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Extractable Organics and Colour in a Bleached Kraft Mill Effluent Land Application System and Recipient Ground Waters

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of the requirements for the degree of

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Abstract

This thesis describes a study of the behaviour of extractable organics and colour in a land application system used to treat highly coloured, organic-rich, alkali extraction stage and foul condensate effluents from a traditional bleached kraft mill. The land application system comprised 44 unlined seepage basins, totalling 86 ha in area, into which approximately 10,000 m^3 d^{-1} effluent was loaded for approximately eight months of each year. The study aimed to determine (1) the effectiveness of the system for treating major effluent organics, including monoterpenes, fatty acids, resin acids, chlorophenolics, and colour, and (2) the effects of the system on organic contamination of sediments, aquifer materials, and ground waters.

The study was carried out in four parts, investigating: (i) the behaviour of extractable organics and colour in the effluent drains and seepage basins; (ii) the penetration of extractable organics into the sediments beneath the seepage basins; (iii) the organic chemistry of shallow ground waters beneath the seepage system, and of deeper off-site ground waters; and (iv) behaviour of extractable organics and colour in laboratory soil-column simulating the land application process. In addition, a review of land application of pulp mill effluents was carried out, and analytical methods for determining extractable organics in effluents, sediments, and ground waters were developed.

Concentrations of extractable organics and chlorophenolics were reduced by >95% over a 40 day period in the seepage basins. Removal rates decreased in the order fatty acids > chlorophenolics ≈ monoterpenes > resin acids. Resin acids underwent reductive and oxidative transformations, producing transient intermediates including 13-abietenoic acid and 13β-hydroxyabietanoic acid. A suite of relatively stable transformed species, dominated by the saturated compound abietanoic acid, remained in the seepage pond after 40 days. Colour removal over the same period was approximately 25%.

High concentrations of effluent-derived extractable organics were found in surficial sediments beneath the seepage basins. Major compounds were resin acids, largely saturated species, and diterpene hydrocarbon transformation products. Diterpene hydrocarbons were dominated by retene, fichtelite, and dehydroabietin. Surficial sediments contained concentrations of total resin acids and diterpene hydrocarbons of up to 10,000 mg kg^{-1}. Concentrations dropped with depth, but high levels were found in discrete zones at depths of up to 5 m beneath the surface. This indicated that effluent movement was occurring through permeable conduits rather than via uniform infiltration through the soil, and was consistent with the fractured geology of the site.

Ground waters taken from seven well clusters, sampling depths between 2 and 15 m beneath the seepage basins, contained elevated sodium and chloride concentrations (200–400 mg L^{-1}), and spatially variable colour levels (100–2000 CPU). Effluent-derived extractable organics were also found in variable concentrations. Major compounds were methyl-substituted 2-cyclopentenones, resin acids, and diterpene hydrocarbons. Resin acids and diterpene hydrocarbons were the generally dominant compound classes, concentrations totalling 20–2600 μg L^{-1}. Preliminary assessment of chlorophenolics found low levels, totalling 2–4 μg L^{-1} in the most contaminated ground waters. The results indicated that contamination of shallow ground water was occurring, but the nature and level of this contamination was highly spatially

variable. As found for the sediment studies, these findings were consistent with effluent infiltration through heterogeneous, fractured, sub-surface geology.

The hydrogeology of the area was determined to be dominated by ground water movement through fractured zones in four major ignimbrite aquifers. Wells were placed at depths between 9 and 110 m, and at distances from immediately adjacent to 2.7 km from the seepage area to sample ground water from these zones. Contamination was found largely within the highly fractured, high flow zones of two of these units, the Marshall A and, to a lesser extent, the Marshall B ignimbrite aquifers. Concentrations of effluent-sourced extractable organics (largely resin acids and diterpene hydrocarbons) and colour were highest immediately beneath the seepage area, maximum concentrations of 110 $\mu g\ L^{-1}$ total resin acids and diterpene hydrocarbons, and 900 CPU colour being found. Concentrations dropped rapidly with distance from the ponds, decreasing by approximately 90% within about 100 m from the seepage area. There was evidence for retardation of organics relative to sodium and chloride in the off-site aquifers.

Laboratory simulations of effluent infiltration through seepage site soils were carried out under two application regimes (permanently flooded, and flood-dry cycle) to determine the range of treatment possibilities occurring in the seepage system. Leachate chemistry was monitored over an approximately two year period, and soil extractives measured at the end of the study. Mass balance was used to estimate effluent treatment efficiency. The flood-dry (aerobic) application regime resulted in essentially compete degradative removal of extractable organics.

Under the flooded (anaerobic) regime, extractable organic removal was limited for all constituents other than fatty acids, which were >90% removed. Resin acids were strongly retained by the soil, approximately 72% remaining in the soil at the end of the study. Approximately 25% was recovered in the leachate. Monoterpenes were highly mobile, moving rapidly through the soil. A relatively stable suite of transformed compounds was found in the leachates. Monoterpene removal was estimated to be approximately 55%. Under flooded conditions, transformation rather than degradative removal of extractable organics occurred.

Colour intensification, rather than reduction, occurred at times in both application regimes. At the end of the study, colour removal in the flood-dry cycle regime was 2%, and in the flooded regime an increase of 51% was measured.

In summary, the study found that the land application system resulted in large decreases (>95%) in the concentrations of extractable organics, but little overall treatment of effluent colour. Ground waters affected by effluent infiltration were highly variable in composition, but in general contained elevated colour levels, and moderate-to-low concentrations of extractable organics. Resin acids and diterpene hydrocarbons were the dominant class of extractable organics found in sediments and ground waters beneath the seepage system.

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Abbreviations

AAS	atomic absorption spectrometry
AOX	adsorbable organic halogen
AR	Access Road (seepage area)
BKME	bleached kraft mill effluent
BOD	biological oxygen demand
CC	chlorocatechol
CF-E	continuously flooded effluent (application regime)
CG	chloroguaiacol
CP	chlorophenolic
CV	chlorovanillin
cv	coefficient of variation (relative standard deviation)
DL	detection limit
DT	diterpene hydrocarbon
EA	Extension Area (seepage area)
EO	extractable organic
FA	fatty acid
FD-E	flood-dry effluent (application regime)
FID	flame ionisation detector
GC	gas chromatography
LA	land application
LLC	land limiting constituent
m/z	mass-to-charge ratio
mamsl	metres above mean sea level
MCP	methy-substituted 2-cyclopentenone
MSD	mass selective detector
MT	monoterpene
mw	molecular weight (relative molecular mass)
NZFP	New Zealand Forest Products Ltd
OF	overland flow
RA	resin acid
RFA	resin and fatty acids
RI	rapid infiltration
S_R	method standard deviation
SR	slow rate (infiltration)
SS	suspended solids
TIC	total ion chromatogram
TOX	total organic halogen

Chapter One

Introduction and Background

1.1 Introduction

Population growth and expanding industrialisation have resulted in the production of increasingly large quantities of domestic and industrial waste water. Contamination of the Earth's soil, water, air, and biota by these waste discharges is a major issue. To protect the environment from harmful constituents in these effluents, treatment is often required before the waste waters are discharged into the receiving environment. Developing effective and affordable treatment processes is a challenge for many industries.

The pulp and paper industry is an example of an industry for which effluent management is a major challenge. The industry uses large amounts of water and, despite well developed recycling and recovery methods, large volumes of effluent are generated. These effluents contain a vast array of organic constituents, reflecting the complex composition of wood and the variety of physical and chemical treatments used in wood processing. Although the processes which generate the liquid wastes within the industry continue to improve, external treatment is still generally necessary to reduce organic pollutant loads on the receiving environment.

Most pulp and paper industry treatment systems discharge to surface waters, where problems such as organic enrichment, dissolved oxygen depletion, discolouration, deposition of fibrous solids, and emission of odours have traditionally been experienced. Due to improved processing technology and higher standards of effluent treatment, most of these gross effects of effluent pollution are now far less prevalent than they have been in the past. However, more subtle effects of effluent contamination are now being observed, particularly on aquatic biota residing in receiving waters. These effects include chronic reproductive and life-cycle effects (e.g. biochemical and physiological changes, changes in organism morphology, and mutagenic and carcinogenic effects), changes in population composition, behaviour modification, and occasionally even acute lethality (e.g. McLeay 1987; Stuthridge 1990; Owens 1991; Environment Canada 1991).

Reducing pulp and paper mill effluent pollutant loadings on surface waters is therefore highly desirable. Reduction can be brought about by changes to the mill processes which generate the constituents of concern, by improving the performance of waste treatment systems discharging to surface waters, or by using treatment systems which minimise direct discharge of effluent to surface water recipients.

An alternative to effluent discharge to surface waters is land application (LA). By applying waste water to the ground, direct discharge to surface waters is avoided and the treatment properties of the soil environment can be used to facilitate effluent renovation. When effluent and site characteristics are favourable, LA can offer an attractive combination of treatment effectiveness, reduced surface water pollution, and lower operating costs than more conventional treatment technologies. In New Zealand, an additional advantage of LA is that it is acceptable to the indigenous Maori people, who consider direct discharge of effluents to surface waters to be culturally offensive.

However, just as surface waters can be contaminated by inadequately treated wastes, the quality of soils, ground waters, and aquifer media can be degraded by inappropriate LA practices. Remediation of contaminated soil and ground water is generally expensive and difficult. It is therefore essential that contamination is avoided by using well tested treatment methods that remove potentially harmful effluent constituents. Reliable information on the behaviour of potential pollutants during the LA process is required as a basis for LA system design and operation. The performance of existing LA systems must be characterised to ensure that environmental effects are acceptable and that continued use is sustainable.

1.2 The Present Study

1.2.1 Background

From 1960 to 1988, the Kinleith mill of New Zealand Forest Products Pulp and Paper Limited (NZFP), an integrated bleached kraft pulp and paper mill, used a LA system to treat and dispose of one of its waste streams. The LA process involved applying untreated waste water containing high concentrations of inorganic and organic constituents, to unlined seepage basins. Contamination of the soils, ground waters, and aquifer media underlying the basins by effluent-sourced chemicals was a potential problem associated with the system. Because it had been operating for 28 years, significant contamination of ground waters by off-site migration of infiltrated effluent was also possible.

In 1985, NZFP initiated studies which aimed to assess the environmental effects of the LA system and its suitability for on-going treatment and disposal of the effluent. This thesis describes chemical aspects of these investigations that were carried out between 1985 and 1990. Subsequent to this study, the mill underwent a process modernisation programme that substantially improved the quality of its effluent, to the point where NZFP no longer considered LA to be an essential component of the effluent treatment system. This thesis therefore describes investigations carried out pre-modernisation.

Despite being an historical account, the findings of the study remain relevant. The constituents which were the prime focus of the study (resin acids and colour) are still environmentally significant contaminants from kraft mills, and their fate and effects in recipients are the subject of on-going research (e.g. Archibald *et al.* 1997; Stuthridge *et al.* 1997). Investigating and documenting the performance of methods of treating these constituents in ways which reduce contaminant loads to surface waters are therefore still required.

Bleached kraft mill effluents (BKMEs) contain a large number of organic compounds. Over 250 have been identified (McKague *et al.* 1989), but many more remain unidentified (Environment Canada 1991). The behaviour and treatability of many of these compounds in a range of physical, chemical, and biological treatment systems, and their fate in surface receiving waters have been widely studied, both overseas (e.g. Keith 1976; USEPA 1982a; Leuenberger *et al.* 1985; McLeay 1987; Lindstrom and Mohamed 1988; Gergov *et al.* 1988; NSEPB 1989; Owens 1991; Environment Canada 1991) and in New Zealand (Wilkins and Panadam 1987; Panadam-Twigley 1988; McFarlane and Clark 1988; Stuthridge 1990; Stuthridge *et al.* 1991; Zender *et. al.* 1994; Tavendale 1994).

In contrast to the extensive literature describing the behaviour of BKMEs in these treatment systems and surface water recipients, there has been little documented work on the behaviour and fate of BKME-derived organic compounds in LA systems or underlying ground water systems. The studies described in this thesis contribute information to this apparently neglected area.

1.2.2 General aim of the thesis study

NZFP's investigations aimed to assess the suitability of the Kinleith LA system for sustainable effluent treatment. The studies described in this thesis contributed to the programme by providing detail on the behaviour of selected organic contaminants in the system. Literature survey (Chapter 2) found little information on the behaviour of organic contaminants in LA systems treating BKMEs that was directly applicable to the investigation. Colour removals in other studies were found to be highly variable and system-specific. Reliably predicting the performance of the Kinleith LA system from literature data was therefore not possible. The fate of organic contaminants, including colour, in the LA system therefore required investigation and was the focus of the thesis study.

The aim of the study was to evaluate the behaviour of major extractable organic (EO) compounds and colour in the Kinleith LA system so that the effects of the system on the receiving environment (underlying sediments, aquifer materials and ground waters) could be determined and the suitability of the LA system for on-going effluent treatment at Kinleith assessed.

The following sections of this chapter describe the Kinleith mill (as it was when the studies were carried out) and the LA system, summarise information from previous studies of the LA system and ground water recipients, and outline the structure of the thesis. Based on the site specific information summarised in this chapter, and from literature survey covered in Chapter 2, study objectives were identified. These are listed at the end of this chapter in section 1.8.

1.3 The Kinleith Pulp and Paper Mill

NZFP's Kinleith mill, New Zealand's second largest pulp and paper mill, is situated in the central North Island of New Zealand, about 6 km south of the nearest urban centre, Tokoroa (Figure 1.1).

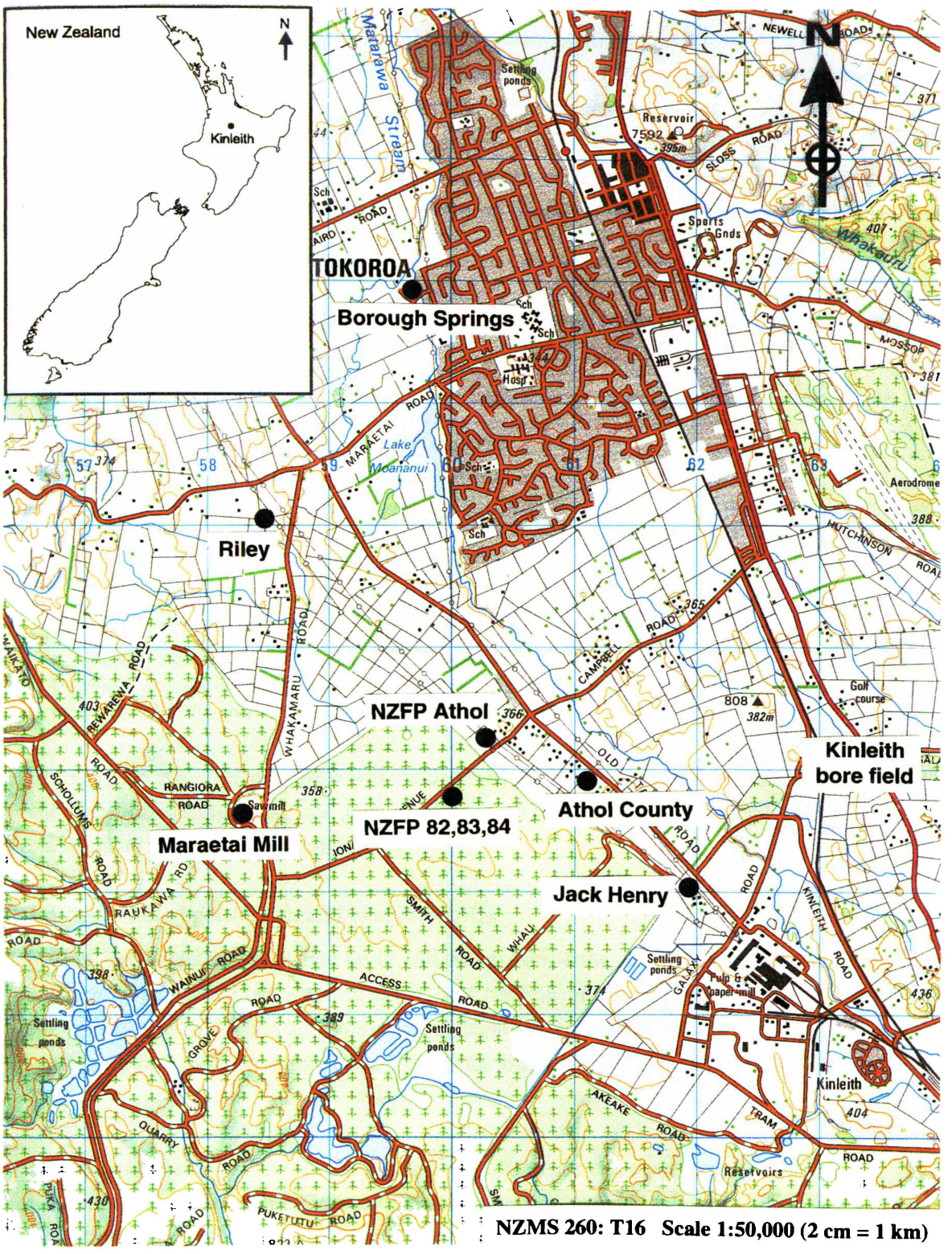


Figure 1.1: Kinleith location map showing selected ground water sampling bores

1.3.1 Mill processes and production

During the study period the Kinleith mill produced about 400,000 ADT yr^{-1} of kraft and neutral sulphite semi-chemical (NSSC) pulp from three pulp lines (Table 1.1). This represented about 30% of New Zealand's total pulp production. The softwood *P. radiata* was the major raw material. Smaller quantities (ca. 25%) of the native hardwood, *Beilschmeldia tawa*, were also used. About 40% of the kraft pulp produced was bleached in two bleach plants, as summarised in Table 1.1. Various paper products were also produced on site, including packaging materials, printing and writing papers.

Table 1.1: Pulping and bleaching processes used at Kinleith during the study period

Plant	Process	Production (ADT d^{-1})
Pulping:		
• No. 1	kraft, six batch digesters	600
• No. 2	kraft, continuous digestion	650
• No. 3	NSSC, continuous digestion	100-250
Bleaching:		
• No. 1	CEHDP sequence [a]	100-150
• No. 2	$(C_{70}+D_{30})E_oDED$ sequence	160-300

a: Bleaching sequence symbols (Casey 1980): C-chlorination; E-alkaline extraction; H-hypochlorite bleaching; D-chlorine dioxide bleaching; P-peroxide bleaching; Eo-alkaline extraction in the presence of pressurised oxygen; (C70+D30) -chlorine plus chlorine dioxide (70:30 mixture).

In 1991, the No. 2 bleach plant was modernised to utilise oxygen delignification and 100% chlorine dioxide bleaching and now produces 146,000 ADT yr^{-1} bleached pulp. The No. 1 bleach plant is no longer operating.

1.3.2 Effluent generation and characteristics

Mill effluent discharges totalled up to 180,000 m^3 d^{-1}, sourced from debarking, pulp washing and screening, bleaching, paper making, and cooling processes. Non-process discharges of stormwater and accidental spills contributed significantly to this total at times. Effluents were segregated into three streams (Table 1.2) on the basis of their chemical characteristics (Table 1.3).

The effluent treated by LA was the No. 2 stream. Its major characteristics were:

- high pH and colour, and high sodium concentration, from alkali extraction stage effluents making up about 9 ML d^{-1} of its total flow; and
- high BOD_5, attributable to high concentrations of biodegradable, low molecular weight organics such as monoterpenes (MTs), organosulphur compounds, and methanol. Foul condensates (about 2 ML d^{-1}) from black liquor evaporator sets, turpentine decanters and blow heat evaporators were the major sources of these compounds.

1.3.3 Effluent treatment

Until late-1988, a combination of LA and biological treatment in lagoons was used to treat and dispose of the mill effluents. Figure 1.2 schematically depicts the treatment systems in operation during this period. The No. 1 and No. 3 effluents were not directly relevant to the LA studies as they discharged to surface water recipients. These effluents have been detailed elsewhere (Stuthridge 1990).

Table 1.2: Sources and typical discharge rates of Kinleith mill's effluent streams

Effluent stream	Discharge rate $m^3 d^{-1}$	Process sources
No. 1	120,000	pulping, papermaking, recaustising, recovery boilers
No. 2	15,000	bleach plants: E, H, P stage filtrates (No.1 BP)
		E_O, D, E, D stage filtrates (No.2 BP)
		foul condensates
No. 3	45,000	bleach plants: C, D stage filtrates (No.1 BP)
		D_{30}+C_{70} filtrate (No.2 BP)
		Stormwater, debarking

Table 1.3: General chemical characteristics of the segregated effluent streams (after Campin 1989)

		Effluent stream		
Determinand	Units	No. 1	No. 2	No. 3
pH	pH units	8.5	10	2
Total Suspended Solids	mg L^{-1}	500	100	20
Sodium	mg L^{-1}	100	600	150
BOD_5	mg L^{-1}	200	800	100
Colour	CPU	650	5500	400

1.3.4 The No. 2 effluent treatment system

Approximately 1 km after leaving the mill, the No. 2 effluent drain divides, allowing effluent to be directed to two separate treatment and disposal areas (Figures 1.2 and 1.3):

1) biological treatment in two mechanically aerated lagoons (K and I basins) followed by a naturally aerated storage lagoon (J basin). Characteristics of these basins are listed in Table 1.4. Effluent leaving J basin flows down a natural stream channel into the Waituna Stream, which joins the No. 1 effluent system prior to its discharge into the Kopakorahi Arm of Lake Maraetai; or

2) direct application of the untreated effluent to land in two sets of seepage ponds, the Access Road (AR), and the Extension Area (EA) systems.

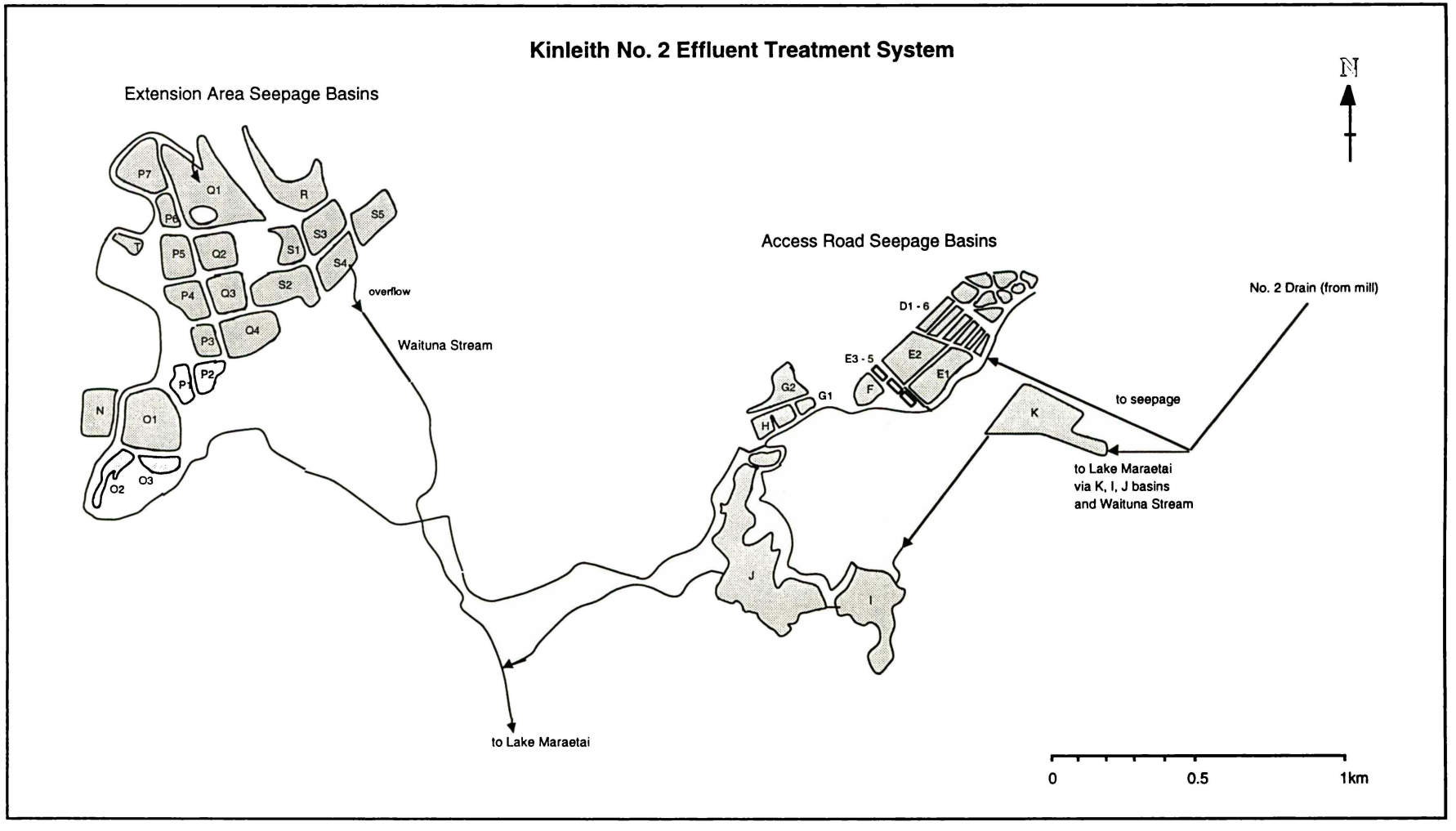


Figure 1.2: Kinleith No. 2 effluent treatment system

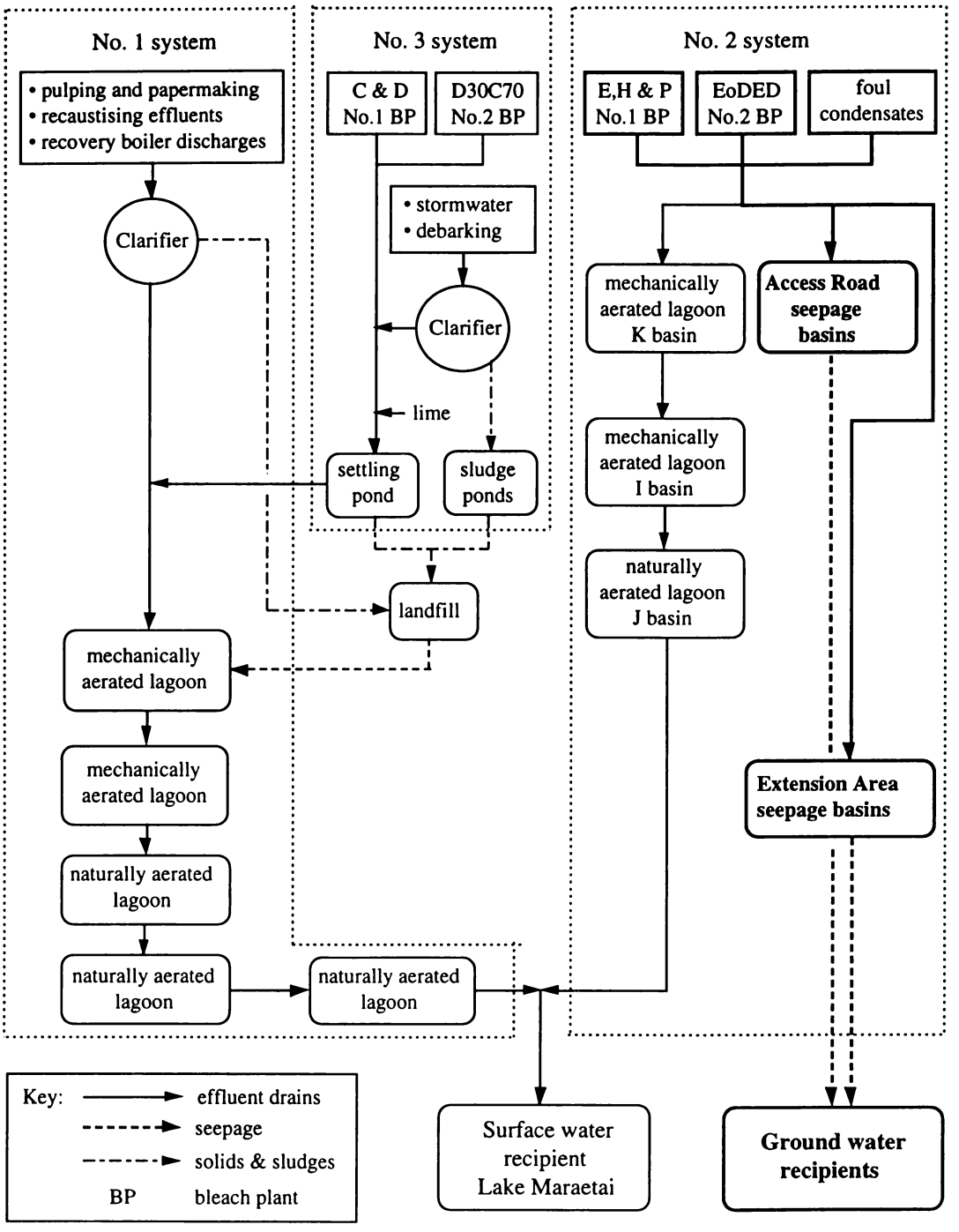


Figure 1.3: Schematic representation of the effluent systems operating during the study. No.2 effluent LA system bolded and shaded (adapted from Stuthridge 1990).

The volume of effluent distributed between each disposal option was determined by receiving water quality at the discharge point in Lake Maraetai and the available storage in the seepage system. During normal operation preference was given to feeding the aeration/storage basins, about 60% of the effluent being directed via this route to the lake. This enabled adequate storage capacity in the seepage pond system to be maintained. When dissolved oxygen conditions at the legally designated effluent discharge point in Lake Maraetai approached the 5

mg L^{-1} permitted minimum, effluent flow from J basin into the Waituna Stream was reduced, and greater use was made of the LA system.

Considerable flexibility and control of effluent disposal could therefore be exercised and the impacts on the surface receiving waters reduced, especially at times when dissolved oxygen conditions within the lake were critical.

Table 1.4: Characteristics of the biological treatment lagoons in the No. 2 effluent system (after Stuthridge 1990)

Parameter	Units	Aerated lagoons I,K basins	Storage lagoon J basin
volume	m^3	277,000	230,000
depth	m	3	3
hydraulic retention time	days	28	23
aeration	kW	260	0
volatile suspended solids	mg L^{-1}	50	50
dissolved oxygen	mg L^{-1}	1.2	0.2
BOD_5 removal	tonne d^{-1}	2.6	1.6
BOD_5 removal	%	45	12.5
COD removal [a]	%	---------- 25 ----------	
temperature range [a]	°C	---------- 11-20 ----------	
pH [a]	pH units	---------- 8 ----------	

a: typical values for the combined K, I, and J basin sequence

1.4 Previous Studies of the Land Application System

When the thesis study was initiated in 1985, a considerable amount of background information relating to the LA system, the geohydrology of the area, and the effect of LA on the inorganic chemistry of the ground water had been accumulated. Some preliminary data on the organic composition of the No. 2 effluent had also been collected. This section summarises the information available at the start of the study (1985/86) and outlines why further study of the LA and ground water systems was warranted. Table 1.5 lists the background information available at, or near, the start of the project.

1.4.1 Operation of the land application system

The 86 ha LA system consisted of 44 shallow seepage basins, each about two metres deep, grouped in two separate areas (Figure 1.3). Table 1.6 provides a summary of the features of the two areas. An indication of the physical setting is given by the aerial photograph of the EA seepage system (Figure 1.4).

Table 1.5: A summary of information available in the initial year of the project

Subject Area	Reference
Ground water resources for mill supply investigated, commentary on seepage disposal system, geological descriptions	Martin (1961)
Isotopic analyses of Kinleith ground waters: attempted use of $^{18}O/^{16}O$ ratios to identify effluent contaminated ground waters	Taylor (1973)
Ground water contamination of Tokoroa ground water by Kinleith effluent: historical ground water monitoring results, geohydrological summaries and implications for effluent movement in ground waters	Nairn (1974)
Placement of cased wells for identification of aquifers contaminated by effluent from the AR seepage system	Houghton (1977)
Trial use of electrical resistivity to determine effluent contamination in the aquifers	Risk (1980)
Summary of investigations of the seepage disposal systems to 1985	Gifford and Campin (1985)
Review of seepage system, geohydrology, extent of effluent migration in ground waters, conceptual model of seepage system hydrogeology	Geo-Engineering (1985)
Geohydrological investigations in Tokoroa-Kinleith area: water balances, geology, aquifer characteristics, effects of effluent seepage on ground water chemistry; initial study of organics in ground water	Tracey (1986)
Ground water contamination from Kinleith: summary of ground water chemical data, contamination patterns	Bird (1986)
Geological investigations south of Kinleith to clarify geology and its implications for effluent migration from seepage ponds; earlier geohydrological models corrected	Houghton (1986)
Interactions of Kinleith seepage pond effluent with a range of soils	Williams (1986)
Identification of critical issues related to effluent management	Campin (1987)

Table 1.6: Summary of seepage area features

	Seepage basin system	
Feature	Access Road	Extension Area
Commissioning date	1960	1966
Location (km west of mill)	2	6
Elevation (m a m s l)[a]	364	360
Total area (ha)	30	56
Number of basins	23	22

a: metres above mean sea level

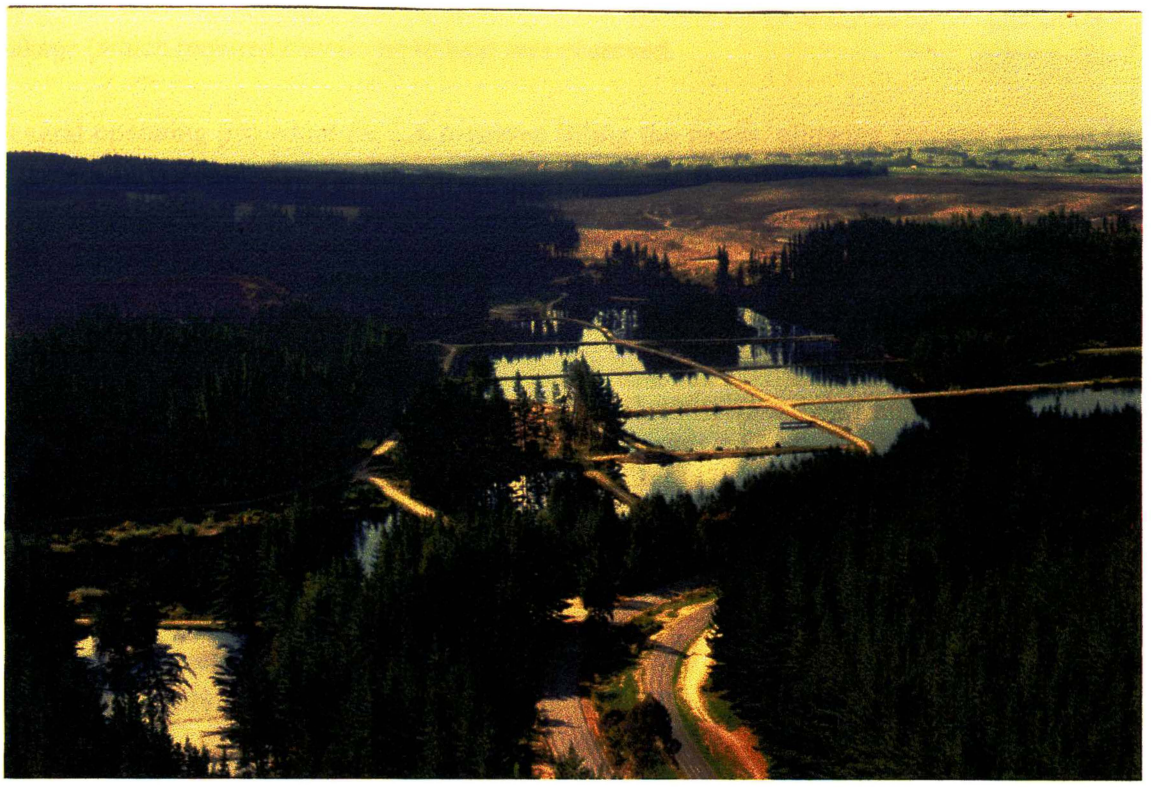


Figure 1.4: Aerial view of the Extension Area seepage basins

The AR basins were the first seepage ponds used, beginning in April 1960. In 1966, an additional set of basins, making up the 56 ha EA, were commissioned. From 1966 to the mid-1970s, effluent flow was divided between these two sets of basins; available storage in each area was used to determine effluent distribution. From the mid-1970s to the mid-1980s, because of public concerns that effluent from the AR basins was causing contamination of ground water supplies, preference was given to the effluent disposal through the EA ponds (Nairn 1974; Gifford and Campin 1985; Bird 1986).

From 1960 to November 1967, the seepage ponds were used for 12 months of the year, with any overflow discharged via the Waituna Stream to Lake Maraetai. From then onwards, the general management approach was to load the LA system from April to mid-November (i.e. Autumn-Winter-Spring), allowing the ponds to dry over summer. In late summer (March-April), to maintain seepage rates, the floors of the basins were disced to a depth of about 0.8 m (Geo-Engineering 1985).

Annual average loading rates of 19,000 m^3d^{-1} for the 1960-67 period (Nairn 1974), 13,500 m^3d^{-1} for the 1968-71 period (Nairn 1974), and 9,200 m^3d^{-1} for the 1976-83 period (Tracey 1986), have been reported. The long term average annual loading was estimated to be 10,000 m^3d^{-1} (Gifford and Campin 1985). Seepage losses from the unlined effluent channels or aeration/storage lagoons of the No. 2 system have been assessed to be less than ±1,000 m^3d^{-1}, the gauging accuracy of the effluent flow monitoring system (Tracey 1986). A notable

exception occurred during the development of the Access Road and K basins, when major leakage (which required clay lining to halt) was observed.

General operating procedure for LA involved filling the ponds, allowing seepage to occur (a process which could take up to 2 months to re-expose the basin floor), then adding more effluent to ponds in which effluent levels had sufficiently dropped. Noticeably variable infiltration rates between the ponds had been observed, but not quantitatively reported.

1.4.2 Hydrogeology of the Kinleith area

Characterisation of the soils, sediments, and aquifers underlying a LA system is required to ensure the hydraulic properties of the system are adequately understood. Five major geological units underlie the Tokoroa-Kinleith area (Houghton 1986; Geo-Engineering 1985; Tracey 1986). All are of volcanic origin, and are classed as ignimbrites. Ignimbrites are extensive, sheet-like masses of poorly sorted pumice and fine ash formed from explosive eruptions of huge volumes of degassing viscous molten rock. Between these major units there may exist further minor layers which, although not important as productive aquifers or effluent disposal zones, have a potentially important role in providing low permeability barriers between the major aquifers.

As the molten rock settles and cools, its density and welding increases. The degree of welding depends on several factors including temperature of the gas-particle mixture on deposition, its chemical composition, rate of cooling, and local temperatures and pressures within the deposit. Welding leads to fracturing of the rock, and it is the nature and extent of these fractures that impart important hydrological properties to the ignimbrite aquifers. Fracture permeability dominates many ignimbrites because of their generally low porosities, and therefore the location, orientation, and continuity of the fractures strongly influence ground water (and hence contaminant) movement. The densely welded zones act as independent aquifers, separated by essentially impermeable unwelded ignimbrite zones (Houghton 1986).

Of the five major units in the Kinleith area, the top three, the Whakamaru, Waiotapu, and Marshall ignimbrites, dominate the geology and hydrology and are of most importance with respect to the fate of effluent in the ground water system. Figure 1.5 depicts the generalised stratigraphic column for these units in the Kinleith area. Two deeper units, the Ongatiti and Rocky Hill ignimbrites underlie these three units, but are present at depths too great to be significantly affected by the LA system. In addition to the ignimbrites, the surficial materials are important because they control the rate at which land-applied effluent infiltrates to ground water. It is also within this shallowest geological zone that most effluent renovation is likely to occur.

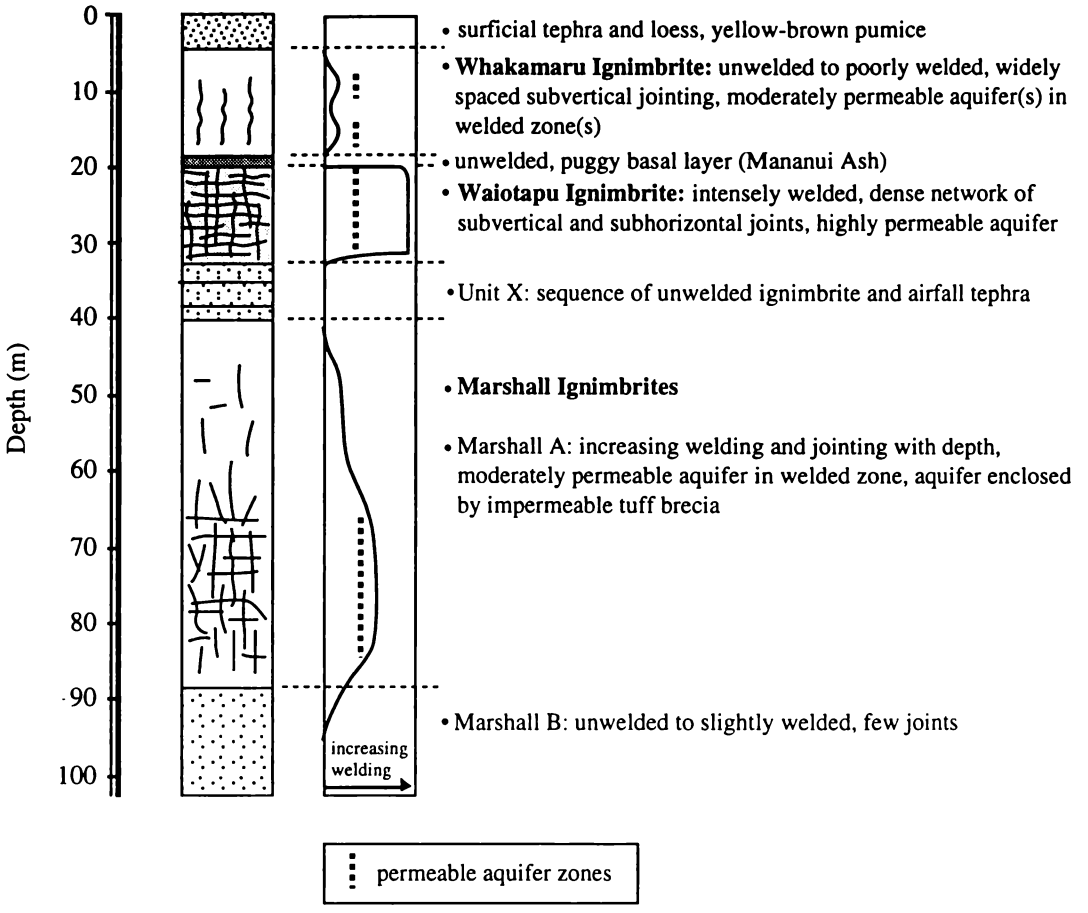


Figure 1.5: Generalised stratigraphy of the ignimbrites underlying the Kinleith area

Surficial materials

Overlying the ignimbrites is a layer of surficial ash. Two to seven metres of these weathered, fine-grained fall deposits and wind-blown loess cover most of the Kinleith area. Depths average about 2.5 m. The ash is highly porous and contributes to low runoff and high ground water recharge. Soils in the area are classed as yellow-brown pumices, and are characterised by coarse textures (sand, silty sand, sandy silt), poor structure, friability, low density, and high porosity (NZ Soil Bureau 1968). The effluent ponds are sited in the surficial ash material.

Whakamaru Ignimbrite

This is the most recent of the ignimbrite deposits, and therefore it is generally found overlying the others. It occurs as a gently northward-dipping sheet which increases in thickness from 20-30 m at Kinleith to 30-60 m near Tokoroa. South of Kinleith it is discontinuous, forming tongues in the deeper valleys which fall sharply to the Waikato River, where its thickness can exceed 200 m (Houghton 1986).

It is typically mildly welded, and contains widely spaced (1-5 m), rounded, sub-vertical joints. Permeability is a combination of limited fracture permeability within the moderately welded basal zones, and porosity permeability in the upper unwelded portion. Close to Kinleith, it appears to form a single aquifer sealed at the base by a thin, puggy, fine ash layer, the Mananui Ash. This layer may not be continuous, and the predominance of vertical jointing in the basal

sections of the ignimbrite may enable ground water interaction with the underlying Waiotapu Ignimbrite aquifer.

Vertical drainage conduits, which are locally referred to as tomos, are easily formed in the unwelded Whakamaru Ignimbrite (and in the overlying unconsolidated surficial ashes), and are features of the surface geology of areas in the vicinity of Kinleith (Geo-Engineering 1985). Rapid transport of land-applied effluent to underlying aquifers may result from preferential flow through these conduits, facilitating effluent disposal but possibly limiting treatment processes associated with effluent-soil interaction.

The Whakamaru Ignimbrite aquifer is generally considered to be low yielding and most suitable for low-use domestic or farm supply.

Waiotapu Ignimbrite

The second ignimbrite of the sequence, the Waiotapu Ignimbrite unit is thin, widespread, and intensely welded, reflecting a high temperature and energy deposit. It forms a north-sloping sheet north of Kinleith, but is not present to the south. Porosity is very low, but bulk permeability is extremely high due to a dense, open jointing system with a significant horizontal orientation. The aquifer is highly productive and has regional significance for water supply; both Kinleith mill and Tokoroa township draw water from this aquifer.

Marshall Ignimbrites

Less information on the characteristics and distribution of the Marshall Igninbrites was available at the start of the study. Their importance with regard to the fate of EA seepage pond effluent was first established in 1986 (Houghton 1986).

Two different units, the "Marshall A" and the underlying "Marshall B", were identified as making up the Marshall Ignimbrites. Welding and fracturing were found to be less intense than in the Waiotapu Ignimbrite and therefore the fracture permeability was expected to be intermediate between that of the Whakamaru and Waiotapu ignimbrites. Thickness of the units in the Kinleith area was estimated to be greater than 70 m, but regionally poorly defined, as most bores did not completely penetrate them.

1.4.3 Ignimbrite distributions relative to the seepage basins

The location of the seepage basins in relation to the sub-surface geological units is an important factor affecting the fate of the land-applied effluent. The rate and direction of effluent transport away from the seepage areas, and the spatial distribution of effluent in the ground water system are largely dependent on the ignimbrite unit into which the effluent is initially introduced, and on the hydraulic connectivity between the ignimbrite aquifers.

Houghton (1986) clarified uncertainties in the earlier hydrogeological models of the area, particularly with respect to the geological position of the EA ponds. The AR basins lie on the southern edge of the Waiotapu Ignimbrite sheet. The ponds most probably discharged effluent to the Waiotapu Ignimbrite either directly or via the Whakamaru Ignimbrite. As the Waiotapu

Ignimbrite does not extend further south than the ponds, the effluent from the ponds could not migrate south, but was contained within the north-draining Waiotapu and, to a lesser extent, Whakamaru ignimbrite aquifers. Movement of effluent into the deeper Marshall Ignimbrites was considered unlikely due to the low permeability zone separating the Marshall and Waiotapu ignimbrite aquifers.

The EA ponds are sited at least 300 m west of the southern edge of the Waiotapu Ignimbrite sheet. Examination of the ignimbrite outcrops closest to the ponds revealed Whakamaru overlying Marshall Ignimbrite, with Waiotapu Ignimbrite apparently absent. This observation suggested that the EA basins would not contribute effluent to any plume moving northwards from the AR seepage ponds, which was contained largely within the Waiotapu Ignimbrite. Further, the presence of large areas of welded Marshall Ignimbrites exposed at the ground surface adjacent to the EA ponds suggested that the Marshall aquifers were probably receiving effluent from this seepage area.

1.5 Ground Water Contamination Studies

In 1961, one year after the commissioning of the AR seepage basins, complaints of contaminated bore water from a bore sited at Maraetai Mill, about 2 km northwest of the ponds (Figure 1.1), were made. Concern was expressed for the potential contamination of the Tokoroa Borough municipal water supplies, which draw from ground water about 6.5 km north of the ponds. In response to these concerns, several investigations into the fate of the seepage effluent and the associated public health implications were initiated by NZFP, the Department of Scientific and Industrial Research (DSIR) Geological Survey, the Department of Health (DoH), and the Waikato Valley Authority (WVA), the regulatory authority responsible for water and soil management at that time.

Two regular ground water quality monitoring programmes, which aimed to check for water supply contamination, had been in operation since 1960 (Gifford and Campin 1985; Bird 1986). In addition, as part of a study of the water resources of the Tokoroa region (Bird 1987), one survey of ground water chemistry, which included bores suspected of contamination, was also carried out.

Of the determinands measured in these surveys, Na^+ was considered the best indicator of effluent contamination because of its high concentration in the seepage pond effluent, its high mobility in ground water systems, and because it was measured in all three surveys (Bird 1986). The Na^+ data from these programmes was analysed by Nairn (1974), Geo-Engineering (1985), and Bird (1986). The following sub-sections summarise their findings.

1.5.1 NZFP fortnightly monitoring

In this programme five bores were sampled fortnightly between 1960 and 1984. Four of these were incompletely cased wells drawing mostly from the Waiotapu Ignimbrite aquifer, and one was the Tokoroa spring, originating from within the Whakamaru unit. Figure 1.6 shows Na^+ concentrations in four of these wells (locations shown in Figure 1.1) between 1960 and 1984.

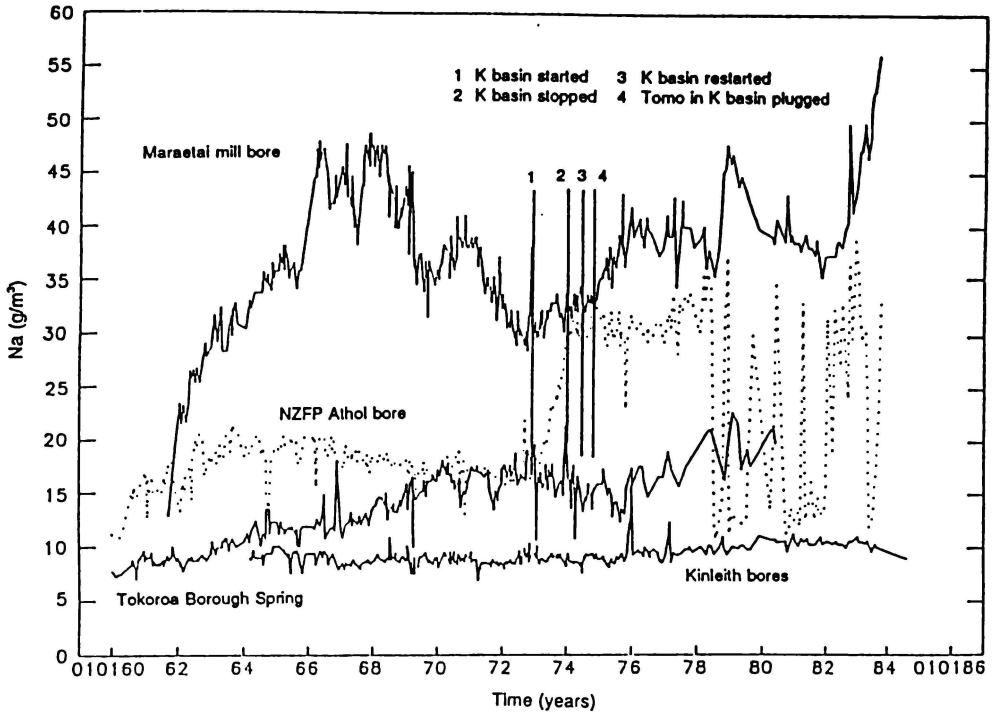


Figure 1.6: Sodium concentrations in ground waters monitored in the NZFP programme (after GeoEngineering 1985)

Major changes in the Na^+ concentrations of bore waters from the Maraetai Mill and NZFP Athol wells were recorded after effluent disposal by seepage began. These changes appeared to coincide with the management regimes operating in the seepage system. Increases in Na^+ concentrations were observed shortly after seepage disposal in the AR system commenced in 1960. Na^+ levels in the Maraetai Mill bore waters began to decrease in 1967. This drop coincided with reduced effluent loading to the AR ponds which occurred at about this time after commissioning of the EA basins.

Substantial increases in Na^+ in waters drawn from the NZFP Athol bore were measured in 1973. These corresponded to the first use of the aerated lagoon K basin. This lagoon, which was believed to have been excavated close to (or into) the Waiotapu Ignimbrite, developed major drainage fissures or "tomos" in its base. Effluent losses of approximately 10,000 m^3d^{-1} for several months were reported to have occurred through K basin leakage. Use of the pond was stopped in early 1974, while attempts were made to seal its base. It was restarted in late 1974, and final sealing was achieved in early 1975.

A drop in Na^+ concentrations in the Athol bore waters was recorded in 1979 and was attributed to a lack of well pumping during 1978. Variability in Na^+ occurring after this was thought to be due to sampling problems (Geo-Engineering 1985).

The Tokoroa Borough Spring showed a gradual increasing trend in Na^+ concentrations over the monitoring period, suggesting that some effluent contamination was occurring. The absence of

any marked changes in ground water chemistry in response to pond management changes was consistent with greater dilution, mixing, and dispersion of effluent by the time sites further from the effluent source were reached.

Waters from the Athol County and Jack Henry bores contained lowest Na^+ concentrations, indicating no appreciable effluent contamination in the waters sampled at these sites.

1.5.2 NZFP-Department of Health monitoring

Nineteen sites were monitored in this programme, two springs and 17 bores, four of which were included in the NZFP programme. Fourteen of the bores were used for farm supply (domestic and stock water). Sampling frequency was twice-yearly between 1970 and 1981, then annually from 1981 to 1985. The data collected in this programme showed that distance from the seepage ponds did not account for the distribution of Na^+ concentrations. Instead, there appeared to be zones affected by effluent (i.e. having elevated Na^+ concentrations) and others approximately equidistant from the ponds which were largely unaffected. Concentrations in some wells were also highly variable.

These effects were attributed to the predominance of fracture flow in the Waiotapu Ignibrite aquifer, with effluent following well defined flow paths rather than a more uniform radial spread as found in homogeneous aquifers.

1.5.3 Waikato Valley Authority survey

In this survey, 61 bores were sampled on one occasion in May 1986. The study obtained results which were consistent with those of the other monitoring programmes and found that between 13 and 16 bores and springs contained Na^+ concentrations sufficiently higher than background levels to be suspected of being effluent contaminated. All but three of these were water supply bores or springs (Bird 1986).

1.5.4 Limitations of these monitoring programmes

These monitoring programmes were able to show that marked changes had occurred in the chemistry of some ground waters north of the seepage ponds. The observed effects were almost certainly attributable to ground water contamination by effluent seepage.

Two problems with the programmes were identified by Gifford and Campin (1985). Firstly, all the bores in the NZFP and NZFP-DoH programmes were uncased, and therefore were yielding water from all aquifers through which the bores passed. Secondly, a number of the bores were too shallow to penetrate the Waiotapu Ignimbrite aquifer, which was believed to be the major recipient for effluent from the AR area. In addition, the quality of the bore logs for most bores sampled was poor, compounding the problem of determining the units from which water was being sampled, and the zones in which effluent was migrating (Tracey 1986).

Confirmation that the effluent contamination north of the AR ponds was confined largely to the Waiotapu Ignimbrite aquifer was obtained by Houghton (1977) from cased bores drilled into each of the Whakamaru, Waiotapu, and underlying ignimbrites (bores 82, 83 and 84; Figure

1.1). Samples from the Waiotapu Ignimbrite aquifer contained Na^+ concentrations of approximately 70 mg L^{-1}, levels which were higher than had been found in any previously sampled ground waters.

In the overlying Whakamaru Ignimbrite aquifer, Na^+ concentrations were approximately 20 mg L^{-1}, while in the ignimbrite beneath the Waiotapu about 7 mg L^{-1} Na^+ was found. This indicated that some contamination of the shallowest ignimbrite aquifer was occurring, but that effluent migration to deeper aquifers was not. The suspected unsuitability of the shallow, uncased wells used for much of the previously described routine monitoring programmes was therefore confirmed.

Other attempts to determine effluent contamination in ground water by ^{18}O isotopic enrichment (Taylor 1973) and surface electrical resistivity soundings (Risk 1980) were unsuccessful. Although not unique to the mill effluent, Na^+ was therefore found to be an effective and practical tracer of effluent in the ground water system.

1.5.5 Organic compounds in effluents and ground waters

Effluent studies

Panadam *et al.* (1984) and Stuthridge (1984) reported the results of initial studies of EOs in the Kinleith mill effluents. A range of compounds including monoterpenes (MTs), saturated and unsaturated fatty acids (FAs), and resin acids (RAs) were identified as dominant species in the No. 2 effluent. This effluent stream was found to contain concentrations of solvent-extractable material totalling over 700 mg L^{-1}, the highest of any of the effluents leaving the mill.

It was tentatively estimated that about 90% of the EO content was being removed from the No. 2 effluent during its passage through the K, I, J basin system. RAs appeared to be relatively more resistant to removal, the principal species leaving J basin being dehydroabietic acid and an hydroxylated resin acid compound of uncertain structure. The processes responsible for the observed removals were not clear from the data collected.

Ground water studies

In response to complaints of oily films, and taste and discolouration problems, "hydroxylated aromatics" were determined on water taken from the Riley farm bore (Figure 1.1) on three occasions in 1971 (Nairn 1974). The results were variable, concentrations of 0.30, 1.90, and 0.01 mg L^{-1} being found in samples taken in February, April, and June respectively.

Absorbance at 270 nm (A270) and BOD_5 levels were measured as part of the WVA ground water survey (Bird 1986). A270 was used as a measure of the concentration of effluent-sourced polyphenolic compounds, as used in studies of the effect of Kinleith effluent on colour in the Waikato River (Timperley 1985). Several sites were found to contain elevated A270 levels, including three which also contained high Na^+ concentrations. However, the non-specific nature of these methods made them no more useful than Na^+ for confirming effluent contamination. The BOD_5 results indicated that some wells contained organic material from sources other than the mill effluent.

In an initial attempt to use tracers more effluent-specific than Na^+ to unambiguously identify contaminated ground water, Tracey (1986) analysed eight bore water samples for EOs. Only the result for water from the bore at Maraetai Mill (Figure 1.1) was presented. RAs, including dehydroabietic acid (a major component of the mill effluent), were found at concentrations of 2–5 $\mu g\ L^{-1}$.

1.6 Summary of Information on the Kinleith LA System

From 1960 to mid-1988, about 10,000 m^3d^{-1} of bleach plant and foul condensate effluent was discharged via seepage to ground water. The effluent contained high concentrations of Na^+, colour, BOD_5, and solvent-extractable organics.

Studies of ground water chemistry, using Na^+ as an effluent tracer, indicated that some ground waters between Kinleith and Tokoroa were contaminated by the effluent. RAs, which were most probably effluent-sourced, were also found in one sample.

The hydrogeology of the area surrounding Kinleith is based on three major ignimbrite units (Table 1.7). Ground water flow in the ignimbrites is largely through fractures, the density, orientation, and continuity of which strongly influence vertical and horizontal ground water movement.

Table 1.7: Characteristics of the three most important hydrogeological units around Kinleith

Ignimbrite unit	Characteristics	Relevance to LA project
Whakamaru	10-60 m thick; unwelded to poorly welded; infrequent, widely spaced vertical jointing; generally low yielding	received some effluent from AR ponds; farm bores tap this unit
Waiotapu	10-50 m thick; highly welded, dense network of horizontal and vertical jointing; high yielding	received effluent from AR ponds; major public and industrial water supply source
Marshalls	>70 m thick; extent of jointing uncertain; moderately permeable aquifer in welded zones	welded portion exposed beside EA basins; suspected to be recipient for EA seepage; flow directions and patterns unknown

Effluent from the AR seepage area seeped through a surficial ash layer into the Whakamaru and/or Waiotapu Ignimbrite(s) then flowed north to north-west towards Tokoroa. A substantial amount of untreated effluent also entered the ground via flow through fissures in K basin.

The Na^+ concentrations in ground waters from some wells between Kinleith and Tokoroa increased in response to the effluent discharge. However, a simple radial plume of effluent contaminated ground water moving away from the ponds was not observed due, in part, to the aquifer's fracture-flow characteristics. Plume definition was hampered by sampling bores which were not aquifer specific, water from both the Waiotapu and Whakamaru Ignimbrite aquifers

being taken from most bores. Samples taken from one set of aquifer specific bores placed in 1977 determined that most contamination was present in the Waiotapu aquifer.

The fate of effluent applied to the EA basins was unknown. Geological studies in 1986 indicated that the Marshall Ignimbrites were likely recipients. The direction and rate of movement of ground water and effluent in these aquifers were unknown.

Volumes of effluent applied to each seepage area were approximately known, but no measures of treatment achieved in the system were documented. Effluent composition was adequately known for colour, sodium, and BOD_5. Some preliminary data on the composition of the EO fraction showed it to contain high concentrations of MTs, FAs, and RAs.

Major areas of uncertainty at the start of the project were: 1) the behaviour and fate of the effluent's EOs and colour in the LA system and underlying ground waters; 2) the fate of effluent from the EA seepage basins; and 3) the nature of the geology and hydrology under and around the EA basins.

1.7 Justification for Further Studies

1.7.1 Company perspectives

In the mid-1980s, NZFP carried out a major review of markets for products from the Kinleith mill. As part of this review, changes in process technology required to produce pulp and paper products of sufficient quality and quantity to meet the requirements of an increasingly demanding market were investigated. Increases in production capacity were likely to be required for economic reasons. Changes to the types of processes used were envisaged to be necessary to achieve higher production, to make products with lower concentrations of chemical contaminants (e.g. chlorinated dibenzodioxins), and also to reduce environmental impacts of mill effluents.

Effluent management strategies which would account for the proposed changes in production methods were developed so that existing and planned operations would meet long-term statutory obligations with respect to effluent quality, quantity, and environmental effects in the receiving waters (Campin 1987). Critical areas requiring immediate study were effluent flow, colour, and BOD discharges to the Waikato River. If mill production was to increase (using conventional technology), it was considered vital that a major portion of the mill's effluent colour continue to be discharged to a recipient other than the Waikato River, to avoid causing unacceptable adverse effects in the surface water receiving environment.

The segregation and separate treatment of the No. 2 effluent stream, the most highly coloured waste water leaving the mill, was considered to be the most practicable method of reducing colour load to the river. Two options for reducing the colour were investigated: 1) physical or chemical treatment to produce a lower-coloured effluent which could then be discharged to the surface water recipient; or 2) using ground waters as effluent recipients.

Literature reviews and world-wide industry liaison carried out by NZFP revealed that no operational plant in the world at that time was providing colour removal performance sufficient to meet the Company goals. Disposal to ground water was therefore considered to be the only practicable option available at that time.

The primary requirement for a LA system was the ability to handle sustained use with acceptable environmental effects. Several methods of achieving effluent discharge to ground water were viewed as possibilities, including:

- the existing LA system, managed as it had been for the previous 25 years;
- LA based on the existing system, but incorporating pretreatment to reduce levels of suspended solids and/or BOD;
- LA using methods other than seepage basins (e.g. spray irrigation); and
- direct injection of effluent into shallow or deep aquifers.

If effluent disposal to ground water proved unsuitable, changing process technology to produce effluent with lower colour and organic content would be required.

LA of some form was therefore considered important for continued operation of a conventional-technology mill. The ability of the LA system to treat and dispose of the effluent needed to be determined to ensure it represented a viable long-term solution for effluent treatment, and that it would meet the environmental standards necessary to obtain discharge permits.

1.7.2 Public concerns and regulatory authority requirements

Public concern about the presence of effluent-sourced contaminants in ground waters used for public and private water supply had been voiced since 1961. Na^+ data indicated that a significant component of ground water drawn from some wells was effluent-sourced. While the Na^+ itself was not constituting a human health hazard at the concentrations found, it was recognised that effluent-affected ground water could contain other constituents, principally organic compounds, that were of uncertain and potentially undesirable character. The regulatory authority therefore recognised that it was necessary to identify and quantify effluent-sourced organic constituents in the ground waters (Marshall 1987).

The status of the LA system as a legally authorised waste discharge was unclear. The environmental protection legislation in operation at the time (Water and Soil Conservation Act 1967) prohibited discharge of any waste to land if contamination of natural water, including ground water, resulted [section 34(1)]. Establishing the nature and extent of the impacts of the LA system on ground water quality was therefore essential information for obtaining discharge permits for the LA system.

1.7.3 Academic interests

Investigation of organic compounds in BKME and recipients was, and continues to be, an area of research interest in the Waikato University's Chemistry Department. Studies of organics in Kinleith's pulp and paper mill process wastes had been underway since 1983 (Stuthridge 1984;

Stuthridge 1987). Over the duration of the LA system investigations, more detailed studies of the mill's effluents and the treatment system discharging to surface waters were carried out (Stuthridge 1990). These have subsequently been extended in studies by Zender *et al.* (1994) and Tavendale (1994). At the other New Zealand kraft mill, Tasman Pulp and Paper Company, studies of EOs in the effluent treatment system and riverine receiving waters were also undertaken (Panadam-Twigley 1988). A study of the behaviour of effluent-sourced EOs in the Kinleith LA system and underlying ground waters was therefore complementary to these studies, and a logical extension to previous studies.

Initial studies by Panadam *et al.* (1984) had found high concentrations of EOs in the No. 2 effluent stream. The behaviour and fate of these compounds in the LA system was unknown. A survey of the literature (Chapter 2) found no published studies of the fate of pulp mill effluent organics in LA systems. It was, however, recognised as an area requiring attention (Thacker 1986). Extrapolating the results from one LA system to another is unlikely to provide reliable information due to the site specific nature of the performance of LA systems. Additionally, the Kinleith situation appeared to be unusual, in that it was one of few pulp mills in the world applying an untreated, segregated, waste stream to the land. Study of the Kinleith system was therefore required to ensure that the potential impacts of LA were adequately evaluated.

1.8 Study Objectives and Approach

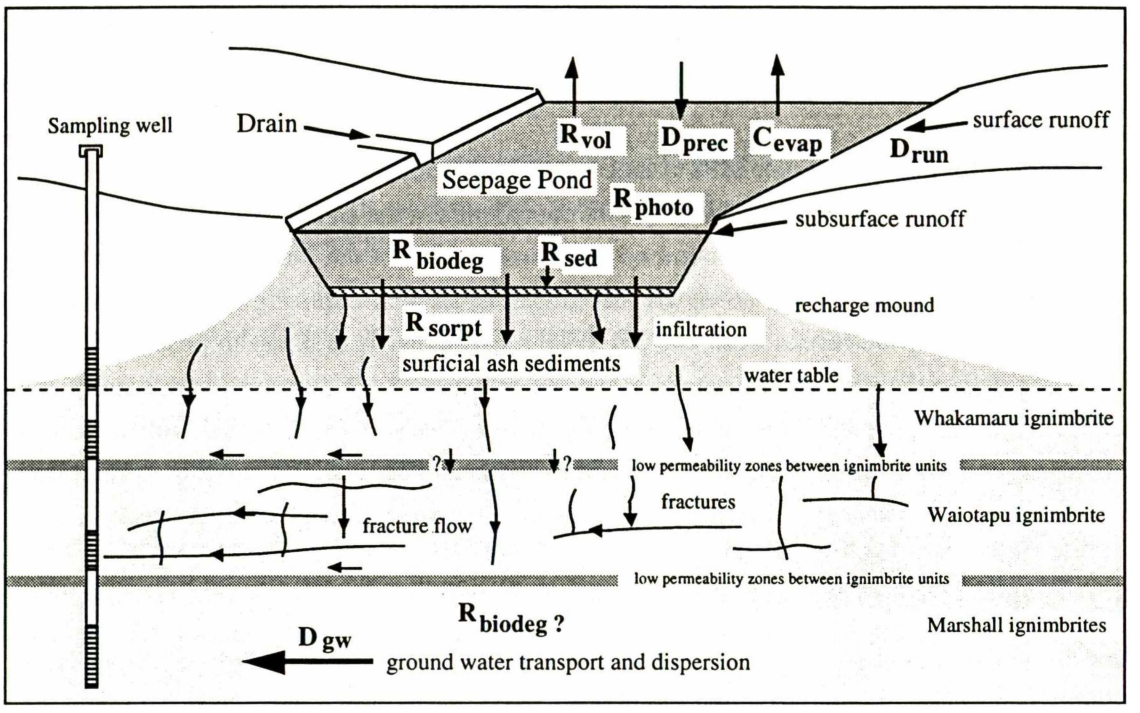
Based on the information available on the Kinleith LA system at the start of the study, a qualitative conceptual model depicting the major compartments of the seepage system, and the treatment processes occurring within these compartments, was constructed (Figure 1.7).

