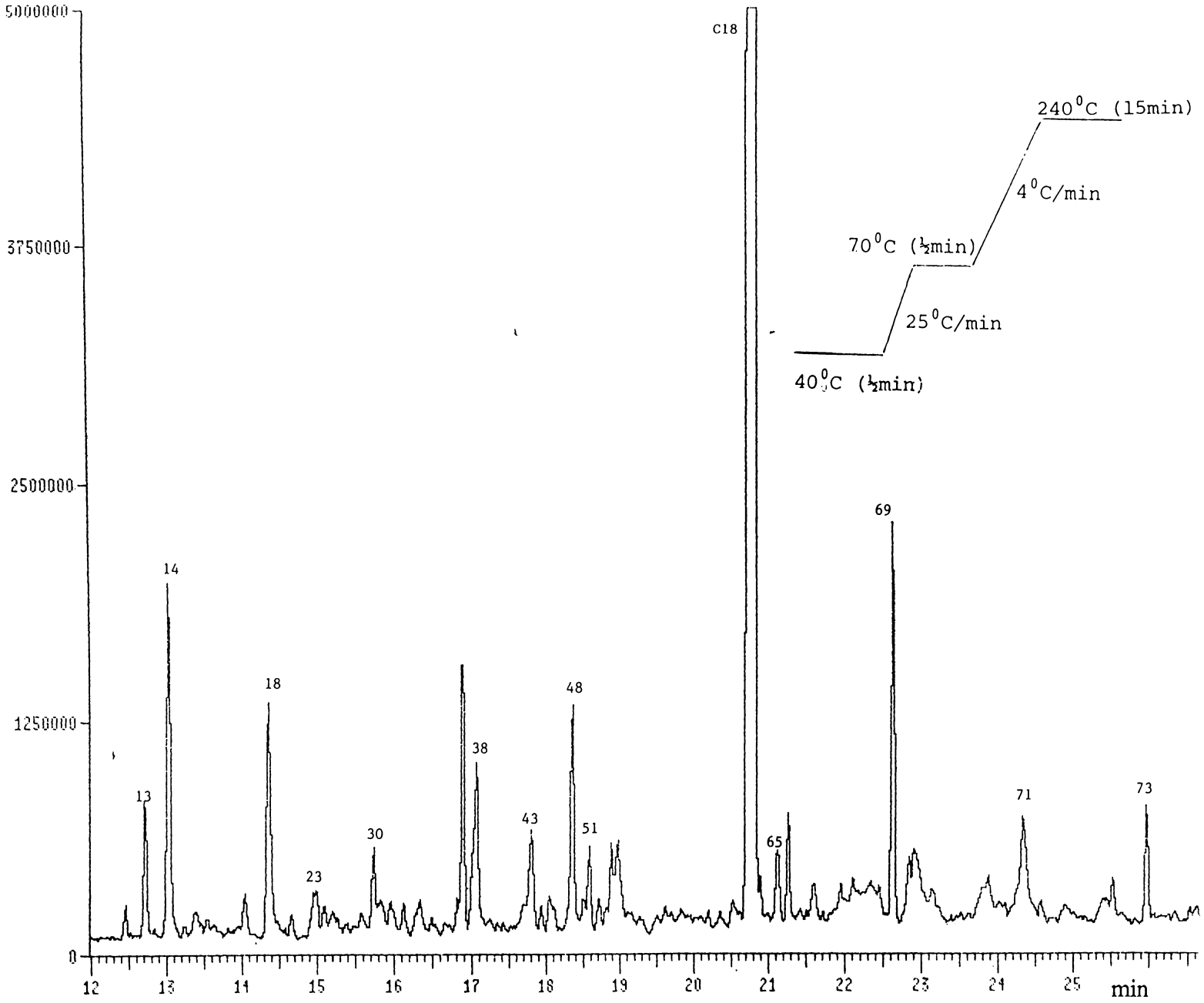


Figure 7.4 GC-MSD profile of an extract of C-stage (No. 1 bleach plant) (April 1986). For peak identifications see Table 7.1.

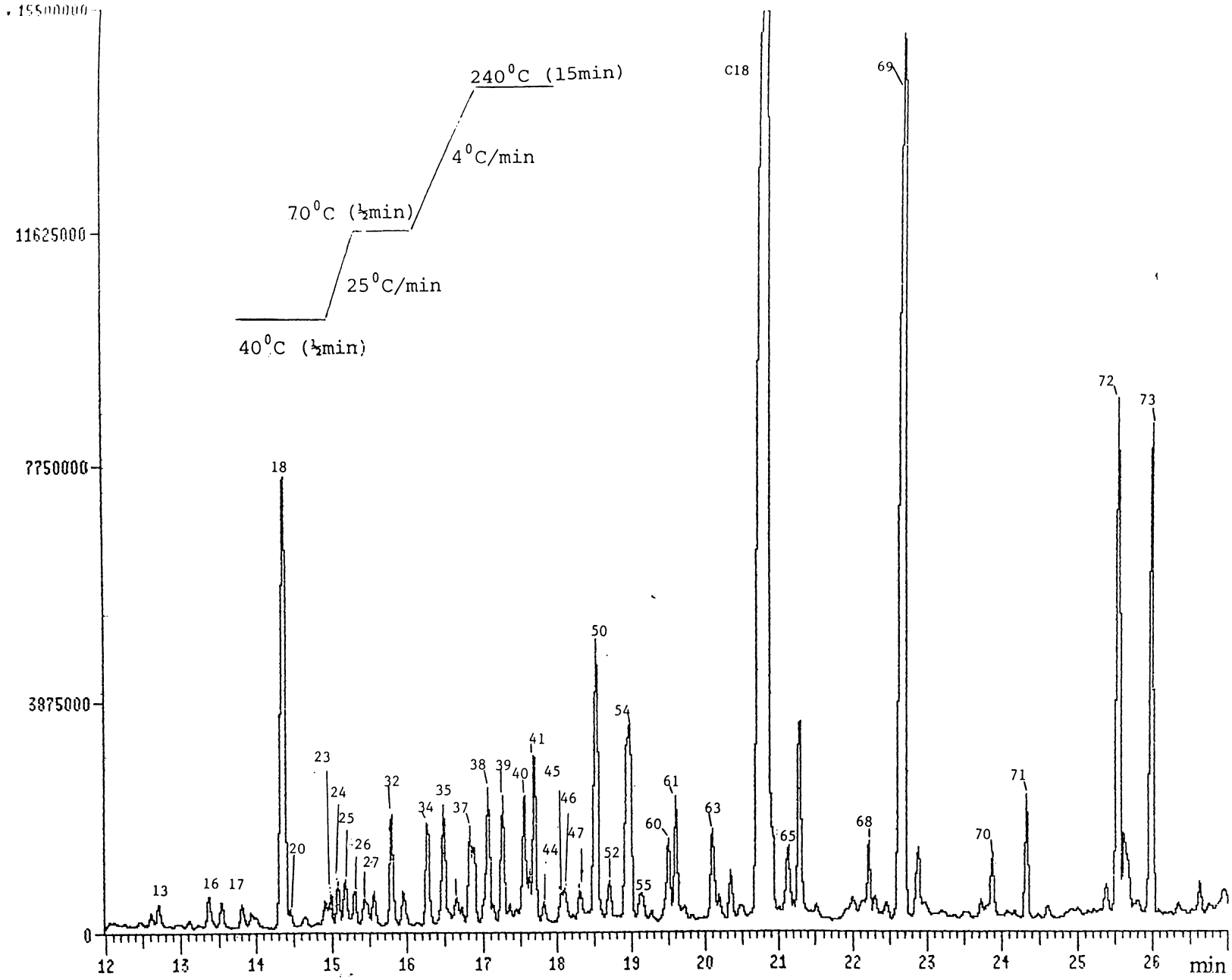


Figure 7.5 GC-MSD profile of an extract of E-stage (No. 1 bleach plant) (April 1986). For peak identifications see Table 7.1.

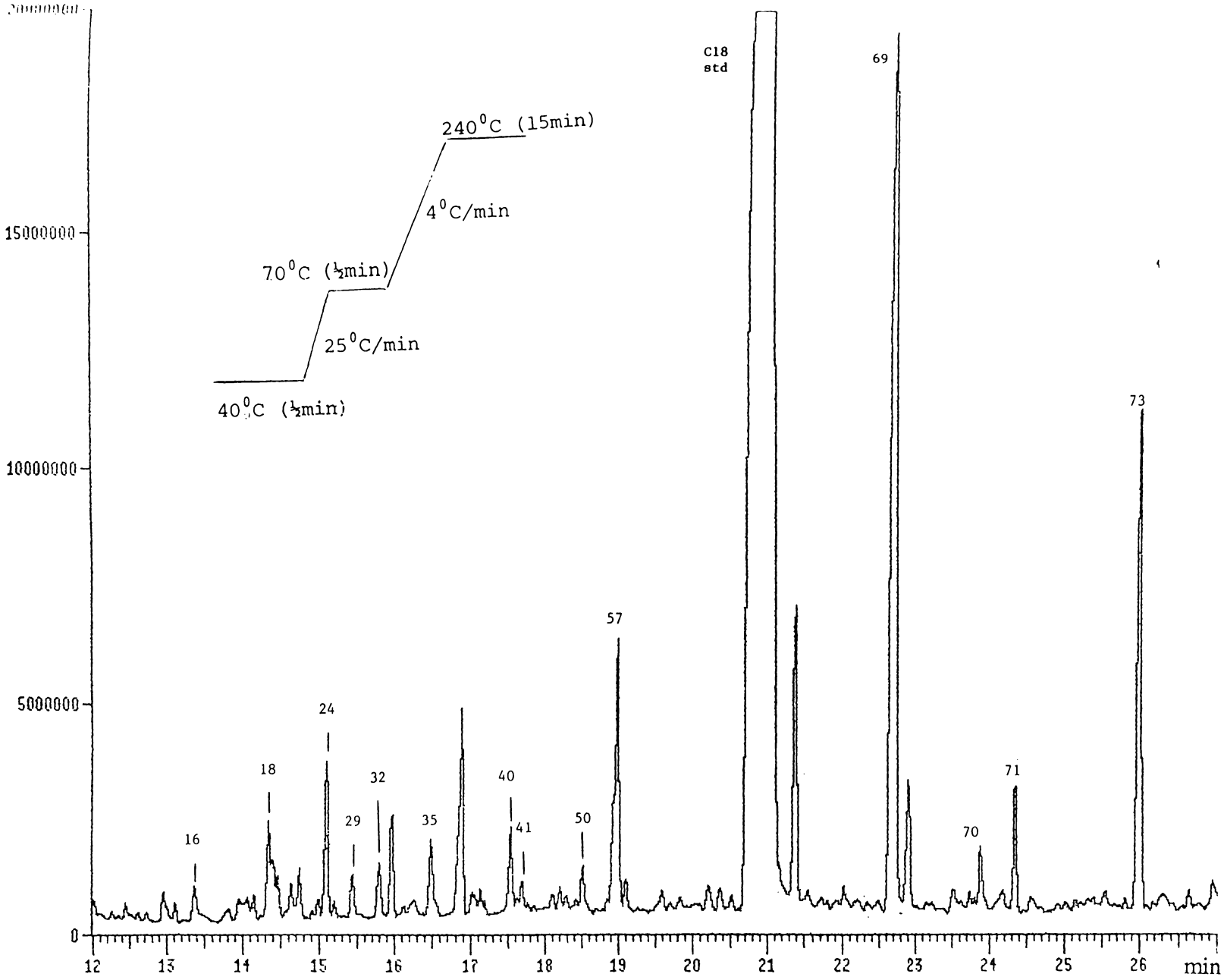


Figure 7.6 GC-MSD profile of an extract of H-stage (No. 1 bleach plant) (April 1986). For peak identifications see Table 7.1.

7.6.1 Aromatic Compounds

GC-ITDS and GC-MSD analyses led to the identification of a large number of aromatic substances, most of which were mono-, di-, tri- and tetrachlorinated. Guaiacol and catechol derivatives are reported in Table 7.1 as the corresponding dimethoxybenzenes since diazomethylation does not distinguish between the parent guaiacols and catechols (see Section 4.3.4). While acetylation (as opposed to methylation) would preserve this distinction, the former procedure suffers from the disadvantage that a greater number of derivatized isomers are produced: *e.g.* there are six possible acetylated dichloroguaiacol isomers; 4 possible dichlorocatechol isomers; and 4 possible dichloro-1,2-dimethoxybenzene isomers. This affords a total of 14 derivatives compared with methylation which produces only a total of 4 isomers from all of these compounds. Given the complexity of the bleaching extracts the fewer number of peaks produced by the methylation procedure facilitates separation of the derivatized extracts.

On the basis of overseas reports it was anticipated that di-, tri- and tetrachlorodimethoxybenzenes (M^+ ion clusters at m/e 206, 208 and 210; 240, 242 and 244; 274, 276, and 278 respectively) would be the dominant constituents of the methylated C-stage extracts. Four isomers of dichloro-1,2-dimethoxybenzene, and two isomers of trichloro-1,2-dimethoxybenzene were detected in the methylated extracts. (see Table 7.1). Amongst these isomers 4,5-dichloro-1,2-dimethoxybenzene and 3,4,5-trichloro-1,2-dimethoxybenzene were predominant. The identification of these compounds was confirmed

by co-injection of authentic specimens prepared by Stuthridge (1986). Minor methylated isomers were considered to elute in the order reported by Knuutinen and Kolehmainen (1982) for the corresponding acetylated isomers; *i.e.* the 3,5-, 3,4- and 3,6-dichloro isomers elute before the dominant 4,5-isomer while the 3,4,6-trichloro isomer elutes before the dominant 3,4,5-trichloro isomer. The relative ratios of the acetylated isomers reported by Knuutinen and Kolehmainen (1982) were similar to those found in the present study. This observation affords support for the assumed elution order of the minor isomers in their methylated forms.

In addition to the chlorinated dimethoxybenzenes, a series of mono-, di- and trichlorinated 3,4-dimethoxy analogues of benzaldehyde (26), acetophenone (28), methyl benzoate (27), phenylpropan-1-one (34) and phenylpropan-2-one isomers were detected in some of the samples. The greatest array was found in the E-stage effluent of the No. 2 bleach plant. The majority of the chlorinated aromatic compounds gave rise to distinctive mass spectra, and selected ion profiles. For example, the mono-, di- and trichloro-3,4-dimethoxybenzaldehyde isomers exhibited M^+ ion clusters at m/e 200 and 202; 234, 236 and 238; and 268, 270 and 272 respectively together with strong M^+-H ion clusters of 199 and 201; 233, 235 and 237; and 267, 269 and 271 respectively. In a like manner the mono-, di- and trichloro- isomers of methyl 3,4-dimethoxybenzoate exhibited M^+ ion clusters at m/e 230 and 232; 264, 266 and 268; and 298, 300 and 302 respectively, while the mono-, di- and trichloro-3,4-dimethoxyacetophenone isomers,

exhibited M^+ ion clusters at m/e 214 and 216; 248, 250 and 252; and 282, 284 and 286 respectively.

The structures of the minor chlorinated 3,4-dimethoxybenzaldehyde, methyl 3,4-dimethoxybenzoate, 3,4-dimethoxyacetophenone and 1-(3,4-dimethoxyphenyl)-propan-2-one isomers are less certain. The C-1 carbonyl group of these derivatives should activate the *ortho-* and *para-* positions (*i.e* the 2, 4 and 6 sites) to a greater extent than would be the case for the C-3 methoxyl group or the C-4 hydroxyl group of the unmethylated 4-hydroxy-3-methoxy-percursor. It can therefore be proposed that the major monochlorinated isomer, for example, of benzaldehyde is C-6 substituted while the lesser isomers are the result of C-2 or C-5 substitution. Hitherto Voss *et al* (1981a) have reported the presence of 6-chloro-3,4-dimethoxybenzaldehyde and 5,6-dichloro-3,4-dimethoxybenzaldehyde in methylated bleach plant effluents.

A number of non-chlorinated aromatic acids were also detected. These were chiefly the methyl esters of benzoic acid, 4-hydroxy-3-methoxybenzoic acid and/or 3,4-dimethoxybenzoic acid. Since the extracts were methylated prior to GC and/or GC-MS analysis the latter pair of acids were not distinguished.

7.6.2 Resin acids and fatty acids.

Significant levels of resin acids were found in the spent liquors. Dehydroabietic acid, 6,8,11,13-abietatetraen-18-oic acid, 12- and 14-chlorodehydroabietic acids, 12,14-dichlorodehydroabietic acid and 7-oxodehydroabietic acid were detected in most of the samples.

Aliphatic fatty acids ranged from C_4 to C_{18} with palmitic acid and stearic acid being the main fatty acids present. Other fatty acids detected (those present in low levels were not quantified) were decanoic, lauric, myristic, pentadecanoic, 14-methylhexadecanoic, heptadecanoic, and behenoic acids together with butanedioic acid and nonanedioic acid. Many of the fatty acids were detected in the GC-ITDS or GC-MSD chromatograms (m/e 74 and m/e 87 ion profiles readily located the methylated fatty acids) but not on the GC-FID profiles, hence they were not quantified. A substance exhibiting strong m/e 155 and 187 ions, together with a weak m/e 74 ion was identified by library searching as the methyl ester of 9,10-dihydroxy-stearic acid. This compound presumably arises by hydroxylation of oleic acid.

7.6.3 Chlorinated Neutral Compounds

A collection of neutral substances, identical to those reported by Stuthridge (1986) were found to be present in the C-stage bleach plant effluent of another New Zealand mill. These have now been identified (Stuthridge, *pers. comm.*) as chlorinated monoterpene hydrocarbons and alcohols derived principally from α- and β-pinene, and α-terpineol. The mass spectra of the monoterpene hydrocarbons, α- and β-pinene include a base peak at m/e 93 (see Chapter Nine); the substances believed to be chlorinated pinenes also displayed base peaks at m/e 93 (see Appendix C). Addition of two chlorine atoms to the double bond of the respective pinenes affords substances of molecular weight 206 amu. Weak ions of m/e 206 (M^+) and 208 appeared in the mass spectra of the dichlorinated hydrocarbons. On the other hand, the dichloroterpineol isomers did not exhibit

molecular ions. As is the case for α–terpineol, the mass spectra of the dichloroterpineol isomers were dominated by a fragment ion of m/e 59 corresponding to the loss of the C-4 hydroxyisopropyl group. Some of the chlorinated monoterpenes appeared to be the dehydrated analogues (*i.e.* limonene derivatives). In these analogues the base peak was an ion of m/e 43 (see Appendix C).

Chlorinated terpineol and pinene isomers, while detected in the bleaching effluents of two New Zealand pulp mills, have not been reported in overseas literature. It appears that turpentine recovery operations and washing of the pulp prior to bleaching, does not result in the complete removal of monoterpenes, which not unexpectedly react with chlorine (or chlorine doxide) during bleaching.

One of the C-stage effluent peaks was tentatively identified as dichlorodimethylsulphone. Preliminary extractions indicated that higher levels (10-40 μg/l) were present in the D_1- and D_2-stage of the No. 2 bleach plant. Only a trace amount was detected in the E-stage by the GC-MSD. This compound is formed by oxidation and chlorination of dimethylsulphide which is a product of Kraft cooking (McKague, 1981; Lindström *et al*, 1981). Another compound identified provisionally was dichloroacetyl chloride. Also detected (but not quantified due to overlap with other peaks) were small amounts of chlorinated hydrocarbons: hexachloroethane, 1,1,1,3,3-pentachloropropan-2-one, and 1,1,1-trichloro-2-methylpropanal. Although it is known that chloroform and dichloromethane are produced in substantial quantities during bleaching, they are not reported in this study as the extraction procedure was not suitable for their detection.

Mass spectra of the dominant mono-, di- and trichlorinated 3,4-dimethoxy analogues of benzaldehyde, acetophenone, benzoic acid methyl ester and phenylpropanone are presented in Appendix C.

7.7 CONCLUSION

The combined discharge of the acid sewers of the bleach plants is 5 Ml per day while the alkali sewers contribute only 2.9 Ml per day to the treatment system (Slabber, *pers. comm.*). While the volume of alkali discharges is smaller than that of the acid discharge, the alkali extration liquor is highly coloured and results in a higher BOD loading. The main concern has been that the majority of extractable chlorinated organic compounds are resistant to biodegradation and toxic.

The No. 1 bleach plant discharges consisted chiefly of fatty acids, resin acids, mono- and dichlorinated aromatic analogues of compounds such as guaiacol, 4-hydroxy-3-methoxyacetophenone, and 4-hydroxy-3-methoxybenzoic acid. While the toxicity of chlorinated guaiacols is well established, the environmental impact of chlorinated 4-hydroxy-3-methoxyacetophenone, and 4-hydroxy-3-methoxy-benzoic acid analogues has not yet been defined.

Besides the range of compounds detected in the No. 1 plant, the No. 2 bleach plant also included significant quantities of trichlorinated analogues. such as guaiacol, 4-hydroxy-3-methoxyacetophenone, and 4-hydroxy-3-methoxybenzoic acid. This may be due to more forcing conditions being used in this bleach plant. In general more highly chlorinated aromatic compounds have

been found to be more resistant to biodegradation than the less chlorinated analogues. Thus it can be concluded that at the time of sampling, effluent from the No. 2 bleach plant possessed higher levels of compounds likely to be more environmentally sensitive.

The uniqueness of the No. 2 C-stage effluent was the presence of chlorinated pinenes and terpineols. Stuthridge (1986) had previously observed a similar array of compounds from the C-stage effluent of another New Zealand pulp and paper mill which, like Tasman's No. 2 plant, bleaches pulp from a continuous digester. The turpentine recoveries from a continuous digester are much lower than batch digester; residual turpentine in the pulp would be the precursors of these compounds. The concentrations found by Stuthridge (1986) were however ten-fold higher than those detected in this study. Chlorinated monoterpenes have not been reported in overseas literature. While the toxicity of these compounds are not known, related chlorinated monoterpenes have been found to exhibit significant toxicity towards *Daphnia magna* (Kopperman *et al*, 1976).

The chlorinated compounds in this study were detected using GC-FID, GC-ITDS or GC-MSD. It is anticipated that by using a GC-ECD (Electron Capture Detector). a much greater diversity of chlorinated components would have been found. GC-ECD is much more sensitive (up to one thousand-fold more sensitive) than either GC-FID, GC-ITDS or GC-MSD systems towards chlorinated compounds particularly polychlorinated compounds. However the quantities detected at such sensitivity (levels down to 0.01 µg/l), while having potential impact on the treatment system, are not likely to be of environmental significance.

CHAPTER EIGHT

PLANT SOURCES III: PAPER MACHINES

8.1 INTRODUCTION

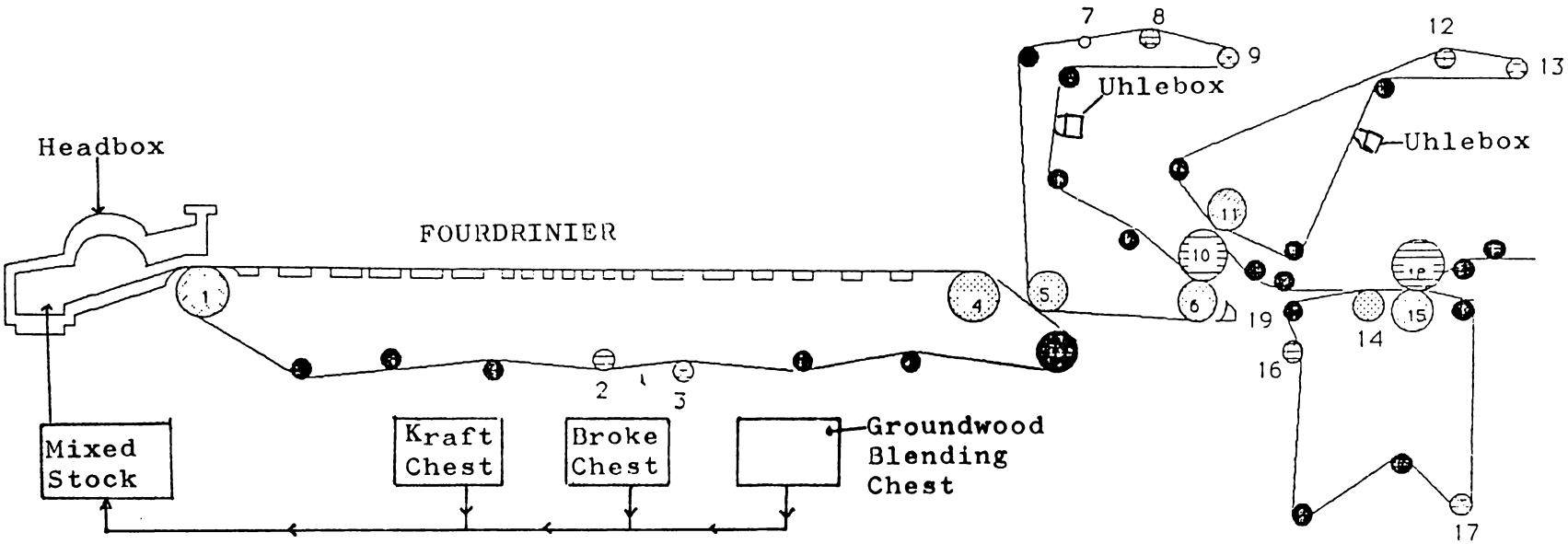
Newsprint at the Tasman mill is made up of 80% mechanical pulp and 20% Kraft pulp. The Kraft pulp is semi-bleached. Newsprint is made on Fourdrinier machines. A newsprint machine comprises of a Kraft chest, groundwood blending chest, broke chest and a mixed stock chest. The broke refers to paper that has been discarded at any stage of its manufacture and is repulped. The groundwood, Kraft and broke are blended in the mixed stock chest to a proportional percentage and consistency. The Kraft and broke are refined in the stock preparation area before entering the mixed stock chest. However, the groundwood is refined prior to entering the stock preparation area.

The most lavish use of water is at the stage when the refined cellulose is suspended in 100 times its volume of water and fed onto a fast moving wire screen. The flow of the stock onto the wire is controlled by the headbox which is situated at the wet end of the Fourdrinier. The paper leaving the couch roll has about 80% water. The water is removed first by table rolls and later by vacuum boxes

(uhle boxes) which assist in further removal of water from the wet web. This water is recycled and used for the dilution of the incoming pulp. The fibre sheet is removed from the wire by the couch roll and passed onto a felt web, after which it is passed through various presses and steam driers. Finally the paper is passed through a calender stack which comprises a series of pressurized polished rolls to give the paper a smooth finish (Figure 8.1).

Mechanical pulping discharges have been considered to have less effect on the environment than Kraft pulping discharges. However, there have been indications that the untreated effluent from mechanical pulping operations may pollute receiving waters (Leach *et al*, 1976a, 1976b). An early study by Leach and Thakore (1976b) found that 12-62 mg/l of toxic constituents (*i.e.* substances having toxicity values at 96-hour LC_{50} towards fish of the order 1 mg/l or less) were present in mechanical pulping spent liquors discharged from a North American mill. They comprised mainly resin acids, resin alcohols, diterpene aldehydes and juvabione analogues. The effect of fibre loss and fines are well-known (Corson and Lloyd, 1978a, 1978b) but little attention has been given to the water soluble compounds of wood that are leached out by the hot white water.

The effluent from the paper machines consists mainly of dissolved wood chemicals and fibre fines, as well as the biocides used on the machines (Cox, 1981). Tasman does not have a saveall filter system whereby the cellulose fibres are recovered, hence they are discharged into the sewers, and thence to the effluent treatment system where their degradation results in an additional BOD loading. The amount of leachable substances is influenced by the bleaching



1. BREAST ROLL
2. FABRIC GUIDE ROLL
3. FABRIC STRETCH ROLL
4. COUCH ROLL
5. PICK-UP ROLL
6. 1ST PRESS SUCTION ROLL
7. MOUNT HOPE ROLL
8. PICK-UP FELT GUIDE ROLL
9. PICK-UP FELT STRETCH ROLL
10. TWINVER GRANITE ROLL
11. 2ND PRESS GROOVED ROLL
12. 2ND PRESS FELT GUIDE ROLL
13. 2ND PRESS FELT STRETCH ROLL
14. 3RD PRESS FELT SUCTION ROLL
15. KUSTER SWIMMING ROLL
16. 3RD PRESS FELT GUIDE ROLL
17. 3RD PRESS FELT STRETCH ROLL
18. 3RD PRESS GRANITE ROLL
19. STEAM BOX

Figure 8.1 No. 2 Paper machine (Headbox, Fourdrinier and Press sections)
(Source: Tasman Pulp and Paper Company Limited)

process. The presence of leachable substances, particularly carbohydrates and resin acids, encourages slime growth in the white water. The build-up of slime can affect the operation of the plant. Currently Tasman uses three types of biocides to prevent this. They are Nalco 7620, Busan 40 and Busan 110. The main constituents of these biocides are shown in Table 8.1. Biocides can lower the efficiency of the biodegradation of the effluent treatment system.

Table 8.1
Constituent of Commercial Biocides

Trade name	Constituents	%
Nalco 7620	methanol	1-2
	dimethylformamide	30
	methyl bisthiocyanate	10
	dispersants and penetrants	1-2
	pine oil (turpentine)	65
Buscan 110	potassium N-hydroxy methyl dithiocarbonate (in water)	41
Buscan 40	methyl bisthiocyanate	10
	dimethyl formamide	27
	surfactants (fatty acids)	63

8.1.1 Pitch Problems

The most frequently occurring problem in paper manufacture is due to the presence of pitch. Pitch consists of wood resins that form sticky deposits on equipment such as screens, wires, filters and felts. They can fill the wire of the paper machines thereby producing holes in the finished paper or aggregate on the felt or machine parts as

sticky dark-coloured lumps which are invariably transferred onto the paper as sticky specks. The presence of pitch reduces operation efficiency. The build-up of pitch on the Fourdrinier machines requires that the machines be stopped and washed with sodium hydroxide solution. These interruptions cost Tasman between $5-10 million per year in lost production (Slabber, *pers. comm.*).

In wood, resins are concentrated in the resin ducts: ray parenchyma and epithelial cells. The ducts of these cells are fractured during the pulping process, thus allowing their resin content to be released to form colloidal particles in the liquid surrounding the fibres. These colloidal particles then coagulate to form pitch deposits (Allen, 1975). This effect is more prominent in sulphite and mechanical pulping than in Kraft pulping since the resins in the latter process dissolve readily in the alkaline solution and are removed as tall oil. An early review by Levitin (1967) indicated that chip or log that had been stored for eight months to two years showed reduced pitch problem as the amount of resins in wood decreased due to oxidation.

8.2 EXPERIMENTAL

On 18th April 1986, samples of white water from the No. 2 paper machine were taken at the Mixed Stock, Headbox and Uhle box regions (see Figure 8.1).

The samples (300 mls in each case) were filtered to remove the fibres. Internal standards, *n*-dodecane and *n*-octadecane, were added at the rate of 1000 µg/l to the filtrates which were extracted with redistilled chloroform in a liquid-liquid extractor for 6 hours.

The extracts were then concentrated, dried, derivatized with diazomethane, and analysed on the capillary GC and the GC-ITDS systems as described in Chapter Four.

A sample of pitch (~ 10 g), taken from the Uhle box region during the same sampling programme, was extracted with chloroform in a Soxhlet apparatus. Prior to extraction *n*-octadecane was added to the solvent at the rate of 1000 μg/g. The pitch dissolved in the course of the extraction, leaving behind some fibres. The chloroform extract was concentrated, dried, derivatized with diazomethane, and analysed on the capillary GC and the GC-ITDS systems as described previously

8.3 RESULTS AND DISCUSSION

The GC-FID profiles of the Headbox and pitch extracts are given in Figures 8.2 and 8.3 respectively. The peaks are numbered with reference to Table 8.2. Methylated white water extracts were, in general, characterized by high concentration of the methyl esters of resin acids and fatty acids together with lesser amount of the methyl esters of aromatic acids such as benzoic acid (peak 5), phenylacetic acid (peak 7), phenylpropanoic acid (peak 14) and cinnamic acid (peak 16) (Table 8.2).

The aromatic methyl esters were easily identified since they displayed strong molecular ions, and usually gave rise to base peaks attributable to the M^+- $COOCH_3$ fragment ion. The monoterpenes detected were borneol, terpen-4-ol and α-terpineol. The relative concentrations of the organic compounds in the samples decreased quite substantially from Mixed Stock to Uhle box. This is as expected

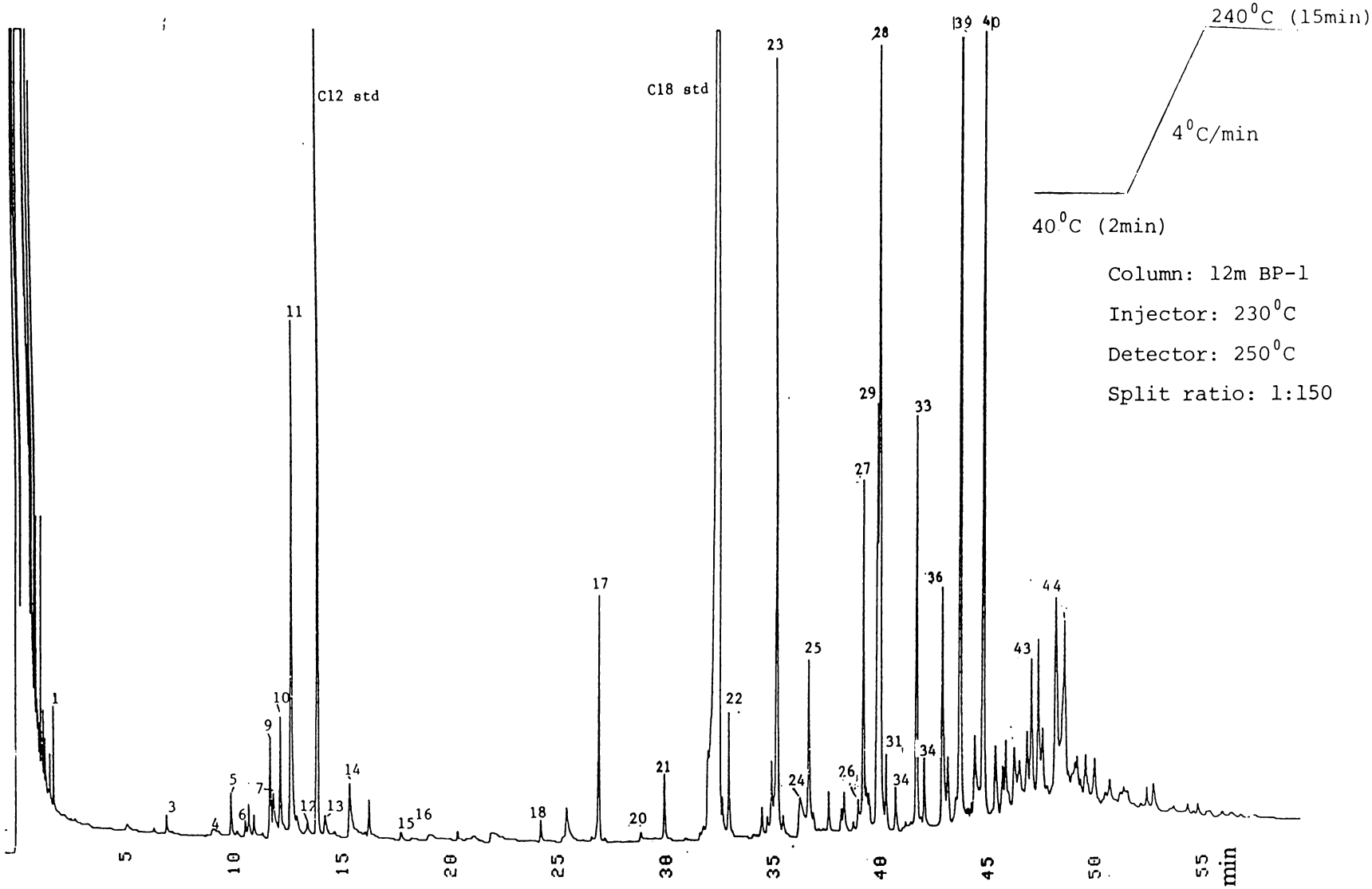


Figure 8.2 GC-FID profile of a derivatized extract of No. 2 paper machine Headbox. For peak identifications see Table 8.2.