This model highlighted the complexity of the Kinleith situation, particularly with respect to the number of possible processes affecting effluent fate and the heterogeneous geology underlying the LA system. This complexity precluded quantitative development of the conceptual model, the use of which was restricted to identifying important treatment processes and compartments for study.

Sustainable effluent treatment is dependent on active removal processes. Biodegradation (R_{biodeg}), preferably complete mineralisation of organic compounds to CO_2 and H_2O, volatilisation (R_{vol}), and possibly photodegradation (R_{photo}), are the removal processes with the capability to provide on-going protection for ground waters, aquifer media, and soils from contamination by organic compounds entering the seepage system.

Sorption (R_{sorpt}) and sedimentation (R_{sed}) remove effluent constituents from the aqueous phase, but lead to accumulation of these constituents in soils, sediments, or aquifer media. They are removal processes in that they provide some protection to ground water from infiltrating contaminants, but in the absence of biodegradation or other sustainable treatment processes, a system dependent solely on sorption or sedimentation for effluent treatment would have a finite lifetime. Ground water contamination could eventually result from exhaustion of sorption sites and desorption of retained compounds.

Other factors affecting the behaviour of effluent in the LA system include 1) dilution by precipitation (D_{prec}), runoff (D_{run}), and mixing with uncontaminated ground water (D_{gw}), and 2) concentration by evaporation (C_{evap}) from the seepage ponds.



Effluent Modification and Treatment Processes

Dilution:	by precipitation, Dprec; surface and subsurface runoff, Drun; dilution and dispersion in ground water, Dgw.
Removal:	by volatilisation, Rvol; photochemical reaction, Rphoto; sedimentation, Rsed; biodegradation, Rbiodeg; and sorption, Rsorpt.
Concentration:	by evaporation, Cevap.

Figure 1.7: Conceptual model of the seepage system

To evaluate the ability of the LA system to sustainably treat the effluent, the nature and performance of the treatment processes occurring in each compartment of the LA system (the effluent drain, seepage ponds, seepage basin sediments, and underlying aquifer media and ground waters) required assessment. To evaluate the effects of the system on the receiving environment, the chemical composition of aquifer media and ground waters needed to be characterised. These study areas formed the basis of the thesis.

Study objectives

Based on the review of site-specific characteristics and information from other systems (presented in Chapter 2), four major objectives were defined:

1. To measure the treatability of effluent colour and major EOs in the drains and ponds of the seepage system;

2. To determine the penetration of effluent-sourced organic contaminants into sediments and aquifer materials underlying the seepage system;

3. To assess the nature and extent of ground water contamination by effluent-sourced EOs and colour; and

4. To measure effluent treatment and chemical modification occurring during percolation through seepage basin sediments.

The complexity of the subsurface geology beneath the seepage ponds, in particular the fractured nature of some of the ignimbrite units, suggested that carrying out detailed studies of chemical processes occurring beneath the seepage site was likely to be difficult. Field studies of the LA system were therefore complemented with laboratory experiments. An outline of the thesis study areas is given in Figure 1.8.

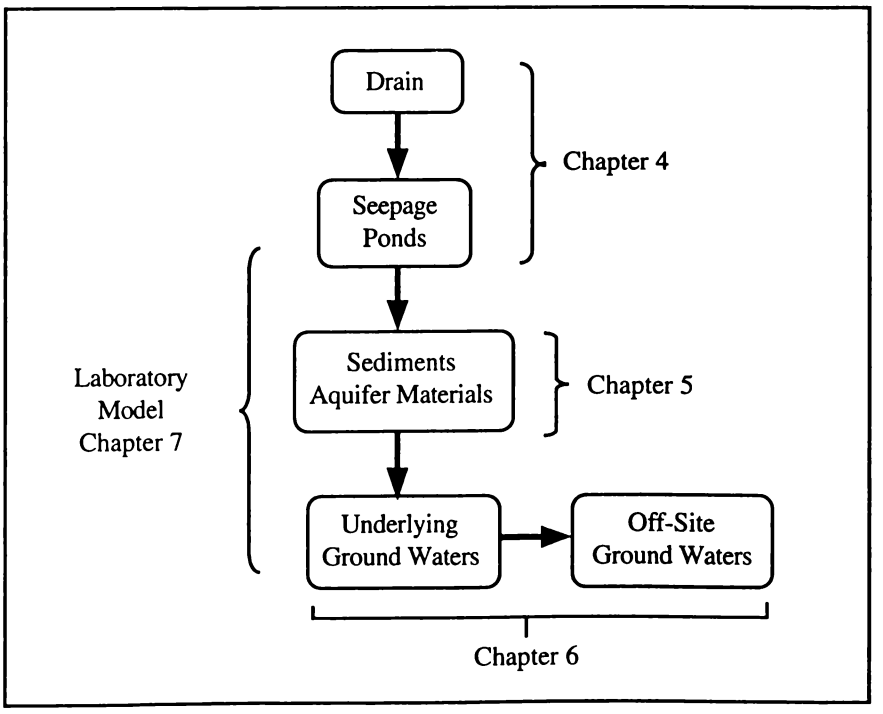


Figure 1.8: Outline of the thesis study, based upon effluent movement through the LA system

The existing information highlighted the need for a multidisciplinary approach to the investigations. An understanding of the geology of the area and the hydrological properties of the ignimbrites was vital for siting sampling wells and for predicting effluent and ground water movement. Study of the physical properties of the surficial materials under the seepage basins and the effect of effluent application on these properties (e.g. infiltration rates) was necessary to predict the system's long term viability for disposal. This hydrogeological work was carried out largely by consultants under contract to NZFP. Hydrological and geological information relevant to the chemical investigations was obtained from the reports of these studies.

In addition to chapters 4–7, the thesis contains a literature review (Chapter 2), a description of analytical methods used in the study (Chapter 3), and a summary and conclusions section (Chapter 8). Appendix 1 lists mass spectra, names, and structures for organic compounds found in the effuents, sediments, ground waters, and soil-column leachates studied in the project. Appendix 2 is a compilation of analytical data tables.

Chapter Two

Pulp Mill Effluent Treatment by Land Application

2.1 Introduction

Pulp and paper production, and the composition and treatment of pulp mill wastes, have been extensively reviewed in books (e.g. Casey 1980; Sjostrom 1981; Springer 1986), critical reviews (e.g. Kringstad and Lindstrom 1984; McLeay 1987; Stuthridge 1990; Tavendale 1994), and many hundreds of research papers. The following overview summarises key features of effluent chemistry which were directly relevant to the Kinleith No. 2 effluent stream as it was at the time of the thesis study.

The site-specific information review (Chapter 1) established that a study of the behaviour and fate of No. 2 effluent in the LA system was required to evaluate the effects of the system on the receiving environment (underlying sediments, aquifer materials and ground waters) and its suitability for on-going effluent treatment at Kinleith. The review of the literature was therefore undertaken to determine:

1. the composition of effluent generated by processes similar to those producing Kinleith's No. 2 effluent;
2. the key effluent constituents whose behaviour and fate in the LA system required assessment; and
3. how these key effluent constituents behave in other LA systems similar to the Kinleith system.

Based on the site-specific information and wider literature assessments, some speculative predictions of the likely perfomance of the Kinleith LA system were made, and information gaps requiring further study defined.

2.2 The Composition of Bleached Kraft Mill Effluent

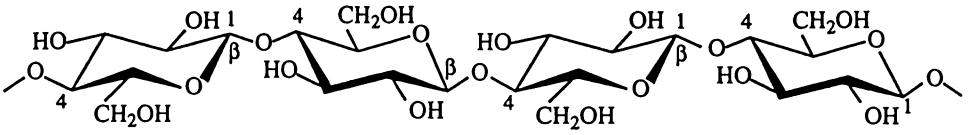
Much of the organic pollutant load of BKMEs is derived from wood constituents, and from derivatives formed during pulp manufacture. Some knowledge of the composition of wood is therefore useful in understanding the composition of the effluents produced during wood processing.

2.2.1 The composition of softwood

The softwood *Pinus radiata* was the major wood species processed at Kinleith. About 90% of a softwood is made up of elongated cells called tracheids (or fibres). The cell walls are made of cellulose and hemicelluloses which are bound together by lignin which permeates the cell walls and intercellular spaces to provide structural rigidity. Onto this matrix is deposited a mixture of low molecular weight compounds called extractives. The relative amounts of these four major organic components in New Zealand *P. radiata* are: cellulose (42% of the dry wood weight), hemicelluloses (29%), lignin (26%), and extractives (3%) (Uprichard and Lloyd 1980).

Cellulose, the major structural component of plant cell walls, is a linear homopolysaccharide, containing at least 10,000 β-D-glucopyranose units joined by 1,4-β-glycosidic linkages. Strong intermolecular hydrogen bonding occurs between cellulose molecules, causing aggregation into microfibrils. These are further associated to make fibrils, and further still to form cellulose

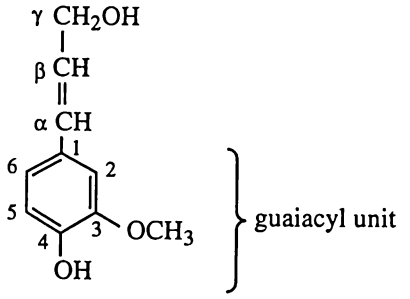
fibres. The fibrous structure and strong hydrogen bonding in cellulose give it high tensile strength (which is required to fulfill its function as a supporting material in the tree) and low solubility in most solvents (Sjostrom 1981).



Cellulose

Hemicelluloses are heteropolysaccharides of much lower molecular weight than cellulose, containing approximately 200 saccharide units per polymer. Principal monomeric components are D-glucose, D-mannose, D-xylose, and L-arabinose. Like cellulose, they provide structural support to the cell.

Lignin is a three-dimensional, branched, heterogeneous, polymer, about 50% of which is aromatic. Its molecular weight in the native state is very high, and could be considered to be infinite (Kringstad and Lindstrom 1984). In softwoods, it is formed by enzyme-initiated polymerisation of 4-hydroxyarylpropenyl alcohols, largely coniferyl alcohol, and therefore guaiacyl groups are the dominant aromatic structural sub-units found in softwood lignin.



coniferyl alcohol

These phenylpropane units, linked by aryl-aryl, alkyl-aryl, and alkyl-alkyl linkages, make up much of the lignin structure (Figure 2.1). In wood, lignin is linked to the polysaccharides by physical sorption and covalent bonding, forming crosslinks between polysaccharide chains (Glasser 1980).

Extractives are low molecular weight compounds which can be removed from the wood with neutral solvents. Softwood extractives are dominated by resin acids (RAs), fats, and terpenes. In *P. radiata,* extractives fall into five major groups: free fatty acids (FAs), fatty acid esters, resin acids (RAs), phenolics, and unsaponifiable neutral compounds (Porter 1969; Lloyd 1978; Uprichard and Lloyd 1980). Figure 2.2 shows the structures of some of the major extractive compounds. RAs and monoterpenes (MTs) protect the wood from biological damage, while FA esters and sterols constitute a store of nutrients required for growth (Sjostrom 1981).

RAs are derivatives of tricyclic diterpenes ($C_{20}H_{32}$ compounds), and in coniferous woods can be classified into two major skeletal types: 1) abietane species, which have a single isopropyl group at C13, and 2) pimarane species, which have both methyl and vinyl substituents at C13. Levopimaric, palustric, and neoabietic acids are present in approximately equal proportions in *P. radiata.*, and together make up about 70% of the total RA content. Smaller amounts of abietic, pimaric, 7,15-isopimaric, 8(9),15-isopimaric, dehydroabietic, and sandaracopimaric acids make up the balance (Lloyd 1978).

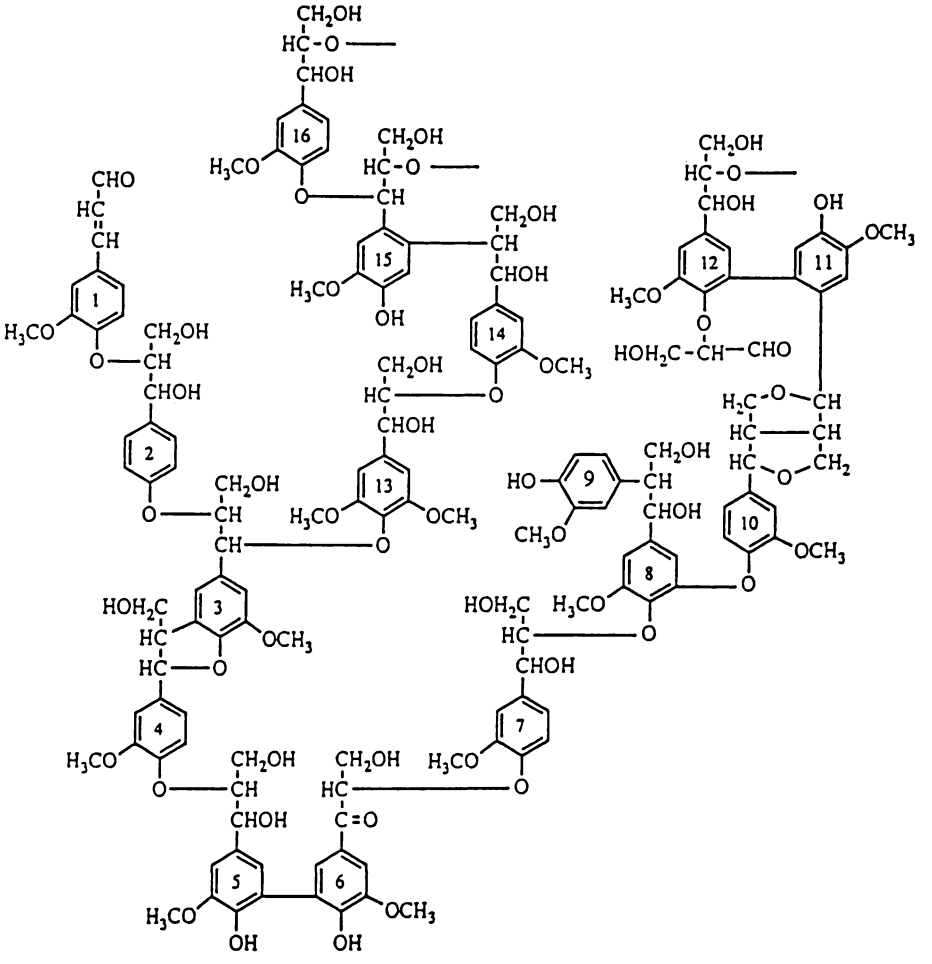


Figure 2.1: Softwood lignin model, showing prominent structural features (after Adler 1977)

FAs are present predominately as triglycerides. Major acid components include a range of unsaturated species, dominated by oleic acid ($C_{17}H_{33}COOH\ \Delta^9$) and linoleic acid ($C_{17}H_{31}COOH\ \Delta^{9,12}$), and C_{10}-C_{24} saturated compounds, of which palmitic acid ($C_{15}H_{31}COOH$) is generally dominant (Lloyd 1978).

About 0.4% of the oven-dry wood weight is made up of volatile constituents (Uprichard and Lloyd 1980). Principal components are the MTs α-pinene (25%) and β-pinene (73%), with minor amounts of camphene, limonene, and β-phellandrene making up the remaining 2% (Blight *et al.* 1964; Bannister *et al.* 1962).

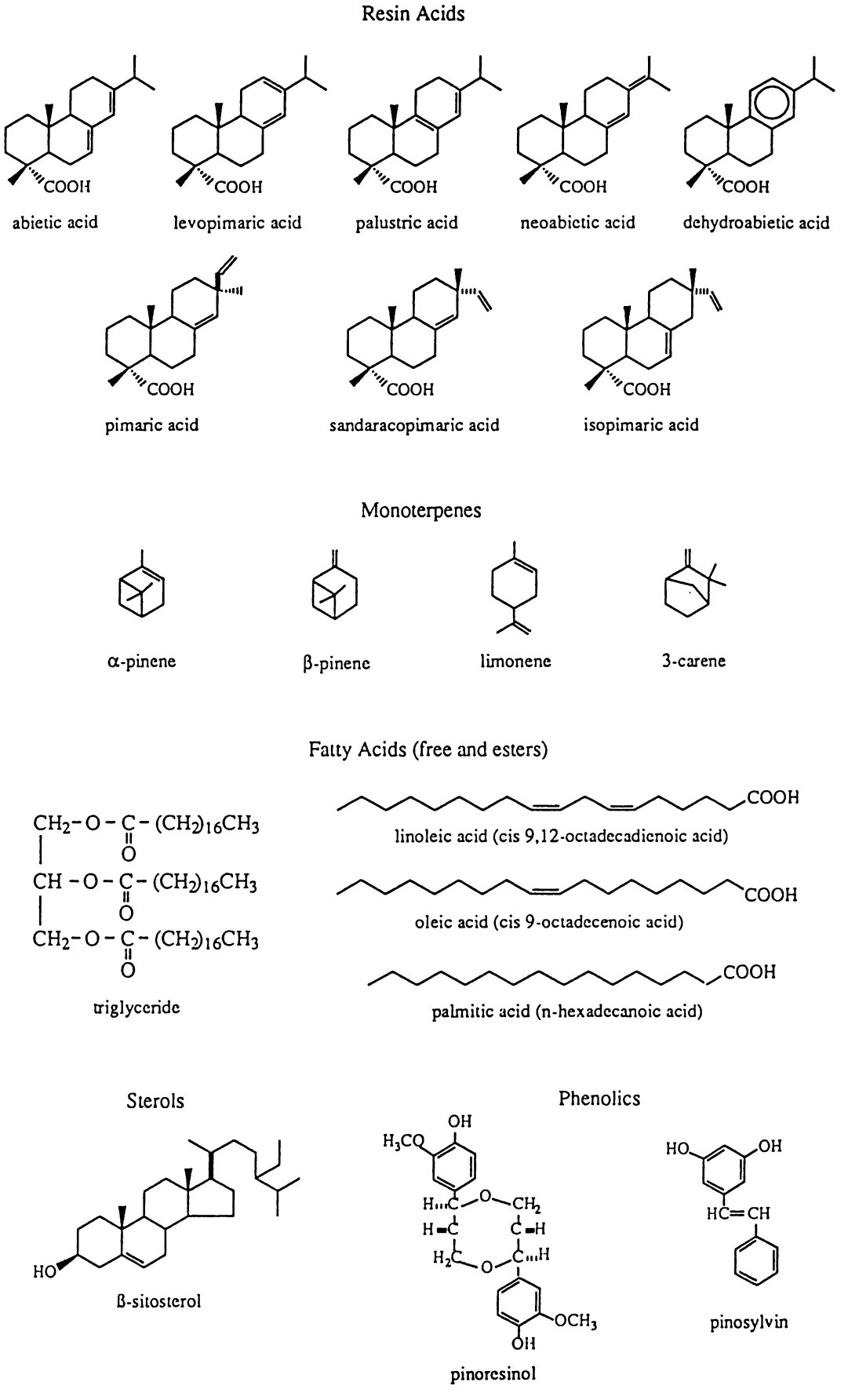


Figure 2.2: Some representative extractive compounds found in *P. radiata* (Sjostrom 1981)

Phenolic compounds are concentrated in heartwood and bark, with only trace levels being present in the xylem (Sjostrom 1981). A wide variety of compounds belonging to groups such as the flavanoids (polyphenols with $C_6C_3C_6$ carbon skeleton), lignans (formed by oxidative coupling of two phenylpropane C_6C_3 units; e.g. pinoresinol), and stilbenes (substituted 1,2-diphenylethylenes; e.g. pinosylvin) have been found.

Unsaponifiable compounds include sterols, of which β-sitosterol is the most abundant. They are also present as the alcohol component of fatty acid ester waxes.

Although extractives are present in relatively minor quantities, they are important because a) they are the source of valuable byproducts from the kraft pulping process (turpentine from MTs, and tall oil from RAs and FAs); b) RAs are major contributors to the acute toxicity of BKME to fish (e.g. McLeay 1987); and c) non-volatile compounds with low water-solubilities (particularly RAs) can cause problems in paper making by polymerising to form resinous "pitch" which deposits on equipment and products and adversely affects paper characteristics (Sjostrom 1981; Suckling and Ede 1990).

2.2.2 The kraft pulping process

The primary aim of pulp production is to isolate, in good yield and with minimal structural degradation, the cellulose and hemicellulose fibres from the rest of the wood matrix. The kraft process has become the most popular chemical pulping process because of its favourable pulping rate, yield, pulp quality and production costs (Bryce 1980).

A mixed NaOH-Na_2S solution called "white liquor" is used at elevated temperature and pressure (170°C, 800 kPa) to remove lignin and extractives. The spent pulping liquor (weak black liquor), which contains high concentrations of process chemicals and dissolved organic materials (about 50% of the total weight of the wood becomes dissolved), is washed from the pulp and sent through a recovery cycle to regenerate the white liquor, energy for heating, and chemical byproducts (Figure 2.3).

The recovery cycle makes the kraft process economical and reduces the amounts of pollutants discharged, both to the air and in liquid effluents. Important steps are:

i) black liquor oxidation, in which sulphides are oxidised, thereby reducing odorous emissions:

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

ii) burning the concentrated black liquor in the recovery furnace, providing energy and process chemicals (Na_2CO_3 and Na_2S, which in aqueous solution is called green liquor):

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$
$$C + O_2 \rightarrow CO_2$$
$$Na_2O + CO_2 \rightarrow Na_2CO_3$$
$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

iii) recausticising, producing NaOH from Na_2CO_3 and CaO:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$Ca(OH)_2 + Na_2CO_3 \Leftrightarrow 2NaOH + CaCO_3$$

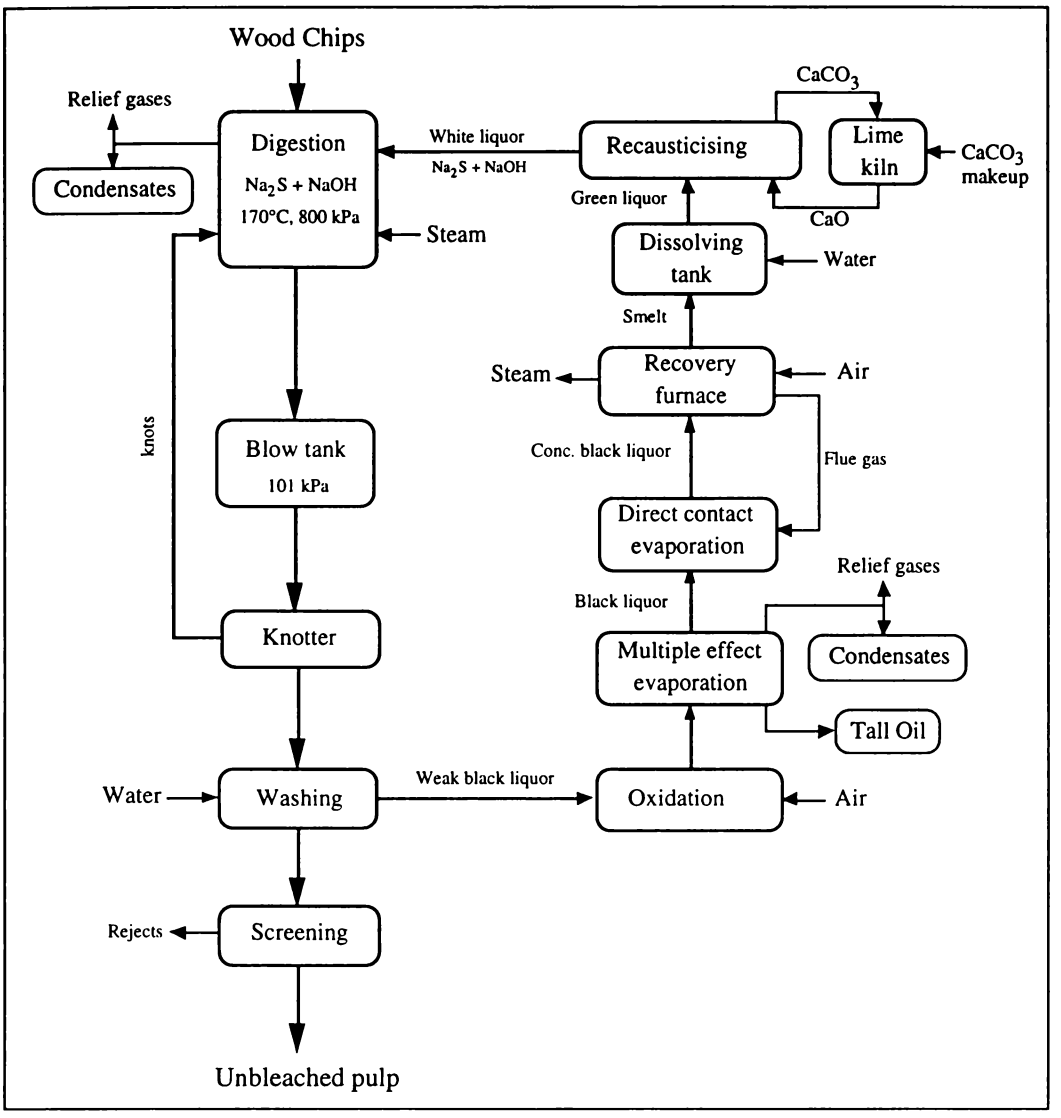


Figure 2.3: Kraft pulping cycle. Sources for Kinleith's No. 2 effluent are shaded (adapted from Bryce 1980)

Lignin reactions during kraft pulping

Making lignin soluble in aqueous systems, thereby facilitating its removal from the pulp, can be achieved by increasing the number of hydroxyl or carboxyl groups in the lignin structure, fragmenting the lignin polymer, or by adding hydrophilic substituents to form soluble lignin derivatives. The reactions which occur in the kraft process are complex and not completely understood. However, the effectiveness of the kraft process is largely attributable to the high reactivity of nucleophilic SH^- ions which facilitate lignin fragmentation.

Nucleophilic substitution reactions between HS^-, CH_3S^- and lignin methoxyl groups result in partial lignin demethylation, enhancing its aqueous solubility. Methylmercaptan and dimethyl sulphide are formed. Subsequent oxidation of methylmercaptan forms dimethyldisulphide:

$$HS^- + \text{Lignin–}OCH_3 + OH^- \rightarrow CH_3S^- + \text{Lignin-}O^- + H_2O$$
$$CH_3S^- + \text{Lignin–}OCH_3 \rightarrow CH_3\text{-S-}CH_3 + \text{Lignin-}O^-$$
$$4CH_3SH + O_2 \rightarrow 2CH_3\text{-S-S-}CH_3 + 2H_2O$$

These organosulphur compounds are volatile and extremely malodorous, creating an air pollution problem characteristic of the conventional kraft process.

A small portion of the lignin is sufficiently degraded so that aromatic monomers such as vanillin, guaiacol, catechol, and 4-hydroxy-3-methoxyacetophenone can be found in softwood pulping liquors (e.g. Niemela and Sjostrom 1986; McKague 1981).

Carbohydrate degradation reactions

Kraft pulping usually removes 90-95% of the lignin, but because the carbohydrate components are sensitive to alkaline degradation, the use of prolonged digestion to give complete lignin removal is not feasible without reducing the yields and quality of the pulp. Approximately 30% of the softwood polysaccharides originally present in the wood are typically lost during kraft pulping (Sjostrom 1981).

The major degradative reaction of hexose polysaccharides in alkaline solutions is the "peeling reaction", which reduces the polymer chain length by a β-elimination mechanism (McGinnis and Shafizadeh 1980; Sjostrom 1981). This process also consumes white-liquor alkali in the neutralisation of the acid products of cellulose depolymerisation. Hydroxy monocarboxylic acids and dicarboxylic acid products of carbohydrate degradation, at concentrations in the spent liqours equivalent to 16-18% of the wood weight, have been identified in softwood kraft pulping liquors (Alen *et al.* 1985).

Other products of carbohydrate reaction during kraft pulping include methyl- and hydroxy-substituted cyclopentenones (Niemela 1988a; Voss 1984), acylthiophenes (Voss 1984), and thiophenecarboxylic acids (Niemela 1989). Condensations of lignin and carbohydrate fragments produce hydroxy-acids with stilbene structures (Niemela 1988b).

Fate of wood extractives during pulping

The FAs, esters, and RAs are dissolved in the alkaline pulping liquor as sodium salts (soaps), which in turn emulsify a large proportion of the unsaponifiable extractives. Most of these components are transferred with the spent pulping liquor to the recovery cycle where they are skimmed from the surface of the aqueous phase. After acidification with sulphuric acid, they are recovered as crude "tall oil", which can be further purified and fractionated by vacuum distillation to give RAs, FAs, light oils, and pitch residue (Sjostrom 1981). RA isomerisation results in abietic acid being the predominant species in *P. radiata* tall oil (McDonald and Porter 1969; Porter 1969). The concentration ratios of major species (abietic, palustric, and neoabietic

acids) approximates the thermal isomerisation equilibrium mixture composition of about 80:15:5 (Takeda *et al.* 1968).

MTs are volatilised during digestion and discharged during digester pressure relief. Most of these compounds are recovered in the condensate as "sulphate turpentine", the composition of which is very similar to the mixture of MTs originally present in the tree (Blight *et al.* 1964). Smaller quantities are carried with the pulping liquor into the recovery cycle where they are recovered in the multiple-effect evaporator foul condensates.

2.2.3 The composition of kraft pulping effluents

The economic viability of the kraft process is dependent on efficient recovery processes which regenerate process chemicals, generate heat, recover valuable chemical byproducts, and reduce organic discharge loads. The effluents from kraft pulping are therefore limited to spills, condensate losses, and wash waters which are too dilute to allow economic recovery of their chemical constituents.

Pulping wastewaters contain a complex array of organic compounds including lignin and carbohydrate degradation products, extractives, and condensable organosulphur compounds. Relatively high levels of sodium, sulphate, and suspended solids are also present in some waste streams. Waste streams contaminated by black liquor are visually highly coloured.

The pulping effluent streams feeding the LA system at Kinleith were sourced from foul condensates associated with black liquor evaporation and MT recovery, and from tall oil recovery (Figure 2.3). Major organic constituents from these sources include MTs, organosulphur compounds, RAs, FAs, and phenolics.

Concentrations of these constituents ranging from $<10\ \mu g\ L^{-1}$ to $>16{,}000\ \mu g\ L^{-1}$ per component have been found in pulping effluents (Stuthridge 1990). Concentrations given in the literature vary widely between mills, reflecting variations in washing efficiencies, pulping conditions, the performance of recovery processes, and the combinations of effluent streams studied. Some literature data is summarised in Table 2.1, which lists major compounds identified in kraft pulping effluents and their relative concentration ranges (based on maximum recorded concentrations, abitrarily assigned as: high $>4\ mg\ L^{-1}$; medium 1-4 $mg\ L^{-1}$; low $<1\ mg\ L^{-1}$).

Foul condensates are high organic strength waste streams (Table 2.2). Methanol, sourced from demethylation of lignin, is the source of most of the BOD_5 with lesser, but still substantial, contributions from MTs and reduced sulphur compounds. Evaporator condensates can also contain high concentrations of RAs and be highly coloured.

Table 2.1: Some major organic compounds found in kraft pulping effluents

Compound class	Relative concentration range			References
	high >4 mg L^{-1}	medium 1 - 4 mg L^{-1}	low < 1 mg L^{-1}	
Monoterpenes	α-pinene β-pinene α-terpineol	borneol terpen-4-ol	fenchone fenchol camphor	1, 2, 3, 4, 5
Fatty acids	linoleic oleic	palmitic	stearic	1, 2, 3, 4, 5, 11, 12
Resin acids	isopimaric dehydroabietic abietic	pimaric palustric neoabietic	seco-dehydroabietic(s) sandaracopimaric	3, 6, 7, 8, 11, 12
Phenolics	guaiacol		vanillin acetovanillone propiovanillone vanillic acid	3, 5, 13
Miscellaneous	hydroxy-carboxylic acids		methyl 2-cyclopentenones acetylthiophenes propionylthiophene phthalic acid esters thiophenecarboxylic acids	4, 9, 10

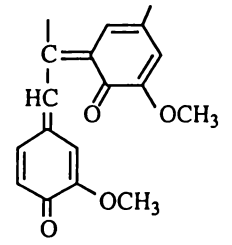
References: 1: Hrutfiord *et al.* (1975), 2: Wilson and Hrutfiord (1975), 3: Stuthridge (1987), 4: Voss (1984), 5: Turoski *et al.* (1983), 6: Wilkins *et al.* (1989), 7: Voss (1987), 8: M^{c}Leay (1987), 9: Alen *et al.* (1985), 10: Niemela (1989), 11: USEPA (1982a), 12: Keith (1976), 13: M^{c}Kague (1981)

Table 2.2: Concentrations of major constituents in foul condensates (after Blackwell *et al.* 1979)

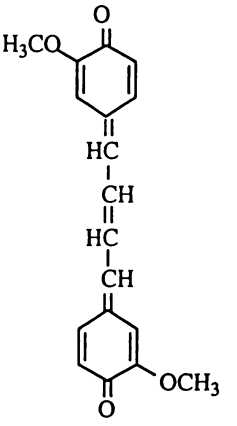
Constituent	Concentration range (mg L^{-1}) in condensates from:		
	Batch digester [a]	Continuous digester [b]	Evaporator [c]
hydrogen sulphide	1-270	210	1-240
methyl mercaptan	20-5000	70	1-410
dimethyl sulphide	15-7000	–	1-15
dimethyl disulphide	2-4000	–	1-50
methanol	250-12000	670-9000	180-1200
ethanol	20-3200	–	1-190
terpenes	0.1-5500	100-25000	0.1-620
guaiacol	–	–	1-10
resin acids	–	–	28-230
BOD_5	720-12000	2000-9000	60-2500
pH (pH units)	9.5	9.2-9.6	6.0-11.1
colour (APHA units)	–	–	280-5500
sodium	–	–	4-370

a: range for vent and blow condensates; b: flash steam condensate; c: range for combined and condenser condensates

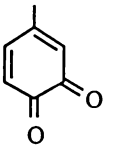
The colour of black liquor and associated waste streams has traditionally been associated with chromophoric, lignin-derived structures containing conjugated double bonds. Much of the colour has been attributed to oxidation or dehydrogenation of leucochromophoric (colourless) lignin degradation products formed during pulping (Sjostrom 1981). Some possible lignin-derived chromophores include stilbene quinones, butadiene quinones, and o-quinoids:



stilbene quinones



butadiene quinones



o-quinoids

Studies by Ziobro (1990a) indicated that much of "kraft colour" may be attributable to carbohydrate degradation products rather than lignin-sourced aromatics.

2.2.4 Pulp bleaching

Pulp produced by the kraft process contains 5-10% of the original cell wall lignin, and is too highly coloured for direct use in high-grade white papers. During pulping, the residual lignin becomes increasingly darker, so that even after removing more than 90% of the lignin, the brightness of the pulp is lower than that of the original wood. To remove residual lignin, multistage bleaching procedures are used. These generally employ an acidic oxidising step followed by an alkaline step which extracts the oxidised products. In hypochlorite, peroxide, and oxygen bleaching, the oxidation steps are performed within the alkaline stage. Common conventional bleaching sequences[1], such as those used at Kinleith during the period of the thesis studies (section 1.3.1, Table 1.1), included (CD)EHDED, (CD)EDED, and (CD)EHD (Sjostrom 1981). Most lignin is removed in the chlorination and extraction pre-bleaching stages, while the subsequent stages are used to bleach residual chromophores.

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[1] Common bleaching sequence symbols include (Casey 1980): C: chlorination with gaseous or aqueous solutions of chlorine. CD: chlorine + chlorine dioxide (chlorine dominant). DC: chlorine dioxide + chlorine (chlorine dioxide dominant). E: alkaline extraction with NaOH solution. E_O: oxidative extraction, where oxygen is included in E stage. D: chlorine dioxide bleaching. H: hypochlorite bleaching with sodium or calcium hypochlorite solution. P: peroxide bleaching with aqueous hydrogen peroxide solution.

The initial *chlorine prebleaching* stage depolymerises the lignin and introduces alkali-soluble functional groups by reactions such as a) aromatic substitution and electrophilic side-chain displacement, forming chlorophenols; b) oxidative cleavage of aryl-alkyl ether linkages, forming quinones; and c) aromatic ring cleavage, by conversion of orthoquinones to muconic acid derivatives (Glasser 1980; Figure 2.4).

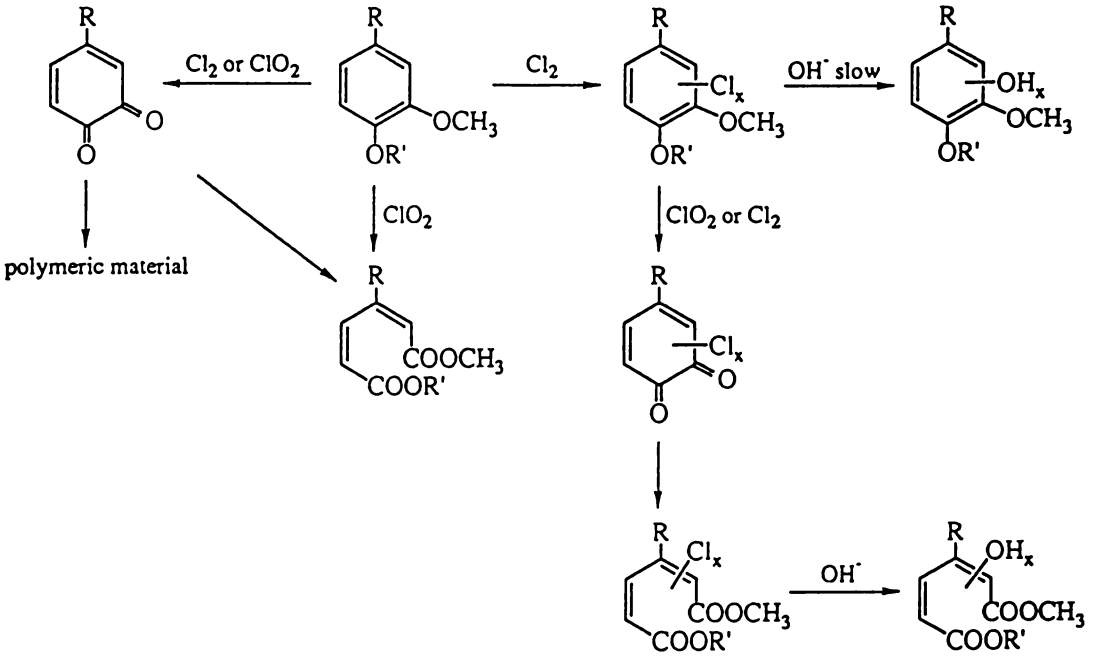


Figure 2.4: Dissolution reactions of residual lignin during chlorination and extraction. Adapted from Glasser (1980) and Kringstad and Lindstrom (1984).

Wood extractives and other organic constituents of black liquor which are carried over from the pulping stage may also be chlorinated. Reaction of chlorine with carbohydrates is much slower than with lignin, but some decomposition does occur by radical reaction, oxidation, and hydrolysis, introducing carbonyl and carboxyl groups.

Modern mills have largely eliminated molecular chlorine from their bleaching sequences. Removing chlorine reduces the amounts of environmentally undesirable chlorinated organic compounds discharged in bleaching effluents, and allows pre-bleaching process waters (which are too corrosive to be recycled when chlorine is used) to be passed through the kraft recovery cycle.

The *alkaline extraction* stage neutralises acids generated in the chlorination stage, solubilises lignin fragments by ionising hydoxyl and carboxyl groups, and produces phenolic hydroxyl groups from chlorine substituted aromatics (Figure 2.4). A reduction in the amount of organically bound chlorine as well as delignification is therefore achieved in the E stage. Coloured compounds can be formed by alkali treatment of oxidised carbohydrates. Much of the

high colour of E stage effluent has been attributed to keto-enols produced from the carbohydrate peeling reaction during pulping (Ziobro 1990b).

Hypochlorite was the first agent used for pulp bleaching but, due to its reactivity towards cellulose, its use has declined. Reaction with cellulose is particularly rapid between pH 6 and 7 when the number of alkali-labile carbonyl groups is at a maximum (Loras 1980). Bleaching occurs by both lignin removal and decolorisation, the latter by oxidation of chromophoric groups in the pulp. Chloroform is a characteristic byproduct of hypochlorite bleaching.

Chlorine dioxide is an oxidative bleaching chemical. It has the important property of being unreactive towards carbohydrate under bleaching conditions. It is used with chlorine in the prebleaching stage as a radical scavenger to prevent chlorine radical attack on cellulose (ClO_2 is oxidised to ClO_3^-, and $Cl^\bullet$ reduced to Cl^-). Lignin oxidation with chlorine dioxide is not as effective as with chlorine because only lignin's aromatic phenolic groups react. Quinones, chlorite, chlorate, and chlorine (in equilibrium with aqueous chlorine species such as hypochlorous acid) are formed. The chlorine subsequently produces chlorinated substitution products, while the quinones may be polymerised to form darkly coloured materials. Oxidation to alkali extractable muconic acid structures also occurs (Figure 2.4). Compared with chlorine bleaching, chlorine dioxide produces smaller amounts of chlorinated organic compounds.

Hydrogen peroxide, and *oxygen*, are used as oxidative delignification agents. Oxidation breaks the lignin into smaller fragments which can be extracted with alkali. Oxygen reaction requires alkaline conditions and elevated temperatures to form anions and radicals, which are the reactive oxidative species. These are somewhat unselective agents, and therefore inhibitors such as magnesium salts are sometimes used to prevent reaction with carbohydrates. The lack of selectivity prevents more than 50-60% of the residual lignin from being removed by oxygen pre-bleaching. Hydrogen peroxide is reactive under less severe conditions than oxygen, and therefore side reactions with carbohydrates are less of a problem.

Oxygen in particular is often used as a pre-bleaching agent before chlorine bleaching. Because effluent from the oxygen stage contains no chlorine, it can be circulated as washing liquor to the mill recovery system. The removal of a large proportion of the lignin prior to chlorine bleaching reduces the amounts of chlorine required to complete the bleaching process and therefore the quantities of chlorinated organics produced and discharged from the mill are greatly reduced.

Hydrogen peroxide can oxidise both lignin and chromophores, enabling it to be used for both pre-bleaching and final brightening. It is expensive and less effective than oxygen, and is sensitive to metal-catalysed degradation. Oxygen is therefore generally used in chlorine-free pre-bleaching delignification. For final bleaching, chlorine dioxide is cheaper and more effective, but peroxide has the advantage that it produces no chlorinated side products.

2.2.5 Extraction stage bleaching effluents

Due to the great variety of reactions taking place, the spent liquors from chlorination and extraction stages have complex compositions. Since only the extraction stage effluents were directed to LA at Kinleith, the following discussion concentrates on summarising their characteristics. A more comprehensive overview of spent bleaching liquor composition has been given by Stuthridge (1990).

Pfister and Sjostrom (1979) performed a detailed characterisation of E stage effluent from a conventional CE prebleaching sequence (Table 2.3). Most of the material was of high relative molecular mass (about 80% M_r >1000), containing about 10% chlorine, and possessing high carboxyl group content. Low numbers of phenolic hydroxyl groups suggested that it was largely non-aromatic. During extraction, about 64% of the combined chlorine in the pulp from the C stage was removed as chloride, 23% remained as organically bound chlorine in the effluent, and 13% was retained in the pulp. Approximately half the BOD_7 load was attributable to carbohydrates (M_r >1000), and half due to the low molecular weight acids and methanol.

Later investigations of the molecular weight distribution of organically bound chlorine in E stage effluent (Lindstrom *et al.* 1981; Lindstrom and Osterberg 1984) have shown that 95% was present in material of M_r >1,000 (Figure 2.5).

Table 2.3: Composition of dissolved organic material in extraction stage effluent (after Pfister and Sjostrom 1979)

	% total organic matter			
Constituent	M_r<1000	1000<M_r<10000	M_r>10000	Total (%)
carbohydrates	0.1	0.6	3.8	4.5
unidentified lignin products	–	28.4	40.6	69.0
combined chlorine	0.2	2.7	4.3	7.2
carbon dioxide	11.7	–	–	11.7
methanol	1.2	–	–	1.2
volatile acids	2.9	–	–	2.9
monocarboxylic acids	1.4	–	–	1.4
dicarboxylic acids	2.6	–	–	2.6
Total	20.1	31.7	48.7	100.5 [a]

a: Total ≠ 100% due to experimental error.

The high M_r material contained (Lindstrom and Osterberg 1984; Kringstad and Lindstrom 1984):

- low aromatic content, with remaining aromatic structures being condensed, mono- to trichloro- substituted catechols;
- approximately 5-10% chlorine, most of which was bound to aliphatic structures;
- abundant primary aliphatic hydroxyls, and carboxyl groups of both aromatic and aliphatic origin; and
- relatively uniform elemental composition of $C_{14}H_{10}O_9Cl$.

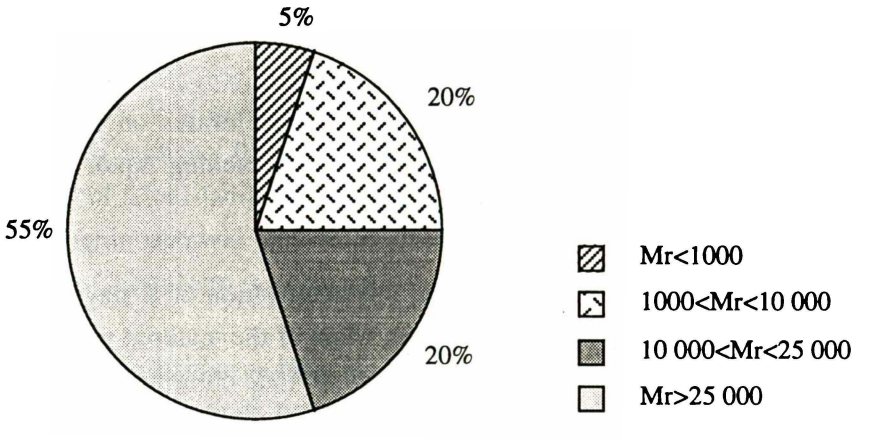


Figure 2.5: Molecular weight (M_r) distribution of total organically bound chlorine (TOCl) in extraction stage effluent (after Lindstrom *et al.* 1981)

The bulk of the native lignin structure, which is based on propylguaiacyl units, is therefore destroyed by the chlorination and extraction processes.

E stage effluents are highly coloured, typically 5,000-20,000 APHA colour units. About 90% of total bleachery effluent colour and 70% of total mill effluent colour discharge originate from caustic extraction (Rush and Shannon 1976). Over 85% of the colour in E stage effluent was associated with material of M_r >1000 (Pfister and Sjostrom 1978).

The low molecular mass fraction (M_r<1000) of bleaching effluents is also complex, with over 300 compounds having been identified (M^{c}Kague *et al.* 1989). In E stage effluent, the dominant compound is CO_2, indicating that considerable decomposition occurs during extraction. Volatile acids (largely formic acid), dicarboxylic acids (dominated by oxalic acid), monocarboxylic acids (mainly glycolic acid), and methanol constitute most of remaining low molecular weight organics (Pfister and Sjostrom 1979).

In this matrix of non-chlorinated compounds, a range of chlorinated acids, phenolics, and neutrals are found at lower concentrations (Table 2.4). Those which have been identified represent approximately 35% of the organic chlorine in the M_r<1000 fraction, indicating that the majority of the low M_r fraction remains uncharacterised (Kringstad and Lindstrom 1984).

Table 2.4: Chlorinated acids, phenolics and neutrals found in E stage bleaching effluents (after McKague *at al.* 1989; Kringstad and Lindstrom 1984; Stuthridge 1990)

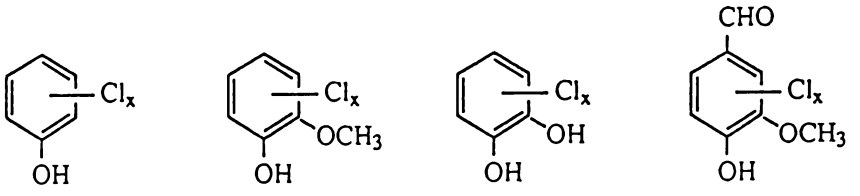
Chlorinated acids	
Compound	g ADT^{-1}
chloroacetic	4
dichloroacetic	20
trichloroacetic	5
dichlorostearic	0.5-190
chlorodehydroabietic (2 isomers)	3-70
dichlorodehydroabietic	3-40

Chlorinated neutrals	
Compound	g ADT^{-1}
chloroform	30
2,3,7,8-TCDD	0.06-36[a]
2,3,7,8-TCDF	0.56-140[a]

Chlorinated phenolics	
Compound	g ADT^{-1}
2,4-dichlorophenol	0.4-2
2,4,6-trichlorophenol	0.5-4
2,3,4,6-tetrachlorophenol	0.03-2.3
4,5-dichloroguaiacol	1.0-9.7
3,4,5-trichloroguaiacol	0.8-19
4,5,6-trichloroguaiacol	0.4-3.7
tetrachloroguaiacol	0.1-40
chlorovanillin (2 isomers)	2-5.5
5,6-dichlorovanillin	1.2-7.1
dichlorocatechols	0.7-2.7
trichlorocatechol (2 isomers)	0.3-3
tetrachlorocatechol	0.3-3.1

a: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) yields in µg ADT^{-1} (Stuthridge 1990)

The chlorophenolics, formed from chlorination of the residual lignin, have been well documented (e.g. Voss *et al.* 1980, 1981a, 1981b; Holmbolm 1980; Lindstrom *et al.* 1981; McLeay 1987; Gergov *et al.* 1988; Stuthridge 1990). E stage effluents from softwood bleaching contain chlorinated phenols, guaiacols, vanillins and, at lower concentrations, catechols:



chlorophenols chloroguaiacols chlorocatechols chlorovanillins

Low M_r chlorinated carboxylic acids constitute about 18 g of organic chlorine (OCl) per tonne of pulp, representing about 60% of the acidic ether-extractable OCl in E stage effluent (Lindstrom and Osterberg 1986). Chloroacetic acids dominate, making up 76% of the identified chlorinated compounds in the acidic fraction.

Chlorinated neutral compounds, such as chloroacetones and chloroaldehydes, are found in C stage effluents, but because of their instability under alkaline conditions they constitute only minor components of E stage effluents. Chloroform and dichloromethane are also found,

although production is greatest in the hypochlorite bleaching stage (Lindstrom *et al.* 1981; Kringstad *et al.* 1983; Kringstad and Lindstrom 1984).

Polychlorinated dibenzodioxins (PCDD) and furans (PCDF) were identified in kraft mill effluents and sludges in the USA and Canada in 1985 (Amendola *et al.* 1989; Clement *et al.* 1989). In a study of five US pulp mills (Amendola *et al.* 1989), E stage effluents were found to contain the highest mass discharges of 2,3,7,8-TCDD (median concentration 0.26 ng L^{-1}) and 2,3,7,8-TCDF (median 0.51 ng L^{-1}). These compounds are formed in the C stage from chlorination of dibenzodioxin and dibenzofuran precursors (Dimmel *et al.* 1993).

In addition to these compounds, variable quantities of wood extractives and their chlorinated products have been found in E stage effluents as a result of incomplete removal from the pulp during washing. Chloro-dehydroabietic acids, 9,10-epoxystearic acid (formed by chlorination of oleic acid in the C stage and subsequent epoxidation under alkaline extraction), and dichlorostearic acid are among the most commonly found chlorinated extractives in E stage effluents (McLeay 1987). Chlorinated thiophenes and MTs (Carlberg *et al.* 1988; Stuthridge *et al.* 1990) have been found in C stage effluents, and at lower concentrations in subsequent E stage wastes.

Inorganic constituents in E stage effluents are dominated by high concentrations of Na^+ from the extraction alkali, and Cl^- sourced from the organochlorine substituted during extraction and from C stage residuals. The high Cl^- levels accelerate corrosion, while the relatively low organic content of spent bleaching liquors make recovery processes uneconomic, and therefore E stage wastes are usually discharged from the mill.

2.3 Environmental Significance of BKME components

The environmental effects of pulp and paper mill effluents have received a great deal of attention, primarily focused on determining impacts on surface receiving waters and associated biota. A number of adverse effects at community, population, whole-organism, and within-organism levels have been linked with BKMEs (Walden 1976; McLeay 1987; NSEPB 1989; Crooks and Sikes 1990; Environment Canada 1991; NPMRP 1991; Owens 1991; Higashi *et al.* 1992). Because of the complexity and site-specific nature of BKME composition, the variety of effluent treatment processes used, and differing receiving ecosystem characteristics, isolating effects due to individual components of the effluents has proved difficult. Despite these difficulties, sufficient evidence of the harmful nature of BKME has been accumulated to enable the Canadian government to class BKMEs as "toxic" substances, thereby requiring regulatory control (Environment Canada 1991).

2.3.1 Conventional pollutants

High concentrations of biodegradable organic matter in pulp mill effluents have historically been of concern, causing oxygen depletion and adverse effects on aquatic life in surface receiving waters. Most mills now employ biological treatment before discharging to receiving waters, greatly reducing BOD-related impacts.

Suspended solids (SS) in mill effluents are made up of organic material, principally fibre, and inorganic particulates such as lime. While in suspension, suspended material may interfere with respiratory systems in aquatic organisms, and impair vision, reducing predatory efficiency. After settling, SS can affect aquatic life by degrading benthic habitat in the receiving waters, thereby changing faunal community structure, and by exerting oxygen demand, which may stress aquatic life and promote the formation of anaerobic conditions, under which release of noxious substances such as H_2S can occur (Walden 1976). Sorption of hydrophobic organic compounds onto particulate and colloidal matter, in particular organic matter, can alter the environmental transport, bioavailability, and reactivity of organic compounds.

Due to the wider use of effluent treatment before discharge, BOD and SS are not the critical issues they once were. However, the large volumes of effluents discharged by the pulp and paper industry ensure that substantial loads of oxygen demand and SS are continually exerted on effluent receiving waters. Intermittent losses of high strength wastes, which have been estimated to contribute about 30-50% of the BOD and SS loads from traditional kraft mills (Springer 1986), can also have major short-term impacts.

The pHs of individual waste streams at source range from acidic (pH<2 for C stage effluents) to alkaline (pH 11 for E stage). Segregated waste streams are seldom discharged individually to receiving waters, but are usually mixed or neutralised prior to final disharge. pH conditions in the receiving waters sufficiently extreme to adversely affect aquatic life, outside the 6<pH<9 range commonly recommended for aquatic ecosystem protection (e.g. ANZECC 1992), are not usually encountered.

Increased in-stream primary production has been observed in response to low concentration nutrient inputs from pulp mill effluents (Hall *et al.* 1991; Owens 1991). At higher effluent concentrations, colour effects increase and primary productivity reduces as a result of limited light transmission.

Bacteria associated with pulp mill discharges have also been a source of some concern. The bacterium *Klebsiella pneumoniae* is commonly found in high numbers (10^6-10^8 per 100 mL) in pulp mill effluents. The nitrogen-depleted, sugar-rich composition of pulping effluents provides ideal conditions for growth of this nitrogen-fixing organism. Because *K. pneumoniae* are included in coliform enumeration tests, meeting coliform-based bacteriological receiving water standards for human health protection has been a problem in waters affected by pulp mill discharges. For some time, the human health implications of the presence of these pathogens was of concern. In the environment in which they are discharged, they are no longer considered to pose a significant threat to human health (Clark *et al.* 1991).

2.3.2 High molecular weight material

The majority of the organic material present in E stage bleaching effluents is of high molecular weight (M_r>1000) and therefore is unable to penetrate cell membranes. Chlorolignin has therefore not generally been considered to be directly biologically active (Kringstad and Lindstrom 1984; Salkinoja-Salonen *et al.* 1981), although a polar, high molecular weight

component has been associated with the toxicity of BKME to early life stages of some marine species (Higashi *et al.* 1992). Instead, the environmental significance of chlorolignin is associated with (Rush and Shannon 1976):

- colour, which is aesthetically displeasing, reduces light transmission and therefore in-stream primary productivity, and may alter movement and feeding abilities of aquatic fauna;
- increased consumption of municipal water treatment disinfection and coagulation chemicals, and fouling of industrial water treatment ion exchange resins;
- long term oxygen demand; and
- precipitation in quiescent zones, resulting in benthic habitat degradation.

The products of chlorolignin degradation and reaction are also of potential concern. Chlorolignin stability studies have shown that slow abiotic degradation can occur in receiving water environments, releasing chlorinated catechols and guaiacols (Eriksson *et al.* 1985). Chlorophenolics have also been found to desorb from chlorolignin (O'Connor and Voss 1992). Some of the chlorophenolic products are amenable to biomethylation by various mixed bacterial consortia, producing more recalcitrant and toxic chloroveratroles. Chlorination of chlorolignin, as could occur in drinking water treatment, has been shown to produce chlorinated phenols, guaiacols, and catechols, as well as low concentrations of mutagenic tetrachloro- and pentachloroacetones (Kringstad *et al.* 1984).

Binding to chlorolignin can decrease hydrophobic pollutant bioavailability and hence toxicity (Priha and Talka 1986; Kukkonen and Oikari 1987; Oikari and Kukkonen 1990; Kukkonen 1992). Enhanced micropollutant solubility, transport, and stability might also be expected, analagous to that observed with other macromolecular organic matter such as humic acids (e.g. Enfield and Bengtsson 1988; McCarthy and Zachara 1989; Kan and Tomson 1990; Dahlman *et al.* 1993).

The cation exchanging ability of lignin is well known and has made it a potentially useful soil amendment agent (Glasser 1980), while its complexation of ferrous and ferric ions are believed to contribute to colour changes in lignin-rich pulps (Jansen and Forsskahl 1989). Lignin, and presumably chlorolignin also, are therefore potentially capable of facilitating transport of metal ions.

2.3.3 Low molecular weight organics

Low molecular weight organic compounds are capable of penetrating biological membranes, and therefore have the potential to induce undesirable toxic effects in aquatic organisms. Other problems attributable to low molecular weight organics found in pulp mill effluents include tainting of fish flesh, and odour production in air and water. Biodegradable low molecular weight constituents also account for a major proportion of the total BOD load.

Acute lethal toxicity

The acute lethal toxicity of untreated kraft mill effluents to fish and, to a lesser extent aquatic invertebrates, has been well documented (eg. McLeay 1987). The range of reported toxicities is

large (Table 2.5), reflecting differences in measurement procedures, species of wood processed, and mill processes. Despite this variability, the data indicate that primary treatment has little effect on removal of toxic constituents, while biological treatment, when properly managed, removes essentially all acute toxicity. The low values in Table 2.5 were associated with inadequate treatment systems (McLeay 1987).

Table 2.5: Acute toxicities of kraft whole mill effluents (after McLeay 1987)

	96 hour LC_{50} to rainbow trout (% v/v)		
Effluent	untreated	primary treated	biologically treated
unbleached	7-100	3-19	80->100
bleached	5-74	5-87	13->100

RAs are largely responsible for acute toxicity of pulping effluents, while chlorophenolics and chlorodehydroabietic acids are the major toxic components of extraction stage liquors (McLeay 1987). About 90% of E stage acute toxicity is due to 3,4,5-trichloroguaiacol, tetrachloroguaicol, mono- and dichlorodehydroabietic acids, and epoxystearic acid (Kringstad *et al.* 1984). Epoxystearic and dichlorostearic acid toxicities (1.5–3.4 mg L^{-1}) are comparable with RAs and chlorophenolics (McLeay 1987). E stage effluents are generally more acutely toxic than those from chlorination, but because of the larger volumes of the latter, C stage effluents contribute most of the total toxicity released.

Unchlorinated RAs are the only compounds usually present at concentrations above acutely toxic levels in untreated whole-mill effluents, but after biological treatment they are almost always reduced to sub-lethal levels (Table 2.6).

Table 2.6: Acute toxicities of major classes of compounds present in BKMEs (after McLeay 1987)

		Concentration ranges in effluents (μg L^{-1})	
Compound Class	96 hour LC_{50}[a]	Untreated	2° treated
resin acids	360-1740	<10-4800	<1-2100
chlorophenolics	200-2800	<1-620	<1-280
saturated fatty acids	>20,000	1600	660
unsaturated fatty acids	2000-8200	<20-9300	<20-2300

a: 96 hour LC_{50}s for rainbow trout under static bioassay conditions

Foul condensate streams may contain reduced sulphur compounds at concentrations above their LC_{50}s, which range from 0.5 mg L^{-1} for CH_3SH to 23 mg L^{-1} for $(CH_3)_2S$ (Blackwell *et al.* 1979). Chlorate, formed during chlorine dioxide bleaching, has been reported to have caused acute lethal toxic effects on some marine macro-algae in Swedish coastal waters (Crooks and Sikes 1990).

While the acute toxicities of individual compounds have been reasonably well defined, relationships between the acute lethal toxicity of whole effluents and the toxicities of the individual components remains uncertain. The sum of individual compound toxicities usually

exceeds the whole-effluent toxicity. Synergistic and/or antagonistic effects in effluent mixtures may occur, making it difficult to evaluate the contributions of individual compounds to whole-effluent toxicity (Priha 1991). Because of the complexity of pulp mill effluents, use of quantitative structure-activity relationships (QSARs) to predict rather than measure the properties of pulp mill effluent organics has been suggested as a way of improving understanding of toxicological properties and environmental behaviour (Suntio *et al.* 1988; Mackay 1989).

Sub-lethal toxicity

These effects do not directly kill the organism, but cause adverse anatomical, behavioural, physiological, or biochemical changes that may reduce its survival or reproductive capabilities (McLeay 1987). They manifest themselves as whole-organism changes (e.g. growth, reproduction, stamina, avoidance behaviour) and/or as sub-organism effects (e.g. changes in blood chemistry, tissue diseases, respiration, circulation). Owens (1991) and NPMRP (1991, pp. 201-311) provide detailed reviews.

Sub-lethal effects have been observed over a very broad range of effluent threshold concentrations of 0.65% to >100% v/v (Stuthridge 1990). Studies on the effects of individual components, for example RAs and chlorophenolics, have found sub-lethal effects on some fish at concentrations in the low $\mu g\ L^{-1}$ range, about 1000 times lower than the acutely toxic levels (e.g. Oikari *et al.* 1983; Tana 1988).

Studies carried out in Canada and the USA indicate that threshold concentrations for sub-lethal effects were between 0.05 and 0.1 of the 96 hour LC_{50} value (Walden 1976), and that major sub-lethal effects were absent when treated BKMEs underwent >20 fold dilution. Scandinavian results however, have shown effects such as skeletal deformations, physiological disorders, and diseases (such as fin rot) at 200-1000 fold dilutions (Stuthridge 1990; SWEPB 1989). This apparent disparity has been attributed to differences in effluent qualities, ecosystem characteristics, and effluent discharge histories, and pollution contributions from other industrial discharges (Procter and Gamble 1989).

Mutagenicity

The genotoxicity of kraft bleaching effluents is largely confined to the C-stage, where the predominate mutagenic compounds are chloroacetones, 2-chloropropenal, and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (Holmbolm and Kronberg 1987; Kringstad *et al.* 1984). Mutagenicity is reduced under neutral and alkaline conditions, and by biological treatment (Salkinoja-Salonen *et al.* 1981; Langi and Priha 1988; Crooks and Sikes 1990).

Bioaccumulation

Octanol-water partition coefficients (log K_{ow}) values of approximately 4.5-8 for RAs and diterpene neutrals (Stuthridge 1990; Holmbolm 1991; Hynning *et. al.* 1993) indicate that these compounds are highly lipophilic and therefore potentially bioaccumulatory. This is consistent with their presence at elevated, but variable, concentrations in fish and molluscs exposed to BKME (McLeay 1987; Niima and Lee 1992; Tavendale 1994).

K_{ow}s of chlorophenolics are dependent on the degree of chlorine substitution and on the non-chlorine substitution of the aromatic ring, and range from $\log K_{ow}<2$ for monochlorovanillin to 5.08 for pentachlorophenol (Stuthridge 1990; Xie *et al.* 1984). For the same degree of chlorination, log K_{ow}s were vanillins ≈ catechols < phenols < guaiacols. All the tri-, tetra-, and pentachloro- compounds have log K_{ow} >3, indicating that they are potentially bioaccumulative (Kringstad *et al.* 1984). Tavendale (1994) reported bioconcentration factors (water to goldfish bile) of 280–9700 for a range of chlorophenolics. Chloroveratroles, bacterial methylation metabolites of chloroguaiacols, have also been reported to accumulate in fish with higher BCFs than the parent guaiacols (Environment Canada 1991).

RAs and chlorophenolics are cleared from fish relatively rapidly (days to weeks) upon transfer to uncontaminated water (McLeay 1987; Niimi *et al.* 1990; Niimi and Lee 1992).

Identified chlorinated species have been found to represent only only 10-15% of the total extractable organochlorine (EOX) in fish exposed to BKME. Less than 1% of the EOX is chlorophenolic, and much appears to be of molecular weight >500 (Stuthridge 1990). Organochlorine from sediments can also be bioaccumulated by fish (Carlberg *et al.* 1987), indicating that even on removal of the pollutant source, long-term effects are possible until access to the sediment is stopped.

Chlorine bleached BKME as a whole has a log K_{ow} identical to water, indicating that the bulk of the organic material associated with the effluent is highly water soluble and should be transported in the water column (Diercks and Banerjee 1993).

Taste and odour problems

Tainting of fish flesh has been attributed to exposure to BKMEs. Foul condensates in particular apparently have a powerful tainting propensity, off-flavours being reported at concentrations of <0.1% v/v. The specific effluent constituents responsible for tainting are uncertain, although di- and trichlorophenol, RAs, organosulphur compounds, terpenes, and cymenes have been proposed as potential off-flavour sources (McLeay 1987; Juttner 1988). Chlorinated phenols, guaiacols, and catechols, and their chlorinated anisole and veratrole biomethylation products, have also been implicated in fish tainting (Paasivirta *et al.* 1987). Taste and odour problems in waters contaminated with these compounds might also be expected.

2.3.4 Summary: Effluent characteristics and environmental effects

Foul condensates and extraction stage waste waters contain complex mixtures of organic materials covering a wide range of molecular weights. High concentrations of Na^+ and Cl^- are found in the wastewaters.

The dominant low M_r organic compounds in effluents sourced from pulping, black liquor evaporation, and turpentine recovery are wood extractives, primarily RAs, FAs, phenolics, and MTs. Literature data shows a high degree of quantitative variability in effluent composition. BOD levels of these waste streams are high.

E stage effluent organic material is predominately high M_r lignin degradation products containing about 10% organically bound chlorine. A complex suite of lower M_r compounds is also present, consisting mainly of carboxylic acids. Chlorinated constituents of the low M_r fraction are dominated by chlorinated acids and phenolics. Chlorinated wood extractives may also be significant components. The effluents are highly coloured, but the identity of the chromophoric groups responsible remains uncertain.

Potential environmental effects associated with these effluents include acute and sub-lethal toxicity to a range of aquatic organisms, bioaccumulation (possibly to levels where sub-lethal effects would result), tainting of fish and water, aesthetic degradation and ecological effects associated with discolouration and reduced light transmission, facilitated transport of organic and inorganic contaminants, dissolved oxygen depletion, and degradation of benthic habitat.

Ensuring these waste waters are well treated before discharge is essential, since biological treatment significantly reduces some adverse effects (e.g. oxygen demand, acute toxicity and mutagenicity). While current understanding of the biological responses to whole-effluents is well advanced, it remains incomplete. There is evidence that adverse effects can occur even at high effluent dilutions. Where possible, reducing the input of pulp mill effluents to surface waters is therefore desirable.

2.4 Wastewater Treatment by Land Application

Treatment and disposal by land application is one method of avoiding the effects associated with direct discharges to surface waters and providing effective treatment of degradable organic materials. However, if effective treatment in a land application system is not achieved, ground water contamination with effluent-sourced chemicals can occur. While direct effects on aquatic biota are not relevant in a sub-surface setting, introducing BKME constituents into a ground water environment is undesirable. Potential effects include degradation of drinking water supplies, for example by aesthetic impacts of colour, taste and odour. Indirect effects on surface water biota are possible, as ground water discharge can contribute significantly to stream baseflows and low flows.

Given that the chemical and toxicological properties of BKME are incompletely characterised, it would be unwise to contaminate ground water with effluent through inadequate treatment and disposal procedures. Ground water remediation is an expensive and difficult process, and should be avoided if possible.

2.4.1 The development of land application for treatment of liquid wastes

The land has served as a giant biodigestion system for many millions of years, accumulating the products of plant and animal matter degradation in the soil. The waste treatment technologies collectively known as *land application* (LA), or land treatment, are the human-managed equivalents of these natural processes. In LA, waste is applied to the land in a manner which encourages the physical, chemical and biological processes associated with the soil system, resulting in assimilation of environmentally undesirable waste constituents.

LA has four objectives (Childs *et al.* 1977): 1) waste treatment, 2) waste disposal, 3) recovery or reuse of waste components, and 4) ground water recharge. The relative importance of each of these for a given situation will depend on a combination of factors including the nature of the waste, the site characteristics, and economics. The primary objective is usually waste treatment.

LA for treatment and disposal of waste water is not a new process. Domestic waste has been treated by LA for centuries, the first documented examples occurring in Poland and Germany in the 16th century. Modern interest in LA began in the 1840s in Britain, due in part to recognition that the nutrient value of municipal waste could be used to replenish nutrients lost from agricultural land by leaching, and also because of the need to improve the quality of receiving waters. LA "sewage farms", became increasingly used around the cities of Europe during the 19th century as a practical measure for reducing surface water pollution and for recovering valuable plant nutrients. During this period (1840-1890), the primary wastewater management objective was to minimise pollution of the receiving waters, especially potential drinking waters. LA represented the most effective process available, and therefore its use expanded (Fuller and Warrick 1985a; Wilcock 1984a).

In the 1880s to 1890s, other effluent treatment technologies became available, leading to debate over the best methods to use. Rapid urban population growth at the end of the 19th century resulted in overloading and failure of many LA systems. A change in philosophy from the "zero discharge" goal of the 1880s to the "permissible pollution, dilution solution to pollution" approach occurred after about 1890 and continued until the 1970s. Treatment of polluted drinking water was seen as more effective and more economical than treatment of wastewater prior to discharge. During this period, the popularity of LA declined.

In the 1960s and 1970s, the deterioration of surface water quality resulting from the discharge of increasingly large amounts of inadequately treated municipal and industrial wastewater lead to another change in attitude towards the handling of wastes. Policies of non-degradation of natural waters, reuse of wastewaters, and discharge minimisation were incorporated into legislation aimed at protecting the quality of water resources. To meet legal requirements for receiving water quality, waste treatment became the norm rather than the exception.

In 1977, the US Clean Water Act recognised the advantages of LA for minimising impacts on surface water quality and the potential it offered for reuse of both waste and water, by placing it into the "innovative and alternate" category of waste treatment processes. By doing so, LA systems were eligible for subsidies not available for conventional technologies. These financial incentives encouraged the use of LA, so that by 1985 the number of municipal wastewater LA systems in the USA had grown to over 1100 (Hutchins *et al.* 1985).

In New Zealand, the first LA system for municipal wastewater was completed in the 1880s in Christchurch. The low population densities in most parts of New Zealand allowed effluents to be discharged to surface waters in most areas without seriously risking public health. In the 1950s, increased population and expanding industrialisation contributed to a decline in water quality in many areas. Growth in the recreational use of surface waters heightened public awareness of the degradation of the natural water resources that was occurring, and calls for

improvements were made. The Water and Soil Conservation Act 1967 resulted from these concerns.

Interest in LA as a method for solving waste disposal problems in New Zealand increased after 1970, so that by 1981 there were 24 local authorities operating LA systems (Wilcock 1984a). The use of LA continues to increase in New Zealand, particularly for agricultural and municipal wastes which together contribute large loads of organic pollutants to surface waters. Regional Councils, the agencies currently responsible for environmental management in New Zealand, encourage the use of LA as an aid to achieving sustainable water and waste management, and for satisfying Maori cultural concerns over the discharge of effluents to surface waters.

The use of LA has not been confined to treatment and disposal of municipal wastewaters. Provided certain conditions are met, effluents from a diverse range of industries have the potential to be treated by LA (Fuller and Warrick 1985a). These conditions include that:

- the waste's organic components must be largely biodegradable;
- at reasonable waste application rates, soil microorganisms will continue to function;
- long-term toxic effects of accumulated residues, and damage to the soil ion exchange complex by ion adsorption, can be mitigated or prevented;
- practical loading rates will not cause ground water pollution; and
- the cost-effectiveness of LA must be comparable with other treatment methods.

With appropriate LA system management, many industries are able to meet these requirements. Industries whose waste streams are considered potentially suitable for LA include those associated with production or processing of food, pharmaceuticals, organic fibres, soap and detergents, organic chemicals, and petroleum. In New Zealand, considerable attention has been directed towards LA of wastes generated by the agricultural sector, including effluents from dairy-sheds, piggeries, wool-scouring, dairy factories, and meat processing facilities (Wilcock 1984b).

The wastes from the pulp and paper industry, which contain large quantities of biodegradable organic matter, are also candidates for effective treatment and disposal by LA.

2.4.2 Land application methods

Three LA techniques have evolved to be the most commonly used for treatment and disposal of liquid wastes. The design features of these are listed in Table 2.7 and hydraulic pathways for each are shown in Figures 2.6, 2.7, and 2.8. These are (USEPA 1981; Hutchins *et al.* 1985; Crites 1984):

1) *Slow rate (SR)*, in which the effluent is applied to a vegetated land surface at rates not greatly exceeding plant requirements. Objectives include waste treatment, economic return from the use of water and waste nutrients in crop production, and water conservation by using wastewater for irrigation. Evapotranspiration and plant/soil uptake are primarily responsible for water uptake and waste treatment. Percolation to ground water is relatively minor. SR systems

are capable of producing the highest degree of treatment of all LA systems largely due to the use of finer textured soils and lower application rates than other methods.

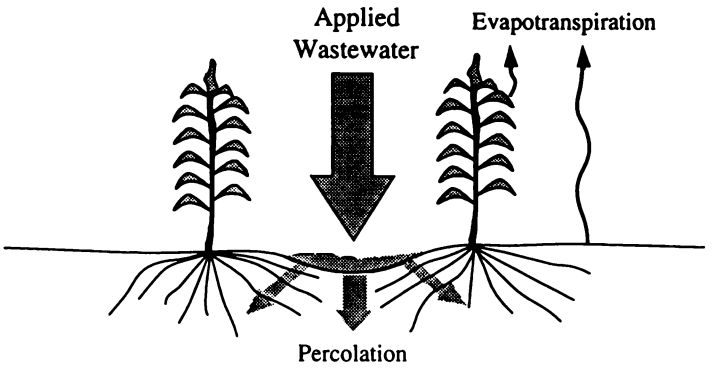


Figure 2.6: Hydraulic pathway for slow rate LA systems (after USEPA 1981)

2) *Rapid infiltration (RI)*, which involves applying effluent to permeable soils at very high rates, typically 6-125 m per annum. The majority of the wastewater percolates to ground water. Treatment occurs by physical, chemical and biochemical processes in the soil and underlying aquifers. Filtration at the soil surface and subsequent biological oxidation of the particulate organic matter account for much of the BOD and SS removals.

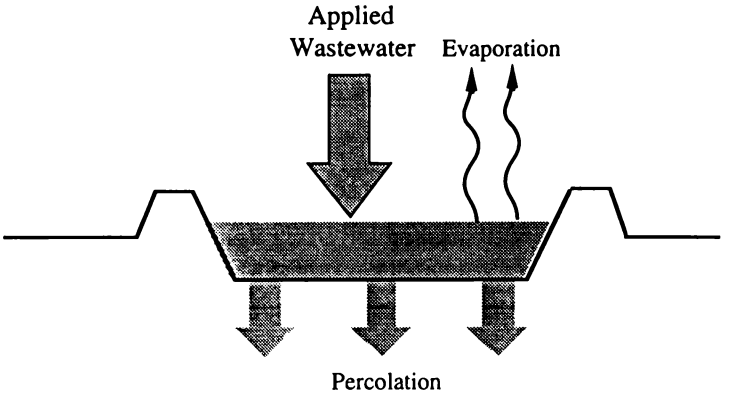


Figure 2.7: Hydraulic pathway for rapid infiltration LA systems (after USEPA 1981)

3) *Overland flow (OF)*, in which the effluent is applied at the top of a vegetated slope, and flows across the surface to be collected at the bottom end of the plot for discharge to surface waters or reuse. Moderately high application rates and low permeability soils prevent significant infiltration from occurring. OF is used to achieve secondary effluent quality from minimally treated wastes, or to polish conventionally treated wastewaters. Treatment occurs via volatilisation, and by physical and biochemical interactions with the soil surface and its microbial populations. Vegetation and litter assist the removal of particulate and colloidal material by sedimentation and filtration. Limited contact between soil and effluent in OF systems can result in relatively low treatment performance.

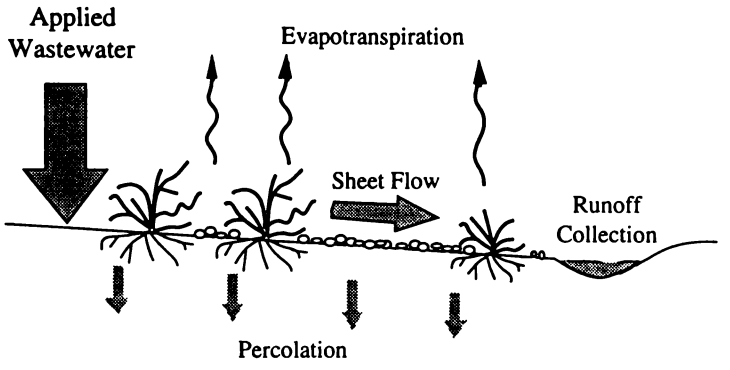


Figure 2.8: Hydraulic pathway for overland flow LA systems (after USEPA 1981)

The SR process is generally the most commonly used method, at least in the USA where 839 SR, 323 RI, and 18 OF publicly owned facilities were operative in 1981 (Hutchins *et al.* 1985).

Table 2.7: Features of the three major types of LA systems (USEPA 1981; Fuller and Warrick 1985a)

	Land application technique		
Feature	Slow rate	Rapid infiltration	Overland flow
Application method	sprinkler or surface	usually surface	sprinkler or surface
Annual application rate (m)	0.5-6	6-125	3-20
Typical weekly application rate (cm)	1-10	10-250	6-40
Minimum depth to ground water (m)	0.6-1	1.5-3	not critical
Minimum pretreatment	1° sedimentation	1° sedimentation	screening, grit removal
Fate of water	Evapotranspiration and percolation	mainly percolation	surface runoff and evapotranspiration, some percolation
Vegetation	required	optional	required
Soil permeability	moderate	high	low

LA systems have different performance characteristics and site requirements, and therefore the best system for a given situation is dependent on a number of factors including the:

- quantity of effluent to be treated;
- principal constituents to be removed;
- degree of treatment required to protect receiving waters;
- effluent pretreatment available;
- prevailing climatic conditions;
- hydrogeological characteristics of the site and surroundings; and
- available land area, and its proximity to urban areas.

The performance of these systems has been extensively studied, particularly for the treatment of municipal effluents (e.g. USEPA 1981). Indicative performance of the three processes for removing major wastewater constituents is shown in Table 2.8.

Table 2.8: Typical perfomance of LA methods for removing major classes of pollutants from municipal wastewaters (after Fuller and Warrick 1985a; USEPA 1981)

	Removals (%) obtained by each land application method		
Waste constituent	Slow rate	Rapid infiltration	Overland flow
BOD	94-99	85-99	30-95
Suspended Solids	>99	99	30-95
Nitrogen	60-90	10-95	30-90
Phosphorus	44-99	30-95	40-60
Trace metals	95-99	50-90	60-90
Organic toxicants	99	70-100	90
Viruses and bacteria	>99	>99	>90
Cations	50-75	30-75	30-50
Anions	0-50	0-10	0-10

2.4.3 Concerns related to land application of wastewater

The use of LA increased largely as a result of concern for the deterioration of surface water quality. However, just as conventional treatment and discharge practices can pollute surface receiving waters, inappropriate LA practices have the potential to contaminate underlying groundwaters. The hydraulic pathways for each of the three major types of LA systems (Figures 2.6 to 2.8) indicate that RI and, to a lesser extent, SR have the potential to contaminate ground water. The degradation of ground water is a serious problem for several reasons including (Pye and Patrick 1983; Hutchins *et al.* 1985):

- many communities and industries are dependent on high quality ground water supplies for drinking and processing waters;
- monitoring involved in locating and characterising ground water contamination is difficult and expensive;
- ground water residence times in aquifers are generally long, and therefore purification by natural volume turnover is often slow;
- dissolved oxygen levels in ground waters are often low, reducing degradation rates of many aerobically-biodegradable organic compounds;
- ground water emerges as baseflow for many surface waters, raising the possibility of adverse effects on biota which occupy or use these waters; and
- remediating contaminated aquifers is difficult, expensive, and sometimes practically impossible.

The increasing costs and regulation associated with discharge to surface waters has contributed to the application of more waste to the land, often in systems which were designed for effluent disposal or containment rather than treatment. Examples of these systems include unlined impoundments used for storage, disposal, and treatment of many industrial waste waters. These represent a major source of ground water contamination in the USA, where leakage to ground water from secondary treatment lagoons alone has been estimated to be in the vicinity of 0.5

billion m^3 per annum (Miller 1980). At that time, the pulp and paper industry contributed the greatest quantity of industrial effluents discharged to ponds, accounting for 29% of the total industry impounded wastewater.

2.5 Land Application of Pulp and Paper Mill Effluents

The following review describes the treatment of pulp and paper mill effluents by LA. It aims to:

- summarise the performance of LA systems for treating major pulp and paper mill effluent constituents;
- identify operational factors which influence LA system performance;
- identify the effects of effluent application on soil characteristics; and
- assess the potential for ground water contamination from LA systems.

Examining the treatability of pulp mill effluents on a constituent-by-constituent basis allows the component which limits the rate of application, or which requires the greatest land area for sustainable treatment, to be determined. The treatment of this component, the "land limiting constituent" (LLC), becomes the controlling factor which determines the viability of LA (Overcash and Pal 1979).

In light of the information obtained from the literature, likely LLCs for pulp and paper mill effluent LA may be identified, the performance characteristics of the Kinleith LA system anticipated, and areas requiring further study identified.

2.5.1 Background

LA for treatment and disposal of liquid effluents from the pulp and paper industry has been studied since the 1950s, interest peaking during the 1960s in the USA. During this period, the impacts of pulp and paper mill effluents on surface receiving waters became increasingly recognised. Economical and effective methods to reduce odour, BOD, colour, and suspended solids in effluents discharged to surface waters were required. The cost of conventional technologies was rising and for some effluent components, particularly colour, the degree of treatment provided was insufficient to allow the industry to meet receiving water quality standards. In many areas, this problem was compounded by large seasonal fluctuations in the flow of receiving waters, making surface water discharge a viable option only during high flow periods. LA was seen to provide solutions to at least some of these problems.

These difficulties are not unique to the USA. In New Zealand, similar problems exist, and studies of LA have been carried out for at least three wood industry plants. Pulp and paper industries in other countries, including India, France, and Canada (as well as USA), have also investigated using LA.

NCASI (1985) reviewed the status of LA of wastewater in the forest products industry in the USA, including the fibreboard and wood preservation sectors. The following summary is based on the NCASI review, and has been limited to describing the use of LA for treating pulp and paper industry waste waters, since these are directly relevant to the Kinleith LA system study.

The impetus for LA of pulp and paper mill wastewaters came largely from the need to meet receiving water quality standards which conventional treatment methods found difficult to attain during low-flow periods. Emphasis in most investigations was directed towards characterising BOD and colour treatment; the following subsections therefore also focus on these constituents.

2.5.2 Biochemical oxygen demand removal

The performance of LA for reducing BOD has been addressed in several laboratory, pilot, and full-scale studies. Results are summarised in Table 2.9.

Blosser and Owens (1963) measured BOD reductions in soil column experiments, using a range of effluent feeds and soil types. Reductions were generally >95% at BOD loadings of <264 kg ha^{-1} d^{-1}, resulting in leachates containing <10 mg L^{-1} BOD_5. Soil and effluent type had no effect on BOD removal. From these results a guideline limit for BOD loading of 225 kg ha^{-1} d^{-1} was recommended. Above this loading, vegetation cover was adversely affected by anaerobic soil conditions, and soil permeability was reduced.

Experiments which simulated percolation through soils beneath seepage ponds or lagoons gave low BOD removals, even at low organic loading rates (Blosser and Owens 1964). The seepage rate, or residence time in the soil, was found to be important in these studies, removals declining as seepage rate increased.

These studies concluded that for most pulp mill effluents, hydraulic loading rather than organic loading would be the controlling design parameter, as at typical application rates of 25 mm d^{-1} and a permissible organic loading of 225 kg ha^{-1} d^{-1}, acceptable treatment of high strength effluents, containing up to 875 mg L^{-1} BOD_5, would be possible.

Studies by Wallace (1976) reinforced the conclusion that hydraulic rather than organic overloading had most effect on BOD removal rates. Much higher removal rates were achievable when soils were not waterlogged, even when organic loadings were very high. In one experiment, anaerobic conditions induced by hydraulic overload caused BOD removal to plateau at about 30 kg ha^{-1} d^{-1}, whereas removal rates of about 900 kg ha^{-1} d^{-1} were achievable when soils were not waterlogged.

Generally therefore, provided adequate drainage is maintained, and organic loadings are within certain limits, the literature indicates that LA is an effective method for removing biodegradable organic matter from a variety of pulp mill effluents.

Table 2.9: BOD removals for a variety of LA process/effluent combinations

Reduction (%)	Process	BOD Loading (kg ha^{-1} d^{-1})	Effluent	Comment	Reference
96-99	I-SC	<263	a, b, c, d, e	laboratory trials	1
94-100	I-SC	197	b, c, f, g	laboratory trials	1
96-99	I-SC	n/s	d, h	laboratory trials	1
96-99	I-SC	143-171	i	laboratory trials	1
90	I-SC	n/s	j	laboratory trials	3
>85	RI	n/s	j	pilot and full-scale systems	4
≥85	OF+SRI	n/s	k	full-scale system	5
99	S+SRI	n/s	l	full-scale system	6
93-96	RI	n/s	m	full-scale system	7
55-84	I-SC	315-502	i	anaerobic, organic overload	1
20-80+	L	31-154	a, c	anaerobic, hydraulic overload	2
10-50	I-SC	1100-10800	g	anaerobic, organic overload	8
15-30	I-SC	110-220	n	anaerobic, hydraulic overload	8
29-46	AM	n/s	o	low BOD feed effluent	9
72-90	I-SR	1.4-8.1	j	field trial	10
50-80	I-SC	n/a	j	laboratory scale	10

Process: I-S.C = irrigation, laboratory scale soil columns; L = percolation under simulated lagoons; RI = rapid infiltration; OF+SRI = overland flow plus slow rate infiltration; S+SRI = seepage from storage lagoons plus slow rate infiltration; AM = artificial marsh; I-SR = irrigation, slow rate

Effluent: a-diluted kraft black liquor (0.3-3%); b-bleached kraft; c-unbleached kraft; d-kraft recovery evaporator condensates; e-caustic extract wash water; f-steamed mechanical insulating boardmill; g-unbleached sulphite; h-raw turpentine suspensions (0.02-0.04% v/v); i-unbleached liner board fortified with wood sugars; j-2° treated whole mill bleached kraft; k-1° treated de-inking waste; l-combined municipal, industrial and whole mill bleached kraft; m-1° treated integrated kraft/semichemical; n-pulping (process unspecified); o-2° treated pulp mill effluent (process unspecified) BOD_5 10-15 mg L^{-1}

Reference: 1-Blosser and Owens (1963); 2-Blosser and Owens (1964); 3-Narum *et al.* (1979); 4-Swaney (1985); 5-Flower (1969); 6-Ellis *et al.* (1979); 7-Edwards and Sweet (1980); 8-Wallace (1976); 9-Thut (1990); 10-Slabber (1990)

Note: n/s – not specified in the reference

2.5.3 Colour removal

Unlike BOD, the documented behaviour of colour was highly variable and depended on both the effluent and soil types (Table 2.10).

Table 2.10: Colour reductions for various effluent-soil combinations

Reduction (%)	Effluent characteristics: Effluent type	Effluent characteristics: Colour (CPU)	Soil type	Reference
93	bleached kraft	1360	silt loam	1
83	unbleached kraft	200	silt loam	1
94	evaporator condensate	295	silt loam	1
75	caustic extraction	8340	silt loam	1
88	steamed mechanical	1015	silt loam	1
99	steamed mechanical	1015	clay loam	1
94	steamed mechanical	1015	sandy loam	1
96	steamed mechanical	1015	clay loam	1
-78	unbleached sulphite	515	silt loam	1
83	unbleached sulphite	515	clay loam	1
-63	unbleached sulphite	515	sandy loam	1
95	unbleached sulphite	515	clay loam	1
95	bleached kraft	1360	silt loam	1
99	bleached kraft	1360	clay loam	1
65	bleached kraft	1360	sandy loam	1
97	bleached kraft	1360	clay loam	1
90	unbleached kraft	544	silt loam	1
99	unbleached kraft	544	clay loam	1
91	unbleached kraft	544	sandy loam	1
98	unbleached kraft	544	clay loam	1
-230	spent sulphite liquor, pH 4.5	n/s	silt loam	1
-300	spent sulphite liquor, pH 2.8	n/s	silt loam	1
-5	sulphite, NH_3 base	n/s	silt loam	1
-120	dilute sulphite liquor, Ca base	n/s	silt loam	1
30	alkaline waste waters	n/s	ground waters	2
46-83	2° treated, bleached kraft	700	sandy loam	3
89-100	2° treated, bleached kraft	1750-3200	not specified	4, 5
0-100	2° treated, bleached kraft	2300	coarse sand, gravel	6
75	diluted black liquor	1200	not specified	7
0	n/s	n/s	sand	8
80-92	n/s	n/s	sandy loam	8
54-64[a]	2° treated, bleached kraft	500-1000	Tarawera Ash	9
10-20[b]	2° treated, bleached kraft	500-1000	Tarawera Ash	9

References: 1-Blosser and Owens (1963); 2-Marchand and Sechet (1975); 3-Narum *et al.* (1979); 4-Swaney (1985); 5-M^{c}Farlane (1987); 6-Grimestad (1977); 7-Joshi and Dutta (1987); 8-Subrahamanyam *et al.* (1972); 9-Slabber (1990)

Notes: a) results from field trials; b) results for same system from laboratory soil column experiment; n/s – not specified in the reference

General findings from these studies were:

a) Colour removals were variable, a large range of reductions being recorded for different effluent-soil combinations. Differences between laboratory soil-column simulations and operative field-scale systems were also reported (e.g. Slabber 1990). Operative systems showed a wide range of colour removals at a given site (e.g. Grimestad 1977), presumably reflecting the heterogeneity of ground water systems and fluctuations in the colour of mill effluents.

b) Soils containing greater amounts of clay (e.g. clay loams) were more effective at removing colour. Sandy soils generally gave lower reductions.

c) Colour intensification (negative reductions in Table 2.10) was observed when sulphite effluents were applied to silt and sandy loams. Analysis of the lignin content of the percolates showed that 35-90% of the applied lignin had been retained in the soils. Constituents other than the unmodified, effluent-sourced lignin were therefore responsible for the colour enhancement (Blosser and Owens 1963). Changes in the light absorption characteristics of the lignin, due to pH change on transport through the soil (pH 2.8 to 7.3 in the most extreme case), was given as a possible explanation. It was noted that ground waters contaminated by sulphite effluents also exhibited persistent colour (Blosser and Owens 1963).

d) Colour was generally leachable by water applied to the soil surface after effluent application had ceased. Leachates contained higher colour levels than the feed effluents, the highest being 50,000 CPU leached from a sandy loam previously fed with bleached kraft effluent of 1360 CPU colour (Blosser and Owens 1963). While an advantage with respect to renewing the colour retention capacity of the soil (Blosser and Caron 1965), it was noted that the leachability of colour represented a potential source of ground water contamination.

Only one study examined the mechanisms for colour removal. In the RI system of Crestbrook Forest Industries Ltd (Skookumchuck, BC, Canada), colour removal was attributed to precipitation of the macro-molecular lignin by Ca^{2+}, Mg^{2+}, and Fe^{3+}, which were present in the site soil in large quantities (McFarlane 1987). During the rest phase of the LA cycle, decomposition of organic residues generated CO_2 and acidified the soil, thereby releasing more cations for precipitating lignin added in the next effluent dosing cycle. The characteristics of the soils on site were the key factor in the success of this system. Because of different soil chemistry, the technology could not be applied to the site of another pulp and paper company which had shared process development costs.

Colour breakthrough has become a problem in two operational RI systems in North America. Colour breakthrough from the RI basins in the Crestbrook system has begun (McFarlane *pers. comm.* 1990), presumably due to the exhaustion of available cation sites and the resistance of lignin to biological degradation. The Champion International RI system described by Grimestead (1977) and Olson *et al.* (1976) has apparently experienced similar problems, necessitating continuing excavation of new RI basins (McFarlane 1987).

Despite the variability in colour behaviour, which lead Blosser and Owens (1963) to recommend that each effluent-soil combination be tested to ensure ground water contamination did not occur, LA showed some potential for effective colour reduction from even highly coloured effluents. The mechanisms of colour removal have not been well established. There is evidence that site-specific factors are likely to be important in determining colour removal performance, and that LA may not be a suitable method for long-term treatment of colour at all sites or with all effluents.

2.5.4 Behaviour of organic compounds during land application

The behaviour of specific organic compounds in pulp and paper effluent LA systems has apparently received little or no attention (Thacker 1986). This is in marked contrast to conventional secondary treatment systems, which have been the subject of considerable study.
In one major US effluent treatment system (at Muskegon, Michigan), BKME made up about half of the 100,000 m^3 d^{-1} of wastewater treated (Hutchins *et al.* 1985). The removal of 56 organic compounds present in the influent was evaluated, only eight compounds being found above 1 μg L^{-1} in the treated percolates. The behaviour of BKME organics was not described.

Given that BKMEs are known to contain a large number of organic compounds of variable degradability, the lack of information on their fate in LA systems represents a significant information gap.

2.5.5 Effects on soil characteristics

The application of large quantities of effluent containing high levels of dissolved organic and inorganic matter, as well as suspended particulates such as wood fibre, has the potential to alter the characteristics of the soil. Of principal concern with regard to the viability of LA systems are reductions in soil permeability and accumulation of chemical residues which are toxic to plants or animals. The pHs of some effluent streams are also potentially detrimental to soil and vegetation.

pH

Most soils and crops generally require the irrigant pH to lie between 6.0 and 9.5 (Blosser and Caron 1965). Some segregated waste streams have pH values well above or below this range (e.g. acidic chlorination stage and alkaline extraction stage bleaching wastes) and may therefore be unsuitable for direct LA without pretreatment. LA of segregated waste streams is no longer practised in the USA (NCASI 1985).

Accumulation of toxic heavy metals

Heavy metal priority pollutants are present only at very low concentrations in most pulp and paper mill effluents. Sludges from pulp mill treatment systems generally contain heavy metal levels lower than those found in municipal sewage sludges (Thacker 1986; EPA 1982; Campin 1981; Springer 1986). Zinc was the only metal included in the USEPA toxic pollutants list for the pulp and paper industry (USEPA 1982a), and this only for groundwood processes using zinc hydrosulphite for bleaching. Concentrations were not considered high enough to reach toxic

levels in receiving waters (Springer 1986). Accumulation of toxic heavy metals in soils from LA of most pulp and paper mill effluents therefore appears to be unlikely.

Soil-colloid deflocculation

The most commonly raised concern regarding the suitability of pulp and paper mill effluents for LA is salinity. High Na^+ levels relative to Ca^{2+} and Mg^{2+} can cause the soil's cation exchange sites to be saturated with sodium. Deflocculation (dispersion) of the soil's clay fraction can result, leading to decreased permeability to both air and water. The sodium adsorption ratio (SAR)[1] is an index of potential sodium hazard of an irrigant with respect to impacts on soil structure. The sensitivity of soils to Na^+ is a function of their texture, clay content, and the nature of the dominant clay minerals present. Coarse textured soils are less susceptible than fine, while those containing expanding-lattice clays such as montmorrillonite are more sensitive to high Na^+ levels. Critical SAR values range from 5 for fine textured soils containing >10% clay content, to 750 for pure sand (Overcash and Pal 1979).

Irrigation of a number of soils with a range of pulp and paper mill effluents showed that when effluents with SARs<8 were used, problems only arose with fine textured, clay loam soils (Blosser and Owens 1963). With clay loam soil, deflocculation consistently occurred when the salt concentration of the irrigant was radically changed, for example upon leaching with water after effluent addition had ceased. Geurri (1973) also found that irrigation with NSSC liquor containing very high Na^+ concentrations (about 1800 mg L^{-1}) caused destruction of soil structure. Two to four years of rejuvenation procedures were necessary to rectify the problems. Techniques employed to amend the depletion of Ca^{2+} and Mg^{2+} generally involve addition of limestone, gypsum, dolomite (Blosser and Owens 1964; Narum *et al.* 1979), or ferrous sulphate (Hayman 1978; Hayman and Smith 1979).

SARs of pulp and paper mill effluents are highly variable, but are generally above the maximum level of 8 recommended for irrigation onto coarse soils (Blosser and Owens 1963). Values ranging between 8 and 67 were reported for US and South African effluents (Percival 1984). For soils other than coarse sands with little clay content, permeability loss associated with effluent salinity is likely to be a problem.

Soil clogging by suspended solids

Pulp and paper mill effluents can contain considerable amounts of organic and inorganic suspensoids (e.g. fibre, lime), concentrations ranging from 100-2500 mg L^{-1} (USEPA 1982). LA is effective for removing SS, but clogging of soil pores can occur. The soil's permeability to air and water is reduced, promoting the formation of anaerobic conditions and limiting infiltration rates. Sedimentation has been used as a preapplication treatment to reduce the impacts of SS (NCASI 1985). Caron and Blosser (1967) recommended fibrous solids contents of <100 mg L^{-1} for spray irrigation. Periodic scouring of the soil surface was commonly practiced for maintaining infiltration rates (NCASI 1985).

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[1] $SAR = \frac{Na^+}{\sqrt{(0.5Ca^{2+} + 0.5Mg^{2+})}}$ where concentrations are measured in meq L^{-1}.

Accumulation of organic compounds

Accumulation of organic compounds of low degradability in soils is a potential problem with LA, but little information on the fate of organic pollutants in pulp and paper mill effluent LA systems was found.

Studies of organic compounds in pulp mill effluent sludges (Thacker 1986; NCASI 1984a; NCASI 1984b), revealed that USEPA priority pollutant levels were much lower than in municipal sludges. The non-hazardous rating applied to pulp mill sludges by USEPA (Hanmer 1988) reflected the low levels of these toxic components.

Major compounds present in sludges at levels above 10 mg kg^{-1} (dry weight basis) included RA species and derivatives (abietic acid, dehydroabietic acid, norabietatriene, tetrahydroretene, and retene), napthalene, phthalates, polychlorinated biphenyls (PCBs), and (surprisingly because of its volatility) chloroform. Total organic halogen (TOX) levels of 600 and 1900 mg kg^{-1} were measured, largely attributable to high molecular weight chlorinated lignin (NCASI 1984b). PCBs were probably sourced from historic recycling of old carbonless copy paper. A wide range of chlorophenolic compounds, dominated by chloroguaiacols and catechols in both free and bound forms, have also been found in BKME sludges (Louch *et al.* 1993).

The fate of five BKME chlorophenolic compounds in soils was investigated in incubated soil reactor studies by Dargitz *et al.* (1991). The compounds were found to be biodegradable, but at different rates. Relative degradabilities were, in decreasing order: 4,5,6-trichloroguaiacol (TCG) > 4,5dichloroguaiacol (DCG) > 2,4,6-trichlorophenol (TCP) > tetrachloroguaiacol (TetCG) > 3,4,5-trichloroveratrole (TCV). TetCG and TCV were degraded by 62% and 12% respectively after 27.5 days, while the other compounds exhibited 88-96% reductions after 13 days.

Brezney *et al.* (1992) described a laboratory study which simulated landspreading of sludges from chlorine bleaching effluents. After lag phases of approximately 5 days, the concentrations of all six chlorophenolic compounds studied decreased with half-lives of between 4.3 days (for 4,5-dichloroguaiacol) and 25 days (for 4,5-dichlorocatechol). Transformation products, primarily chlorocatechols from O-demethylation of chloroguaiacols and chloroveratroles, were produced and were also degraded. Little formation of chloroveratrole O-methylation products, which were of concern due to their greater bioaccumulative potential (e.g. Neilson *et al.* 1990), was observed. Biodegradation by native soil microorganisms was shown to be responsible for the transformations and removals.

Polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) have also received some attention, after being found at parts per trillion (ppt) levels in paper industry effluents and sludges in the USA (Amendola *et al.* 1989), Canada (Clement *et al.* 1989), and New Zealand (Campin *et al.* 1990). The use of BKME sludges for land spreading declined in the USA after these findings became known, but the toxicity related implications remain unclear. Insignificant effects on wildlife in a plantation receiving sludge containing 50-80 ng kg^{-1} of 2,3,7,8-tetrachlorodibenzodioxin (TCDD) have been reported (Thiel *et al.* 1989).

Chlorolignin has been shown to adsorb strongly onto freshwater and marine sediments (Pellinen 1994) and soil (Brezny *et al.* 1993). Sorption kinetics and partitioning were found to be dependent on molecular weight, pH, and the sediment source. Sorption was strongest at low pH and for high molecular weight materials. Leaching of chlorolignin from soil to ground water was considered improbable. Mineralisation of 11% of the chlorolignin organic chlorine occurred after 90 days of aerobic soil incubation (Brezny *et al.* 1993).

2.5.6 Impacts on ground water quality

Most pulp and paper industry LA systems described in the literature depended on some seepage through the soil for effluent disposal. Ground water contamination was therefore possible. Factors which influence the risk of ground water contamination include soil permeability and type, depth to ground water, application rates, and the nature of the waste applied.

Reports of ground water contamination originating from pulp and paper mill effluent LA are limited. Grimestad (1977), Marchand and Sechet (1975), and Hansen *et al.* (1980) provided data from (then) operative, full scale, systems. The information obtained in soil column experiments (e.g. Blosser and Owens 1963) provides useful indications of possible effects. The levels of various constituents reported in ground waters influenced by pulp and paper LA systems is provided in Table 2.11.

Na^+ is mobile in soil-water systems, so elevated Na^+ levels in ground water will inevitably result from the application of many pulp and paper industry effluents. This has been observed in both operational and experimental LA systems (Blosser and Owens 1963, and Table 2.11). The exchange of Ca^{2+} and Mg^{2+} for Na^+ may also raise the concentrations of these, and possibly other multivalent ions in the ground water. Hansen *et al.* (1980) measured such an effect in shallow ground waters.

In soil column trials, colour was found to be leachable by water during the LA rest phase, intensification of percolate colour commonly occurring (Blosser and Owens 1964). Coloured ground waters beneath LA sites may therefore result. Grimestad (1977), and Marchand and Sechet (1975), recorded elevated colour levels in ground waters influenced by operational LA systems. Coloured material of molecular weight >2000 daltons was highly mobile in a sandy aquifer beneath a waste pulp liquor disposal pit, migrating at the same rate as ground water (Robertson *et al.* 1984; McCarthy and Zachara 1989).

These examples demonstrate the potential for marked degradation of ground water quality when wood industry wastes are applied to the land in systems designed for disposal rather than treatment. No reports of ground water contamination by low molecular weight organic compounds sourced from BKME LA systems were found in this review.

Table 2.11: Concentrations of constituents in ground waters influenced by pulp and paper effluent LA systems, field trials, or waste disposal

Constituent	Concentration ($mg\ L^{-1}$)	Sampling depth (m)	Reference
Na^+	320	3-10	Marchand and Sechet (1975)
	300	0.4-4.5	Hansen *et al.* (1980)
	493	3-15	Grimestad (1977)
	3000	4-25	Robertson *et al.* (1984) [a]
Cl^-	400	0.4-4.5	Hansen *et al.* (1980)
	600	4-25	Robertson *et al.* (1984) [a]
SO_4^{2-}	200	0.4-4.5	Hansen *et al.* (1980)
Ca^{2+}	100	0.4-4.5	Hansen *et al.* (1980)
COD	10800	4-25	Robertson *et al.* (1984) [a]
BOD	1650	4-25	Robertson *et al.* (1984) [a]
Fe (total)	13	n/s	Sweet and Fetrow (1975) [b]
Mn	106	n/s	Sweet and Fetrow (1975) [b]
Tannin and lignin	780	4-25	Robertson *et al.* (1984) [a]
	7.5	n/s	Sweet and Fetrow (1975) [b]
colour (CPU)	1200	3-10	Marchand and Sechet (1975) [c]
	3242	3-15	Grimestad (1977)
	205	35-45	McFarlane (1987)

Notes: a: ground water contamination from waste pulp liquor application to disposal pit in sandy soil; b: ground water contamination from wood waste disposal in gravel pits; c: colour measured by non-standard method, therefore approximate value calculated from data given in the publication, assuming effluent colour 2000 CPU. Maximum colour reductions reported were 30%; n/s = not specified in reference

2.5.7 Summary: Pulp mill effluent treatment by land application

In 1985, 17 pulp and paper mills in the USA were using LA (NCASI 1985), a decline from the 30 which were in operation in the 1965. Reasons given for the reduced usage were a) mill closure, b) improved water conservation or wastewater treatment removing the need for LA, and c) problems associated with reduced soil permeability, uncontrolled runoff, or ground water contamination, attributable to inadequate design or operation. More recent information (Dr. A Springer, *pers. comm.* 1993; APPITA 1993) indicates that while LA continues to be used as a sludge disposal method in the pulp industry, its use for effluent treatment and disposal has declined markedly in the USA, partly as a result of possible liability issues associated with site and ground water remediation. The number of currently operational LA facilities is unknown.

Spray irrrigation was the preferred application technique. The majority of mills applied less than 4500 $m^3\ d^{-1}$, with average hydraulic loading rates varying between 3.8 and 940 $m^3\ ha^{-1}d^{-1}$. LA of segregated waste streams was no longer practised at any facilities. Treatment prior to LA ranged from primary screening only to secondary aerobic biological processes.

Most sites employed vegetation, usually grasses, to help maintain soil permeability. Crop yields were able to be maintained or improved by appropriate irrigation management. Unvegetated

sites were periodically disced or ploughed to regenerate infiltration capacity, although not always successfully.

LA was effective for BOD removal, provided aerobic conditions were maintained in the soil. In flooded soils, such as found beneath seepage ponds, BOD removal was poor unless very slow seepage rates and low organic loadings were used.

The behaviour of colour was less predictable, a range of colour removals, as well as some increases, being reported. Sandy soils generally gave lower performance. Colour was leachable in laboratory simulations, generating intensely coloured percolates. Operational systems gave variable performance. Some ground waters beneath operating LA systems were highly coloured. It would appear that the processes operating in the soil are consumptive; colour is retarded until the soil capacity is exhausted, after which breakthrough occurs. The mechanisms of colour retention and/or removal were unclear. The relationship between colour and chlorolignin behaviour seemed contradictory; chlorolignin was reported to be strongly bound to soils, yet colour was not generally effectively removed. It seemed that chlorolignin was not solely responsible for leachate colour.

The combination of high colour and Na^+ in many effluents presents a problem. Best colour reductions were obtained from fine textured clay-loam soils, but these were most sensitive to deflocculation-induced permeability losses. Both coloured organic material and Na^+ have the potential to contaminate ground water. From existing information therefore, these components would appear to be the LLCs for sustainable treatment of many pulp and paper mill effluents by LA. Colour may be of particular concern because of possible intensification, rather than removal, arising from LA.

Information on the fate of low molecular weight organics in pulp and paper LA systems was limited. Studies of effluent treatment system sludges suggested that wood extractives and their derivatives were potentially important low molecular weight components in soils exposed to effluents. Chlorophenolics were likely to be present at lower concentrations. The majority of the chlorinated organic material was likely to be of high molecular weight.

The major information gap identified by the literature survey was the behaviour and fate of low molecular weight organic compounds in pulp and paper mill LA systems. Study of major effluent-sourced compounds in the Kinleith system was therefore required. The documented behaviour of colour was highly variable. Laboratory studies of chlorolignin mobility in soil indicated that it was immobile, while laboratory soil column studies and ground water studies of operational systems suggested colour mobility could be high. Because of these factors, as well as the potential for significant aesthetic degradation of the ground water resource by BKME-sourced colour, the fate of effluent colour in the Kinleith LA system and underlying ground water also needed to be determined.

In light of the lack of relevant information on the behaviour and fate of low molecular weight organics in LA systems, and the design of the Kinleith LA system, in which the quiescent seepage ponds were potentially active treatment zones, broadening the scope of the literature

review to include the behaviour of BKME components in pond-based treatment system environments was considered worthwhile. This provided additional information on possible effluent behaviour in the pond-soil-ground water environments of the Kinleith system.

2.6 BKMEs in Pond-based Treatment Systems

Effluent passing through the Kinleith LA system was exposed to a range of treatment environments. Anaerobic conditions would be anticipated to be present in the ponds during loading with high BOD effluent. After biological oxidation of degradable organic matter, aerobic status would gradually be re-established by natural re-aeration. The hydraulic retention characteristics of the seepage basins approximated those of "storage oxidation ponds", the earliest biotreatment systems used in the treatment of pulp and paper mill effluents. 50-90% BOD removal at loading rates of 60-70 kg ha^{-1} d^{-1} and retention times of 20-60 days were achievable with these types of biotreatment systems (Springer 1986).

The sediments and shallow ground waters immediately beneath the ponds were probably anaerobic, especially during effluent loading and extended flooded periods. As the ponds dried out during their summer rest phase, aerobic conditions would be reestablished, at least at the sediment-air interface.

A combination of anaerobic, facultative, and aerobic biotreatment processes would therefore be expected to operate in this system and it is therefore relevant to consider the behaviour of BKME organic constituents under these environmental regimes.

Examining effluent treatment performance in aerated treatment systems provides information on the behaviour of effluent constituents in aerobic environments. In these systems, dominated in the pulp and paper industry by aerated lagoons and activated sludge reactors, degradation of oxidisable organic matter is optimised by employing turbulent mixing and high rates of oxygen transfer to ensure high concentrations of active microbial biomass are maintained. The results from these systems therefore represent the upper limits of removals that could be expected in aerobic environments.

Information on effluent behaviour in anaerobic environments can be found from studies on anaerobic treatment system performance, and also from examination of the composition of sediments in effluent receiving waters. Information on the behaviour of effluent components in these systems can be used to provide an indication of the nature of the transformations which could occur within and beneath the seepage basins.

2.6.1 Aerobic environments

High molecular weight materials

The primary aim of aerated treatment systems is BOD removal, and for pulp and paper mill effluents reductions of the order of 80-95% are generally achieved with retention times of 5-10 days (Keith 1976; Lindstrom and Mohamed 1988; Boman *et al.* 1988; Springer 1986). The reduction in total organic material (e.g. COD) is generally much lower, of the order of 20-60%,

due to the large proportion of high molecular weight material of low biodegradability present in most BKMEs (Lindstrom and Mohamed 1988; Stuthridge 1990; Randle *et al.* 1991).

Chlorolignin mineralisation of less than 4% after 3 months resulted from incubation with bacteria isolated from an aerated lagoon (Eriksson and Kolar 1985). Long-term studies of lignin degradation in an aerobic aquatic environment indicated that significant lignin removal was unlikely on the time-scale usually employed in treatment systems (Rush and Shannon 1976).

Colour removals are therefore also low in aerobic biological treatment systems, 30% reductions at best (generally <10%) being achieved (Springer 1986). Aeration of diluted (1:10) spent alkali extraction liquor, with and without microbial activity, decreased the colour by 20% and 33% respectively after 5 months (Hardell and de Sousa 1977). No statistically significant colour reduction was measured in the Kinleith biological treatment system (Stuthridge *et al.* 1991). Colour increases have even been observed in some biological treatment systems (Larrea *et al.* 1989; Cecen *et al.* 1992).

Removals of total organically bound chlorine, measured as AOX, TOCl, or TOX[1] are generally comparable with COD reductions, 20-65% removals having been reported in a number of studies (Bryant *et al.* 1988; Randle *et al.* 1991; Gergov *et al.* 1988; Lindstrom and Mohamed 1988; Stuthridge *et al.* 1991; Ferguson and Dalentoft 1991; Saunamaki *et al.* 1991; Nevalainen *et al.* 1991). Activated sludge system performance is generally better than aerated lagoons, probably because of the longer solids retention times in the former (Boman *et al.* 1988). AOX reduction in aerated lagoons occurs largely by dehalogenation and mineralisation in anaerobic benthal zones, to which AOX is transported by adsorption onto settling biomass (Bryant *et al.* 1988; Stuthridge 1990; Randle *et al.* 1991; McFarlane *et al.* 1991). The nature of the dehalogenation process is not clear, but there is evidence that both biotic and abiotic processes operate (McFarlane *et al.* 1991; Fergusson and Dalentoft 1991). Association with biosludges and volatilisation is relatively minor. In activated sludge systems, biodegradation of AOX in the recycled sludge is the major removal process, although some (generally <10%) is removed with the sludge and/or volatilised (McFarlane *et al.* 1991; Saunamaki *et al.* 1991; Randle *et al.* 1991).

Low molecular weight compounds

The removal of specific organic constituents in aerated lagoons and activated sludge plants has been extensively documented in overseas systems (e.g. Keith 1976; Easty *et al.* 1978; Hrutfiord *et al.* 1975; Wilson and Hrutfiord 1975; USEPA 1982a; Voss 1984; Voss and Rapsomatiotis 1985; Holmbolm and Lehtinen 1980; Leuenberger *et al.* 1985; McLeay 1987; Gergov *et al.* 1988; Lindstrom and Mohamed 1988; Boman *et al.* 1988), and in New Zealand (Stuthridge *et al.* 1991; Zender *et al.* 1994).

It is generally accepted that well operated systems reduce the concentrations of MTs, FAs, and RAs by >90% (McLeay 1987). However, the range of removals documented for operative

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[1] Generic measures of total organically bound chlorine: AOX = adsorbable organic halide; TOCl = total organic chlorine; TOX = total organic halide

systems is large, especially for RAs, for which reductions of between 39% (for 2 day retention time aerated lagoon; Keith 1976) and 96% (Voss and Rapsomatiotis 1985) have been recorded. This is reflected in historical reports of a 20% failure rate of aerated lagoons (5-day hydraulic retention time) in eliminating acute toxicity (Leach *et al.* 1978; Kutney *et al.* 1981a).

Metabolic pathways for RA biodegradation proceed via oxidation and hydroxylation, a range of oxy- and hydroxy- metabolites having been reported for a number of bacteria and fungi incubated under laboratory conditions (e.g. Biellmann *et al.* 1973a, 1973b; Ekman and Sjoholm 1979; Kutney *et al.* 1981a, 1981b; Kutney *et al.* 1982). Hydroxylated RA intermediates were found to be less toxic than the parent species (Kutney *et al.* 1982).

In aerated treatment systems, biotransformation products have not been extensively reported. 7-oxodehydroabietic acid (Brownlee and Strachan 1977) and 13-abieten-18-oic acid (Keith 1976) are two relatively commonly detected compounds. The absence of high levels of RA metabolites in aerobic effluent treatment systems suggests that mineralisation or deposition in settled biomass occurs during treatment. Major MT metabolites found in aerobic treatment systems are camphor and fenchone, formed by oxidation of borneol and fenchyl alcohol respectively (Wilson and Hrutfiord 1975).

Methyl substituted 2-cyclopentenones and acetyl thiophenes, which are relatively minor BKME constituents, appear to be relatively resistant to biological treatment. Removals of 17% and 50% respectively have been measured in an aerated lagoon (Voss 1984).

Reductions in the concentrations of chlorophenolics are typically about 30-40% in aerated lagoon systems (Lindstrom and Mohamed 1988; Holmbolm and Lehtinen 1980; McLeay 1987) but again literature data are somewhat variable. Stuthridge *et al.* (1991) measured reductions of about 70% in the aerated lagoon system at NZFP Kinleith. Activated sludge systems are generally reported to be more effective, giving reductions of 60-95% (Stuthridge 1990). Gergov *et al.* (1988) measured reductions of 86% and 95% with an activated sludge plant, in contrast to 25-37% reductions reported by Randle *et al.* (1991) and 13-36% by Leuenberger *et al.* (1985). Removals of individual chlorophenolic compounds are variable. Some species even increase in concentration during treatment, for example chlorocatechols (Holmbolm and Lehtinen (1980), and chloroguaiacols (Stuthridge *et al.* 1991). Chloroguaiacols have been reported to be the most resistant to degradation (Lindstrom and Mohamed 1988), but are apparently well sorbed to sludge (Leuenberger *et al.* 1985). Hydroxylation, followed by cleavage of the aromatic ring and Cl^- elimination is a major degradative mechanism for mono- and dichlorinated phenols, while reductive dechlorination and hydroxylation, followed by aromatic ring cleavage has been identified as being responsible for degradation of more highly chlorinated chloroguaiacols and phenols (Neilson *et al.* 1990).

2.6.2 Anaerobic environments

High molecualr weight materials

Lignin is recalcitrant under anoxic conditions because of its high molecular weight and structural disorder, the latter preventing effective enzymatic depolymerisation (Zeikus *et al.*

1982; Evans and Fuchs 1988; Lettinga *et al.* 1991). Chemical oxidants such as oxygen-containing radicals, which are unlikely to be present in anaerobic treatment environments, are thought to be required for lignin degradation to proceed. Decomposition of kraft lignin to CO_2 and CH_4 amounting to 11% was measured after incubation for 30 days in an anaerobic lake sediment (Zeikus *et al.* 1982). Studies of $M_r \geq 850$ and $M_r \leq 850$ fractions revealed that the lower M_r fraction was significantly degraded, while the higher fraction was not. Lignin model dimers containing the β-aryl ether linkage were also decomposed, indicating that the interunit ether linkage does not limit anaerobic degradation. Zeikus *et al.* (1982) concluded that lignin must be modified or depolymerised before significant anaerobic degradation would occur.

Low molecular weight components

In poorly aerated treatment systems, RAs and their metabolites are more persistent than in aerobic environments. Reductions in total RAs of about 20% were recorded in a quiescent storage basin with 3-6 month hydraulic retention time (HRT), 13-abieten-18-oic acid and, to a lesser extent, dehydroabietic acid, increasing in concentration (Keith 1976).

A saturated hydroxylated RA, 13β-hydroxyabietanoic acid, was found as a major species in a 45 day HRT naturally-aerated storage lagoon at Kinleith (Wilkins *et al.* 1989). This compound and dehydroabietic acid were the dominant compounds, with modest amounts of 13-abieten-18-oic acid also being found. Total RA levels were reduced by only 44% during treatment in this predominately anaerobic system, resulting in mean total RA concentrations of 46 mg L^{-1} exiting the lagoon (Stuthridge *et al.* 1991).

Saturated RAs, and both saturated and aromatic diterpene hydrocarbons (DTs) were found in an anaerobic sludge lagoon in a New Zealand kraft mill treatment system (Wilkins and Panadam 1987; Panadam-Twigley 1988). Major compounds were abietan-18-oic acid and dehydroabietic acid.

The behaviour of resin constituents in anaerobic effluent treatment systems, and the toxicity of RAs to the methanogenic organisms required in anaerobic reactors, have also been investigated (M^{c}Farlane and Clark 1988; Lettinga *et al.* 1991; Sierra-Alvarez and Lettinga 1990; Sierra-Alvarez *et al.* 1990; M^{c}Carthy *et al.* 1990; Rintala *et al.* 1991). Some MTs and RAs are inhibitory to methanogenic processes, and interfere with metabolism of readily biodegradable substrates, contributing to poor BOD removal from some wastes during anaerobic treatment. Kraft evaporator condensates, however, are well treated anaerobically (Qiu *et al.* 1988), indicating that the alcohols and volatile FAs which make up the majority of their organic loading are readily degradable. Monomeric lignin-related compounds such as guaiacol, and ferulic and vanillic acids are also anaerobically biodegradable, although aromatic compounds with alkyl side-chains (e.g. eugenol) or those without polar functional groups (e.g. benzene and alkyl-benzenes) are not. Long chain FAs, such as oleic and linoleic acids, which are major kraft effluent constituents, are readily degradable during anaerobic treatment (Sierra-Alvarez *et al.* 1990).

The recalcitrance of RAs (dehydroabietic and abietic acids) and MT hydrocarbons (α-pinene and limonene) under methanogenic conditions was demonstrated by their insignificant

degradation after incubation for 123 days (Sierra-Alvarez *et al.* 1990). Poor removals of RAs, particularly dehydroabietic acid which was found at higher concentrations in the treated effluent than in the influent, were also recorded by Qiu *et al.* (1988).

McFarlane and Clark (1988) detailed the behaviour of RAs in the anaerobic treatment of screw press effluent from a medium density fibreboard plant and a synthetic wastewater, using upflow anaerobic sludge blanket (UASB) and continuously stirred tank reactor (CSTR) systems. Dehydroabietic acid was the only component which left or accumulated in the UASB reactor, but even at levels in the sludge 13 times higher than the feed concentration, methanogenesis was not inhibited. A range of metabolites arising from double bond saturation were identified, indicating a reductive degradation/transformation pathway was operating. In the CSTR, which was fed with abietic and dehydroabietic acids, abietic acid was metabolised producing 8(14)-abieten-18-oic acid as the sole intermediate. Dehydroabietic acid was not degraded.

Anaerobic treatment of effluents containing sulphur compounds may result in odour problems. Qiu *et al.* (1988) determined that about 30% of the total sulphur was transferred to the gas phase as H_2S, with most of the remainder remaining as organic sulphur compounds or HS^-. Subsequent aerobic treatment removed essentially all of this to SO_4^{2-}.

The resistance of RAs and some other extractive compounds to biodegradation in poorly aerated and anaerobic systems is therefore well documented. A range of degradation intermediates have been identified, although mostly for systems which are predominately anaerobic.

Chlorophenolic compounds are at least partially degradable under anaerobic conditions, microbially-mediated, sequential reductive dechlorination being the predominant degradation mechanism (Guthrie *et al.* 1984; Woods *et al.* 1989; Neilson *et al.* 1990; Mikesell and Boyd 1988). Chloroveratroles are de-O-methylated, forming chloroguaiacols, then chlorocatechols, before undergoing reductive dechlorination. Degradation is not always complete, and compounds with lower chlorine substitution are found as products, particularly in sludges and sediments (Neilson *et al.* 1990).

Treatment systems using high-rate anearobic systems (Parker et al. 1993), or sequential anaerobic and aerobic conditions (e.g. ENSO-FENOX process), have been shown to be effective for BKME treatment. The anaerobic stage provides dechlorination of high and low molecular weight material, resulting in high AOX and chlorinated phenolics removals, while subsequent aerobic treatment reduces BOD (Randle *et al.* 1991; Haggblom and Salkinoja-Salonen 1991; Frostell *et al.* 1991).

2.7 BKME Behaviour in Receiving Environments

Despite being degradable in effluent treatment systems, RAs and chlorophenolics have been found in effluent receiving waters and sediments. Highest concentrations have been associated with discharges from mills employing limited or no treatment. McLeay (1987), Environment Canada (1991) and Tavendale (1994) provide compilations of literature data.

Recent studies have shown that AOX and colour of biotreated BKME were degraded by sunlight (Archibald *et al.* 1997). Neither AOX nor colour were susceptible to biological degradation, and natural organic matter reduced the photomineralisation process.

Sorption to effluent-sourced fibre, and consequent sedimentation, have been reported to influence the distribution and fate of chlorophenolic compounds in receiving waters (Xie *et al.* 1986). High concentrations of BKME-sourced organic compounds and biotransformation products have therefore been found in sediments close to mill outfalls (Xie *et al.* 1986; McLeay 1987; Crooks and Sikes 1990; Remberger *et al.* 1990; Tavendale 1994). At more distant locations, dilution has been found to be an important mechanism in reducing concentrations of effluent-sourced compounds (e.g. Fox 1976). Chlorinated guaiacols and catechols have been found in waters and sediments up to 700 km from pulp mill sources (Environment Canada 1991).

Chlorocatechols, in particular tetrachlorocatechol, are generally the dominant chlorophenolic compounds found in sediments (McLeay 1987). This observation is consistent with the biotransformation pathways of chlorophenolics (summarised in Neilson *et al.* 1990) in which the end-products are chlorocatechols. Under aerobic conditions, O-methylation of chloroguaiacols and catechols forms chloroveratroles, while under anaerobic conditions chloroguaiacols and chloroveratroles are de-O-methylated to chlorocatechols. The catechols have higher aqueous-sediment partition coefficients than guaiacols or veratroles (Remberger *et al.* 1986) and therefore would be expected to be found bound to sediments. While partitioning to sediment-phase organic carbon is believed to be primarily responsible for sorption of chloroguaiacols, there is evidence that an important mechanism in the binding of chlorocatechols to sediments is complexation with sediment-phase iron and aluminium cations (Remberger *et al.* 1993). Bound chlorocatechols can be released from contaminated sediments into the aqueous phase, a process which is facilitated by iron and aluminium complexing agents, and by elevated pH.

Dehydroabietic acid is the most often reported RA in sediments, although a number of other RAs, including abietanoic acid, various abietenoic acids, pimaric and isopimaric acids, have also been found both overseas (e.g. McLeay 1987; Remberger *et al.* 1990; Lee and Peart 1991) and in New Zealand (Wilkins and Panadam 1987; Tavendale 1994). DTs, which are well documented anaerobic transformation products of RAs (e.g. Simoneit 1986), have also been found in sediments of both natural origin (Simoneit 1977; Wakeham *et al.* 1980; Tan and Heit 1981) and those contaminated by pulp and paper mill effluent (Yamaoka 1979; Kinae *et al.* 1981; Tavendale 1994).

No accounts of BKME-sourced organic compounds in ground waters were found in this literature survey. MTs and dehydroabietic acid have been found in ground water contaminated by landfill leachate (Reinhard *et al.* 1984). Camphor and fenchone were the major MTs present, indicating that sub-surface biotransformations, for example those occurring within the landfill, were similar to those operating in effluent treatment systems.

Chlorinated phenols have commonly been found as ground water contaminants, often associated with timber treatment plants (e.g. Valo *et al.* 1984, 1985) or disposal of chemical industry waste waters (e.g. Johnson *et al.* 1985). Although chlorinated phenols are biodegradable in aerobic and anaerobic treatment systems (e.g. Mikesell and Boyd 1988; Guthrie *et al.* 1984), degradation under environmental conditions is slow (Valo *et al.* 1990). Sorption is pH dependent, but under most environmental conditions is dominated by partitioning of the undissociated molecule between the aqueous phase and the organic phase of the sediment (Schellenberg *et al.* 1984; Lagas 1988). In sediments and aquifer materials containing low organic carbon contents, and in high pH waters, chlorinated phenols could be expected to be relatively mobile compounds.

2.8 Implications of the Literature for the Kinleith LA System

The literature provided a substantial body of information upon which to base some speculative predictions of the likely performance characteristics of the Kinleith LA system. The review also identified areas in which insufficient information was available for adequate prediction. These areas formed the basis for the thesis investigations.

2.8.1 Treatment characteristics of the Kinleith LA system

From the literature survey and site specific information on the Kinleith system (Chapter 1), a number of performance characteristics of the LA system at Kinleith were at least tentatively predictable:

1) The average effluent application rate (10,000 m^3 d^{-1}) and area of the seepage fields (80 ha), gave an average infiltration rate of 12.5 mm d^{-1}. Assuming disposal by LA for 8 months of the year (section 1.4.1), this equated to an annual application rate of 2.8 m $year^{-1}$. This placed the Kinleith system into the "slow rate" LA category (Table 2.7), for which maximal treatment performance is generally obtained.

2) The BOD application rate, assuming effluent BOD of 800 mg L^{-1} (Table 1.3) and application rate of 10,000 m^3 d^{-1}, was 100 kg ha^{-1} d^{-1}. This was below the recommended maximum of 225 kg ha^{-1} d^{-1} (section 2.5.2), suggesting that adequate BOD removal should have been achieved in the Kinleith LA system. During extended flooded periods however, anaerobic conditions could be expected beneath the seepage ponds, reducing the BOD removal capability and allowing survival of aerobically degradable organic compounds.

3) Using No. 2 effluent composition data supplied by NZFP, a sodium adsorption ratio (SAR) of approximately 42 was calculated. This was well above the recommended value of 8 (section 2.5.5), indicating that degradation of soil structure, and consequent reductions in infiltration rates might become a problem in the Kinleith LA system.

Colour removal data given in the literature were highly variable, preventing any reliable prediction of colour removal performance to be made. Given the recalcitrance of colour to biological treatment, it seemed unlikely that sustainable treatment would occur in the LA system.

The literature contained no information on fate and behaviour of BKME low molecular weight organic compounds in LA systems. The predominant compounds in the No. 2 effluent were MTs, FAs, RAs, and at lower concentrations, chlorophenolics. Information on the behaviour of these constituents under aerobic and anaerobic conditions suggested that:

a) FAs would be readily degradable under most environmental conditions, and should therefore be readily treated in the LA system;

b) MTs would be readily degraded and/or volatilised under aerobic conditions, but could be somewhat resistant to removal under anaerobic conditions. They would also be expected to be relatively mobile in soil-water systems, and could therefore pass through the seepage system soils. Once in low dissolved oxygen ground waters, they could be relatively persistent species;

c) RAs would be degradable during aerobic treatment, but could be persistent under anaerobic conditions. The degradation rates in facultative quiescent oxidation basins could be relatively slow and degradation incomplete, resulting in transformed compounds percolating into ground water. However, the high K_{ow} values of RAs suggested that they should be strongly associated with soil organic matter and biosludges, and therefore their movement through the sediments beneath the seepage ponds should be limited. During the summer rest phase in the Kinleith LA system cycle, sorbed RAs could undergo aerobic degradation, thereby providing a mechanism for remediation of contaminated surficial sediments and providing for sustainable treatment;

d) chlorophenolics should be at least partially degradable under both aerobic and anaerobic conditions, and the major degradation products (chlorocatechols) strongly bound to sediments. The anaerobic-aerobic cycle of the Kinleith LA system could provide good treatment conditions for chlorinated compounds. Degradation of chlorophenolics in aerobic soils occurs at rates sufficient to permit sorbed compounds to be removed during the rest cycle. Given that a) the concentrations of chlorophenolics in the effluent were 10-100 times lower than RAs, b) the toxicities of RAs and chlorophenolics to aquatic life are similar, and c) chlorophenolics are possibly more amenable than RAs to treatment during LA, the environmental significance of the chlorophenolics was considered lower that the RAs.

2.8.2 Uncertainties requiring clarification

Based on the information review, it was hypothesised that the Kineith LA system should adequately treat MTs and FAs, but remove chlorophenolics, and more particularly RAs, to a lesser extent. While it was probable that chlorolignin would be removed by sorption to soil, it seemed unlikely that colour removal of sufficient magnitude to be useful would be achievable. Any removal that did occur would almost certainly be unsustainable in the longer term.

The physical characteristics of the Kinleith LA system, in particular the influence of the fractured geology on effluent transport and soil-effluent interactions, compounded the uncertainty. Similarly, the role of high molecular weight chlorolignin in facilitating sub-surface transport of low molecular weight organic compounds was unknown.

Site-specific studies were therefore required to adequately establish the performance of the Kinleith LA system. Areas requiring evaluation were:

1. the behaviour of extractable organics (in particular RAs) and chlorophenolics in the quiescent seepage ponds;

2. the effect of BKME infiltration on the chemistry of sediments underlying the seepage basins, in particular accumulation of chemical residues;

3. the behaviour of effluent-sourced organic compounds and colour during passage through these sediments;

4. the effect of the LA system on shallow ground waters underlying the seepage system, with particular reference to effluent-sourced organics and colour; and

5. the effect of the LA system on the quality of off-site ground waters, in particular migration of effluent-sourced organics and colour away from the LA site.

These aspects were addressed in the investigations described in this thesis.

Chapter Three

Analytical Procedures

3.1 Introduction

This chapter describes the analytical procedures used in the study. Methods used for estimating method performance (e.g. detection limits and precision) are summarised, and some discussion of the limitations of the analytical methods is included.

3.1.1 Performance assessment procedures

Precision and bias of the analytical procedures were assessed to ensure analytical results were sufficently reliable to meet the objectives of the project.

Estimating precision
Precision was estimated in two ways:

1) calculation of the "within-batch standard deviation" (swb), or coefficient of variation (cv; 100 x swb/mean), from repeated analysis of several identical samples and/or standards under the same conditions. The precision estimate obtained from this exercise is termed "repeatability" (Hunt and Wilson 1986; TELARC 1987) and does not take into account long-term variations which may arise; and

2) calculation of an "overall method standard deviation" (S_R), from duplicate analyses of samples and standards performed throughout the duration of the project. This precision estimate is termed "reproducibility", and for analysis of duplicates, is defined by (*eqn. 3.1*):

$$S_R^2 = \frac{1}{2p} \sum_{i=1}^{p} | y_{i1} - y_{i2} |^2$$

where p = number of duplicates analysed, and $y_{i1} - y_{i2}$ = difference between duplicate results (TELARC 1987).

The second approach gives a more realistic estimate of the performance of an analytical method over a given period, as it accounts for method variation over time. It does, however, require a considerable amount of replication, at least 10 sets of duplicates covering five or more concentration ranges being recommended to provide reliable S_R estimates (TELARC 1987). This approach is therefore better suited for relatively simple analytical procedures, and was used to estimate precision for sodium, chloride, colour, and iron determination methods.