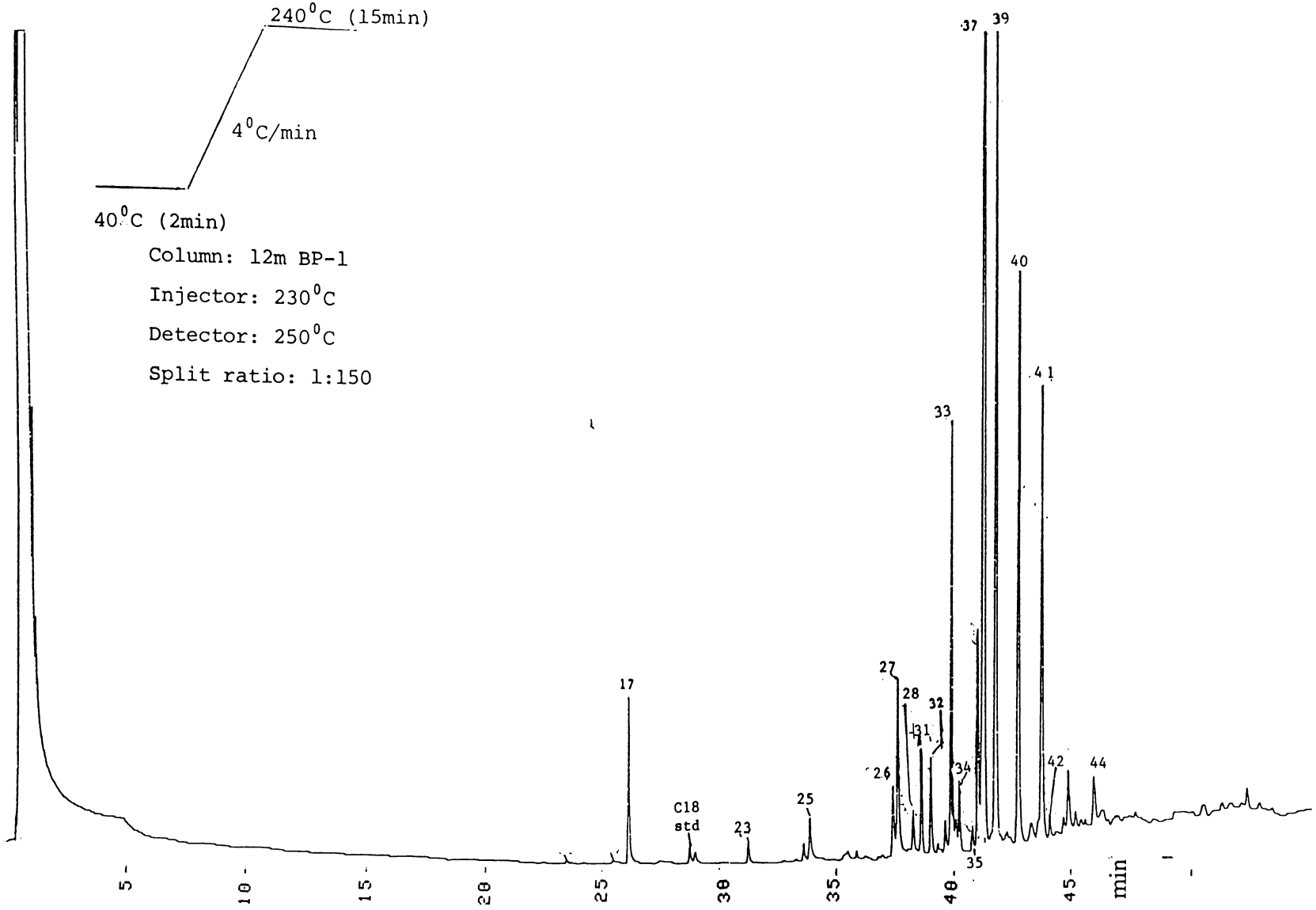


Figure 8.3 GC-FID profile of a derivatized extract of No. 2 paper machine pitch. For peak identifications see Table 8.2.

Table 8.2

Extractable organic compounds present in No. 2 paper machine white water (μg/l) and pitch samples (μg/g).

Peak	Compound	Mixed stock (μg/l)	Head box (μg/l)	Uhle box (μg/l)	Pitch (μg/g)
1	Toluene	-	*	-	-
2	Benzaldehyde	-	-	*	-
3	*p*-Cymene	-	*	*	-
4	Dimethyl butanedioate	-	*	-	-
5	Methyl benzoate	*	10	*	-
6	Dimethyl-2-cyclopentenone	-	*	-	-
7	Methyl phenylacetate	48	11	*	-
8	Phenylmethanol	*	-	-	-
9	Borneol	58	12	*	-
10	Terpen-4-ol	-	-	12	-
11	α-Terpineol	493	62	*	-
12	Dichloropinene (135,93)	*	*	*	-
13	Methyl nonanoate	*	-	-	-
14	Methyl phenylpropanoate	20	19	*	-
15	Methyl decanoate	-	*	*	-
16	Methyl cinnamate	5	2	-	-
17	Methyl 3,4-dimethoxybenzoate	12	*	-	26
18	Methyl laurate	18	4	*	-
19	Dimethyl nonanedioate	6	-	*	-
20	Pentachloromethoxybenzene	-	1	-	-
21	Methyl myristate	13	12	*	*
22	Methyl pentadecanoate	26	25	*	*
23	Methyl palmitate	126	148	*	5
24	Juvabione	20	22	*	-
25	Methyl heptadecanoate	40	15	*	1
26	Methyl oleate	269	44	*	8
27	Methyl linoleate	787	66	*	20
28	Methyl stearate	723	274	*	4
29	Methyl octadecenoate	125	15	*	*

Table 8.2 cont....

Peak	Compound	Mixed stock (µg/l)	Head box (µg/l)	Uhle box (µg/l)	Pitch (µg/g)
30	Hydrocarbon	-	7	-	-
31	Methyl secodehydroabietate-1	332	7	1	6
32	Methyl secodehydroabietate-2	195	2	1	6
33	Methyl pimarate	2036	53	11	25
34	Methyl sandaracopimarate	336	10	2	4
35	Unknown (resin acid)	-	-	-	1
36	Methyl isopimarate	1170	38	9	14
37	Methyl palustrate	-	11	-	1
38	Methyl 6,8,11,13-abietatetraen-18-oate	161	4	2	-
39	Methyl dehydroabietate	5443	143	48	108
40	Methyl abietate	3642	128	16	57
41	Methyl neoabietate	357	-	4	38
42	Methyl 8,11,13,15-abietatetraen-18-oate	318	-	13	*
43	Hydroxylated methyl abietate	327	30	-	-
44	Methyl 7-oxodehydroabietate	823	-	13	*

* detected on the GC-ITDS but not on the GC-FID; not quantified.
- not detected on the GC-FID or GC-ITDS.

as the Mixed Stock sample consists of pulp coming directly from the pulp mills while the Uhle box sample has undergone several washings.

The major methylated resin acid was methyl dehydroabietate (peak 39) followed closely by methyl abietate (peak 40). The other resin acids present were methyl secodehydroabietates-1 and 2 (peaks 31 and 32), methyl pimarate (peak 33), methyl sandaracopimarate (peak 34), methyl isopimarate (peak 36) and methyl palustrate (peak 37).

Besides the usual methylated pulp mill fatty acids (methyl palmitate, methyl stearate, methyl oleate, etc), dimethyl nonanedioate and dimethyl butanedioate (dimethylsuccinate) were also observed. The mass spectrum of the dimethyl nonanedioate displayed a weak molecular ion at m/e 216 and two consecutive losses of methanol [M^+-(2 x CH_3OH)] to give the fragment ion at m/e 152. Dimethyl butanedioate, on the other hand, did not show a molecular ion; only a base peak of m/e 115 (M^+-OCH_3) was seen.

A trace amount (<0.001 mg/l) of the methyl ether of pentachlorophenol (PCP) was detected in the Headbox sample. PCP is used as a wood preservative. This compound is easily recognized by its mass spectral fragmentation pattern (see Figure 8.4); M^+ ion clusters at m/e 278,280 and 282 together with a strong M^+ - CH_3 ion clusters at m/e 263, 265 and 267.

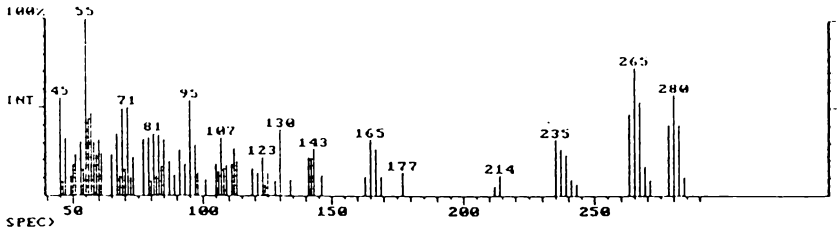
A white water sample collected in July, 1984 was found to include high concentrations of fatty acid methyl and ethyl esters. Since only methyl esters were expected from the methylation with diazomethane, the presence of ethanol in the extract was suggested. It would appear that in the presence of ethanol, fatty acids (but not the more highly hindered carboxyl group of resin acids) are slowly esterified. Presumably this is a consequence of acid-catalysed thermal esterification during liquid-liquid extraction. The origin of the ethanol is unclear; one possibility is that it may have arisen from carbohydrate fermentation. The presence of fatty acid ethyl esters was not observed in later samples.

It is notable that while 4-hydroxy-3-methoxybenzoic acid is only a minor constituent of the black liquor (the dominant aromatic constituents of black liquor are 4-hydroxy-3-methoxybenzaldehyde and 4-hydroxy-3-methoxyacetophenone; see Chapter Six), this acid is present in significant amount in the Headbox and pitch samples. Since the phenolic hydroxyl groups of these compounds react with diazomethane (see Chapter Six) they appear in Table 8.2 as the corresponding 3,4-dimethoxy analogues. Clearly 4-hydroxy-3-methoxybenzoic acid, a comparatively polar substance, has a greater tendency to accumulate in pitch than is the case for 4-hydroxy-3-methoxybenzaldehyde and 4-hydroxy-3-methoxyacetophenone. Likewise amongst the turpentine monoterpenes (see Chapter Nine) only the comparatively polar alcohols, borneol (peak 9), terpen-4-ol (peak 10) and α-terpineol (peak 11) are present in significant quantities (see Table 8.2), but not the ketones (*e.g.* camphor and fenchone) and hydrocarbons (*e.g.* α- and β-pinene).

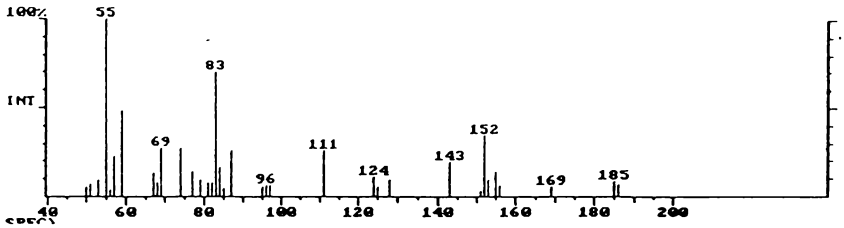
8.4 CONCLUSION

White water contributes about 10% of the total effluent volume (Piper, *pers. comm.*). It is apparent from Table 8.2 that resin acids are the major components of the white water but the levels are such that the white water discharges contribute only a minor part of the resin acids loading in the effluent. Only the resin acids persist in the wash waters through to the Uhle box which is consistent with high affinity between these species and the fibres.

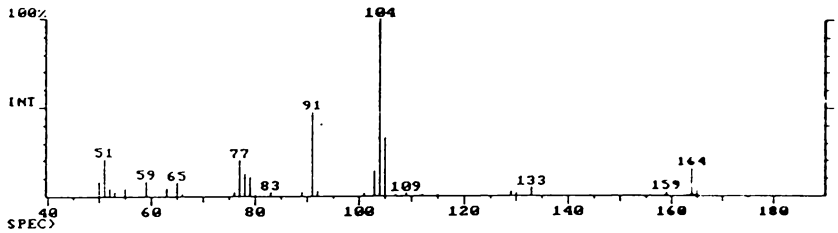
Resin acids and fatty acids are the main constituents of pitch formed at the Tasman mill. Pitch problems are likely to be accentuated when the resin and fatty acid concentrations in the recycled wash waters become sufficiently high.



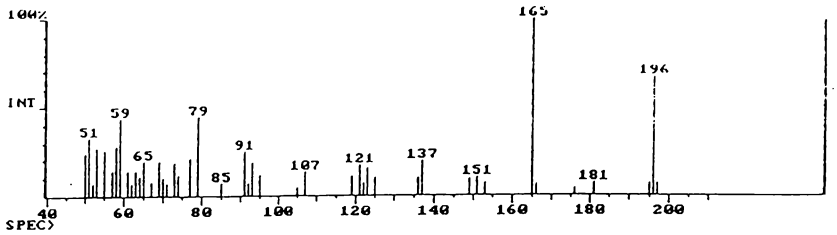
Peak 20 Pentachloromethoxybenzene



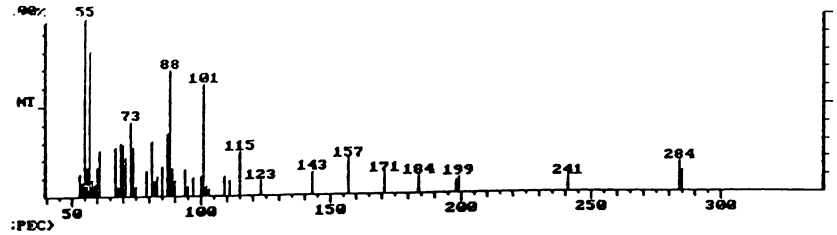
Peak 19 Dimethyl nonanedioate



Peak 14 Methyl phenylpropanoate



Peak 17 Methyl 3,4-dimethoxybenzoate (27)



Ethyl palmitate

Figure 8.4 Mass spectra of some white water compounds

CHAPTER NINE

PLANT SOURCES IV: BY-PRODUCTS

9.1 INTRODUCTION

Oleoresin, which is secreted by some pine species contains about 25% volatile oil (turpentine) and the remainder is chiefly resin acids. From this oleoresin gum, tar and pitch have been isolated and used historically for the protection and tightening of the hulls of wooden ships and for the preservation of ropes. This gave rise to the naval stores industry. Hence tall oil and turpentine are often referred to as naval store products. Now tall oil and turpentine are obtained as by-products from Kraft pulping.

9.2 BY-PRODUCTS

9.2.1 Tall Oil

The production of tall oil in connection with Kraft pulping is the dominant source for naval stores. In New Zealand, about 8,000 tonnes of tall oil are produced by Kraft pulping of radiata pine (*P. radiata*) (Uprichard, 1978). The main constituents of crude tall oil are resin acids (rosin), fatty acids and neutral substances (unsaponifiable material). The average proportions are 35% resin

acids, 55% fatty acids and about 10% unsaponifiable substances. Tall oil has a wide range of applications *e.g.* core oil, flotation agent and production of surface-active agents (Zinkel, 1975; Herrick and Hergert, 1977; Uprichard, 1978; McGovern, 1980). The resin acid fraction is utilized in sizing paper to control water absorptivity, synthetic adhesives, surface coatings, paints and varnishes, and in the synthesis of pharmaceuticals. The fatty acids are used as detergent and soap components, and in alkyd resin production.

The fatty and resin acids present in wood are converted to the sodium salts (soap) in the Kraft digester. This soap is only partially soluble in the weak black liquor and settles out as a thick curd on the surface of the liquor on storage. The soap is then skimmed off and pumped to the tall oil plant. Here, the soap is converted to tall oil by acidifying with sulphuric acid (Cooney and Dixon, 1982). Sufficient acid is added to bring the pH to 3.5. The soap and acid are mixed together and heated to 105^{o}C. After 3-4 hours, the mixture settles into three layers. The top layer is crude tall oil which is skimmed off, washed to remove any residual acid and pumped to storage. The middle layer contains a mixture of lignin, tall oil, and spent liquor. The bottom layer contains sodium sulphate and is pumped back to the soap washing tank.

9.2.2 Turpentine

Turpentine may be obtained as gum turpentine, wood turpentine and sulphate turpentine. The volatile portion of the exudate of 'wounded' living pine trees is steam distilled to give gum turpentine. Wood turpentine is mainly from the stumps of trees

which are chipped and extracted with solvent while the sulphate turpentine is obtained as a by-product of sulphate (Kraft) pulping. Much of today's turpentine is obtained by the last method (Uprichard, 1978). Turpentine is dominantly a mixture of unsaturated bicyclic hydrocarbons with empirical formula $C_{10}H_{16}$, alcohols ($C_{10}H_{18}O$) and ketones ($C_{10}H_{16}O$).

New Zealand *P. radiata* turpentine is notable in that β-pinene is present in substantial quantities. Drew and Pylant, Jr. (1966) investigated the turpentine recovered from the major species of wood used in the United States and Canada and in every case found α-pinene to be the major component. On the other hand, Smith (1964) found β-phellendrene to be the major constituent of turpentine from lodgepole pine (*P. contorta* Douglas).

Turpentine is volatilized and discharged along with the non-condensable gases and steam during regular relief in the Kraft process. In batch cooking, turpentine and steam are relieved from the digester along with air and other non-condensable gases. A centrifugal cleaner (cyclone) is used to remove fibres and cooking liquor which have been carried over in the gas stream. The vapour is cooled in a condenser where the condensate is separated out into a turpentine phase and an aqueous phase. They are separated either by gravity decantation or centrifugation (Figure 9.1).

There is no gas relief during the heating period in the Kamyr (continuous) digester as it is completely filled with liquid. Turpentine is flashed from the spent cooking liquor in the first digester flash tank. This flashed vapour is condensed into the pre-steaming tube,

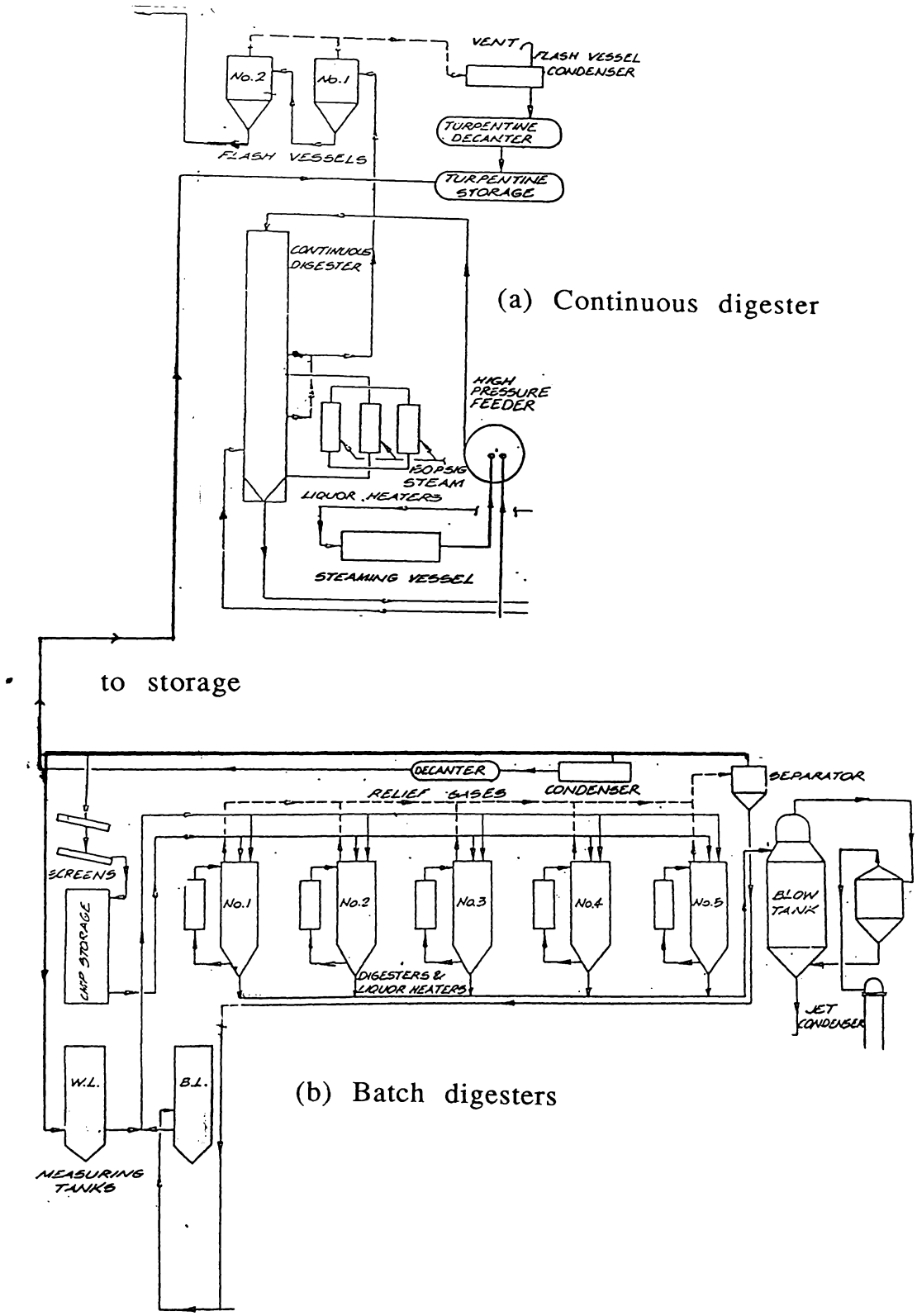


Figure 9.1 Turpentine recovery

(Source: Tasman Pulp and Paper Company Limited)

where the steam is used to preheat the chips fed to the digester. The gases vented from the pre-steaming tube are combined with the vapour from the second flash tank, cooled in a condenser and turpentine is separated from the resulting condensate. Turpentine yields from the continuous digester are about 3 kg/tonne (air-dried) compared with 14 kg/tonne (air-dried) obtained from the batch process (Slabber, *pers. comm.*).

Turpentine was originally used as a solvent for oil- and resin-based paints but is now used as a major component in perfume and α-terpineol manufacture. Flavour chemicals such as menthol, myrcene and camphor can be synthesized from turpentine components (Palmer, 1942). β-Pinene is used as a starting material for the synthesis of terpineol, menthol and hydroxycitronellal.

9.3 EXPERIMENTAL

Samples of tall oil soap, crude tall oil, crude and refined turpentine were collected on 5th December 1984. Since the crude tall oil sample was already acidified, it was extracted directly with chloroform in a 1-litre separating funnel. The soap sample was weighed and acidified using 6 M hydrochloric acid and then extracted as for the crude tall oil. *n*-Octadecane was added to the soap and tall oil samples prior to extraction at the rate of 0.1 mg/g and 10 mg/l respectively. Extracts were concentrated, dried, methylated with diazomethane, and analysed by GC and GC-ITDS as described in Chapter Four.

The refined turpentine sample was diluted in chloroform (with the addition of *n*-nonane as internal standard at the rate of 1 mg/l) and analysed by GC-FID and GC-ITDS, or GC-MSD. The crude turpentine sample was acidified to pH 2 and then extracted with chloroform in a 1-litre separating funnel. Turpentine extraction trials (see Section 9.3.2) were performed by diluting crude turpentine ten-fold with distilled water, and extracting 150 ml of the diluted mixture with: (i) chloroform in a separating funnel, (ii) pentane in a separating funnel, (iii) chloroform for 1 hour in a liquid-liquid extractor and (iv) chloroform for 2 hours in a liquid-liquid extractor. Extractions (i), (iii) and (iv) were carried out at pH 2 while extraction (ii) was carried out at pH 10. Thereafter, the extracts were concentrated on a rotatory evaporator and and analysed by GC-FID as described in Chapter Four.

9.4 RESULTS AND DISCUSSION

9.4.1 Tall Oil

The identification of resin acids and fatty acids has been discussed in previous chapters (Chapters Four and Five). The concentrations of the components found in the tall oil soap and crude tall oil samples are given in Table 9.1. On non-polar GC stationary phases levopimaric acid and palustric acid invariably co-elute. Holmbom (1974, 1977) has indicated that both of these compounds are usually present in tall oil samples. A comparison of the published mass spectral fragmentations of the two methyl esters of these two resin acids led to the conclusion that in the present study the levopimarate/palustrate peak arose dominantly from methyl

TABLE 9.1
Dominant Methylated Tall Oil and Soap Extractives

Peak No.	Compound	soap (mg/kg)	tall oil A (mg/l)	tall oil B (mg/l)
1	Methyl myristate	34	8	6
2	Methyl pentadecanoate	-	6	5
3	Methyl palmitoleate	186	94	-
4	Methyl palmitate	1229	259	310
5	Methyl 14-methylhexadecanoate	300	67	65
6	Methyl heptadecanoate	70	16	-
7	Methyl pinolenate	271	116	121
8	Methyl linolenate	132	30	33
9	Methyl oleate	3154	1667	1069
10	Methyl linoleate	8082	1000	1747
11	Methyl octadecenoate isomer	409	72	104
12	Methyl octadecadienoate isomer	236	62	77
13	Methyl octadecadienoate isomer	-	79	-
14	Methyl stearate	391	194	247
15	Methyl secodehydroabietate -1	1019	129	161
16	Methyl octadecadienoate isomer	252	78	103
17	Methyl octadecadienoate isomer	294	52	17
18	Methyl secodehydroabietate-2	552	136	173
19	Methyl pimarate	3009	389	491
20	Methyl sandaracopimarate	562	80	112
21	Methyl isopimarate	4168	515	663
22	Methyl palustrate	202	624	772
23	Methyl abieta-6,8,11,13-tetraen-18-oate	376	97	-
24	Methyl dehydroabietate	9315	459	666
25	Methyl abietate	401	2249	311
26	Methyl neoabietate	-	490	636

palustrate. Levopimaric acid is one of the unstable resin acids and is easily isomerized to abietic acid.

The major component in the crude tall oil was abietic acid while that in soap was dehydroabietic acid. It is possible that the soap sample had undergone isomerization prior to extraction and GC analysis. The absence of neoabietic acid from the latter sample appears to support this proposal since neoabietic acid is another acid that is easily isomerized.

A GC-FID profile of the tall oil A sample is shown in Figure 9.2. The tall oil was found to be made up of 0.5% monoterpenes, 98% fatty and resin acids and 1.5% of oxygenated resin acids. The soap sample, collected from an external tank overflow pipe, was found to contain a relatively high level of dehydroabietic acid, and reduced levels of abietic acid, neoabietic and palustric acids. Thus appreciable conversion of the latter resin acids to dehydroabietic acid (via dehydrogenation and isomerization) appears to have occurred prior to analysis, possibly while the soap sample was exposed to the atmosphere at the overflow point.

9.4.2 Turpentine

Studies directed towards the characterization and quantification of resin acids and phenolic substances invariably resulted in the detection of significant quantities of monoterpenes, the major source of which is overflows from the turpentine recovery operations. While α-terpineol was usually the dominant constituent of the crude turpentine extracts, the dominant monoterpene in the refined turpentine was β-pinene. The refined turpentine is crude turpentine that has been distilled and so the monoterpene hydrocarbons with lower boiling points predominate over the

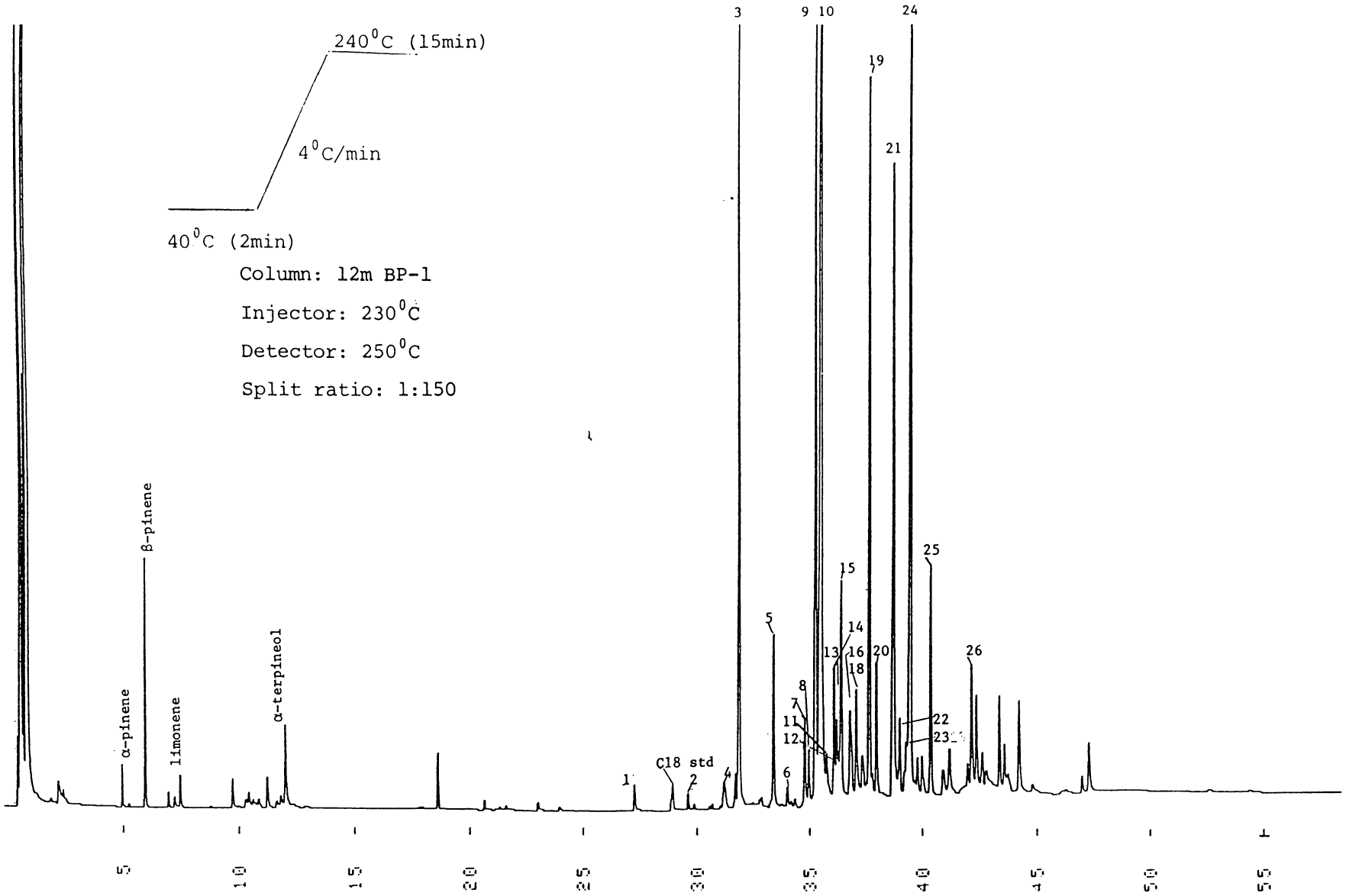


Figure 9.2 GC-FID profile of a derivatized extract of tall oil
For peak identifications see Table 9.1.

monoterpene alcohols. As it is the crude turpentine that is usually lost, α-terpineol is the major monoterpene detected in mill sewers and the treatment system. Hitherto, Uprichard (1978) has reported the major turpentine component of *P. radiata* to be β-pinene followed by α-terpineol.

Figure 9.3 is a GC-FID profile of a crude turpentine sample rich in α-terpineol while Figure 9.4 is a GC-MSD profile of a refined turpentine sample rich in β-pinene. Some of the minor components were resolved only when chromatographed on a 25 m HP-1 (methylsilicone gum) column installed in the GC-MSD (as opposed to the 12 m BP-1 column routinely used in the GC-FID system). Table 9.2 lists the concentrations of the dominant monoterpenes found in some of the turpentine samples investigated during the present study.

Compounds were identified by comparing the retention times and Kovats indices of standards and by comparisons of reported mass spectral fragmentation patterns (Von Sydow, 1963, 1964, 1965; Ryhage and Von Sydow, 1963; Vernin, 1969; Swigar and Silverstein, 1981). Standards of the following compounds were available: α-pinene, β-pinene, camphene, limonene, *p*-cymene, camphor, borneol, menthol and terpineol isomers. In addition to the compounds mentioned above, a number of other monoterpenes were detected. For example, peak 4 was found to have strong ions at m/e 91, 119 and 134, suggesting it to be a non-aromatic analogue of *p*-cymene (58), possibly possessing structure (51) or (52).

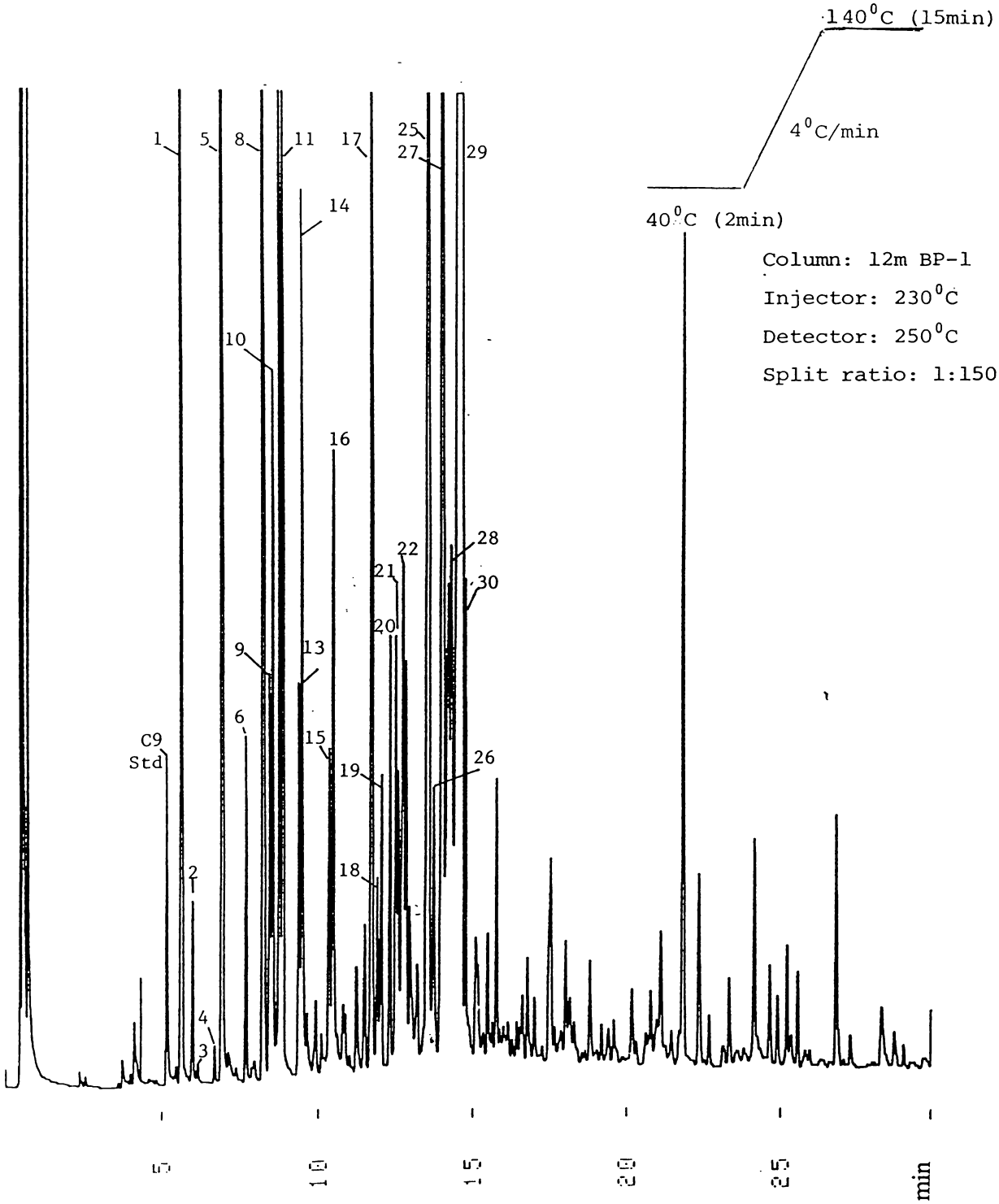


Figure 9.3 GC-FID profile of crude turpentine. For peak identifications see Table 9.2.