The "within-batch" replication approach was used to determine the precision (or rather repeatability) of the procedures used for organic contaminant analysis. The on-going replication method (approach 2) would have required overly large amounts of sample (which were not always available) and more time than was available. Few comparisons of data obtained in separate analytical batches were made in the project, and therefore the use of repeatability as a precision estimate was acceptable. For future work, especially contaminant temporal trend monitoring, greater emphasis on between-batch quality assurance may well be required.

Estimating bias

Bias was assessed for analysis of sodium and iron because the instrument used in the determination of these elements exhibited significant drift. Calibration standards with concentrations similar to the samples analysed in the batch were reanalysed at the end of each batch of samples. The differences between the remeasured values and the true concentrations of these standards were used to estimate average bias at five concentrations. Bias was less than ±10% for all analyses except iron, where average bias of +19% was measured at 1 mg L^{-1} (near the detection limit (DL) for the method used).

Detection limits

The majority of the samples analysed had high analyte concentrations and therefore DLs were of little importance. Detection limits for sodium and colour analysis procedures were estimated from the S_Rs of low concentration samples and blanks, using detection limit, DL ≅ $5S_R$ (TELARC 1987). Insufficient data was available to determine DLs for other determinands.

3.2 Inorganic and Physical Determinands

3.2.1 Sodium

Sodium concentrations in most of the samples analysed were high, typically 300-1000 mg L^{-1}. A method which gave reliable quantitation at high concentrations was therefore used. Atomic absorption spectrometry (AAS) at 330.3 nm was employed, using a Philips SP9 instrument coupled to a Philips PU2000 computer for quantitation. The relatively low sensitivity at this wavelength allowed most high concentration samples to be analysed without dilution.

Method precision (cv; %), estimated from a total of 164 standard replicates analysed throughout the project, at concentrations 25–1000 mg L^{-1}, was 2.3–7.0%, greater variability occurring for the lowest and highest concentrations. Analysis of 101 sample duplicates of 6–1030 mg L^{-1} gave cv's of 1.6–2.7%. The DL was estimated to be 3 mg L^{-1} from between-batch replicate analysis of blanks .

3.2.2 Chloride

Chloride was determined by ion selective electrode (ISE) and colorimetry.The ISE method was briefly trialled but was soon abandoned as the performance of the electrode system deteriorated, possibly because of poisoning by effluent sulphide. No method performance data was acquired. The ISE data were used in preliminary investigations of the No. 2 effluent (section 4.3).

A manual version of the DSIR (1978) modification to the ferricyanide method 407D (APHA 1985) was used for the rest of the project. Method precision was evaluated from 12 sample between-batch duplicates in the 340–680 mg L^{-1} concentration range. A S_R of ±16 mg L^{-1} was calculated for this range giving a cv of ±3.1% (for a mid-range concentration sample).

3.2.3 Colour

The National Council of the Paper Industry for Air and Stream Improvement (NCASI) method for measurement of pulp mill effluent colour was used (NCASI 1971). This procedure involves the spectrophotometric comparison of the filtered sample with cobalt-platinum colour standards,

at a wavelength of 465 nm. The resulting units of colour are "chloroplatinate units" (CPU), 1 CPU being the colour produced by 1 mg L^{-1} Pt in the form of chloroplatinate ion ($PtCl_6^{2-}$).

50 mL samples were adjusted to pH 7.6 with 2 mol L^{-1} NaOH, then 0.8 µm membrane filtered. The absorbances of the filtered samples at 465 nm were measured in 1 cm quartz cells, using either Pye Unicam SP1800 or Hitachi 150-20 spectrophotometers.

A cv of ±1–4% was obtained between-batch duplicate analysis of 61 samples of 30–6500 CPU, and a DL of 20 CPU from 13 low level samples (12–100 CPU) and 23 distilled water blanks.

3.2.4 Iron

Iron was determined by AAS at 248.3 nm using the same instrument used for Na^+ analysis. The cv was ±2.2–2.6% from duplicate analysis of 30 samples and ±3.5–10% from 52 standards (0.95–48 mg L^{-1}). A DL of 0.6 mg L^{-1} was estimated from between-batch duplicate analyses of 10 low level (0.95 mg L^{-1}) calibration check standards.

3.3 Extractable Organics

3.3.1 Definition

The term "extractable organics" (EOs) describes organic compounds which can be recovered from a sample by extraction with organic solvents. The compounds isolated and identified are dependent on both the extraction method and the technique used to analyse the extract.

The EO constituents targeted in this study were monoterpenes (MTs), resin acids (RAs), and fatty acids (FAs). Analytical techniques used for their determination also allowed a range of other compounds to be recovered and at least tentatively identified. These included monomeric phenolics, organosulphur compounds, and cyclopentenones.

3.3.2 General preparatory procedures for reagents and materials

To minimise interference from extraneous contaminants during sample collection and analysis for EOs, sample bottles and analytical materials were pretreated as follows:

- Glass sampling bottles were cleaned by scrubbing and overnight soaking in laboratory detergent solution (Decon 90®or Pyroneg®), followed by hot tap-water rinsing, acid and alkaline rinsing (2 mol L^{-1} HCl and NaOH), tap water flushing and, finally, rinsing with distilled water. Bottles were left to drain overnight before sealing with aluminium foil lined caps until use. Once dry, bottles for ground water sampling were rinsed with doubly-distilled dichloromethane (DCM), before draining and capping. Glassware used for analysis was subjected to the same washing procedure, but oven drying was used after the distilled water rinse. A single solvent rinse was employed as a final cleaning step immediately prior to use.

- Solvents used for extraction, glassware rinsing, or preparation of standards were either singly distilled (for use in effluent sample analysis only), or doubly distilled, through a 50 cm glass fractionation column. Distilled solvents were checked for interfering impurities by

concentrating the solvents by the same factors as occurred during sample analysis (100-500 times), and analysing by gas chromatography (GC) prior to use.

- Sodium sulphate (BDH, granular Analar) was furnaced at 600°C overnight and stored in airtight screw-top bottles until use. Material which was visibly grey coloured after heating was well mixed and reheated overnight. Florisil® was treated in the same way before deactivating by adding 2 g distilled water to 98 g activated Florisil®, and tumbling for at least 4 hours prior to use. Glass wool and glass fibre filters (Whatman GF/C) were baked at 600°C for at least 3 hours and rinsed with distilled DCM before use.

- Anti-bumping granules were Soxhlet extracted overnight with DCM, then stored in screw-top vials.

- Aqueous acids and bases (2 mol L^{-1} HCl and NaOH) were solvent extracted (twice, with distilled DCM in separating funnels) and stored in glass reagent bottles.

- Ethereal diazomethane (CH_2N_2) was generated from either nitrosomethylurea (Vogel 1978), or from N-methyl-N-nitroso-*p*-toluene sulphonamide (Diazald®; Aldrich). A one-piece still/condensor with clear-glass joints was used to isolate the purified product. The resulting bright yellow solution was stored for up to 5 days at -20 °C until use.

- Standards were generally >95% pure when analysed by gas chromatography (GC) prior to use. Where necessary, concentrations were corrected to account for impurities. Standard solutions were stored in volumetric flasks at 4 °C (EOs) or -20 °C (chlorophenolics).

3.4 Extractable Organics in Effluents

3.4.1 Background

Procedures for analysis of organics in BKMEs developed considerably over the period spanned by this project. Prior to 1985/86, the extraction conditions required for optimal recovery of resin and fatty acids (RFA) from BKMEs were not well defined, and a range of procedures had been reported in the literature (Table 3.1). Subsequent to the studies described in this thesis, new methods, or variations of established methods, have been reported (e.g. Lee *et al.* 1990; Morales *et al.* 1992a).

The methods published prior to 1986 followed two general approaches (Voss and Rapsomatiotis 1985): 1) solvent extraction of the acidified (pH 2-3) effluent with diethyl ether or chloroform, and 2) adsorption onto polymeric XAD-2 resin under alkaline (pH 9-10) conditions. Solvent extraction under acidic conditions was commonly used to maximise recoveries of organic acids, a procedure consistent with accepted practice for recovery of acidic organic compounds from aqueous matrices (e.g. Valkenburg *et al.* 1989).

Table 3.1: Some procedures published prior to, or during, the thesis study period for extraction of resin and fatty acids from pulp and paper mill effluents and receiving waters

	Extraction variables			
Method [a]	pH	solvent	internal standards [c]	Reference
XAD-2	acidic	diethyl ether	none	Fox (1976)
L/L-SF	acidic	chloroform	none	Keith (1976)
L/L-C	ambient	chloroform	none	Brownlee and Strachan (1977)
XAD-2	2	diethyl ether	FA17:0, FA23:0	Oikari *et al.* (1980)
L/L-SF	2-3	diethyl ether	FA17:0, FA23:0	Holmbolm (1980)
L/L	≤2	dichloromethane	FA17:0	USEPA (1982a)
XAD-2	>7-5	diethyl ether	FA17:0	Richardson and Bloom (1983)
L/L-SF	9	MTBE [b]	FA17:0, PDHA	Voss and Rapsomatiosis (1985)
L/L-C	2	dichloromethane	*n*-octadecane	Wilkins and Panadam (1987)
L/L	acidic	dichloromethane	FA20:0	M^{c}Farlane and Clark (1988)

a: XAD-2 = adsorption onto XAD-2 porous polymer resin, L/L = liquid-liquid extraction using separating funnel (SF) or continuous (C) extractors; b: MTBE = methyl *tert.*-butyl ether; c: FA17:0 = *n*-heptadecanoic acid, FA20:0 = n-dicosanoic acid; FA23:0 = *n*-tricosanoic acid, FA18:0 = *n*-octadecanoic acid, PDHA = propyl dehydroabietate.

In New Zealand, solvent extraction at low pH using either chloroform or DCM, was the established procedure prior to late 1988 (Wilkins and Panadam 1987; M^{c}Farlane and Clark 1988). After the investigations described in this thesis and studies carried out concurrently by Stuthridge (1990), a change to extraction under alkaline conditions was subsequently made to overcome a number of problems associated with the low pH approach.

Two methods were therefore used in this study: 1) solvent extraction at pH 2, in the initial phases of the project, and 2) extraction at pH 10–11, after mid-1988. The following sections describe these procedures, and summarise their performance characteristics.

3.4.2 Effluent extraction at pH 2

Extraction procedure

Samples were well mixed before transferring 450 mL to a continuous liquid-liquid extractor. Surrogate standard, *n*-heptadecanoic acid (FA17:0[1]) dissolved in acetone, was added and the sample mixed with a glass stirring rod. Acidification to pH 2 by dropwise addition of dilute HCl with stirring was then carried out. This resulted in precipitation of lignin, which subsequently formed a 0.5-1.0 cm layer at the interface between the aqueous phase and extraction solvent. Extraction with DCM at rapid reflux rate for 18–24 hours gave a pale yellow extract, to which *n*-octadecane (HC18) internal standard was added for calculating surrogate recovery.

[1] Fatty acid abbreviated nomenclature given as number of carbons:number of double bonds (e.g. FA18:1 is fatty acid with 18 carbons and 1 double bond).

The extracts were concentrated by rotary evaporation to a volume of about 2 mL then derivatised with ethereal diazomethane for at least 30 minutes (Schlenk and Gellerman 1960). Remaining diazomethane was removed by further rotary evaporation to a volume of less than 2 mL. The extracts were stored at 4 °C in screw-top vials until GC analysis. Quantitative analysis of EOs was carried out by capillary GC using flame ionisation detection (GC-FID) as described in section 3.8. Compound identifications were made by GC using mass selective detection (GC-MSD) as outlined in section 3.7.

Performance

The performance of this procedure was assessed in several extraction trials with effluents and soil column leachates. Major features were:

Standard recoveries: The FA17:0 surrogate was incompletely extracted, recoveries ranging from 23–53%. In contrast, *n*-alkane standards added before extraction, *n*-dodecane (HC12), *n*-hexadecane (HC16), and *n*-tetracosane (HC24), were well recovered (84–101%).

Compound recoveries: Sequential extractions of the same effluent sample showed that the RFAs were incompletely extracted after 22 hours. MTs, guaiacol, and the hydroxylated RA, 13β-hydroxyabietan-18-oic acid (Kinleithic acid; Wilkins *et al.* 1989), were isolated largely (>84%) in the first 22 hour extraction.

Repeatability: Replicate analyses (n = 5) of a No. 2 effluent sample gave cv's of ±23% (total MTs), ±12% (total FAs) and ±10% (total RAs). Surrogate recoveries and repeatabilities were (mean recovery ± cv): 53 ± 13% (FA17:0), 84 ± 12% (HC12), and 98 ± 14% (HC24).

Discussion

Four major problems were identified with this procedure: 1) poor recovery of most, but not all, acidic compounds; 2) relatively poor quantitative repeatability; 3) large differences in the recoveries of the major compound classes; and 4) compositional changes in the RA fraction upon extraction.

Recoveries of acids: The poor recovery of organic acids at pH 2 was consistent with the findings of Voss and Rapsomatiosis (1985), who reported 68% and 55% recoveries for RFAs respectively when whole-mill, biologically treated BKME was extracted at pH 2. The lignin which flocculated during the extraction of the Kinleith No. 2 effluent was almost certainly responsible for the low recoveries of the RAs and FAs. Evidence to support this hypothesis was provided by the following observations:

a) substantial quantities of RFAs were recovered from the solids precipitated during the effluent extractions, indicating that at least some of the compounds unrecovered during liquid-liquid extraction were associated with the flocculated lignin;

b) essentially quantitative recovery (94–102%) of FA17:0 standard was obtained when a medium density fibreboard (MDF) effluent was extracted using the pH 2 procedure. The MDF

effluent contained high levels of RFAs but low colour, and no appreciable solids precipitation occurred on acidification or extraction; and

c) recovery of FA17:0 surrogate was low when the high molecular weight fraction (M_r >1000 amu) of an ultrafiltered Kinleith No. 2 effluent sample was extracted at pH 2. Complete FA17:0 recovery was achieved by pH 2 extraction of the M_r<1000 amu fraction. Smaller quantities of MT hydrocarbons and RFAs were recovered from the M_r<1000 amu ultrafiltrate than from an unfiltered sample. This indicated that some EOs were associated with high relative molecular mass material (M_r>1000 amu) and/or suspended solids (fibre), or were present in aggregates (micelles) of M_r>1000 amu. These results were consistent with the association of BKME extractives with high molecular weight lignin (Priha and Talka 1986) and fibre (Lindstrom *et al.* 1988), and the formation of micellar aggregates by low M_r species (Jokela and Salkinoja-Salonen 1992).

Binding between lignin and RFAs would be expected to be stronger at lower pHs, due to the greater hydrophobicity of acidic organic components when protonated. Physical enmeshment of extractives in the lignin floc/precipitate was also possibly occurring, limiting contact between extraction solvent and EOs. The low recoveries obtained from extraction of Kinleith No. 2 effluent reflected the very high concentrations of macromolecular material present in this effluent stream.

Quantitative variability: GC-sourced variability contributed much of the variation observed in extraction trials. In a later pH 2 extraction trial using automated GC analysis (rather than the manual injection system used in early work), improved repeatability was obtained, cv's for MT and RFAs of ±1.3–6% being measured in triplicate analyses.

An indication of the variability attributable to manual injection was provided by GC-FID analysis repeatabilities (cv's) of ±8% (total FAs), ±12% (total RAs), and ±13% (HC24 standard) measured from five replicate analyses of an effluent-contaminated sediment extract.

Differences in compound extractability: While low analyte recovery was undesirable, it would have been acceptable if the major compounds and the surrogate were equally affected. Extraction trials showed that this was not the case, and therefore the best method for using the data collected from pH 2 extractions for quantitative assessments needed to be determined (until a better analytical method was developed).

MTs, guaiacol, and Kinleithic acid recoveries were comparable with those of *n*-alkane standards (i.e. essentially completely recovered). Concentrations of these compounds were therefore calculated by reference to the HC18 standard, which was added to the extract immediately after the liquid-liquid extraction step.

The FA17:0 surrogate was chosen to mimic semi-volatile organic acids during extraction, workup, and GC analysis, as used elsewhere (USEPA 1982a; Holmbom 1980; McFarlane and Clark 1988; Voss and Rapsomatiosis 1985; Volkmann *et al.* 1993). It was generally extracted to

the same extent as the RFAs (with the exception of the hydroxylated resin acid, Kinleithic acid) and was therefore appropriate for quantifying most RFAs.

The hydroxylated resin acid Kinleithic acid was more readily extracted than other RAs, presumably as a result of weaker associations with lignin as a result of the hydroxyl group. Since it was largely extracted in the first pH 2 liquid-liquid extraction quantification from the HC18 internal standard was considered appropriate.

Resin acid speciation: The composition of the RA fraction recovered from the pH 2 extraction method, and from an extraction in which the pH was not adjusted before extraction (pH 11), were different. Extraction at pH 2 recovered little palustric and neoabietic acids, compounds which are major RA constituents of *P. radiata* (Lloyd 1978) and which were therefore expected in the effluent. After exhaustive extraction at pH 2, relatively larger amounts of isopimaric and dehydroabietic acids were recovered.

These results were consistent with isomerisation of levopimaric, palustric, and neoabietic acids, which has been found to occur under a variety of conditions including:

- kraft pulping and acidification of the tall oil soap, producing abietic acid as the major constituent of tall oil, with lesser quantities of palustric and neoabietic acids (Porter 1969);
- heating, which gives a similar product mixture (Takeda *et al.* 1968);
- extraction with DCM, which has been reported to promote the isomerisation of levopimaric, palustric and neoabietic acids under acidic extraction conditions (the reason for the use of diethyl ether by some workers, e.g. Holmbolm 1980);
- GC analysis, where high temperatures, in conjunction with acidic column sites, have been reported to convert levopimaric and palustric acids to abietic and dehydroabietic acids (Hudy 1959); and
- storage in hydrocarbon solvents, in which levopimaric and palustric acids produced dehydroabietic acid, even when held under N_2 at -10 °C (Nestler and Zinkel 1963; Chang *et al.* 1971).

Given the well documented sensitivity of some RAs to isomerisation, especially under acidic conditions, it was unlikely that pH 2 extraction would adequately recover the full suite of RAs originally present in the Kinleith No. 2 effluent.

Summary
The pH 2 extraction procedure was successful in recovering a range of organic species known to be major effluent constituents. However, the qualitative composition of the extracts indicated that RA isomerisation was occurring. In addition, recoveries of the major compound classes were different. To obtain useful semi-quantitative data, quantification from two standards was required; 1) FA17:0 for RFAs (other than hydroxylated species), and 2) HC18 for MTs, guaiacol, and hydroxylated RAs.

Substantial improvements in method performance were obtained when No. 2 effluent was extracted at ambient pH (pH 10–11). Extraction under alkaline conditions was an approach

consistent with that developed in Canada by Voss and Rapsomatiotis (1985), and that adopted by Forest Research Institute, Rotorua after studies carried out concurrently with the work described in this thesis (Stuthridge 1990). Automated purged-splitless GC injection significantly improved in quantitative precision.

3.4.3 Effluent extraction under alkaline conditions

Extraction procedure

450 mL effluent was, if necessary, adjusted to pH 10–11 with NaOH (2 mol L^{-1}) and liquid-liquid extracted with DCM for 18 hours. A mixed *n*-hexadecane:*n*-octadecane (HC16:HC18) standard (1:10 concentration ratio) was added to the extract, which was then concentrated by rotary evaporation (T<25 °C) to 4–5 mL. The extract was methylated with ethereal diazomethane, an additional 3 mL DCM added, and further rotary evaporated 4 mL to ensure complete removal of CH_2N_2. Extracts were stored in 5 mL screw top vials at 4 °C until GC analysis. The extracts produced by this procedure were very pale yellow (as compared with the highly coloured red/brown extracts produced by extraction at pH 2). Preliminary work (Chapter 4) showed the No. 2 effluent to be variable in its extractive content. The mixed standard at the 1:10 ratio was used to ensure a level of standard appropriate for quantitation was present in the sample.

Performance

Performance of this procedure (subsequently termed the "pH 11" procedure) was investigated in several trials, a summary of which follows:

Standard recoveries: Surrogate recoveries from eight replicate analyses were (mean ± cv): 91 ± 6% for FA17:0, and 66 ± 4% for HC9. HC16 recoveries were 100–102% in four extractions.

Compound recoveries: After 18 hours, >98% of the EOs recoverable by exhaustive extraction (48 hours) were isolated.

Repeatability: From eight replicate extractions of a Kinleith No. 2 effluent sample, using automated purged splitless injection in the GC-FID analysis of the extract, cv's of ±1.4–5.6% were measured (Table 3.2). These were comparable with repeatabilities reported by Voss and Rapsomatiosis (1985) and Stuthridge (1990) for analysis of high concentration effluents.

Table 3.2: Repeatability and standard recoveries for the pH 11 effluent extraction procedure

Compound	Units	Mean (n = 8)	cv (%)
Guaiacol	mg L^{-1}	12	2.5
Total monoterpenes	mg L^{-1}	39	1.5
Total fatty acids	mg L^{-1}	81	5.6
Total resin acids	mg L^{-1}	89	1.4
FA17:0 surrogate standard	% recovery	91	5.7
HC9 surrogate standard	% recovery	66	3.6

Discussion

Comparison with the pH 2 procedure: Greater quantities of EOs were recovered at pH 11 than at pH 2. Quantifying RFAs from the FA17:0 internal standard, and MTs and guaiacol from the HC18 standard provided the best semi-quantitative data from the pH 2 method. EO concentrations estimated by this approach were, however, still only 71–77% of those obtained from the pH 11 method (Table 3.3). Concentrations of EOs obtained by the pH 2 method were therefore likely to underestimate the actual levels present.

Table 3.3: Recoveries of EOs by the pH 2 procedure, relative to those obtained from pH 11 extraction, using various quantitation procedures

Constituent	Relative Recovery (%) [a]	Quantitation calculated from:[b]		
		HC16 standard	FA17:0 standard	HC16 and FA17:0 standards
Total Monoterpenes	73	74	140	74
Guaiacol	103	105	198	105
Total Fatty Acids	40	41	77	77
Total Resin Acids	37	38	71	71
FA17:0 standard	52	–	–	–
HC18 standard	98	–	–	–

a: Recoveries of MTs, guaiacol, FA, and RAs obtained from the pH 2 procedure, expressed as a percentage of the concentrations obtained by pH 11 extraction. Standard recoveries are percentages of the amounts added; b: Recoveries from the pH 2 procedure (relative to the pH 11 procedure) using various quantitation procedures: HC16 standard – quantitation from a HC18 surrogate standard; FA17:0 standard – quantitation from FA17:0 surrogate standard; HC18 and FA17:0 – RFAs quantified from FA17:0, guaiacol and MTs from HC standard (as described in section 3.4.2)

Resin acid speciation: The pH sensitive RAs palustric and neoabietic acids were recovered as significant components in the pH 11 method. and therefore the qualitative data obtained from the alkaline extraction regime more accurately reflected the "real" extractive composition of the effluent. The absence of appreciable quantities of levopimaric acid in the extracts from either procedure was presumably due to the sensitivity of this compound to isomerisation.

Monoterpene recovery: The magnitude of the volatile MT hydrocarbon losses in the alkaline extraction procedure was assessed by comparison with a separating funnel extraction with pentane. This experiment indicated that about 64% recovery of the α-pinene (the most volatile MT) was achieved in the liquid-liquid extraction and workup, a result which was consistent with a mean HC9 standard recovery of 66% (bp α-pinene = 154°C, HC9 = 158°C). The recoveries of MT alcohols (principally α-terpineol) were better in the DCM liquid-liquid extraction, and since these compounds dominated the MT fraction of the effluent in the seepage pond system (Chapter 4), this method was judged to be more appropriate for the thesis studies.

Contribution of the GC analysis step to method variability: Variability for the GC analysis step were (cv's, n = 8) ±0.2–2.2%.

Comparison with similar methods: A variation of the alkaline extraction procedure, which used a 4 hour extraction of a 125 mL sample at pH 9, was developed concurrently at Forest Research Institute, Rotorua, New Zealand (Stuthridge 1990). This method was compared with the 450 mL pH 11 procedure using high and low concentration effluent samples. Agreement between the methods was good for the high concentration sample (RFA results differed by <5%), but less so for the low level sample (24% higher RA result, and 100% higher FA result from the 450 mL pH 11 method).

Using the 125 mL pH 9 method, Stuthridge (1990) reported spike recoveries of 86–95% for isopimaric and dehydroabietic acids, but only 33% and 55% for neoabietic acid at low and high concentrations respectively. This confirmed that the latter compound was unstable, even under alkaline extraction conditions. FAs were well recovered (85–100%). RFA recoveries increased with increasing pH in these trials, the highest results being obtained at pH 11, which was the maximum pH tested.

Another well documented study of RFA extraction (Voss and Rapsomatiosis 1985), found that recoveries dropped at pH >10, especially for resin acids. The reason for the difference in the effect of pH on recovery observed in this and the New Zealand studies was unclear, but may have been due to the differences in extraction solvent (methyl *tert.*-butyl ether rather than DCM), or effluent composition (more dilute whole-mill effluent compared with Kinleith's segregated No. 2 effluent, which contained high concentrations of high relative molecular mass material).

Summary

Extraction at pH 11 solved most of the major problems associated with the pH 2 procedure. Greater quantities of RFAs were recovered, and near quantitative recoveries of the FA17:0 RFA surrogate standard were obtained. The qualitative composition of the RA fraction isolated by the pH 11 method more closely resembled that expected from a *P. radiata*–sourced effluent. The composition of the pH 11 extracts and the results of spiking trials using pH 9 extraction (Stuthridge 1990) showed that isomerisation and/or degradation of some RA species (particularly levopimaric and neoabietic acids) during alkaline extraction with DCM was still occurring. Repeatability was improved and was comparable with documented precision estimates (Stuthridge 1990; Voss and Rapsomatiosis 1985). About 35% of the most volatile extractable compounds, largely the MT hydrocarbons, were lost in the extraction and workup, limiting the reliability of quantitative data for these compounds.

3.5 Extractable Organics in Ground Waters

Ground water samples were extracted by the same procedures as the effluents, except that larger volumes (1 or 2 L depending on the expected concentration range), and lower surrogate concentrations, typically 5–100 $\mu g\ L^{-1}$, were used. Before GC analysis, extract volumes were reduced to 0.25–1 mL in a stream of N_2. Both pH 2 and pH 11 procedures were used during the project.

As found for effluents, low and variable FA17:0 surrogate recoveries were obtained when effluent-contaminated ground waters were extracted at pH 2. Median FA17:0 recoveries for eight ground waters from beneath the seepage basins was 44% (range 24–78%, at 58 μg L^{-1}). Recoveries of 85–101% were obtained when these samples were extracted at pH 11.

An effluent dilution experiment was carried out to confirm that major effluent constituents could be adequately recovered from ground waters at concentrations found in effluent-affected wells. J basin effluent (location shown in Figure 4.4) was characterised by 4 replicate analyses. A composite ground water sample made up from from uncontaminated wells near Kinleith was prepared and 1.2 L aliquots spiked with 5 mL of the J Pond effluent. Six 1.2 L samples of spiked ground water were extracted by the pH 11 procedure. The concentrations obtained from analysis of the diluted samples were compared with the expected concentrations (J Pond concentrations divided by 240 dilution factor).

The pH 2 and pH 11 extraction procedures were also compared, and the repeatability of the sampling, transportation and analysis procedure was assessed, by replicate analysis of two effluent-affected ground waters.

Recoveries and extraction repeatability

Mean recoveries of MTs at a total concentration 45 μg L^{-1}, and RAs plus diterpene hydrocarbons (DTs) totalling 150 μg L^{-1}, were 102% and 89% respectively of the expected concentrations (diluted J Pond). RA and DT recovery was significantly lower than 100% (t-test, p = 0.025, n = 4). Analysis repeatabilities (cv's) were ±11% for MTs and ±9% for RAs and DTs. Figure 3.1 summarises the trial results.

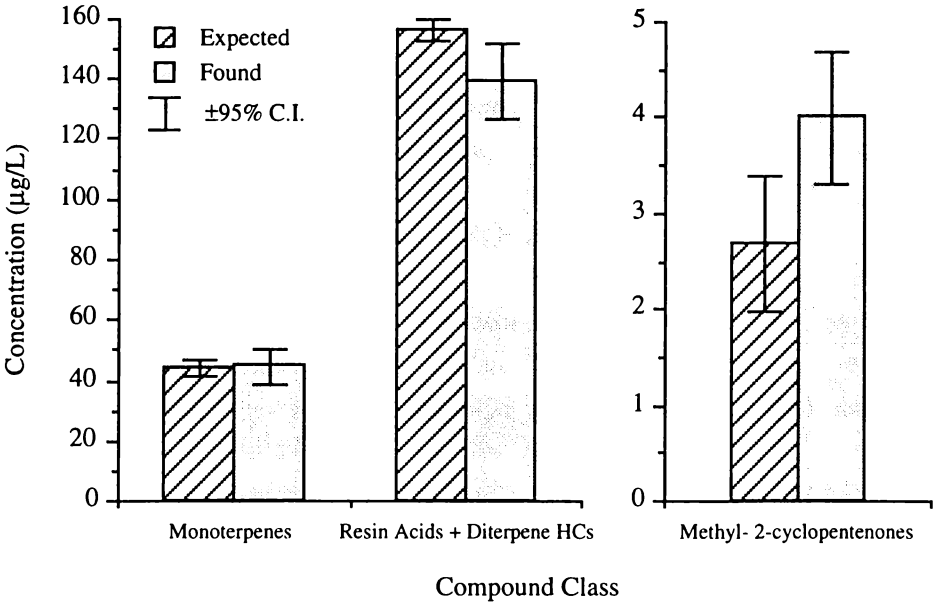


Figure 3.1: Comparison of expected and found concentrations in the ground water spiking trial. Concentrations are means ± 95% confidence intervals.

Repeatability of the sampling, transport, and analysis protocol

Analysis of ground water samples taken sequentially from two effluent-affected wells gave an indication of the repeatability of the entire analysis protocol used for the analysis of the "off-site" ground waters described in Chapter 6. Results are summarised in Table 3.4 (graphically depicted in Chapter 6, Figure 6.7).

Table 3.4: Repeatability of the ground water sampling, transport and analysis protocol

			Bore 74/1		Bore 83	
Constituent	Units	n	mean	cv (± %)	mean	cv (± %)
Total FAs	$\mu g\ L^{-1}$	5	16	6.6	5	14
Total RAs+DTs	$\mu g\ L^{-1}$	5	56	5.4	12	8.4
sodium[a]	$mg\ L^{-1}$	6	260	2.8	78	1.6
colour[b]	CPU	6	410	8.2[d]	28	16
absorbance 270 nm[c]	cm^{-1}	6	1.64	7.2[d]	0.111	5.0

a, b, c: increases in sodium (7.5%), colour (26%) and absorbance 270 nm (20%) were observed during sampling of bore 74/1; d: indicative only due to the increasing trend.

Comparison of pH 2 and pH 11 extraction procedures

The lignin content of the ground waters, as indicated by the colour of the samples, appeared to influence the relative performance of these procedures. The pH 11 procedure recovered greater quantities of effluent-derived organics than the pH 2 method from ground water containing high colour levels. Amounts of RA and DTs recovered by pH 11 extraction from highly coloured ground water (bore 74/1, 410 CPU) were approximately double those obtained using pH 2 extraction. In contrast, no difference in the quantities of extractives recovered by the two methods was observed from ground waters with little colour (bore 83, 28 CPU). These results were consistent with interference by lignin as was proposed to account for the poor recoveries of RFAs in pH 2 extraction of No. 2 effluent.

The pH 2 procedure recovered nearly four times greater amounts of a group of late eluting, unidentified compounds (possibly resin acid derivatives) of molecular weight 348–402. Whether these compounds were formed in the extraction by acid-catalysed reaction, or were more readily extracted at pH 2 remained undetermined. The results highlighted the complexity of the extractive chemistry of effluent-affected ground waters.

The analysis trial results indicated that EOs could be determined in effluent contaminated ground waters with acceptable repeatability. As expected, variability was greater for the lower concentration bore water samples. The high variability observed for analysis of colour in bore 83 was consistent with that expected at concentrations approaching the analytical detection limit, which for colour was estimated to be 20 CPU (section 3.2.3). The data also showed that while EOs exhibited no obvious trend during sampling, increasing levels of colour, sodium, and absorbance (270 nm) were observed during sampling water from one well. The ground water constituents under investigation were therefore not behaving identically during sampling, and that each well could exhibit different sampling characteristics. Ground water sampling problems

of this kind have been encountered elsewhere (e.g. Rivett *et al.* 1990; Backhus *et. al.* 1993), and should be studied in more detail in future work at Kinleith.

Summary of ground water analysis trials

Consistent with the results from effluent extraction studies, effluent contaminated ground waters were best analysed by extraction under alkaline conditions. Using this procedure, adequately reliable quantitative data for the MTs, RFAs, and DTs present in seepage basin effluent were obtained at concentrations above about 1 $\mu g\ L^{-1}$ per component. Sampling procedures for off-site ground waters were a potentially major source of error for some constituents. Unlike sodium, colour, and absorbance, EOs appeared not to be affected.

3.6 Extractable Organics in Sediments and Aquifer Materials

3.6.1 Background

No standard procedure for extracting pulp and paper mill effluent constituents from sediments was available at the time of the thesis studies (Table 3.5). None of the reported procedures gave details of performance characteristics nor specified surrogate or internal standards.

Table 3.5: Some documented procedures for extraction of pulp and paper mill effluent constituents and diterpene hydrocarbons (resin acid metabolites) from sediments

Extraction Method	Sample Pretreatment	Extraction Solvent(s)	Reference
Soxhlet	none (wet)	acetone, then diethylether	Fox (1976)
Soxhlet	freeze dried	chloroform	Brownlee and Strachan (1977)
Soxhlet	none (wet)	acetone, then diethylether	Brownlee *et al.* (1977)
not stated	freeze dried	toluene-methanol (3:1)	Simoneit (1977)
not stated	none (wet)	isopropanol-heptane (4:1)	Simoneit (1977)
ultrasonic	none (wet)	chloroform-methanol (2:1)	Yamaoka (1979)
Soxhlet	air dried	dichloromethane	Wakeham *et al.* (1980)
Soxhlet	air dried	diethylether and methanol	Kinae *et al.* (1981)
shake flask	none (wet)	cyclohexane	Remberger *et al.* (1990)

Subsequent to this study, several more sophisticated methods have appeared in the literature. These include:

- freeze drying, hydrolysis (2 mol L^{-1} KOH in ethanol), then extraction with methyl *tert.*-butyl ether (Holmbolm 1991);
- Soxhlet extraction of air-dried samples with acetone-methanol (88:12) in the presence of HCl (Lee and Peart 1991);
- extraction by shaking with methyl *tert.*-butyl ether/DCM (1:1) at pH 5 (Morales *et al.* 1992a), and
- Soxhlet Dean-Stark extraction followed by solvent partitioning/fractionation for separate analysis of chlorophenols, RA, and DT (Tavendale *et. al.* 1995).

In the present study, two procedures were used for extraction of organic compounds from sediments and aquifer solids. The first, Soxhlet extraction, was used to evaluate the nature and concentrations of extractives in the sediments and aquifer materials beneath the seepage basins (Chapter 5). The second method was a composite alkaline hydrolysis and DCM liquid-liquid extraction procedure developed for recovering extractives from sediments in laboratory-scale soil columns (Chapter 7). The success of the pH 11 effluent extraction procedure for recovering effluent-derived compounds, and the need for a rapid and simple analytical procedure, provided the impetus for developing the latter method.

3.6.2 Analysis of seepage basin sediments

Extraction procedure

Sediment samples were dried at 40 °C overnight, before extracting subsamples with $CHCl_3$ in all-glass Soxhlet apparatus for 20 hours. HC18, applied to the sediment in the Soxhlet thimble, was used as a surrogate standard for RAs and DTs. Extracts were rotary evaporated to a volume of 1–2 mL, methylated with ethereal diazomethane, further evaporated to 1 mL, and transferred to screw-top vials for storage at 4 °C until GC analysis. Extracts were analysed by GC-FID using manual, split injection (section 3.8.1).

Before extraction, two sample preparation procedures were used:

1) sediments taken from the Extension Area seepage basins, which were used in the initial isolation and identification studies of the extractives, and for assessing a coarse concentration profile beneath one basin (section 5.4), were dried, obvious coarse materials (e.g. twigs) removed, then gently ground with a pestle and mortar to produce a visually uniform powder; and

2) core samples taken from beneath Pond E in the Access Road seepage area for detailed concentration profile evaluation (section 5.4.2) were sieved (250 μm) after air drying to remove larger particles (pumice, twigs, root fragments). Variability due to gross particle size heterogeneity was thereby reduced.

Performance assessment

Using sieved samples, replicate analysis (n = 5) of a seepage basin sediment containing high concentrations of EOs was carried out (Table 3.6).

Further extraction of once-extracted sample with a more polar solvent mix (chloroform/acetone 4:1 v/v) released an additional 5% RAs and DTs. This indicated that the single $CHCl_3$ Soxhlet extraction was recovering most of the freely available EOs. Rigorous alkaline hydrolysis extraction (reflux in dilute KOH in MeOH) released an additional 38% of RFA in a single sample trial. There was, therefore, a more tightly bound residual, comprised largely of RFAs, that the single solvent Soxhlet procedure did not recover. The EOs' data presented in Chapter 5 are therefore best described as "freely available" residues.

Table 3.6: Repeatability and surrogate standard recoveries for the analysis of EOs in seepage basin sediment using Soxhlet extraction

Constituent	units	mean n = 5	cv %
Total fatty acids	mg kg^{-1}	43	22
Total resin acids and diterpene hydrocarbons	mg kg^{-1}	2610	2.9
FA17:0 surrogate standard	% recovery	75	8.9
HC24 surrogate standard	% recovery	73	9.9

3.6.3 Extraction of aquifer solids

Extraction procedure

Aquifer solids taken during coring of shallow ground water monitoring wells were dried by grinding the wet samples with anhydrous Na_2SO_4 before Soxhlet extracting with DCM for 18-20 hours. FA17:0 was used as a surrogate, and HC18 added to the DCM extract as an internal standard for calculating surrogate recovery. Extracts were rotary evaporated to a volume of 1-2 mL, methylated with ethereal diazomethane, further evaporated to 1 mL, and transferred to screw-top vials for storage at 4 °C until GC analysis. Quantitative analysis of these extracts was performed by GC-FID using automated, purged-splitless injection (section 3.8.1).

The Na_2SO_4 drying method was used as an alternative to air drying to minimise potential losses of more volatile constituents and to reduce the potential for analyte binding that can occur as a result of air drying. The significance of RFA binding on sediment dehydration was uncertain. Some work suggested it may not be a significant issue, complete recoveries of most RAs being achieved by Soxhlet extraction of air-dried sediments (Lee and Peart 1991). However, limited trials carried out during development of a method for analysing soil-column sediments (section 3.6.4) suggested that for some samples, low recovery of RAs can result from sample drying. One more recently published method (Tavendale 1995) avoids sample pre-treatment by Soxhlet extracting wet sample with a Dean Stark apparatus to remove water during extraction. This represents an improvement over other methods in which sample matrix is altered prior to analysis.

Performance assessment

FA17:0 recoveries were 73±9% (mean ± cv) in 40 aquifer material analyses. Uncontaminated seepage area sediment spiked with eight compounds representing MTs, hydrocarbons, and RFAs at concentrations of 10 mg kg^{-1} dry weight per component was analysed by this method. Essentially quantitative recoveries (95–105%) were obtained for all compounds except the volatile species HC9 (46%) and α-pinene (63%). Extract workup (rotary evaporation and N_2 blow-down of the methylated extract) was responsible for 28% and 9% of the HC9 and α-pinene losses respectively.

Ten replicate Soxhlet extractions of effluent-contaminated soil-column experiment sediment (Chapter 7) gave repeatabilities (cv's) for FAs of ±16% (at 20 mg kg^{-1} total FAs), and for RAs ±3.8% (at 184 mg kg^{-1} total RAs).

3.6.4 Extraction of soil column sediments

An extraction method that would quantitatively recover MTs and RFAs, principally RAs, from effluent-treated sediments was required for mass-balance estimation in soil-column experiments (Chapter 7). Using the experience gained from the seepage pond sediment studies, a hybrid extraction method best suited for this purpose was developed.

Extraction procedure

Residual liquid was removed from the wet sediment sample by low vacuum suction (water pump, 10 minutes) before transferring 6 g to a 250 mL Schott bottle. Water (80 mL), NaOH (4 mol L^{-1} dropwise to give a pH of 11), and 50 mL DCM were added. The mixture was stirred vigorously on a mechanical stirring bench for one hour then transferred into a round bottomed flask by filtering under gentle suction through a glass frit (#1 porosity) overlain by 5 cm glass wool bed. The Schott bottle was rinsed with water (2 x 30 mL), then DCM (2 x 30 mL), and these rinsings passed through the glass wool filter. The resulting turbid mixture was then transferred to a 125 mL continuous liquid-liquid extractor and extracted with DCM for 4 hours.

After extraction, HC18 standard was added to the DCM extract, which was then concentrated by rotary evaporation to a volume of about 3 mL and methylated with ethereal diazomethane. 30 minutes were allowed for methylation, after which further rotary evaporation to about 2 mL was carried out. Cleanup of the yellow extracts was achieved by passage through Pasteur pipette mini-columns containing 3 cm of 2% deactivated Florisil® topped with 1 cm anhydrous Na_2SO_4. Elution with an additional 2 mL DCM recovered all constituents found in the crude extracts and gave very pale yellow solutions. Extract volume was reduced to 2 mL with a gentle stream of dry N_2. Samples were stored in crimp top GC vials at 4 °C until analysis.

Performance

Recoveries from soil-column sediment spiked with eight compounds representing the major classes of extractives at 10 mg kg^{-1} per component were 87–100% for all compounds except HC9 and HC16, for which 30% and 66% recoveries respectively were measured. Unlike the sediments from the Kinleith seepage system, the soil-column sediments did not contain large amounts of DTs (as assessed by Soxhlet extraction trials), and therefore the procedure adequately recovered all compound classes of major interest.

Compared with Soxhlet extraction, the "alkaline aqueous-liquid-liquid extraction" method (AA-LL) recovered significantly greater amounts of MTs and FAs, and equal quantities of RAs, from effluent-contaminated soil-column sediments. Data from a comparative trial are summarised in Table 3.7 and Figure 3.2.

Table 3.7: Comparison of Soxhlet and AA-LL extraction procedures

Constituent	Soxhlet [a]		AA-LL no DCM [b]		AA-LL with DCM [c]	
	mean mg kg^{-1}	cv %	mean mg kg^{-1}	cv %	mean mg kg^{-1}	cv %
Total monoterpenes	9.0	36	11.5	8.9	33	18
Total fatty acids	19.7	16	43	18	36	14
Total resin acids	184	3.8	160	8.5	188	7.3

a: 10 replicates; b: 5 replicates, no DCM present in hydrolysis step; c: 5 replicates, DCM included in hydrolysis step

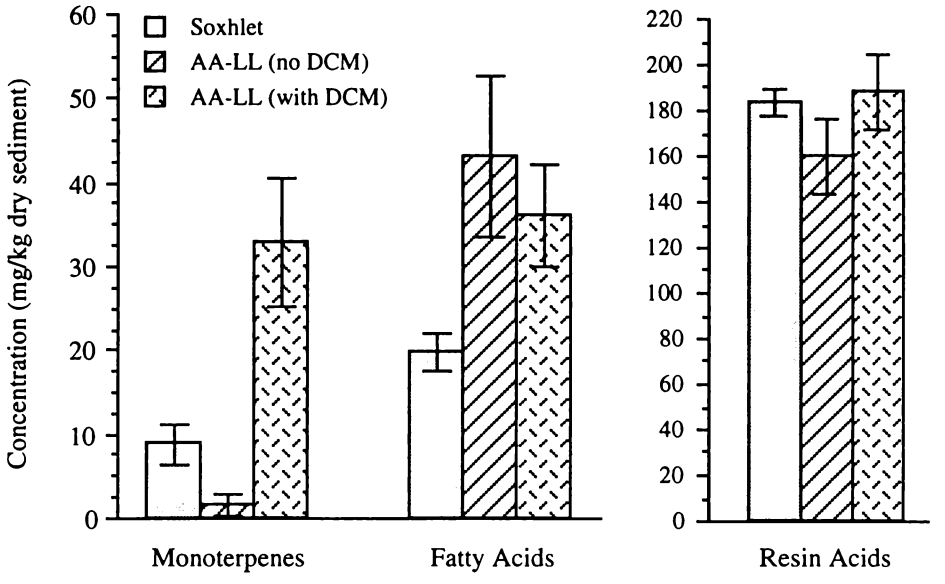


Figure 3.2: Comparison of EOs recovered from effluent-contaminated soil-column sediment by i) Soxhlet extraction, and ii) aqueous alkaline-liquid liquid extraction (AA-LL) with and without DCM in the hydrolysis step. Error bars are ±95% confidence intervals.

No single extraction procedure gave highest recoveries of all compound classes, best precision, and fastest sample analysis time. AA-LL (with DCM in the hydrolysis step) and Soxhlet extraction yielded the same concentrations of RAs, but AA-LL recovered significantly greater quantities of FAs and MTs. For this section of work, maximum recovery and rapid analysis were important. Although the amount of operator involvement was greater with the AA-LL method, it had about half the total analysis time of the Soxhlet method (for the 30–40 samples analysed, using the equipment available at the time).The AA-LL procedure, including DCM in the initial stirring phase, was therefore selected, even though it was less reproducible than Soxhlet extraction.

3.7 Identification of Extractable Organics

Capillary column gas chromatography using mass selective detection (GC-MSD), as described in Table 3.8, was used to identify the compounds found in the extracts generated by the procedures described in sections 3.4 to 3.6. The names, structures, and mass spectra of the compounds described in Chapters 4–7 are listed in Appendix 1. The compounds are referenced in the body of the thesis as an italicised number in square parentheses (e.g. dehydroabietic acid *[128]*, where *128* is the compound number used in Appendix 1).

Table 3.8: Instrument and operating conditions used for most GC-MSD analysis

Instrumental Component	Description
gas chromatograph	Hewlett Packard HP 5890A
column types and stationary phase	Hewlett Packard HP-1 fused silica capillary
column length, internal diameter, film thickness	12.5 m, 0.25 mm, 0.25 μm
typical oven program	50°C (3 min.), 4°C min^{-1} to 260°C (15 min.)
injection method, purge time, temperature	manual purged splitless, 30 s, 250°C
detector	HP 5970B mass selective detector (MSD)
mode, ionisation potential	electron impact, 70 eV
carrier gas, linear velocity	helium, 30 cm s^{-1}

Additional confirmations were made using longer columns (20 m DB-1, 0.18 mm i.d., 0.2 μm film; and 30 m DB-5ms, 0.25 mm i.d., 0.25 μm film, J&W Scientific) under a variety of temperature programmes to optimise separation of peaks of interest. Examples of total ion chromatograms (TICs) of representative effluent, sediment, ground water, and soil-column leachate extracts have been included in the relevant chapters.

The identity of a peak eluting in a GC chromatogram can only be considered to be confirmed when either:

- its retention time is matched with that of an authentic reference compound on two or more columns of differing polarity; or
- the peak and the reference compound have matching retention times and mass spectra when analysed by GC-MS.

Confirmation of identity is therefore dependent on the availability of reference standards. Reference materials were available for only a selection of the compounds detected in the extracts, and therefore a number of tentative identifications were made, using the methods summarised in Table 3.9.

Table 3.9: Procedures used for identification of extractable organic compounds

Identification Method	Status
1. GC retention time and mass spectral match with authentic compounds	confirmed
2. GC retention times and mass spectra matching with reference mixtures of well documented composition (e.g. RFAs in BKME extracts)	confirmed
3. Comparison with published mass spectra and GC elution orders for compounds of the same origin	probable
4. Mass spectra matched NBS mass spectral library [a]	possible
5. interpretation of mass spectral features - molecular ion, fragmentation pattern, comparison with spectra of related compounds	possible

a: Using the National Bureau of Standards (NBS) mass spectral libraries supplied with the Hewlett Packard 5970 and 5972 GC-MSD systems

Compounds whose identity was confirmed

Major FAs (palmitic, stearic, oleic, linoleic) and RAs (dehydroabietic, abietic), were available as reference compounds. The identities of the remaining parent effluent RAs were confirmed by GC-FID and GC-MSD comparison of extracts from the present study with those characterised by other investigators of New Zealand BKMEs (Wilkins and Panadam 1987; Panadam-Twigley 1988; Stuthridge 1990). Identifications were consistent with the documented composition of *P. radiata*-sourced BKME (e.g. Holmbolm 1980; Voss and Rapsomatiosis 1985). Minor saturated FAs were present in a homologous series and were readily identified from their characteristic mass spectra (*m/z* 74 and 87 fragment ions).

Major MTs were available either as individual reference compounds, as mixtures of isomers (e.g. terpineol isomers), or as well characterised sulphate turpentine (Panadam-Twigley 1988). 13β-hydroxyabietan-18-oic acid (Kinleithic acid), a major resin acid metabolite found in the Kinleith No. 2 effluent treatment system, was identified by GC-MSD comparison with a structurally characterised sample isolated from J basin effluent (Wilkins *et al.* 1989).

Dehydroabietin, 1,2,3,4-tetrahydroretene, and abietan-18-oic acid (as the methyl ester) were isolated from seepage basin sediments by preparative thin-layer chromatography (PLC). Seepage pond sediment was Soxhlet extracted with $CHCl_3$ and the concentrated unmethylated extract was separated into "neutral" and "acid" fractions by partitioning between diethylether and dilute NaOH respectively. The acids were recovered from the alkaline aqueous phase by acidifying with HCl and extraction with ether. Derivatision with diazomethane gave the methylated acid fraction. PLC of the neutrals on silica gel with petroleum spirit separated fichtelite (R_f=0.8), dehydroabietin (R_f=0.65), 1,2,3,4-tetrahydroretene (R_f=0.50), and retene (R_f=0.35). Methyl-abietan-18-oate was recovered by PLC of the methylated acid fraction (silica, 20% diethylether in petroleum spirits; R_f = 0.7).

Dehydroabietin and methyl abietan-18-oate were isolated in sufficient quantities and with adequate purity for analysis by nuclear magnetic resonance spectroscopy (NMR). ^{13}C chemical shifts for dehydroabietin were consistent with those reported by Hynning *et al.* (1993) for 18-

norabieta-8,11,13-triene. ^{13}C chemical shift data are listed below. The quantity of 1,2,3,4-tetrahydroretene was insufficient for complete structural assignment, aromatic singlet signals being undetectable. Retene was identified by GC-MSD comparison with a sample provided by Forest Research Institute, Rotorua.

^{13}C NMR (Jeol FX-90Q spectrometer at 22.5 MHz (^{13}C) in $CDCl_3$): chemical shifts, δ in ppm relative to TMS, (carbon number):

dehydroabietin: 15.2 (C-18); 18.1 (C-6); 24.0 (C-16, 17); 24.6 (C-2); 25.6 (C-19); 30.4 (C-7); 33.2 (C-1); 33.5 (C-15); 34.0 (C-4); 37.3 (C-10); 38.7 (C-3); 44.9 (C-5); 123.8 (C-12); 124.3 (C-11); 127.0 (C-14); 135.1 (C-8); 145.4 (C-9); 147.2 (C-13).
methyl abietan-18-oate: 14.5 (C-19); 16.8 (C-20); 18.1 (C-2); 19.85 (C-16, C-17); 24.5 (C-6); 24.9 (C-11); 29.9 (C-12); 32.8 (C-15); 35.3 (C-7); 36.3 (C-10); 36.6 (C-8); 37.1 (C-3); 38.2 (C-1); 38.5 (C14); 43.7 (C-13); 47.7 (C-4); 50.0 (C-5); 51.8 ($COO\underline{C}H_3$, C-21); 56.2 (C-9); 179.1 (C-18).

Tentatively identified compounds
Principal classes of tentatively identified compounds were:

Methyl substituted 2-cyclopentenones: Identification of these compounds was based on comparison with documented mass spectra and GC retention orders (Voss 1984), and matches with NBS library spectra.

Minor and transformed resin acids: Identifications of monoenic and saturated RAs were based on mass spectral characteristics (Chang *et al.* 1971; Zinkel *et al.* 1971), GC elution order (Foster and Zinkel 1982), and comparison with previously characterised extracts from the other New Zealand kraft mill effluent treatment system (Wilkins and Panadam 1987). Identification of 7-oxodehydroabietic acid (Brownlee and Strachan 1977), 12-chloro- and 14-chlorodehydroabietic acids, and 12,14-dichlorodehydroabietic acid was based on mass spectral comparison with published data (Remberger *et al.* 1990).

Diterpene hydrocarbons: DTs other than retene, tetrahydroretene, and dehydroabietin (which were identified as described previously) were identified by comparison with published mass spectra and consideration of plausible chemical relationships with related compounds. The principal compound in this class was fichtelite, a well documented anaerobic degradation product of coniferous resin (e.g. Simoneit 1986), and BKME treatment system sediments (Wilkins and Panadam 1987; Tavendale 1994). A series of structurally related compounds were tentatively assigned by comparison with literature mass spectra (e.g. Tan and Heit 1981; Barrick and Hedges 1981; Hynning *et. al* 1993; Singh-Thandi 1993).

Organosulphur compounds: Most compounds have been identified previously in BKMEs (Stuthridge 1987; Voss 1984; Panadam-Twigley 1988). Other minor organosulphur compounds were identified on the basis of NBS MS library match.

All other compounds, which were generally very minor components of the EO fraction, were identified by comparison with literature GC-MS data, by NBS MS library search, or by interpretation of mass spectra. Where literature data was the basis of identification, this is referenced in the text and in Appendix 1.

All extracts obtained in this project were methylated before GC analysis and therefore the RFAs were detected as their methyl esters. To check the possibility that RFA methyl esters were present in the original samples (Rogers *et al.* 1979), an unmethylated extract from a Kinleith seepage basin sediment was analysed by GC-MSD. The most highly modified array of reduced, oxidised, and decarboxylated RA transformation products were found in the sediment extracts, and it was therefore expected that if methylated RFAs were present in the LA system, they would have been present in the sediments. No RFA methyl esters were found. It was therefore a reasonable assumption that all RFAs were present as the parent acids in the effluents, sediments and ground waters.

Quantitative data have therefore been calculated for the parent acid species, while the relative molecular masses and mass spectra given in the thesis are those of the RFA methyl esters.

3.8 Quantitative Analysis of Extractable Organics

Extractable organics were quantified using capillary column gas chromatography with flame ionisation detection (GC-FID). Over the time in which the work was carried out, the GC procedures employed evolved considerably as improved technology became available. A change from manual, split-injection to an automated, purged-splitless system was made to improve quantitative precision, to more easily process larger batches of samples, and to provide greater sensitivity.

3.8.1 Instrumentation

The results of the initial investigations of the effluent characteristics and seepage pond sediments were obtained using the instrument and conditions described in Table 3.10.

Table 3.10: Instrumental configuration used for GC analysis during initial investigations

Instrumental Component	Description
gas chromatograph	Varian 3700
column, stationary phase, film thickness, i.d.	12.5 m, BP-1 (SGE), 0.25 μm, 0.2 mm
injection method, temperature	manual, split, split ratio ca. 1:50; 250°C
detector, temperature	FID, 250°C
carrier gas, linear velocity	hydrogen, 40 cm s^{-1}
makeup gas, flow rate	nitrogen, 30 mL min^{-1}

Two oven temperature programs were used with this system:

1) 40 °C (2 minute hold), then 6 °C min.$^{-1}$ to 240 °C (15 minute hold), for analysis of effluent and pond samples containing MTs and RFAs; and
2) 140 °C (2 minute hold), then 4 °C min.$^{-1}$ to 240 °C (15 minute hold), for analysis of RFAs and DTs in sediment extracts (in which lower boiling point components were not present in significant quantities).

The relatively poor precision obtained with this system (within-batch cv's of ±8–15%) limited the use of the manual split injection system to semi-quantitative assessments where large changes occurred (e.g. preliminary investigations of effluents, section 4.3, and those found in sediment profiles, section 5.4).

Quantitative results generated after the initial investigation phase, including investigations of seepage pond effluent (section 4.4), aquifer materials (section 5.5), ground waters (Chapter 6), and soil column leachates and sediments (Chapter 7), were generated using the instrumental configuration described in Table 3.11. The repeatability obtained with this system was substantially better (e.g. within-batch cv's for repeated effluent extract of ±0.2–2.2%).

Table 3.11: Instrumentation used for the majority of quantitative GC analyses

Instrumental Component	Description
gas chromatograph	Hewlett Packard HP 5890A
column type, stationary phase	fused silica capillary, DB-1 (J&W Scientific)
length, internal diameter, film thickness	10 m, 0.2 mm, 0.25 μm
injector, mode	HP 7673A, automated purged splitless
injector purge time, temperature	30 s, 250°C
oven temperature program	40°C (2 min.), 6°C min^{-1} to 240°C (15 min.)
detector, temperature	FID, 250°C
carrier gas, linear velocity	hydrogen, 40 cm s^{-1}
makeup gas, flow rate	nitrogen, 30 mL min^{-1}

3.8.2 Calibration

The linear range of GC-FID analysis was established from calibration curves for 8 compounds representing the compound classes quantified in the samples (HC9, α-pinene, fenchol, camphor, HC16, FA17:0, elaidic acid (FA18:1), and dehydroabietic acid). The linear range (R^2= 0.993–0.998) extended to at least 500 ng per component. Sample extracts were therefore diluted or concentrated as appropriate to ensure that the amounts of major components injected fell within the linear range.

Relative response factors (RRFs) for each compound class were established at the start of each batch of analyses by injecting a 100 ng μL^{-1} standard solution for the splitless system, or 1 μg μL^{-1} for split injection. 1 μL injections of standards and samples were made with both systems.

MTs and miscellaneous early eluting compounds (principally guaiacol, organosulphur species, and alkyl substituted cyclopentenones) were quantified from the RRF of camphor, saturated FAs from FA17:0, unsaturated FAs from elaidic acid, and RAs and DTs from dehydroabietic acid. The response factors were calculated relative to HC18.

Peak areas were determined with either a Shimadzu CR3-A integrator or Hewlett Packard Chemstation data system, and subsequent calculations were performed with Excel (Microsoft Corp.). Statistical analysis of quantitative data was performed using Excel, and the statistical analysis software DataDesk (Data Description Inc.) and Systat (SYSTAT Inc.).

3.9 Chlorinated Phenolics

The GC equipment and authentic reference compounds necessary for chlorophenolics analysis became available at a relatively late stage in the project, enabling some preliminary assessments of these compounds in drain and pond effluents and shalllow ground waters to be made.

3.9.1 Extraction of effluents

Extraction of effluents was carried out by *in-situ* acetylation and extraction into hexane (Stark *et al.* 1985). Heavy emulsions were formed on hexane extraction of effluent samples, and were not adequately broken with isopropanol. Filtering the extract through a Pasteur pipette mini-column packed with 2 cm anhydrous Na_2SO_4 was required to obtain a sample suitable for GC analysis. Apart from this step, the "Stark method" was used without modification for the analysis of drain and seepage basin effluent samples.

3.9.2 Extraction of ground waters

Analysis of ground waters using the Stark method was unsuccessful due to the low concentrations of the chlorophenolics present in these samples. Abrahamsson and Xie (1983) described a procedure based on the same *in-situ* acetylation and extraction chemistry, but which achieved higher sensitivity by extracting 100 mL samples with only 0.5 mL hexane. Emulsion formation caused difficulties in separating the small volumes of hexane used in this extraction procedure, particularly when the higher coloured ground waters were extracted. As an initial screening tool for assessing the approximate levels of chlorophenolics in the shallow ground waters beneath the seepage ponds, a scaled-up procedure using 500 mL sample and larger volumes of hexane extraction solvent was therefore employed for a limited selection of ground water samples.

Extraction procedure

To a 500 mL sample contained in a 1 L separating funnel, internal standard (2,3,6-trichlorophenol, 100 µL, 8.3 µg mL^{-1}) and K_2CO_3 (10 mL, 5.3 mol L^{-1}) were added before mixing for 1 minute. Acetic anhydride (5 mL) was then added, and the mixture shaken for 3 minutes with frequent venting. Hexane (10 mL) was then added and a further 3 minutes extraction performed. The mixture was allowed to stand for 10 minutes, allowing a heavily emulsified hexane layer to separate. This was partially broken by dropwise addition of isopropanol (1 mL), then the emulsion passed (under gentle suction) through a 5 cm bed of anhydrous Na_2SO_4 into a 100 mL round bottom flask. The extract was concentrated by rotary

evaporation to a volume of ca. 2 mL, and additional Na_2SO_4 added if necessary to complete drying. Approximately 1.5 mL of the extract was passed through a pasteur pipette packed with a 1 cm bed of Na_2SO_4 into a crimp-top GC vial where final volume reduction to 1 mL by N_2 blowdown was carried out.

3.9.3 Analysis of acetylated extracts

GC with electron capture detection (GC-ECD) was used for both identification and quantitation of chlorophenolics. Compounds were identified by comparing GC retention times with 11 authentic compounds supplied by Forest Research Institute, Rotorua (Table 3.11).

In addition to the reference compounds, four further species were identified in the extracts. 5,6-dichlorovanillin and 4,5,6-trichloroguaiacol were present as impurities in the 5-chlorovanillin sample, allowing confirmation of identity by GC-MSD. Isomer assignments for the trichloroguaiacol and dichlorovanillin were based on published GC retention data (Knuutinen and Korhonen 1983; Stark *et al.* 1985; Lee *et al.* 1989) and the documented composition of chlorophenolics in Kinleith No. 2 effluent (Stuthridge 1990). 6-chlorovanillin was a major species in the effluent (Stuthridge 1990) which was located in the GC-ECD chromatograms by comparison with the published GC retention data, and by GC-MS in selected ion monitoring (SIM) mode (*m/z* 186; $[M–CH_2CO]^{\bullet+}$, and *m/z* 228; $M^{\bullet+}$).

The 5-chlorovanillin sample also contained a third compound with mass spectral characteristics consistent with the acetate derivative of a dichlorohydroxybenzaldehyde (*m/z* 232 $[M^{\bullet+}]$; *m/z* 189 $[M–CH_2CO]^{\bullet+}$). 4-hydroxybenzaldehyde has been found in kraft black liquor and in unbleached kraft pulp mill waste waters (Knuutinen *et al.* 1982), and 3,5-dichloro-4-hydroxybenzaldehyde has been reported in BKMEs, particularly in E stage effluent (Voss *et al.* 1980).

The mass spectrum of the compound found in the No. 2 effluent *[65]* compared well with that of 3,5-dichloro-4-hydroxybenzaldehyde acetate (Wallis *et. al.* 1993). It was therefore possible that the dichlorohydroxybenzaldehyde tentatively identified in the Kinleith No. 2 effluent, which was 80-90% E-stage effluent, was the 3,5-dichloro-4-hydroxy substituted species.

GC analysis

Extracts were analysed using the GC instrumental configuration and conditions listed in Table 3.12.

Table 3.12: Instrumental configuration used for analysis of chlorinated phenolics

Instrumental Component	Description
gas chromatograph	Hewlett Packard HP 5890A
column type and stationary phase	fused silica capillary, DB-1 (J&W Scientific)
column length, internal diameter, film thickness	20 m, 0.2 mm, 0.25 μm
oven program: temperature program 1	50°C (1 min.), 20°C min^{-1} to 110°C
then: temperature program 2	110°C, 2°C min^{-1} to 250°C
injector, mode	HP7673A, automated purged splitless
injector purge time, temperature	30 s, 250°C
detector, temperature	ECD, 275°C
carrier gas, linear velocity	hydrogen, 40 cm s^{-1}
makeup gas, flow rate	nitrogen, 30 mL min^{-1}

The GC temperature program used gave good separation of the major compounds. However, two pairs of compounds, 1) pentachlorophenol and 3,4,5-trichlorocatechol, and 2) 5-chlorovanillin and tetrachlorophenol, were not baseline resolved in chromatograms of the standard mixture. Pentachlorophenol was a very minor constituent in the samples analysed, while 5-chlorovanillin and 2,3,4,6-tetrachlorophenol coeluted with at least two other minor compounds in the effluent extract chromatograms (Figure 4.3 shows a typical effluent extract GC-ECD chromatogram). These compounds were therefore seldom quantifiable.

Repeatabilities of GC analysis of standard mixture and effluent extracts, and of the entire extraction and GC analysis procedure are listed in Table 3.13.

Calibration

Single point calibration, using 2,3,6-trichlorophenol as the surrogate standard, was used for quantitation, as described by Stark *et al.* (1985). RRFs for the three compounds for which no pure standards were available were assigned either arbitrarily (dichlorohydroxybenzaldehyde, RRF = 2.0) or from values determined at Forest Research Institute, Rotorua from authentic standards (6-chlorovanillin RRF=4.5; 5,6-dichlorovanillin RRF=4.0; J. Zender, *pers. comm.*). The quantitative data for these compounds should therefore be considered indicative. The major use of chlorophenolics' data was in investigating the degradability of effluent in a seepage pond (sections 4.4.5 and 4.4.9) where changes in relative concentrations, rather than absolute levels, were of primary interest. The quantitative limitations of the data were therefore of little practical importance and did not affect the conclusions of the study.

Table 3.13: Chlorophenolic compounds analysed and repeatability of analysis

	Standard solution GC repeatability		Effluent extract GC repeatability		Effluent Analysis Extraction and GC	
	mean concn	cv	mean concn	cv	mean concn	cv
Compound	$\mu g\ L^{-1}$	%, n = 11	$\mu g\ L^{-1}$	%, n = 11	$\mu g\ L^{-1}$	%, n = 5
2,4-dichlorophenol*	266	1.2	14	1.3	nq [d]	–
2,4,6-trichlorophenol*	40	0.3	32	1.2	42	3.2
2,3,6-trichlorophenol*[a]	33	–	33	–	33	–
dichlorohydroxybenzaldehyde	na [b]	–	na [b]	–	34	7.1
4,5-dichloroguaiacol*	536	2.5	78	9.1	180	14
5-chlorovanillin*	122	1.8	ur [c]	ur [c]	ur [c]	ur [c]
2,3,4,6-tetrachlorophenol*	44	2.2	ur [c]	ur [c]	ur [c]	ur [c]
6-chlorovanillin	na [b]	–	77	5.9	150	9.0
3,4,5-trichloroguaiacol	na [b]	–	340	12	210	18
4,5,6-trichloroguaiacol*	29	4.6	52	4.7	48	9.0
5,6-dichlorovanillin	na [b]	–	52	2.5	96	20
pentachlorophenol*	29	5.3	nq [d]	–	nq [d]	–
3,4,5-trichlorocatechol*	39	2.4	nq [d]	–	nq [d]	–
tetrachloroguaiacol*	28	5.8	120	7.7	63	12
tetrachlorocatechol*	40	2.7	38	4.9	18	28
Total chlorophenols	379	0.3	46	1.1	42	3.0
Total chloroguaiacols	593	2.7	590	9.7	501	14
Total chlorovanillins	122	1.8	129	4.4	246	9.0
Total chlorocatechols	79	2.5	38	4.9	18	28
Total chlorophenolics	1173	1.6	803	7.6	841	9.0

a: surrogate standard; b: na = not analysed; c: ur = unresolved peaks in these extracts; d: nq = not quantifiable due to coeluting interferences; * indicates compounds for which reference standards were used for identification and quantitation

Summary of chlorophenolics analysis

The method enabled the behaviour of major chlorophenolic compounds in the drains and ponds of the seepage system to be assessed (section 4.4). Ground water samples gave GC-ECD chromatograms which were very complex, and generally lacked the pattern of major analytes seen in effluent samples. The method was therefore less suitable for providing reliable quantitation for these complex, low level, samples. GC-MSD analysis in single ion monitoring (SIM) mode would be more appropriate for accurate quantitation and reliable identification in such samples. Subsequent to the thesis work, such methods have been reported (Lee *et al.* 1989; Morales *et al.* 1992b; Tavendale *et. al.* 1995). In addition, a wider range of chlorophenolic standard compounds, including major known chlorophenolic metabolites (e.g. chloroveratroles; Neilson *et al.* 1990), could be needed to more completely characterise the composition of ground waters.

3.10 Summary

Investigating the behaviour of effluent-sourced organic compounds in the LA system required robust analytical methods capable of detecting the widest possible range of parent species and transformation products. Non-specific extraction and analysis techniques were therefore used (GC-FID and full scan GC-MSD). These methods gave detailed qualitative information on the chemistry of the system, but, because of their broad scope, gave quantitative data which was likely to be less accurate than techniques which target selected compounds. The quantitative limitations did not, however, affect the major conclusions relating to the fate of the major organic compounds in the LA system.

The major factor limiting quantitative analysis and unequivocal qualitative characterisation of the organic chemistry of the system was a lack of authentic reference compounds. Future work will require a wider range of RFAs, DTs, methyl substituted 2-cyclopentenones, and chlorophenolic reference materials to better characterise effluent-contaminated ground waters and sediments. Compound-specific analytical procedures (e.g. GC-MSD in SIM mode) will be necessary to obtain more rigorous quantitative data, especially in complex, low level samples containing interfering background "unresolved complex mixtures" (UCMs), such as those found in some ground waters. Reference compounds are required for compound-specific analytical procedures, and therefore the acquisition, synthesis, or isolation of these compounds is important for future studies of the Kinleith LA system and associated ground waters.

Chapter Four

Effluent Behaviour in the No. 2 Drain and Seepage Ponds

4.1 Introduction

Review of the Kinleith LA system (Chapter 1) indicated that infiltration rates in the seepage ponds were generally low, of the order of 10-12 mm d^{-1}. Effluent storage times in the ponds of up to 100 days were therefore possible before complete seepage of a typical 1 m deep batch of effluent into the ground occurred. There was therefore potential for significant effluent treatment and/or modification in the ponds.

In addition, changes in effluent composition in the No. 2 drain system were also possible. The No. 2 drain system was long (approximately 6 km from the mill to the EA seepage ponds) and consequently it was possible that residence times were sufficient to allow some treatment to occur during transport from the mill to the ponds.

Literature review (Chapter 2) indicated that many BKME organics were degradable under aerobic conditions. However, the rates and chemistries of degradative processes in quiescent ponds were not well documented. Investigation of the chemical behaviour of effluent in the drain and seepage ponds of the Kinleith LA system was therefore carried out.

4.1.1 Objectives

The investigations described in this chapter aimed to evaluate effluent treatability in the drain and seepage ponds of the LA system by:

1) measuring the rates of disappearance of MTs, FAs, RAs, chlorophenolics (CPs), and colour in a seepage pond; and

2) assessing chemical transformations of the major EOs occurring in the drain–pond system.

4.1.2 Experimental Approach

The investigations were carried out in two parts: 1) a preliminary study, which was used to obtain semi-quantitative information on changes in effluent composition occurring in the system; and 2) a quantitative study which focused on monitoring changes in effluent chemistry in one seepage pond. The two studies are described separately in sections 4.3 and 4.4 respectively. Section 4.2 describes the extractable organic (EO) composition of the No. 2 effluent.

4.2 The Extractable Organic Composition of No. 2 Effluent

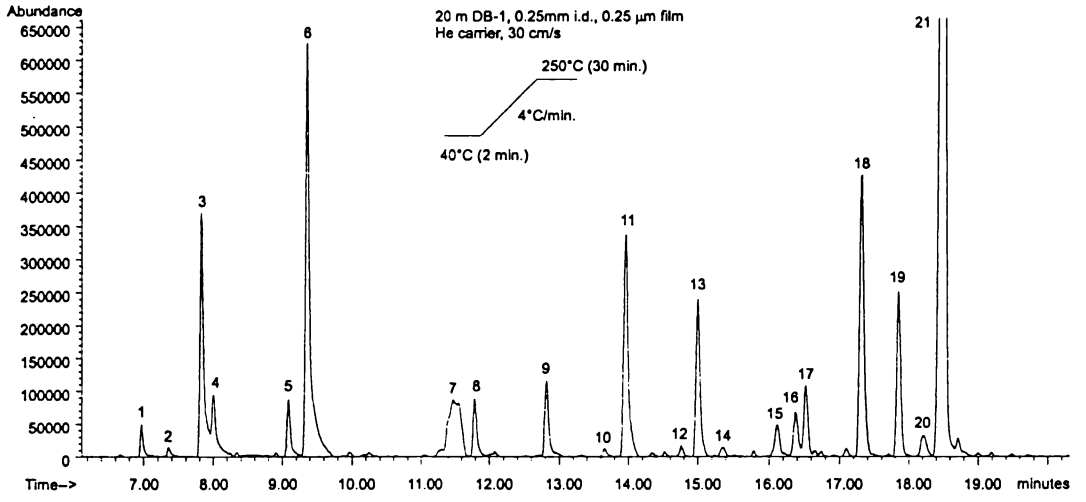
The EO composition of No. 2 effluent was first documented by Panadam *et al.* (1984) and Stuthridge (1984). The effluent was found to contain high concentrations of solvent-extractable organic material, dominated by MTs, FAs, and RAs. In addition, organosulphur compounds and monomeric phenolics were found at lower concentrations.

The composition found in the present study was consistent with that found in the these and later studies (e.g. Stuthridge 1990; Zender *et. al.* 1994), and is summarised in sections 4.2.1 to 4.2.5.

Representative GC traces of EOs (GC-MSD) and chlorophenolics (GC-ECD) are shown in Figures 4.1–4.3.

4.2.1 Monoterpenes

The MT fraction was dominated by α-pinene *[5]*, β-pinene *[9]*, and α-terpineol *[48]* (Figure 4.1). Compounds identifiable at lower concentrations were fenchol *[32]*, borneol *[44]*, 4-terpineol *[45]*, limonene *[17]*, *p*-cymene *[15]*, fenchone *[29]*, and camphor *[34]*. These compounds collectively made up ≥95% of the monoterpene fraction.



Peaks:

1. 2-methyl-2-cyclopentenone *[3]*; 2. dimethyldisulphide *[4]*; 3. α-pinene *[5]*; 4. 2,5-dimethyl-2-cyclopentenone *[6]*; 5. dimethyltrisulphide *[8]*; 6. β-pinene *[9]*; 7. limonene *[17]* + p-cymene *[15]* + unid. MT136; 8. 2,3-dimethyl-2-cyclopentenone *[18]*; 9. 2,3,5-trimethyl-2-cyclopentenone *[21]*; 10. 3-acetylthiophene *[23]*; 11. guaiacol *[24]*; 12. tetramethyl-2-cyclopentenone *[30]*; 13. fenchol *[32]*; 14. unidentified MT138; 15. unidentified MT *[33]*; 16. camphor *[34]*;17. veratrole *[38]*; 18. borneol *[44]*; 19. terpin-4-ol *[45]*; 20. propionylthiophene *[47]*; 21. α-terpineol *[48]*

Figure 4.1: GC-MSD total ion chromatogram of monoterpenes in No. 2 effluent

4.2.2 Fatty Acids

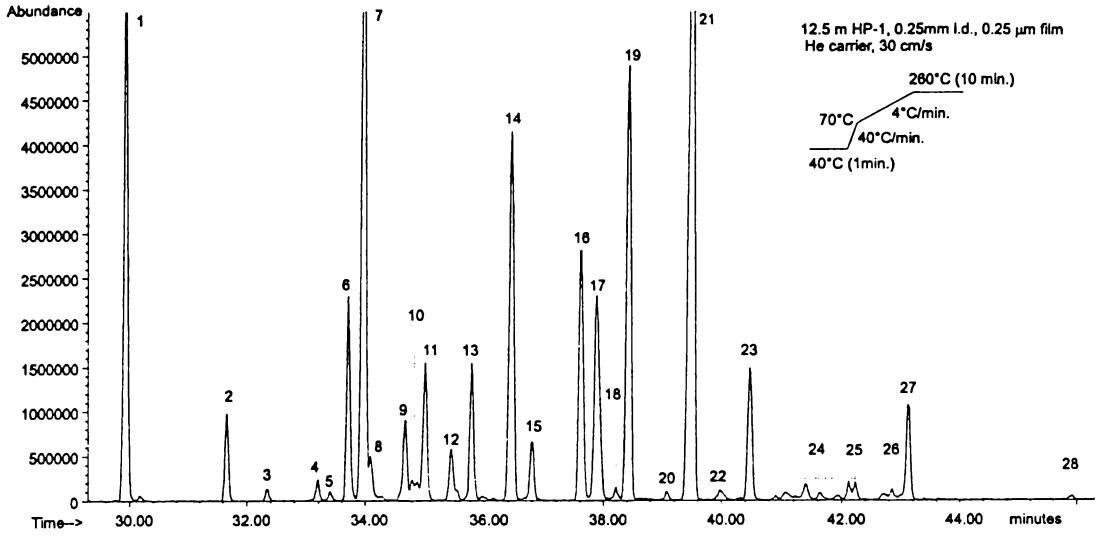
Oleic acid *[101]* and linoleic acid *[100]* were the major FAs present. In addition to these compounds, saturated compounds from FA14:0 to FA26:0, dominated by palmitic acid *[81]*, were present. Several unsaturated FAs, largely FA18:1, 18:2 and 18:3 compounds were also present at lower concentrations.

4.2.3 Resin Acids

Nine major compounds made up about 90% of the total RA fraction (Figure 4.2). These were abietic *[131]*, dehydroabietic *[128]*, pimaric *[110]*, isopimaric *[121]*, palustric *[123]*, neoabietic

[133], secodehydroabietic isomer 1 *[103]*, sandaracopimaric *[113]*, and secodehydroabietic isomer 2 *[104]* acids.

Also present at lower concentrations were 6,8,11,13-abietatetraenoic acid *[125]*, 7-oxodehydroabietic acid *[139]*, 12,14-dichlorodehydroabietic acid *[143]*, and two monochlorodehydroabietic acids (the 12- and 14-chloro isomers;e.g. *[140]*). A poorly resolved complex mixture of compounds having mass spectral features similar to RAs eluted after abietic acid, and remained unidentified. These collectively constituted up to approximately 10% of the GC-FID peak area of the RA fraction.



Peaks:

1. FA16:0 *[81]*; 2. *anteiso*-FA17:0 *[91]*; 3. FA17:0; 4. FA18:3; 5. FA18:2; 6. FA18:2 (linoleic acid) *[100]*; 7. FA18:1 (oleic acid) *[101]*; 8. FA18:1; 9. FA18:0 *[102]*; 10. FA18:2 (2 isomers); 11. seco-dehydroabietic acid #1 *[103]*; 12. seco-dehydroabietic acid #2 *[104]*; 13. FA18:2 *[108]*; 14. pimaric acid *[110]*; 15. sandaracopimaric acid *[113]*; 16. isopimaric acid *[121]*; 17. palustric acid *[123]*; 18. 6,8,11,13-abietatetraenoic acid *[125]*; 19. dehydroabietic acid *[128]*; 20. FA20:0 *[129]*; 21. abietic acid *[131]*; 22. unidentified resin acid *[132]*; 23. neoabietic acid *[133]*; 24. resin acid derivatives unidentified, unresolved; 25. FA22:0 + 12-chlorodehydroabietic acid; 26. 14-chlorodehydroabietic acid *[140]*; 27. unidentified, unresolved RA's *[141]*; 28. 12,14-dichlorodehydroabietic acid *[143]*; NB: all acids present as methyl esters

Figure 4.2: GC-MSD total ion chromatogram of fatty acids and resin acids in No. 2 effluent

4.2.4 Other non-chlorinated compounds

Non-chlorinated compounds other than MTs, RAs, and FAs were quantitatively relatively minor and included organosulphur compounds, methyl-substituted 2-cyclopentenones, phenolics, and sterols.

Dimethydisulphide *[4]* and dimethytrisulphide *[8]* were the major organosulphur compounds. Smaller amounts of 2-acetylthiophene *[25]*, 3-acetylthiophene *[23]*, and propionylthiphene *[47]*, were also present.

Methyl-substituted 2-cyclopentenones included mono-, di-, tri-, and tetra-methyl species. Tentative isomer assignments, in increasing retention time order (Voss 1984), were the 2-methyl- *[3]*, 2,5-dimethyl- *[6]*, 2,3-dimethyl- *[18]*, 2,3,5-trimethyl- *[21]*, and 2,3,4-trimethyl-

[26] compounds. At least two tetramethyl-substituted compounds (e.g. *[30]*) were also present but were poorly resolved from other compounds.

The major phenolic compound found was guaiacol *[24]*, but smaller amounts of veratrole (dimethoxybenzene) *[38]* and 3,4-dimethoxyacetophenone *[68]* were also present at lower concentrations. 3,4-dimethoxybenzaldehyde *[67]* and 3,4-dimethoxybenzoic acid *[69]* were also found in some samples. These aromatics were products of diazomethane methylation of 4-hydroxy-3-methoxy- substituted parent phenolic compounds.

Sterols were dominated by β-sitosterol *[152]* and a related compound, possibly the saturated analogue *[153]*.

4.2.5 Chlorophenolics

The chlorophenolic composition was consistent with that reported by Stuthridge (1991). Chloroguaiacols were the dominant class of chlorophenolics. 3,4,5-trichloroguaiacol and tetrachloroguaiacol were the major compounds, with lower levels of 4,5,6-trichloroguaiacol also present. Chlorovanillins were also major components, of which the 6-chloro- and 5,6-dichloro-compounds were the major species detected. 2,4,6-trichlorophenol was the major chlorophenol analysed, with 2,4-dichlorophenol present at lower concentrations. 2,3,4,6-tetrachlorophenol and pentachlorophenol were present, but at levels too low relative to other compounds to quantify. 3,4,5-trichlorocatechol and tetrachlorocatechol were relatively minor components. Dichlorohydroxybenzaldehyde, possibly the 3,5-dichloro-4-hydroxy- isomer *[65]*, the dominant chlorinated hydroxybenzaldehyde reported in E stage bleaching effluents (Voss *et al.* 1980), was also found. A typical GC-ECD chromatogram is shown in Figure 4.3.

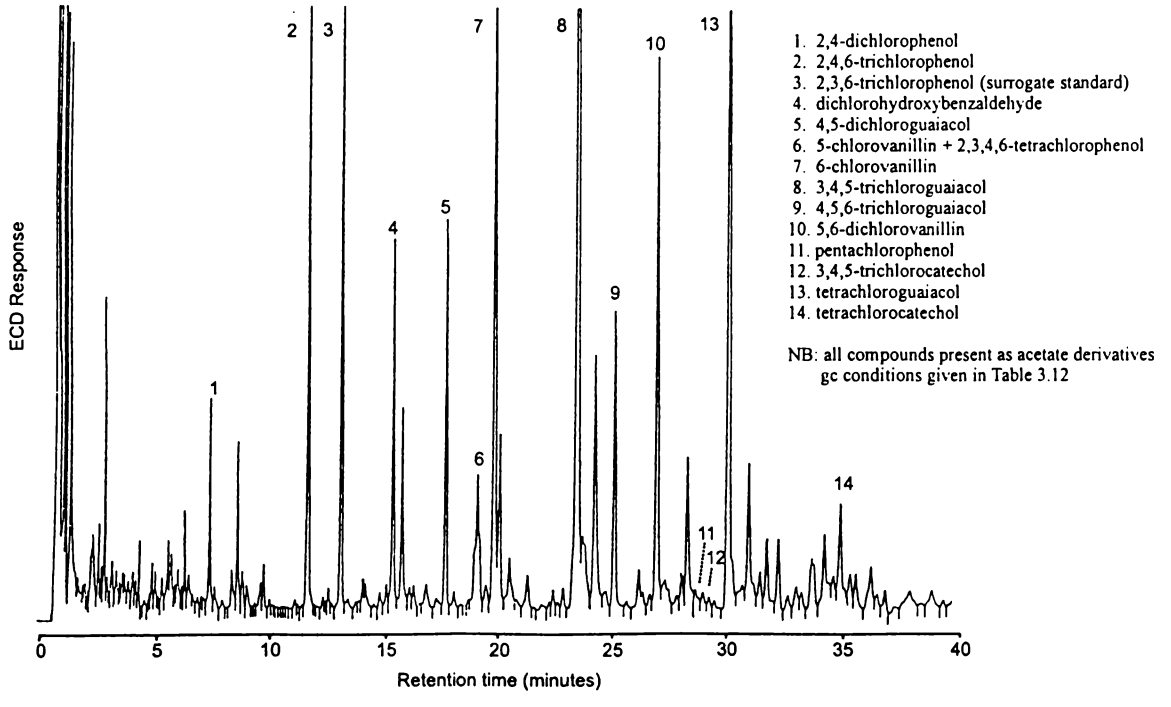


Figure 4.3: GC-ECD chromatogram of an acetylated No. 2 effluent extract

4.3 A Preliminary Study of Effluent Behaviour

4.3.1 Objective

The study set out to obtain information on effluent composition and changes occurring in the ponds and drains of the LA system by comparing effluent composition at three locations (Figure 4.4): 1) the drain near its source from the mill, 2) the exit from J pond, and 3) Q basin, in the EA. J pond samples were included because transformations of EOs in poorly aerated conditions were of interest. Q Basin was the largest seepage basin in the EA and always contained effluent during the LA investigations. It was considered that the composition of effluents from this seepage basin would best represent changes due to long-term transformation and degradation processes. Analytical data from the study are tabulated in Appendix 2, Tables A2.1, A2.2, and A2.3.

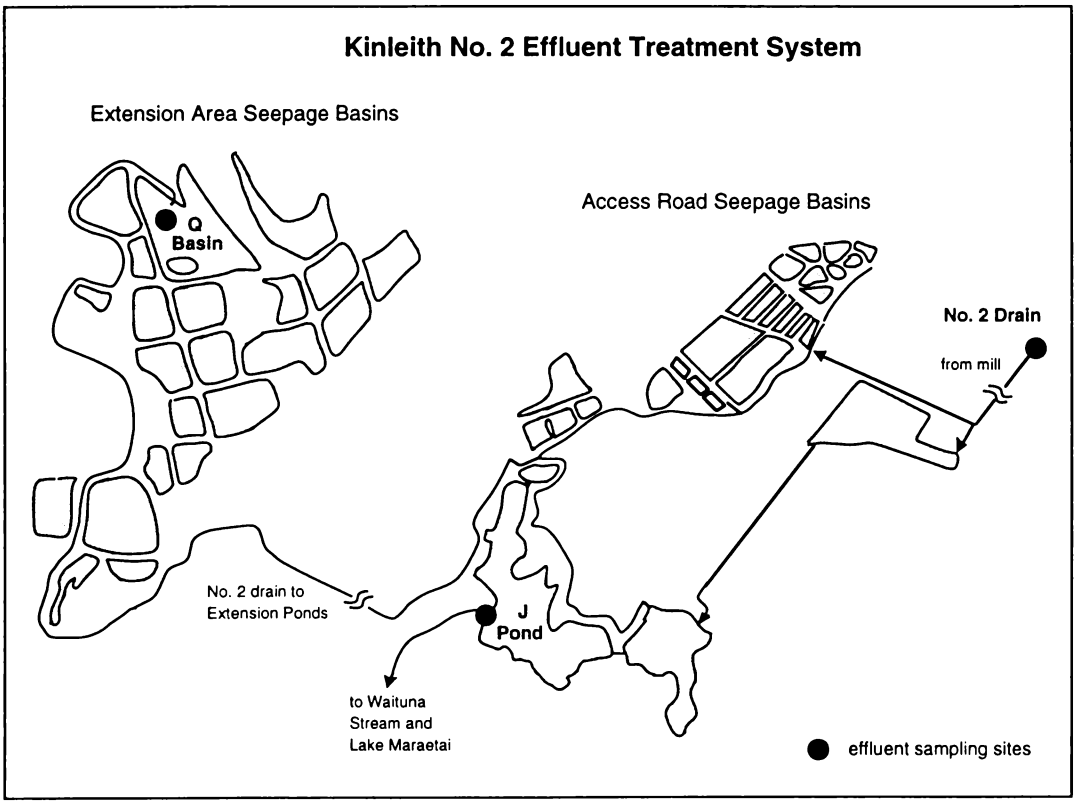


Figure 4.4: Sampling locations used in the preliminary study of effluent behaviour

4.3.2 Sampling and analysis

One litre grab samples were collected from each location at approximately weekly intervals and analysed for EOs, sodium, chloride, and colour by the procedures summarised in Table 4.1. In addition, pH, conductivity, dissolved oxygen, temperature, and effluent flow rates were measured by NZFP staff.

Table 4.1: Analytical procedures used in the preliminary study of effluent behaviour

Determinand	Analytical procedure	Section
extractable organics	pH 2 liquid-liquid extraction; GC-FID-MSD	3.4.2, 3.7, 3.8
sodium	AAS	3.2.1
chloride	ion selective electrode	3.2.2
colour	absorbance at 465 nm	3.2.3

4.3.3 Characteristics of No. 2 drain effluent

No. 2 drain effluent was warm, low in dissolved oxygen (DO), and had high conductivity and pH. Sodium and chloride concentrations were high, as was effluent colour. The physical and chemical characteristics of the drain effluent are summarised in Tables 4.2 and 4.3 respectively. The EO compounds making up the totals summarised in Table 4.3 are listed in Table 4.12 (appended to this chapter). On average, MTs made up 75% of the total concentration of EOs, 10% were RAs, 8% were miscellaneous compounds, and 7% were FAs.

Table 4.2: Physical characteristics of No. 2 drain effluent (data from NZFP files)

Characteristic	Units	Mean	Minimum	Maximum
Temperature	°C	30	21	37
pH	pH units	9.6	7.1	11.0
Dissolved oxygen	mg L^{-1}	0.6	0.4	1.1
Conductivity	mS m^{-1}	2710	1480	4970
Flow	m^3 d^{-1}	16000	9800	27900

Table 4.3: Chemical characteristics of No. 2 drain effluent

Constituent	Units	N	mean	s	median	minimum	maximum
Total monoterpenes	mg L^{-1}	19	63	67	42	5.9	300
Total fatty acids	mg L^{-1}	26	5.9	11	1.9	0.18	56
Total resin acids	mg L^{-1}	26	8.5	11	3.5	0.7	43
Total miscellaneous	mg L^{-1}	19	6.3	4.0	5.8	0.2	19
Sodium	mg L^{-1}	29	630	210	640	290	1100
Chloride	mg L^{-1}	29	490	150	490	170	800
Colour	CPU	29	2600	1020	2600	970	5100

4.3.4 Characteristics of J Pond effluent

Compared with the No. 2 drain effluent, samples from J pond had lower pH, DO, and temperature (Table 4.4). Chemical characteristics are summarised in Table 4.5, and EO compounds quantified are listed in Table 4.12.

Table 4.4: Physical characteristics of J Pond effluent (data from NZFP files)

Characteristic	Units	Mean	Minimum	Maximum
Temperature	°C	15	10	21
pH	pH units	7.6	7.4	8.0
Dissolved oxygen	mg L^{-1}	0.34	0.1	1.0
Conductivity	mS m^{-1}	2870	2500	3270
Flow	m^3 d^{-1}	13	10	15

Table 4.5: Chemical characteristics of J Pond effluent

Constituent	Units	N	mean	s	median	minimum	maximum
Total monoterpenes	mg L^{-1}	9	7.8	2.3	7.8	3.9	12
Total fatty acids	mg L^{-1}	14	0.20	0.19	0.14	<0.1	0.67
Total resin acids[a]	mg L^{-1}	14	23	11	20	10	51
Total miscellaneous	mg L^{-1}	9	0.86	0.51	0.77	0.24	1.9
Sodium	mg L^{-1}	17	720	71	750	600	830
Chloride	mg L^{-1}	17	610	90	630	440	740
Colour	CPU	17	3600	510	3500	2900	4400

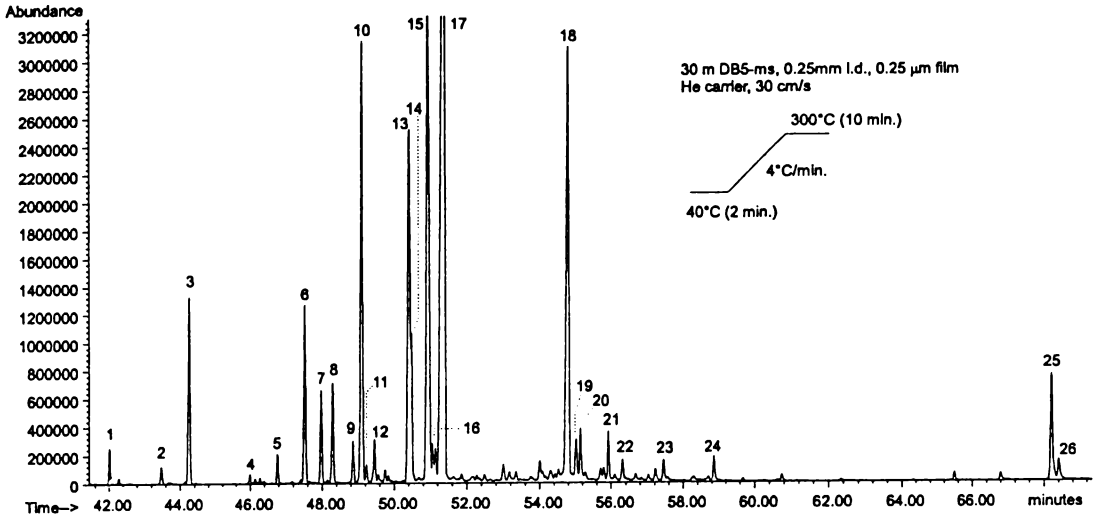
a: including diterpene hydrocarbon transformation products

The major class of EOs found in J Pond effluent were RAs, on average making up 73% of the total concentration of quantified compounds. Dehydroabietic acid *[128]* was the dominant compound, whereas abietic acid *[131]*, which was a major constituent of the drain effluent, was present in relatively minor amounts. Several RA transformation products were present including 13β-hydroxyabietanoic acid *[136]* (Kinleithic acid; Wilkins *et al.* 1989), abietanoic acid *[127]*, 8,15-pimaradienoic acid *[107]*, 8,15-isopimaradienoic acid *[109]*, and 13-abietenoic acid *[120]*. Small quantities of the diterpene hydrocarbons (DTs) dehydroabietin *[90]* and fichtelite *[87]* were also found. Figure 4.5, a partial GC-MSD TIC depicts the RAs and DT distribution in J Pond effluent.

Unsaturated FA18:1 and 18:2 species, which were the major FA species in the drain effluent, were present in very small amounts in J Pond. Relatively low concentrations of saturated compounds, mainly FA16:0, FA18:0, F22:0, and FA24:0 remained.

A group of poorly resolved compounds with mass spectral fragmentation similar to RAs eluted after dehydroabietic acid. Compounds with similar mass spectra have been reported in laboratory studies of the microbial degradation of dehydroabietic acid (Kutney *et al.* 1982) and

in BKME treatment systems (Panadam-Twigley 1988) and attributed to hydroxylated and oxidised (keto) resin acids.



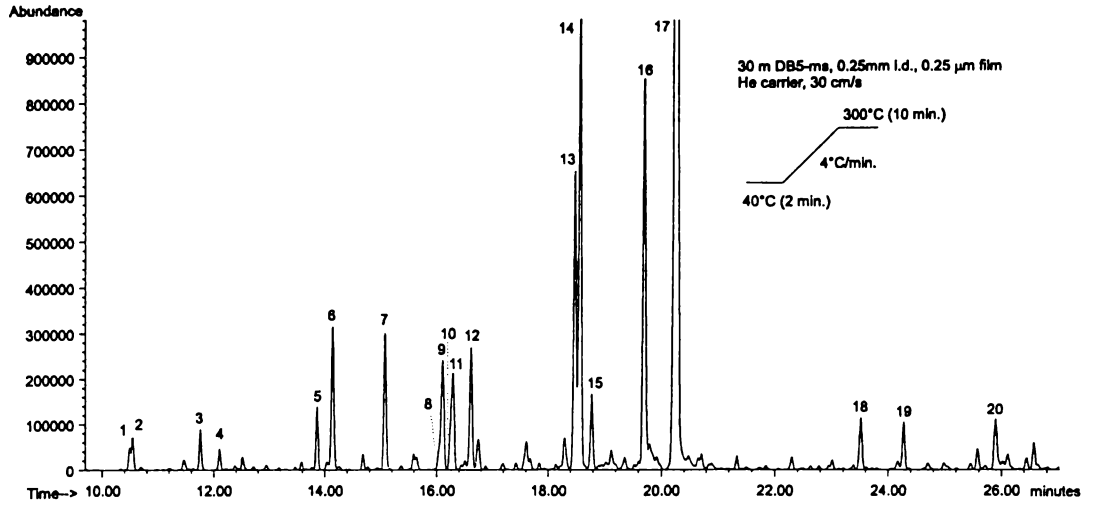
Peaks:

1. FA16:0 *[81]*
2. fichtelite *[87]*
3. dehydroabietin *[90]*
4. tetrahydroretene *[98]*
5. FA18:0 *[102]*
6. seco-dehydroabietic acid #1 *[103]*
7. seco-dehydroabietic acid #2*[104]*
8. 8,15-pimaradienoic acid *[107]*
9. 8,15-isopimaradienoic acid *[109]*
10. pimaric acid *[110]*
11. 8-pimarenoic acid *[111]*
12. sandaracopimaric acid *[113]*
13. 13-abietenoic acid *[120]*
14. isopimaric acid *[121]*
15. abietanoic acid *[127]*
16. FA20:0 + unidentified FA
17. dehydroabietic acid *[128]*
18. 13β-hydroxyabietanoic acid *[136]*
19. 14-chlorodehydroabietic acid *[140]* + unresolved RA
20. FA22:0 *[138]*
21. 7-oxodehydroabietic acid *[139]*
22. unidentified RA348 *[147]*
23. unidentified RA344 *[142]*
24. FA24:0 *[144]*
25. β-sitosterol *[152]*
26. sitosterol analogue? *[153]*

NB: all acids present as methyl esters

Figure 4.5: A GC-MSD TIC of RAs, FAs, and DTs in J Pond effluent

Compared with the drain effluent, MTs were relatively minor constituents, constituting on average only 24% of the total quantified EOs. The dominant compound was α-terpineol *[48]*. Camphor *[34]* and fenchone *[29]*, oxidation products of borneol *[44]* and fenchol *[32]* respectively, were significant components, as was "dihydro-α-terpineol" (DHT) *[35]*, a transformation product of α-terpineol reduction. The MT hydrocarbons α-pinene *[5]*, β-pinene *[9]* and limonene *[17]* were very minor components. The other feature of J pond effluent was a complex mixture of compounds eluting after α-terpineol. Some of these had mass spectra consistent with hydroxylated and alkyl-substituted monoterpenes, phenols, and thiophenes. Guaiacol *[24]*, the dominant monophenolic compound in the drain effluent, was not present in significant amounts in the J pond. Trimethyl-2-cyclopentenones remained as the most significant compounds in this class. Figure 4.6, a GC-MSD TIC of early eluting compounds, illustrates the distribution of these compounds.



Peaks:

1. α-pinene *[5]*
2. 2,5-dimethyl-2-cyclopentenone *[6]*
3. dimethyltrisulphide *[8]*
4. β-pinene *[9]*
5. *p*-cymene *[15]*
6. 2,3-dimethyl-2-cyclopentenone *[18]*
7. 2,3,5-trimethyl-2-cyclopentenone *[21]*
8. 3-acetylthiophene *[23]*
9. 2,3,4-trimethyl-2-cyclopentenone *[26]*
10. 2-acetylthiophene *[25]*
11. fenchone *[29]*
12. trithiolane *[31]*
13. camphor *[34]*
14. dihydro-α-terpineol *[35]*
15. unidentified MT154 *[42]*
16. terpin-4-ol *[45]*
17. α-terpineol *[48]*
18. unidentified MT *[52]*
19. unidentified MT *[54]*
20. tetrathiolane *[66]*

Figure 4.6: A GC-MSD TIC of monoterpenes in J Pond effluent

4.3.5 Characteristics of Q Basin effluent

The composition of Q Basin effluent changed markedly during the sampling period. This change was brought about by addition of fresh drain effluent to the seepage basin. The first seven samples taken contained much lower concentrations of EOs than either No. 2 Drain or J Pond effluents, while sodium, chloride, and colour levels were only slightly lower. The composition of the remaining 13 samples was very similar to J Pond effluents. As the composition of degraded effluent was of primary interest in this study, and because the composition of J Pond effluent has already been described, the characteristics of only the first seven Q Basin samples are discussed in the following section.

The chemical and physical characteristics of Q Basin effluent are summarised in Tables 4.6 and 4.7 respectively. EO compositional data are listed in Table 4.12.

Table 4.6: Chemical characteristics of Q Basin effluent

Constituent	Units	N	mean	s	median	minimum	maximum
Total monoterpenes	mg L^{-1}	7	<0.1	–	<0.1	<0.1	<0.1
Total fatty acids	mg L^{-1}	7	0.16	0.06	0.15	0.08	0.26
Total resin acids[a]	mg L^{-1}	7	0.53	0.33	0.39	0.15	1.0
Total miscellaneous	mg L^{-1}	7	<0.1	–	<0.1	<0.1	<0.1
Sodium	mg L^{-1}	5	480	31	480	440	520
Chloride	mg L^{-1}	5	410	28	420	370	450
Colour	CPU	5	2800	210	2800	2500	3100

a: including diterpene hydrocarbon transformation products

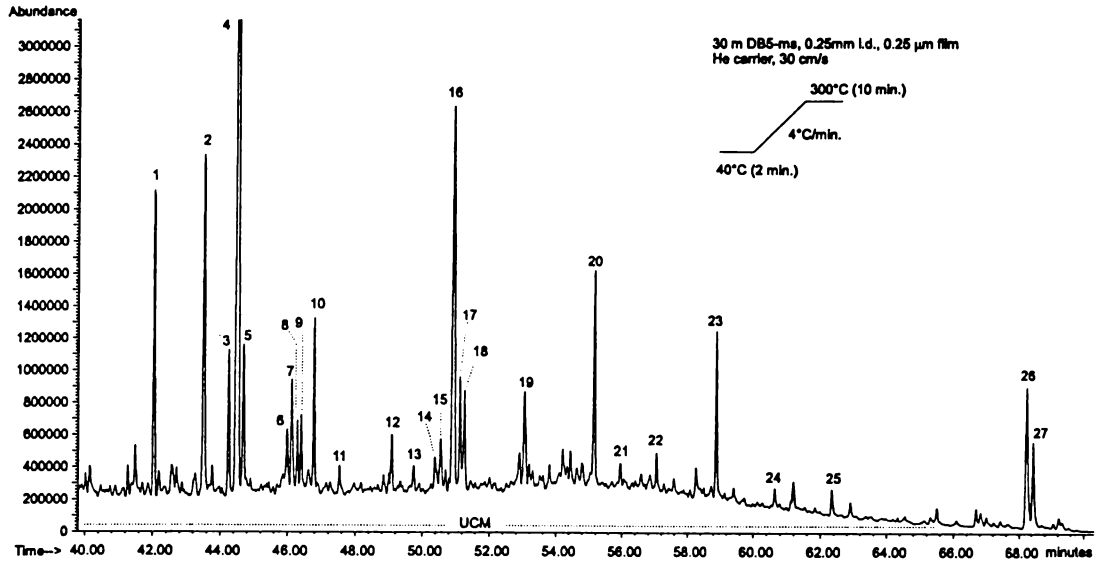
Table 4.7: Physical characteristics of Q Basin effluent (data from NZFP files) [a]

Characteristic	Units	Mean	Minimum	Maximum
Temperature	°C	14	8	23
pH	pH units	7.4	5.7	8.2
Dissolved oxygen	mg L^{-1}	0.7	0.1	3.2
Conductivity	mS m^{-1}	2310	1571	2760

a: data for all 20 Q Basin samples

EO chromatograms of Q Basin extracts lacked the clearly resolved compound signatures observed in the drain and J Pond samples. Instead, the GC-MSD and GC-FID traces were dominated by a complex, elevated baseline ("unresolved complex mixture", UCM), above which relatively few peaks were readily identifiable (Figure 4.7). Among these were several RAs and DTs, the major species being abietanoic acid *[127]*, dehydroabietin *[90]*, fichtelite *[87]*, and dehydroabietic acid *[128]*. Pimaric acid *[110]*, 13-abietenoic acid *[120]*, tetrahydroretene *[98]*, and the seco-dehydroabietic acids *[103* and *104]* were also present at lower levels. A compound of molecular weight 332 was found by GC-MSD, coeluting with abietanoic acid. Based on comparison with NBS library mass spectra, this compound was tentatively assigned as 7-oxokauran-18-oic acid *[126]*. As was found in J Pond effluent, a group of compounds which appeared to be related to the RA class were also present eluting after dehydroabietic acid.

Trimethyl-2-cyclopentenones were the major remaining miscellaneous compounds. In addition, sulphur compounds such as dimethyltrisulphide *[8]* and a compound tentatively identified from MS library search as methyl 5-methylthiophene-2-carboxylate *[50]*, were identifiable by GC-MSD. The FA fraction was composed of saturated species, largely FA16:0 to FA24:0.



Peaks:

1. FA16:0 *[81]*
2. fichtelite *[87]*
3. dehydroabietin *[90]*
4. FA17:0 surrogate standard
5. unidentified mw=290 *[94]*
6. FA18:2
7. FA18:3
8. FA18:1
9. FA18:1
10. FA18:0 *[102]*
11. seco-dehydroabietic acid #1 *[103]*
12. pimaric acid *[110]*
13. pimaranoic acid *[119]*
14. 13-abietenoic acid *[120]*
15. unidentified RA314? (weak ms)
16. abietanoic acid *[127]* + 7-oxokauranoic acid *[126]*
17. FA20:0 *[129]*
18. dehydroabietic acid *[128]*
19. unidentified RA348? *[132]*
20. FA22:0 *[138]*
21. 7-oxodehydroabietic acid *[139]*
22. FA23:0
23. FA24:0 *[144]*
24. FA25:0
25. FA26:0
26. β-sitosterol *[152]*
27. sitosterol analogue *[153]*

Figure 4.7: GC-MSD total ion chromatogram (RA, FA, DT region) of Q Basin effluent extract

4.3.6 Compositional changes occurring in the effluent system

The EO chemistry of J Pond and Q Basin effluents was markedly different from that of the parent drain effluent. MTs were essentially absent in Q Basin, indicating they were degradable in the seepage ponds. J pond effluent contained largely MT ketones (e.g. fenchone and camphor) and tertiary alcohols (e.g. DHT and α-terpineol). The increase in relative abundances of fenchone and camphor, and decreases in fenchol and borneol respectively (Figure 4.8) was evidence of oxidative degradation. This was consistent with the documented behaviour of MT secondary alcohols in aerobic lagoons (Wilson and Hrutfiord 1975). The appearance of DHT indicated that a reductive degradative pathway, as required to degrade tertiary alcohols (since oxidation to the corresponding ketones is not possible), was also operative in the pond. A comparison of the average composition of major components of the MT fractions of No. 2 drain and J Pond effluent is shown in Figure 4.8.

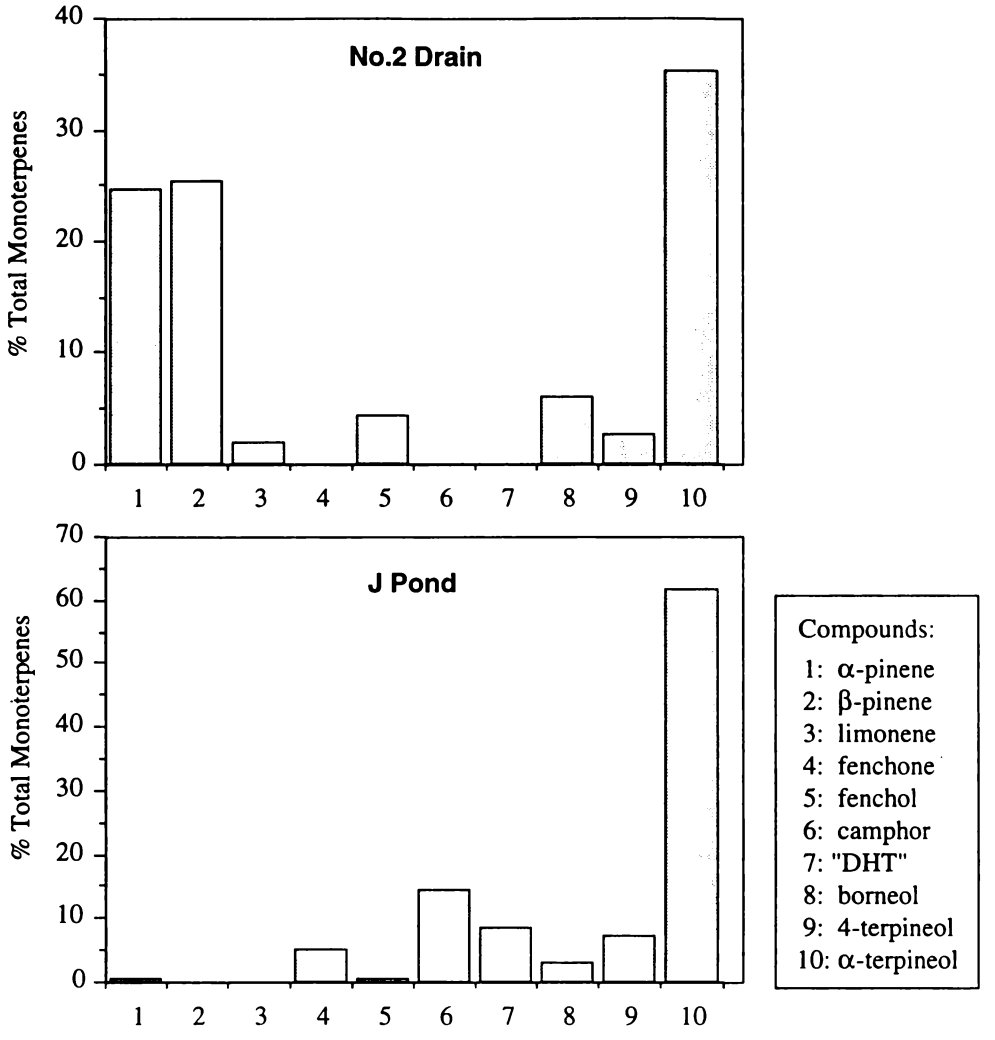


Figure 4.8: Comparison of average monoterpene composition in No. 2 drain and J pond effluents

Microbial metabolism of camphor proceeds via a sequence of hydroxylation, oxidation to a diketone, O-insertion, and ring cleavage (Trudgill 1984). It is possible that the complex mixture of compounds eluting after α-terpineol in GC traces reflected the presence of such oxidised and hydroxylated MT transformation intermediates in J Pond.

The degradation of α-pinene is complex, and has been found to proceed via limonene, producing a complex mixture of compounds. Hydroxylation of methyl substituents is followed by an oxidative sequence (via aldehydes and carboxylic acids) before ring cleavage and β-oxidation produces acetyl coenzyme A for the citric acid cycle (Trudgill 1984, 1990). Apart from limonene, which was also present in the drain effluent in larger relative amounts than in J Pond, no plausible pinene transformation products were observed in the effluent system. Volatilisation of MT hydrocarbons, which are significantly more volatile than the alcohols, was a probable contributing factor in the disappearance of the pinenes.

A possible degradative scheme for MTs, based on the compounds observed in the Kinleith effluent system, is shown in Figure 4.9.

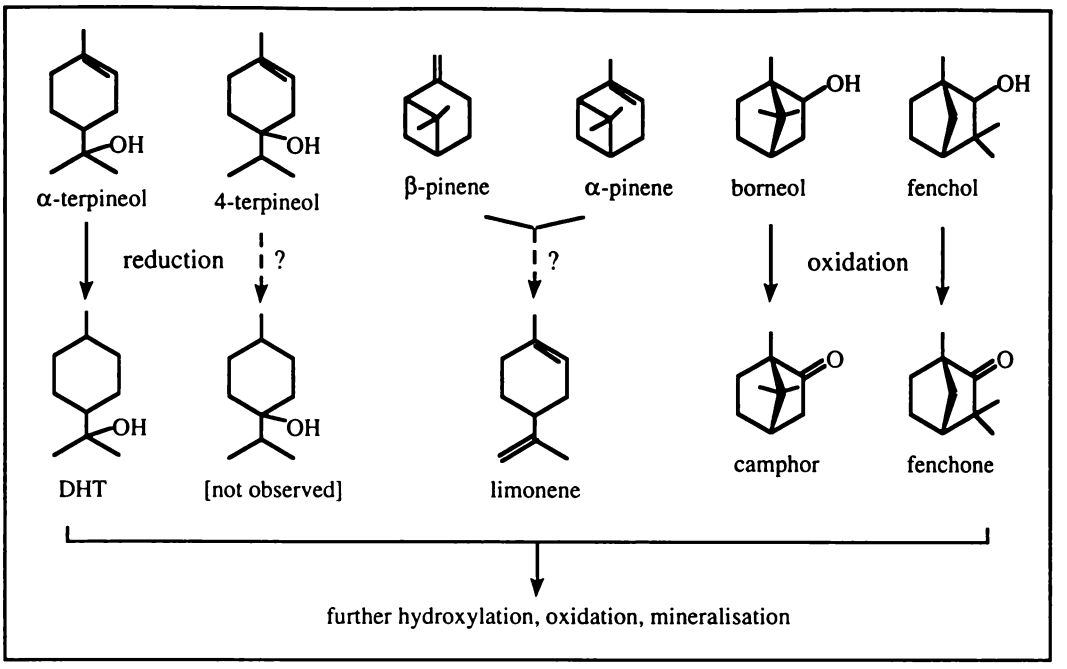


Figure 4.9: Possible degradation scheme for monoterpenes, based on compounds observed in J Pond

Similar processes were apparently transforming and degrading RAs. From the compounds found in the ponds, oxidative and reductive transformation pathways consistent with those documented for RAs in natural environments (e.g. Simoneit 1986) were being followed, as summarised in Figure 4.10. In addition, the presence of 13β-hydroxyabietanoic acid *[136]* was evidence for a further step in the degradation of abietane RAs. Hydroxylated RAs have been identified as intermediates in the aerobic degradation of RAs (e.g. Kutney *et al.* 1982). Hydroxylation increases the water solubility of hydrophobic organic compounds, thereby facilitating microbial assimilation. As such it represents an important step in organic compound mineralisation and biological detoxification.

The tentatively identified compound 7-oxokauranoic acid *[126]* was possibly an intermediate in the degradation of pimarane RAs, involving ring C rearrangement (Dev 1979):

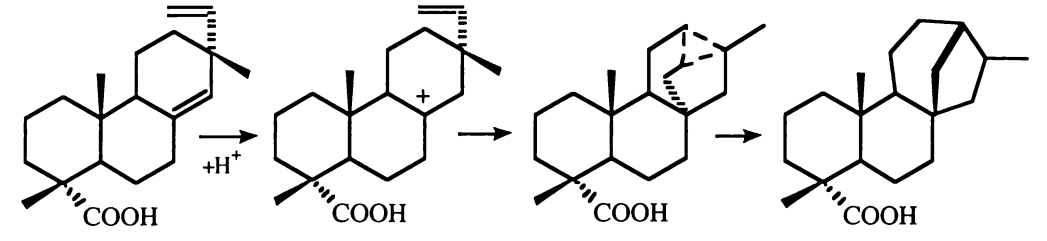


Figure 4.11 provides a graphical summary of the qualitative differences in effluent composition observed at each effluent sampling site. The major feature was the dominance of transformed RAs and DTs in the pond effluents.

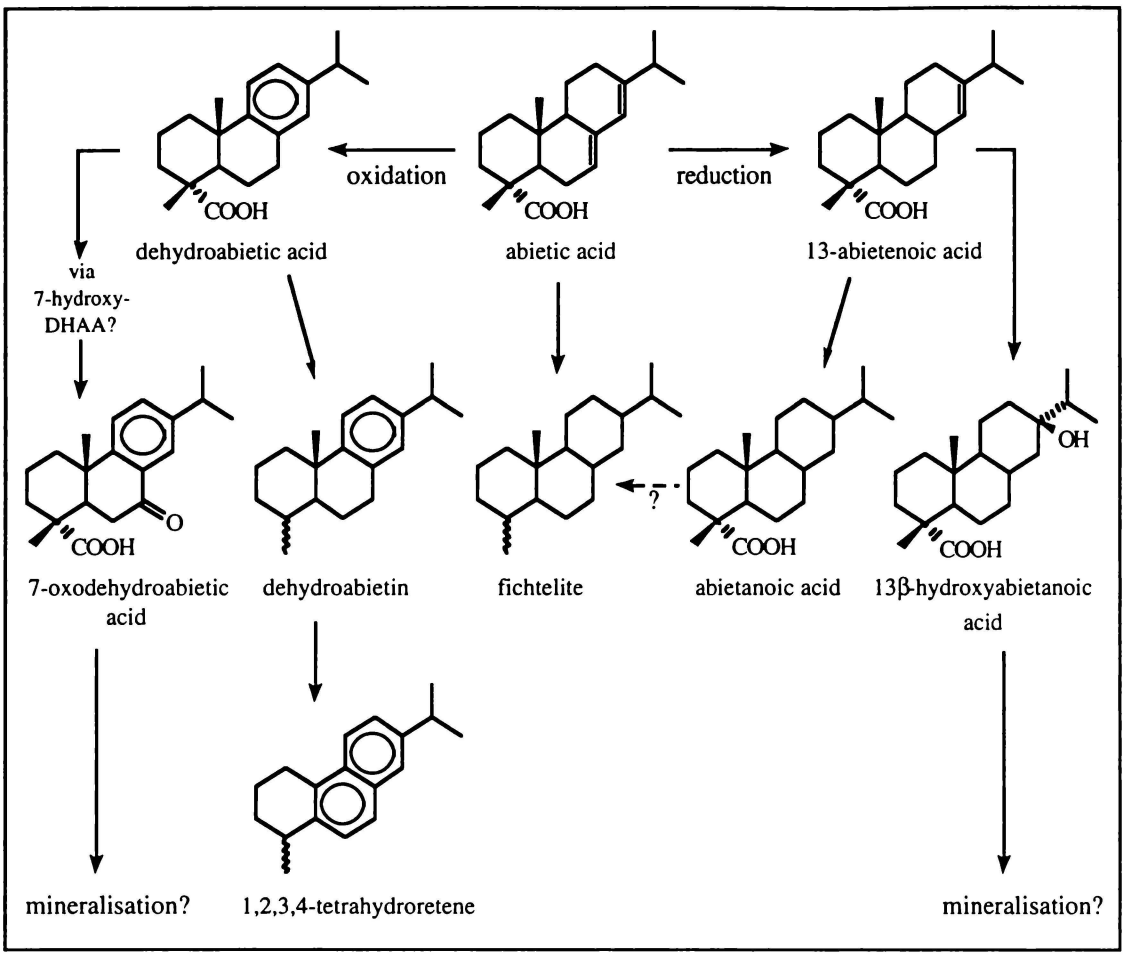


Figure 4.10: Possible transformation scheme for resin acids based on compounds observed in the No. 2 effluent ponds during the preliminary study

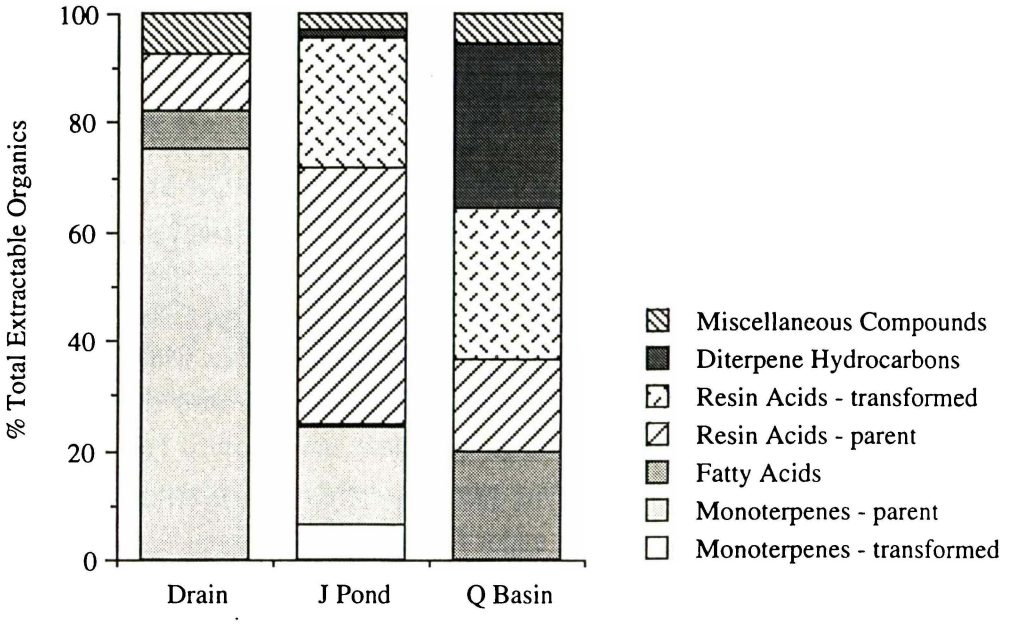


Figure 4.11: Comparison of the extractable organic composition of No. 2 system effluents

Unlike the MTs and RAs, FAs disappeared without observable transformation intermediates. FA degradation occurs via β-oxidation, which sequentially reduces the compound chain length in two-carbon unit steps, producing acetyl coenzyme A for the citric acid cycle (Overcash and Pal 1979). The shortened chain-length FA (C_{n-2}) re-enters the β-oxidation cycle and degradation continues. It was therefore reasonable that no intermediates were found.

4.3.7 Quantitative changes occurring in the effluent system

Despite the quantitative limitations of the analytical procedures used (section 3.4), useful information was obtained from the preliminary survey. Quantitative comparisons of effluent composition at each sampling location are summarised in Figure 4.12. The major features of the data were:

- concentrations of major components were much more variable in the drain than in J Pond or Q Basin effluents;

- concentrations of MTs, FAs and miscellaneous compounds were much lower in J Pond and Q Basin than in No. 2 drain effluent, indicating that these constituents were being removed from the aqueous phase in the ponds (note the log scales for EOs in Figures 4.12d, e, f, and g);

- RA concentrations in J Pond were higher than in the drain effluent (Figure 4.12f);

- colour was similar at all three locations, suggesting limited treatability in the system (Figure 4.12c);

- sodium and chloride concentrations in Q Basin were lower than in J Pond or drain effluents (Figures 4.12a and b), suggesting that dilution was a potentially important factor to be taken into account when assessing effluent treatment in the seepage basins.

The higher levels of sodium, chloride, colour and RAs present in J pond than in the drain effluent was subsequently found to be an artifact of the sampling program used for the drain. Sampling carried out by NZFP staff often coincided with short maintenance cuts and process changes within the mill, possibly producing atypical effluent composition. Later analyses of drain effluents confirmed this, yielding higher concentrations of RAs and FAs. In contrast, the large volume and residence time of the I-K-J pond system dampened out such short-term temporal variations in drain composition. To adequately characterise drain effluent composition, composite sampling was therefore required to avoid the problems associated with short term fluctuations.

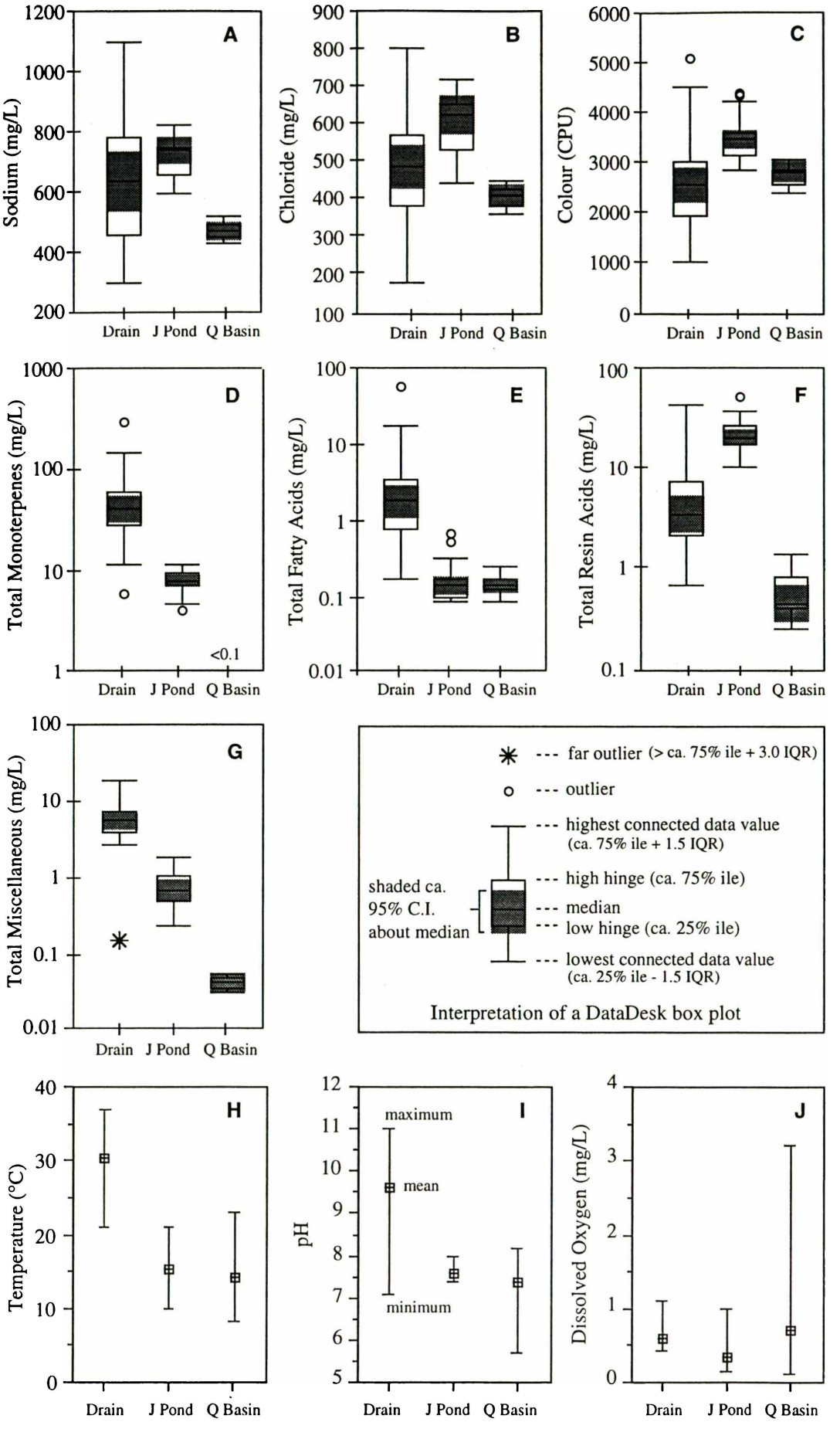


Figure 4.12: Quantitative comparisons of effluent composition in the No. 2 system

RAs were the most persistent group of EOs analysed, and remained at identifiable concentrations in Q Basin effluent. Trimethyl-2-cyclopentenones also persisted at low concentrations, consistent with their resistance to aerobic treatment (Voss 1984). The absence of guaiacol at significant levels in J Pond effluent was consistent with the degradability of non-chlorinated monomeric phenolics in both aerobic and anaerobic environments (Sierra-Alvarez *et al.* 1990).

No significant decreases in colour were observed. Comparison of relative colour levels in the drain, J Pond and Q Basin (after correcting for dilution by dividing colour by sodium or chloride concentration), indicated that highest colour levels were present in the seepage basin (Figure 4.13). This suggested that colour could increase slightly upon standing in quiescent ponds. Increases in kraft effluent colour during secondary treatment have been reported, and attributed to oxidation of lignin to chromophoric quinonoid compounds (Davis *et al.* 1978; Larrera *et al.* 1989; Cecen *et al.* 1992). The only evidence for lignin modification or fragmentation obtained in the preliminary survey was the appearance of small amounts of phenylacetic acid *[36]* in J Pond. This compound has been identified as a plausible intermediate of lignin degradation (Healy *et al.* 1980; Reinhard *et al.* 1984).

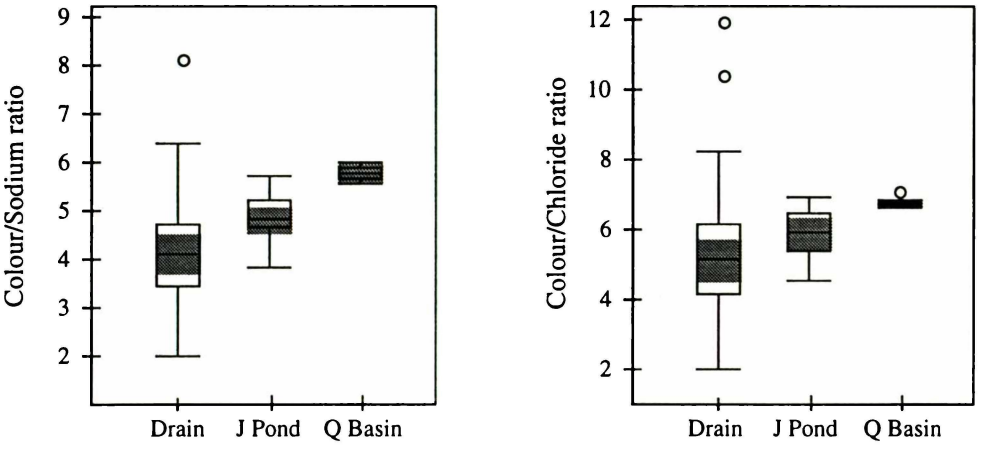


Figure 4.13: Comparisons of dilution corrected colour in the No. 2 effluent system

4.3.8 Conclusions from the preliminary study

The preliminary study established that considerable modification and disappearance of EOs occurred in the ponds of the No. 2 effluent system. Both oxidised and reduced EO transformation intermediates were detected in the pond effluents indicating that both oxidative and reductive degradation pathways were operative in the system. RAs, especially transformed RAs and DTs, were found to be a persistent group of EO compounds and were therefore candidates for transport to ground water or accumulation in sediments beneath the seepage ponds.

The semi-quantitative data indicated that reductions in EO concentrations of >90% could be achieved in the seepage ponds, but the rates of the removal processes could not be determined from the data collected. Colour remained essentially unchanged, although the data collected raised the possibility of increases in colour occurring upon standing in the seepage ponds.

4.4 A Quantitative Study of Effluent Behaviour

The preliminary experiment gave useful information about the behaviour of the No. 2 effluent in the pond system. However, neither the chemical sequences of degradative processes occurring in the ponds, nor the rates at which these processes occurred, could be determined from the data collected. To obtain this information, a further experiment was carried out.

4.4.1 Objectives

The study's main objectives were to:

1) measure the rates at which EOs, chlorophenolics, and colour disappeared from ponded effluent during seepage; and
2) investigate the degradative sequences leading to the disappearance of EOs, in particular RAs.

In addition, changes in effluent composition occurring during transport along the drain from the mill to the EA seepage ponds were assessed.

4.4.2 Sampling and analysis

Sampling of No. 2 drain effluent and ponded seepage basin effluent was carried out at the sites shown in Figure 4.14. Seepage basin P7 was used for the study because it had been designated by NZFP for use in field studies of the LA system, and was the focus for investigations of ground water from beneath the seepage site (Chapter 6).

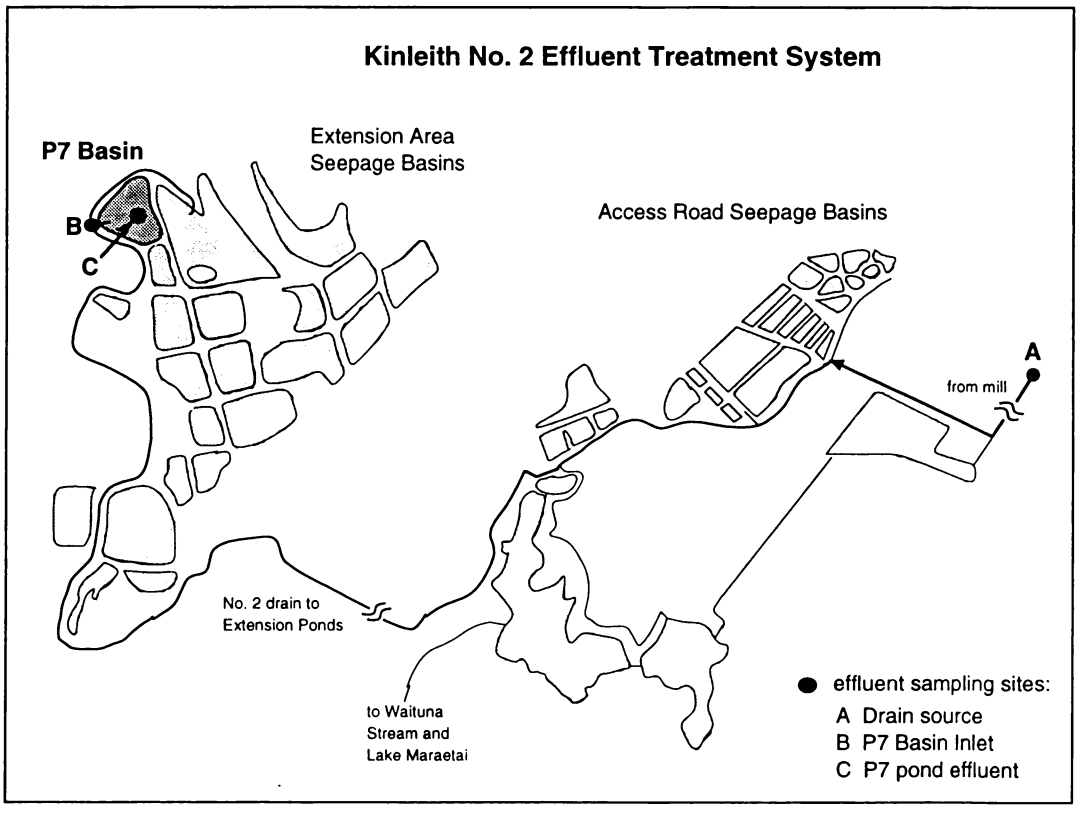


Figure 4.14: Sampling sites used in the second effluent monitoring study

At the drain source (the No. 2 effluent flow-monitoring station), a permanently installed composite sampler was used to deliver 100 mL effluent aliquots, at 15 minute intervals, into a 10 L covered plastic bucket surrounded by crushed ice enclosed in a polystyrene box. This maintained the temperature of the effluent below 10°C for the 24 hour collection periods. The 9.6 L samples collected were well mixed before taking 2.5 L subsamples in glass winchesters for analysis.

At the other end of the drain (the inlet to seepage basin P7), an ISCO autosampler was used to take both 24 hour and 1 hour composite samples. The sampler was programmed to deliver four 250 mL aliquots, each taken at 15 minute intervals, into each 1 L sample bottle. Each bottle was therefore a 1 hour composite sample. 100 mL taken from each bottle were mixed to produce a 2.4 L, 24 hour composite sample. The interior cavity of this autosampler was also packed with crushed ice, again keeping temperatures below 10°C for the 24 hour sampling periods.