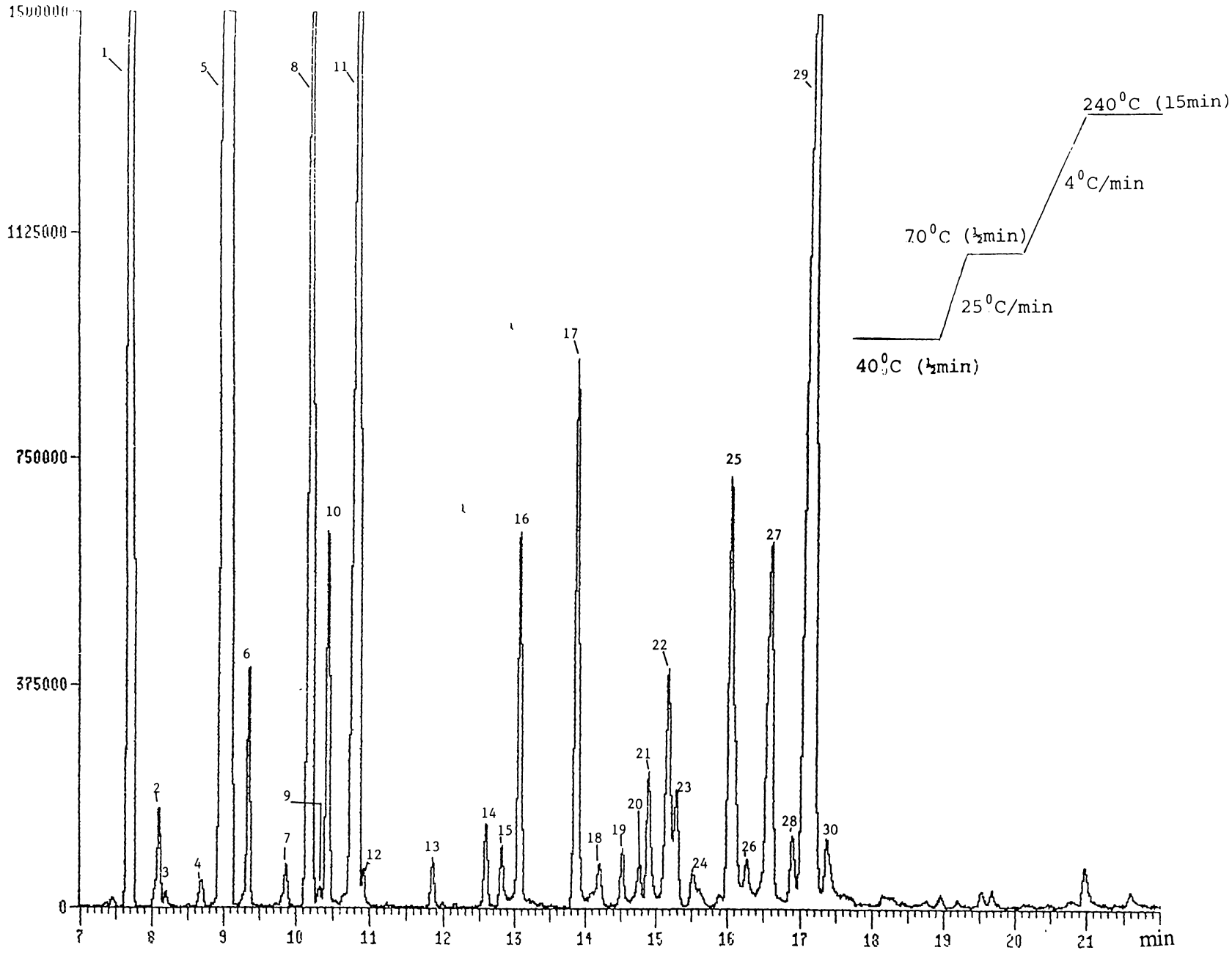


Figure 9.4 GC-MSD profile of refined turpentine. For peak identifications see Table 9.2.

Table 9.2
Monoterpenes present in some turpentine samples (g/l)

Peak	Compound	A	B	C
1	α–Pinene	35	68	51
2	Camphene	2	2	2
3	*p*- Mentha-1,3,8-triene	0.5	*	*
4	*t*- Butylbenzene	1	*	*
5	β–Pinene	237	73	57
6	Myrcene	3	4	4
7	3-Carene and α–Phellandrene	1	-	-
8	α–Terpinene	12	21	19
9	Ocimene	0.7	6	6
10	*p*- Cymene	15	10	8
11	Limonene	42	65	52
12	Unknown (138, 123, 95)	*	*	*
13	γ–Terpinene	5	21	19
14	Fenchone	4	12	11
15	α,*p*- Dimethylstyrene	1	6	6
16	Terpinolene	33	11	12
17	Fenchol	36	28	28
18	Limonene-1,2-epoxide-1	5	3	4
19	Limonene-1,2-epoxide-2	6	4	5
20	Camphor	9	5	6
21	*ttrans*- Pinocarveol	14	8	12
22	Unknown (156, 141, 59)	26	11	12
23	Unknown (154, 136, 71)	19	6	6
24	Pinocamphone	8	2	2
25	Borneol	29	62	64
26	Unknown (156, 95, 96)	6	6	6
27	Terpen-4-ol	37	59	58
28	Myrtenal	11	13	15
29	α-Terpineol	87	181	229
30	Myrtenol	2	8	7

A - refined turpentine

B and C - crude turpentine

Peak 3 also exhibited strong m/e 91 and 119 ions, but lacked a molecular ion. Library search suggested peak 7 to be either 3-carene (56) or α-phellandrene (55), while peaks 12 and 22 were identified as 1(1-methylethylene)-4-methylcyclohexane (60) and 1(1-hydroxy-1-methyl)-4-methylcyclohexane (69) respectively [*i.e.* the dihydro analogues of limonene (59) and α-terpineol (74) respectively]. Although not positively identified, the mass spectral fragmentation patterns and retention times of peaks 18 and 19 suggested them to be limonene-1,2-epoxides-1 (66) and 2 (Swigar and Silverstein, 1981). Other minor components detected were *trans*-pinocarveol (68) (peak 21), pinocamphone (70) (peak 24), myrtenal (73) (peak 28) and myrtenol (75) (peak 30), all of which are oxygenated analogues of α- or β-pinene. Some of the turpentine samples were also found to contain low levels of compounds believed to be carvone (76) and piperitone (77). These compounds eluted after α-terpineol. The mass spectrum of the monoterpene hydrocarbons, alcohols and ketones are shown in Appendix C.

In addition to the expected monoterpenes, a series of peaks were found with a possible molecular ion at m/e 204 and daughter ions at m/e 161, 149, 132, 119, and 91. These appear to be sesquiterpenes of molecular formula $C_{15}H_{24}$. No attempt was made to identify individual sesquiterpenes.

The extraction and derivatization procedures used when recovering resin acids, fatty acids, aromatic compounds and monoterpenes from aqueous samples while appropriate for comparatively non-volatile fatty acids and resin acids, have major shortcomings when applied to monoterpenes, the chief of which is

loss of volatile substances (especially monoterpene hydrocarbons) during the evaporation and concentration stages. Table 9.3 compares the recovery of monoterpenes from an aqueous turpentine sample (prepared by diluting a neat crude turpentine sample), using three extraction techniques. In the case of the liquid-liquid extractions, small volume extractors (150 ml) with a high solvent turnover rate, and dual condensers were used in an effort to reduce losses of monoterpenes by evaporation during the extraction period. However these precautions do not preclude the losses of volatile compounds occurring after extraction, *i.e.* during concentration of the extracts by rotatory evaporation.

Table 9.3.

Recovery of major turpentine components from a diluted crude turpentine sample. Concentrations are expressed as mg/l of undiluted turpentine.

	$CHCl_3$ (funnel)	Pentane (funnel)	$CHCl_3$/liquid-liquid (1 hour)	(2 hour)
α-Pinene	53	48	19	90
Camphene	3	2	1	4
β-Pinene	61	82	28	106
Limonene	55	63	25	82
Fenchone	12	9	5	7
Fenchol	34	26	24	27
Camphor	8	5	4	5
Borneol	79	51	50	53
Terpen-4-ol	73	68	63	78
α-Terpineol	275	248	220	240

It is apparent (see Table 9.3) that while in each of the extraction procedures the recoveries of monoterpene alcohols (*e.g.*

α-terpineol, terpen-4-ol, borneol and fenchol) and ketones (*e.g.* camphor and fenchone) were comparable, this was not the case for monoterpene hydrocarbons (*e.g.* α-pinene, β-pinene and limonene). Attempts were made to limit the hydrocarbon loss by maintaining the water bath of the rotary evaporator at room temperature and concentrating the extracts to similar volumes. Support for the view that hydrocarbon losses occur during evaporation was afforded by the continued evaporation of extracts; this was found to further reduce hydrocarbon levels, and ultimately also monoterpene alcohol and ketone levels. However, it should be noted that longer extraction times yielded a higher recovery of the hydrocarbons compared with the small increase for the alcohols and the ketones.

9.5 CONCLUSION

The main constituents of tall oil are fatty acids and resin acids. In most instances tall oil soap enters the treatment system through accidental spills. While the levels involved are often low, the high concentrations of acids in tall oil mean that spillages result in increased levels of resin acids and fatty acids being discharged to the treatment system.

Tall oil soap has a higher proportion of unsaturated fatty acids than black liquor. These are known to be more toxic than the corresponding saturated analogues. Unlike black liquor, tall oil soap has negligible levels of aromatic and sulphonated compounds, hence elevated levels of resin and fatty acids in the absence of aromatic and sulphonated compounds distinguishes black liquor spills from tall oil soap spills.

Both refined and crude turpentines have been characterized in this study. It was found that while β-pinene is the major turpentine component in the refined sample, α-terpineol is the dominant component in the crude sample. Hence turpentine that usually escapes to the treatment system is crude turpentine. Thus, by monitoring the α-terpineol concentration in the treatment system, an assessment of the turpentine loss may be made.

CHAPTER TEN

TREATMENT SYSTEM

10.1 INTRODUCTION

With increasing restrictions on the quality of water being discharged into public waterways, it has become necessary for pulp and paper mills to utilize some form of treatment for the effluents. In many countries, regulations exist limiting the suspended solids content, biological oxygen demand (BOD), toxicity and in some instances, the colour of the pulp effluents. For example, in Canada toxicity is a major concern and research has led to the identification of the nature and sources of toxic constituents in bleached Kraft mill effluents, knowledge of the biodegradability of the various toxicants and the detoxification capability of biological waste treatment systems (Rogers *et al*, 1975; Brownlee *et al*, 1977; Voss, 1983, 1984, 1987).

Biological detoxification of pulp mill effluent is accomplished by the attack of micro-organisms on the toxic substances. Analysis of the products of microbial degradation of resin acids, in particular dehydroabietic acid, has been the subject of several laboratory studies (Biellmann *et al*, 1973; Ekman and Sjöholm, 1979; Kutney *et al*, 1981, 1982a, 1982b, 1985; Kutney and Dimitriadis, 1982). A recent study by Remberger *et al* (1986) examined the transformations of

chloroguaiacols, chlorocatechols and chloroveratroles in sediments. In another study, Salkinoja-Salonen *et al* (1981) found that tetrachlorocatechol was the major chlorophenol in freshwater sediment near pulp mills. It can be stated that adsorption is generally greater when sediment particles are smaller, *i.e.* have a larger surface area, as in the case of pulp mill fibres.

10.1.1 Aerated Stabilization Basins

Effluent may be treated aerobically or anaerobically (absence of oxygen). Aerated stabilization basins (ASB) are the predominant form of biological treatment used by the pulp and paper industries for wastewaters. The effectiveness of ASB has been well researched in terms of the conventional pollution parameters such as BOD_5 and the fate of the individual organic compounds (Servizi and Gordon, 1973; Hrutfiord *et al*, 1975; Keith, 1976; Voss, 1983, 1984, 1987). Leach and Meier (1978) observed the ease of treatment of extractable organic compounds in aerated systems to follow the order: unsaturated acids > resin acids > juvabione > chlorinated resin acids > chlorinated guaiacols. Naturally-occurring wood extractives were more biodegradable than the chlorinated constituents in wastewaters.

Most of the aerated systems were designed for 3-10 days retention. For effective performance, the pH of the influent should be controlled near neutral; nitrogen (N) and phosphorus (P) must be added to give a BOD_5 : N: P ratio of about 100: 3: 0.5 and dissolved oxygen levels should be kept above 0.5 mg/l (Leach *et al*, 1976; Mueller *et al*, 1977).

10.1.2 Activated Sludge Treatment

Activated sludge digestion is another form of biological treatment used especially where the availability of land is limited (Alleman *et al*, 1982). In this system the biomass is settled and recycled to the incoming influent. The active concentration of biomass in the aeration tank is thus increased and biodegradation rates are improved proportionately. The hydraulic retention time in the aeration tank is typically 6-8 hours whereas extended activated sludge systems operate at 16-24 hours retention times. Studies carried out by Mueller *et al* (1977) found that such systems detoxified effluent only 50-70% of the time and that a 90% detoxification success rate could be achieved by protecting against toxicity shocks. Leuenberger *et al* (1985) reported that chlorinated phenols were poorly eliminated in the activated sludge treatment plant of a Swiss sulphite pulp mill.

Richardson and Bloom (1983) followed the start-up of an activated sludge treatment plant at the Australian Newsprint Mill Limited, Albury (NSW) mill and investigated the chemical composition of the treated thermomechanical pulp effluent. While the concentration of resin acids at the time of start-up was significant (>0.5 mg/l), this was reduced to less than 0.05 mg/l under stable operating conditions.

10.1.3 Anaerobic Treatment

Anaerobic decomposition is a spontaneous process occurring in nature when suitable conditions of temperature and absence of oxygen prevail. The anaerobic process is dependent upon the density

of the biological population, pH and temperature for optimization of the rate of decomposition. A recent review by Dorica (1985) states that anaerobic treatment reduces aeration costs, reduces the generation of methane, and lowers the quantity of sludge.

10.1.4 Tasman's Treatment System

The mill has two main sewers to the wastewater treatment system: the general sewer and the acid sewer. The general sewer has a total volume of 190 Ml/day and the major contributors are the alkaline extraction stages of the bleach plants and chemical preparation (80 Ml/day, 42%), Kraft pulping (30 Ml/day, 16%), groundwood pulping and paper machines (40 Ml/day, 21%) and ancillary operations like debarking, log-washing, etc make up the balance. Discharges from the acid stages of the bleach plants (10 Ml/day) are directed into a separate sewer as they do not contain much (if any) solids. The general sewer is subjected to primary clarification whereas the acid sewer is piped directly to the treatment ponds.

The effluent treatment system operated by Tasman Pulp and Paper Company Limited at Kawerau has been described in Section 3.6. The plan of the treatment system is shown in Figure 3.2 (see page 42). The total volume of the influent to the system is 200 Ml/day while the outflow is approximately 210-230 Ml/day. This is due to a contribution from a freshwater stream into Pond 3. This study involves the identification of the extractable organic compounds present in the primary sludge and the treatment ponds.

The objective of the present study was to quantify selected extractable organic compounds present in Tasman's treatment system and to follow the degradation of these compounds in both the aeration ponds and the anaerobic primary sludge lagoon. During the course of the study, there were opportunities to monitor the effects of adding an additional aerated pond to the treatment system and to study assimilative capacity of the system during the start-up after a prolonged period of mill closure.

10.2 EXPERIMENTAL

Grab samples were taken from the primary sludge lagoon and the treatment ponds on various occasions over a two-year period. The treatment ponds were monitored in greater detail on three occasions: 31st October 1985 to 8th November 1985; 6th October 1986 to 21st October 1986; and 9th February 1987 to 25th February 1987. The first of the extended studies followed the start-up of the mill after it had been closed for three weeks due to industrial action. The second of the extended studies followed the start-up of the mill after an eleven-week closure. This start-up also corresponded to the introduction of an additional aeration pond (Pond 3), the effect of which was to extend the retention time of the treatment ponds from 4 days to 8 days. The last study occurred when the mill was running at almost full capacity, with two of its three paper machines in operation.

On the first occasion, surface water samples were collected by mill staff from Pond 1 inlet and Pond 4 outlet and sent to the University. The samples were acidified to pH 2 with 2 M hydrochloric

acid. Two internal standards, *n*-octadecane and *n*-dodecane were added to the effluent at the rate of 1,000 µg/l and 100 µg/l respectively. These were then extracted with redistilled chloroform by continuous liquid-liquid extraction for 12 hours. The chloroform extracts were concentrated, dried and methylated with diazomethane. The methylated extracts were analysed on the GC-FID.

On the next two occasions, water samples were taken from Pond 1 inlet (Pin), Pond 1 outlet (P1-2), Pond 2 outlet (P2-3), Pond 3 outlet (P3-4) and Pond 4 outlet (Pout). During the second sampling programme, samples were collected in plastic containers by mill staff and sent to the University of Waikato. These were extracted by continuous liquid-liquid extraction. This sampling programme was carried out for three weeks from the time the mill re-opened. On the last occasion, samples were collected and extracted at the mill laboratory using the separating funnel extraction method.

n-Octadecane was added routinely as internal standard at the rate of 1,000 µg/l (or occasionally 100 µg/l) during both sampling dates. The extracts were prepared as previously reported (Wilkins and Panadam, 1987). These were analysed by GC-FID and GC-ITDS (and later by GC-MSD). Due to a malfunction of the GC-ITDS system, only one sample from each sampling point was characterized exhaustively by GC-ITDS. However extensive quantitative GC-FID data was obtained.

A sediment sample from the primary sludge lagoon was collected using a metal scoop. Sediment samples were also taken from Pond 1, Pond 2 and Pond 4 on the day the mill re-started (3rd

October 1986). These were filtered by suction and dried at *ca* 130°C. While the sludge and the Pond 1 sediment samples comprised mainly of pulp fibres, the Pond 2 and 4 sediment samples were grainy in nature. The sediment samples were weighed (~1 g) and extracted for 12 hours with redistilled chloroform using an all-glass Soxhlet apparatus. A standard solution (1,000 µg/ml) of *n*-octadecane in chloroform was introduced into the extraction thimble at the rate of 100 µg/g. The extracts were concentrated, dried and methylated as previously described in Chapter Four and by Wilkins and Panadam (1987).

The compounds selected for quantification were monoterpenes, fatty acids and resin acids. Chlorinated aromatic compounds were excluded principally because of identification difficulties at the time of the study (MSD and ITDS techniques were not routinely available). GC-FID data indicated that while significant levels of aromatic compounds entered the system, only low levels survived to the outlet. River samples were typically found to contain less then 0.5 µg/l of chlorinated aromatic compounds (see Chapter Five).

The detection limit of this investigation is typically 1 ppb. However the use of the GC-ITDS's selected ion monitoring techniques when available, enabled the detection of sub-microgram/litre levels of compounds of concern. Some samples were re-examined on the Hewlett-Packard 5980/5970 GC-MSD system while this work was being written up.

10.3 RESULTS

10.3.1 Treatment System - October-November 1985

The Pond 1 inlet sample comprised chiefly of the following classes of compounds: monoterpenes (α-pinene, β-pinene, *p*-cymene, fenchol, camphor, α-terpineol), 2-cyclopentenone derivatives, a vast array of aromatic compounds (guaiacol derivatives, benzoic acid, 4-hydroxy-3-methoxybenzaldehyde, cinnamic acid, 4-hydroxy-3-methoxyacetophenone), sesquiterpenes, fatty acids (C_6-C_{24}), resin acids (secodehydroabietic-1 and -2 acids, pimaric acid, sandaracopimaric acid, isopimaric acid, dehydroabietic acid, abietic acid), and chlorinated analogues (tetrachloroethane, trichlorophenol, dichloroguaiacol, chloro-4-hydroxy-3-methoxybenzaldehyde, trichloro-3,4-dimethoxybenzene, 12- and 14-chlorodehydroabietic acids). These compounds are typical of those that have been reported in overseas studies (Voss, 1987; Fox, 1977; Brownlee and Strachan, 1977).

Pond 4 outlet comprised of fatty acids, resin acids, chlorinated compounds and occasionally monoterpenes such as borneol, terpen-4-ol and α-terpineol. While the effluent treatment was efficient in removing the monoterpene hydrocarbons, the monoterpene ketones (*e.g.* camphor and fenchone) and alcohols (*e.g.* α-terpineol and terpen-4-ol) were more persistent (see Table 10.1). The monoterpenes were not detected in the outlet extracts during the first five days of sampling as the mill had just resumed operations and there was a time lag. Keith (1976) had observed that the

Table 10.1

Concentration of selected compounds in the treatment ponds when the mill re-opened after a 3-week closure. (µg/l)

COMPOUND	Site	31-Oct	1-Nov	2-Nov	3-Nov	4-Nov	5-Nov	6-Nov	7-Nov	8-Nov
Fenchol	Pin	-	5	115	185	275	134	a	a	a
	Pout	1	-	-	a	-	95	55	33	29
Camphor	Pin	-	3	32	176	195	102	a	a	a
	Pout	-	-	a	-	-	-	54	19	15
Borneol	Pin	-	4	316	277	330	140	a	a	a
	Pout	-	-	a	-	-	46	73	49	24
Terpen-4-ol	Pin	-	-	215	217	252	109	a	a	a
	Pout	-	-	a	-	-	46	34	30	15
a-Terpineol	Pin	-	-	1039	1562	2000	889	a	a	a
	Pout	-	-	a	-	-	410	125	87	69
Methyl Palmitate	Pin	488	80	117	207	444	86	a	a	a
	Pout	569	499	a	191	548	686	63	121	41
Fichtelite	Pin	-	-	-	-	-	-	a	a	a
	Pout	-	-	a	-	-	18	-	-	-
Dehydroabietin	Pin	-	-	-	-	-	-	a	a	a
	Pout	69	85	a	98	117	97	29	10	4
1,2,3,4-Tetrahydroretene	Pin	-	-	-	-	-	-	a	a	a
	Pout	70	-	a	106	349	305	78	27	24

Table 10.1 cont....

COMPOUND	Site	31-Oct	1-Nov	2-Nov	3-Nov	4-Nov	5-Nov	6-Nov	7-Nov	8-Nov
Methyl linoleate	Pin	153	-	54	-	190	30	a	a	a
	Pout	-	-	a	-	-	144	46	-	-
Methyl oleate	Pin	530	35	219	134	448	101	a	a	a
	Pout	64	-	a	-	233	218	55	24	20
Methyl stearate	Pin	332	160	231	214	471	245	a	a	a
	Pout	299	200	a	134	397	542	138	128	87
Methyl secodehydroabietate-1	Pin	217	29	186	283	589	86	a	a	a
	Pout	124	119	a	85	466	676	145	58	53
Methyl secodehydroabietate-2	Pin	124	22	127	170	405	62	a	a	a
	Pout	66	60	a	50	307	396	131	56	58
Retene	Pin	-	15	-	-	-	-	a	a	a
	Pout	-	-	a	110	261	189	-	9	5
Methyl Pimarate	Pin	321	134	678	1248	2493	404	a	a	a
	Pout	330	325	a	179	792	1033	282	108	105
Methyl Sandaracopimarate	Pin	55	23	71	178	367	54	a	a	a
	Pout	1492	151	a	824	276	233	58	22	26
Methyl pimaran-18-oate	Pin	-	-	-	-	1959	-	a	a	a
	Pout	250	252	a	97	305	279	68	25	28

Table 10.1 cont....

COMPOUND	Site	31-Oct	1-Nov	2-Nov	3-Nov	4-Nov	5-Nov	6-Nov	7-Nov	8-Nov
Methyl isopimarate	Pin	196	107	343	1290	-	518	a	a	a
	Pout	399	403	a	184	779	874	216	93	84
Methyl abietan-18-oate	Pin	-	-	-	-	-	-	a	a	a
	Pout	1851	1911	a	749	2044	1789	357	139	120
Methyl dehydroabietate	Pin	853	490	2709	3844	7841	1271	a	a	a
	Pout	1146	1117	a	636	2403	2246	545	235	241
Methyl abietate	Pin	756	235	148	2920	3924	570	a	a	a
	Pout	94	93	a	-	895	872	341	162	93
Methyl neoabietate	Pin	87	-	39	372	792	332	a	a	a
	Pout	-	-	a	-	-	-	-	61	-

N.B: The first row denotes concentration at Pond inlet while the second row is for the outlet concentrations. Pin - Pond inlet sample; Pout - Pond outlet sample; (a) No sample was obtained.(-) not detected

concentrations of ketones actually increased on treatment due to oxidation of alcohols.

Table 10.1 gives the concentrations of the more persistent compounds that exit from the treatment system and compares the levels of these compounds in the inlet point of the treatment system. The concentrations of fatty acids were found to be highly variable. The inlet concentrations of resin acids were significantly variable, however the outlet concentrations were more uniform, presumedly because of the dampening effect of the treatment ponds.

10.3.2 Extended Treatment System - October 1986

The concentrations of selected compounds are summarized in Table 10.2. The fatty acid concentrations remained fairly constant through the treatment ponds while a substantial decrease was observed for the resin acids in the pond outlet samples. The concentrations of the total resin acids in the final discharge (Pond 4 outlet) during the re-start were very low (~300 μg/l) compared with that when the mill was operating at full capacity (Table 10.1).

It was noted that the concentrations of α-pinene was higher than for β-pinene. This is in contrast to the usual dominance of β-pinene in *P. radiata* extracts. The elevated α-pinene concentration may be due to the wood pile being kept in storage during the period of mill closure. β-Pinene appears to be selectively reacted and is readily isomerized to the α-form (Palmer, 1942). It has also been observed by Palmer (1942) that very little trace of β-pinene remained in old pine stumps; α-pinene was the major monoterpene.

TABLE 10.2

Selected organic compounds (µg/l) present in the treatment ponds following the start-up of the mill on 6th October to 21st October 1986.

COMPOUND	Site	6th	13th	21st
α–Pinene	Pin	522	-	34
	P1-2	a	-	182
	P2-3	-	-	14
	P3-4	69	a	84
	Pout	a	40	-
β-Pinene	Pin	28	-	-
	P1-2	8	a	28
	P2-3	-	-	-
	P3-4	3	a	3
	Pout	a	28	-
α–Terpineol	Pin	823	-	-
	P1-2	a	-	-
	P2-3	-	-	-
	P3-4	-	a	-
	Pout	a	-	-
Methyl palmitate	Pin	72	122	141
	P1-2	a	230	245
	P2-3	107	53	128
	P3-4	72	a	87
	Pout	a	87	273
Methyl linoleate	Pin	13	a	-
	P1-2	a	-	-
	P2-3	-	-	15
	P3-4	7	a	8
	Pout	a	-	8
Methyl oleate	Pin	70	44	96
	P1-2	a	80	101
	P2-3	67	16	58
	P3-4	48	a	75
	Pout	a	43	121

Table 10.2 cont....

COMPOUND	Site	6th	13th	21st
Methyl stearate	Pin	43	34	62
	P1-2	a	75	16
	P2-3	69	76	65
	P3-4	36	a	25
	Pout	a	31	65
Dehydroabietin	Pin	-	-	-
	P1-2	a	95	83
	P2-3	79	-	181
	P3-4	48	a	40
	Pout	a	-	4
1,2,3,4-Tetrahydroretene	Pin	-	-	-
	P1-2	a	-	12
	P2-3	9	-	3
	P3-4	-	a	2
	Pout	a	-	-
Retene	Pin	-	-	-
	P1-2	a	-	13
	P2-3	84	a	-
	P3-4	4	a	2
	Pout	a	-	-
Methyl pimarate	Pin	251	8	431
	P1-2	a	370	325
	P2-3	189	2	171
	P3-4	218	a	74
	Pout	a	38	45
Methyl sandaracopimarate and methyl 8(14)-pimaren-18-oate	Pin	77	-	81
	P1-2	a	61	69
	P2-3	75	-	54
	P3-4	63	a	15
	Pout	a	6	2
Methyl pimaran-18-oate	Pin	-	-	-
	P1-2	a	-	13
	P2-3	124	-	22
	P3-4	27	a	7
	Pout	a	7	7

Table 10.2....

COMPOUND	Site	6th	13th	21st
Methyl isopimarate and	Pin	204	2	316
Methyl 13-abieten-18-oate	P1-2	a	420	238
	P2-3	79	1	147
	P3-4	191	a	56
	Pout	a	32	35
Methyl abietan-18-oate	Pin	-	-	-
	P1-2	a	10	274
	P2-3	241	9	28
	P3-4	225	a	87
	Pout	a	68	93
Methyl dehydroabietate	Pin	829	53	1070
	P1-2	a	1380	938
	P2-3	717	22	195
	P3-4	168	a	90
	Pout	a	64	64
Methyl abietate	Pin	528	-	795
	P1-2	a	474	400
	P2-3	54	-	120
	P3-4	53	a	64
	Pout	a	30	29
BOD_5 (mg/l)	Pin	-	-	-
	P1-2	116	146	208
	P2-3	95	87	100
	P3-4	23	37	49
	Pout	8	21	17

Pin Pond 1 inlet; P1-2 Pond 1 outlet; P2-3 Pond 2 outlet;
P3-4 Pond 3 outlet; Pout Pond 4 outlet; a sample not available;
- not detected

10.3.3 Extended System At Steady State - February 1987

An extensive range of GC-FID data was acquired over a three-week sampling programme. The concentrations of a selected number of compounds present in the system are listed in Table 10.3.

Comparison of the total extractable organic substances in the Pond 1 outlet (P1-2) and Pond 4 outlet (Pout) during the start-up and steady state was made. This was plotted against time and the result is presented in Figure 10.1. (a) and (b). Even though the inlet concentration on the second week of start-up was very low, it could be seen that the treatment system was capable of assimilation. During steady state (February 1987), it was observed that while the inlet concentrations were highly variable, the outlet concentrations were stable. The assimilative capacity of the treatment ponds was found to be greater during steady state.

A set of samples were identified on the GC-ITDS and GC-MSD. The concentrations for this set (9th February 1987) are given in Table 10.4. The GC-FID profiles of the Pond 1 outlet, Pond 2 outlet, Pond 3 outlet and Pond 4 outlet are presented in Figures 10.2, 10.3, 10.4 and 10.5. Given the sensitivity of the GC-FID with regard to sulphonated, chlorinated and unmethylated aromatic compounds, these were not quantified even though their presence was detected on the GC-ITDS or GC-MSD. Many of the compounds were present in modest amount and Table 10.4 includes only those above 5 μg/l.

Table 10.3
Concentrations of selected compounds in the treatment system at steady state (February 1987) µg/l

COMPOUND	Site	9th	11th	16th	18th	23rd	24th	25th
α-Pinene	P1-2	71	1102	-	-	974	-	-
	P2-3	53	78	a	-	11	50	-
	P3-4	106	158	4	-	12	53	a
	Pout	-	-	26	-	-	-	a
	S	92	-	1817	603	a	a	a
β-Pinene	P1-2	87	82	-	-	192	-	-
	P2-3	12	6	a	-	5	16	-
	P3-4	-	-	5	-	15	-	a
	Pout	-	-	12	-	-	-	a
	S	63	-	137	85	a	a	a
Camphor	P1-2	101	244	117	359	105	134	-
	P2-3	225	-	a	-	66	91	128
	P3-4	-	93	-	-	30	-	-
	Pout	-	-	-	-	-	-	a
	S	237	323	237	798	a	a	420
Borneol	P1-2	681	347	523	254	594	612	-
	P2-3	551	-	a	-	261	391	319
	P3-4	-	30	-	-	44	110	-
	Pout	-	-	-	-	-	-	a
	S	279	94	174	313	a	a	139
Terpen-4-ol	P1-2	292	129	184	-	242	203	-
	P2-3	225	-	a	-	113	167	68
	P3-4	-	35	-	-	18	-	-
	Pout	-	-	-	-	-	-	a
	S	160	59	107	269	a	a	192
α-Terpineol	P1-2	3143	1158	1711	890	2409	1791	-
	P2-3	1859	-	a	-	1113	1657	160
	P3-4	-	196	-	-	41	120	-
	Pout	-	-	-	-	-	-	a
	S	920	107	443	903	a	a	162
Methyl palmitate	P1-2	113	69	193	23	554	242	140
	P2-3	114	36	a	120	401	118	67

Table 10.3 cont....

COMPOUND	Site	9th	11th	16th	18th	23rd	24th	25th
Methyl palmitate	P3-4	36	40	65	-	144	65	45
	Pout	22	19	51	23	-	56	a
	S	1656	1256	1900	3108	a	a	517
Methyl linoleate	P1-2	17	-	152	21	462	-	29
	P2-3	13	5	a	21	90	33	30
	P3-4	-	45	13	-	39	-	-
	Pout	7	-	-	-	-	-	a
	S	568	50	329	682	a	a	-
Methyl oleate	P1-2	52	24	404	180	1145	94	104
	P2-3	67	18	a	93	400	101	65
	P3-4	-	55	58	-	125	42	26
	Pout	24	15	-	35	33	32	a
	S	1248	151	735	1876	a	a	60
Methyl stearate	P1-2	64	64	114	50	162	162	57
	P2-3	61	33	a	79	156	124	37
	P3-4	28	34	34	-	94	-	12
	Pout	25	26	67	31	-	16	a
	S	189	120	221	294	a	a	49
Methyl secodehydroabietate-1	P1-2	62	75	103	86	166	104	49
	P2-3	93	21	a	100	132	88	52
	P3-4	46	70	46	27	118	86	21
	Pout	31	24	22	36	-	14	a
	S	175	61	77	219	a	a	47
Methyl secodehydroabietate-2	P1-2	22	42	52	18	88	51	28
	P2-3	52	12	a	115	77	50	23
	P3-4	-	31	22	-	59	28	13
	Pout	19	7	-	30	-	11	a
	S	126	37	47	189	a	a	24
Retene	P1-2	-	-	-	-	-	-	-
	P2-3	57	7	a	43	-	33	10
	P3-4	-	25	11	-	36	-	6
	Pout	9	-	-	-	-	-	a
	S	89	82	-	154	a	a	39

Table 10.3 cont....

COMPOUND	Site	9th	11th	16th	18th	23rd	24th	25th
1,2,3,4-Tetrahydroretene	P1-2	-	-	-	-	-	-	-
	P2-3	86	17	a	75	95	80	32
	P3-4	72	48	62	-	144	86	7
	Pout	8	-	-	-	-	-	a
	S	106	80	47	137	a	a	63
Dehydroabietin	P1-2	-	-	-	-	-	-	-
	P2-3	-	-	a	-	-	-	15
	P3-4	-	-	16	-	29	-	-
	Pout	8	-	-	-	-	-	a
	S	15	-	10	-	a	a	54
Fichtelite	P1-2	-	-	-	-	-	-	-
	P2-3	21	7	a	-	19	20	6
	P3-4	-	8	9	-	13	-	4
	Pout	-	-		-	-	-	a
	S	11	24	15	-	a	a	-
Methyl pimarate	P1-2	610	457	488	416	725	574	285
	P2-3	525	112	a	585	627	334	196
	P3-4	203	339	227	146	527	368	134
	Pout	161	136	134	156	a	79	a
	S	886	392	377	795	a	a	258
Methyl sandaracopimarate	P1-2	142	98	110	74	176	119	41
	P2-3	59	9	a	33	166	40	49
	P3-4	-	80	27	-	139	27	12
	Pout	19	34	33	26	-	a	a
	S	215	68	84	153	a	a	37
Methyl pimaran-18-oate	P1-2	-	-	-	-	-	-	-
	P2-3	78	19	a	74	88	61	19
	P3-4	35	39	40	18	100	70	16
	Pout	50	33	47	37	-	12	a
	S	52	54	32	126	a	a	31
Methyl isopimarate	P1-2	649	684	522	557	647	641	373
	P2-3	478	123	a	586	841	367	186
	P3-4	235	326	236	148	535	378	116
	Pout	184	147	147	157	a	77	a
	S	1782	613	644	2306	a	a	510

Table 10.3 cont....