Sampling at the seepage basin inlet was performed 36 hours later than at the drain source, to account for effluent residence time in the drain, which had been determined by NZFP staff in a separate tracer experiment. Drain sampling was carried out for the period in which the seepage pond was being filled. This took only four days, a time shorter than was expected, and gave a smaller than desirable sample set upon which to assess changes in effluent composition (section 4.4.3).

One litre grab samples of seepage basin effluent were taken daily from the same location in the pond. The sampling program is summarised in Table 4.8. Samples were analysed by the procedures summarised in Table 4.9. Analytical data are tabulated in Appendix 2, Tables A2.4 (drain monitoring data) and A2.5 (seepage pond data). A summary of the seepage pond data is appended to this chapter as Table 4.13.

Table 4.8: Sampling program used in the second effluent monitoring study

Location	Type	Frequency	Total samples	Analyses [a]
K2 drain source	24 hour composite	1 per day	5	Na, Col, EO, CP
seepage basin inlet	24 hour composite	1 per day	3	Na, Col, EO, CP
	15 hour composite	1 only	1	Na, Col, EO, CP
	1 hour composite	24 per day (+16)	88	Na
seepage basin	grab	~1 per day	30	Na, Col, EO, CP

a: Col = colour; EO = extractable organics; CP = chlorinated phenolics; Na = sodium

Table 4.9: Analytical procedures used in the second effluent monitoring study

Constituent	Procedure	section
sodium	atomic absorption spectrometry	3.2.1
colour	absorbance 465 nm (NCASI 1971)	3.2.3
extractable organics	450 mL liquid-liquid extraction at pH 11; GC-FID, GC-MSD	3.4.3
chlorophenolics	50 mL, acetylation, hexane extraction; GC-ECD	3.9.1

4.4.3 Effluent behaviour in the No. 2 drain

Na^+ concentrations in the 1 hour composite samples from the seepage basin inlet were used to monitor the movement of the effluent in the drain. This was possible because the drain feeding the pond had not been used for several weeks prior to the experiment, and the small quantity of stagnant effluent remaining contained relatively low Na^+ levels. Figure 4.15 shows the changes in Na^+ measured in each of the 1 hour and 24 hour composite samples.

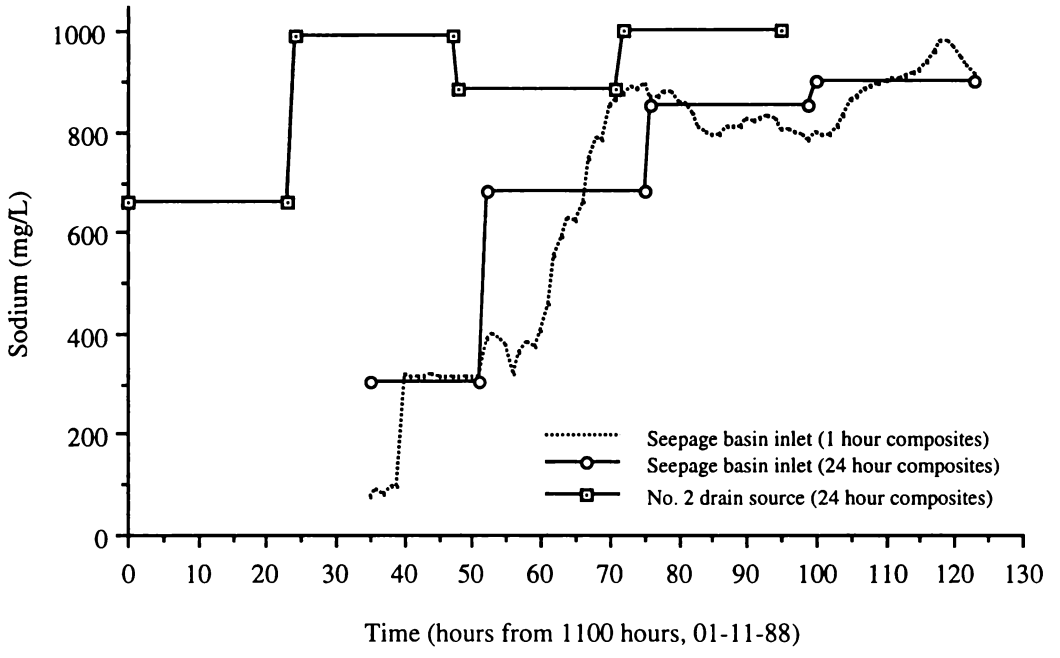


Figure 4.15: Sodium concentrations in the No. 2 drain during effluent loading to the seepage pond

Stable Na^+ levels at the seepage basin inlet were not reached in the 36 hours predicted by the tracer study. "Steady state" was not reached until the third day, when the Na^+ in the seepage basin inlet samples approached those taken from the drain source samples about 36 hours earlier. The reason for this delay in effluent arrival was not established.

In combination with the small data set caused by the pond filling more quickly than was anticipated, this delayed effluent arrival made comparison of the compositions of source and seepage basin inlet effluent possible from only the last two 24 hour composite samples.

Changes in effluent composition in the No. 2 drain, as estimated from the two sets of composite samples, are listed in Table 4.10. The masses entering the drain at its source and leaving at the seepage basin inlet were calculated assuming a flow of 5,000 m^3 d^{-1} in the drain feeding the EA seepage basins, as estimated by NZFP staff for the duration of the experiment.

Table 4.10: Quantitative changes in effluent composition occurring in the No. 2 drain

Constituent	Total masses (kg) [a] determined at:		Ratio
	Drain Source	Seepage Basin Inlet	Basin Inlet / Drain Source
Sodium	9420	8765	0.93
Colour	55700	51100	0.92
Total methyl-2-cyclopentenones	14.8	11.8	0.80
Total monoterpenes	370	255	0.69
Total fatty acids	384	336	0.87
Total resin acids	684	688	1.01
Total chlorophenols	1.60	1.31	0.82
Total chloroguaiacols	9.14	6.49	0.71
Total chlorovanillins	5.51	4.91	0.89
Total chlorocatechols	0.57	0.62	1.09
dichlorohydroxybenzaldehyde	1.07	0.97	0.91
Total chlorophenolics	17.9	14.3	0.80

a: sum of the two one-day composite sample values

Given the very small data set, and the uncertainties inherent in the analytical methods, the mass balance (as indicated by unreactive species, Na^+ and colour) was reasonable. However, the small data set obtained, and the failure to reach a well established steady-state, precluded estimating the significance of the changes observed. Changes of a magnitude likely to be important with respect to the performance of the LA system appeared to be occurring for relatively volatile constituents, in particular α- and β-pinene, and possibly also for chloroguaiacols. MT hydrocarbons (α- and β-pinene and limonene) made up 29% of the total MTs at the drain source, 17% at the seepage basin inlet, and only 13% in the seepage pond effluent at the completion of effluent addition. Transport from the mill to the seepage basin therefore resulted in a substantial reduction in these constituents.

No significant qualitative changes to the suite of EO compounds were detected in the drain, suggesting that physical processes (e.g. volatilisation), rather than chemical or biological degradation, were probably responsible for the reductions observed in the drain. This was reasonable, given the combination of warm effluent (T~30 °C) and summer daytime temperatures (afternoon T~24 °C) at the time of the study.

The small amount of degraded effluent in the drain at the start of the experiment had a higher colour:sodium ratio (9.65) than in fresh drain effluents (3.66 to 6.55). Assuming Na^+ to be conservative, this suggested that effluent colour increased on standing in the drain system. A similar result was observed in the preliminary study of Q basin effluent (section 4.3.7, Figure 4.13).

4.4.4 Colour change in the seepage pond

The colour of the effluent ponded in the seepage basin decreased with time, paralleling changes in sodium concentrations (Figure 4.16). The greatest reductions coincided with periods of rainfall (NZMS 1988), while increases reflected periods of greater evaporation than rainfall and accumulated runoff. Effluent dilution by rainfall and runoff from the catchment surrounding the EA was therefore occurring at times. To estimate changes in effluent composition due to processes other than dilution or concentration, dilution correction was therefore necessary. Assuming Na^+ to be a conservative constituent, "dilution corrected" concentrations $[\ ]_{dc}$ at each sampling time (t) in the seepage basin were calculated and normalised to the concentration measured in the pond when effluent addition ceased (t_{in}):

$$[\ ]_{dc}(\%) = 100 \times \frac{[\ ]_t}{[\ ]_{in}} \times \frac{[Na]_t}{[Na]_{in}}$$

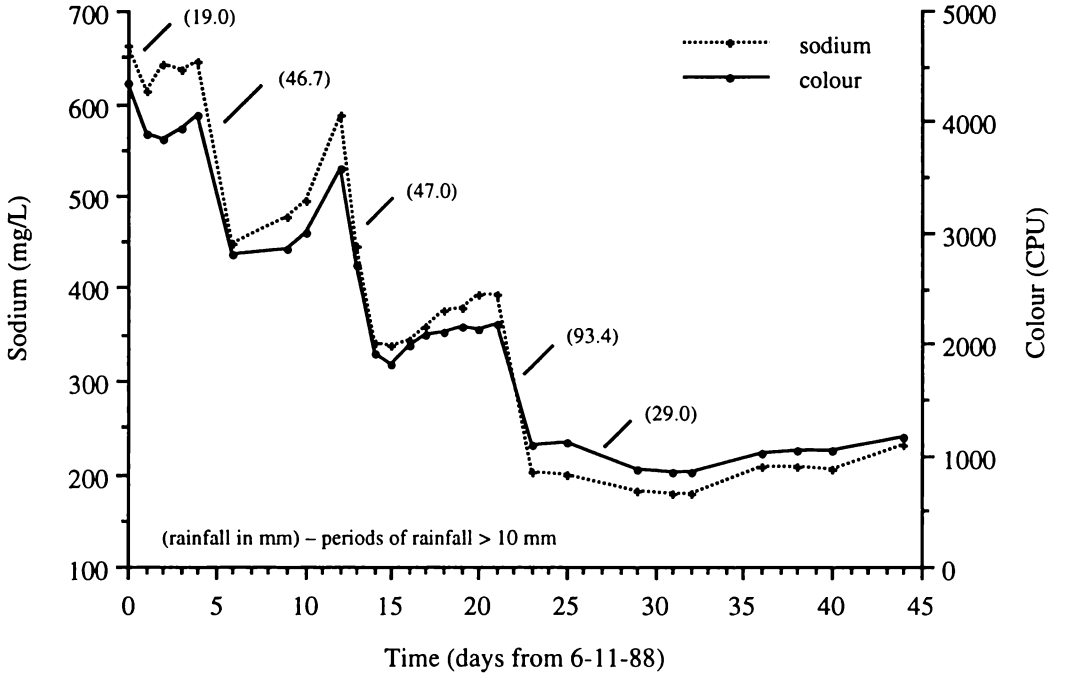


Figure 4.16: Changes in the concentrations of colour and sodium in the seepage pond

Significant dilution-corrected colour reduction was measured. However, the data was insufficiently precise to reliably determine the form of the colour disappearance kinetics. Analytical uncertainties in colour and sodium determination, compounded by the calculation procedure, potentially contributed about ±15% to the 95% confidence interval about each corrected colour value. The disappearance trend was adequately described by linear regression, giving a significant but relatively imprecise estimate of colour reduction: % colour remaining = 96.6–0.58·days (R=0.914; p=0.0001; 95% C.I. in slope = ±0.11; n=27). Second-order polynomial fitting gave a slightly better fit (R = 0.927), and is shown in Figure 4.17.

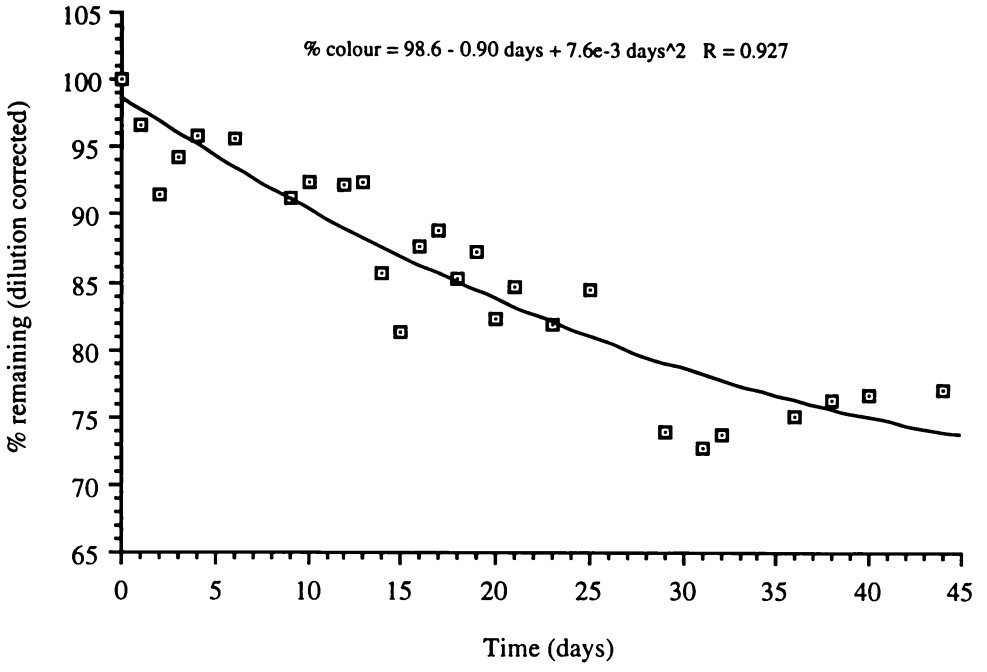


Figure 4.17: Disappearance of dilution corrected colour in the seepage pond effluent

Colour reduction mechanisms in addition to dilution were therefore operating in the pond, producing a decrease of about 25% after 30 days. This was comparable with reported reductions in colour of filter-sterile, hardwood C+E stage effluent exposed to glass-filtered daylight at a dissolved oxygen level of 2.1 mg L^{-1} (Roy-Arcand and Archibald 1993). The reduction measured in the seepage pond was, however, insufficient to be a practical benefit for the land application process, as the colour of the diluted pond effluent remaining at the end of the experiment was still high (approximately 1000 CPU, even after dilution).

Chlorolignin degradation by aerated lagoon bacterial consortia is known to be slow. Erikkson and Kolar (1985), for example, found <4% removal over 3 months. Roy-Arcand and Archibald (1993) found that settling pond sludge microorganisms had no effect on colour reduction of BKME high molecular weight material, indicating that abiotic processes were responsible for observed chromophore bleaching. The change in colour observed in the seepage pond was therefore probably associated with photodegradation (Archibald and Roy-Arcand 1995) or physical processes such as deposition.

4.4.5 Changes in the concentrations of EOs and chlorophenolics

Concentrations of total MTs, FAs, RAs, and chlorophenolics (CPs) decreased by between 98% (CPs) and >99.9% (MTs) during the experiment. Concentrations of EOs remaining in the seepage basin effluent after 44 days ranged from <20 $\mu g\ L^{-1}$, for total MTs, to approximately 300 $\mu g\ L^{-1}$, for total RAs.

Dilution corrected disappearance profiles revealed marked differences in behaviour of the major classes of EOs (Figure 4.18).

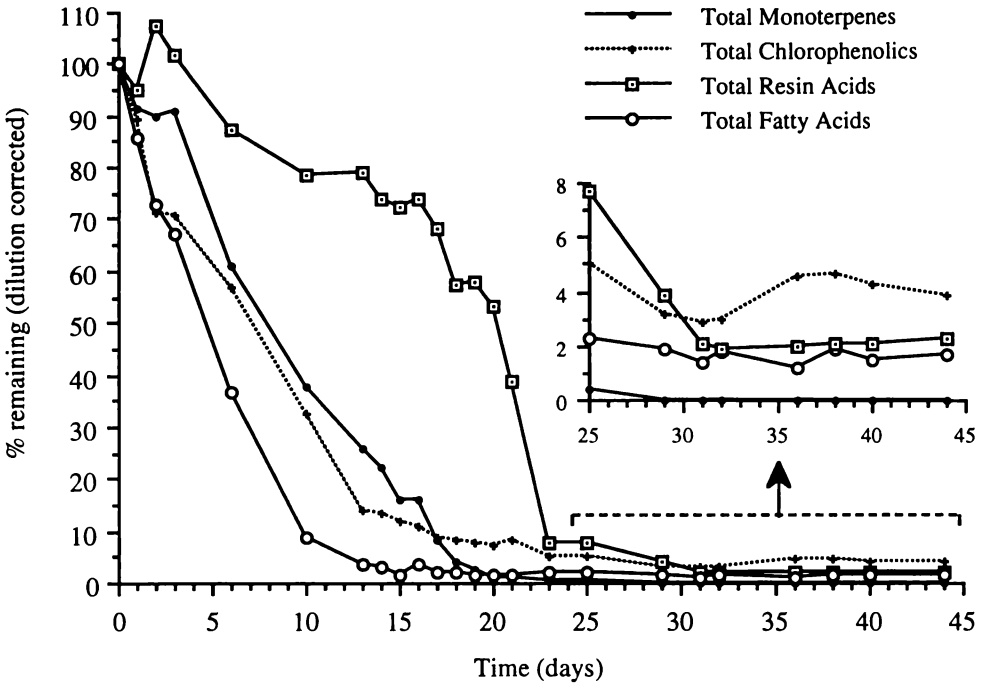


Figure 4.18: Disappearance of extractable organics and chlorophenolics in the seepage pond

The major features of the disappearance profiles were a) the differences between the disappearance rates of the compound classes, in particular the markedly different behaviour of the RAs, and b) the presence of RAs and FAs and CPs at low but relatively stable concentrations after about 30 days.

RA behaviour was distinctly different from that of the other major compound classes. The rate of disappearance was relatively slow for the first 15–20 days, then increased dramatically between 20 and 23 days. Concentrations then stabilised at relatively low levels.

FAs were the most rapidly removed compounds. This was consistent with their documented degradability, with little necessary acclimation, even under anaerobic conditions (Sierra-Alvarez *et al.* 1990).

The behaviour of MTs was intermediate between that of the RAs and FAs. In contrast to the other classes of compounds, which remained detectable throughout the monitoring period, levels of MTs were undetectable (<2 $\mu g\ L^{-1}$) after about 20-25 days.

CPs disappeared at a similar rate to the MTs for the first 15 days, but higher relative concentrations remained at the end of the experiment. The disappearance of CPs was unexpectedly rapid, but was consistent with their degradability under both aerobic and anaerobic conditions (Neilson *et al.* 1990; Woods *et al.* 1989; Reineke and Knackmuss 1988), and treatability in the facultative I-K-J basins of the Kinleith No. 2 effluent system (Stuthridge *et al.* 1991), in which 76% removal of CPs was measured (compared with 44% for RAs).

Possible reasons for the presence of relatively stable residuals of RAs and CPs at the end of the monitoring period include:

a) equilibrium between removal, by biotic or abiotic processes, and release, from sediments or chlorolignin. CP release has been reported as a result of chlorolignin degradation (Eriksson *et al.* 1985), desorption from chlorolignin (O'Connor and Voss 1992), and release from contaminated sediments (Remberger *et al.* 1993);

b) concentration thresholds, below which microbially-mediated removal stops. Lower thresholds to microbial degradation of organics have been proposed to be responsible for the environmental persistence of low levels of even relatively biodegradable species (Alexander 1985);

c) the physico-chemical form of the organic compounds in the effluent matrix. Compounds weakly associated with chlorolignin may be unavailable to degrading organisms, yet still be solvent extractable. Neilson *et al.* (1990) suggested that inaccessibility may be a contributory factor in the environmental persistence of apparently biodegradable compounds such as CPs; and

d) cometabolic biodegradation. The observed removals may have occurred coincidentally with degradation of more abundant, and more readily degradable, organic material which was the primary substrate for microbial growth. In the absence of primary substrate, the remaining organics were either present at insufficient concentrations to support growth (i.e. below a critical threshold concentration) or were no longer being cometabolised. Cometabolic degradation of abietic acid has been reported in anaerobic systems (McFarlane and Clark 1988).

The rates of disappearance observed in this experiment were likely to be near maximal for the Kinleith seepage system. Temperatures were warm (afternoon effluent T 17–26°C) enhancing microbial growth rates, chemical reaction rates, and volatilisation. The ponded effluent was relatively shallow (depth <1 m), facilitating reaeration and mixing. Removal of CPs in facultative stabilisation basins increases with temperature, possibly because of the higher temperature optima exhibited by anaerobic bacteria (Randle *et al.* 1991). BKME photo-decolourisation has been found to be dependent on DO levels, proceeding more rapidly at higher DO (Archibald and Roy-Arcand 1995).

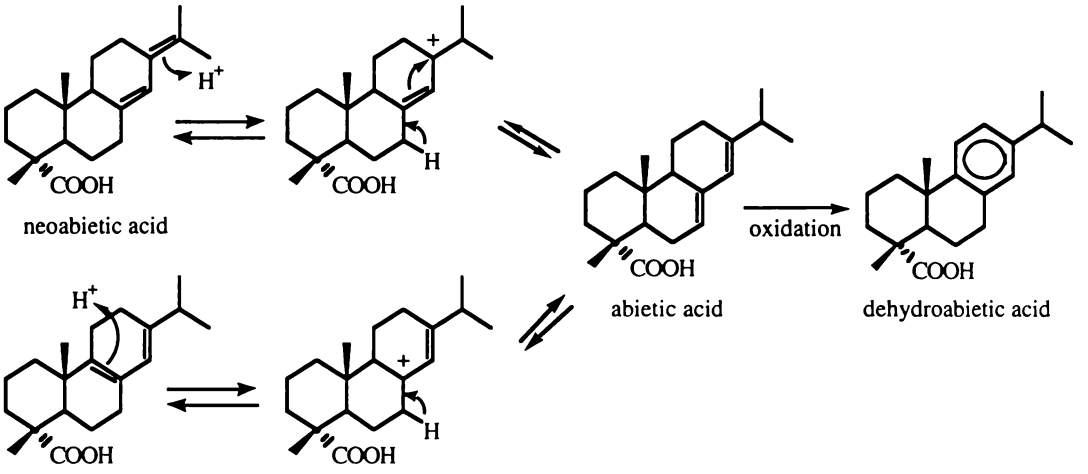
Since the seepage basins at Kinleith were used for effluent disposal largely during winter (mean temperature about 7.5 °C compared with summer mean of about 17 °C), treatment achieved in the ponds during normal operation would probably have been considerably slower than that measured in this trial.

4.4.6 Qualitative changes in composition of the resin acid fraction

Most chemical modification was observed for the RAs. A range of compounds which were plausible degradation intermediates were identifiable. The unusual decay profile observed for

the total RAs (Figure 4.18) was attributable to the formation, and subsequent disappearance, of these transformation intermediates in the first 20 days.

Not all the parent RAs present in the No. 2 drain effluent were detected in appreciable quantities in the seepage basin effluent. Palustric *[123]* and neoabietic *[133]* acids, which together constituted approximately 10% of the total RA concentration of the drain effluent, were never significant components in the pond. These compounds were therefore very sensitive to either degradation to species undetectable by the procedures used, or to transformation to other abietane resin acids, probably dehydroabietic acid or abietic acid which were the principal species present immediately after effluent addition to the pond:



The major remaining compounds exhibited very different disappearance profiles (Figure 4.19). Temporal changes in the concentrations of abietane RAs revealed the disappearance of parent compounds, and the formation, then disappearance, of intermediates. After a short acclimation period, abietic acid disappeared pseudo-exponentially.

Two major degradation intermediates, 13-abietenoic acid *[120]* and 13β-hydroxyabietanoic acid *[136]* appeared, and were subsequently removed (Figure 4.20). Dehydroabietic acid concentrations increased slightly over the first 15 days, then decreased rapidly. The sequence of observed chemistry was consistent with the two-route scheme involving both oxidative and reductive processes that was suggested in the preliminary study to account for the compounds found in J Pond and Q Basin (section 4.3.6, Figure 4.10). This sequence appeared to be:

1) oxidation of abietic to dehydroabietic acid and removal of dehydroabietic acid via undetected or minor metabolites; and

2) saturation of the C7 double bond in abietic acid to produce 13-abietenoic acid, hydroxylation of the 13(14) double bond to form 13β-hydroxyabietanoic acid, then assimilation of 13β-hydroxyabietanoic acid via undetected species.

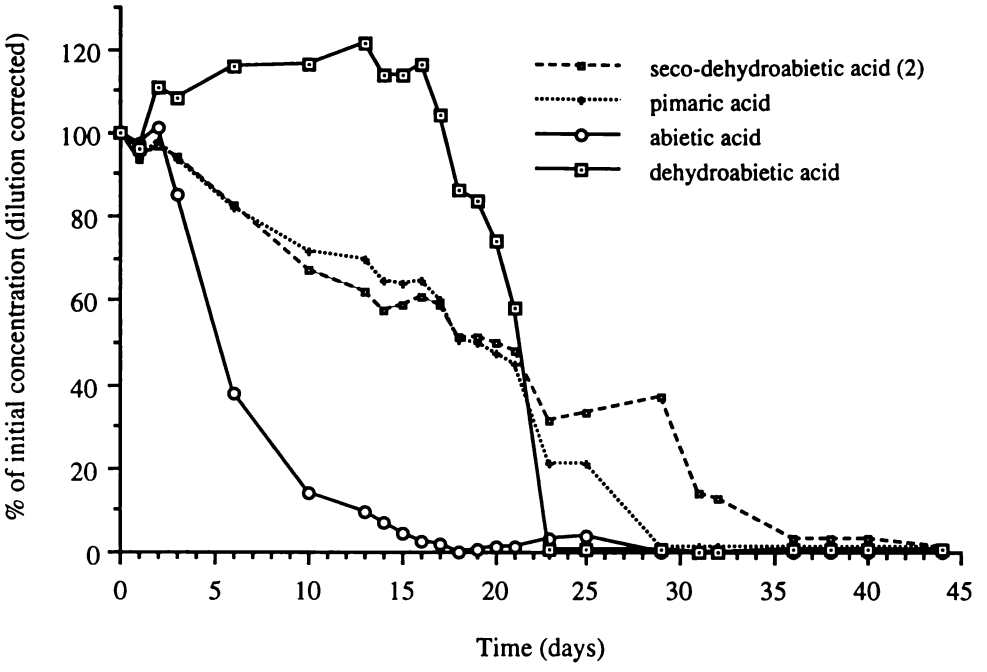


Figure 4.19: Changes in relative concentrations of major parent resin acids in the seepage pond

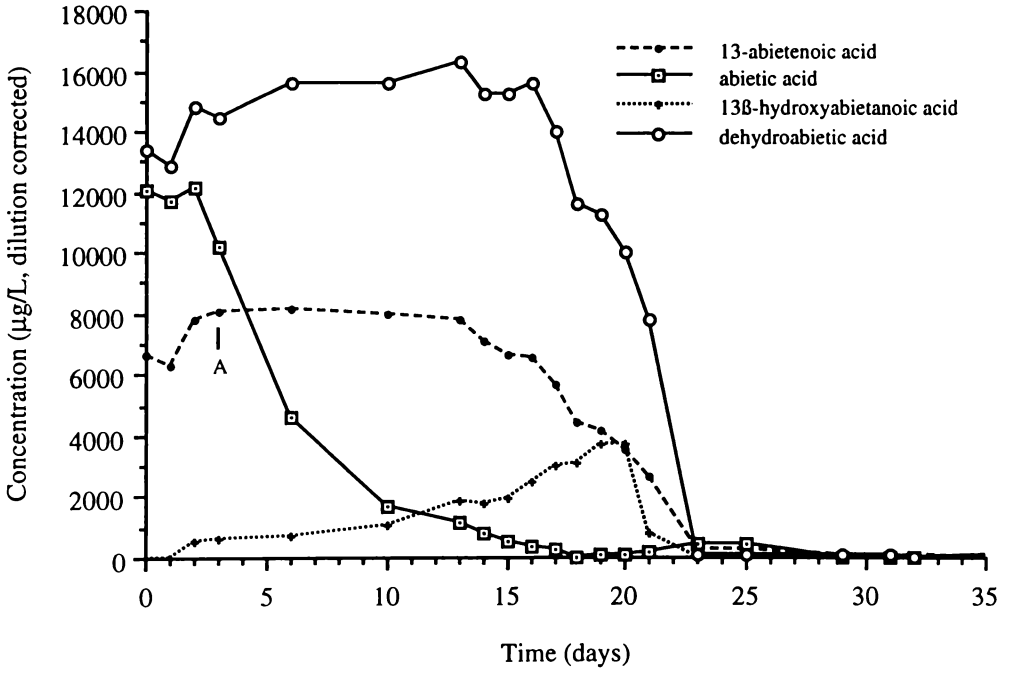


Figure 4.20: Changes in the concentrations of major abietane resin acids in the seepage pond [1]

[1] Isopimaric acid and 13-abietenoic acid coeluted in GC-FID analysis. GC-MSD established that the peak was >80% 13-abietenoic acid at point A, after which isopimaric acid was a very minor constituent.

The relatively stable concentration of dehydroabietic acid over the initial 15 day period suggested that formation and removal were at approximately steady state. Its subsequent disappearance could therefore have been associated with the exhaustion of abietic acid precursor. The disappearance of dehydroabietic acid may also have been a response to changing DO levels in the pond. No. 2 drain effluent had low DO levels (<1 mg L^{-1}, Table 4.2), and after addition of effluent to the seepage basin, microbial assimilation of readily degradable organic matter would be expected to inhibit rapid increases in DO concentration. Under these conditions, dehydroabietic acid degradation is likely to be slow, as shown by its persistence during anaerobic treatment (McFarlane and Clark 1988). As the organic matter was consumed, and reaeration of the pond by wind-induced mixing and diffusion continued, DO levels would have increased. The reductions in dehydroabietic acid observed in the seepage basin may therefore have been the result of aerobic degradation, which did not become appreciably rapid until the majority of the effluent's oxygen demand had been expressed.

The concentrations of 13β-hydroxyabietanoic acid remained relatively low, and declined rapidly when 13-abietenoic acid became depleted. This suggested that the hydroxylated compound was readily metabolised. Further products of this degradative sequence were not detected, suggesting that either mineralisation of the hydroxylated compound rapidly occurred, or (probably less likely) that the products of further degradation, such as the di-hydroxylated species found in laboratory studies of RA metabolism (e.g. Kutney *et al.* 1982), were not detected by the analytical regime employed. The initial hydroxylation step is often the rate limiting step in the anaerobic degradation of unsubstituted hydrocarbons, after which metabolism proceeds more rapidly. Resin acids appeared to behave similarly in the seepage basin.

Reductions in the concentrations of pimaric acid *[110]*, sandaracopimaric acid *[113]*, and both seco-dehydroabietic acid isomers *[103* and *104]* were approximately linear (zero order) for the 29–36 day period before concentrations stabilised at low levels (Figure 4.21). Reductions of 2.5–3.5 % d^{-1} occurred for these compounds in this period. In contrast to the abietane species, for which major transformation products were observed, plausible intermediates of the degradation of these compounds were very minor constituents, and were limited to 8,15-pimaradienoic *[107]*, 8,15-isopimaradienoic *[109]*, 8(14)-pimarenoic *[118]*, 8-pimarenoic acids *[111]*, and extremely low levels of 7-oxokauranoic acid *[126]*.

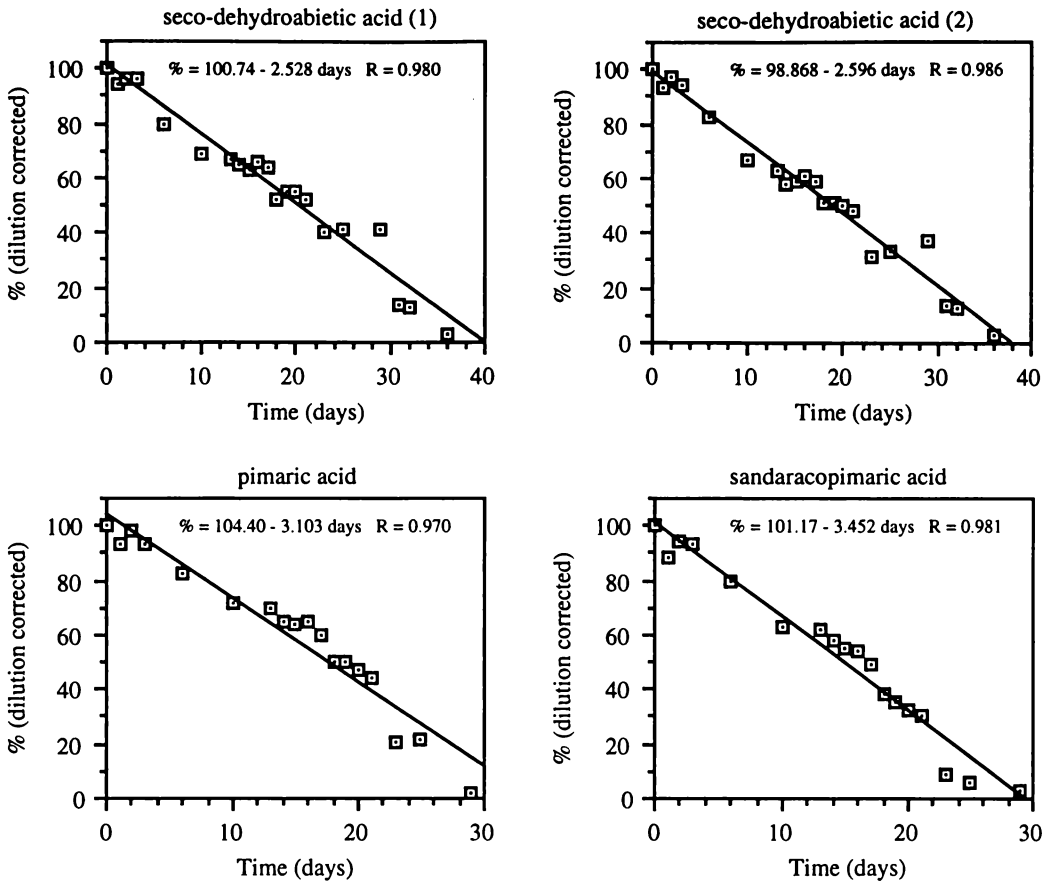


Figure 4.21: Disappearance of seco-dehydroabietic and pimarane resin acids in the pond

Attention was focused on evaluating the behaviour of the major species, and therefore accurate assessment of quantitative changes in minor components was not realistically achievable. A species-specific quantitative detection method, such as GC-MSD in selected ion monitoring mode, rather than the non-specific GC-FID used in this experiment, would have been required to reliably quantify small peaks, which were sometimes poorly resolved and superimposed on a complex baseline.

Despite these quantitative limitations, several minor species were identifiable. These included 8,15-pimaradienoic acid *[107]*, 8,15-isopimaradienoic acid *[109]*, 8(14)-pimarenoic acid *[118]*, 8-pimarenoic acid *[111]*, abietanoic acid *[127]*, 7-oxodehydroabietic acid *[139]*, dehydroabietin *[90]*, and fichtelite *[87]*. 7-oxodehydroabietic acid appeared to increase in concentration in the period between 10 and 20 days, consistent with some oxidative degradation of dehydroabietic acid. Dehydroabietin *[90]* appeared as a transient, low concentration component at about the same time. Abietanoic acid concentration increased during the final stages of monitoring. Figure 4.22 shows the changes in the concentrations of some of the minor RAs.

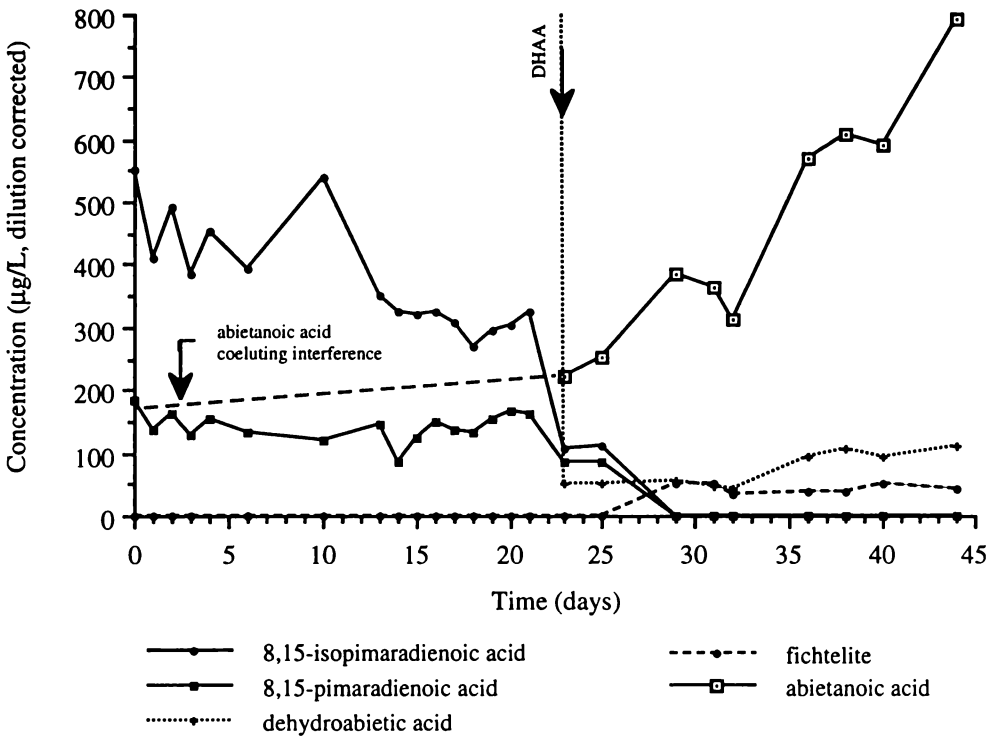


Figure 4.22: Changes in the concentrations of some minor RAs and DTs in the seepage pond[2]

Saturated (abietanoic *[127]* and pimaranoic *[119]* acids) and monoenic (13-abietenoic acid *[120]*) RAs were the dominant compounds in the seepage basin effluent at the end of the experiment. Abietanoic acid, making up approximately 65% of the total RAs present at this stage, was the major compound. Dehydroabietic acid constituted less than 10%. Pimaric and seco-dehydroabietic acids were the major parent dienes remaining. Abietic acid, despite its degradability, was also still detectable at very low levels. Fichtelite *[87]*, a smaller amount of dehydroabietin *[90]*, and a DT260 *[86]* were also present.

The dominance of abietanoic acid in the degraded effluent was consistent with the composition of the small amount of effluent lying in the seepage basin before the experiment began. Effluent had not been added to the pond for 7 weeks prior to the trial. Immediately before the experiment began, 170 µg L^{-1} abietanoic acid was present in the remnant effluent, constituting over 80% of the RA fraction. The saturated compound was therefore a persistent species, having survived 7 weeks since effluent had last been added to the seepage basin. It was somewhat surprising that a reduced RA was the dominant species present in what should have been an aerobic environment, and suggests that once formed, saturated species are somewhat resistant to further transformation under the conditions prevailing in the pond system.

4.4.7 Changes in the composition of the monoterpene fraction

The disappearance of total MTs was shown in Figure 4.18. The profile largely reflected the behaviour of α-terpineol *[48]*, which was the dominant species present at the start of the pond

[2] Coelution of abietanoic acid and 6,8,11,13-abietatetraenoic acid prevented reliable quantitation of abietanoic acid by GC-FID in the initial 23 days.

monitoring (making up 61% of the total MTs). Disappearance of this compound appeared to proceed by 1) an initial acclimation phase of about 3 days, during which concentrations were little changed, 2) an approximately exponential decay for about 12 days, followed by 3) a more rapid removal process for the remaining 4 days until the compound was no longer detectable.

Other MTs behaved similarly, although disappearing at greater rates (Figure 4.23). DHT *[35]* was detected as a metabolite which increased in concentration (after correction for dilution) during the exponential decay phase of α-terpineol, then was itself removed. Camphor *[34]*, the oxidation product of borneol *[44]*, was also produced. Fenchone *[29]*, the oxidation product of fenchol *[32]*, was observed in J pond effluent (section 4.3.4). It was therefore expected to appear as an intermediate in the seepage pond. It was, however, not detected in quantifiable amounts, presumably due to rapid removal after formation.

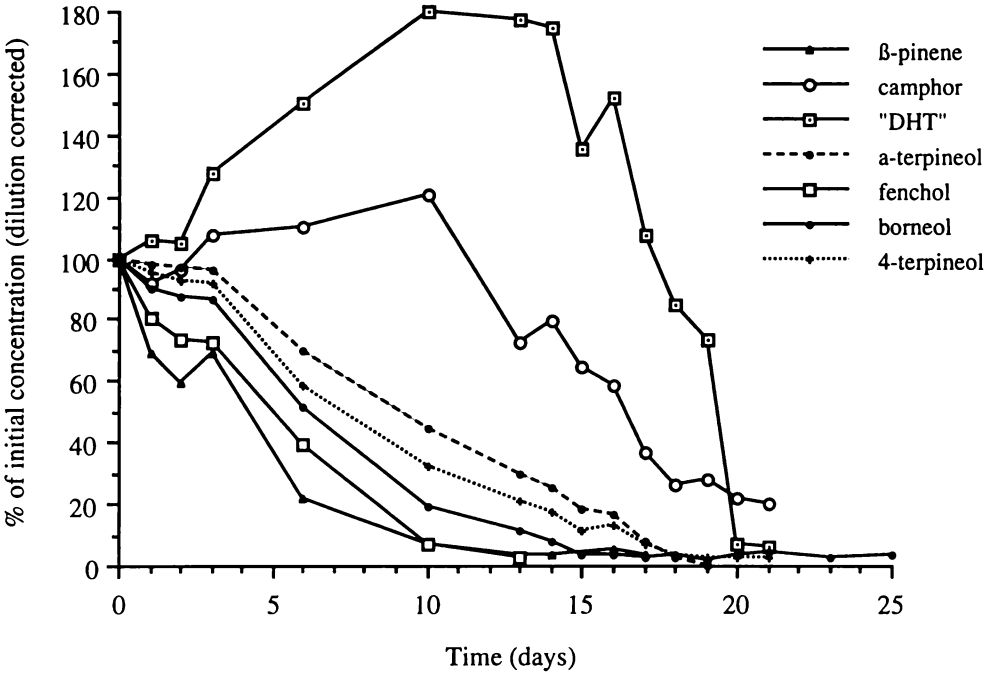


Figure 4.23: Disappearance and appearance of monoterpenes in the seepage pond effluent

Both DHT and camphor were quantitatively minor species, indicating that the majority of MT removal occurred by processes giving either no detectable intermediates, or intermediates which were readily further metabolised (presumably mineralised). The formation of DHT and camphor indicated that both reductive and oxidative degradative processes were occurring in the seepage pond. This was consistent with RA behaviour, and with observations made in the preliminary effluent study.

Volatilisation was also a plausible contributory mechanism for MT removal resulting in compound removal without formation of chemically modified species. Consistent with volatilisation, the rates of MT disappearance were inversely related to the compounds' boiling points.

4.4.8 Changes in fatty acid fraction composition

The effluent remaining after 44 days contained 18 FAs detectable by full-scan GC-MSD. FA16:0, FA18:0, and FA18:1 species dominated, all of which were compounds found in the parent drain effluent. No transformation products were detected.

4.4.9 Behaviour of chlorophenolic compounds

CPs were present in the ponded effluent at the end of the experiment at low levels, ranging from approximately 0.2 μg L^{-1} chlorovanillins to 9 μg L^{-1} chlorocatechols (Table 4.13).

The chlorocatechols, which were minor components of the No. 2 effluent, behaved quite differently from the other chlorophenolics. After a short lag period, corrected concentrations increased, then decreased to approximately 50–60% of the initial concentration (Figure 4.24). Reductions of the other classes of chlorophenolic compounds amounted to between 96 and >99%. Chloroguaicols appeared, at least initially, to be more readily removed than chlorophenols. This was consistent with their behaviour in soils (Dargitz *et al.* 1991). 3,4,5-trichlorocatechol was the dominant identified compound remaining in the degraded seepage pond effluent.

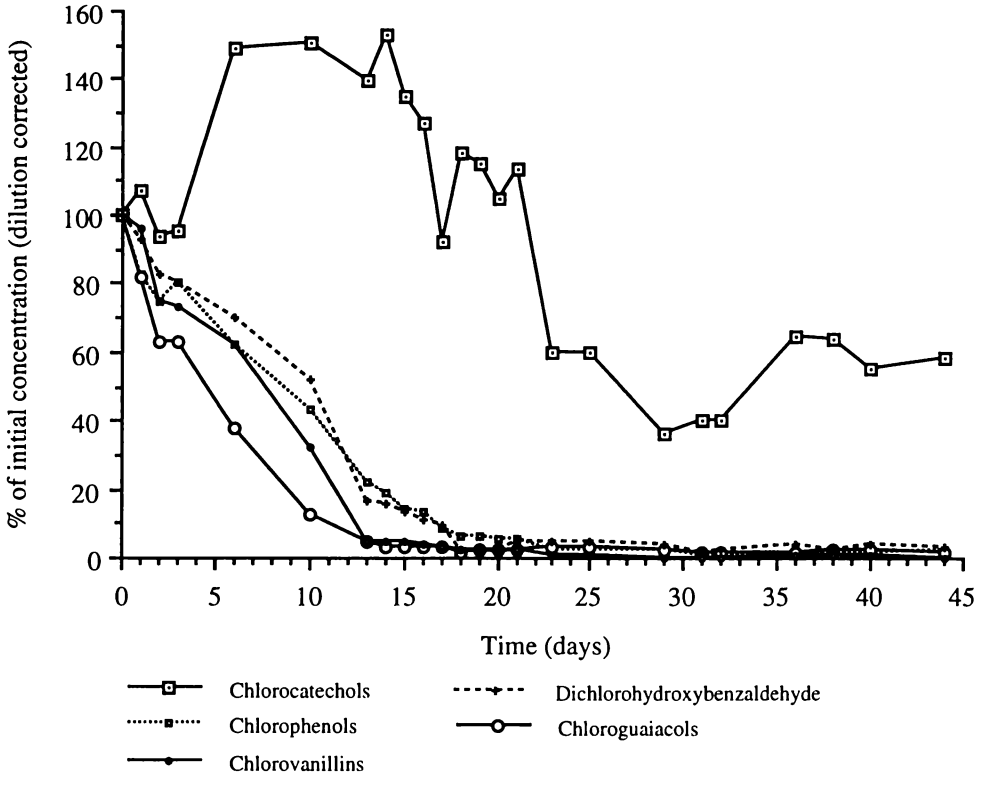


Figure 4.24: Changes in relative concentrations of the major classes of chlorophenolics in the seepage basin

Chlorocatechols have been identified as products of microbial demethylation of chloroguaiacols under anaerobic conditions in sediments (e.g. Neilson *et al.* 1990), and in anaerobic treatment reactors (Woods *et al.* 1989). Similar processes appeared to be occurring in the seepage pond. The relative persistence of the chlorocatechols in the seepage pond was consistent with the

statistically insignificant reductions in chlorocatechols resulting from effluent passage through the K-I-J basins of the Kinleith No. 2 effluent treatment system (Stuthridge *et al.* 1991).

The persistence of chlorocatechols under seepage conditions may be an important factor affecting the fate of chlorophenolics in land application systems, as they have markedly higher affinity for sediment phase organic matter and multivalent inorganic cations than either chloroguaiacols or chloroveratroles (Remberger *et al.* 1986; Remberger *et al.* 1993). Transport to ground water might therefore be influenced by two competing processes: 1) enhanced attenuation by sorption to soil or aquifer materials, which could reduce the potential contamination of ground water, or 2) strong association with dissolved chlorolignin, which could facilitate transport in the aqueous phase.

Paasivirta *et al.* (1990) showed that chlorocatechols have a high affinity for high molecular weight chlorolignin, and are the major chlorophenolic compounds bound to both sediments and chlorolignin. Under anaerobic conditions, chlorocatechols undergo dechlorination, although they remain the dominant class of chlorophenolics recovered from sludges in effluent treatment systems (Neilson *et al.* 1990).

In facultative environments such as the seepage ponds, the behaviour of CPs is potentially complex. The formation (and degradation) of a variety of possible biotransformation products by O-methylation, O-demethylation, reductive dehalogenation, and hydroxylation of parent CPs, is possible under these conditions. Further complication arises because the products of some transformations (e.g. the O-methylation of 3,4,5-trichloroguaiacol) are dependent on the concentration of substrate (Allard *et. al.* 1985).

Neilson *et al.* (1990) summarised the environmental fate of CP compounds and emphasised that, due to the complexity of transformations possible, the disappearance of substrate was not sufficient evidence for the biodegradation of these compounds. While removal of CPs from facultative stabilisation basins is believed to be almost entirely due to biodegradation (e.g. Randle *et al.* 1991), the potential for abiotic photodegradation of at least some BKME-sourced CPs has also been demonstrated (Roy-Arcarnd and Archibald 1993).

In summary, the data acquired in the seepage basin experiment showed that removal of CPs from the aqueous phase was occurring, and that chlorocatechols were produced during CP removal. This was consistent with, but not definitively attributable to, microbial demethylation of chloroguiacols.

4.5 Comparison of Results from the Two Studies

The major results from the preliminary study (section 4.3) and the seepage trial (section 4.4) studies were generally consistent. EOs were effectively removed in the seepage ponds, leaving effluent containing low concentrations of transformed RAs and DTs as the major components. The chemical transformations observed in the second study were consistent with the degradation routes proposed from compounds observed in the preliminary study (Figures 4.8 and 4.9). The EO composition of the effluent at the end of the second study was, however,

somewhat different from that observed in the preliminary study of Q Basin. The composition of the RA and DT fractions found in Q Basin during the preliminary study, and in P7 Basin at the end of the second study, are shown in Figure 4.25.

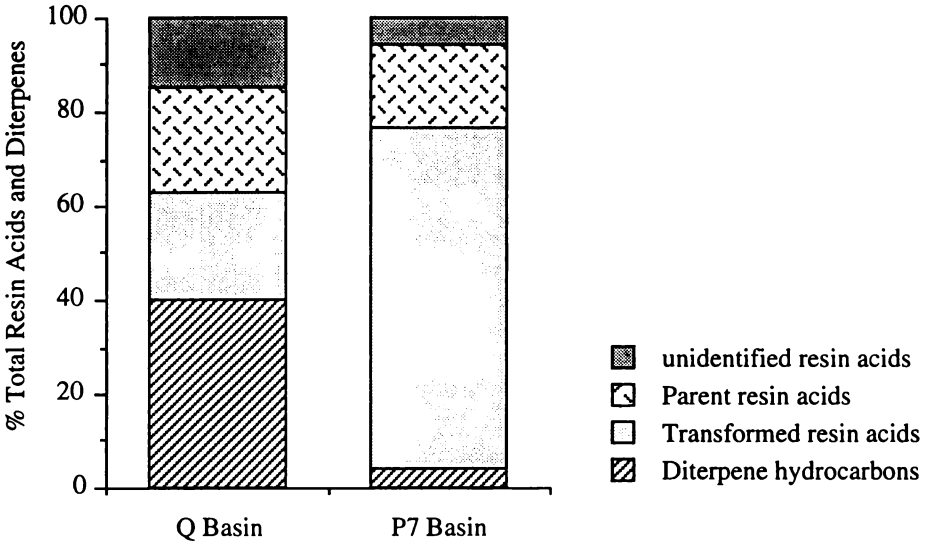


Figure 4.25: Comparison of the resin acid and diterpene composition of two degraded pond effluents

The major difference between the effluent compositions found in the two studies was the larger proportion of DTs in the Q Basin effluent. The reasons for this difference were not determined, but may have been associated with the time required to form significant concentrations of DTs, and the environmental conditions required to maintain these compounds in solution. Q Basin was deeper and contained effluent for the entire 4 year duration of the LA system investigations. It was therefore probably more suited to formation and maintenance of these compounds, which are known to be formed under anaerobic conditions (Simoneit 1986; Tavendale 1994).

A small degree of colour removal was measured in the second study, while in the preliminary study, evidence for small increases in colour was obtained. This difference remained unexplained, but may have been associated with slow changes in chromophore chemistry not observed in the relatively short duration of the seepage pond trial, or more simply to uncertainties associated with the limited data acquired, particularly in the preliminary study.

4.6 Summary and Conclusions

4.6.1 Effluent behaviour in the seepage pond: quantitative changes

The disappearance of major EOs, chlorophenolics, and colour in a seepage basin was followed. After correction for dilution, the concentrations of all the classes of low molecular weight organics analysed were reduced by ≥95% after 44 days. The rates at which these reductions occurred varied with time, so that direct comparison of disappearance kinetics was not possible. For the first 15 days, removal rates decreased in the order FAs>CPs≈MTs>RAs. RA behaviour was distinctly different from the other compound classes due to the appearance of major transformation intermediates, the formation and persistence of dehydroabietic acid, and

different removal kinetics of individual RA compounds. Colour reductions were smaller, amounting to approximately 25%.

The disappearance rates for the effluent organics have been summarised in Table 4.11 by listing the times required to reduce the dilution corrected concentrations by 50, 90 and 95%. The maximum reductions measured are also listed.

Table 4.11: Summary of quantitative changes in the concentrations of organics in the seepage basin

	Time (days) required for reduction of:			Maximum reduction
Compound Class	50%	90%	95%	%
Total monoterpenes	7	17	18	>99
Total fatty acids	4	10	17	98
Total resin acids	20	23	28	98
Total chlorophenolics	6	17	25	95
Colour	not reached	not reached	not reached	25

4.6.2 Effluent behaviour in the seepage pond: compositional changes

The experiment enabled the chemical transformations of major EOs to be followed. The greatest variety of chemistry was observed for RAs, both oxidised and reduced transformation products being detected.

At the end of the experiment, reduced RAs, in particular abietanoic acid, were the dominant species present. Parent species, mainly pimaric acid, seco-dehydroabietics, and dehydroabietic acid, were also present at lower levels. Fichtelite was the major DT found.

MT degradation intermediates were also detected, although only in very minor amounts. As was found for the RAs, both oxidative and reductive degradative routes were operating, producing camphor and DHT as transient intermediates.

Chlorocatechols were the most persistent detectable chlorophenolic compounds.

4.6.3 Significance of the results for seepage system performance

The experiment demonstrated that the seepage basin was an active treatment zone, removing ≥95% of the total RAs, FAs, MTs, and CPs monitored. In combination with a slow seepage rate, this activity should have provided a considerable degree of protection for underlying ground water. Colour was not reduced to a practically useful extent, and therefore colour removal by effluent-sediment interactions were necessary to prevent ground water contamination.

The mechanisms responsible for the disappearance of EOs and CPs were not determined. However, the appearance of compounds which were plausible metabolites of MTs, RAs, and (to

a lesser extent) CPs, was evidence of some biodegradative removal. Volatilisation was probably responsible for some of the disappearance of MT hydrocarbons.

Proof of biodegradation on a field scale is difficult, and for this study was limited to the detection of plausible intermediates. This does not represent definitive proof (Madsen 1991), and therefore the nature of the mechanisms responsible for the observed removals from the aqueous phase of the pond, in particular the balance between biotic and abiotic processes, remained uncertain. However, the results were consistent with a growing body of information on the chemistry of RA degradation (e.g. Zender *et. al.* 1994; Tavendale 1994), adding weight to the probability of degradative removal in the seepage pond.

Deposition of organics with settling biomass was a potentially important abiotic removal mechanism. Investigation of the composition of sediments beneath the seepage ponds, in particular those near the effluent-sediment interface, was required to assess its significance.

The monitoring results showed that the composition of the effluent changed both quantitatively and qualitatively during seepage. The response in ground water chemistry was therefore likely to be complex. Effluent entering the ground in the first few days contained high concentrations of EOs, raising the possibility of significant ground water contamination by these compounds. The role of the sediments and aquifer materials underlying the seepage basins in attenuating and retaining these compounds was therefore important and needed to be investigated. RAs were found to be the slowest class of compounds to disappear from the seepage pond effluent, and were therefore anticipated to be present in highest concentrations in the sub-surface environment beneath the ponds.

Studies of the EO composition of sediments and aquifer materials from beneath the seepage ponds were therefore carried out, and are described in Chapter Five.

Table 4.12: Extractable organics in effluents in the preliminary study

	Drain (mg L^{-1})		J Pond (mg L^{-1})		Q Basin (µg L^{-1})	
Compound	mean	range	mean	range	mean	range
2,5-dimethyl-2-cyclopentenone	0.4	0.1-0.9	0.05	<0.05-0.15	–	–
α-pinene	15	0.3-114	0.03	<0.05-0.29	–	–
dimethyltrisulphide	1.6	<0.1-4.0	0.03	<0.05-0.13	P	–
β-pinene	16	<0.1-142	<0.05	<0.05-0.09	–	–
limonene	1.3	<0.1-3.8	–	–	–	–
2,3-dimethyl-2-cyclopentenone [a]	P	–	0.25	0.07-0.66	P	–
p-cymene [a]	P	–	P	–	P	–
2,3,5-trimethyl-2-cyclopentenone	0.63	<0.1-1.0	0.36	0.1-1.0	22	15-32
2,3,4-trimethyl-2-cyclopentenone	P	–	0.16	0.07-0.33	21	17-23
guaiacol	3.6	<0.1-16	–	–	–	–
fenchone	P	–	0.38	<0.1-0.65	P	–
fenchol	2.7	0.5-6.0	0.05	<0.05-0.1	–	–
camphor	P	–	1.1	0.23-1.8	–	–
MT154 UR[b]	0.8	0.15-1.7	P	–	–	–
DHT [b]	–	–	0.65	0.36-1.3	–	–
borneol [c]	3.8	0.47-7.2	0.22	0.06-0.51	–	–
phenylacetic acid [c]	–	–	P	–	–	–
4-terpineol	1.6	0.2-3.4	0.56	0.30-0.87	–	–
α-terpineol	22	3.5-54	4.8	1.9-7.8	–	–
palmitic acid (FA16:0)	1.2	<0.1-7.3	0.13	<0.05-0.34	33	13-45
fichtelite	–	–	<0.05	<0.05-0.13	98	33-220
dehydroabietin	–	–	0.47	0.1-1.2	110	12-350
anteisoheptadecanoic acid (FA17:0)	0.19	<0.1-1.0	P	–	P	–
1,2,3,4-tetrahydroretene	–	–	–	–	13	4-20
pinolenic acid (FA18:3 Δ5,9,12)	0.15	<0.1-1.4	–	–	–	–
linolenic acid (FA18:2)	<0.1	<0.1-0.9	–	–	–	–
linoleic acid (FA18:2)	1.5	<0.1-17	P	–	P	–
oleic acid (FA18:1)	2.5	<0.1-3.0	P	–	P	–
stearic acid (FA18:0)	0.36	<0.1-1.3	0.07	<0.05-0.33	18	7-32
secodehydroabietic acid (isomer 1)	0.38	<0.1-2.6	0.65	0.22-1.2	35	5-140
secodehydroabietic acid (isomer 2)	0.20	<0.1-0.79	0.37	0.18-0.63	21	3-81
8,15-isopimaradienoic acid	–	–	0.52	0.21-1.2	–	–
8,15-pimaradienoic acid	–	–	0.29	0.13-0.51	–	–
pimaric acid [d]	1.1	0.06-5.0	2.4	1.3-4.8	24	11-46
8-pimarenoic acid [d]	–	–	–	–	P	–
sandaracopimaric acid	0.28	<0.1-1.2	0.28	0.1-0.48	10	3-21
8(14)-pimarenoic acid	–	–	0.20	0.08-0.46	–	–

continued over....

Notes: 1) superscripted letters after compound names refer to compounds which co-eluted in the GC-FID chromatograms (e.g. "c" indicates borneol and phenylacetic acid coeluted). GC-MS used to identify which compounds were dominant; 2) P indicates compound was present but not quantifiable due to its low concentration relative to other compounds in the sample; 3) "less than" values (<'s) are approximate quantitation limit estimates.

Table 4.12 (cont.): Extractable organics in effluents in the preliminary study

	Drain (mg L^{-1})		J Pond (mg L^{-1})		Q Basin (µg L^{-1})	
Compound	Mean	Range	Mean	Range	Mean	Range
13-abietenoic acid [e]	–	–	1.7	0.67-4.6	24	9-48
isopimaric acid [e]	0.46	<0.1-2.3	–	–	–	–
palustric acid [e]	0.64	<0.1-3.1	–	–	–	–
abietanoic acid [f]	–	–	2.0	<0.1-8.1	110	58-170
7-oxokauranoic acid [f]	–	–	–	–	P	–
6,8,11,13-abietatetraenoic acid [f]	0.36	<0.1-1.9	P	–	P	–
dehydroabietic acid	2.8	0.1-11	11	3.6-24	45	24-55
arachidic acid (FA20:0)	P	–	P	–	30	17-61
abietic acid	2.2	<0.1-17	0.62	<0.1-2.8	–	–
neoabietic acid	0.1	<0.1-1.6	–	–	–	–
13β-hydroxyabietanoic acid	–	–	2.1	0.8-4.0	–	–
7-oxodehydroabietic acid	P	–	0.62	0.16-1.4	P	–
behenic acid (FA22:0)	P	–	P	–	51	26-77
lignoceric acid (FA24:0)	P	–	P	–	29	14-52

Notes: 1) superscripted letters after compound names refer to compounds which co-eluted in the GC-FID chromatograms (e.g. "c" indicates borneol and phenylacetic acid coeluted). GC-MS used to identify which compounds were dominant; 2) P indicates compound was present but not quantifiable due to its low concentration relative to other compounds in the sample; 3) "less than" values (<'s) are approximate quantitation limit estimates.

Table 4.13: P7 Seepage Basin effluent monitoring summary data

Date 1988	Days from pond full	Na mg/L	Colour CPU	Total MCP µg/L	Total MT µg/L	Total FA µg/L	Total RA µg/L	Total CP µg/L	Total CG µg/L	Total CV µg/L	Total CC µg/L	DCHB µg/L	Total CPh µg/L
02-11	-4	190	764	NQ	NQ	69	196	NA	NA	NA	NA	NA	NA
04-11	-2	296	NA	414	8278	7676	16392	24	110	83	19	17.1	253
05-11	-1	564	2327	686	15102	22691	52802	58	261	236	32	46.0	634
06-11	0	661	4338	737	15182	20833	44633	84	380	331	44	64.2	904
07-11	1	614	3892	630	12879	16624	39408	65	290	294	44	55.6	748
08-11	2	641	3851	657	13220	14699	46448	61	233	240	40	51.3	626
09-11	3	636	3938	673	13300	13442	43629	65	230	233	41	49.6	618
10-11	4	644	4050	438	7452	9097	37938	43	86	144	55	36.5	364
12-11	6	448	2813	328	6292	5166	26385	36	98	139	45	30.5	348
16-11	10	494	3000	128	4283	1385	26153	27	36	80	50	24.8	219
19-11	13	445	2700	220	2636	506	23801	12	12	10	42	7.2	84
20-11	14	340	1913	97	1750	335	16921	8.4	6.7	8.1	35	5.1	63
21-11	15	337	1800	92	1250	157	16417	6.0	6.0	7.5	31	4.4	54
22-11	16	343	1973	201	1252	366	17153	6.0	6.4	6.4	29	3.6	52
23-11	17	358	2089	192	684	246	16537	3.9	6.4	6.3	22	3.2	42
24-11	18	376	2104	146	368	233	14604	3.0	4.2	4.6	30	0.8	42
25-11	19	377	2160	159	221	171	14725	3.0	4.5	3.9	29	0.6	41
26-11	20	393	2122	146	83	170	14156	2.8	4.7	3.8	28	1.0	40
27-11	21	392	2180	152	84	194	10205	2.8	4.9	4.5	30	1.8	44
29-11	23	202	1087	19	13	145	1047	0.7	3.8	0.7	8.1	0.9	14
01-12	25	199	1103	23	17	125	1059	0.6	3.4	0.7	8.0	0.9	14
05-12	29	181	878	5.9	2	94	489	0.5	2.1	0.2	4.5	0.7	8
07-12	31	177	845	5.2	NQ	68	260	0.2	1.6	0.2	4.8	0.3	7
08-12	32	177	856	16	NQ	84	238	0.2	1.6	0.2	4.8	0.4	7
12-12	36	206	1017	11	NQ	68	281	0.4	2.1	0.5	8.9	0.8	13
14-12	38	208	1043	9.7	NQ	108	304	0.4	2.5	0.7	8.9	0.6	13
16-12	40	204	1028	9.2	NQ	83	292	0.3	2.5	0.5	7.6	0.7	12
20-12	44	229	1160	3.5	NQ	104	361	0.6	1.6	0.3	9.0	0.7	12

Notes: MCP: methyl-2-cyclopentenones; MT: monoterpenes; FA: fatty acids; RA: resin acids and diterpene hydrocarbons; CP: chlorophenols; CG:chloroguaiacols; CV: chlorovanillins; CC: chlorocatechols; CDHB: dichlorohydroxybenzaldehyde; CPh: Chlorophenolics; NA: not analysed; NQ: not quantifiable (below peak detection threshold)

Chapter Five

Extractable Organics in Sediments and Aquifer Media

5.1 Introduction

The effluent studies described in Chapter 4 found that large reductions in the concentrations of EOs present in the No. 2 effluent occurred in the seepage ponds. The mechanisms responsible for the removal of EOs from the aqueous phase were not definitively established, although the observed RA chemistry was consistent with transformation and degradation.

The effluent studies showed that disappearance of RAs was slow compared with that for MTs, FAs, and CPs. Effluent seepage occurring in the first 15–20 days after effluent addition to the ponds would have exposed the sediments and ground waters beneath the ponds to high concentrations of EOs, in particular RAs. Retention of EOs by the surficial sediments was required to prevent ground water contamination. Assessing the EO chemistry of sediments beneath the seepage basins was therefore considered an important part of the LA system investigations.

5.1.1 Sediment-organic compound interactions in LA systems

Interaction with solid-phase materials is a major factor influencing the transport and fate of organic substances in subsurface environments. Sorption retards the migration of organic solutes in ground water, and may affect the rates, nature, and extent of chemical and biologically-mediated transformation processes. The solid phase may also influence the behaviour of an organic compound by controlling chemical release into the aqueous phase, by providing surface sites for accumulation and immobilisation of microbial biomass (thereby enhancing microbial contact with the compound), or conversely by binding the compound in a way that reduces compound availability to extra-cellular enzymes (Mackay *et al.* 1985; Hutchins *et al.* 1985; Karickhoff 1984).

In LA systems, interaction of organics with sediments reduces the concentrations of organic compounds transported into underlying ground water. The most important processes are sorption and biodegradation. Biodegradation rates can be highly variable and dependent on factors such as redox conditions, the nature of the organic compounds present, and nutrient supply.

The soil environment possesses a wide range of chemical and physical microhabitats capable of supporting a diverse microbiological community. Microbial activity can be stimulated by an effluent application regime of repeated flooding and drying, resulting in effective removal of degradable organics. Prolonged flooding, however, generally results in less effective degradation, and can allow transport of organics through the soil profile and into ground water (Hutchins *et al.* 1984; Hutchins *et al.* 1985). In addition, without frequent aerobic rest periods, during which a substantial portion of the microbial population is removed by death and mineralisation, accumulation of viable and incompletely decomposed microbes and metabolic products at the effluent-sediment interface can occur. This can cause soil plugging, thereby reducing infiltration rates (NCASI 1990).