COMPOUND	Site	9th	11th	16th	18th	23rd	24th	25th
Methyl abietan-18-oate	P1-2	-	-	-	-	-	-	-
	P2-3	621	157	a	566	576	393	184
	P3-4	323	314	316	162	639	439	184
	Pout	372	275	236	157	a	126	a
	S	366	517	302	649	a	a	241
Methyl dehydroabietate	P1-2	2058	1642	1186	1367	1682	1797	830
	P2-3	481	159	a	753	1343	376	254
	P3-4	316	447	360	186	726	455	151
	Pout	348	272	223	160	a	116	a
	S	4614	3080	2312	4802	a	a	2323
Methyl abietate	P1-2	1493	602	829	738	1352	1179	293
	P2-3	607	155	a	416	991	526	256
	P3-4	332	452	311	186	572	462	151
	Pout	234	182	135	74	a	104	a
	S	1355	115	627	219	a	a	180
Methyl neoabietate	P1-2	522	180	153	172	402	405	37
	P2-3	115	-	a	-	194	88	-
	P3-4	-	90	45	7	-	-	-
	Pout	-	-	-	-	-	-	a
	S	-	-	-	-	-	-	-
BOD_5 (mg/l)	P1-2	186	288	200	184	199	162	177
	P2-3	73	186	102	126	72	100	79
	P3-4	20	38	40	56	32	35	29
	Pout	18	28	31	24	17	18	19

P1-2 Pond 1 outlet; P2-3 Pond 2 outlet; P3-4 Pond 3 outlet;
Pout Pond 4 outlet; S Sludge lagoon; a sample not available;
- not detected

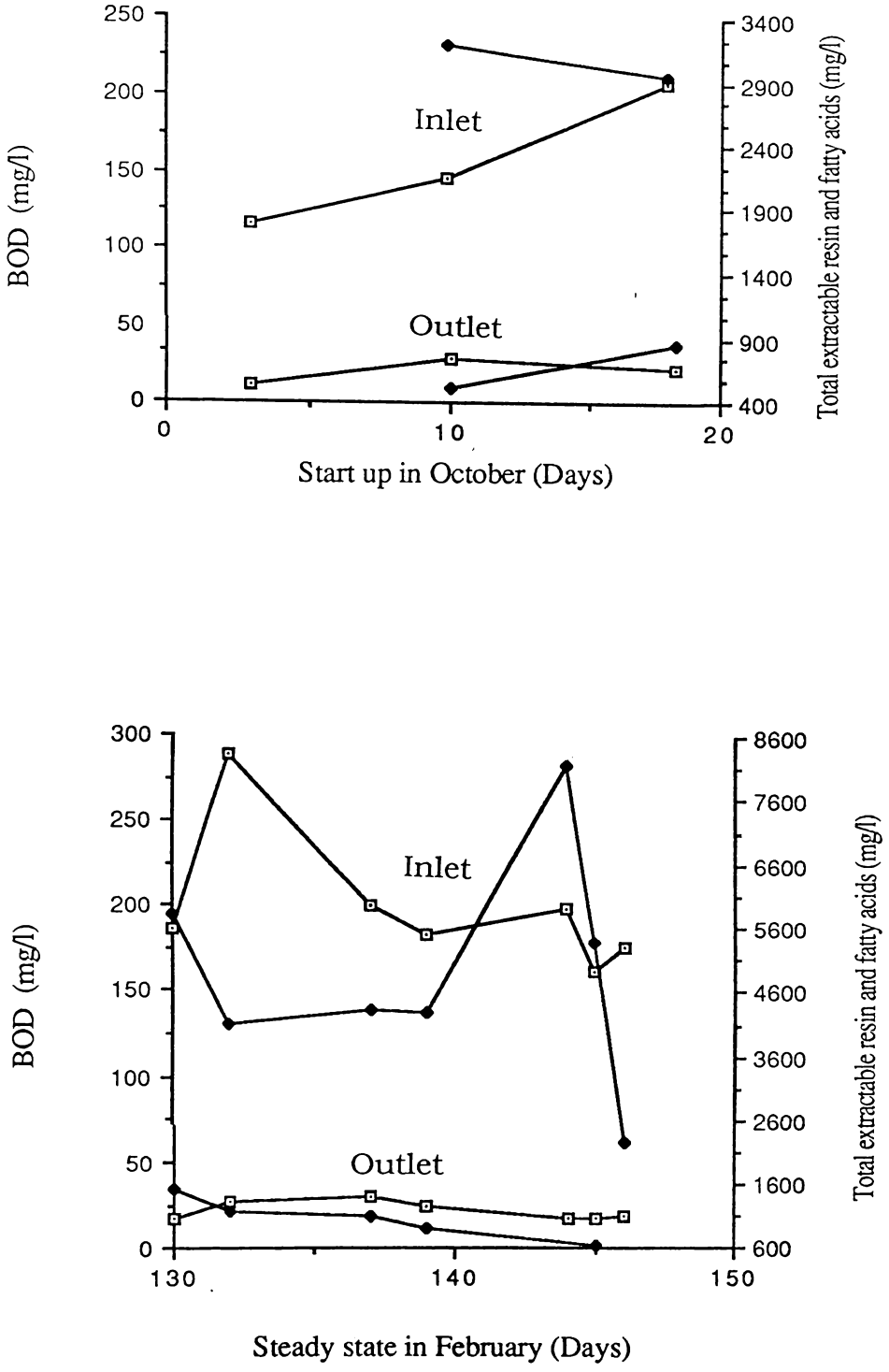


Figure 10.1 Comparison of BOD_5, total extractable organic compounds in the inlet and outlet with time.

▫ BOD_5, ◆ total extractable organic compounds

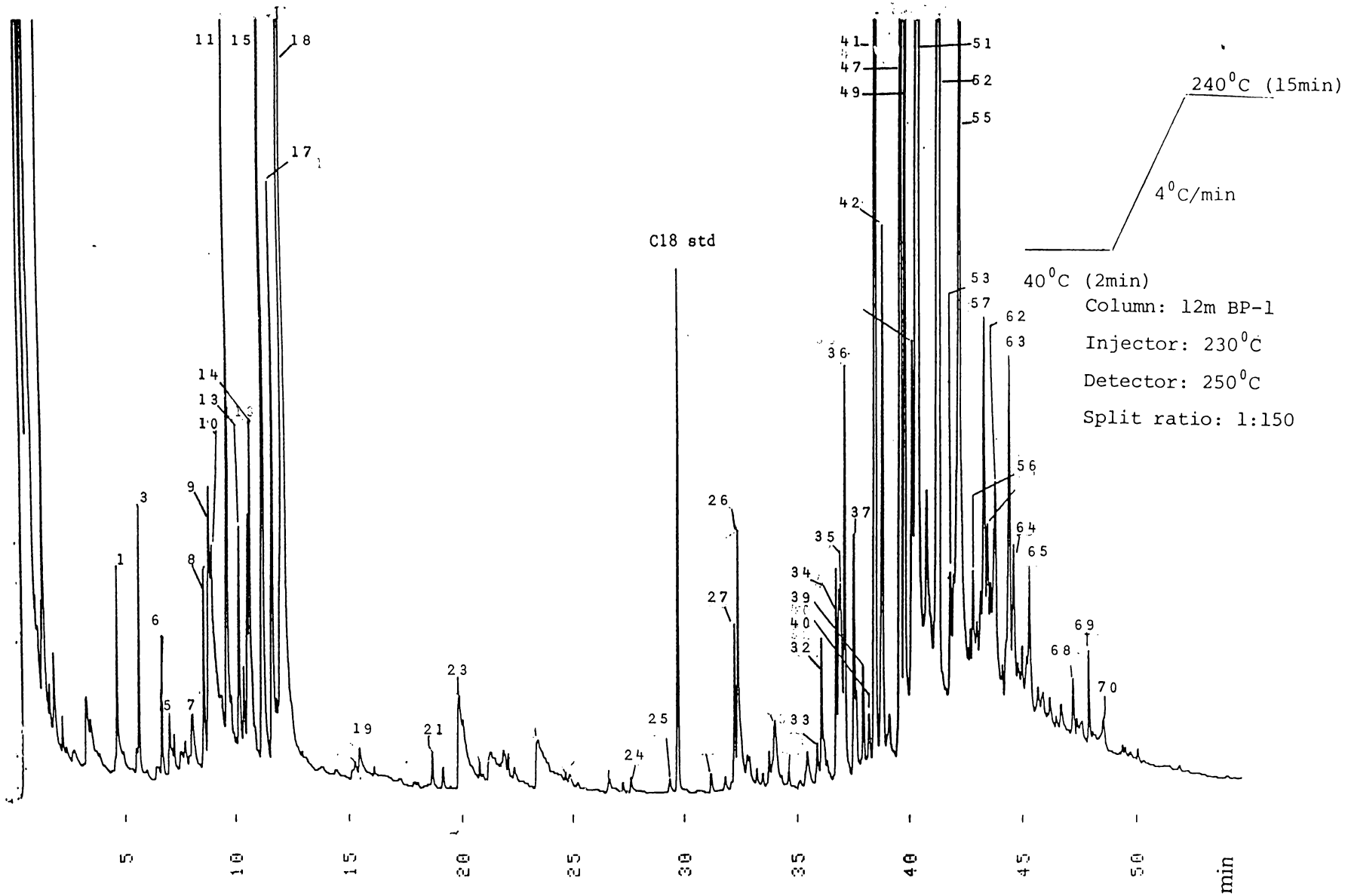


Figure 10.2 GC-FID profile of an extract of Pond 1 outlet at steady state (9th February 1987). For peak identifications see Table 10.4.

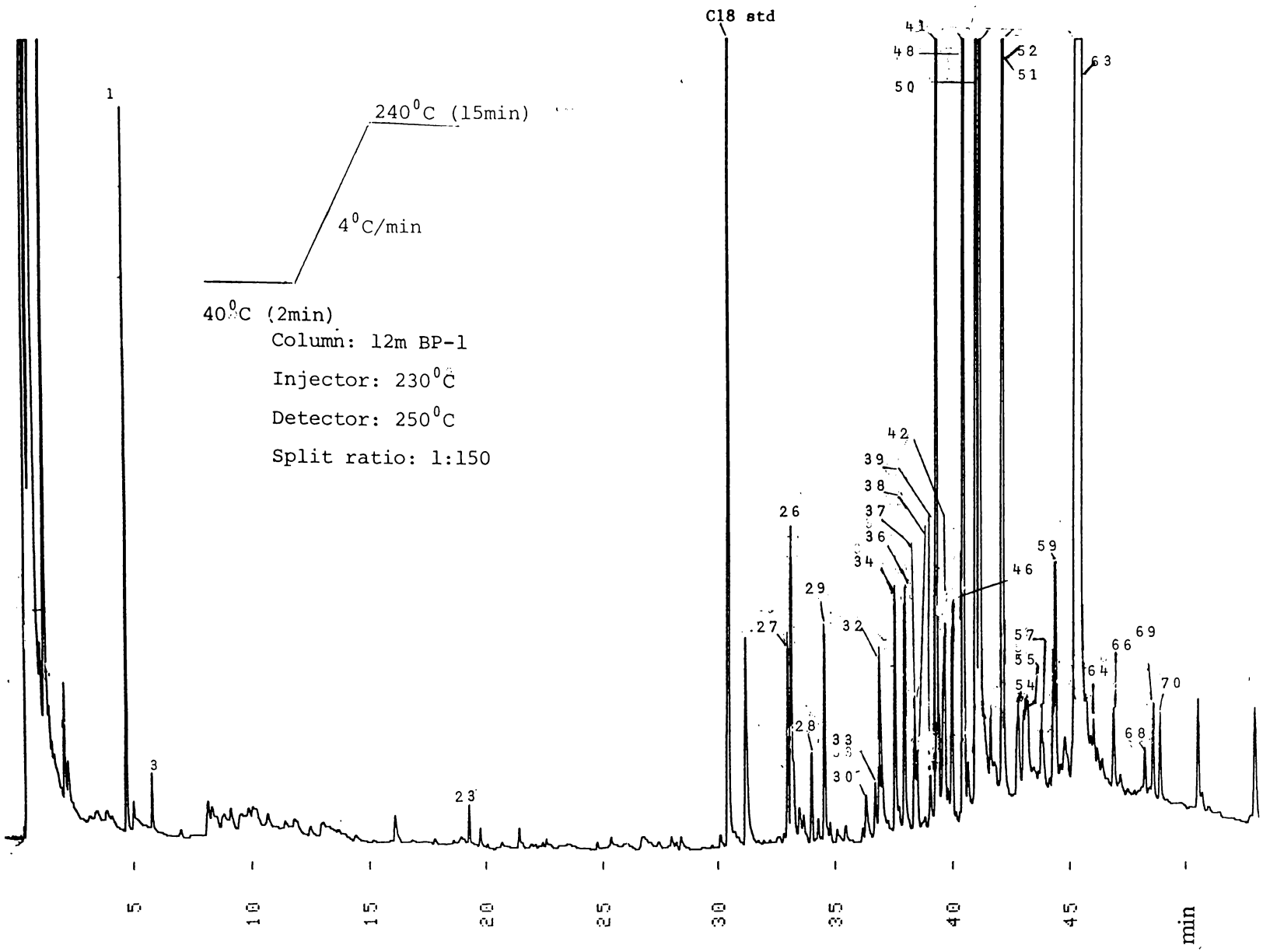


Figure 10.3 GC-FID profile of an extract of Pond 2 outlet at steady state (9th February 1987). For peak identifications see Table 10.4.

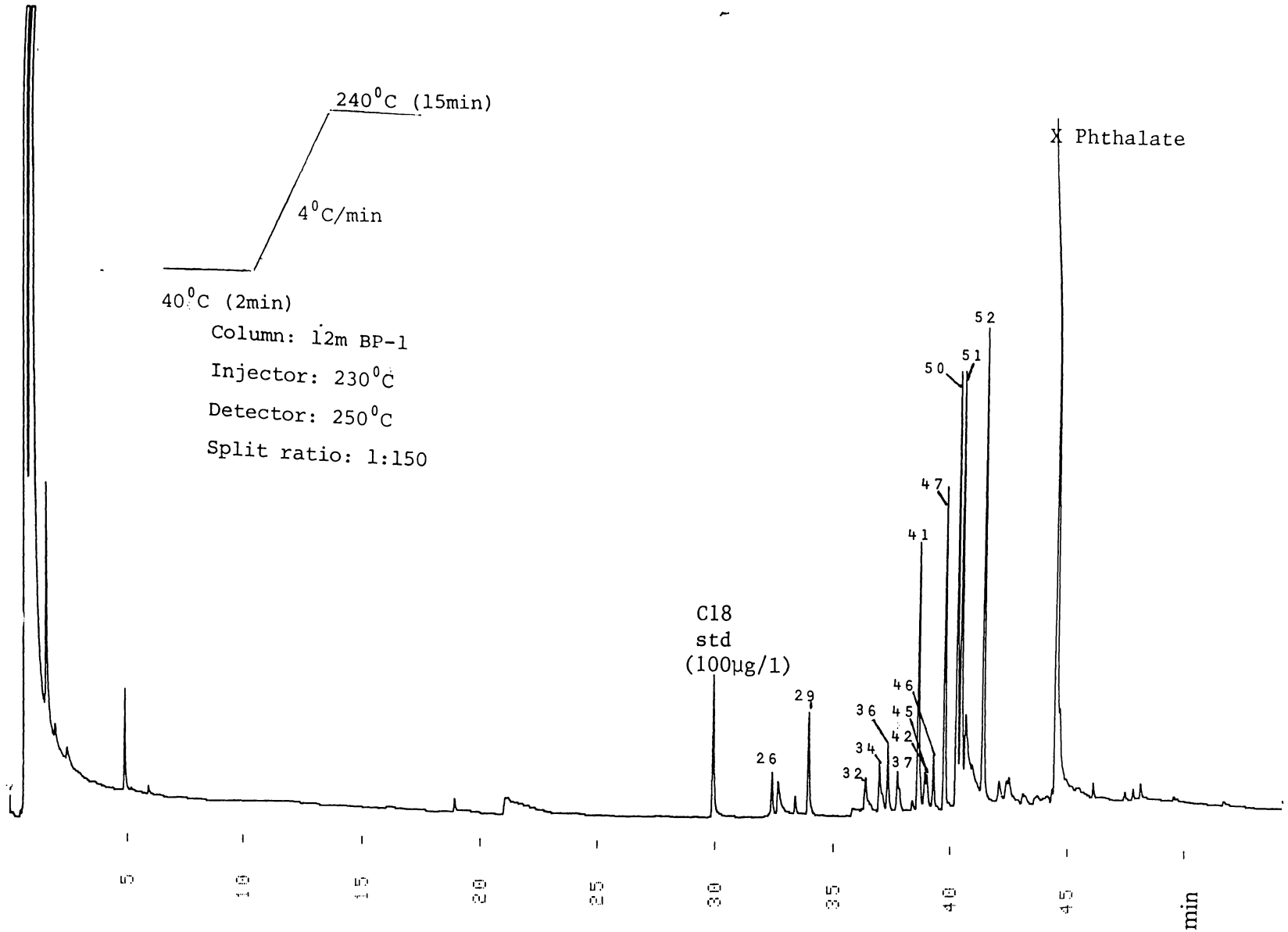


Figure 10.4 GC-FID profile of an extract of Pond 3 outlet at steady state (9th February 1987). For peak identifications see Table 10.4.

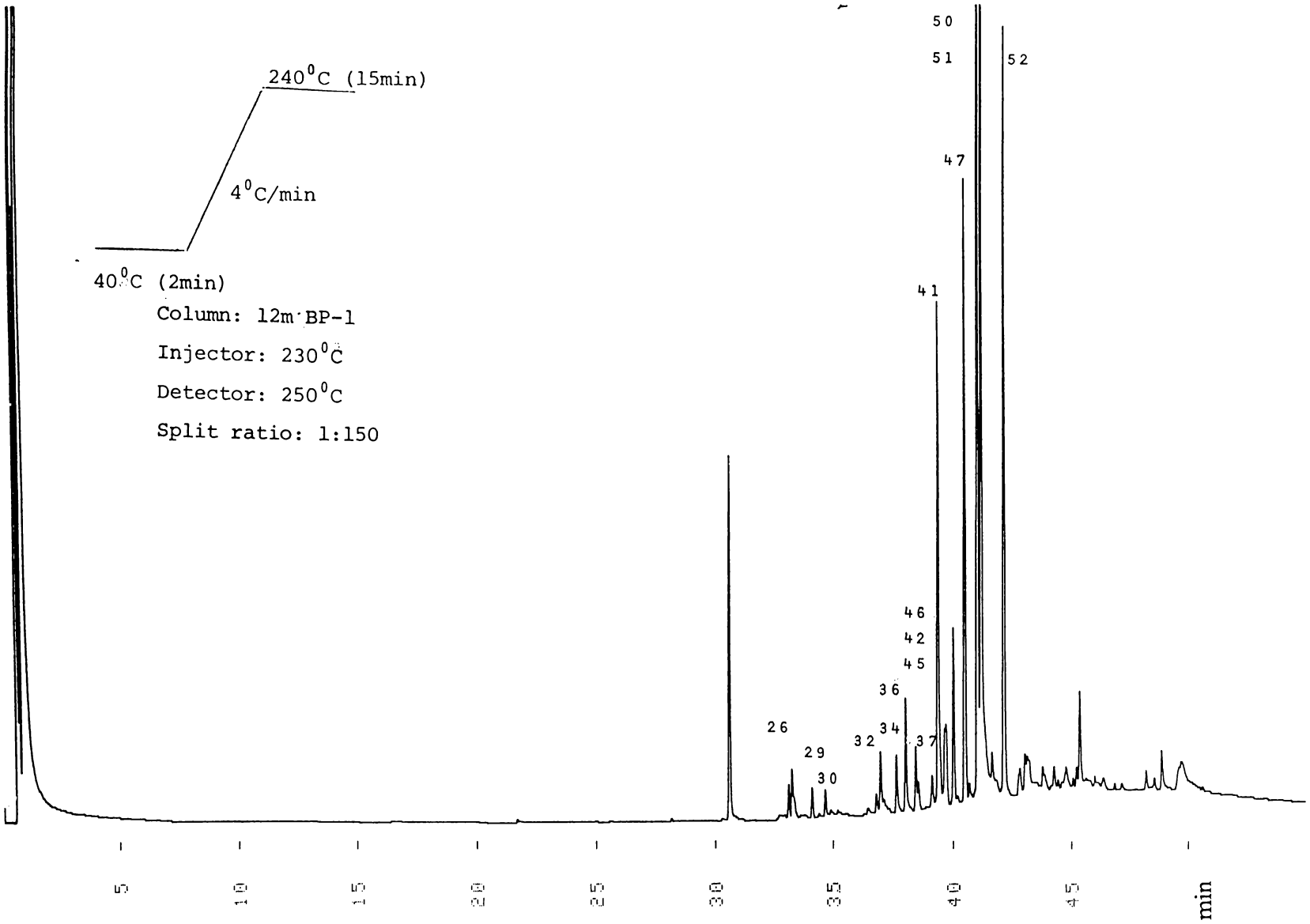


Figure 10.5 GC-FID profile of an extract of Pond 4 outlet at steady state (9th February 1987). For peak identifications see Table 10.4.

Table 10.4
Concentrations of organic compounds present in the treatment system (9th February 1987)

Peak	Compound	P1-2	P2-3	P3-4	Pout	Sludge
		µg/l				µg/g
1	α-Pinene	71	53	106	-	92
2	Methyl hexanoate	-	-	-	-	8
3	β–Pinene	87	12	-	-	63
4	α-Terpinene	50	-	-	-	78
5	Dimethyl-2-cyclopentenone	32	-	-	-	-
6	*p*-Cymene	9	-	-	-	203
7	Limonene	94	-	-	-	52
8	Trimethyl-2-cyclopentenone	532	-	-	-	99
9	Guaiacol	-	-	-	-	13
10	Methyl benzoate	368	69	-	-	27
11	Fenchol	100	120	-	-	149
12	Methyl Guaiacol	80	62	-	-	-
13	Camphor	101	25	-	-	237
14	β-Terpineol	-	-	-	-	958
15	Borneol	681	551	-	-	279
16	Methyl phenylacetate	21	96	-	-	12
17	Terpen-4-ol	292	225	-	-	160
18	α-Terpineol	3143	1859	-	-	920
19	Methyl phenylpropanoate	-	-	-	-	286
20	Methyl decanoate	143	-	-	-	5
21	Methyl cinnamate	25	24	-	-	-
22	1-(3,4-Dimethoxyphenyl)-propan-2-one	-	-	-	-	33
23	3,4-Dimethoxybenzaldehyde	102	-	-	-	40
24	Methyl myristate	-	-	-	-	56
25	Methyl isopentadecanoate	6	2	-	-	-
26	Methyl palmitate	113	114	36	22	1656
27	Unknown (M+ 272)	1668	1024	-	-	-
28	Fichtelite	-	21	-	-	11
29	Dehydroabietin	-	-	-	8	15
30	1,2,3,4-Tetrahydroretene	-	86	72	8	106
31	Methyl heptadecanoate	525	-	-	-	158

Table 10.4 cont....

Peak	Compound	P1-2	P2-3	P3-4	Pout	Sludge
32	Methyl oleate	52	67	-	24	357
33	Methyl linoleate	17	13	38	7	241
34	Methyl stearate	64	61	28	25	189
35	Methyl octadecanoate-1	34	55	-	-	138
36	Methyl secodehydroabietate-1	62	93	46	31	173
37	Methyl secodehydroabietate-2	22	52	-	19	126
38	Retene	-	57	-	9	89
39	Methyl 8,15-pimaradiene-18-oate	15	10	-	-	45
40	Dehydroabietol	6	-	-	-	49
41	Methyl pimarate	610	525	203	161	886
42	Methyl sandaracopimarate	142	59	-	19	215
43	Unknown	(co-eluted with peak 42)				
44	Methyl 8-abieten-18-oate	-	-	-	20	-
45	Methyl 8(14)-pimaren-18-oate	13	-	26	20	52
46	Methyl pimaran-18-oate	-	78	35	50	52
47	Methyl isopimarate	649	478	236	184	1782
48	Methyl 13-abieten-18-oate	(co-eluted with peak 47)				
49	Methyl palustrate	286	70	-	-	180
50	Methyl abietan-18-oate	-	621	333	372	366
51	Methyl dehydroabietate	2058	481	316	348	4614
52	Methyl abietate	1493	607	332	234	1355
53	Unknown (310)	20	-	-	-	-
54	Methyl 8,11,13,15-abietatetraen-18-oate	86	-	24	58	-
55	Methyl neoabietate	522	115	-	-	-
56	Hydroxylated RAME	15	-	-	-	322
57	Methyl alburate	88	20	-	-	50
58	Methyl 7β-hydroxydehydroabietate	115	-	-	-	-
59	Dihydroxylated RAME	-	30	-	-	-
60	Methyl behenoate	-	-	-	10	-
61	Methyl 7-oxodehydroabietate	118	-	12	11	-
62	Hydroxylated RAME	40	-	-	-	-
63	Dihydroxylated RAME	65	20	-	-	179
64	Hydroxylated RAME	30	12	-	-	35
65	Dihydroxylated RAME	38	-	-	-	96

Table 10.4 cont....

Peak	Compound	P1-2	P2-3	P3-4	Pout	Sludge
66	Methyl kinleithoate	-	-	69	32	278
67	Methyl hydroxyabietate	110	96	44	12	143
68	Methyl 12,14-dichlorodehydroabietate	10	18	18	18	10
69	Methyl tetracosanoate	22	14	9	-	-
70	Hydroxylated RAME	10	5	2	-	30

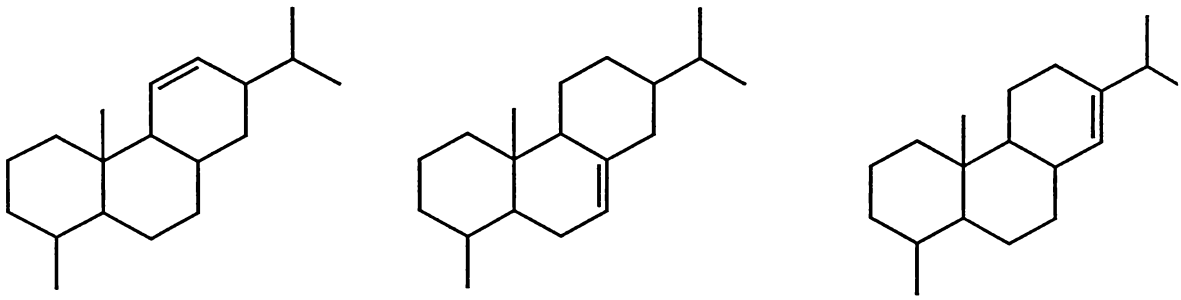
P1-2 Pond 1 outlet; P2-3 Pond 2 outlet; P3-4 Pond 3 outlet;
Pout Pond 4 outlet; Sludge Sludge lagoon; a sample not available;
- not detected; RAME Resin acid methyl ester

In addition to the usual range of resin acids, eight other resin acids and resin acid derivatives were detected in the Pond 4 outlet samples [abietan-18-oic acid (8), pimaran-18-oic acid (9), 8(14)-pimaren-18-oic acid (10), 13-abieten-18-oic acid (11), fichtelite (17), dehydroabietin (18), 1,2,3,4-tetrahydroretene (19) and retene (16)]. These substances were also found to be present in the early Pond 2-4 transfer cutting samples (*i.e.* those collected before the inclusion of Pond 3).

Three minor compounds were detected (below the normal quantification limit) in the February 1987 samples which appeared to be resin hydrocarbons. They had molecular masses of 270 amu and 260 amu (2 isomers). The mass spectrum of the first compound corresponded with that reported for abieta-8,11,13-triene (79). The fragmentation pattern of this compound was similar to that of dehydroabietin (14) except for a fourteen mass unit difference attributable to the replacement of a CH_3 group in the former compound by a proton in the latter compound. Kitadani *et al* (1970)

have previously isolated this compound from *Podocarpus Ferrugineus*. It is possible that abieta-8,11,13-triene was in fact present in earlier samples but in quantities below the detection limit.

The other two compounds had mass spectral fragmentation patterns similar to that of fichtelite (262 amu) (13) except for the difference of two mass units which suggests the presence a double-bond. Possible structures for these compounds include (a), (b) and (c) of Figure 10.6.



(a) (b) (c)

Figure 10.6 Possible structures for compounds of 260 amu.

A compound (peak 44) detected in the extended system eluted close to sandaracopimaric acid (4). No molecular ion was observed; the highest observable ion occurred at m/e 303 with a base peak at m/e 243. The ion of m/e 303 appears to arise from the loss of a methyl group which would suggest that the molecular ion was 318 amu. This is typical of resin acids possessing one double-bond. The base peak (m/e 243) can be envisaged as being derived from the ion of m/e 303 by loss of methyl methanoate ($HCOOCH_3$).

The mass spectrum of this compound (see Appendix C) was similar to that of methyl palustrate (27) save for the displacement of the m/e 301 and 241 ions to m/e 303 and m/e 243 respectively. The

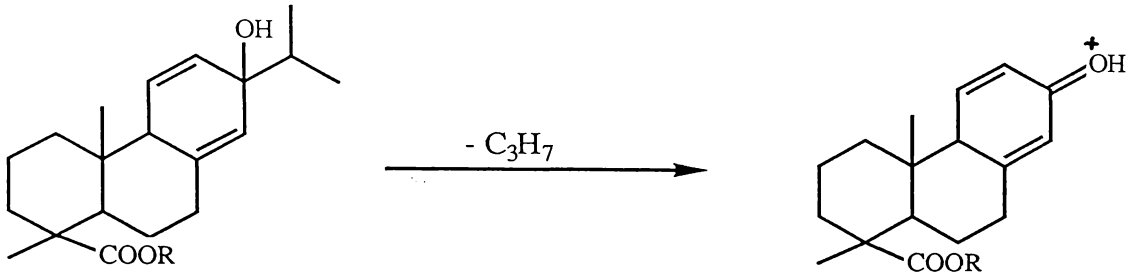
relative retention time coincided with that reported for the methyl ester of 8-abieten-18-oic acid (80) (Zinkel et al, 1971; Foster and Zinkel, 1982).

The occurrence in the latter pond samples of a compound (peak 40) of molecular mass 286 amu suggested the presence of a resin alcohol. This compound eluted close to secodehydroabietic acid-1 (1), and was identified as dehydroabietol (47).

Six compounds were detected in the February Pond 1 outlet samples which displayed molecular ions of 330 amu (four isomers) and 332 amu (two isomers). Molecular masses of 330 amu are typical of resin acids possessing two double bonds and a keto-group, or three double bonds and one hydroxyl group, while molecular masses of 332 amu are typical of hydroxylated diene resin acids. A similar range of compounds were detected in effluent samples taken from two Australian mills by Wilkins and Richardson *(pers. comm.)*. The compounds of molecular mass 330 amu displayed a base peak of m/e 255. The structures of these compounds are not yet known; the parent acids were designated as Boyeric acids-1, -2, -3 and -4 by Wilkins and Richardson.

The compounds of molecular mass 332 amu had base peaks at m/e 289. They appear to possess abietic-type skeletons, hydroxylated at C-13 position and the loss of the isopropyl radical gives rise to an oxonium ion (Figure 10.7). A loss of an isopropyl group is believed to be responsible for the corresponding saturated ion of m/e 293 which appears in the mass spectrum of methyl kinleithoate (48).

The foregoing compounds were also detected by Wilkins and Richardson *(pers. comm.)* and the parent acids were designated as alburic and isoalburic acids.



Possible structure for alburic acid

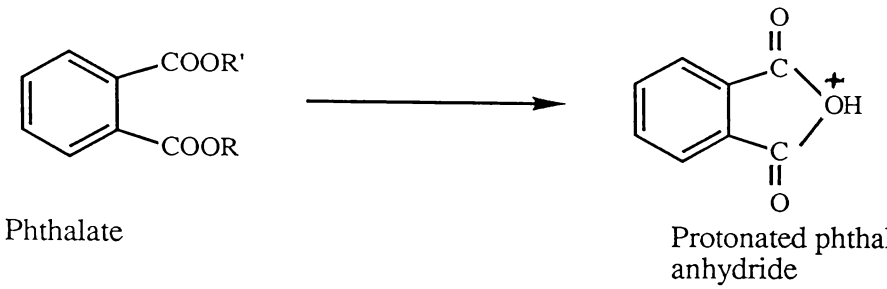
Oxonium ion

Figure 10.7 Possible fragmentation of methyl alburate.

7-Oxodehydroabietic acid (15) is a well-known degradation product of dehydroabietic acid. It has a molecular mass of 328 amu and a base peak at m/e 253 arising from the loss of a methyl radical (CH_3.) and methyl methanoate ($HCOOCH_3$).

12,14-Dichlorodehydroabietic acid was persistent and the concentration was found to be typically 16 µg/l in both the inlet and outlet effluents. Mass spectral data displayed a molecular ion at 382 amu with base peak at m/e 307 (M^+ - CH_3 - $HCOOCH_3$). The 12- and 14-chlorodehydroabietic acid isomers were not detected.

While every effort had been made to prevent contamination by platicizers (phthalates), these compounds have been occasionally encountered. They have a characteristic fragment at m/e 149 due to the formation of a protonated phthalic anhydride ion (Figure 10.8). Phthalates may arise from the use of plastic containers, plastic piping and seals.



Phthalate

Protonated phthalic anhydride

Figure 10.8 Characteristic fragmentation of phthalate (plasticizers).

10.3.4 Sludge Lagoon

The source of the resin hydrocarbons [fichtelite (17), dehydroabietin (18), 1,2,3,4-tetrahydroretene (19) and retene (16)] discussed in Chapter Five was eventually traced to the primary sludge lagoon. Samples taken at various points in the treatment system indicated the presence of these compounds only from the point where the sludge lagoon outflow joined the aeration ponds. Sludge from the clarifier is disposed of in the sludge lagoon (Section 3.6.1) and typically anaerobic conditions exist. When a breach in the sludge lagoon embankment (8th July 1984) resulted in the effluent entering the Tarawera River, a water sample taken at that time contained a high concentration of fichtelite (17), dehydroabietin (18), 1,2,3,4-tetrahydroretene (19), retene (16), abietan-18-oic acid (8) and pimaran-18-oic acid (9). The sludge sediment also afforded a similar array of saturated resin acids and resin hydrocarbons (See Table 10.5).

Besides the above-mentioned compounds, the aqueous sludge sample also comprised of resin acids, fatty acids (C_4 to C_{18}), monoterpenes, 2-cyclopentenone derivatives, aromatic and sulphur compounds. The GC-FID profile of the sludge lagoon appears in

TABLE 10.5
Concentrations of the resin acids and resin hydrocarbons in the sludge lagoon aqueous and sediment samples.

Compound	Sediment µg/g	Aqueous µg/l
Fichtelite	2	47
Dehydrobietin	50	416
1,2,3,4-Tetrahydroretene	9	214
Methyl secodehydroabietate-1	25	82
Methyl secodehydroabietate-2	16	52
Retene	44	199
Methyl pimarate	56	1146
Methyl sandaracopimarate	5	612
Methyl pimaran-18-oate	21	395
Methyl isopimarate	140	1894
Methyl abietan-18-oate	123	4538
Methyl dehydroabietate	342	6115

Figure 10.9 and the concentrations of the compounds are given in Table 10.4. Only compounds with concentrations above 5 µg/l are listed.

Two sulphur compounds were detected on the GC-ITDS and identified by the NBS mass spectral library as 1,2,4-trithiolane ($C_2H_4S_3$) and 1,2,3,4-tetrathiepane ($C_3H_6S_4$). The fragmentation pattern for both the compounds were quite similar except that the latter compound differed by 46 mass units (CH_2S). The mass spectra of these compounds are given in Appendix C.