If degradation rates are low, or degradation incomplete, organic compounds can accumulate in soils and sediments, and mobile compounds can leach to ground water. In anaerobic sediments,

aerobic degradation can slow or even stop, allowing organic compounds which would be readily degraded under aerobic conditions to persist and, if of low mobility, accumulate.

In the Kinleith LA system, the seepage basins were flooded for extended periods with effluent containing high concentrations of organic matter, a combination likely to promote oxygen deficiency in underlying pond sediments. The organic-rich, poorly aerated environment in the sediments beneath the Kinleith seepage ponds was therefore potentially suitable for accumulating effluent-sourced organic compounds and their transformation products. Organic matter, both effluent-sourced and microbially-derived, which was deposited on the floor of the basins, would enhance accumulation of hydrophobic extractable organic compounds in the pond sediments. The sediments were therefore plausible sinks for effluent-derived organics.

5.1.2 Extractable organics in sediments contaminated by BKMEs

The EO composition of receiving water sediments exposed to BKME has been well documented, both overseas (e.g. Fox 1976; Brownlee *et al.* 1977; Yamaoka 1979; Kinae *et al.* 1981; Remberger *et al.* 1990; Lee and Peart 1991; Hynning *et. al.* 1993) and in New Zealand (Panadam-Twigley 1988; Tavendale 1994; Judd *et. al.* 1995; Wilkins *et. al.* 1996).

Sediment EOs are dominated by RAs and diterpene hydrocarbons (DTs), indicating that RAs and their transformation products can accumulate in anaerobic sediments.

Sediments beneath the Kinleith LA system seepage ponds were therefore likely to contain BKME-sourced compounds, particularly RAs and transformed DT metabolites. The resistance of RAs and DTs to degradation in poorly oxygenated environments made these compounds potentially useful markers of effluent movement in the deeper sediments and aquifer media beneath the ponds.

5.1.3 Objectives of the sediment studies

The studies of sediments and shallow aquifer materials were carried out to gain an understanding of the behaviour of effluent-sourced EOs during passage through the sediments beneath the seepage basins by:

1) characterising the chemistry of effluent-derived EOs in the sediments beneath the seepage ponds;

2) measuring EO concentration–depth profiles to assess penetration of effluent–sourced organics into the sediment profile beneath the ponds; and

3) evaluating the use of EOs in sediments and aquifer materials as markers of effluent movement beneath the seepage basins.

5.2 Sampling and Analysis

Sediment samples were taken from beneath three seepage basins (ponds P6 and P7 in the Extension Area, and pond E in the Access Road seepage area) and from three cores recovered

during the drilling of ground water investigation wells beneath and adjacent to seepage basin P7. Samplings are summarised in Table 5.1, and locations are shown in Figure 5.1.

Table 5.1: Sediment sampling summary

Location	Date	Depth (m)	No. samples
Pond P6	April 1985	0–1.4	11
Pond P7	April 1985	0–0.5	5
Pond E	September 1985	0–1.25	26
Bore 10	July 1987	0–13	13
Bore 11	July 1987	0–13	11
Bore 16	July 1987	0–15	11
Pond P7 Pit C3	September 1987	0–3.5	7

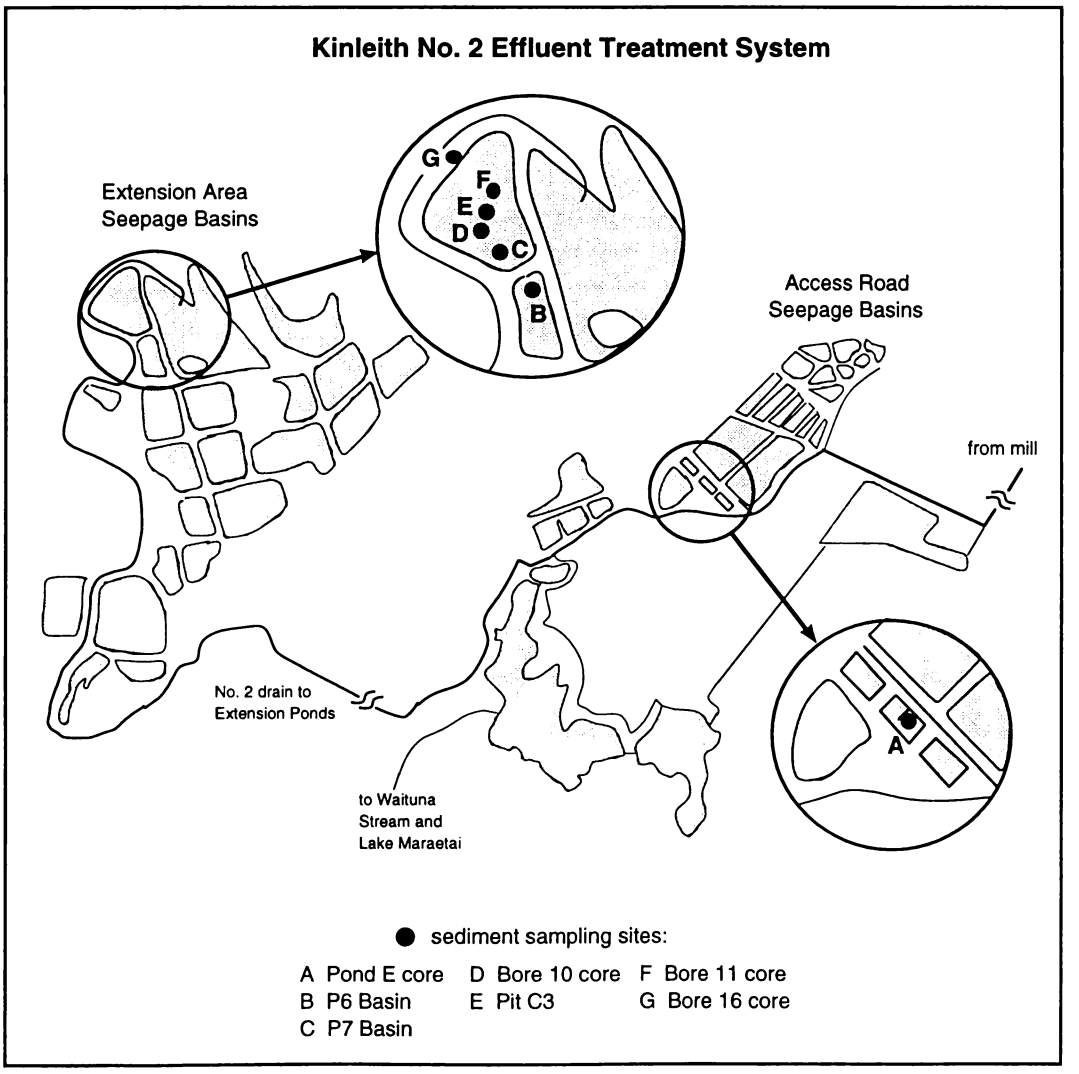


Figure 5.1: Sediment and core sampling locations

5.2.1 Samples taken from beneath ponds P6 and P7

In April 1985, shallow sediment samples were taken from basins P6 and P7 in the Extension Area. Basin P7 was essentially empty, enabling samples to be taken from its floor with a spade. Five surficial samples (top ca. 0.5 m) from basin P7 were composited and used for qualitative characterisation of sediment phase EOs.

Basin P6 contained a small amount of ponded effluent. A post-hole borer was used to recover 11 samples from depths between 0 and 1.4 m beneath ground level from a position immediately adjacent to the ponded effluent. These samples were quantitatively analysed to obtain a coarse concentration versus depth profile.

The surficial sediments beneath basins P6 and P7 were disturbed samples, having been annually disced to depths of ≤0.8 m to regenerate permeability in the seepage basins (section 1.4.1).

In September 1987, Groundwater Consultants of New Zealand (GCNZ), under contract to NZFP, used a mechanical backhoe to excavate four pits 3.5–4.5 m deep in basin P7. These pits were used to examine the geology of the sediments beneath the seepage basin and to assess infiltration rates at various depths in the sediment profile. Sediment samples from selected depths in one of these pits, "Pit C3", were taken by NZFP staff and provided for analysis of EOs. The nature of the materials encountered, the infiltration rates measured by GCNZ, and the depths from which sediments were taken for EO analysis are shown in Figure 5.2.

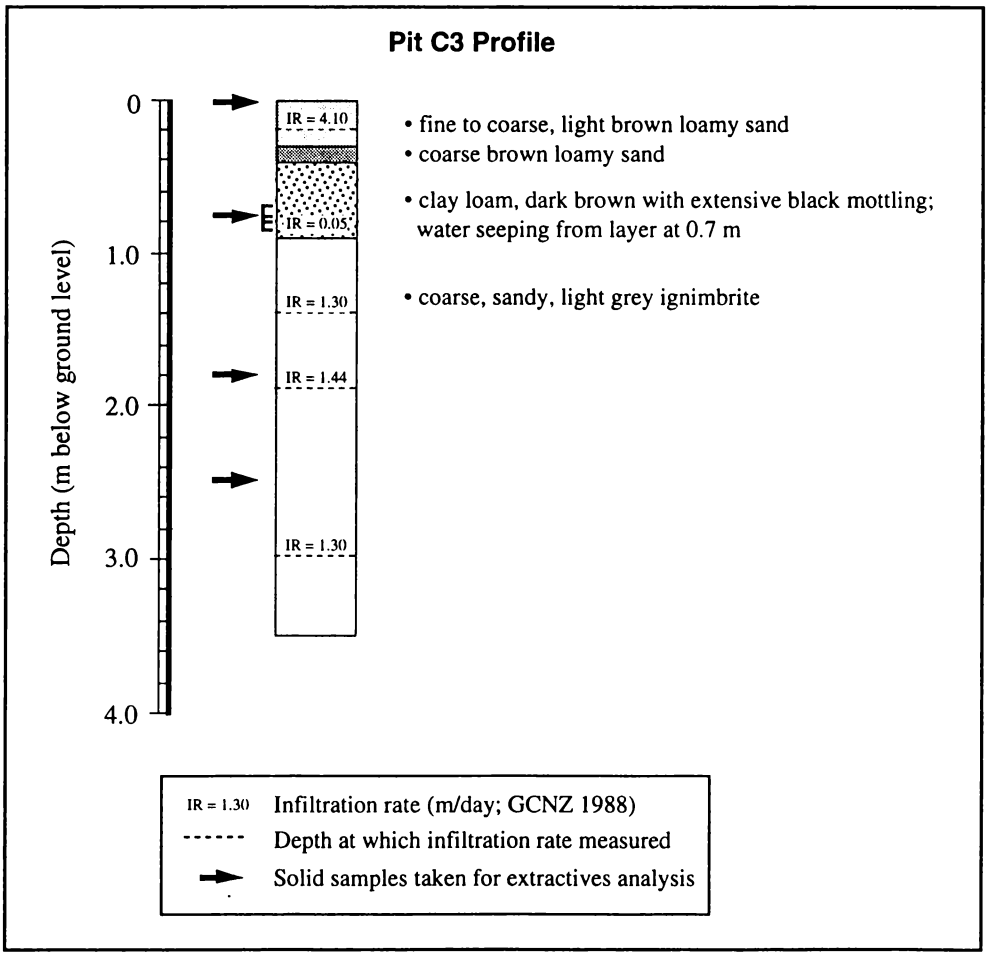


Figure 5.2: Pit C3 sediment profile showing infiltration rates and sediment sampling depths

5.2.2 Samples from beneath seepage Pond E

In September 1985, a core sample from beneath seepage Pond E in the Access Road basin system (Figure 5.1) was taken. A 50 mm diameter PVC piston corer, similar to that described by Munch and Killey (1985), was used to retrieve an intact core, 1.25 m in length. This was sectioned in the laboratory to provide 30 samples from discrete zones, 26 of which were quantitatively analysed for EOs. The core is described in Figure 5.3.

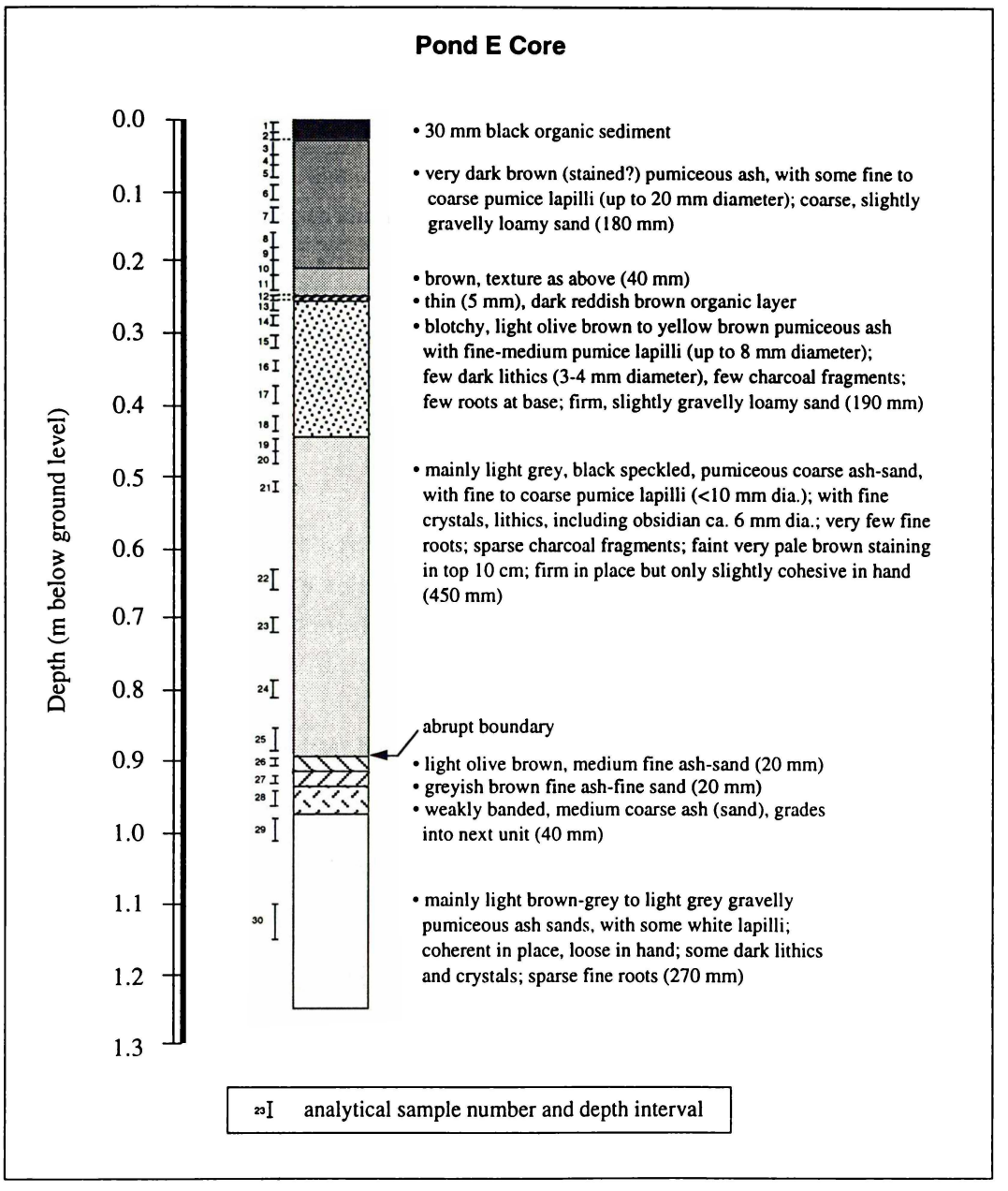


Figure 5.3: Pond E sediment core showing samples analysed for extractable organics

In contrast to basins P6 and P7, the sediments sampled from beneath Pond E were undisturbed. The core was taken from immediately adjacent to a pier which extended over the pond, a position which earthworking equipment would have found difficult to reach. The Pond E core therefore allowed measurement of the distribution of organic compounds in an undisturbed sediment profile, and examination of materials at the effluent-sediment interface to be examined to assess whether deposition of EOs was occurring at this boundary.

When sampled, approximately 1 m of ponded effluent, of unknown history, covered the floor of the basin. The EO composition of this effluent showed it to be substantially degraded, containing relatively low concentrations of RAs, mainly transformed species totalling ca. 400 $\mu g\ L^{-1}$. Based on the degradability of effluent extractable organics in the seepage ponds (section 4.3), pond E had not received any fresh effluent additions for at least 20–25 days.

5.2.3 Samples taken from borehole cores

In July 1987, seven ground water investigation wells were drilled beneath and adjacent to seepage basin P7. Cores were recovered from three holes; bores 10, 11 and 16 (Figure 5.1). Solid phase samples (11-13 samples from each core), taken from depths between 0 and 12 m beneath ground level, were analysed for EOs. Figures 5.4, 5.5, and 5.6 depict the appearance of these cores and indicate sampling depths. The relative positions of ground water sampling well screens and ground water levels are also shown.

More detailed technical descriptions of the geology and hydrological properties of aquifer materials and sediments beneath the seepage basins are given in consulting reports (GCNZ 1987a; Beca Simons 1988).

5.2.4 Sample processing and analysis

Sediment samples from beneath seepage basins P6 and P7 were placed into plastic bags, as much air as possible squeezed out, and the bags secured with ties. Core samples from bores 10, 11, and 16, and infiltration Pit C3 samples were received from NZFP in similar packages. Samples were stored frozen until analysis.

Some samples showed visible signs of alteration upon removal from the ground. Black material became paler and the outer materials exposed to residual air in the bags turned brown. When each sample was sectioned, the altered appearance was found to be confined to a thin (<3 mm) crust, beneath which the black parent material remained. Samples for analysis were therefore taken from the inner portions of the bagged bulk samples, to minimise the potential effects of sample alteration from sampling and storage.

The core from Pond E was sliced longitudinally with a fine wire, the two halves firmly wrapped in plastic film, and cold stored overnight at 4 °C. Samples from 30 measured depths were then removed and stored frozen in glass jars until extraction. EOs were analysed by the procedures described in sections 3.6.

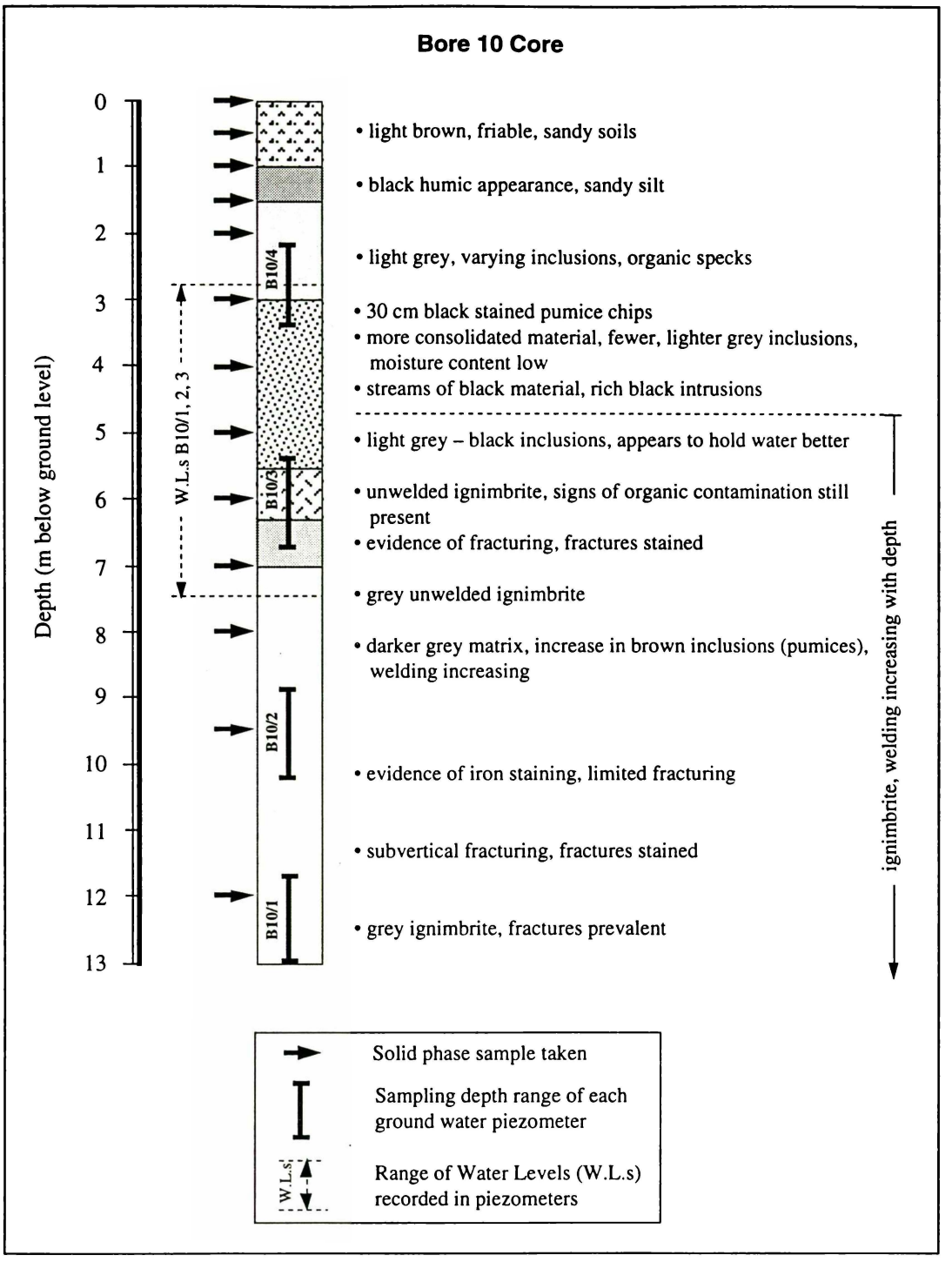


Figure 5.4: Description of core from borehole B10 showing sampling points

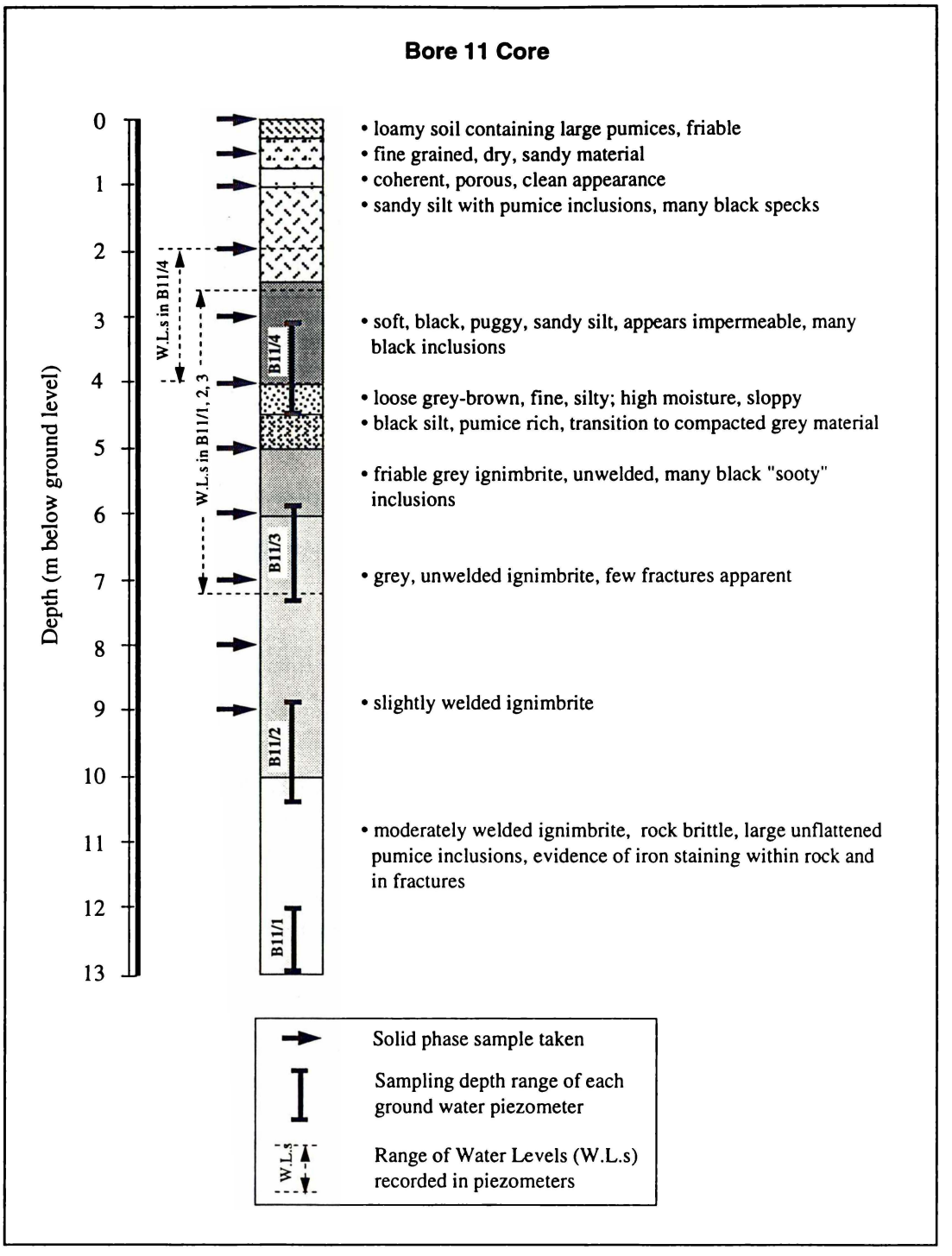


Figure 5.5: Description of core from borehole B11 showing sampling points

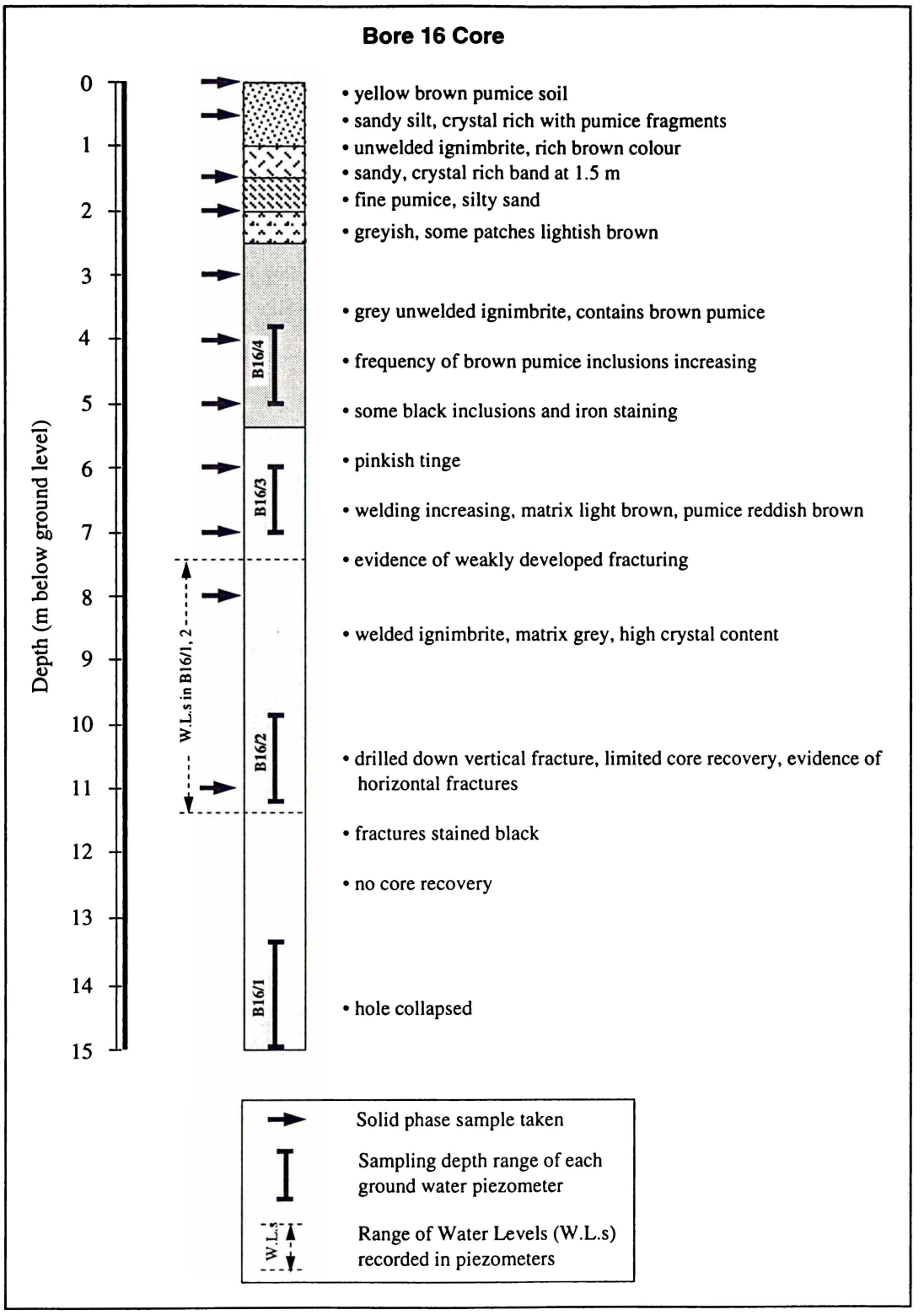


Figure 5.6: Description of core from borehole B16 showing sampling points

5.3 Extractable Organics in Sediments and Aquifer Media

Sediment and aquifer media extracts were dominated by DTs and RAs. FAs and sterols were also significant components. Figure 5.7, a GC-MSD chromatogram of EOs recovered from surficial sediments underlying seepage Pond E, shows a typical distribution of compounds detected.

5.3.1 Diterpene hydrocarbons

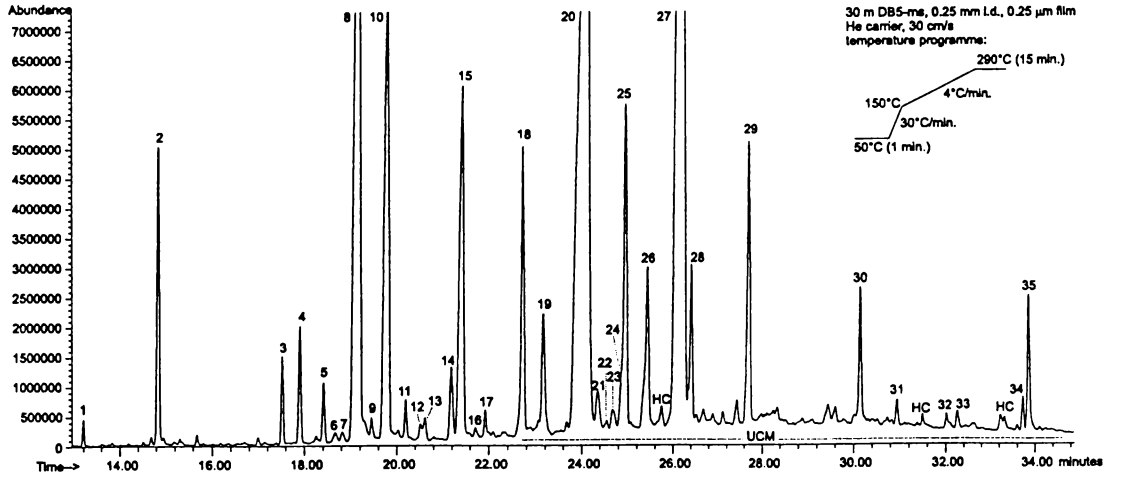
Four compounds, fichtelite *[87]*, dehydroabietin *[90]*, 1,2,3,4-tetrahydroretene *[98]*, and retene *[105]*, collectively constituted >95% of the total DT fraction. Close examination of GC-MSD chromatograms enabled a range of quantitatively minor, structurally related compounds to be tentatively identified. These included:

DT270 species

Two compounds of molecular weight (mw) 270 were found. Mass spectral features of one of these was consistent with the published spectrum of dehydroabietane *[95]* (Kitadani *et al.* 1970; Tan and Heit 1981), a DT found in both plants and sediments (La Fleur 1983). No structural assignment for the second compound *[116]* could be made from its mass spectrum.

DT 262 compounds

Three DTs of mw=262 were found. Fichtelite *[87]* was the major species. The other two compounds had mass spectra consistent with saturated diterpene hydrocarbons with pimarane, DT262P *[79]*, or sandaracopimarane/isopimarane, DT262S/I *[80]*, skeletons (Barrick and Hedges 1981).



Peaks:

1. FA14:0 *[75]*; 2. HC18 internal standard; 3. FA16:0 *[81]*; 4. DT262P *[79]*; 5. DT262I/S *[80]*; 6. DT242P *[82]*; 7. DT260 *[86]*; 8. fichtelite *[87]*; 9. DT254 *[88]*; 10. dehydroabietin *[90]*; 11. Caxtonellite *[93]*; 12. dehydroabietane *[95]*; 13. S_8 *[96]*; 14. DT236 *[97]*; 15. tetrahydroretene *[98]*; 16. DT254 *[99]*; 17. FA18:0 *[102]*; 18. seco-dehydroabietic acid #1 *[103]*; 19. seco-dehydroabietic acid #2 *[104]*; 20. retene *[105]*; 21. DT236 *[106]*; 22. chlorodehydroabietin *[114]*; 23. DT254 *[115]*; 24. DT270 *[116]*; 25. pimaranoic acid *[119]*; 26. isopimaranoic acid *[122]*; 27. abietanoic acid *[127]*; 28. dehydroabietic acid *[128]*; 29. HC24 standard; 30. FA22:0 *[138]*; 31. 7-oxodehydroabietic acid *[139]*; 32. FA23:0; 33. RA350? *[146]*; 34. 12,14-dichlorodehydroabietic acid *[143]*; 35. FA24:0 *[144]*. HC. hydrocarbons above UCM (unresolved complex mixture). All acids detected as methyl esters.

Figure 5.7: GC-MSD TIC of EOs recovered from sediment underlying seepage Pond E.

DT260 compounds

A group of minor compounds of mw=260 were found in some samples. These compounds were probably DTs with one double bond. Two of these *[77]* and *[78]* had almost identical mass spectra showing M^+–15 and M^+–29 fragment ions consistent with losses of the 13-methyl and 13-ethyl radical substituents, losses characteristic of pimarane or isopimarane skeleton RAs. Another showed a *m/z*=217 fragment ion (M^+–43), suggesting an abietane DT, possibly *[84]*.

DT242 compounds

Two mw=242 species were observed. The mass spectrum and gc retention time of the dominant species matched with Caxtonellite *[93]*, a DT isolated from the anaerobic treatment system of a New Zealand tissue paper mill, and and structurally characterised by NMR (Singh-Thandi 1993). A compound with very similar mass spectrum was found in fish from the Gulf of Bothnia and assigned as 10,18{19}-bisnorabieta-8,11,13-triene, a compound with an aromatic ring C (Hynning *et. al.* 1993). The second, minor, DT242 compound was possibly a pimarane analogue *[82]*.

DT236 species

Three minor compounds of mw=236 (e.g. *[97]*) were found. These species may be intermediates in the step-wise oxidation of RAs, for example linking 1,2,3,4-tetrahydroretene and retene via a DT236A (Figure 5.8).

Chlorinated diterpene hydrocarbons

Two compounds with mass spectra consistent with literature data (Hynning *et. al.* 1993) for chlorodehydroabietin *[114]*, and dichlorodehydroabietin *[130]* were found. A third, very minor, compound with mw=272, was possibly chlorotetrahydroretene *[117]*. These compounds were also found at low concentrations in J Pond sediments (Tavendale 1994).

The presence of these chlorinated DTs suggested that both chlorinated and non-chlorinated dehydroabietic acid followed similar transformation pathways in the seepage sediments. Since retene was a major DT constituent in most sediment samples, chlorinated derivatives were expected to be present. However, selected ion searches for chlorinated derivatives of retene were unsuccessful at locating such species.

In summary, the sediments contained four dominant DT compounds and a complex array of minor components, some of which could be tentatively ascribed structures based on mass spectra and literature data from related systems.

5.3.2 Resin acids

The major RAs present were saturated and monoenic species. Saturated species, of which three compounds were found, dominated. Abietanoic acid *[127]* was the major species, and dominated the RA fraction. The structures of the other two saturated compounds were not confirmed, but both possessed mass spectral features consistent with literature data for pimaranoic *[119]* and isopimaranoic *[122]* acids (Chang *et al.* 1971). Three RA monoenes, 13-abietenoic acid *[120]*, 8-isopimarenoic acid *[112]*, and 8-pimarenoic acid *[111]*, were found in

minor quantities. 7-oxodehydroabietic acid *[139]* and the tentatively identified 7-oxokauranoic acid *[126]* were also present as minor components of some samples.

Parent-effluent RAs were relatively minor constituents, only pimaric acid *[110]*, dehydroabietic acid *[128]*, and two secodehydroabietic isomers *[103* and *104]* being found in significant quantities. Of these, dehydroabietic and secodehydroabietic acids were generally dominant. Very minor amounts of 6,8,11,13-abietatetraenoic acid *[125]* were found coeluting with abietanoic acid. 8,15-pimaradienoic acid *[107]* and abietic acid *[131]* were also detected as minor constituents in some samples.

Chlorodehydroabietic acids were found by GC-MSD but could not be unequivocally located in, or quantified from, GC-FID traces due to the minor quantities of these compounds relative to the major constituents. 12,14-dichlorodehydroabietic acid *[143]* was the major chlorinated RA species and was clearly identifiable in the total ion GC-MS analyses. 12-chloro- and 14-chlorodehydroabietic acids *[114]* were also present at lower concentrations.

The RAs and DTs found in the sediments included those found in the drain and seepage pond effluents (Chapter 4). In the sediments, however, more diverse and quantitatively dominant DT chemistry was present. As was found in the effluent studies, both oxidised and reduced transformation RA and DT products were present in the sediments. The compounds found were consistent with those reported in New Zealand kraft mill effluent treatment systems and recipient sediments (Wilkins and Panadam 1987; Panadam-Twigley 1988; Tavendale 1994), and marine sediments contaminated by pulp mill effluent (e.g. Remberger *et al.* 1990; Hynning *et. al.* 1993). The compounds found were also consistent with transformation pathways proposed for the degradation of RAs (e.g. Wakeham *et. al.* 1980; Simoneit 1986; Hynning *et. al.* 1993; Tavendale 1994). Figure 5.8 depicts such as scheme, based on species observed in the Kinleith LA seepage basin sediments.

5.3.3 Fatty acids

FAs, mainly saturated compounds ranging in chain length from FA14:0 *[75]* to FA24:0 *[144]*, were present but were quantitatively minor EOs. Behenic acid *[138]* (FA22:0), lignoceric acid *[144]* (FA24:0), and palmitic acid *[81]* (FA16:0) were the major components.

5.3.4 Sterols and miscellaneous compounds

Two sterols, β-sitosterol *[152]* and a saturated analogue, possibly *[153]* were major constituents in some samples, together constituting up to 10% of the total extractives. These compounds are present in *P. radiata* (Sjostrom 1981; Suckling *et al.* 1990), and have been found as major extractive components in sediments contaminated by pulp mill effluents (Remberger *et al.* 1990). β-sitosterol was also present in the No. 2 effluent.

In addition to these major classes of compounds, sulphur was also present, largely as S_8 *[96]*.

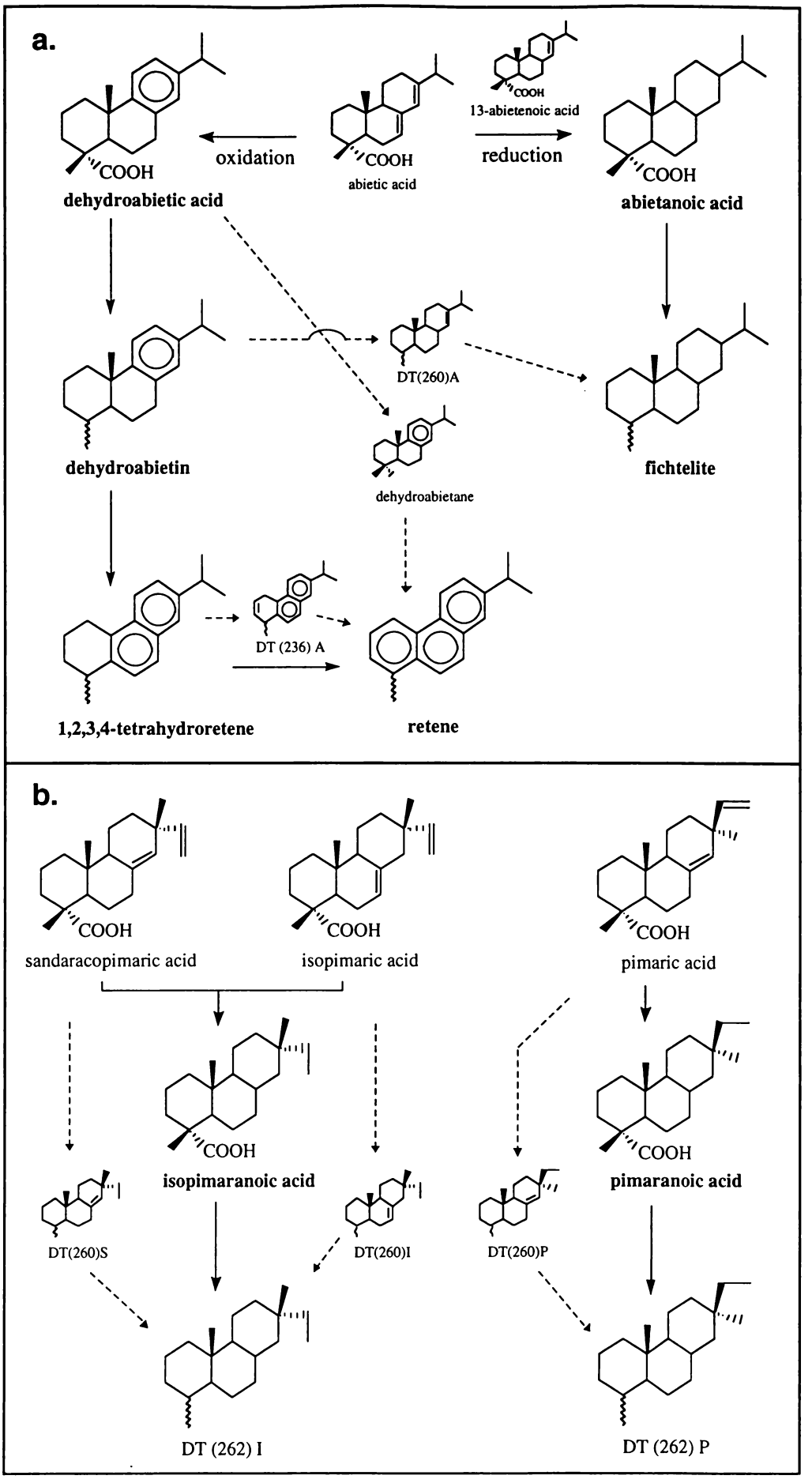


Figure 5.8: Possible resin acid transformation scheme in seepage basin sediments: a) abietanes and b) pimaranes. Major compound names in bold.

5.4 Depth Profiles of Extractable Organics in Surficial Sediments

Concentrations of the major consitituents in the sediment extracts were quantified and depth profiles plotted (Figures 5.9–5.14). Quantitative data are listed in Appendix 2, Tables A2.6–2.11.

5.4.1 EO profiles beneath seepage basin P6

RAs and DTs were present at high concentrations in the surface sample, totalling about 4,000 mg kg^{-1} dry weight sediment (Figure 5.9a). FAs were present at lower concentrations, totalling approximately 400 mg kg^{-1}. Attenuation with depth was rapid, concentrations of <2% of those present at the surface being found at depths between 0.3 and 0.6 m (Figure 5.9b). Concentrations at these depths were similar to "background" levels of 6.7 mg kg^{-1} RAs and DTs, and 7.2 mg kg^{-1} FAs found in a forest soil taken from adjacent to the Extension Area seepage basins. Reductions in RA and FA concentrations with depth were similar (RA = 94.2+10.9xFA; $R^2 = 0.927$).

Concentrations increased significantly below 0.5 m, showing that although EOs were accumulating in the surficial sediments, they were also penetrating the sediments to depths of greater than 1 m. The increases observed below 0.5 m may have reflected the disturbance caused by annual discing (section 1.4.1) and/or the presence of preferential effluent transport pathways through the sediments to deeper zones.

The EO composition varied with depth (Figure 5.9c). Transformed RAs, largely saturated species, dominated the RA and DT fraction. DTs were comparatively minor constituents, although in some samples they collectively made up approximately 30% of the RA and DT fraction. Retene *[105]* and dehydroabietin *[90]* were the major DT compounds.

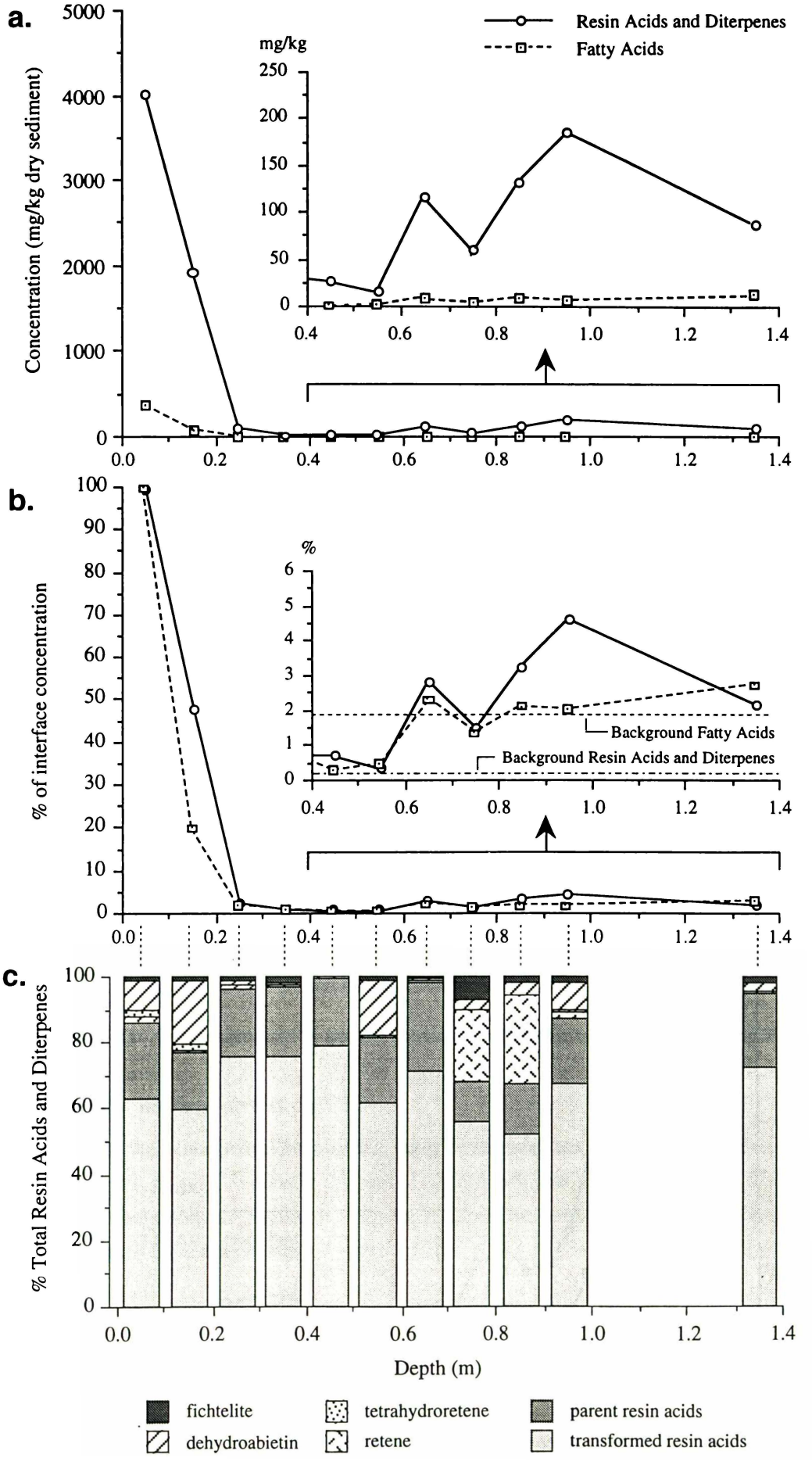


Figure 5.9: Extractable organic profiles in sediments beneath seepage basin P6

5.4.2 Profile of EOs beneath Pond E

Concentrations of RAs and DTs were very high in the surficial sediments, but dropped very rapidly with depth (Figure 5.10a). RA and DT concentrations followed very similar trends with depth (RA = 20.3+0.49 x DT; R^2 = 0.983). Sterols (sum of β–sitosterol *[152]* and its saturated analogue *[153]*) also behaved similarly to RA and DT, while FA reductions were somewhat less rapid (Figure 5.10b).

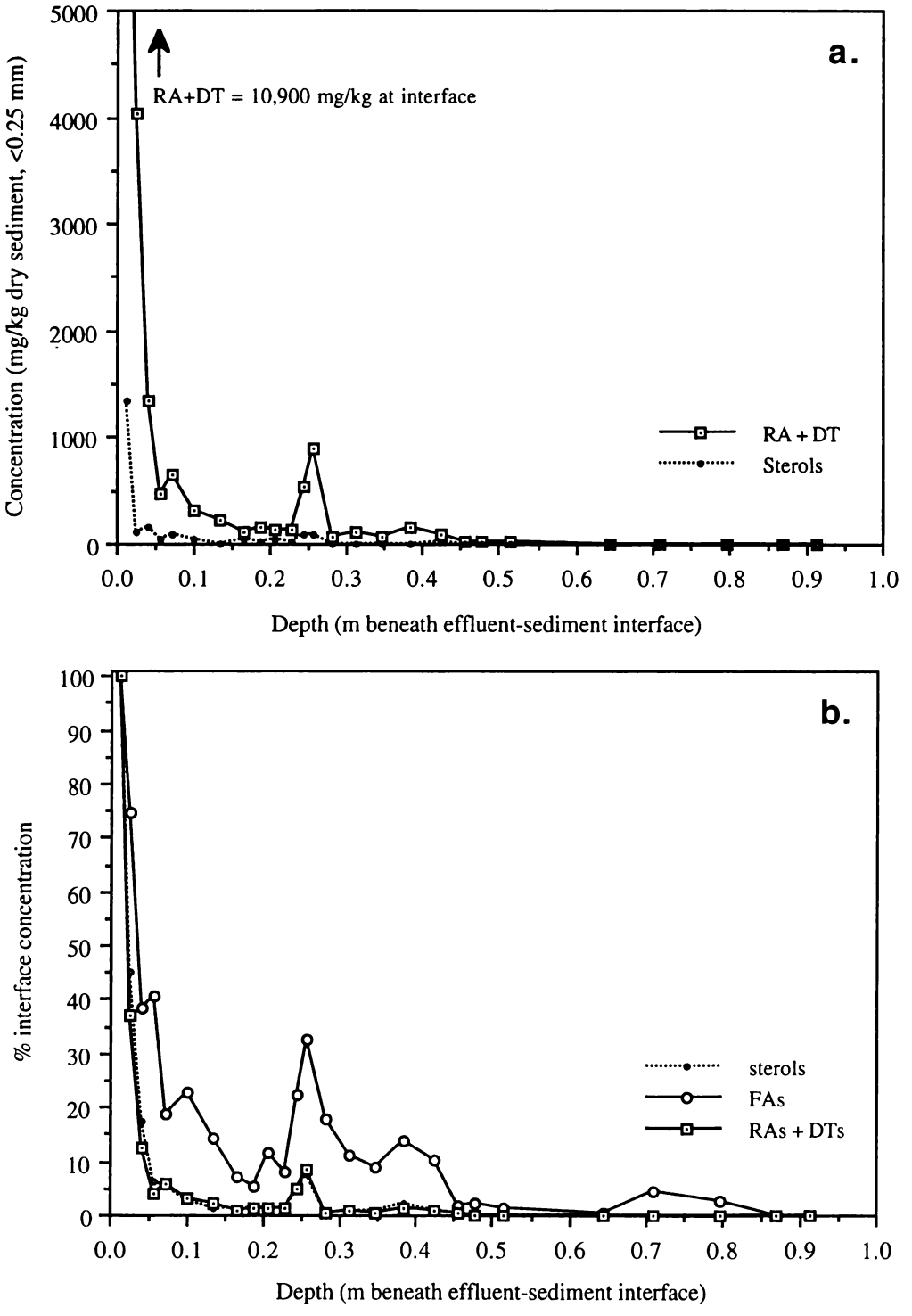


Figure 5.10: EO concentration–depth profiles in sediments beneath Pond E

The high concentrations of EOs were largely confined to the organic sediment layer closest to the effluent-sediment interface (Figure 5.3). However, a significant increase in EOs occurred at a depth of about 0.25 m, coinciding with a thin dark reddish-brown organic textured layer in the sediment core profile. The presence of EOs in this layer at higher concentrations than immediately above or below indicated that some organics were passing through the Taupo pumice sediments, and were accumulating in discrete zones. Composition of the RA and DT fraction varied with depth, but with no consistent trend with depth (Figure 5.11; data from below 0.5 m omitted as concentrations were too low for reliable compositional assessment).

The top 30 mm of the core was fine, black, organic sediment. Approximately 90% of the mass of EOs present in the 1 m of pumiceous sediment beneath the pond was associated with this organic sediment layer. This suggested that filtration or deposition at the effluent–sediment interface was a significant EO removal process.

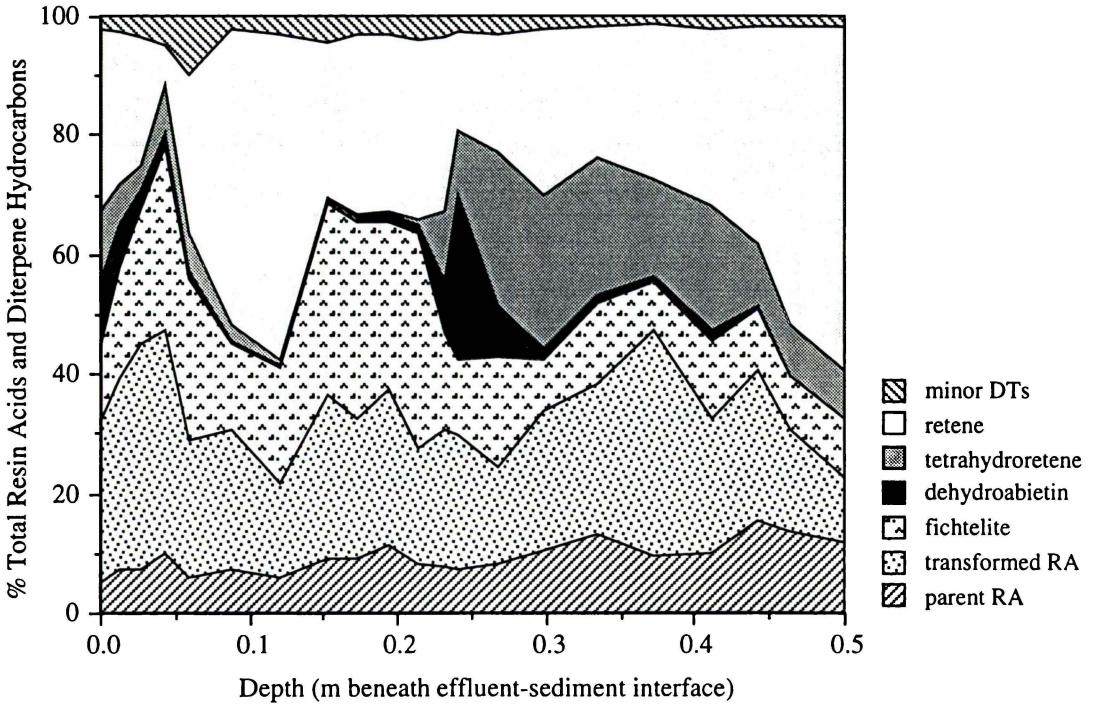


Figure 5.11: Composition of RA and DT fraction in sediments beneath seepage pond E

5.4.3 EOs from infiltration test pit C3

As was found in the other sediment profiles, high concentrations of EOs were present in the surficial sediments of pit C3. Levels decreased with depth, but were also found at elevated concentrations deeper in the sediment (Figure 5.12a). The composition of the RA and DT fraction was again variable with depth (Figure 5.12b).

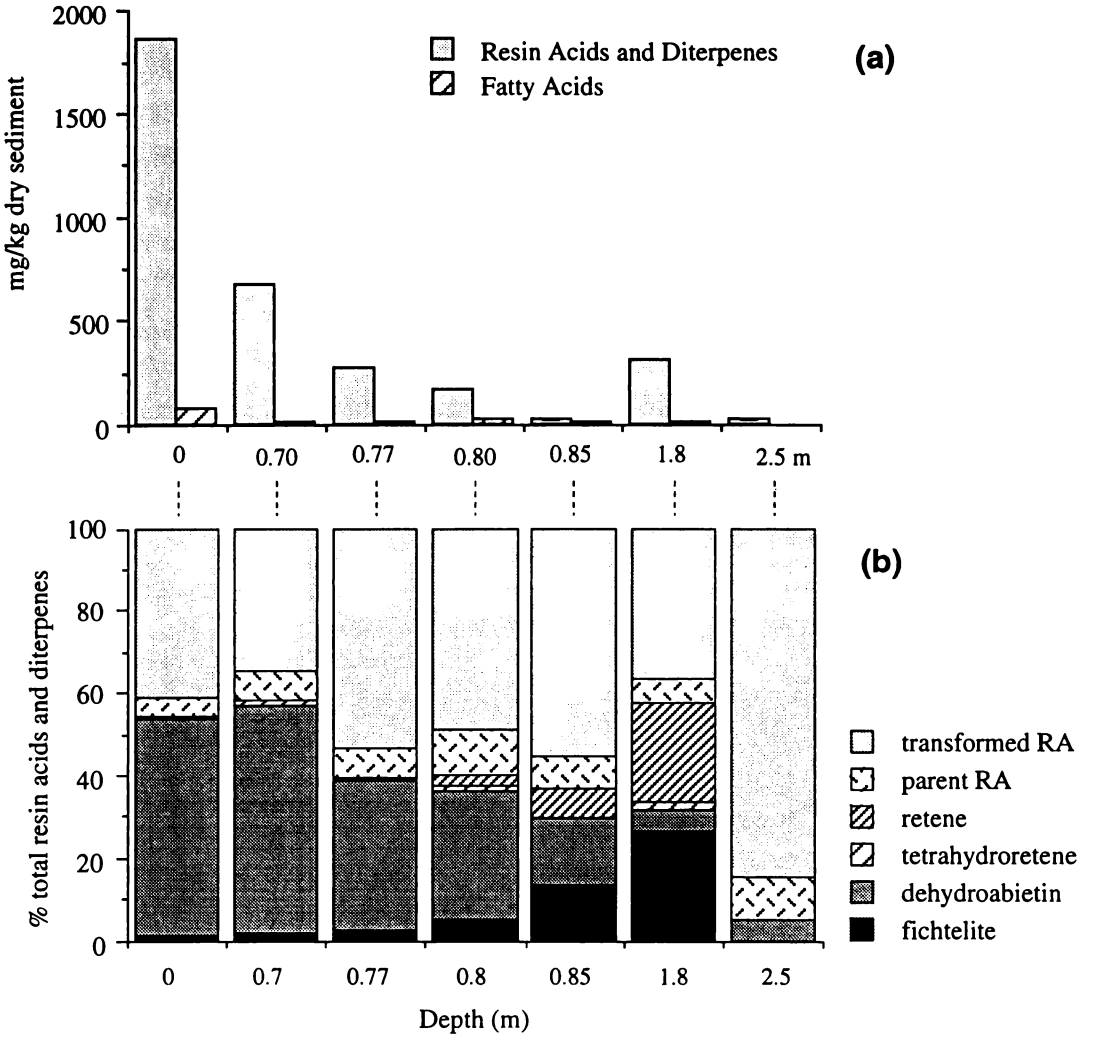


Figure 5.12: Profile of EOs in sediments from infiltration test pit C

5.5 Depth Profiles of Extractable Organics in Bore-hole Cores

5.5.1 Depth profile of EOs from bore 10

The core recovered from bore 10 had three zones (at 0, 1, and 3 m beneath the floor of the seepage basin) which contained elevated concentrations of EOs (Figure 5.13a). It appeared that EOs were being transported through the sediments to zones where accumulation occurred. The sediment at 1 m depth was a black sandy silt (Figure 5.4), while at 3 m, the approximate depth of ground water, a boundary between light grey and black-stained pumiceous material was present.

EO chemistry varied with depth (Figure 5.13b). Most noticeable was the dominance of retene *[105]* in the sediment at 3 m, a depth which coincided with ground water level.

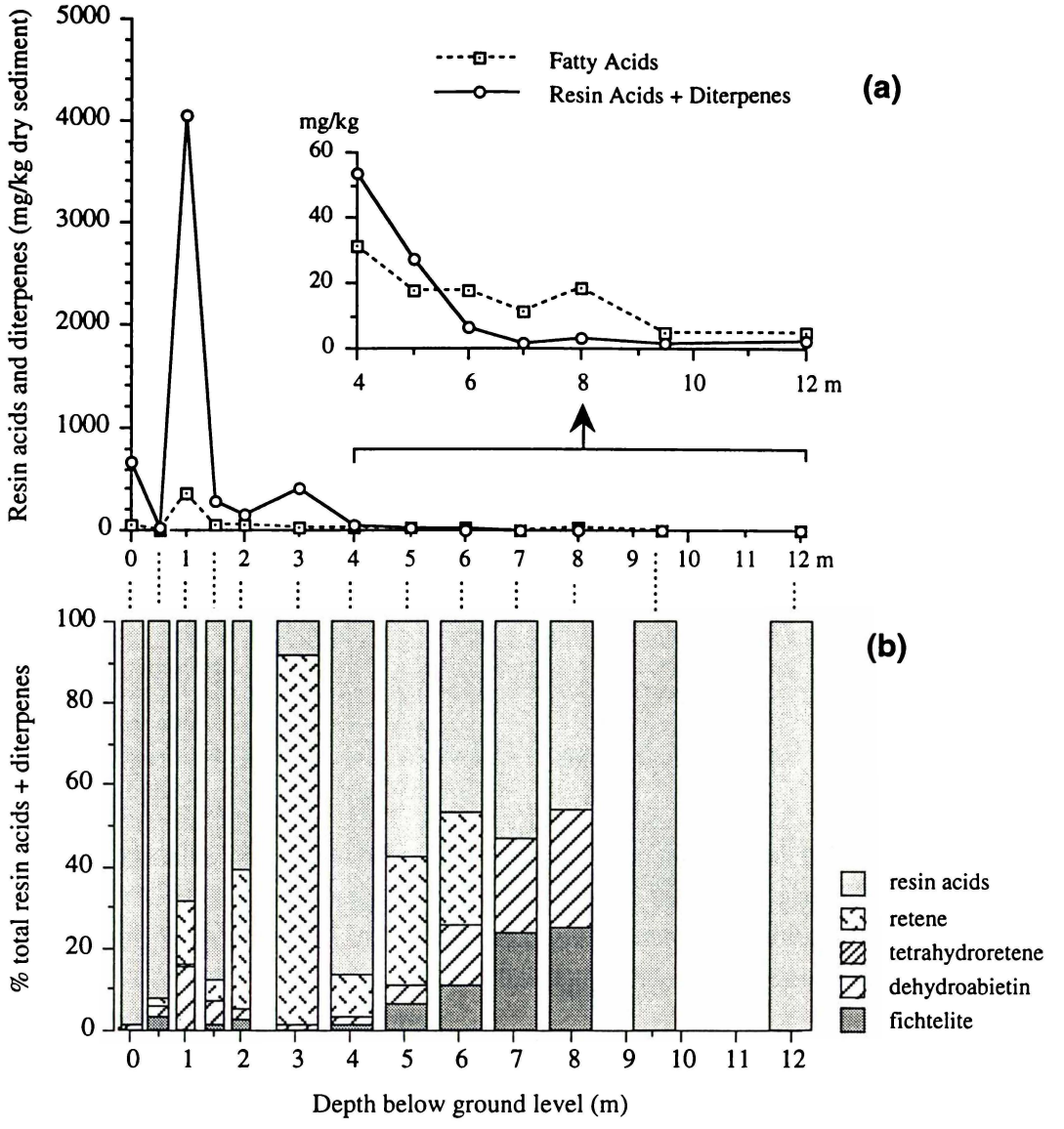


Figure 5.13: Extractable organic profile from bore 10 core

5.5.2 Depth profile of EOs from bore 11

The bore 11 core also contained discrete zones in which EOs had accumulated (Figure 5.14a). These zones, at 3 and 5 m beneath the seepage basin, again coincided with black, silty materials (Figure 5.5). The EO data clearly showed that effluent was being transported through the sediments and aquifer materials in a non-uniform way. The layers in which EOs acumulated appeared to be associated with boundaries between pumiceous sediments and lower-permeability materials. Preferential effluent flow or ponding in these zones of hydraulic restriction was a possible reason for the presence of elevated concentrations of EOs in these areas.

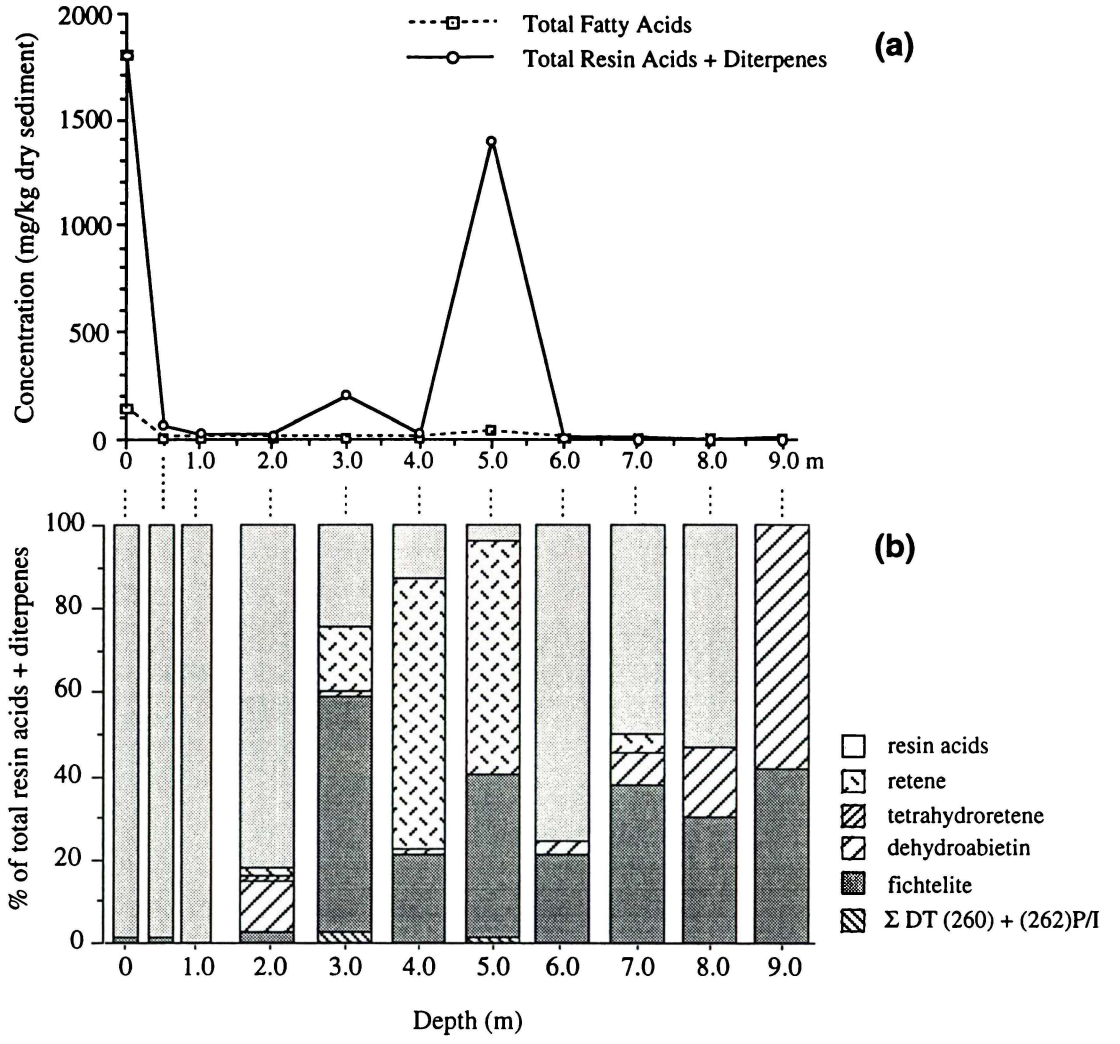


Figure 5.14: Extractable organic profile from bore 11 core

5.5.3 Depth profile of EOs from bore 16

In contrast to the cores from beneath the seepage basin, the sediments in the bore 16 core contained low levels of RAs and FAs (Figure 5.15). No obvious trends with depth were observed. The chemistry and appearance of the core materials indicated that little or no effluent contact with the recovered sediments had occurred. Unfortunately, samples from depths greater than 12 m were not recovered due to collapse of the borehole during drilling. It was subsequently found that ground waters from bore 16/1, which was screened in the 13.3–15 m zone, contained elevated levels of EOs (section 6.5.4). The chemistry of the sediments from this zone would therefore have been of interest.