A major peak was found to elute after neoabietic acid. The mass spectrum of the compound showed a base peak at m/e 293 and the highest observable ion occurred at m/e 318. This compound had

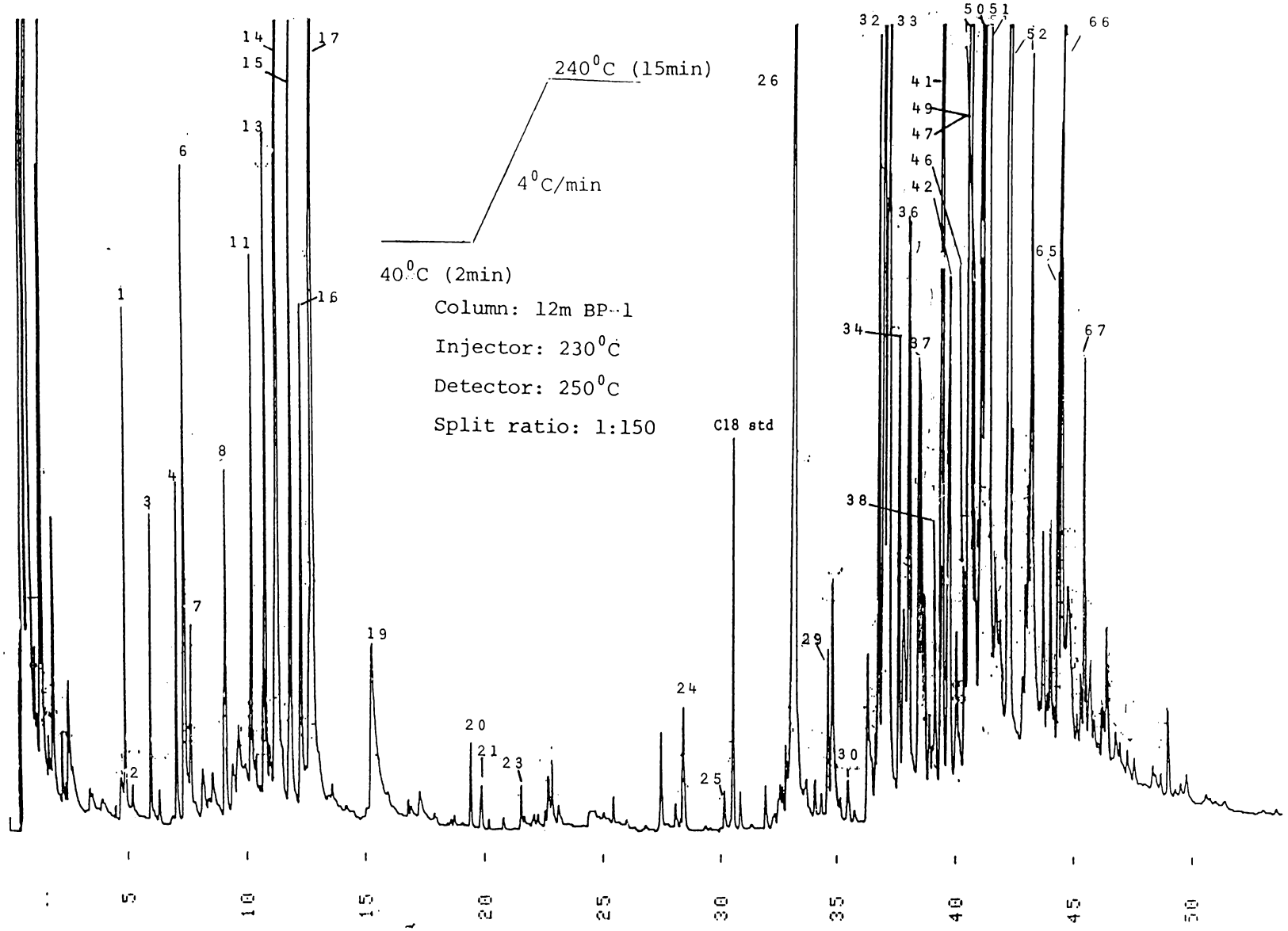


Figure 10.9 GC-FID profile of an extract of the Sludge lagoon (aqueous) at steady state (9th February 1987). For peak identifications see Table 10.4.

been recently isolated from another pulp mill and been identified as methyl kinleithoate (48), a saturated hydroxylated derivative of abietic acid (Wilkins *et al*, in press). The molecular ion of 336 amu ($C_{21}H_{36}O_3$) was not observed.

Four compounds of molecular weight 204 amu and one of molecular weight 206 amu were also found in the sludge samples. A similar range of compounds was reported by Richardson and Bloom (1983) and they were denoted as sesquiterpenes. These compounds were similar to those detected in the crude turpentine extract (see Section 9.3.2).

10.3.5 Treatment System - Sediment Samples

The major classes of compounds found to be present in the sediment samples were monoterpenes, sesquiterpenes, fatty acids, resin hydrocarbons, resin acids, and chlorinated compounds. Only the major components present (> 5 µg/l) are listed in Table 10.6. The GC-FID traces of the sediment extracts of Pond 1, Pond 2 and Pond 4 are shown in Figures 10.10-10.12 while the peak numbers refer to those listed in Table 10.6.

A variety of polychlorinated low molecular weight hydrocarbons were present in trace amounts in the Pond 2 and 4 sediment samples. Several of these chlorinated compounds were tentatively identified by recognizing the chlorine isotope pattern while others were identified using the NBS mass spectral library.

It appeared that many of these chlorinated compounds were hydrocarbons ranging from C_2 to C_6 units. Once the unit is fully

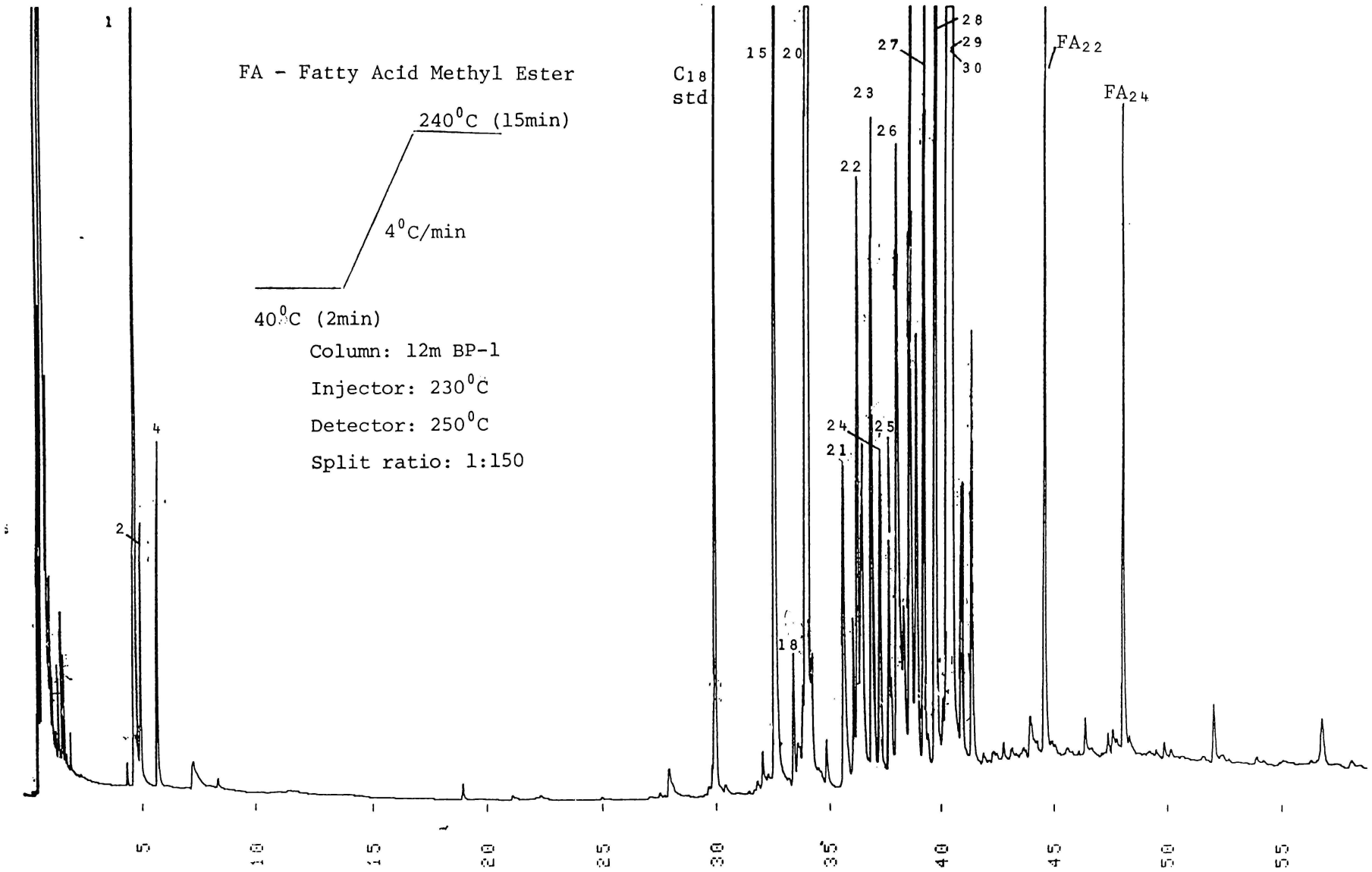


Figure 10.10 GC-FID profile of an extract of a Pond 1 sediment sample (6th October, 1986). For peak identifications see Table 10.6.

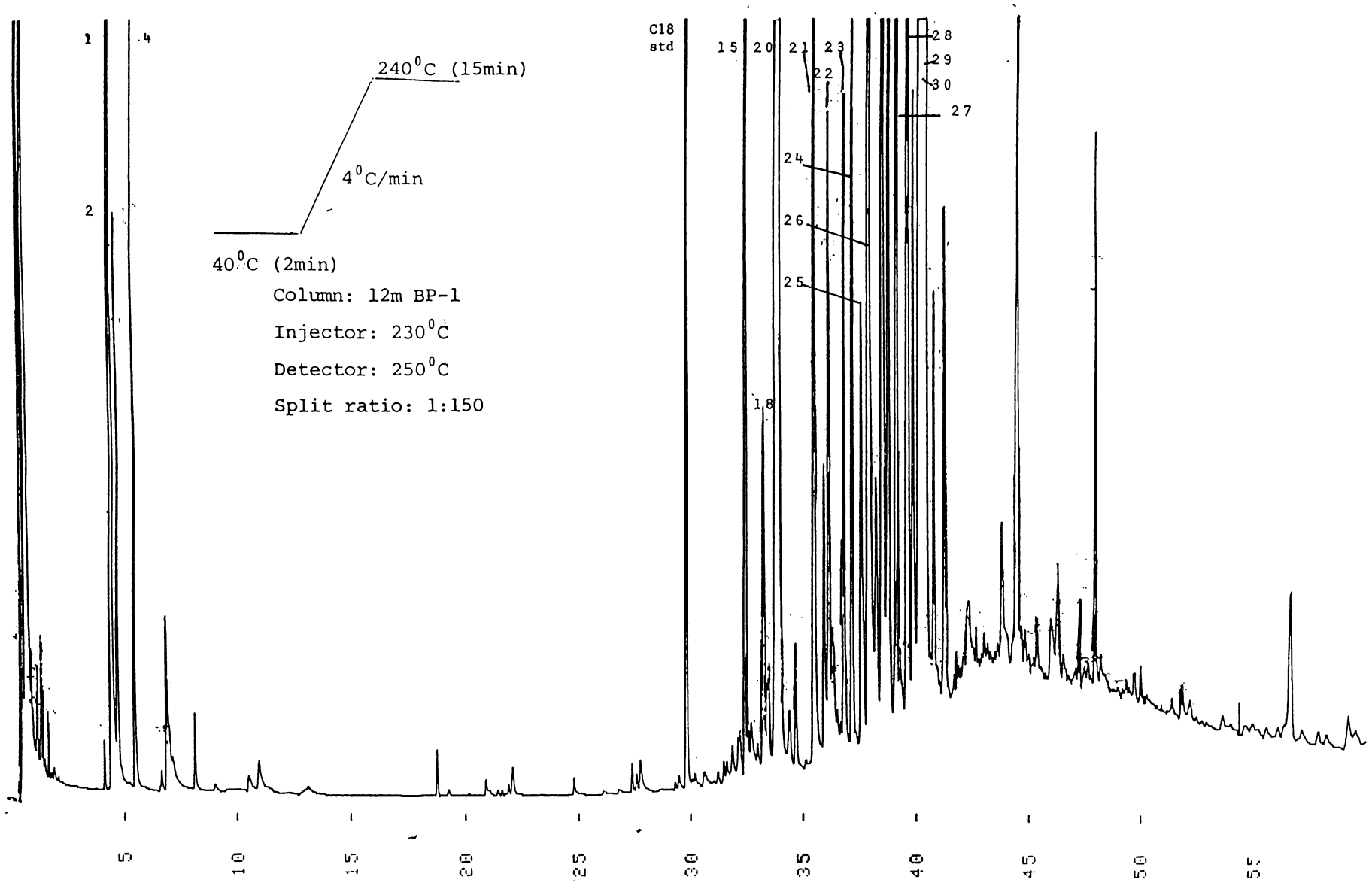


Figure 10.11 GC-FID profile of an extract of a Pond 2 sediment sample (6th October, 1986). For peak identifications see Table 10.6.

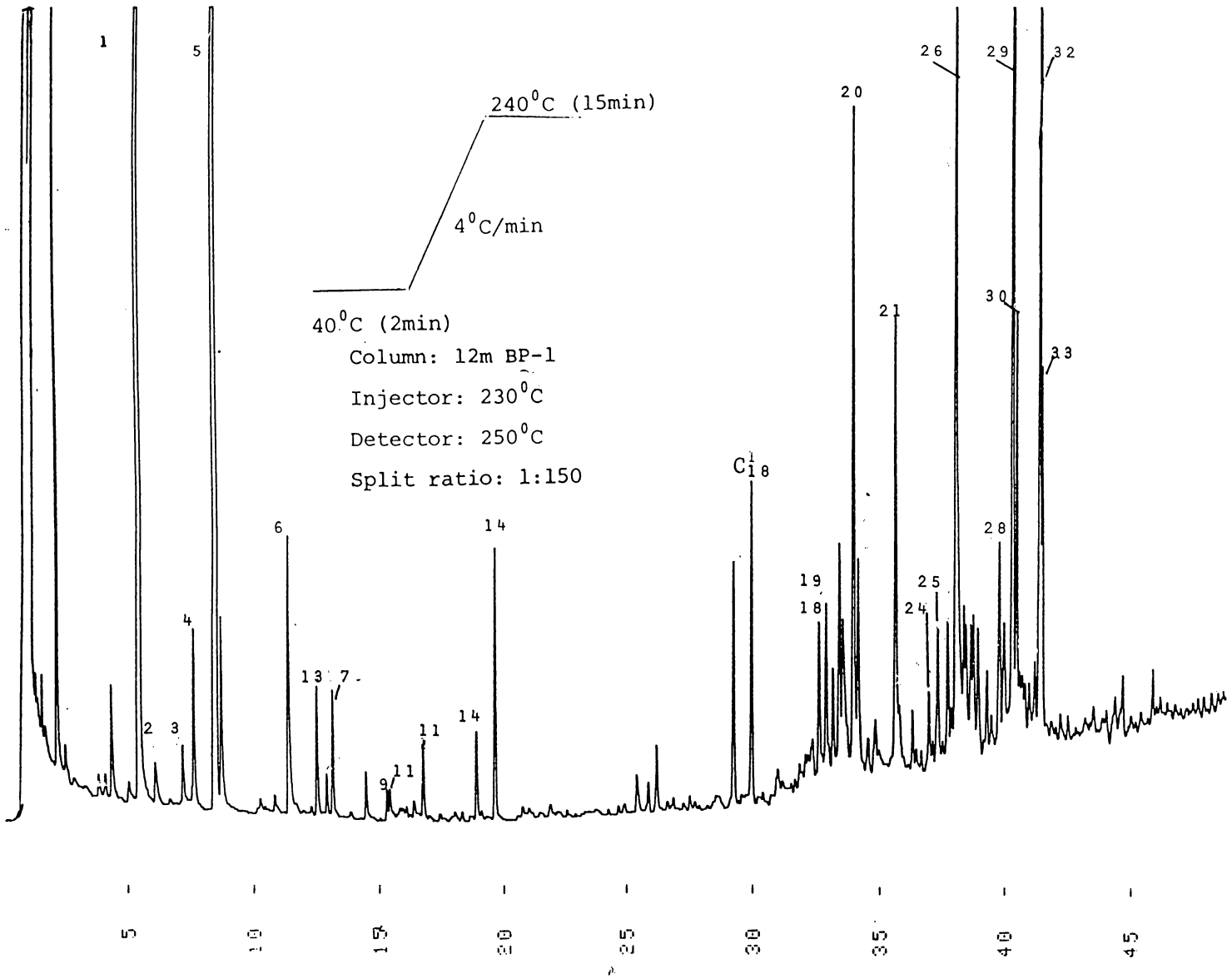


Figure 10.12 GC-FID profile of an extract of a Pond 4 sediment sample (6th October, 1986). For peak identifications see Table 10.6.

Table 10.6

Organic compounds detected in the treatment pond sediments (μg/g)

Peak	Compound	Pond 1	Pond 2	Pond 4
1	α-Pinene	505	1082	2224
2	Camphene	19	43	18
3	Tetrachloroethane	-	-	21
4	β-Pinene	33	61	67
5	Hexachloroethane	-	-	1788
6	Pentachlorobutene	-	-	120
7	Hexachloro-1,3-butadiene	-	-	14
8	Hexachlorobutadiene	-	-	39
9	Hexachlorobutene	-	-	10
10	Hexachlorobutene	-	-	16
11	Hexachloro-1,3-cyclopentadiene	-	-	26
12	Pentachloropropene	-	-	1788
13	Hexachloropropane	-	-	41
14	Heptachlorobutane	-	-	114
15	Methyl palmitate	211	262	105
16	8(14)-Abietene	-	5	78
17	8(14)-Abietene (Isomer)	-	-	60
18	Fichtelite	12	42	105
19	Ethyl palmitate	6	18	110
20	Dehydroabietin	950	1673	260
21	1,2,3,4-Tetrahydroretene	47	131	215
22	Methyl oleate	54	99	31
23	Methyl stearate	55	106	50
24	Methyl secodehydroabietate-1	32	90	77
25	Methyl secodehydroabietate-2	16	65	75
26	Retene	115	289	497
27	Methyl 8-abieten-18-oate	53	162	77
28	Methyl 13-abieten-18-oate	76	232	119
29	Methyl abietan-18-oate	1080	2412	493
30	Methyl dehydroabietate	420	512	162
31	Methyl alburate	-	-	64
32	Hydroxylated RAME	-	-	361
33	Hydroxylated RAME	-	-	150

chlorinated, the molecule tends to break down by losing HCl molecules. Compounds identified were tetrachloroethane, pentachloropropene, hexachloropropene, pentachloro-1,3-butadiene, hexachloro-1,3-butadiene, octachlorobutane and nonachlorobutane. Losses of chlorine radicals (Cl$^{\cdot}$), HCl and/or Cl_2 are prominent in the fragmentation patterns of these compounds. The mass spectra of these compounds are presented in Appendix C.

Another class of chlorinated compounds found is the cyclopentadienes. The fragmentation pattern for this class of chlorinated species also seemed to be as for the hydrocarbons *i.e.* sequential loss of chlorine radicals, HCl and/or Cl_2.

Tetrachloroethane and hexachloroethane were the only chlorinated compounds detected in Pond 1 sediment. However, Pond 1 and 2 had a higher concentration of resin acids and resin derivatives. Also detected in the Pond 1 samples were four compounds of molecular mass 142, 156, and 170 amu (2 isomers). The first compound was identified by the NBS mass spectral library as methylnaphthalene. This then made it apparent that the other three compounds were dimethylnaphthalene and two isomers of trimethylnaphthalene respectively as the molecular mass of these compounds differed by 14 mass units (CH_2).

10.3.6 Biological Oxygen Demand (BOD_5)

Data for the BOD_5 were determined during the periods of start-up and steady state (6th October to 21st October 1986 and 9th February to 25th February 1987). It can be seen from Figure 10.13 that the decrease in BOD_5 through the treatment system is roughly

exponential. The time axis on Figure 10.13 was determined by using the mean retention times of the various ponds. The data of Table 10.3 was analysed with a view to determine whether any correlation existed between the extractable organic compounds (taken individually, as classes of compounds, or as total extractable organic compounds) and BOD_5. The results for methyl pimarate (chosen because of its lack of isomerization/interconversion such as that associated with abietic, neoabietic and dehydroabietic acids), selected resin acids (excluding those produced in the anaerobic sludge lagoon *e.g.* abietan-18-oic acid) and total extractable organic compounds shown in Figure 10.14 (a), (b) and (c). As apparent from the figures a better correlation exists between the total extractable organic compounds and the resin acids than with pimaric acid. However resin acids contribute a large portion of the total extractable organic compounds. This may be due to the overall variability of the system and/or the limitations of the analytical data.

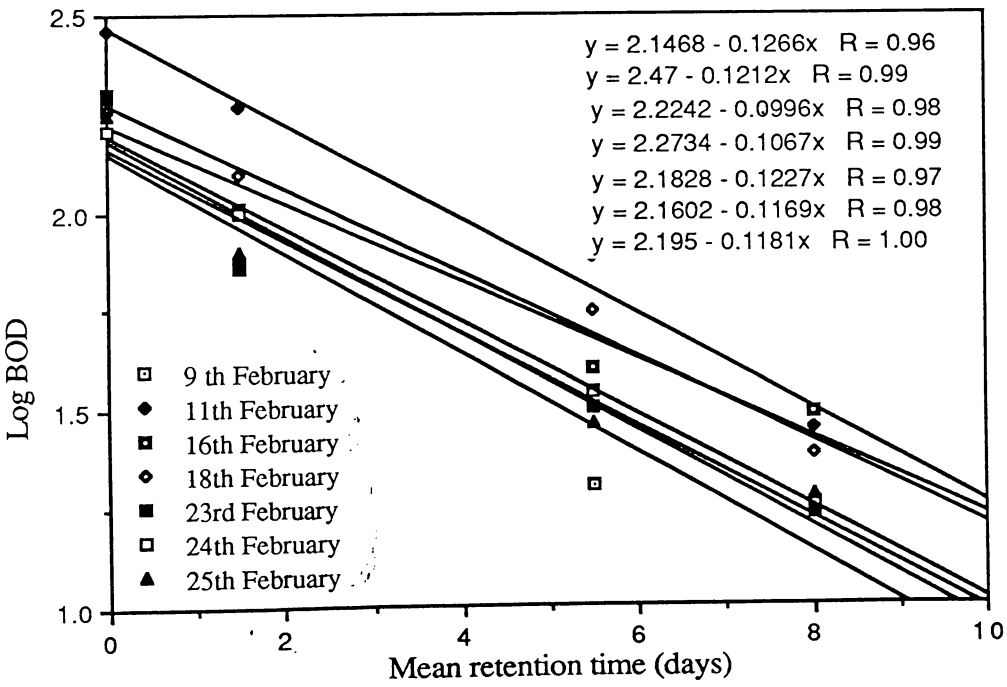


Figure 10.13 Decrease of BOD_5 through the treatment system (February 1987)

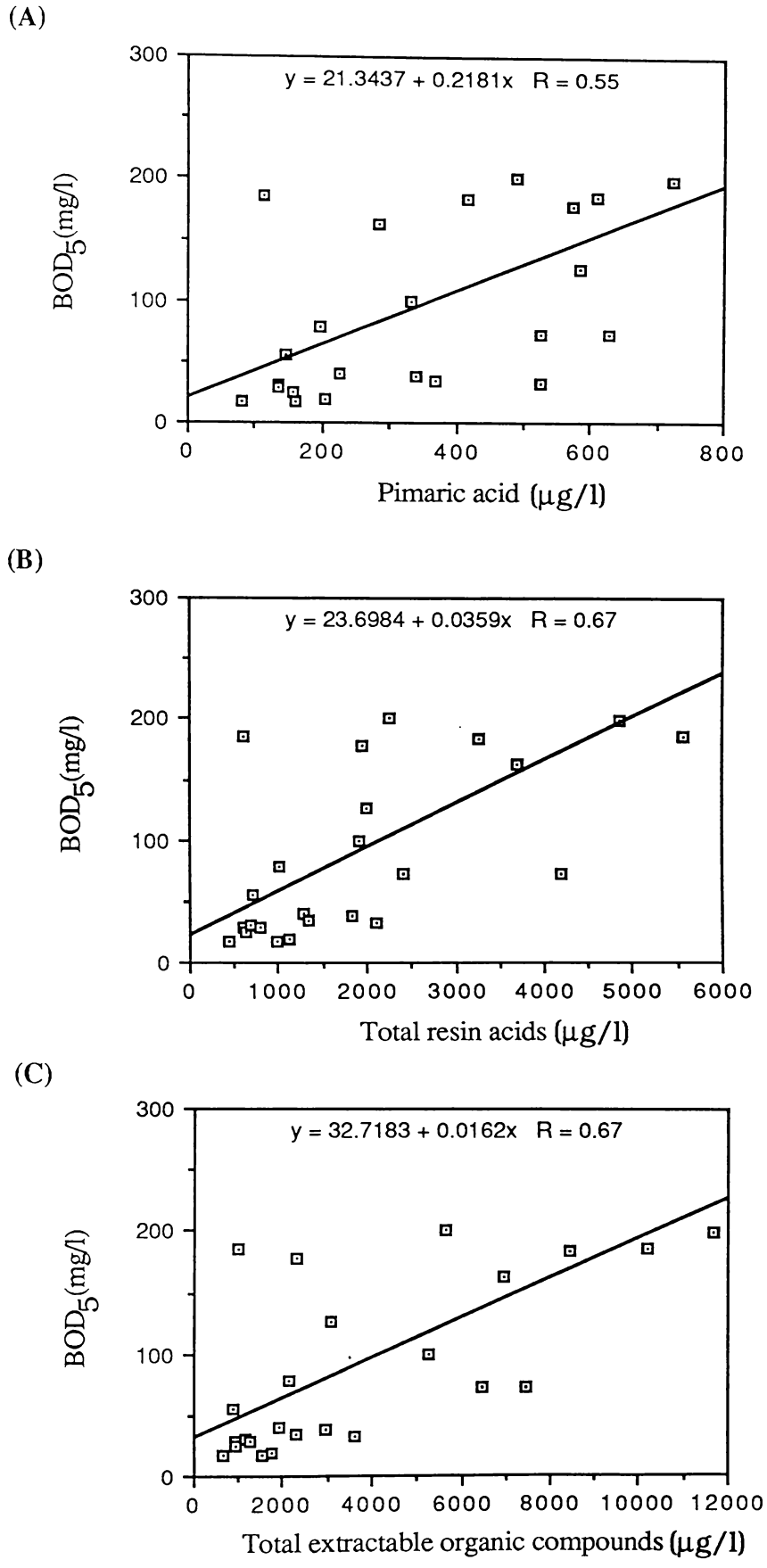


Figure 10.14 Correlation of BOD_5 with the concentration (µg/l) of: (A) Pimaric acid, (B) Total resin acids and (C) Total extractable organic compounds

10.4 DISCUSSION

10.4.1 Pond treatment

The presence of resin hydrocarbons [fichtelite (17), dehydroabietin (18), 1,2,3,4-tetrahydroretene (19), retene (16)] and saturated resin acids [pimaran-18-oic acid (9) and abietan-18-oic acid (8)] which suggests anaerobic modification of abietic acid (Section 5.4.) was intriguing since both Ponds 2 and 4 are extensively aerated. It was however noted that the primary sludge lagoon outflow joined the aeration ponds at the Pond 2-4 transfer cutting (see Section 10.3.4). Once these compounds entered the aeration ponds, little degradation occurred. Although the toxicity of unsaturated resin acids is well documented (Rogers, 1973; Leach and Thakore, 1973, 1975; Rogers *et al*, 1975), no toxicity data is as yet available for saturated resin acids.

Although aromatic compounds (guaiacol, 4-hydroxy-3-methoxy-benzaldehyde, 4-hydroxy-3-methoxyacetophenone) were detected in early outlet samples, these appeared to be eliminated in Pond 3 of the extended system. 2-Cyclopentenone derivatives also appeared to have been eliminated. However, trichlorophenol, pentachlorophenol and tetrachloroguaiacol were detected in some outlet samples. While the period of dormancy (August/September 1986) allowed the treatment system to reduce the concentrations of most organic compounds to very low levels, even after eleven weeks of mill closure, chlorobenzoic acids, trichlorophenol, dimethyl-dichlorosulphone (bleach plant products) were detected.

A range of hydroxylated and dihydroxylated resin acids were found in the influent samples during normal operations, but only trace quantities were detected in the outlet samples. Introduction of hydroxyl-functions increases the water solubility of a compound. This in turn increases the penetrability of the substance into the cell walls of micro-organisms which degrade the substance. Biological degradation studies (Kutney *et al*, 1982) have shown that resin acids are more readily degraded once they are hydroxylated. Comparison of the pond inlet and the pond outlet data taken before and after the inclusion of Pond 3 makes it apparent that the extension of the retention time of the treatment system has substantially reduced the levels of extractable organic compounds as well as BOD.

10.4.2 Sludge Lagoon

The sludge lagoon contributes significant quantities of resin hydrocarbons and saturated resin acids which appear to be resistant to further degradation in the aerated treatment system. If it ever became necessary to reduce the levels of resin acids in the final discharge of the aerated treatment system, consideration should be given to finding an alternative method of disposal of the sludge lagoon effluent (15 Ml/day). However the toxicity of resin hydrocarbons and saturated resin acids characteristic of the sludge lagoon has yet to be ascertained.

10.4.3 Sediment Samples

The presence of polychlorinated hydrocarbons (pentachloro-1,3-butadiene, hexachlorobutane, octachlorobutane) was unexpected since they were not detected in the mill sources. Lindstrom and

Österberg (1986) have reported that 10% of the chlorine charge is organically bound (see Section 7.1) to lignin. Lindstrom *et al* (1981) indicated that it is possible for chlorinated low molecular mass compounds to be formed from high molecular mass chlorolignins in the receiving waters. Degradation may be caused by chemical, biochemical or photochemical means.

A range of chlorinated aliphatic compounds, monoterpene hydrocarbons and resin acids were found in sediment samples taken from Ponds 1, 2 and 4. The latter two classes of compounds are common in pulp effluent. The presence of aliphatic chlorinated compounds could suggest the degradation of chlorolignin or carbohydrates may be occurring in the sediments. The presence of the degraded products in the sediments suggest that they tightly bound (*i.e.* they are not released in detectable quantities to the aqueous phase).

The bacterial degradation of chlorinated compounds in sediments has been investigated by Remberger *et al* (1986) and Steiert *et al* (1987) who reported the degradation of chlorinated guaiacols, catechols, veratroles and phenols by bacteria. These studies have shown that substrates which are strongly adsorbed to sediments are nonetheless accessible to biological degradation.

The presence of relatively volatile substances such as monoterpene hydrocarbons (*e.g.* α-pinene, camphene and β-pinene) in the pond sediments was unexpected as these have been known to be the first class of substances to be removed from aqueous systems during aeration (Keith, 1976; Garrison *et al*, 1970). From Figure 10.6

(Pond 4 outlet aqueous), it is evident that the monoterpene hydrocarbons are efficiently removed from the aqueous phase during aeration. On the other hand, the oxygenated analogues (alcohols and ketones), are quite persistent and are often present in the final effluents of biologically treated systems. Of these substances, α-terpineol is most persistent and has been implicated in fish tainting. Yet these compounds are present in lesser amounts in the sediments than the more volatile hydrocarbons. This would suggests that either the monoterpenes are adsorbed onto sediment particles (clay minerals or macromolecular substances such as lignin or cellulose) and are degraded at a slower rate.

10.4.4 BOD_5

BOD_5 is currently the means by which wastewaters are regulated. The disadvantage of this method is that it takes at least five days for the results to be obtained. With the previous system of 4-day retention time, this meant that the effluent would have been discharged into the river before the BOD_5 results were obtained. Hence, a faster means of monitoring the treated effluents was needed. COD analysis offers a more rapid (but legally less acceptable) method for assessing the oxygen demand of an effluent. Any method that can be used more accurately than COD analysis would have an advantage.

A valid method based on GC analysis of extractable organic compounds would be attractive. Richardson and Bloom (1983) have proposed a GC procedure for estimating toxicity. As yet no workable

relationship between BOD_5 and extractable organic compounds has been described.

10.5 Conclusion

The principle extractable organic compounds exiting from the treatment system have been identified. These are mainly resin acids, together with lower levels of fatty acids. The extractable organic profiles are unusual in that significant levels of saturated resin acids (mainly abietan-18-oic acid) are present. Extractable chlorinated compounds were generally present in the final discharge at levels below the nominal detection limit (1 µg/l) of the present study, however evidence exists for the presence of extractable organic substances in pond sediment.

While no useful relationship was found between BOD_5 and the levels of extractable organic compounds, some similarities in trends were noticed.

CHAPTER ELEVEN

TARAWERA RIVER-PHASE II

11.1 INTRODUCTION

On July 1986 there was a disagreement between the Management of Tasman Pulp and Paper mill at Kawerau and the Pulp and Paper Workers' Union. This resulted in the mill being shut down indefinitely until the problem was resolved. This closure provided an opportunity to study the persistence of the extractable organic compounds in both the river water and its sediments; the time required for the river to recover from the effects of effluent discharge; and the capability of the river to assimilate the extractable organic compounds after the resumption of effluent discharge.

11.2 EXPERIMENTAL

11.2.1 Sampling

The mill remained closed for eleven and a half weeks, and reopened on 3rd October 1986. During this time the effluent loading to the river was slowly decreased and eventually ceased altogether. Water samples were taken periodically at the State Highway 30 and State Highway 2 bridges from 31st August 1986 to 16th October 1986. These samples were collected from the centre of the river by

throwing a pail attached with a length of rope from the bridges. River samples were taken again during February 1987 when the mill was operating at near normal capacity.

During the first sampling period (31st August to 16th October 1986), a set of sediment samples was also taken from the river banks at the Tarawera Park (upstream of where the river is affected by the Kawerau Borough Council, Caxton Paper Mill or Tasman Pulp and Paper Mill discharges), the State Highway 30 bridge, and the State Highway 2 bridge. A clean spade was used to scoop surface sediment from the river bank. The sample obtained from the river bank above the discharge point was fibrous, dark, and slimy whereas those taken from below Tasman's discharge point had the same appearance but also a strong odour. Both types of the river samples formed fine powders when dried.

A river survey was carried out on 26th September 1986 in conjunction with the Ministry of Works, Water Quality Centre, Hamilton. During the survey, water and sediment samples were obtained from the centre of the river at several points along its length, beginning at the site of Tasman's water intake and finishing at the river mouth at Matata (Figure 11.1). A motorboat was used for the survey. There was a lag time of 5 hours from the start of the sampling programme to its completion at the river mouth. Water samples were collected directly into alkali-rinsed glass winchesters and stored in an ice-chilled container while being transported to the University of Waikato laboratory where they were stored at 4^{o} C until required for analysis.

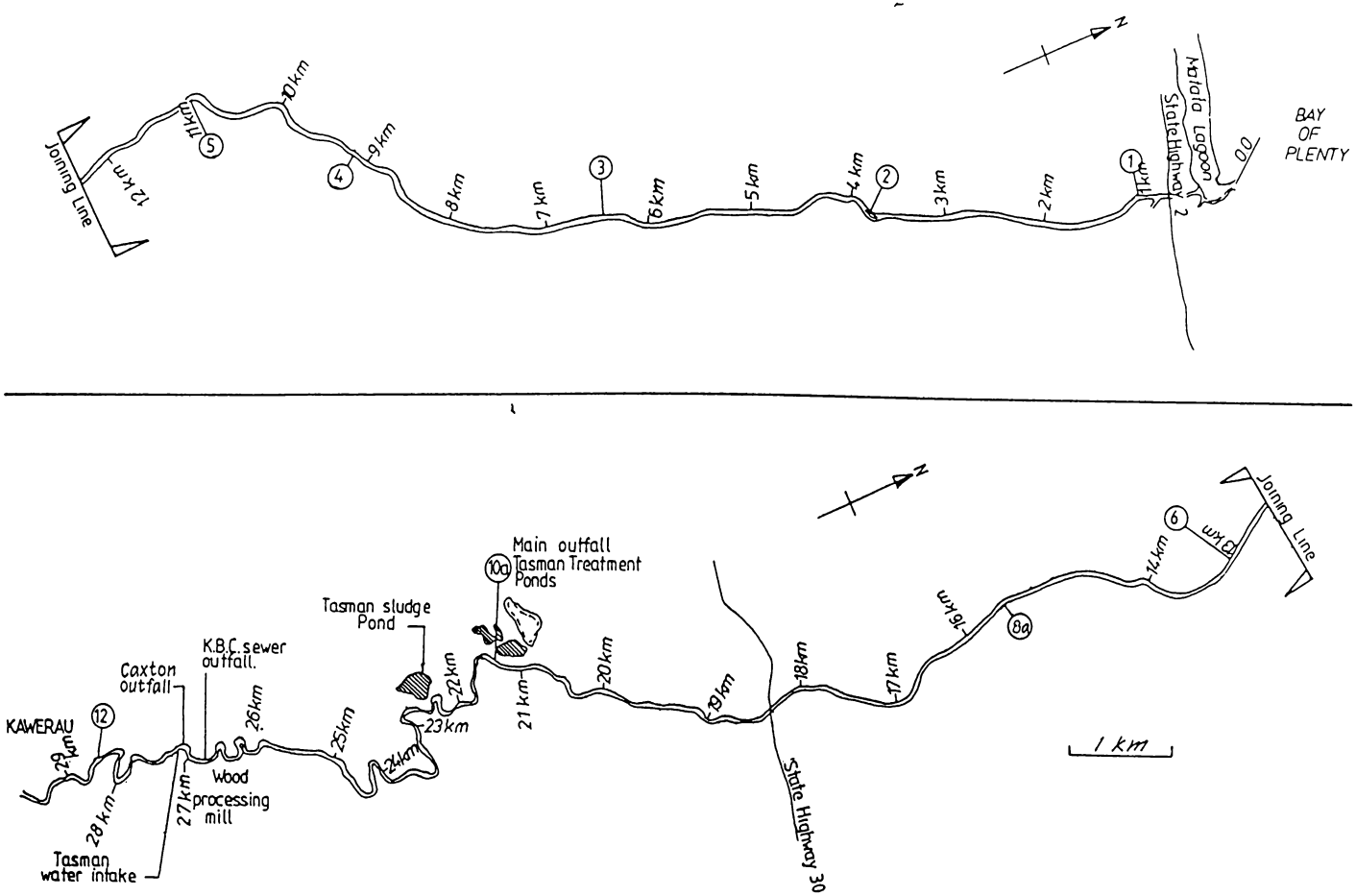


Figure 11.1 Tarawera River survey (26th September 1986) sampling sites (Source: Bay of Plenty Catchment Commission)

Sediment samples collected during the survey were dredged using a weighted metal container. These were then transferred to polythene bags and were stored in ice-chilled containers while being transported. In contrast to the river bank samples, these samples were granular in nature comprising mainly of pebbles and pumice sand, and were odourless.

11.2.2 Extraction and Analysis

The river water samples were extracted either for 12 hours with redistilled chloroform using continuous liquid-liquid extraction or separating funnel procedures. *n*-Octadecane was added as internal standard at the rate of 100 µg/l. The extracts were concentrated, dried, methylated with diazomethane and analysed by capillary GC-FID and GC-ITDS in the manner reported previously.

The sediments were dried at *ca* 100°C, and known weights (~1 g) were extracted for 12 hours with redistilled chloroform in an all-glass Soxhlet apparatus. A standard solution (1,000 µg/ml) of *n*-octadecane in chloroform was introduced into the extraction thimble at the rate of 100 µg/g. The extracts were concentrated, dried and methylated with diazomethane as previously described in Chapter Four. These were analysed by GC-FID and where necessary by GC-ITDS.

BOD_5 measurements for the aqueous samples collected during the survey were carried out by the Water Quality Centre, Hamilton using standard procedures (Standard Methods for the Examination of Water and Wastewater, 1971).

11.3 RESULTS

11.3.1 Periodic Sampling at SH30 and SH2

The concentration of the extractable organic compounds present in the river samples taken from August 1986 to February 1987 are summarized in Table 11.1. In February 1987, data was obtained for a period of three weeks when mill operations were normal except that only two of the three paper machines were in operation. Figure 11.2 illustrates the variation of concentration of the extractable organic compounds with time.

River water concentrations remained low and fairly constant during the period of closure when there was little discharge from the treatment system. Comparisons of the levels for total extractable organic compounds in the discharge during start-up and steady state (Figure 10.2) with the levels found in the river at SH30 and SH2 provided no evidence of the river having appreciable assimilative capacity for effluent species observed either during the period of start up or steady state. River samples taken on 31st August, 13th October and 14th October were found to contain palmitic acid at levels higher than expected. Since palmitic acid was not a major constituent of Tasman's discharge on these dates, another source of palmitic acid is implicated.

11.3.2 River Survey: 26th September 1986

The total amount of extractable organic compounds present in the various aqueous samples taken during the survey was very low (<20 μg/l). The majority of the characteristic mill effluent compounds

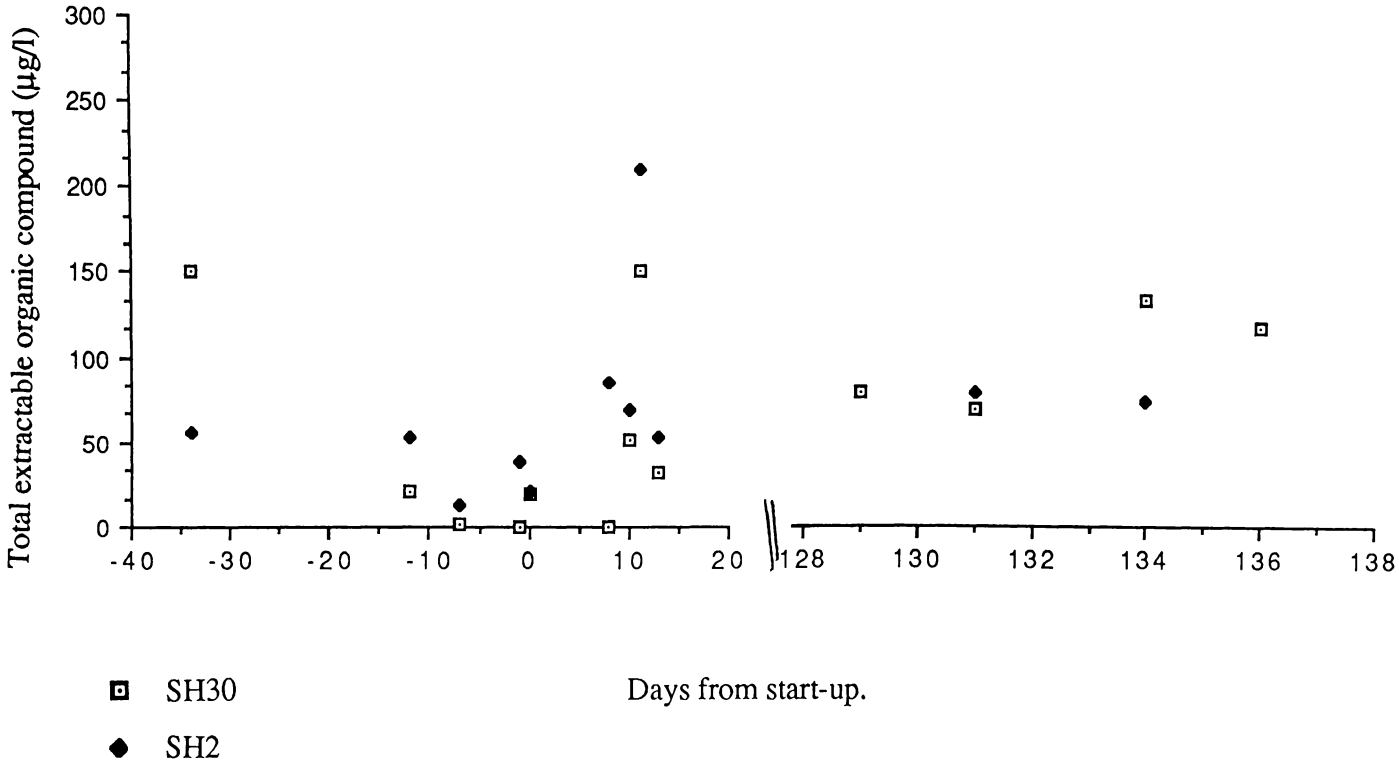


Figure 11.2 Profile of the Tarawera River at State Highways 30 and 2 during start-up and steady state

Table 11.1

Concentrations (µg/l) of derivatised extractable organic substances in Tarawera River water samples (SH30 and SH2 bridges) before and after start-up (days before or after startup are given in brackets).

		August-October 1986									February 1987			
		31.9	21.9	26.9	2.10	3.10	11.10	13.10	14.10	16.10	10.2	13.2	16.2	18.2
Compound	Site	(-34)	(-12)	(-7)	(-1)	(0)	(8)	(10)	(11)	(13)	(129)	(131)	(134)	(136)
Methyl palmitate	SH30	103	21	2	-	7	-	51	103	12	10	-	22	-
	SH2	30	27	5	24	7	36	40	144	14	-	-	-	-
Dehydroabietin	SH30	3	-	-	-	-	-	-	3	0.2	-	-	-	-
	SH2	1	0.5	-	-	-	-	0.5	-	0.2	-	-	-	
1,2,3,4-Tetrahydroretene	SH30	-	-	-	-	-	-	-	-	-	-	-	-	-
	SH2	1	0.7	-	-	-	-	0.7	-	2	-	-	-	-
Methyl oleate	SH30	9	-	-	-	3	-	-	9	2	5	-	20	31
	SH2	-	6	3	3	7	22	10	18	2	-	-	-	-
Methyl stearate	SH30	30	-	-	-	5	-	-	30	3	5	-	21	34
	SH2	14	10	2	10	4	18	10	38	5	-	-	-	-
Methyl pimarate	SH30	1	-	-	-	-	-	-	1	2	15	14	23	11
	SH2	-	2	0.6	0.8	0.5	4	2	-	5	-	15	15	-
Methyl isopimarate	SH30	-	-	-	-	-	-	-	-	2	12	16	15	14
	SH2	-	-	0.4	-	0.6	2	-	-	3	-	17	15	-
Methyl abietan-18-oate	SH30	1	-	-	-	3	-	-	1	5	21	22	24	18
	SH2	2	0.8	1	-	2	3	2	-	12	-	20	22	-
Methyl dehydroabietate	SH30	3	-	-	-	2	-	-	3	6	25	24	23	21
	SH2	8	6	1	1	2	3	4	10	11	-	26	23	-

were either not detected or were present at levels at or below the 0.1 µg/l quantification limit. Only acid species were found consistently in the river water samples. Of these, the fatty acids, palmitic acid and stearic acid, were the major components. These were found at fairly constant levels above and below the various discharge points along the river's course. Of the resin acids, only dehydroabietic acid and abietan-18-oic acid were found in significant concentrations below the Tasman discharge point.

The data for the acid compounds detected in river water samples are presented in Table 11.2. No systematic trends was observed, however the absence of resin acids at SH30 and SH2 may be significant. SH30 is close to the discharge point and so the river water at this point would have had only a short period of contact with sediment-bound resin acids previously absorbed onto the river bottom material. The absence of resin acids at SH2 could be due to the tidal nature of the river at that point. It is not known whether the tide was in or out at the time of sampling.

Included in Table 11.2 is data for BOD_5. An abrupt increase in BOD_5 occurred below the Caxton and Kawerau Borough discharges but no significant further change occurred below this point in the river. Presumably the river's assimilative capacity was being balanced by other discharges.

Samples of mid-river sediments were taken at the same time as the river water samples. Table 11.3 summarizes the extractable organic compounds of these samples. No resin acids were observed at the discharge point or at the SH30 (3 km downstream from the

Table 11.2

Concentrations (µg/l) of derivatised extractable organic compounds detected in Tarawera River water samples of 26th September 1986. Site locations are as in Figure 11.1.

Compound	12	10B	SH30	8A	6	3	SH2
Methyl myristate	-	-	2.8	2.8	2.5	2.6	2.0
Methyl palmitate	5.0	-	3.3	2.3	3.1	5.1	1.0
Fichtelite	-	-	-	-	-	-	-
Methyl anteisoheptadecanoate	1.4	-	-	-	-	-	-
Methyl oleate	2.0	-	-	1.8	1.7	-	-
Methyl linoleate	-	-	-	-	-	-	-
Methyl stearate	2.2	-	1.3	1.3	1.2	2.1	-
Retene/methyl secodehydroabietate-2	-	-	0.7	-	0.3	-	0.2
Methyl pimarate	-	-	0.6	0.3	-	0.6	-
Methyl isopimarate	-	-	-	-	-	-	-
Methyl abietan-18-oate	-	-	0.3	0.6	-	5.8	-
Methyl dehydroabietate	-	-	0.7	0.5	-	4.7	-
BOD_5 (mg/l)	0.06	1.02	1.08	1.43	1.23	1.06	1.1

Table 11.3

Concentrations (µg/g) of derivatised extractable organic substances in Tarawera River sediment samples of 21st and 26th September 1986. Site locations are as in Figure 11.1.

	Gravel and sand material[a]							Clay material[b]	
Compound	12	10B	SH30	8A	6	3	SH2	SH30	SH2
Methyl myristate	-	0.5	-	0.5	0.4	0.4	0.1	-	-
Methyl palmitate	6.3	8.0	2.3	10	8.8	5.5	5.4	15	6.8
Fichtelite	-	-	-	-	-	-	-	-	2.5
Methyl anteisoheptadecanoate	-	-	-	0.6	0.5	0.3	0.3	-	2.4
Methyl oleate	2.6	1.3	-	4.7	4.2	2.9	2.7	12	2.4
Methyl linoleate	-	-	-	-	0.3	0.7	0.5	-	-
Methyl stearate	2.2	3.2	-	0.9	3.5	2.2	2.1	9.0	7.0
Retene/methyl secodehydroabietate-2	-	-	-	-	0.3	-	0.2	16	3.5
Methyl pimarate	-	-	-	-	1.5	0.2	0.6	57	25
Methyl isopimarate	-	-	-	-	1.6	0.3	0.4	83	27
Methyl abietan-18-oate	-	-	-	2.1	1.6	0.6	1.0	344	97
Methyl dehydroabietate	-	-	-	2.1	2.3	0.9	1.3	185	76

[a] Mid-river sediment samples (26th September 1986).

[b] River bank sediment samples (21st September 1986).

discharge point). Resin acids were first detected at a site 7 km downstream from the discharge point. Except for the sample taken at SH30, the levels of fatty acids remain essentially constant down the river's length.

11.3.2 River Bank Sediment Studies

The GC profiles of the river bank sediment extracts appear in Figures 11.3 to 11.5 and the peak numbers refer to compounds listed in Table 11.4. In contrast to the low organic content of the sediment extracts from the mid-river samples, the river banks afforded a wider range of extractable organic compounds, namely fatty acids, resin acids and resin hydrocarbons.

The major components detected were pimaric acid, 8-abieten-18-oic acid (8), pimaran-18-oic acid (9), 8(14)-pimaren-18-oic acid (10), 13-abieten-18-oic acid (11), abietan-18-oic acid (8), dehydroabietic acid (6), abietic acid (7) and 7-oxodehydroabietic acid (15). Trichloroguaiacol and pentachlorophenol were detected on the GC-ITDS using selected ion monitoring. This is consistent with the earlier findings of tetrachloroguaiacol and pentachlorophenol in Tarawera River samples (Wilkins and Panadam, 1987). Other compounds detected were methyl nonanoate, methyl decanoate, methyl dodecanoate, methyl myristate, methyl *iso*- and *anteiso*pentadecanoate, methyl 14-methylhexadecanoate, methyl heptadecanoate, dehydroabietane, pentachlorophenol, fichtelite (17), 1,2,3,4-tetrahydroretene (19), and methyl linoleate. These compounds were present in quantities lower than 5 µg/l and were not listed in Table 11.2.

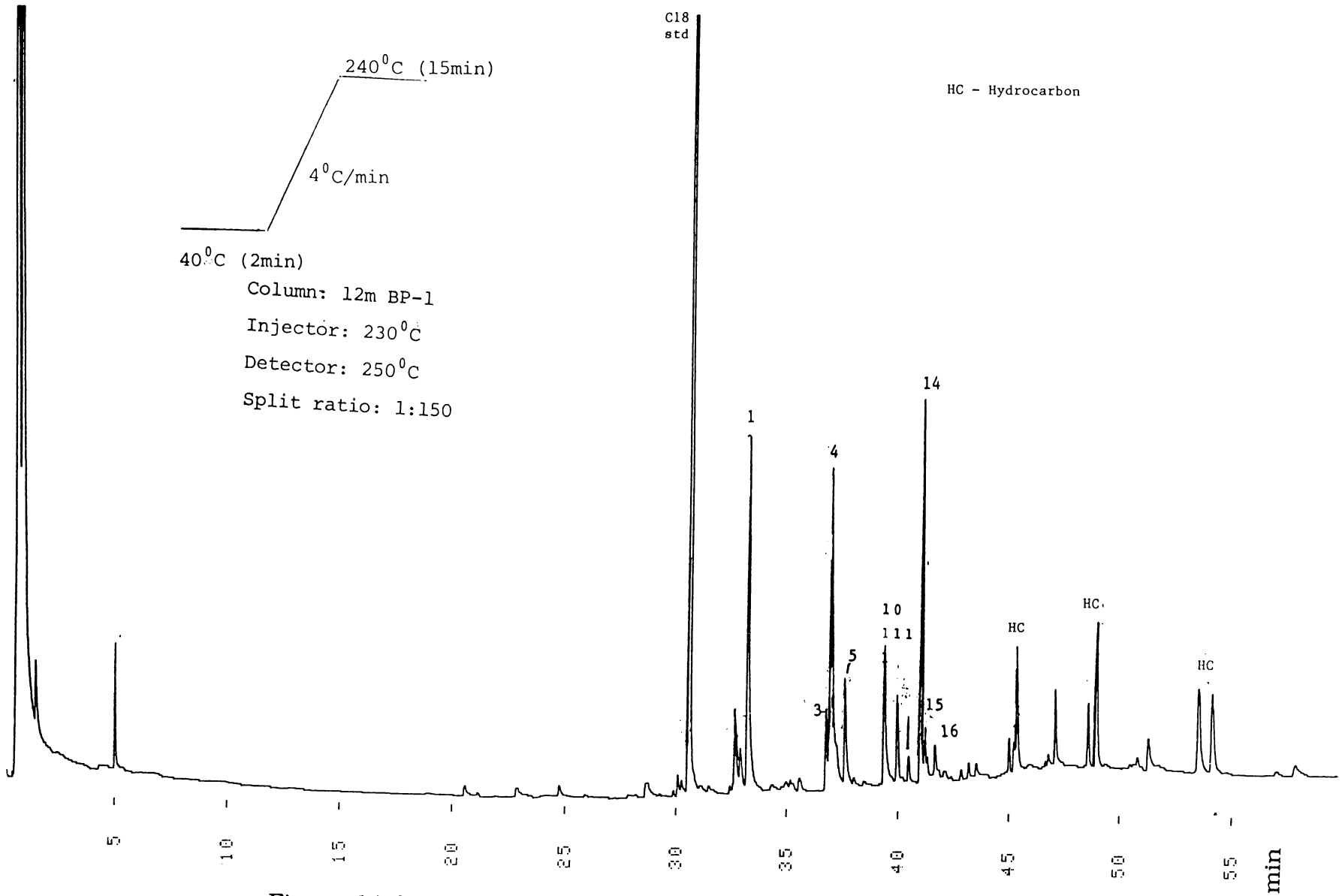


Figure 11.3 GC-FID profile of an extract of the Tarawera Park bank sediment (21st September 1986) For peak identifications see Table 11.4.

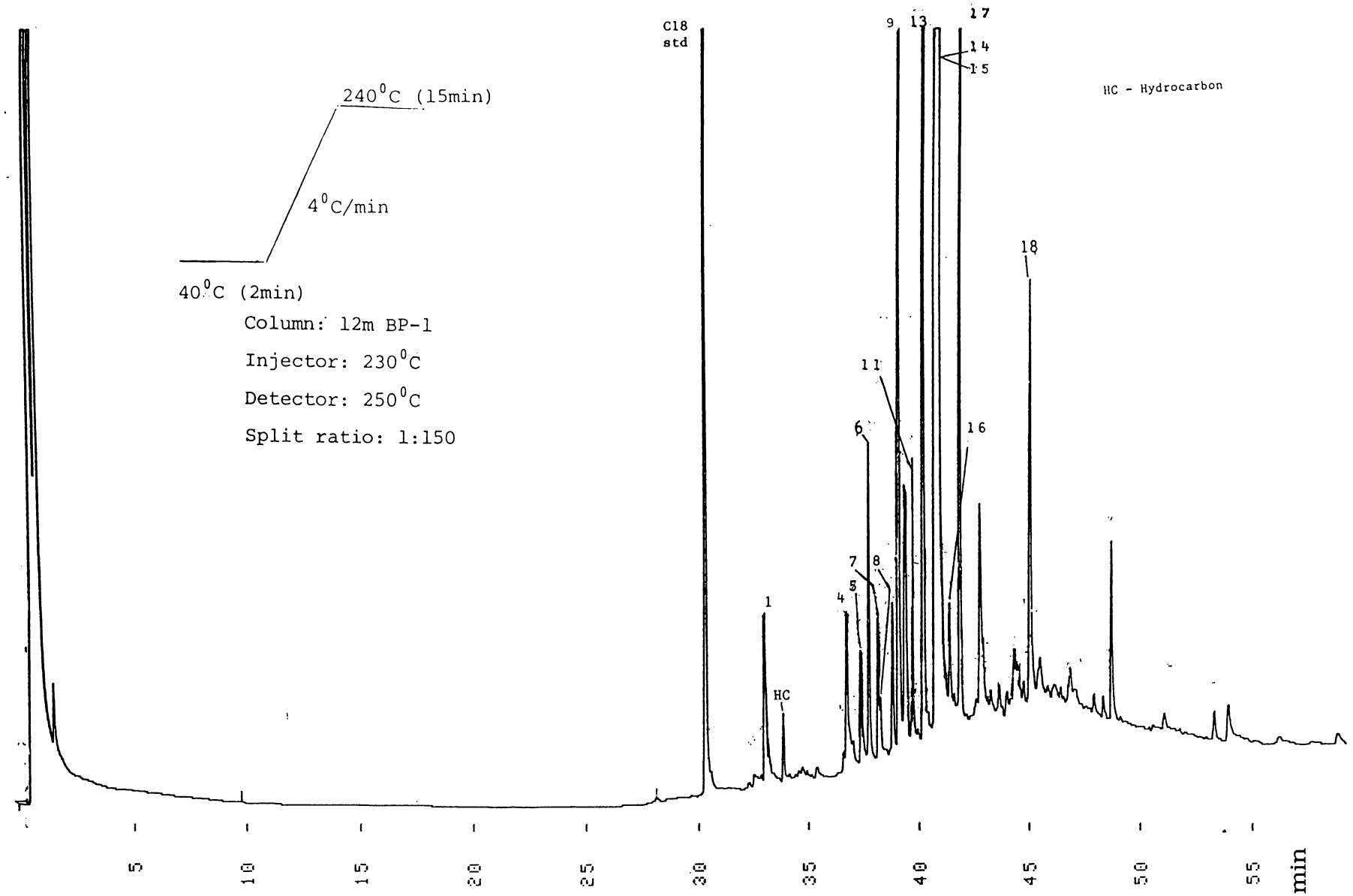


Figure 11.4 GC-FID profile of an extract of SH30 bank sediment (21st September 1986) For peak identifications see Table 11.4.

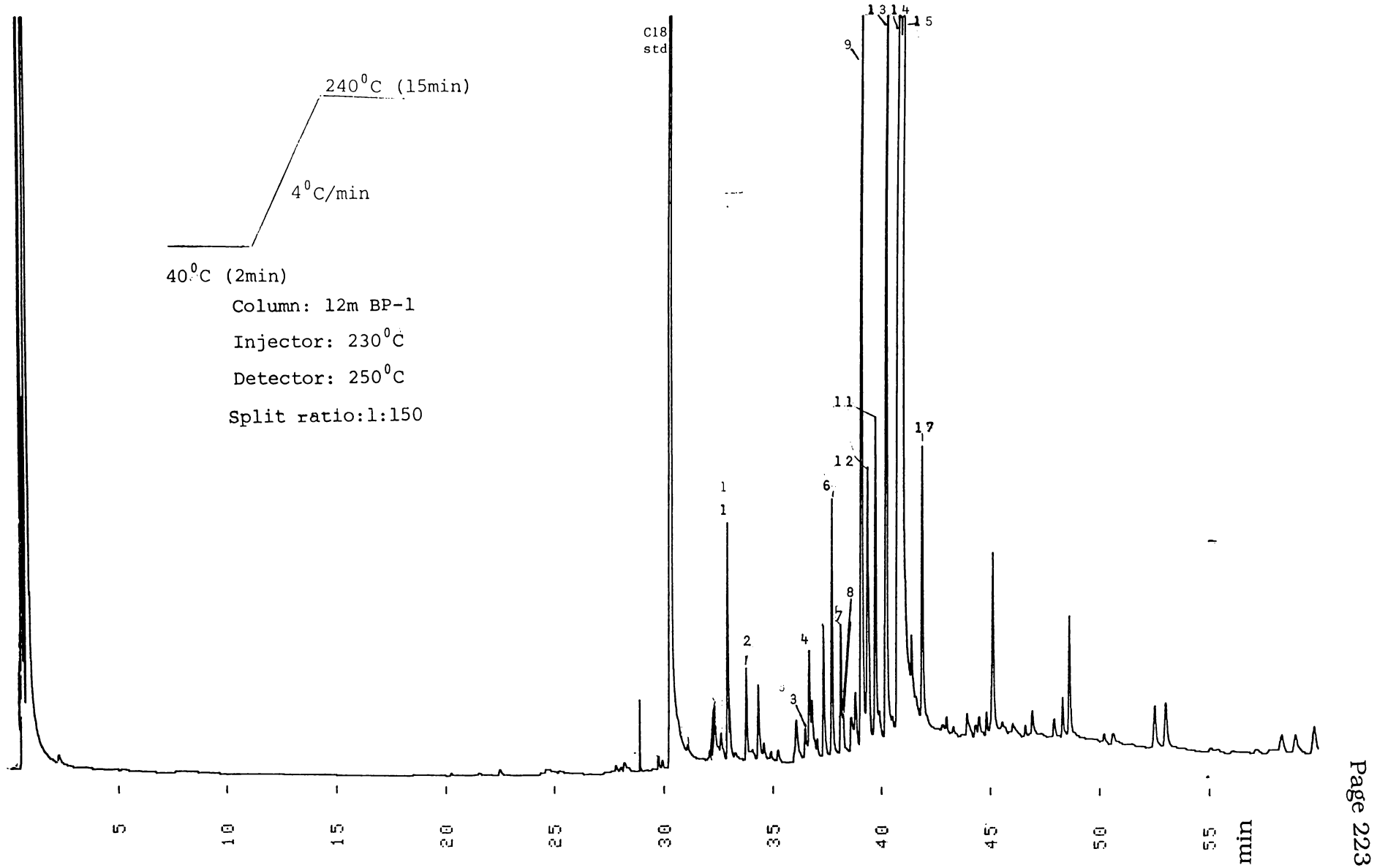


Figure 11.5 GC-FID profile of an extract of SH2 bank sediment (21st September 1986) For peak identifications see Table 11.4.

TABLE 11.4
Concentrations of extractable organic compounds detected in the Tarawera River bank sediments. 21st September 1986.

Peak No	Compound	Park (µg/g)	SH30 (µg/g)	SH2 (µg/g)
1	Methyl Palmitate	15	23	10
2	Dehydroabietin	*	9	-
3	Methyl linoleate	2.6	-	3.5
4	Methyl oleate	12	28	5
5	Methyl stearate	5	15	6
6	Methyl secodehydroabietate-1	*	42	7
7	Methyl secodehydroabietate-2	-	18	-
8	Retene	-	9	-
9	Methyl pimarate	-	94	25
10	Methyl 8-abieten-18-oate	-	33	*
11	Methyl pimaran-18-oate	-	17	-
12	Methyl 8(14)-pimaren-18-oate	-	23	11
13	Methyl 13-abieten-18-oate	-	92	10
14	Methyl abietan-18-oate	8	92	98
15	Methyl dehydroabietate	-	75	76
16	Methyl eicosanoate	-	23	-
17	Methyl abietate	-	89	13
18	Methyl 7-oxodehydroabietate	-	54	-

(-) Not detected in the sample; (*) present in less than 5 µg/l.

11.3 DISCUSSION

While the hydrodynamics of the Tarawera River are not yet fully understood, it is known that the river bed consists of fine pumice material over its lower reaches formed as a result of previous volcanic activity (Tarawera River Management Plan, 1985). Due to the low specific gravity of pumice, the bed is relatively mobile down to depths in excess of 1 metre. The pumice bed material acts as a

medium and supports an active biological community. Hence, organic substances bound to the pumice are constantly being moved.

The presence of extractable organic compounds in the mid-river sediments could result from two causes: adsorption by the pumice material of the river bottom or precipitation/co-precipitation from the river water due to interactions between the effluent species and river water components such as suspended clay, iron [Fe(III)], and silica. Laboratory studies (Panadam, unpublished) have shown that fatty acids are bound to lignin and therefore will be removed from solution by processes that cause lignin removal. It has not been possible to discriminate between the possibility of adsorption or precipitation in this study.

While it has not been proven, it seems most likely that during the period of mill closure, river water levels of resin acids were maintained by desorption from the large effective surface area of the river bottom pumice or the water entrapped in this pumice. The fatty acid concentrations were highly variable both above and below the discharge point. No systematic increase in fatty acid levels was observed after the re-start of mill operations. This suggests other sources *e.g.* natural, agricultural, or municipal (runoff) are responsible for the bulk of the fatty acids found in the river samples.

The extracts of samples taken from the river banks contained a higher concentration of extractable organic compounds than those from the mid-river samples. This could be related to river flow rates. The slower, less turbulent flow at the banks could facilitate precipitation. It is also possible that when ground water meets river

water close to the banks, precipitation and flocculation occurs. The ground waters of the Rangitaiki plains are high in iron [Fe(III)] content and laboratory studies (Panadam, unpublished) have shown that flocculation with iron [Fe(III)] resulted in the removal of 95% of the resin acids and fatty acids present in an effluent sample. In addition, the smaller particle size and higher clay content of bank sediments would give rise to greater adsorptive capacity.

Traces of chlorinated organics (>0.1 μg/l) were found to be present in the river bank sediments below Tasman's discharge point even though they were not detected in the aqueous samples during the period of closure. Chlorinated compounds can be concentrated in sediments from low water concentrations (Kinae *et al*, 1981; Salkinoja-Salonen *et al*, 1981). Once bound by the sediment, they are highly persistent. Given the thousand-fold increase in sensitivity that can be achieved by GC-ECD method (Lindström and Nordin, 1976; Lindström *et al*, 1981) it is likely that further studies of chlorinated compounds in the river bank sediments will yield results of environmental significance.

CHAPTER TWELVE

CONCLUSION

The principal classes of extractable organic substances found in the black liquor, white water, tall oil and bleach plant samples were in keeping with those reported in overseas studies. The high levels of aromatic compounds in black liquor enables them to be used as source markers. Monitoring of the levels of 4-hydroxy-3-methoxy-benzaldehyde and 4-hydroxy-3-methoxyacetophenone is a feasible procedure for determining the progress of black liquor spills through the treatment system.

Tasman's No. 1 bleach plant effluent contains fatty acids, resin acids, and mono- and dichlorinated analogues of guaiacol and other aromatic substances including 4-hydroxy-3-methoxyacetophenone and 4-hydroxy-3-methoxybenzoic acid. The No. 2 bleach plant effluent also included a similar array of aromatic mono- and dichlorinated compounds together with significant quantities of the corresponding trichlorinated aromatic compounds, and a number of chlorinated monoterpenes. The presence of chlorinated pinenes and terpineols in the No.2 bleach plant effluents is a feature of chlorine bleaching of New Zealand *P. radiata* pulp from continuous digestion.

The resin acids are present in low levels in white water although they are the major constituents. Pitch from the paper machines was found to comprise mainly fatty acids and resin acids

together with modest levels of aromatic acids. The presence of these compounds in the recycled wash water could accentuate pitch problems in paper manufacture.

Refined turpentine from Tasman is typical of that reported for *P. radiata i.e.* β-pinene is the major component. However, α-terpineol is the dominant component in crude turpentine. Monitoring of α-terpineol in the treatment system can be used to assess turpentine losses.

The effluent treatment system was studied at steady state before and after the introduction of a third aerated pond, and also at start-up after a prolonged mill closure. On each of these occasions the treatment system was found to have an immediate assimilation capacity. Increasing the average retention time from 4 to 8-days resulted in the discharge of lower levels of extractable organic compounds. This reduction in the levels of extractable organic compounds was reflected in lower BOD_5 values. Aromatic compounds and 2-cyclopentenone derivatives were usually reduced to levels below that of the detection limit of the present study, though traces of trichlorophenol and tetrachloroguaiacol were detected on some occasions. The use of GC-ECD would enable the detection of chlorinated compounds in much lower levels while integrated time average sampling and the use of an auto sampler would improve the reliability and precision of the data.

A unique aspect of Tasman's treatment system is the relatively high levels of anaerobic degradation products, typically up to 50% of

the total resin acid component of the final discharge. The effect of these compounds on the biological community is as yet uncertain.

The sediment from the treatment ponds was found to include monoterpene hydrocarbons and polychlorinated aliphatic compounds.

BOD_5 was found to decrease exponentially through the treatment system. There was only a limited degree of correlation between BOD_5 and total extractable organic compounds, total resin acids and pimaric acid. However, due to the overall variability of the treatment system and/or the limitations of the analytical techniques, further research is required to assess whether a relationship between extractable organic compounds and BOD_5 could be used as a management tool.

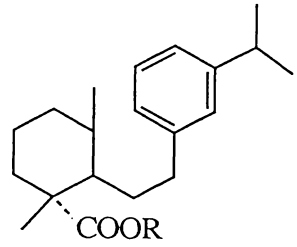
The Tarawera River was found to have little assimilation capacity during start-up after a period of mill closure and at steady state. The river sediments were observed to have retained resin acids and chlorinated compounds strongly even after six weeks of mill closure. Concentrations in bank sediments were higher than in mid-river sediment.

APPENDIX A

Resin acid structures

a: R = H

b: R = CH_3



Secodehydroabietic acid-1
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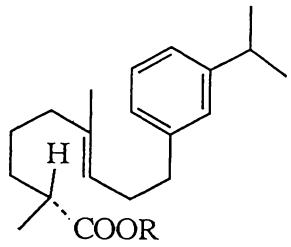

Secodehydroabietic acid-2
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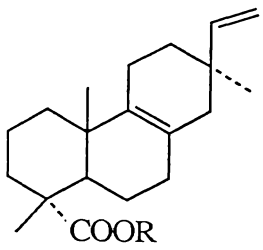

Pimaric acid
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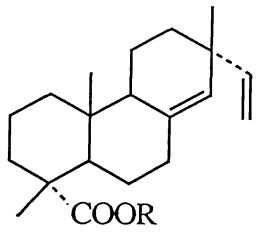

Sandaracopimaric acid
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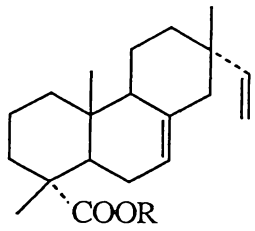

Isopimaric acid
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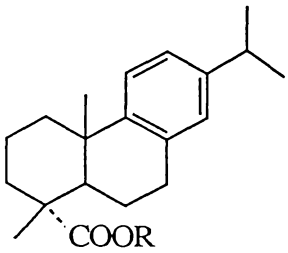
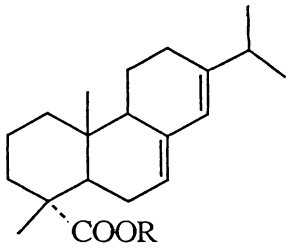
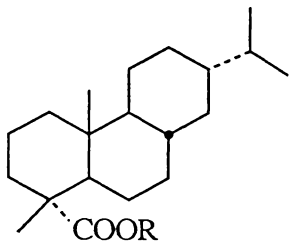


Dehydroabietic acid
6



Abietic acid
7



Abietan-18-oic acid
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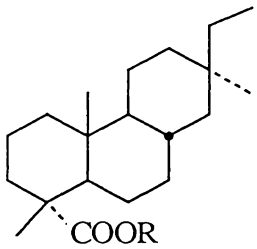

Pimaran-18-oic acid
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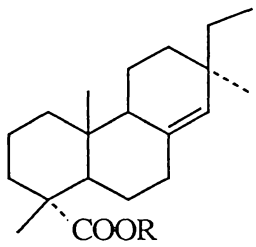
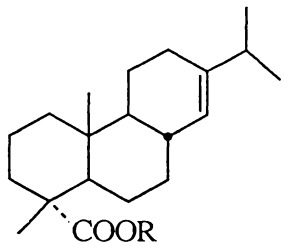


8(14)-Pimaren-18-oic acid
10

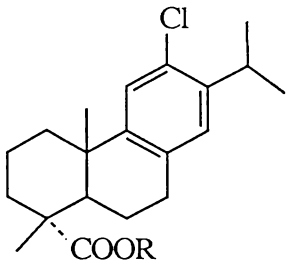


13-Abieten-18-oic acid
11

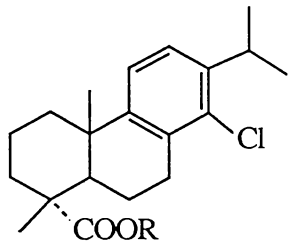
Resin acid structures

a: R = H

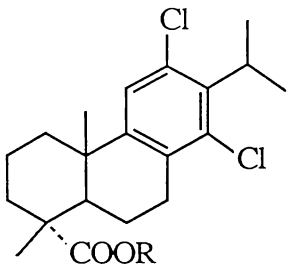
b: R =CH_3



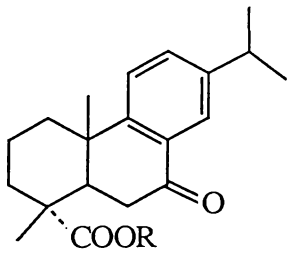
12-Chlorodehydroabietic acid
12



14-Chlorodehydroabietic acid
13



12,14-Dichlorodehydro-abietic acid
14



7-Oxodehydroabietic acid
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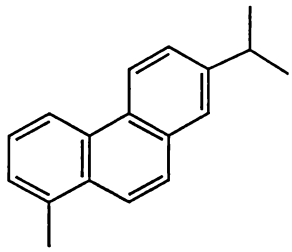

Retene
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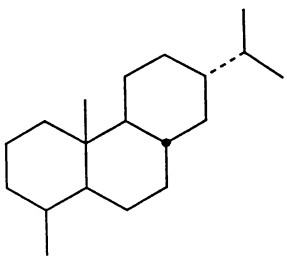

Fichtelite
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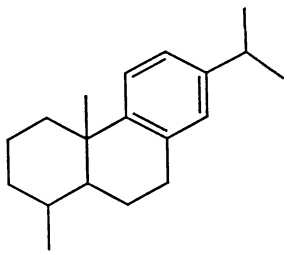

Dehydroabietin
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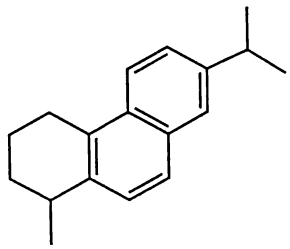
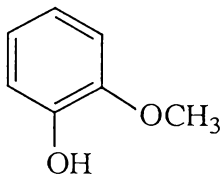
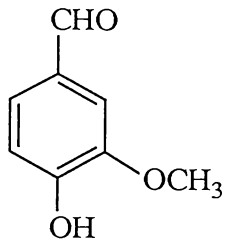


1,2,3,4-Tetrahydroretene
19



2-Methoxyphenol
20



4-Hydroxy-3-methoxy-benzaldehyde
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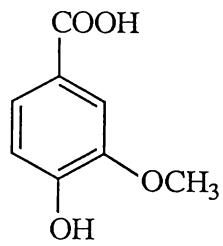

4-Hydroxy-3-methoxy-benzoic acid
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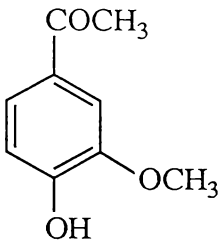

4-Hydroxy-3-methoxy-acetophenone
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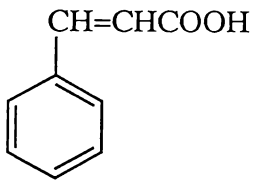
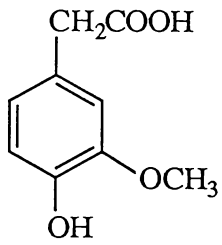


Cinnamic acid
24



4-Hydroxy-3-methoxy-phenylacetic acid
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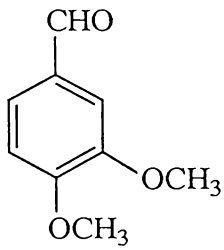
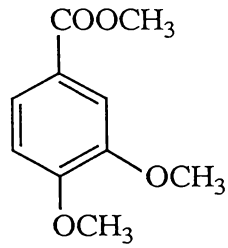


3,4-Dimethoxybenzaldehyde
26



Methyl 3,4-dimethoxy-benzoate
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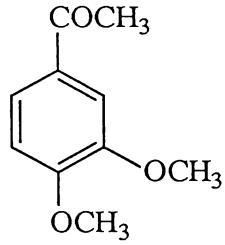
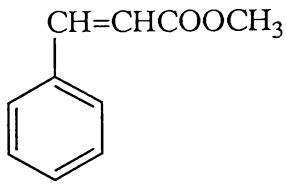
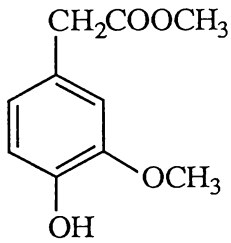


3,4-Dimethoxyacetophenone
28



Methyl cinnamate
29



Methyl 4-hydroxy-3-methoxyphenylacetate
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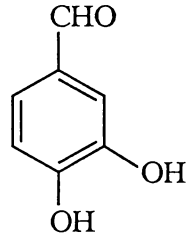
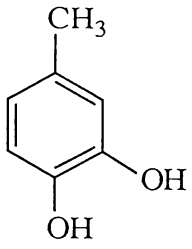


3,4-Dihydroxybenzaldehyde
31



3.4-Dihydroxytoluene
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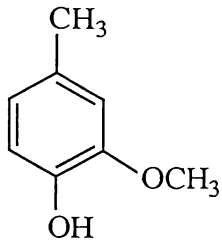
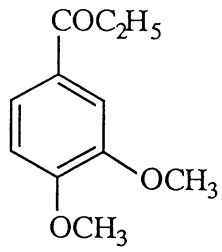
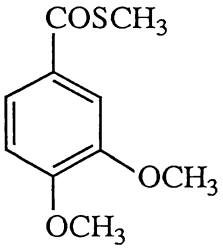


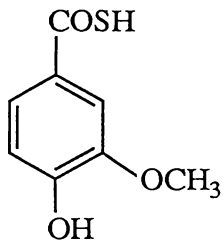
4-Hydroxy-3-methoxy-
toluene
33



3,4-Dimethoxy-
phenylpropan-1-one
34



Methyl 3,4-dimethoxy-
phenylthioate
35



4-Hydroxy-3-methoxy-
phenylthioic acid
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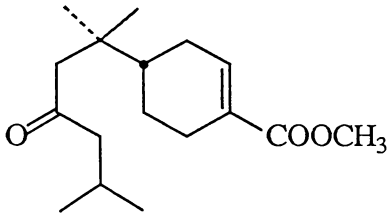

Juvabione
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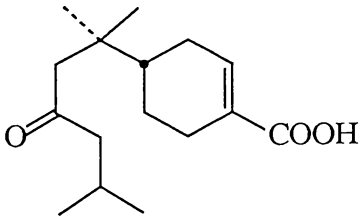

Todomautic acid
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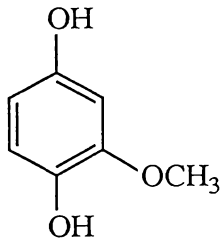
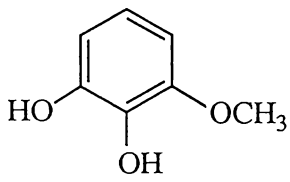


2-Methoxybenzene-
1,4-diol
39

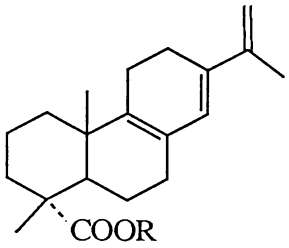


3-Methoxybenzene
1,2-diol
40

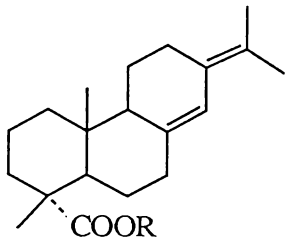
Resin acid structures

a: R = H

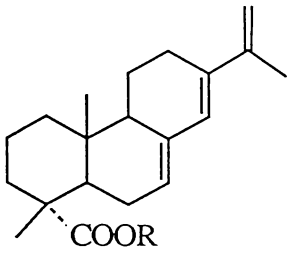
b: R =CH_3



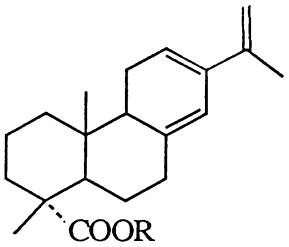
Palustric acid
41



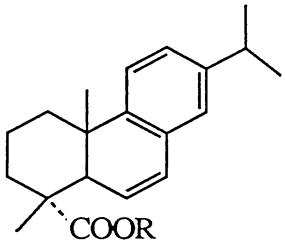
Neoabietic acid
42



7,13,15-Abietatrien-18-oic acid
43



Levopimaric acid
44



6,8,11,13-Abieta-
tetraen-18-oic acid
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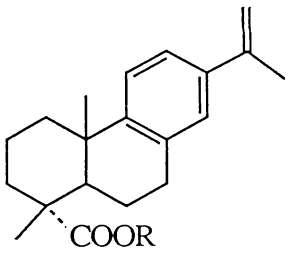

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tetraen-18-oic acid
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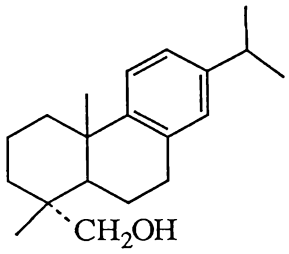

Dehydroabietenol
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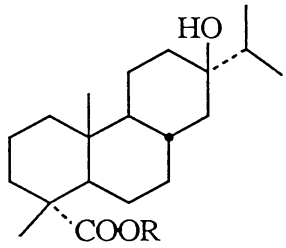
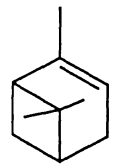


13β-Hydroxyabietan-18-oic
acid (Kinleithic acid)
48



α-Pinene
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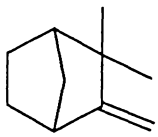

Camphene
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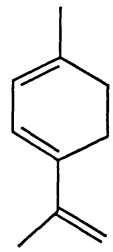

p-Mentha-1,3,8-triene
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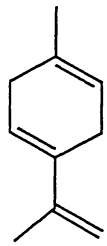
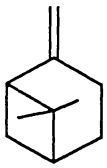


1-Methyl-4-(1-methylethenyl)-
1,4-cyclohexadiene
52



β-Pinene
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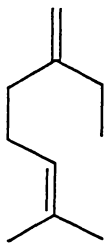

Myrcene
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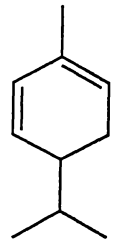

α-Phellendrene
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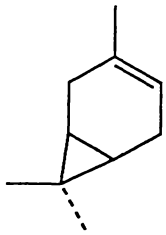

3-Carene
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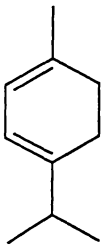
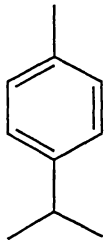


α-Terpinene
57



p-Cymene
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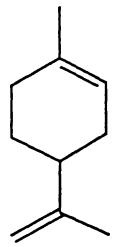

Limonene
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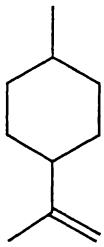

1-(1-Methylethylene)-
4-methylcyclohexane
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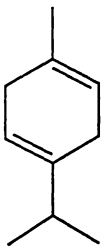

γ-Terpinene
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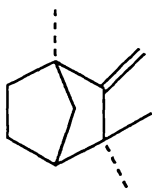

Fenchone
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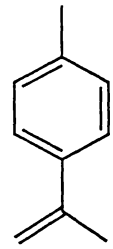

α,*p*-Dimethylstyrene
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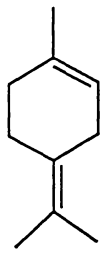

Terpinolene
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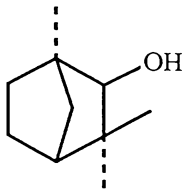

Fenchol
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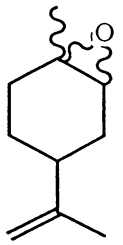
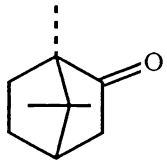


Limonene-
1,2-epoxide Fr.1
66



Camphor
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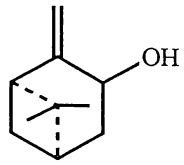

Trans-pinocarveol
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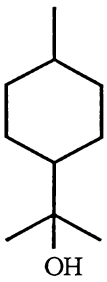
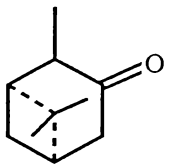


1-(1-hydroxy-1-methyl)-
4-methylcyclohexane
69



Pinocamphone
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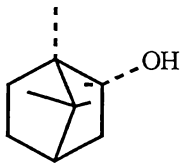

Borneol
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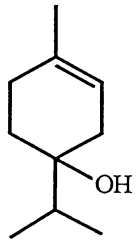

Terpen-4-ol
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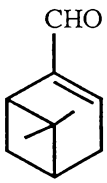

Myrtenal
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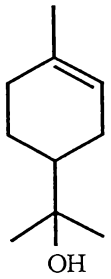
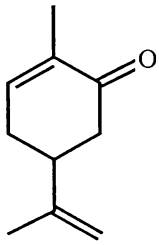


α-Terpineol
74

Myrtenol
75



Carvone
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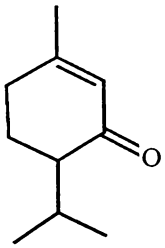

Piperitone
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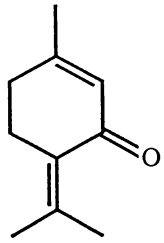

Piperitenone
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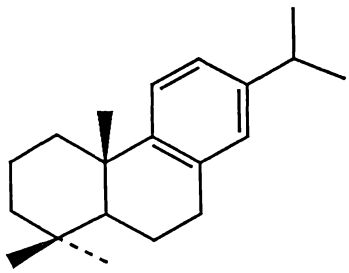
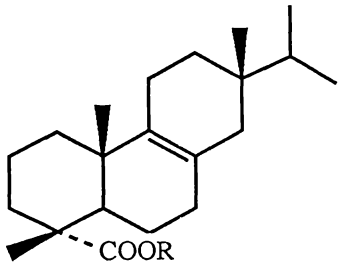


Abiet-8,11,13-triene
79



8-Abieten-18-oate
80

APPENDIX B

Extractable organic substances from the discharges of a New Zealand pulp and paper mill

ALISTAIR L. WILKINS* AND SIVA PANADAM†

SUMMARY

The extractable organic substances in the final discharge and in river water collected downstream from the discharge point of a New Zealand pulp and paper mill utilizing radiata pine have been investigated. Whilst biological treatment proved to be an effective procedure for reducing the levels of the majority of extractable species, some substances formed in an anaerobic region of the treatment system proved to be resistant to subsequent aerobic degradation and were persistent in the final discharge and downstream river water samples. The characterization of these substances by gas chromatographic-mass spectrometric procedures is discussed.

More than a thousand extractable organic substances have been isolated from the effluent streams and treatment systems of pulp and paper mills. Many of these substances are present in comparatively small quantities, and can only be detected with high performance instruments, the chief of which are a capillary column gas chromatograph interfaced to a mass spectrometer (GC-MS). Such instruments are expensive and usually found only in research institutions. These systems are capable of detecting constituents present in concentrations in the mg/L to μg/L ranges. Ion trap and mass selective detectors have also proved useful in confirming peak identifications.

Once the identity of the peaks appearing in the GC trace have been established it is generally possible to routinely monitor the concentrations of individual species without the requirement of a MS interface since the resolving power of narrow bore fused silica capillary columns, as short as 12 metres, is such that few peaks co-elute.

Because some of the substances which are released into the effluent streams of pulp and paper mills are environmentally sensitive there is an increasing awareness of their presence amongst organizations responsible for water management.

Classes of low molecular mass extractable substances which are widespread in pulp and paper mill effluents include monoterpenes, aromatics, fatty acids and resin acids(1,2,3,4,5,6). Bleaching operations are responsible for the presence of chlorinated substances such as chlorinated aromatics, fatty acids and resin acids(7,8,9,10).

Monoterpenes such as α- and β-pinene, limonene, fenchyl alcohol, terpene-4-ol and α-terpineol are major constituents of wood turpentine. Whilst most pulp mills seek to recover turpentine some of it escapes into mill effluent streams. Aromatic substances, like fatty acids and resin acids are major constituents of kraft pulp mill black liquors, and they escape in quantities, depending on plant design and operating practices, to effluent streams. Guaiacol and related derivatives have been regularly reported in the literature. Oxidized analogues such as 4-hydroxy-3-methoxybenzaldehyde and 4-hydroxy-3-methoxybenzoic acid are also frequently detected. Amongst the fatty acids, palmitic acid, oleic acid and linoleic acid are commonly encountered whilst abietic acid, dehydroabietic acid (DHAA) and pimaric acid are representative of resin acids. Abietic acid is the dominant resin acid constituent of New Zealand *Pinus radiata*.

The LD-50 (96 hour) of chlorinated guaiacols and resin acids towards fish are of the order of 300 to 1000 μg/L(11,12,13,14). In the case of DHAA the relationship between pH and observed LD-50 has been explored by McLeay *et al*(15,16). Biological treatment in aerated lagoons(17,18,19) or activated sludge treatment(20) is often employed to reduce the levels of low molecular mass substances in the final discharges of a pulp and paper mill, and thus lessen the impact which the final discharge has on the receiving water.

Whilst much is known about the discharges of overseas pulp and paper mills, little information is available in respect to New Zealand pulp and paper mills which primarily utilize radiata pine. As part of an assessment of the impact which industrial discharges have on waterways in the Waikato-Poverty Bay region of New Zealand's North Island, we had occasion to investigate the discharges of a major New Zealand pulp and paper mill. The combined kraft and mechanical pulp mill produces about 1200 tonnes per day. In the process the mill takes and discharges approximately 200 000 m^3 of water a day into the adjacent Tarawera River. This can represent up to 10% of the total river flow depending on the time of the year.

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Paper presented at 40th Annual General Conference, Auckland, New Zealand, 1986

EXPERIMENTAL PROCEDURES AND EVALUATION

Water samples were extracted using well established liquid-liquid or XAD-2 resin adsorption procedures. In our hands the former procedure gave more consistent results, this despite the more lengthy extraction time. When using XAD-2 difficulties were experienced in obtaining reliable recoveries of phenolic and acidic compounds. Previous workers have varied the pH of the effluent samples to optimize the recovery of resin acids, fatty acids and phenolic substances. The merits of the XAD-2 resin absorption techniques versus liquid-liquid extraction procedures has recently been discussed by Voss and Rapsomatiotis(21) who proposed the alternative of direct extraction in a separating funnel of an effluent sample acidified to pH 9 an equal volume of methyl-*tertiary*-butyl ether.

Water samples (1.5 or 2.3 litres) were acidified to pH 2 in a liquid-liquid extractor and extracted with chloroform for 16 hours. Acidification resulted in flocculation of polyphenolic material. If the flocculated material was filtered prior to extraction lesser levels of acidic compounds were recovered. After concentration under reduced pressure, to *c.* 0.5 mL the extractive solutions were derivatized with an ethereal diazomethane solution (*c.* 1.0 mL) and after further evaporation of the derivatized extracts to *c.* 150 μL, portions of the derivatized extracts were analysed by capillary column GC on 12 metre BP-1 columns installed in Varian 3700 and Pye 4500 instruments.

Typically 1 to 3 μL injections were split 1 to 50 in an SGE unijector (split mode). Analyses were temperature programmed over the ranges 60°C, hold 3 min; up 4°C/min to 250°C; hold 15 min (monoterpene, aromatic, fatty acid and resin acid analysis) or 150°, hold 2 min; up 4°C/min to 250°C; hold 15 min (fatty acid and resin acid analysis only). Hydrogen was employed as the carrier gas, the linear velocity of which was maintained in the region 350 to 400 mm/s. Under these conditions dehydroabietic acid, as its methyl ester was eluted from the BP-1 column at *c* 200°C and the methyl esters of dehydroabietic and abietan-18-oic acids were essentially baseline resolved. Higher elution temperatures (lower carrier gas linear velocities) resulted in a decreased degree of resolution for these methyl esters.

Internal standards, *n*-nonane and *n*-octadecane, (1 mg/mL in chloroform) were injected directly in the water samples immediately prior to liquid-liquid extraction at the dosages of 100 μg/L (river samples), 1000 μg/L (treatment pond samples) or 10 000 μg/L (selected mill sewers). A determination of the *n*-nonane/*n*-octadecane ratio allowed for an assessment of the extent to which comparatively volatile substance (*eg* monoterpene hydrocarbons such as α-pinene, bp 154°C, *n*-nonane bp 158°C) had been lost during evaporation and concentration of the extractives. With care the ratio of recovered *n*-nonane/*n*-octadecane versus added *n*-nonane/*n*-octadecane could be maintained in the region 0.7 to 0.8. It is apparent that some losses of the more volatile components (especially monoterpene hydrocarbons) occurs during the recovery and concentration procedure. The procedure described here allows for the estimation (and correction) of these losses, which in the absence of a correction will result in an under estimate of the actual concentration.

n-Heptadecanoic acid has commonly been used as an internal standard by other workers. Whilst *anteiso*-heptadecanoic acid was the dominant seventeen carbon fatty acid which occurred in the effluent samples, a significant quantity of the *n*-isomer (*c.* 40% of the *anteiso*-isomers concentration) was invariably present in the radiata pine effluents, hence the use of *n*-heptadecanoic acid as the internal standard was not considered to be appropriate. The selection of *n*-octadecane as internal standard was based on considerations of retention time and non-overlap with extractive peaks; thermal stability (not decomposed by extended periods of refluxing); chemical stability (does not react with alcohols or phenols to give esters); and partition coefficient. One of the mill sewers contained significant amounts of ethanol; extraction at pH 2 resulted in the partial formation of the ethyl esters of fatty acids (but not resin acids), and further mitigated against the use of a fatty acid as internal standard.

In the initial stages of the investigation the chloroform extractives were recovered after 16 hours, *n*-hexadecane internal standard solutions (concentrations as for *n*-octadecane) were injected into the water sample, and extraction continued for a further 16 hours. The second extract was devoid of extractives and *n*-octadecane. Response factors for α-terpineol, guaiacol, palmitic acid methyl ester and dehydroabietic acid methyl ester were determined in separate experiments. The response factors thus determined were applied as group response factors for monoterpenes, aromatics, fatty acid methyl esters and resin acid methyl esters as appropriate. Integration was performed using a Shimatzu CR3A reporting integrator.

Combined GC-MS analyses were performed on a Hewlett Packard HP 5985 system operated by the Forest Research Institute, Rotorua, or a Finnigan MAT ion trap detector system (ITDS) operated in the split interface mode. Helium was used as the carrier gas in the GC-MS and ITDS instruments.

RESULTS AND DISCUSSION

Analysis of the extractable organics entering the mill sewers established that in accord with overseas findings monoterpenes (chiefly α-pinene, β-pinene, limonene, fenchyl alcohol, borneol, terpene-4-ol and α-terpineol), aromatics, (chiefly guaiacol derivatives), fatty acids (chiefly palmitic, oleic and linoleic acids), and resin acids (chiefly abietic and pimaric acid derivatives) were the dominant extractable constituents. Biological treatment in an aerated lagoon with an average five day retention time was shown to be effective in eliminating most of the monoterpenes and aromatic substances. Since this aspect of the treatment system proved to be unexceptional it is not further explored in this paper.

Significant quantities of fatty acids and resin acids were however present in the final discharge and readily recovered from water samples taken several kilometres downstream from the final discharge point.

When the extractives were first chromatographed it appeared that the major component of the extractives corresponded to methylated dehydroabietic acid (DHAA), a particularly well documented and persistent constituent of pulp and paper mill discharges(22,23,24). Co-injection of an authentic specimen of methylated DHAA resulted in reinforcement of the major peak,

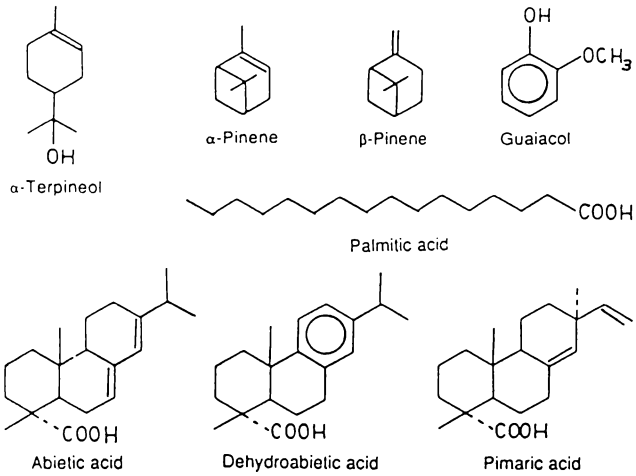

Fig. 1 — Some persistent substances in *P. radiata* effluents.

however combined GC-MS analysis established that two components contributed to this peak. Careful attention to the chromatographic conditions (see Experimental section) allowed for the resolution of the 'dominant' peak into two components, the lesser of which was methylated DHAA. The major component (that with the lesser retention time), was demonstrated by GC-MS analysis to have a molecular mass of 320 atomic mass units (amu). Prominent ions of mass to charge ratio (m/z) 277 ($M^+ - C_3H_7\cdot$), m/z 259 ($M^+ - COOCH_3\cdot$) m/z 245 ($M^+ - HCOOCH_3 - CH_3\cdot$) and m/z 163 (base peak) appeared in the mass spectrum of this compound. These data suggested this substance to be the methyl ester of a saturated tricyclic resin acid of the abietane series.

Extrapolation of the GC retention time data reported by Foster and Zinkel(28) for the methyl esters of a variety of resin acids on an SE-30 (a methyl silicone gum) capillary column, operated at 170 and 190°C, leads to the conclusion that on the BP-1 column used in the present study (BP-1 is a bonded phase methyl silicone gum) co-elution of the methyl esters of DHAA and the 8β-isomel-isomer of abietan-18-oic acid should occur in the vicinity of 220°C. It is thus apparent that considerable care must be exercised in the choice of chromatographic conditions when identifications are based on single column GC analysis, and are not supported by GC-MS data.

Lesser amounts of some other resin acids, including secodehydroabietic acid (two isomers), pimaric acid, sandaracopimaric acid, isopimaric acid, abietic acid and on some occasions neoabietic acid, levopimaric acid and palustric acid were also observed. Sub-μg/L quantities of 7-oxo and monochloro (two isomers) and dichloro DHAAs were detected on most occasions. Fatty acids (chiefly palmitic acid and modest amounts of stearic, oleic and linoleic acids) were also routinely encountered. Selected ion monitoring proved to be an effective procedure of the detection of these substances. For example the ions of m/z 74 and 87 are indicative of the presence of the methylated derivatives of straight chain fatty acids. In addition to palmitic acid and stearic acid, selected ion monitoring thus allowed for the routine detection of lesser quantities of lauric acid, *anteiso*- and *n*-pentadecanoic acid, *anteiso*- and *n*-heptadecanoic acid, arachidonic acid, behenic acid and lignoceric acid. Modest quantities of some unsaturated fatty acids, mainly 18:1 isomers with retention times on the non-polar BP-1 column used in this study, greater than those of linoleic acid methyl ester were also detected. Holmbom(25) has discussed the separation and identification of these fatty acids and other tall oil constituents on more polar capillary columns.

The mass spectrum of methylated DHAA has as its base peak an ion of m/z 239(26), corresponding to the losses of $HCOOCH_3$ and a methyl radical. Equivalent ions appear in the mass spectra of oxidized or chlorinated analogues of DHAA. Thus responses at m/z 253, 273 and 275, or 317 and 319 (selected ion mode) indicated the presence of the methylated 7-oxo, 12- or 14-chloro or 12,14-dichloro analogues respectively of DHAA. Selected ion monitoring also established the presence of sub-μg/L levels of tetrachloroguaiacol and pentachlorophenol. These fully substituted aromatic compounds appear to be more resistant to degradation, at least in the mill biological treatment system, than is the case for less highly substituted analogues such as dichloro or trichloroguaiacol isomers.

In addition there also appeared significant quantities of four other compounds, the molecular masses of which were established by GC-MS analyses to be 262, 256, 238, and 234 amu. A lesser amount of a second compound of molecular mass 320 amu was also detected. Initially it proved difficult to identify these substances since they are not commonly reported as constituents of pulp and paper mills effluent streams. Once it was recognized that the substance of molecular mass 234 was retene it became apparent that the substances of molecular mass 262, 256 and 238 amu were probably fichtelite, dehydroabietin and 1,2,3,4-tetrahydroretene respectively, whilst the second substance of molecular mass 320 amu was the methyl ester of a saturated analogue of pimaric acid.

The mass spectra determined for the substances of molecular mass 234, 238 and 256 amu correspond to those presented elsewhere(26,27) for retene, 1,2,3,4-tetrahydroretene, and dehydroabietin respectively. We have now isolated three of the substances which occur in the Tarawera River samples taken adjacent to the state highway (SH-30) bridge. These substances are dehydroabietin, 1,2,3,4-tetrahydroretene and abietan-18-oic acid in quantities sufficient to confirm their structures by ^{13}C NMR analysis, whilst the presence of retene was established by a direct comparison with an authentic specimen.

In the absence of an authentic specimen, or supporting ^{13}C NMR data, the structure proposed for the second component of molecular mass 320 amu is tentative, however given the presence of resin acids of the abietic and pimaric acid series, the occurrence of a saturated pimaran-18-oic acid is to be expected. The GC retention time of the second component of molecular mass 320 amu is also in accord with that established by Foster and Zinkel(28) for the methyl ester of the 8β-isomer of pimaran-18-oic acid. The co-occurrence of an abietan-18-oic acid with fichtelite, a compound for which the 8β-stereochemistry has been established(29), supports the conclusion that the former acid is the 8β-isomer, since a common metabolite pathway for abietic acid is implied. It is thus reasonable to also expect enzyme mediated hydrogenation of pimaric acid to afford the 8β-isomer.

Table 1 summarizes the fatty acids and resin acid concentrations found in the SH-30 water samples. The results of a typical analysis are followed by an indication (in brackets) of the range of concentrations observed over a 12 month period. Figure 2 is a representative GC profile of the extractable organic substances recovered from a SH-30 water sample.

The presence of fichtelite, retene, dehydroabietin, 1,2,3,4-tetrahydroretene and saturated resin acids in the final discharge and river water samples, but not in any of the mill sewers, is intriguing since they are indicative of the anaerobic modification of abietic acid; this despite the aerobic nature of the treatment system. This apparent paradox was resolved when the source of these compounds was located.

Solid materials from the pulp mill, including reject pulp and solids which settle out from an effluent stream clarifier, are dumped in a separate sludge lagoon. This lagoon is basically a reclaimed swamp and a small water flow exits from it. This outflow is directed into the aerated lagoon system.

GC and GC-MS analysis confirmed the presence of the substances of molecular mass 262, 256, 238, 234, and 320 amu in the sludge lagoon outflow. Quantitative analyses established that these substances pass through the aerated lagoon system with only a modest reduction in their levels (typically of the order of 35% or less) whereas resin acids such as abietic acid are substantially reduced (greater than 90% reduction).

On one occasion during the sampling period a small earthquake collapsed a wall of the sludge lagoon with the result that the outflow from the lagoon passed directly to the river. A water sample subsequently taken from the river at the SH-30 bridge contained elevated levels of fichtelite, 1,2,3,4-tetrahydrodehydroabeitic, dehydroabietin, retene, abietan-18-oic acid and pimaran-18-oic acid, together with some additional aromatic substances (chiefly guaiacol derivatives) and monoterpenes (chiefly α-terpineol).

The resistance of the 'anaerobic' substances to biological degradation is in keeping with their formation and survival in deep sea sediments(26) and in some recent lake sediments(27), particularly those whose drainage basins contain predominantly conifers. Fichtelite has long been known(30) to be a decomposition product of decaying conifers.

Thus since abietic acid is also the dominant resin acid which enters the sludge lagoon, it appears that once anaerobic degradation products, such as fichtelite, dehydroabietin, and retene have been formed from it, they are resistant to subsequent aerobic degradation. This proposition is currently being tested in microbiological trials.

The present results indicate that two distinct 'anaerobic' degradation pathways are operative in the sludge lagoon. Either abietic acid is saturated to afford abietan-18-oic acid which is then decarboxylated to afford fichtelite, or it is dehydrogenated and aromatized to give dehydroabietic acid, which after decarboxylation is progressively demethylated at C-10, and dehydrogenated in rings B and A to sequentially afford, dehydroabietin, 1,2,3,4-tetrahydroretene and retene. The absence of metabolites such as 1,2,3-trihydro-

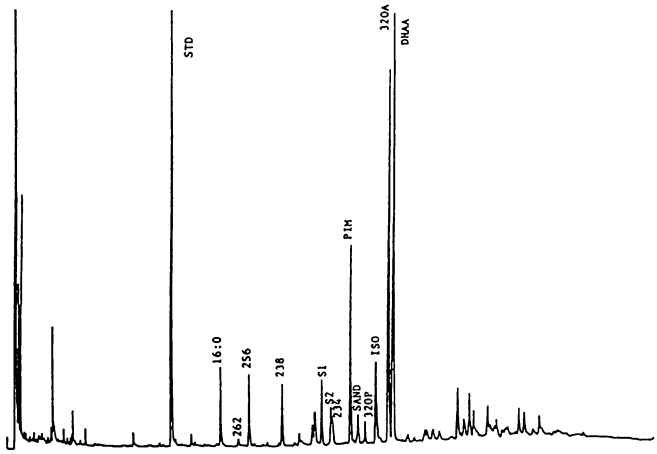

Fig. 2 — GC profile of methylated extractable organic substances recovered from a Tarawera River water sample collected at the SH-30 bridge. Peak identifications; STD, internal standard, *n*-octadecane; 16:0, palmitic acid; 262, fichtelite; 256, dehydroabietin; 238, 1,2,3,4-tetrahydroretene; S1, secodehydroabietic acid-1; S2, secodehydroabietic acid-2; 234, retene; PIM, pimaric acid; SAND, sandaracopimaric acid; 320P, pimaran-18-oic acid; ISO, isopimaric acid; 320A, abietan-18-oic acid; DHAA, dehydroabietic acid.

Table 1
Concentrations of extractable organic substances recovered from Tarawera River water samples at the state highway 30 bridge

	μg/L	
Palmitic acid	10	(2-12)*
Stearic acid	2	(0.5-4)
Oleic acid	0.5	(0-3)
Linoleic acid	0.5	(0-2)
Secodehydroabietic acid-1	7	(1-10)
Secodehydroabietic acid-2	2	(0.5-6)
Pimaric acid	21	(6-24)
Sandaracopimaric acid	3	(0.5-5)
Isopimaric acid	21	(6-24)
Dehydroabietic acid	46	(11-83)
Abietic acid	—	(0-30)
Fichtelite	2	(0.5-5)
Dehydroabietin	8	(2-12)
1,2,3,4-tetrahydroretene	9	(2-14)
Retene	5	(2-10)
Pimaran-18-oic acid	2	(0.5-5)
Abietan-18-oic acid	40	(15-80)
7-Oxodehydroabietic acid	0.5	(0-2)
12-Chlorodehydroabietic acid	1	(0-2)
14-Chlorodehydroabietic acid	1	(0-2)
12,14-Dichlorodehydroabietic acid	0.5	(0-2)

* Typical range of concentrations found over a 12 month sampling period.

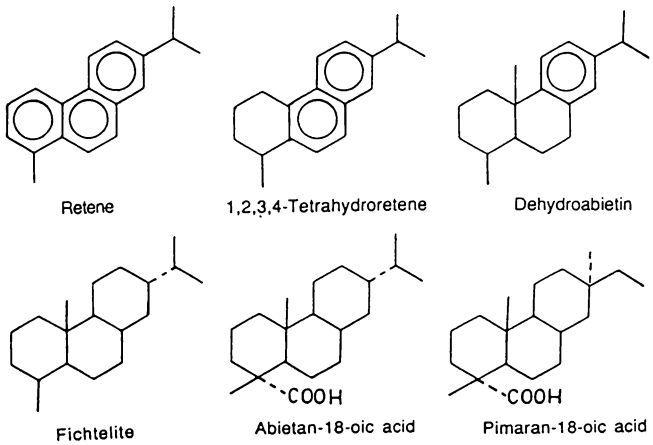

Fig. 3 — Persistent resin acid and resin acid degradation products identified in Tarawera River samples, sludge lagoon effluents, and in the final discharge from the treatment system.

retene-4α-carboxylate indicates that decarboxylation occurs before demethylation and aromatization of ring B. Two routes from abietic acid to retene have been suggested by Wakeham *et al*(27). Conversion of the 4α-carboxyl function to a methyl group is proposed for the route in which dehydroabietane and simonellite are intermediates, whilst in the other route in which dehydroabietin and 1,2,3,4-tetrahydroretene are intermediates, direct decarboxylation and aromatization is proposed. Thus far we have not detected the presence of dehydroabietane, simonellite or pimanthrene (the fully aromatized analogue of pimaric acid)(27) in SH-30 river water samples, or in the sludge lagoon effluent.

CONCLUSIONS

It is clear that the design and operation of biological treatment systems can influence the characteristics of the final discharges, especially if discharges from aerobic and anaerobic systems are mixed. Whilst the toxicity of unsaturated resin acids towards fish is now well documented, no toxicity data are presently available for saturated resin acids. In this context it can be noted that whilst unsaturated fatty acids have significant toxicity, saturated fatty acids are essentially non-toxic. It is thus apparent that when saturated resin acids are present in substantial quantities, toxicity calculations(21,22) based on an assessment of the total resin acid content should presently be viewed with caution.

Despite the wealth of information available in the literature, new substances, and differing system characteristics continue to emerge. Clearly in the New Zealand context each treatment system needs to be carefully investigated before generalizations based on overseas experience can be applied to them, if at all. Detailed investigations of the characteristics of the treatment systems of two New Zealand pulp and paper mills are now in progress at the University of Waikato and will shortly be reported elsewhere.

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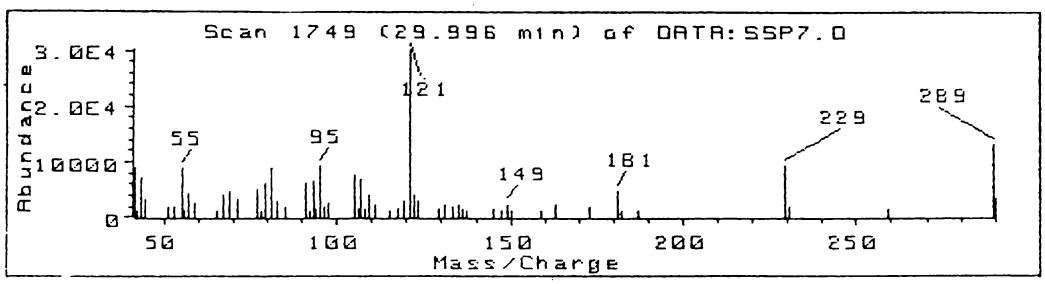
APPENDIX C



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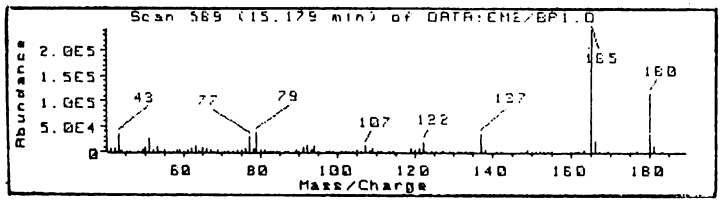

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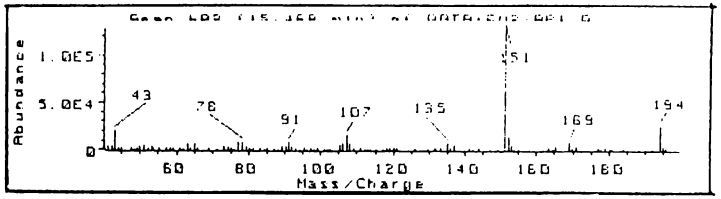

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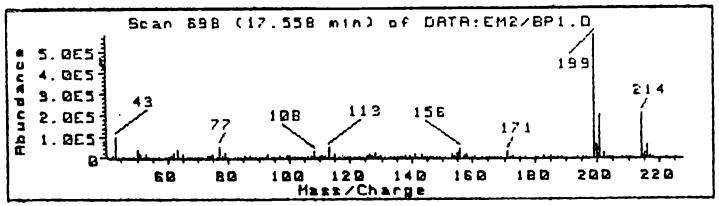

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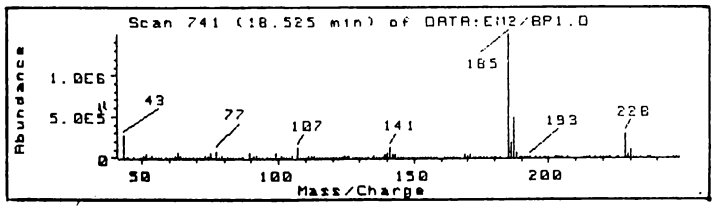

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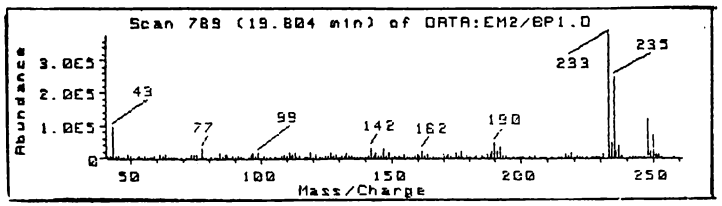

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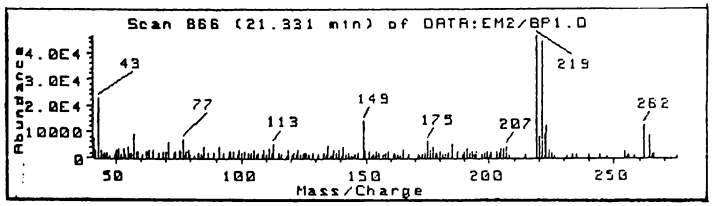

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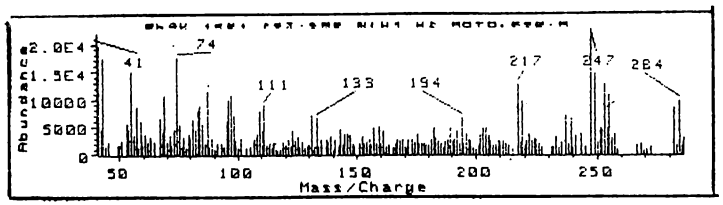

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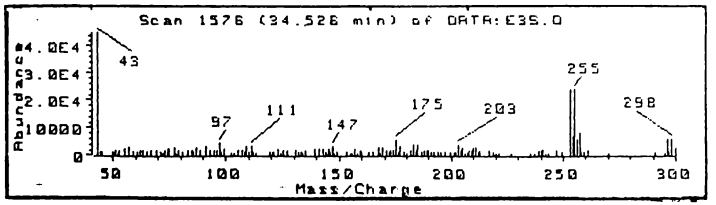

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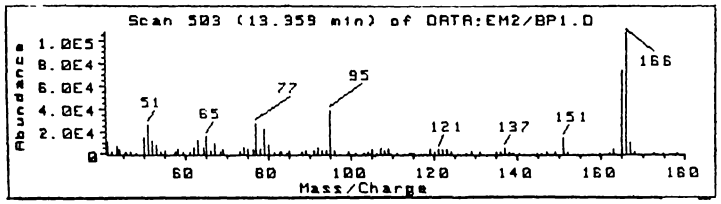

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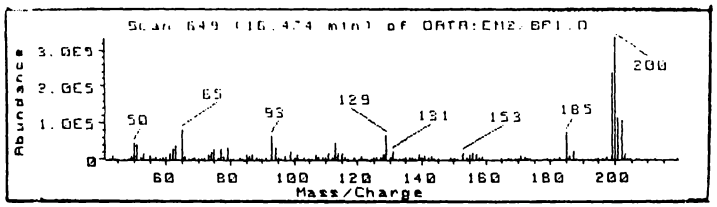

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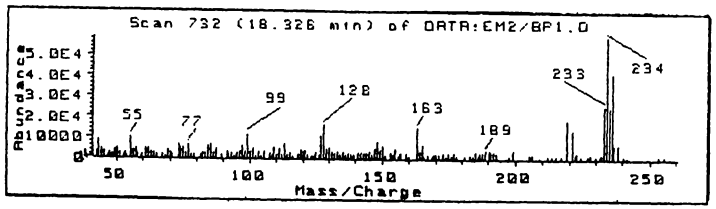

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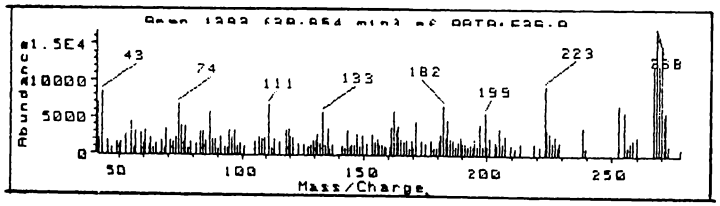

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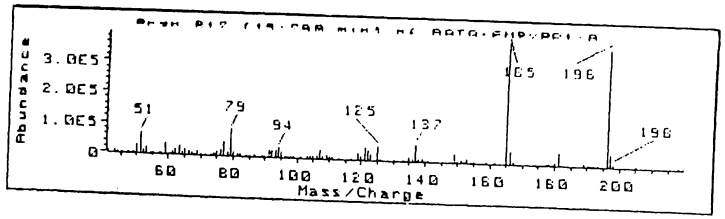

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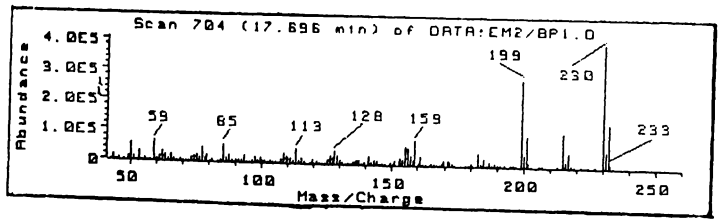

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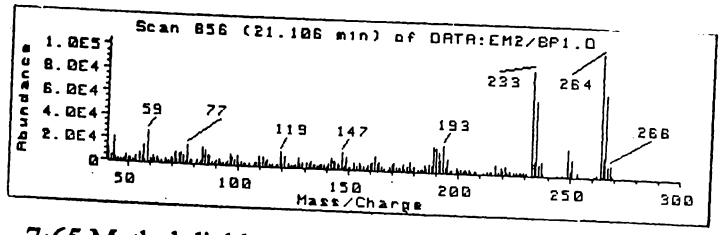
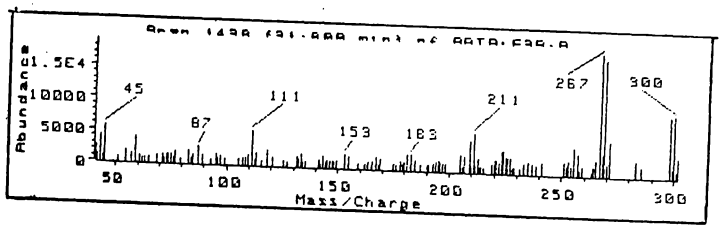
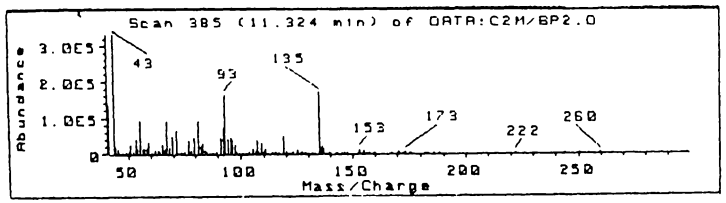


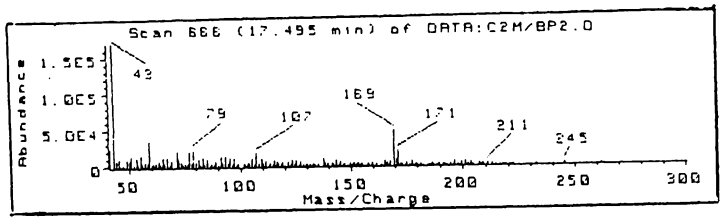
7:65 Methyl dichloro-3,4-dimethoxybenzoate



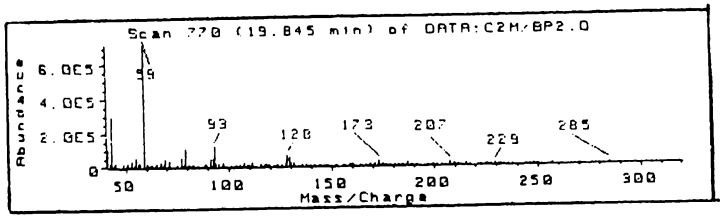
7:66 Methyl 2,4,6-trichloro-3,4-dimethoxybenzoate



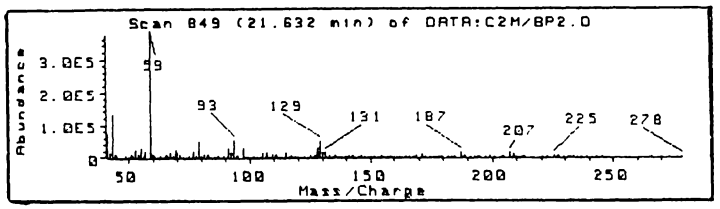
7:5 Dichloropinene



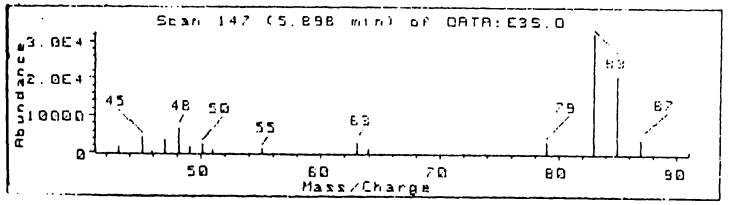
7:11 Dichlorolimonene



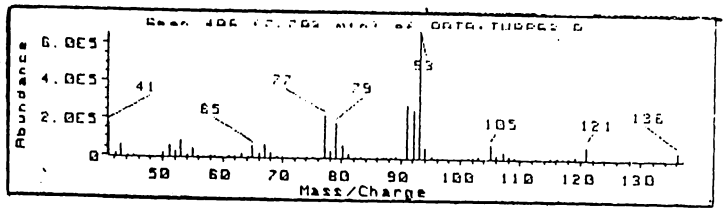
7:15 Dichloroterpineol



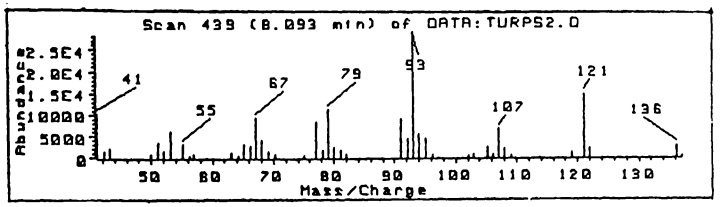
7:20 Dichloroterpineol



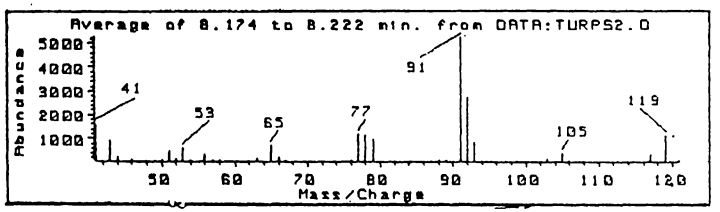
7: Dichlorodimethylsulphone



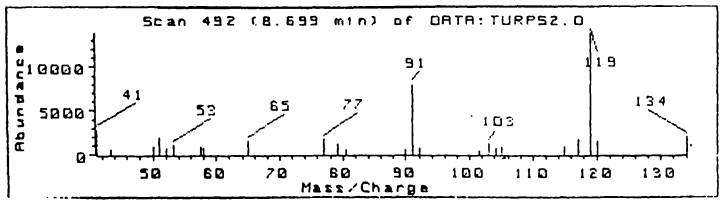
9:11 (2) α-Pinene (49)



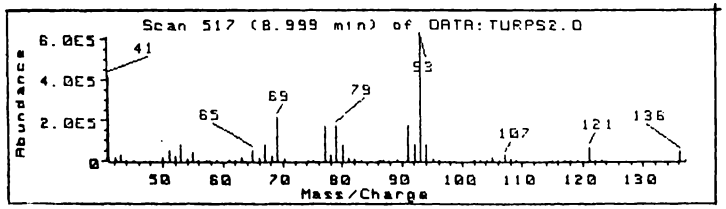
9:2 (2) Camphene (50)



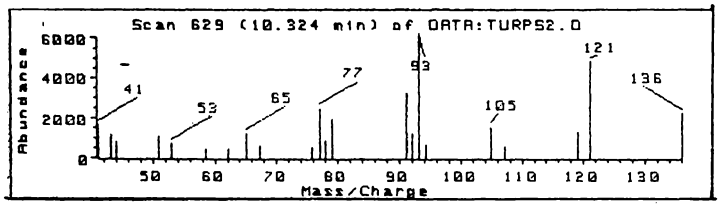
9:3 (2)*p*-Mentha-1,3,8-triene (51)



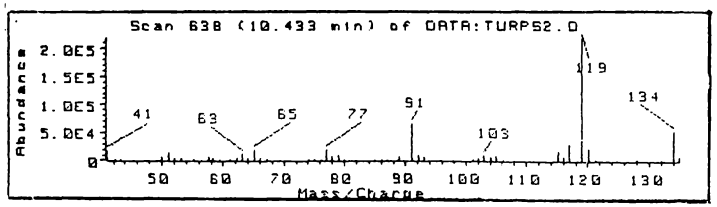
9:4 (2)*t*-Butylbenzene



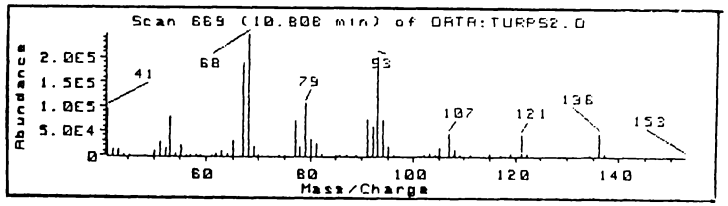
9:5 (2) β-Pinene (53)



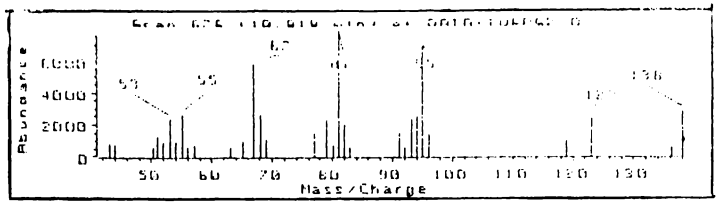
9:8 (2) α–Terpinene (57)



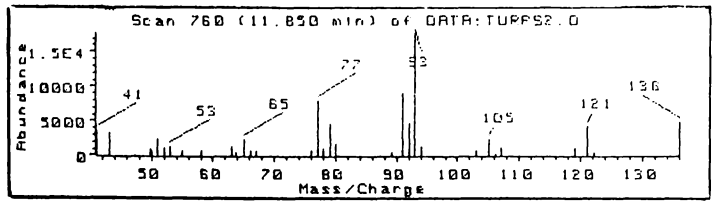
9: 9 (2) *p*-Cymene (58)



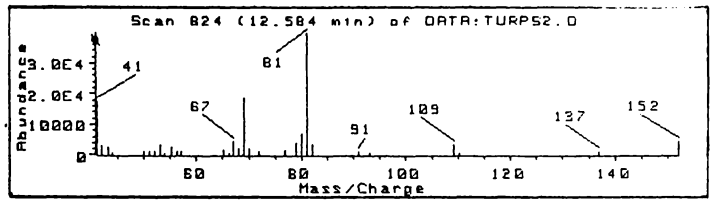
9:11 (2) Limonene (59)



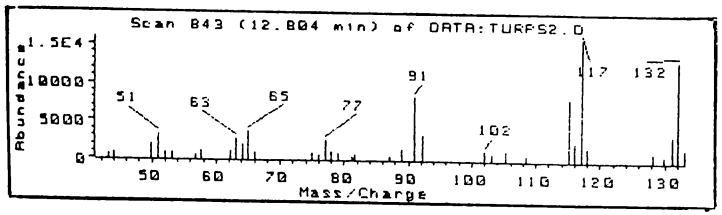
9:12 (2) Unknown



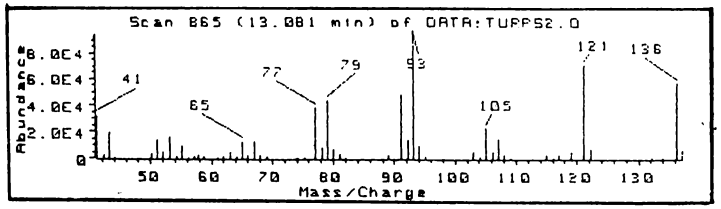
9:13 (2) γ-Terpinene (61)



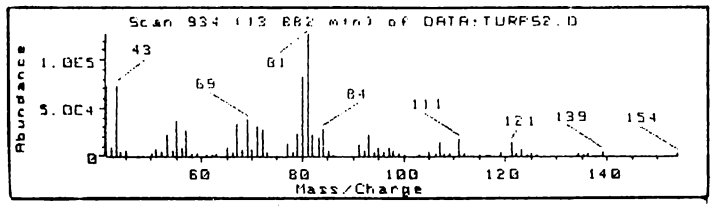
9:14 (2) Fenchone (62)



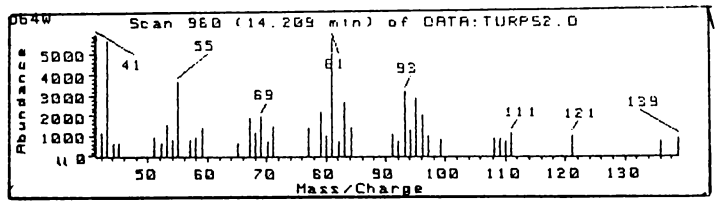
9:15 (2) α,*p*-Dimethylstyrene (63)



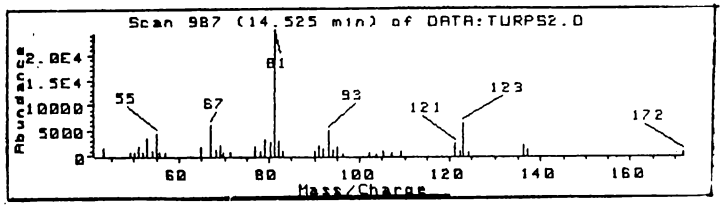
9:16 (2)Terpinolene (64)



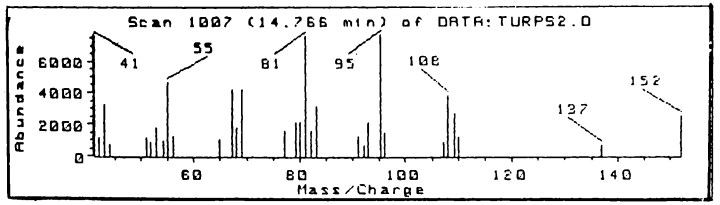
9:17 (2) Fenchol (65).



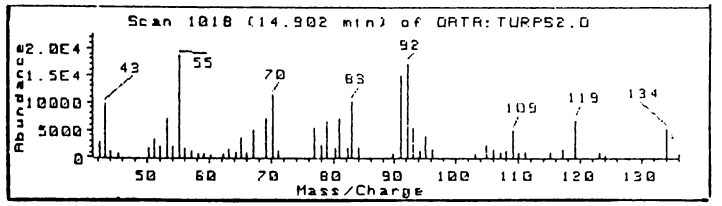
9:19 (2) Limonene-1,2-epoxide-2



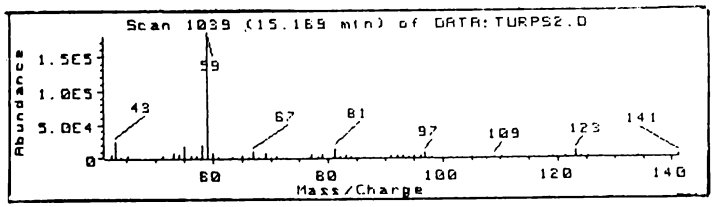
9:18 (2)Limonene-1,2-epoxide-1 (66)



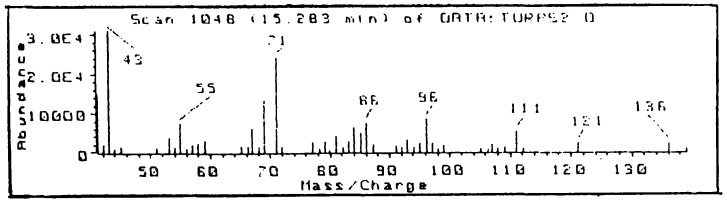
9:20 (2) Camphor (67)



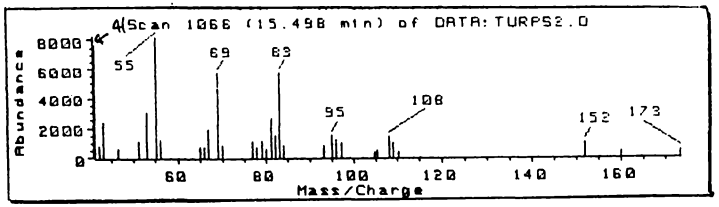
9:21 (2) *trans*-Pinocarveol (68)



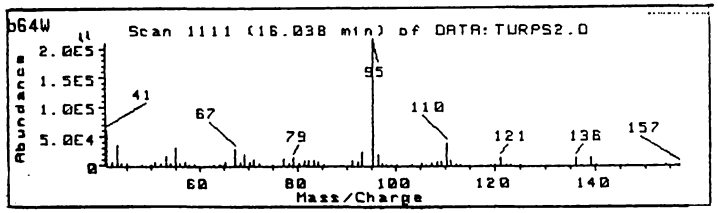
9:22 (2)Unknown



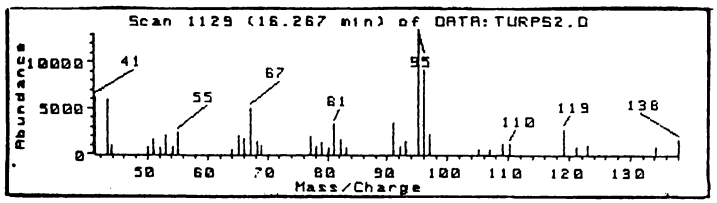
9:23 (2) Unknown



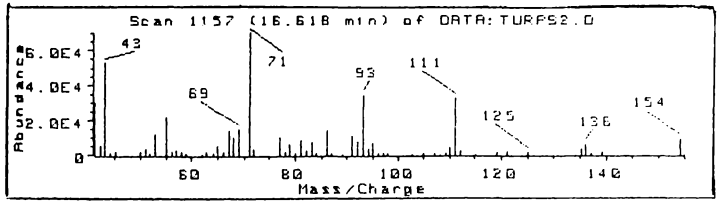
9:24 (2) Pinocamphone (70)



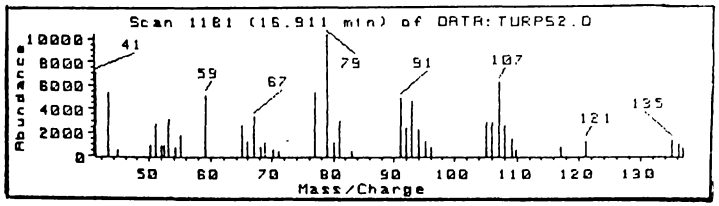
9:25 (2) Borneol (71)



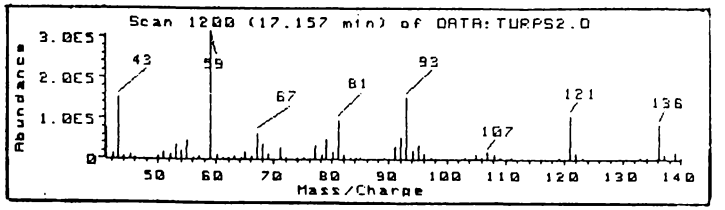
9:26 (2) Unknown



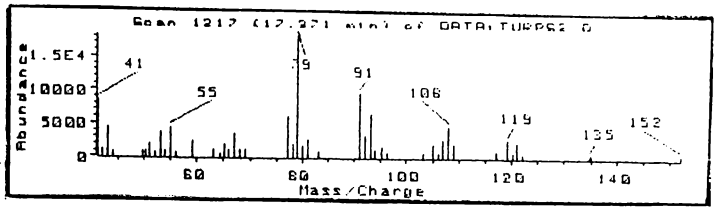
9:27 (2) Terpen-4-ol (72)



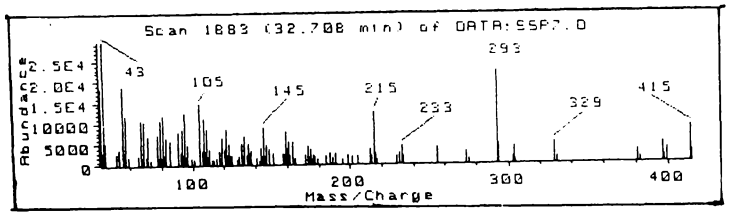
9:28 (2) Myrtenal (73)



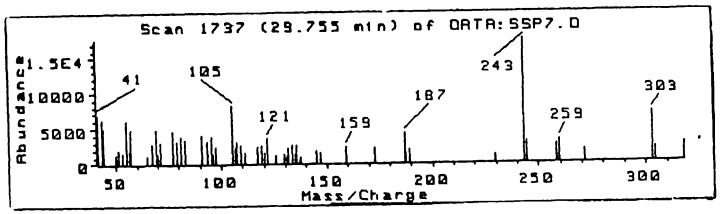
9:29 (2) α–Terpineol (74)



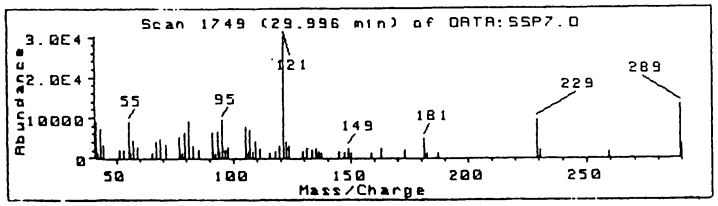
9:30 (2) Myrtenol (75)



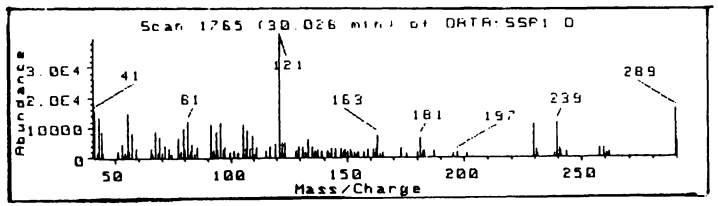
10:66 (4) Methyl kinleithoate (48)



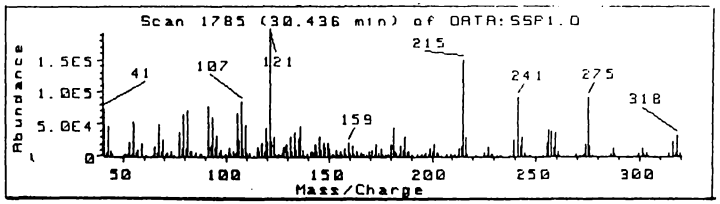
10:44 (4) Methyl 8-abieten-18-oate (80)



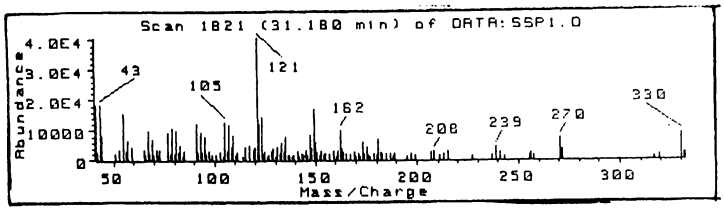
10:57 (4) Methyl alburate



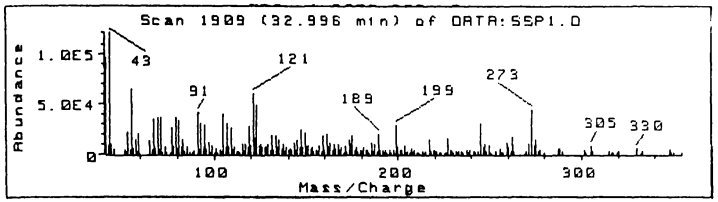
10:45 (40) Methyl 8(14)-pimaren-18-oate (10)



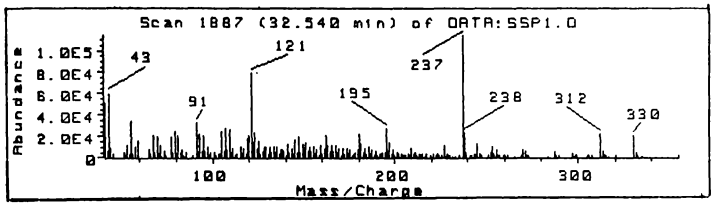
10:48 (4) Methyl 13-abieten-18-oate (11)



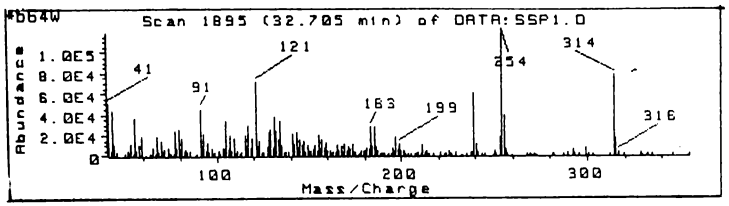
10:56 (4) Hydroxylated RAME



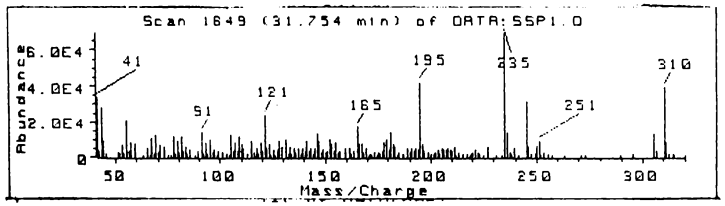
10: (4) Keto-diene resin



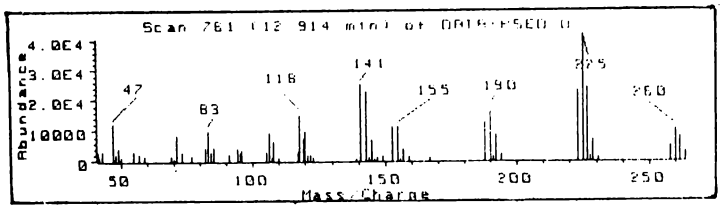
10:58 (4) Methyl 7β-hydroxydehydroabietate



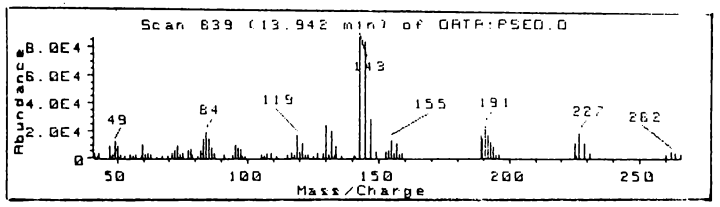
10:67 (4) Methyl hydroxyabietate



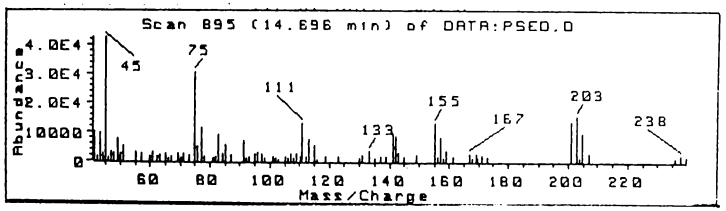
10:53 (4) Unknown



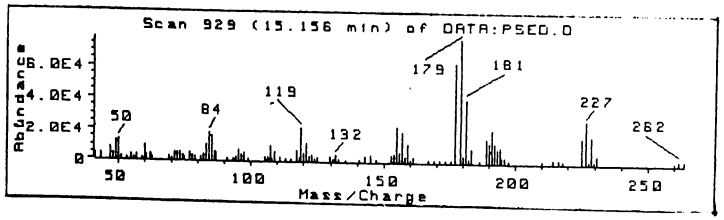
10:7 (6) Hexachloro-1,3-butadiene



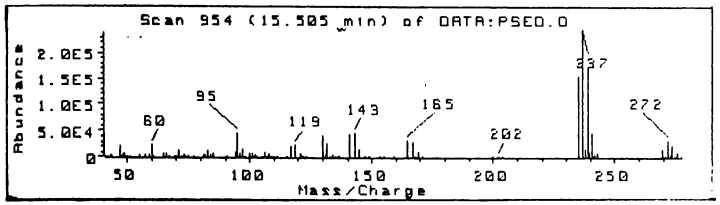
10: (6) Hexachlorobutane



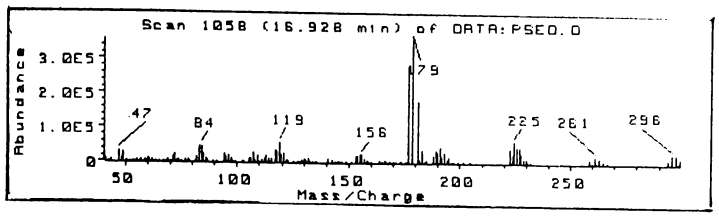
10: (6) Pentachloro-1,3-cyclopentadiene



10:10 (6) Hexachlorobutene



10:11 (6) Hexachloro-1,3-cyclopentadiene



10:14 (6) Heptachlorobutane

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