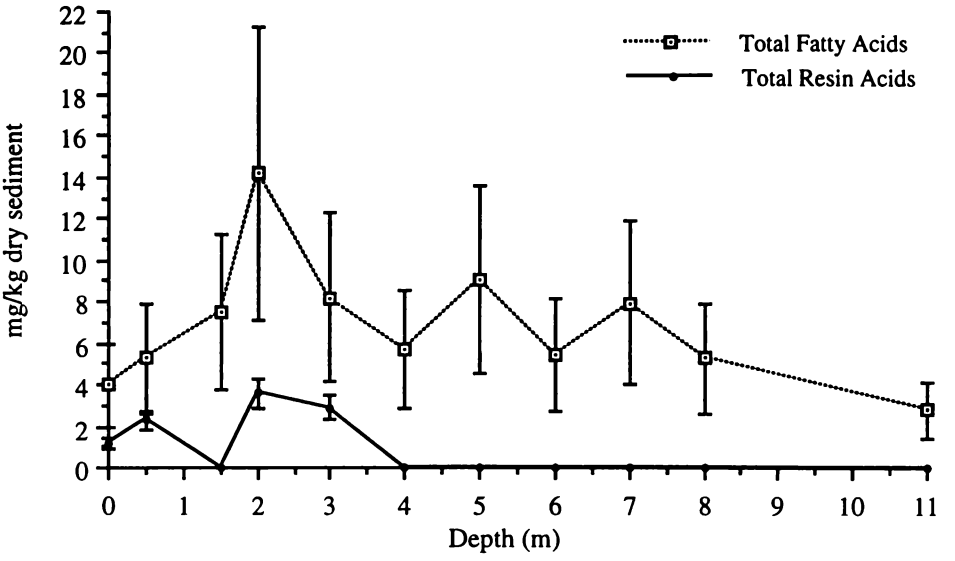


Figure 5.15: Profile of EOs in the core from bore 16. Error bars are analytical 95% confidence intervals.

5.6 Retention and Deposition as EO Removal Mechanisms

Retention of EOs in sediments

High concentrations of EOs were found in sediments beneath the ponds, indicating that retention by sediments was a significant mechanism for EO removal from infiltrating effluent. Estimating how much of the RA input to the seepage system was retained in the sediments was not accurately assessable from the available information. However, a very crude estimate could be made using the following assumptions:

- effluent flow to EA seepage system averaged 10,000 m^3 d^{-1}. Effluent distribution was 50% to EA between 1966–1975 and 100% to EA between 1976–1985.
- seepage was used for 8 months of each year.
- average total RA concentration in No. 2 effluent was 120 g m^{-3} (Stuthridge 1990).
- area of the EA seepage basins = 56 ha.
- average total RA plus DT concentration in the EA sediments was 2,000 mg kg^{-1}, and all was confined to the surficial 0.2 m sediment.
- sediment density 1.25 g cm^{-3}.

Using these assumptions, the total input of RAs to the EA seepage system from 1966–1985 was 4.4×10^6 kg. The total mass of RA plus DT residing in the seepage basin sediments was 2.8×10^5 kg. Based on this estimate, approximately 6% of the RA input was retained in the sediments. This estimate is subject to considerable uncertainty, particularly as long-term average data for RA concentrations in effluent, and average sediment RA and DT levels were not well defined. However, the estimate suggests that there was considerable loss of RAs and transformation products from the seepage system. This was consistent with the large reductions in EOs observed in the effluent studies described in Chapter 4.

Concentrations of sediment-associated extractives generally dropped rapidly with depth beneath the basins, but discrete zones with elevated EO levels were also found.

Possible explanations for this observation included:

a) that there were areas in the sediments which had a greater capacity for organic sorption, possibly related to greater amounts of fine particle size fraction and/or higher organic matter content in these zones, or

b) that these zones may have been in greater contact with infiltrating effluent, either because of their higher permeability (and therefore being effluent migration paths) or because of their lower permeability (and therefore acting as traps for infiltrating effluent).

Whichever the mechanism, the system was clearly not spatially homogeneous.

Deposition as a mechanism for EO removal

Examination of the pond E core revealed a thin (30–50 mm) band of organic sediment at the effluent-sediment interface. The concentrations of RAs and DTs were high in this material, averaging approximately 5,000 mg kg^{-1}. Deposition of effluent-sourced organic matter and accumulation of EOs at the sediment-effluent interface therefore appeared to be occurring. The available data were insufficient to estimate how important this process, relative to other removal mechanisms (e.g. degradation in the ponded effluent) was for EO removal.

5.7 Summary and Conclusions

5.7.1 EO chemistry of effluent-affected sediments and aquifer materials

The EO chemistry of sediments and aquifer materials beneath the seepage basins was dominated by transformed RAs, largely saturated species, and DTs. This chemistry was consistent with that found in natural sediments (e.g. Simoneit 1986), effluent-contaminated sediments in recipients (e.g. Remberger *et al.* 1990; Hynning *et. al.* 1993), and effluent treatment systems (Panadam-Twigley 1988; Tavendale 1994). The proportions of the compounds making up the RA and DT fractions varied substantially between sites and with depth at each site.

5.7.2 EOs as markers of effluent migration beneath the seepage basins

RAs and DTs were sensitive markers of effluent movement beneath the seepage basins. Zones of EO accumulation showed that effluent–sourced organics were penetrating to depths of at least 5 m beneath the ponds, and that effluent movement was not uniform percolation through the sediments. Rather, the results indicated that effluent flow was occurring through discrete, localised, zones in the sediments and aquifer materials. This was consistent with the fractured nature of the sub-surface geology of the area.

5.7.3 Implications of the results for seepage system performance

Despite the high concentrations of EOs found in the sediments, only a relatively small fraction (very approximately 6%) of the effluent–sourced RAs entering the LA system could be

accounted for as RAs and DTs in the seepage basin sediments. The fate of the balance of the EOs was unknown but could have included:

a) degradative removal in the ponds during seepage, as observed in studies described in Chapter 4; and/or
b) aerobic decomposition during the pond discing and resting phase between November and April each year; and/or
c) movement to ground water.

For RAs and DTs to accumulate to the high concentrations observed in the sediments, the sediments beneath the seepage ponds must have been exposed to high concentrations of RAs. The presence of DTs in high concentrations in the sediments but not in the seepage pond effluents (Chapter 4), was evidence that relatively undegraded effluent had penetrated the sediments, where it had undergone anaerobic transformation. This was consistent with the formation of DTs from RAs in anaerobic conditions (Tavendale 1994).

Effluent-sourced EOs were present in the ground at depths below the water table in bores 10 and 11, and therefore ground water contamination by EOs was probable. It was clear that ground water from directly beneath and around the seepage pond system would need to be obtained to assess the nature and extent of the potential contamination. Chapter 6 describes studies of the ground water from directly beneath and immediately adjacent to seepage pond P7. The behaviour of EOs during passage through surficial pumice sediments was further investigated as part of soil-column experiments described in Chapter 7.

Chapter Six

Ground Water Investigations

6.1 Introduction

Effluent-derived RAs and DTs were found in high concentrations in the sediments and shallow aquifer materials directly beneath the seepage ponds. The presence of EOs in discrete zones in these materials below the water table indicated that EOs were reaching ground water, probably by movement through permeable fractured zones in the pumiceous sediments underlying the ponds. Investigations of ground water underlying the seepage system were therefore undertaken to provide information on the effects of the LA system on ground water quality.

Ground waters in two zones were studied. The first was the shallow ground water present in the unconsolidated sediments and shallowest ignimbrite directly beneath the seepage ponds. Investigation of these waters gave measures of the maximum impact of the LA system on ground water quality, and of effluent treatment and modification occurring during infiltration.

The second zone was that present in the ignimbrite aquifers at locations from the perimeter of the pond system to distances of about 3 km down-gradient from the seepage system. Investigation of these ground waters provided information on the transport of effluent away from the ponds, the distribution of effluent-sourced water in the ignimbrite aquifers, and attenuation and modifications to effluent-sourced organic contaminants occurring in the deeper ground water system.

6.1.1 Objectives

The ground water studies were carried out to evaluate the impact of the LA system on ground water quality and investigate effluent modification occurring during infiltration.

The objectives of the ground water studies were to:

1) Determine the effect of infiltrating effluent on ground water chemistry by

- characterising the EO chemistry of ground waters beneath the seepage basins; and
- measuring concentrations of effluent-derived EOs, colour, and sodium in effluent-affected ground waters.

2) Estimate treatment of effluent colour and EOs resulting from effluent percolation through the sediments beneath the ponds, by comparing ground water chemistry with that of overlying seepage pond effluent; and

3) Assess off-site migration of effluent in ground water by measuring EOs, colour, and sodium in ground waters within individual ignimbrite units down gradient from the seepage ponds.

6.2 Ground Water Sampling

6.2.1 Shallow ground waters

An ideal sampling method for shallow ground water studies is one which is rapid, inexpensive, recovers water samples with minimal modification of chemical composition, and is capable of sampling with a high degree of spatial resolution. Methods which minimise disturbance of the sediments during sampler installation are also desirable.

Suction probes and ceramic cups

One technique which had several of the ideal features was the suction probe method, in which a thin metal probe is driven into the sediments and water withdrawn from a port in the probe tip by suction (John *et al.* 1977). This method was tried, but while it worked well in coarse sands (for which the sampler was designed), it was unsuccessful in obtaining water from beneath or adjacent to the seepage ponds. The failure of this sampling approach was probably associated with the depth at which consistently saturated conditions in the sediments were present. While pits dug into the seepage basins revealed narrow zones in the sediment profile from which water seeped (e.g. Figure 5.2), data subsequently collected from drilled wells indicated that water table levels were approximately 2 m or more (e.g. Figures 5.3–5.5).

Sampling from the unconsolidated sediment zone between 0.5 and 3 m beneath seepage pond P7 was also attempted using ceramic cup suction lysimeters (e.g. Stevenson and Beaumont 1984; Everett and McMillion 1985). However, the relatively large volumes (0.5–1 L) of water required for EO analysis were not reliably recovered from these samplers. Successful operation of suction lysimeters requires good contact between the ceramic cup and the fine pore sequences in the soil (Everett *et al.* 1984). To ensure optimal contact under a range of soil texture conditions, a silica flour slurry packing around the cup is recommended (Everett and McMillion 1985). The silica packing was not used in the thesis study because it was felt that silica may have retained or retarded EOs, thus providing samples which were not representative of the ground water. The absence of the silica packing may have been responsible for the inconsistent performance of the samplers. Another potential problem with ceramic cup samplers is their retention of hydrophobic organic contaminants during sampling (Everett *et al.* 1984; Alhajjar *et al.* 1990). Because of these problems, few ceramic cup samples were taken and analysed.

Despite these reservations, ceramic cup samplers have the potential to provide useful data for estimating LA treatment efficiency. They sample from the unsaturated (vadose) zone, and therefore water collected in them represents only infiltrating effluent, enabling direct comparisons with applied effluent composition to be made. They have, therefore, been recommended for monitoring hazardous waste land treatment facilities (Durant *et al.* 1993). The behaviour of BKME organics during ceramic cup sampling would need to be evaluated before adopting them for LA performance monitoring.

Cased wells

Cased wells proved to be a more reliable method for obtaining suitable ground water samples. In August 1987, seven sampling wells around and beneath seepage pond P7 (Figure 6.1) were

installed by rotary wash drilling (Brown Brothers Ltd, Hamilton). Several bores were installed to obtain information on spatial variability of ground water composition. Two bores, B10 and B11, were placed directly beneath pond P7 to obtain vertical profiles of the chemistry of ground water affected by vertical infiltration of effluent.

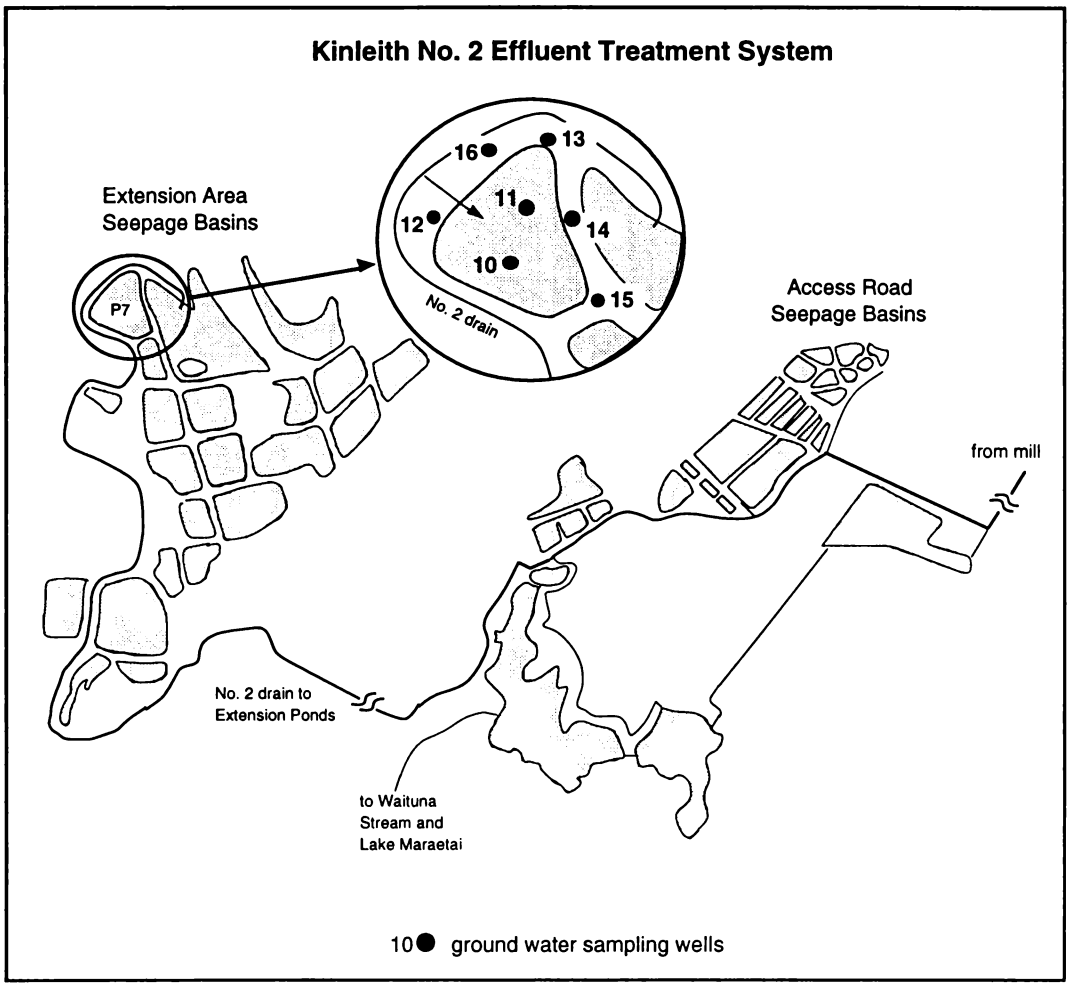


Figure 6.1: Locations of ground water sampling wells placed beneath the EA seepage area

Multi-level well clusters were constructed from 25 mm diameter PVC piezometers. Slotted PVC screens, 1 m in length, were placed in each bore hole at depths between 2 and 15 m below ground level. Each screened section was surrounded with clean gravel (3–10 mm diameter pea metal) topped by 10 cm sand (Perry Aggregates Ltd, Hamilton), and sealed with a 30 cm layer of bentonite. The holes were back-filled to ground level with clean pumiceous ash taken from the site. Bores 10 and 11, which were drilled in the base of the seepage pond, were fitted with steel covers, which were concreted in place. Well construction is shown in Figure 6.2. Each well was assigned a numerical code for its location (bores 10 to 16, Figure 6.1) and depth (/1 to /4, /1 being the deepest well and /4 the shallowest in a given well cluster).

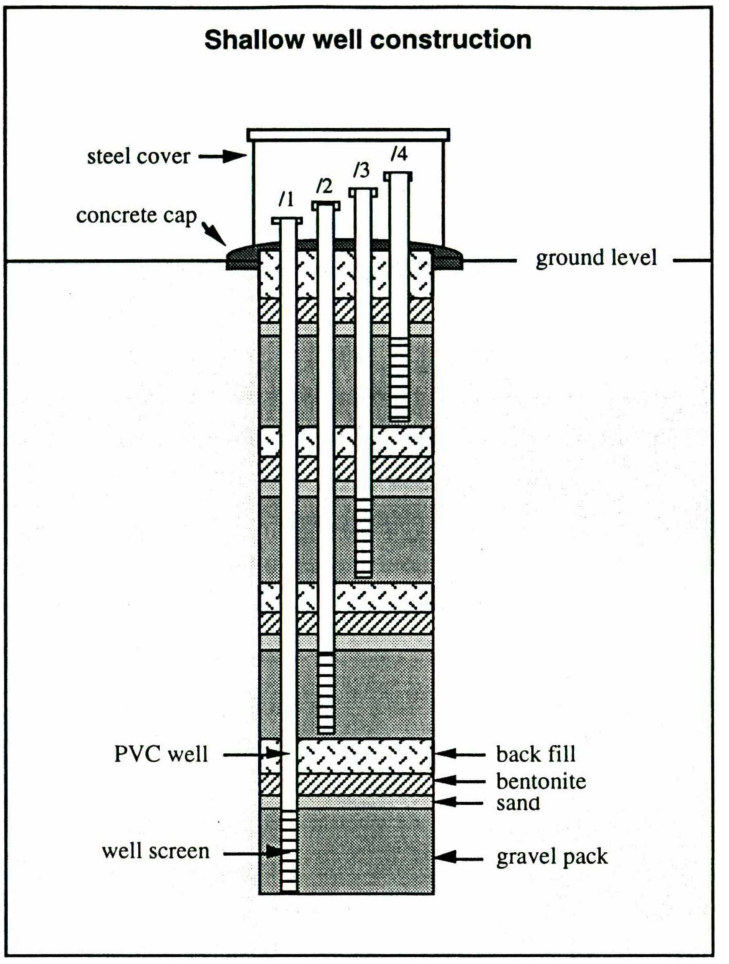


Figure 6.2: Sampling well construction (not to scale)

The multi-level wells enabled ground water to be sampled from discrete depths at each location, providing a vertical profile of ground water chemistry. Cores were recovered from bores 10, 11 and 16 for assessment of sediment stratigraphy and EO chemistry (Figures 5.3–5.5). The sampling depths and elevations (above mean sea level datum; amsl) of the screened sections in these multi-level wells are listed in Tables 6.1 and 6.2, and depicted graphically in Figure 6.3.

Table 6.1a: Sampling depths in ground water monitoring wells beneath seepage pond P7

	Sampling Depth (m below ground level)			
Bore	/1	/2	/3	/4
10	13.0-11.7	10.3-8.9	6.7-5.4	3.3-2.2
11	13.0-12.0	10.4-8.9	7.3-5.9	4.5-3.1
12	11.0-9.7	6.6-5.0		
13	11.0-10.0	6.4-4.5		
14	13.2-11.8	6.7-5.8		
15	13.0-11.8	7.7-6.1		
16	15.0-13.3	11.2-9.9	7.0-6.0	5.0-3.8

Table 6.1b: Elevation of the sampling zones in wells beneath seepage pond P7

	Sampling Elevation (m above mean sea level)			
Bore	/1	/2	/3	/4
10	340.70-342.00	343.40-344.80	347.00-348.30	350.40-351.50
11	340.55-341.55	343.15-344.65	346.25-347.65	349.05-350.45
12	343.60-344.90	348.00-349.60		
13	343.70-344.70	348.00-350.20		
14	342.35-343.75	348.85-349.75		
15	342.50-343.70	347.80-349.40		
16	342.59-344.29	346.39-347.69	350.59-351.59	352.59-353.79

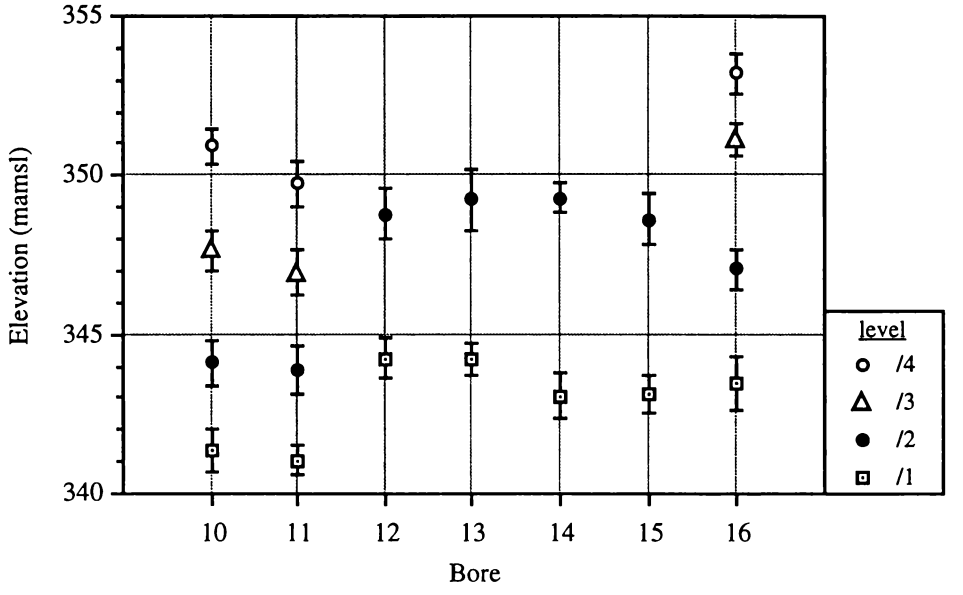


Figure 6.3: Elevations of sampling bores beneath pond P7. Error bars show the range of sampling depths at each level (i.e. the distance between the bentonite seals above and below each screen).

Well construction materials

The most appropriate material for construction of ground water monitoring wells has been the subject of on-going debate in the literature (e.g. Nielsen 1988). The two major issues associated with well construction are contamination of the water sample with substances leached from the well casing or screen packing, and sorption of analytes by well casing materials.

Plastics, in particular PVC and polyethylene (PE), are commonly used casing materials for ground water monitoring wells. Leaching studies of trace organics from plastics have shown that poly-tetrafluoroethylene (PTFE or Teflon) is the least contaminating plastic material (Curran and Tomson 1983), but for most applications, rinsed PVC has proven to be an acceptable alternative to the much more expensive PTFE. Phthalic acid esters are commonly leached from plastic sampling apparatus (e.g. Junk *et al.* 1974). Sorption of organic compounds to PVC has been found to be less than to PTFE (Parker *et al.* 1990). Stainless steel has the least effect on organics, but does leach and sorb various inorganic species. Except in situations where

high concentrations of synthetic organic chemicals such as ketones, esters and aromatics (which degrade PVC) are present, PVC is a cost effective, general purpose well casing material (Nielson 1988; Nacht 1983).

The Kinleith study targeted only pulp mill effluent-derived organic compounds, none of which have been reported to be associated with PVC sampling apparatus. PVC well casings were therefore considered appropriate for the study. Phthalic acid esters, largely *bis*(2-ethylhexyl)phthalate *[145]*, were found in most ground water samples, probably arising from well materials. Cyclohexanone, 2-hexenol, 2-ethylhexanol, and in some samples, 2-ethylhexanoic acid were also found in shallow ground waters (section 6.5.4) and may also have been well construction residuals.

Sampling procedure

Sampling was carried out using a PVC bailer fitted with a glass ball-valve (Nielson and Yeates 1985). Sodium concentrations were measured in sequential samples withdrawn from bore 11/1 to determine the volume of stagnant water present that needed to be removed to obtain a representative ground water sample. Bore 11/1 was chosen because it contained the greatest volume of standing water in its casing, and therefore required most purging. Concentrations were slow to reach steady state on the first purging, but were more rapidly attained on the second sampling (Figure 6.4). This presumably reflected recovery of the aquifer surrounding the well screen after disturbance caused by bore placement.

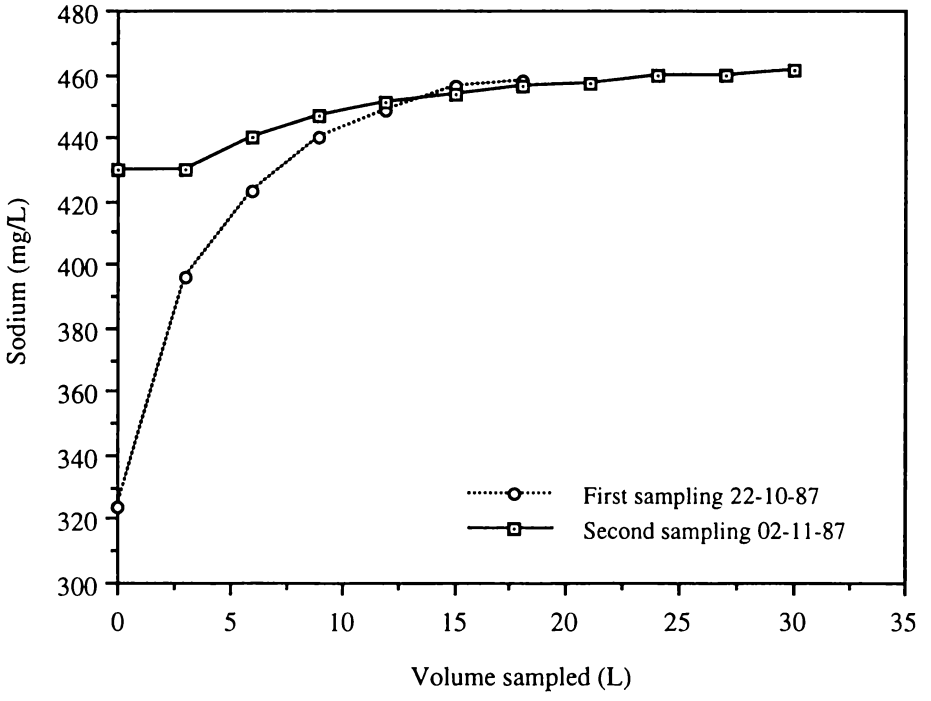


Figure 6.4: Well purging data from bore 11/1 on the first and second samplings

Based on these data, a sampling protocol aimed at obtaining good quality samples in a reasonable time was adopted. Five litres of water were bailed and discarded before collecting a 2.5 L sample for analysis. Based on the sodium data from bore 11/1, samples obtained in this

way contained at least 95% of the maximum "steady state" ground water concentrations. Some wells, such as B15 and the upper level (/4) piezometers in bores 10 and 11, did not always provide enough sample to allow the first 5 L to be purged to waste. For these wells, the first 2.5 L was discarded and an additional 2.5 L taken for analysis.

6.2.2 Off-site ground waters

Well placement

Ground water contamination attenuation with distance from the Extension Area seepage ponds was investigated from waters taken from seven wells shown in Figure 6.5. These wells were cased into individual ignimbrite units so that zones of effluent contamination and migration could be identified. Construction was similar to the shallow wells, piezometers being made of 25 mm i.d. Class E PVC pipe sealed between sampling zones with bentonite, and backfilled with sand. Holes were cased with 100–150 mm diameter steel tubing to the first consolidated ignimbrite unit. Installation and construction details are given in NZFP internal files and consultancy reports (GCNZ 1987; Hassan 1989a; Hassan 1989b). NZFP's numerical well coding has been retained in the descriptions.

Bore 83 was drilled in 1977 (Houghton 1977) and subsequently cleaned to original depths for resampling in June 1988. This well was influenced by seepage from the Access Road basins, and was used to obtain water for analytical method evaluation (section 3.5 and Figure 6.7). Bores 89, and 90 were installed in April 1987, and existing bores 73 and 74 were redeveloped and fitted with multi-level piezometers at this time (GCNZ 1987). Bore 86 was cleaned, deepened into the Marshall B ignimbrite, and equipped with sealed piezometers in June 1988. Bore 94 was drilled in January 1989 (Hassan 1989a). Table 6.2 summarises depth, elevation and aquifer data for these wells. Figure 6.6 schematically depicts the relative elevations of the wells, and their siting in the ignimbrite units.

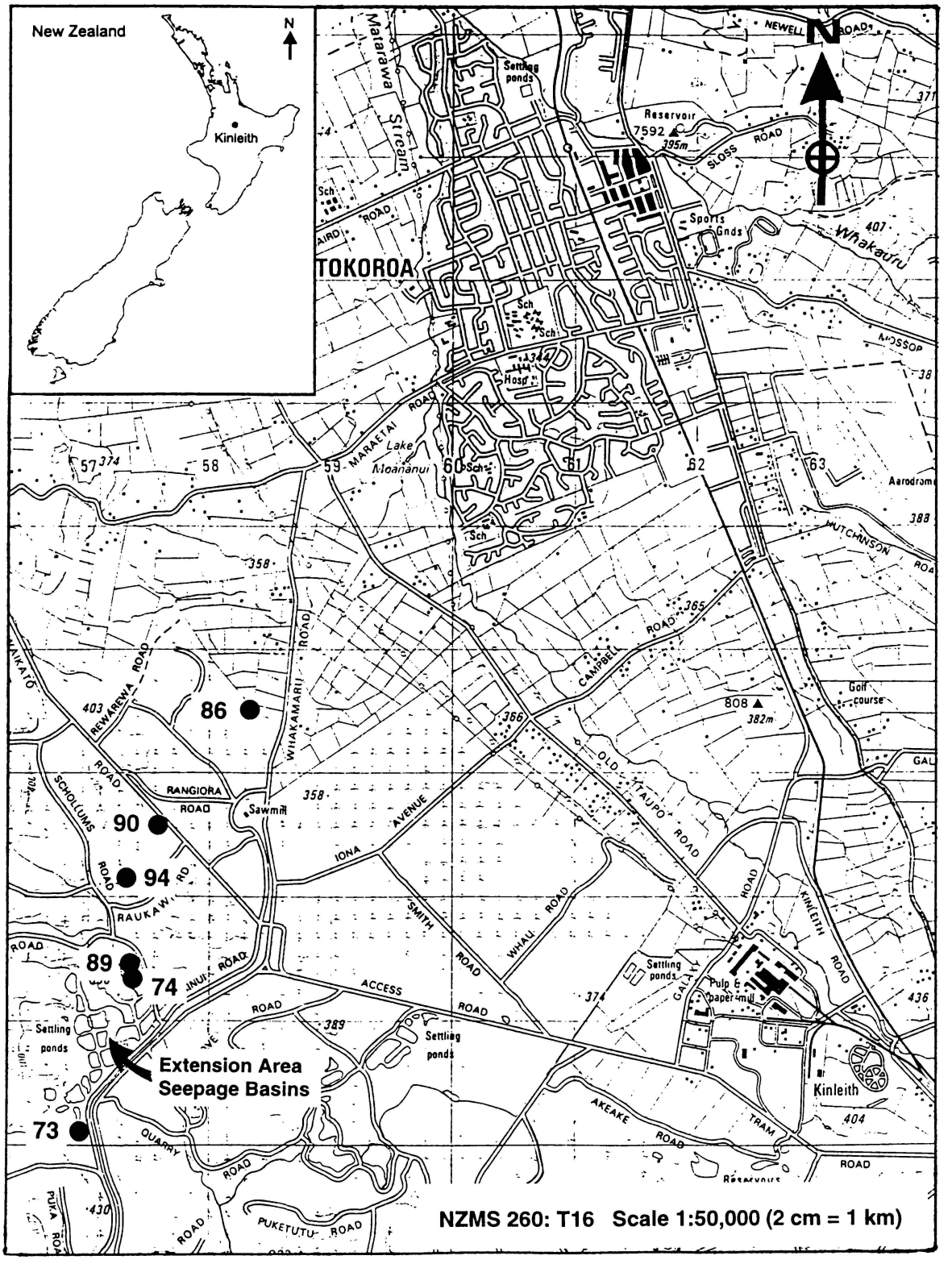


Figure 6.5: Locations of off-site wells sampled in the study

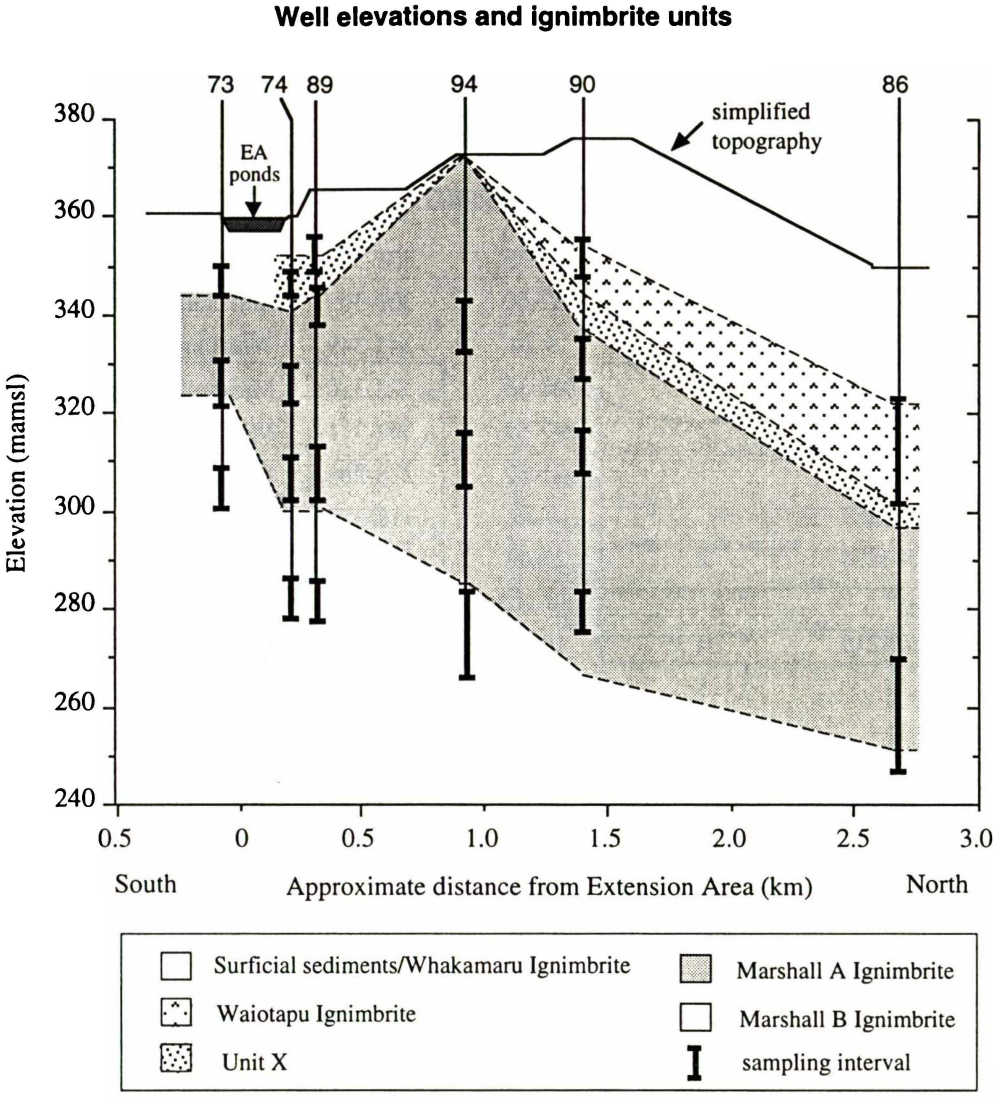


Figure 6.6: Schematic north-south cross section showing relative positions of off-site sampling wells and sampling intervals in major ignimbrite units

Sampling

Wells were sampled by NZFP staff by either compressed air lifting or, for upper level wells in which water levels were below the top of the well screen, by bailing. At least three times the stagnant volume of water in the well was removed by air-lift before taking samples for analysis, while any water present in the upper level wells was taken by bailing and used directly for analysis (Hassan 1989b).

Air-lifting is generally not recommended for ground water sampling because it introduces air into the sampling zone, raising the possibility of losing volatile constituents and promoting oxidation of chemically sensitive species (Nielson and Yeates 1985). The constituents under investigation in this work were not volatile and were not considered susceptible to significant alteration from oxidation during sampling and therefore it was considered adequate for the study.

Table 6.2: Well depths, elevations, and ignimbrite aquifer unit data for off-site wells

Bore	Grid Reference	Level	Sampling Interval[a]		Ignimbrite Unit
NZFP#	NZMS 260 T16	(/)	mbgl	mamsl	
73	569201	3	11-17	344-350	Whakamaru
		2	30-39	321-331	Marshall A (mod. welded)
		1	52-60	300-309	Marshall B
74	574214	4	9-14	344-349	Whakamaru
		3	28-36	322-330	Marshall A (mod. welded)
		2	47-55	302-311	Marshall A (highly welded)
		1	71-80	278-286	Marshall B
83	599227		0-39	318-357	Waiotapu
86	583235	2	27-48	302-323	Waiotapu
		1	80-103	247-270	Marshall A (welded)
89	574215	4	10-17	349-356	Whakamaru/Unit X
		3	20-28	338-346	Marshall A (mod. welded)
		2	53-64	302-313	Marshall A (highly welded)
		1	81-89	277-285	Marshall B
90	576226	4	21-29	347-355	Waiotapu
		3	41-49	327-335	Marshall A (unwelded)
		2	60-68	308-316	Marshall A (welded)
		1	93-101	275-284	Marshall B
94	573222	3	30-41	332-343	Marshall A (welded)
		2	57-68	305-316	Marshall A (unwelded)
		1	90-107	266-283	Marshall B

a: depth interval sampled (gravel packing interval) in metres below ground level (mbgl) and metres above mean sea level (mamsl).

One additional potential problem with the technique is that contaminants can be introduced into the well from the compressor and hoses used. Some compounds which were unrelated to pulp mill effluent (e.g. substituted morpholines and benzothiazoles; section 6.7.3) were observed in some samples, possibly being introduced by the sampling method. Although these compounds did not interfere with the effluent-derived compounds of interest in the present study, future work should avoid using air-lifting for sampling.

Sequential sampling of two wells, bores 83 and 74/1, was carried out to evaluate the effectiveness of the sampling method in obtaining representative ground water data, and to determine repeatability of sampling and analysis procedures. The wells were purged by the standard NZFP procedure, then six 4 L samples collected. The results are summarised in Table 3.4 and shown in Figure 6.7.

Significant increasing trends in sodium, colour and absorbance (270 nm) levels occurred with increasing sampling of bore 74/1, but no such trends were observed for EOs. There were no

observable trends in the concentrations of any monitored analytes in bore 83. The results indicated that analyte behaviour within, and between, each well could be somewhat different. Ground water sampling problems of this kind have been encountered elsewhere (e.g. Rivett *et al.* 1990; Backhus *et. al.* 1993). While not ideal, the variability of the data obtained was considered acceptable for the thesis studies. Calibrating each well for the constituents of interest may be necessary for future work (for example trend monitoring) where reducing variance is critical.

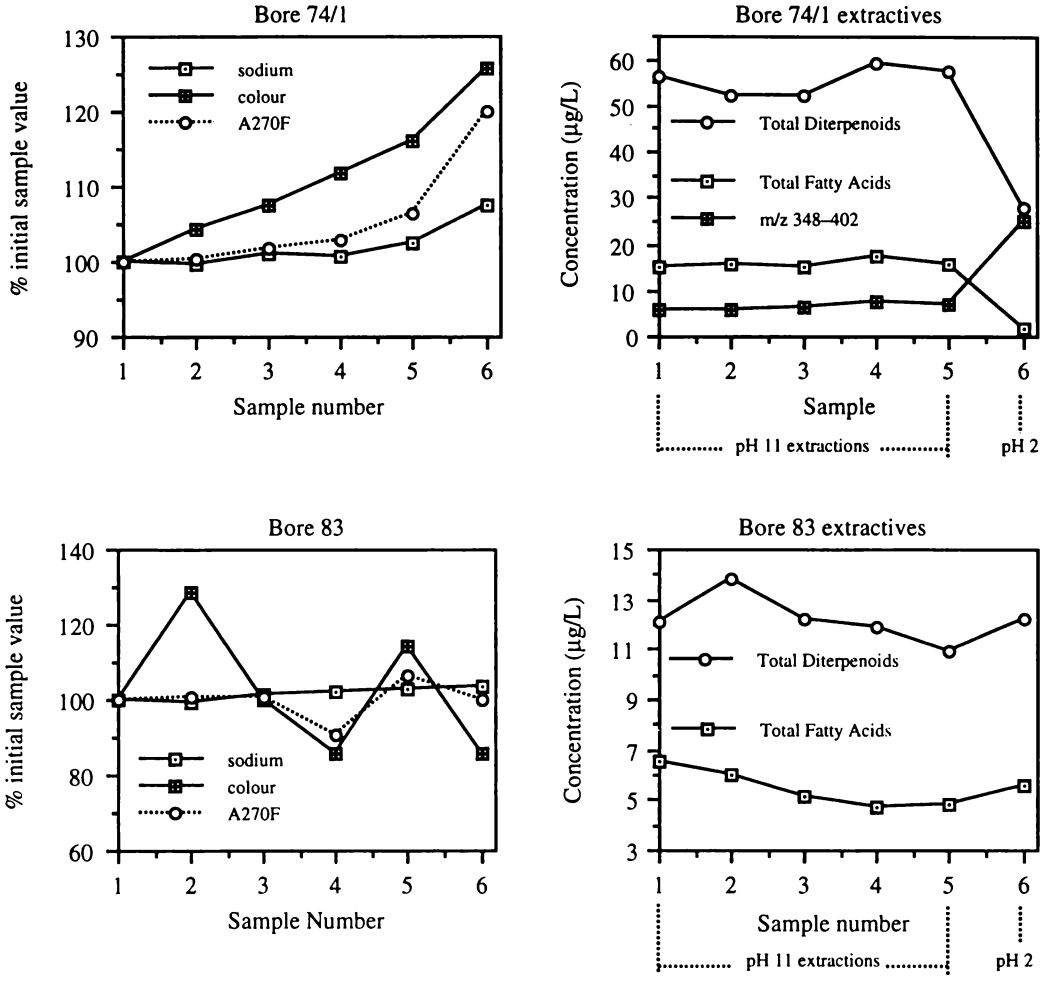


Figure 6.7: Trends in EOs, colour, sodium and absorbance at 270 nm (A270F) in ground waters sequentially sampled from wells 74/1 and 83.

6.3 Analytical procedures

Sodium, chloride, colour, and EOs were analysed by the procedures summarised in Table 6.3. Water levels were measured using a tape fitted with an electronic probe. In addition, five ground water samples taken in 1990 were analysed for adsorbable organic halide (AOX). These analyses were performed by Forest Research Institute Rotorua according to the SCAN-test Standard SCAN-W9-89 (SPPBTC 1989). A small set of preliminary chlorophenolics' data was also obtained using procedures described in section 3.9.2.

Table 6.3: Analytical procedures used in the ground water studies

Determinand	Analytical procedure	Section
extractable organics	Extraction at pH 2 and pH 11; GC-FID-MSD	3.5
sodium	AAS	3.2.1
chloride	ferricyanide method	3.2.2
colour	absorbance at 465 nm and 270 nm	3.2.3

6.4 Shallow Ground Water Study Outline

Three sets of shallow ground water studies were undertaken. The first studies aimed to assess the EO composition, sodium, and colour of ground waters beneath the P7 seepage basin, and to assess hydrology from water levels. EOs were analysed by the pH 2 procedure (section 3.5), and were therefore semi-quantitative assessments. This section of the study gave information about the spatial variations in ground water chemistry under the pond.

EOs, sodium, chloride, and colour were analysed in samples taken in October, November, and December 1987, and in March and July 1988. In addition, NZFP sampled the wells at approximately monthly intervals between October 1987 and October 1988 for sodium analysis. Both sets of data are described in section 6.5.

The second study monitored ground waters from a selection of wells under the pond over a two month period in November/December 1988 to improve quantitative assessment of EO chemistry and to evaluate short-term temporal variability. EOs were analysed by the pH 11 procedure (section 3.5) to obtain more reliable quantitative EO data. The seepage basin monitoring experiment (section 4.4) was also carried out during this period. Ground water chemistry was compared with seepage basin effluent chemistry to determine whether infiltrating effluent was being intercepted in the wells and to estimate effluent treatment occurring during effluent infiltration.

The third work was carried out in October 1990, some 2 years after the last effluent had been applied to the EA seepage basins. Waters from three wells beneath pond P7 were analysed to determine whether contaminant levels had decreased in response to retirement of the seepage system.

The results from each of these sections of work are presented separately in the following sections. Analytical data are tabulated in Appendix 2 (Tables A2.12–A2.18 and A2.21).

6.5 Shallow Ground Water Characteristics from Initial Studies

6.5.1 Water levels

Water levels were recorded to gain an understanding of local hydrology, in particular the relationship between water levels in the bores and effluent loading to the seepage basins, and hydrological connection between sampling zones in each well cluster.

Water levels showed a cyclic trend, lowest levels being recorded in May-June (e.g. Figure 6.8) due to recharge lagging behind rainfall (which, at Kinleith, was highest in July). There was no clear relationship between water levels in the wells and the amount of effluent in the seepage basins, indicating that larger scale hydrological factors (e.g. regional rainfall and recharge) were responsible for water level variations in the wells.

Water levels in the top (/4) piezometers of bores 10 and 11 were higher than in the lower three sampling levels (/1, /2, /3), as shown for bore 11 in Figure 6.8. The similarity in water levels in the bottom three piezometers indicated that these wells were sampling water from zones which were hydrologically well connected. The distinctly different levels in the higher (/4) piezometers showed that the connection between the upper level and the lower sampling zones was poor. This was consistent with the presence of a low permeability layer at, or slightly above, the sediment-ignimbrite interface as proposed by GCNZ (1987) and Beca Simons (1988) from field investigations of the shallow subsurface geology.

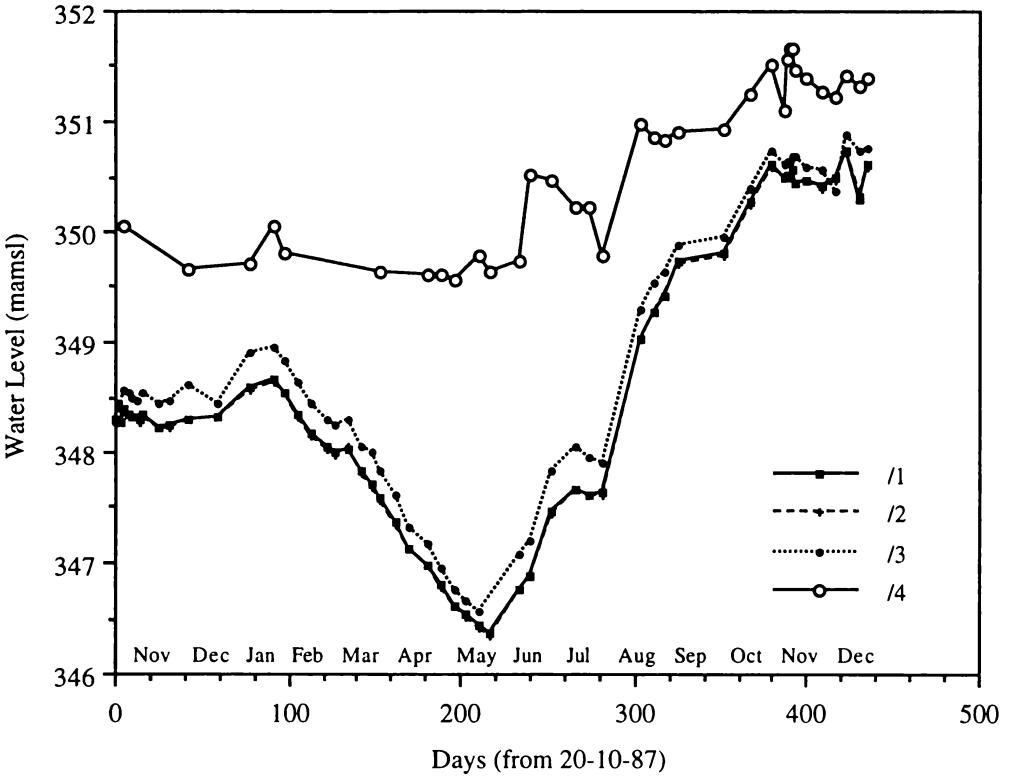


Figure 6.8: Water levels in bore 11 piezometers

6.5.2 Sodium

Sodium concentrations in each well ranged between 200 and 480 mg L^{-1}, averaging 370 mg L^{-1} for all the ground waters (Table 6.4). Substantial variation both between, and within, each well cluster was observed (Figures 6.9 and 6.10a). This indicated that effluent distribution in the shallow ground water system was not homogeneous.

The low outlying values in bore 11 were samples from the upper /3 and /4 piezometers, which were significantly lower in sodium concentration than underlying (/1 and /2) waters (see Figure 6.18a). Comparison of sodium concentrations in piezometers from the same elevations (/1 levels for all wells except B10 and B11 for which the /2 levels were at similar elevations as the /1 piezometers in the other wells; Figure 6.3) showed very similar relationships to those shown in Figure 6.9. Concentrations in B10/1 and 10/2 were not significantly different from each other, but were both significantly ($p<0.05$) lower than those in B11/1 and /2 (which in turn were not significantly different from each other). Figure 6.10a illustrates these differences (using data from four samplings between October 1987 and March 1988).

Table 6.4: Sodium concentrations (mg L^{-1}) in shallow ground waters between October 1987 and October 1988

Bore	n	mean	min	max	cv (%)	median	LQ[a]	UQ[b]
10/1	11	370	350	400	4.3	380	360	380
10/2	8	380	360	400	4.5	370	360	390
10/3	2	360	360	360	–	360	–	–
11/1	10	420	390	460	6.2	420	400	430
11/2	10	420	360	480	9.0	430	390	440
11/3	6	310	230	370	21	340	230	360
11/4	2	230	200	250	–	250	–	–
12/1	11	410	310	460	11	420	390	430
13/1	11	320	230	390	18	330	280	360
14/1	11	400	330	440	11	430	370	440
15/1	9	350	300	380	8.9	370	330	370
16/1	11	280	220	320	11	270	270	290
all bores	102	370	200	480	17	370	330	410

a: LQ–lower quartile; b: UQ–upper quartile,

Sodium levels in ground water were, on average, 44% (range 24–57%) of the parent No. 2 drain effluent concentrations (mean sodium = 841 mg L^{-1}; Stuthridge 1990). Assuming sodium to be conservative, this indicated that the ground waters contained effluent that had been diluted by a mean factor of 2.3 (range 1.8–4.2). Compared with seepage basin effluent (e.g. Q basin, mean sodium = 480 mg L^{-1}, section 4.3.5), dilutions were substantially lower, concentrations averaging 77% (range 42–100%) of those present in the seepage pond. Relatively little dilution was therefore occurring in the ground waters under the ponds.

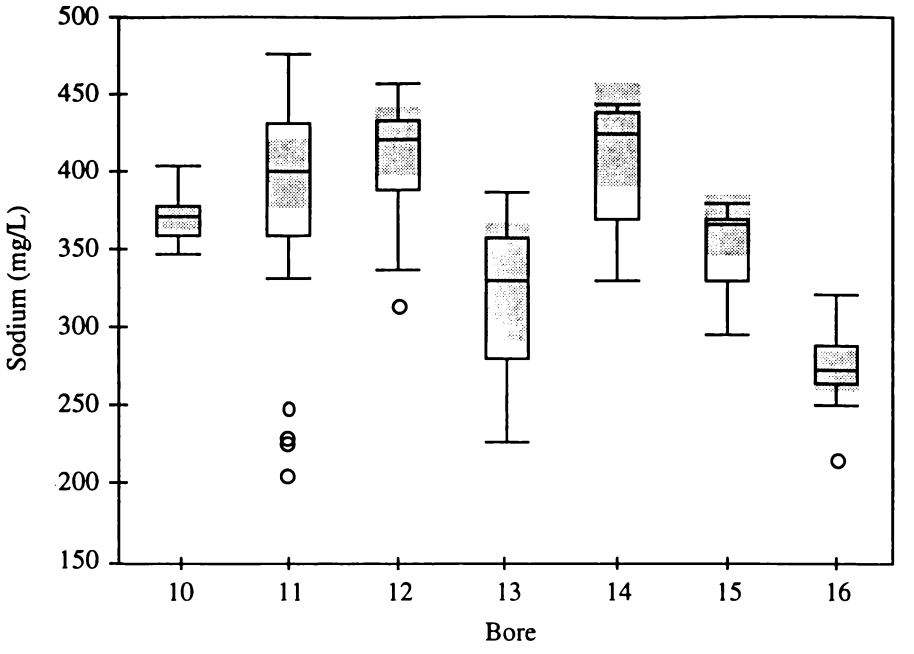


Figure 6.9: Sodium concentrations in shallow ground waters beneath seepage basin P7.

6.5.3 Colour

Colour data from the four sets of samples taken between October 1987 and March 1988 are summarised in Table 6.5 and shown in Figure 6.10c. Sodium and chloride data for the same samplings are plotted in Figures 6.10a and b. Data are listed in Table A2.15 (Appendix 2).

Colour levels were highly variable, ranging between 67 and 2100 CPU, averaging 650 CPU (median 570 CPU) for all the ground waters (Table 6.5).

Table 6.5: Colour, and colour reduction estimates, in ground waters taken October 1987 to March 1988

		Colour (CPU)			median % reduction[a] based on:	
Bore/level	n	median	min	max	Na^+ tracer	Cl^- tracer
10/1	4	770	500	900	64	67
10/2	4	400	160	530	81	83
11/1	4	1200	640	1500	54	51
11/2	4	1800	1600	2100	34	24
11/3	1	1200	–	–	48	50
12/1	4	630	610	660	75	75
13/1	4	120	67	260	94	94
14/1	4	580	540	730	73	77
15/1	4	100	83	130	94	93
16/1	4	130	110	210	92	92
all bores	37	570	67	2100	75	77

a: assuming Q Basin effluent as source (refer to text, equation 6.1, for calculation method)

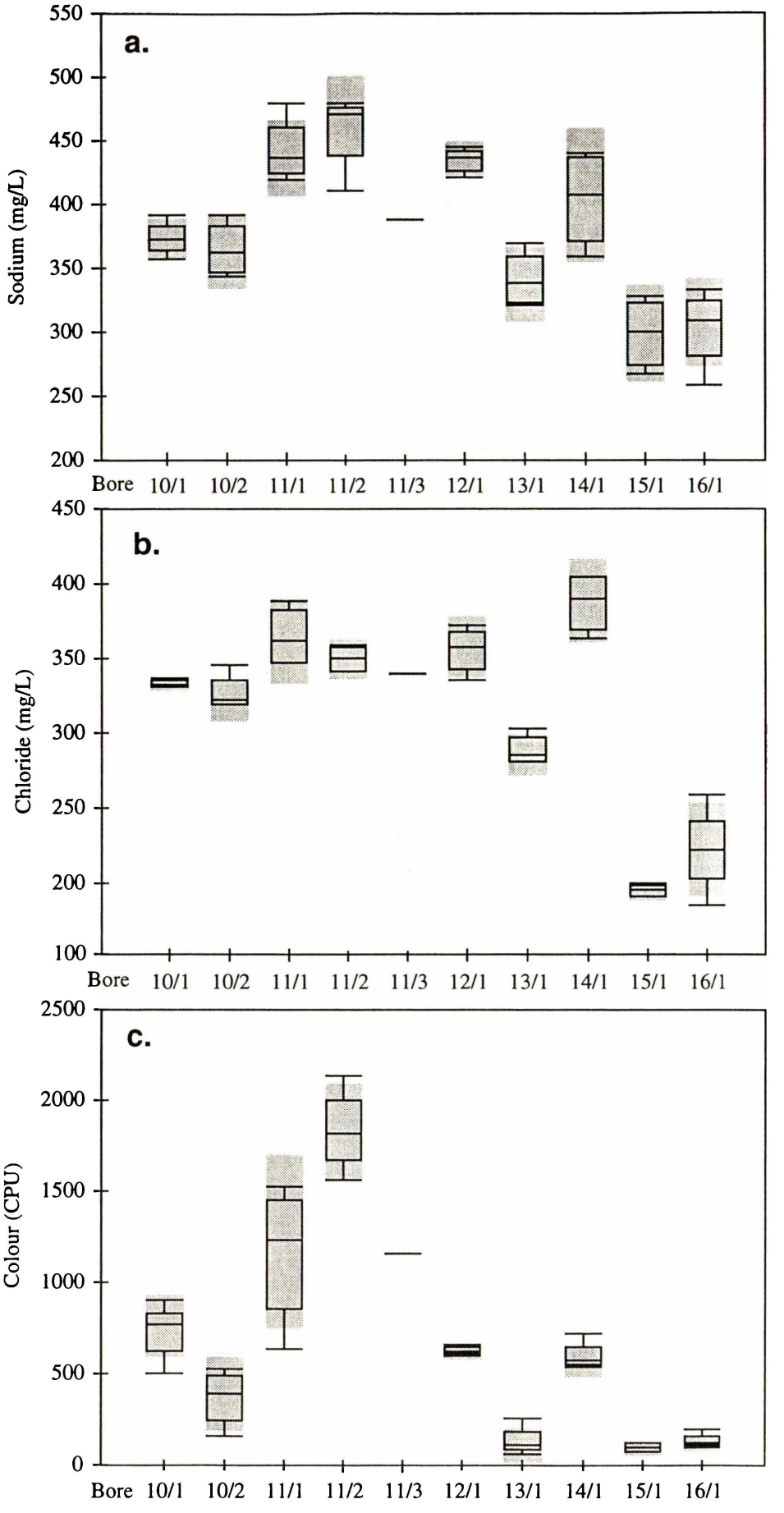


Figure 6.10: Sodium, chloride, and colour in ground waters taken October 1987-March 1988 (n=4)

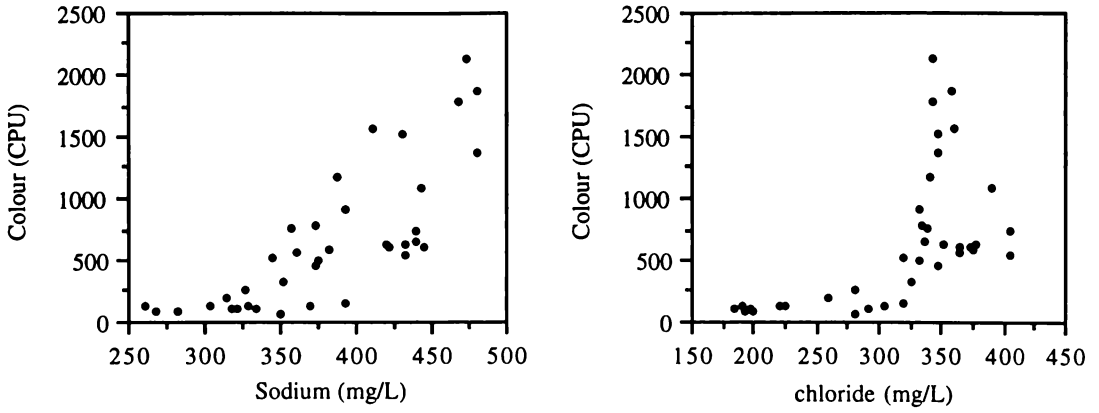


Figure 6.11: Colour-sodium and colour-chloride relationships in ground waters

Relationships between colour levels and sodium or chloride concentrations are shown in Figure 6.11. Linear regressions were statistically significant ($p<0.001$), but highly variable ($R^2=0.600$ for colour vs sodium; $R^2=0.311$ for colour vs chloride) and visually non-linear. The relationship between sodium and chloride was similar to the colour–sodium plot in Figure 6.11, and had similar linear correlation coefficient ($R^2=0.628$; $p<0.001$).

Sodium, chloride, and colour in the shallow ground waters therefore followed similar general trends, but the relationships between these constituents were not simple.

The colour of some ground waters was relatively low, suggesting that significant colour reduction was occurring in some sub-surface zones. Colour reductions were therefore estimated, using the approach of Grimestad (1977) to account for dilution:

$$PCR = 100 \left[1 - \frac{C_m(T_e-T_g)}{C_e(T_m-T_g) + C_g(T_e-T_m)}\right] \qquad \textit{(eq. 6.1)}$$

where PCR = percentage of the effluent-sourced contaminant removed;
C_m = concentration of the contaminant measured in the affected ground water;
T_e = concentration of unreactive tracer in the effluent;
T_g = concentration of unreactive tracer in unaffected ground water;
C_e = concentration of the contaminant in the effluent;
T_m = concentration of the tracer measured in the affected ground water;
C_g = concentration of the contaminant in unaffected ground water;

Degraded Q Basin effluent (section 4.3.5) was chosen as the effluent source, as it was the largest body of ponded effluent in the seepage area during the study and best represented the kind of effluent seeping to ground water. Mean sodium, chloride, and colour levels (Table 4.6) were used in the calculation. Background ground water concentrations of 10 CPU colour, 8 mg L^{-1} sodium (Tracey 1986), and 5 mg L^{-1} chloride (NZFP data) were taken. Calculations using both chloride and sodium as unreactive tracers were made.

Results from each set of calculations were very similar, and were well correlated ($\%reduction_{Na} = 0.898 \cdot \%reduction_{Cl} + 8.17$; $R^2=0.975$; $p<0.001$). Differences between median colour removals in each well estimated using sodium or chloride as tracer were between 0.1 and 3.5% for all wells except B11/2, which differed by 10% (Table 6.5). Colour reductions calculated using chloride as the tracer are shown in Figure 6.12, and median data are listed in Table 6.5. Similar results were obtained using No. 2 drain as the effluent source (using mean concentrations from Stuthridge 1990).

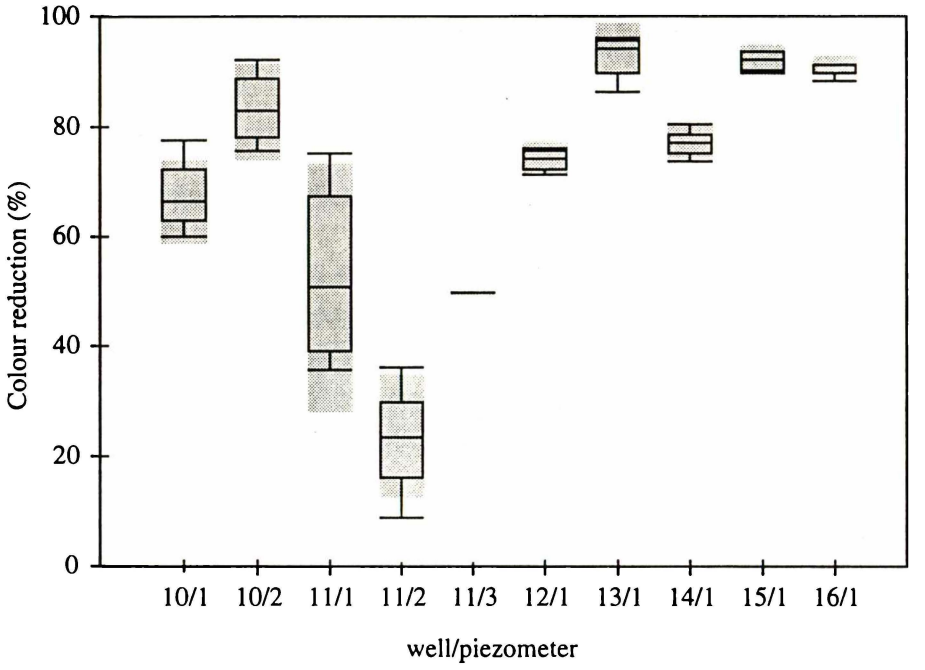


Figure 6.12: Colour reductions calculated using chloride as tracer and Q Basin as effluent source

After accounting for dilution, median colour reductions ranged between 92-94% (B15/1, B13/1 and B16/1) and 24% (B11/2), the overall ground water median being 77%. Colour removals were variable, indicating that subsurface transport and attenuation mechanisms were non-uniform. While there were zones which were effective at removing or retarding the colour, there were also zones which were allowing effluent colour to pass into the ground water system with relatively little reduction.

6.5.4 Extractable organics

The GC-FID and GC-MSD chromatograms of most ground water extracts contained large UCM. MCPs, FAs, RAs, DTs, DEHP, and a group of late eluting compounds of highest observed mass m/z=348–402, were identifiable above the complex baseline. The combination of UCM, relatively low concentrations of targeted EOs, and limitations of the pH 2 extraction method (section 3.5) restricted quantitation to major species. Despite these limitations, useful data was acquired which established the general EO chemistry of the ground waters, the approximate concentrations of key species, and enabled spatial variation in EO chemistry to be assessed. GC-MSD chromatograms of bores 11/1 and 12/1 (Figures 6.13 and 6.14) illustrate the range of EO profiles found.

Major MCPs were trimethyl (probably 2,3,5- and 2,3,4-trimethyl) and tetramethyl- substituted compounds, with trace levels of dimethyl species also present in some samples. These compounds were found in No. 2 drain, J pond and Q basin effluents (Chapter 4) and have been reported as persistent compounds in overseas mill effluents (Voss 1984). Also present in the elution region of the MCPs were compounds which gave MSD library matches for cyclohexanone, 2-hexenol, 2-ethylhexanol, and in some samples, 2-ethylhexanoic acid. These compounds were possibly residuals from the PVC well casings. None of these compounds was considered to be effluent derived.

MTs were very minor constituents in the ground waters, trace amounts of camphene *[7]*, *p*-cymene *[15]*, camphor *[34]*, fenchone *[29]*, and DHT *[35]* being detectable in bores 11/2 and B12/1. The low levels of MTs indicated that the ground water sampled was sourced from degraded pond effluent, or that these compounds were effectively retarded or degraded in the sediments beneath the ponds. Two acetylthiophenes, propionylthiophene, and phenylacetic acid were also identifiable as relatively minor components of the early part of the chromatograms.

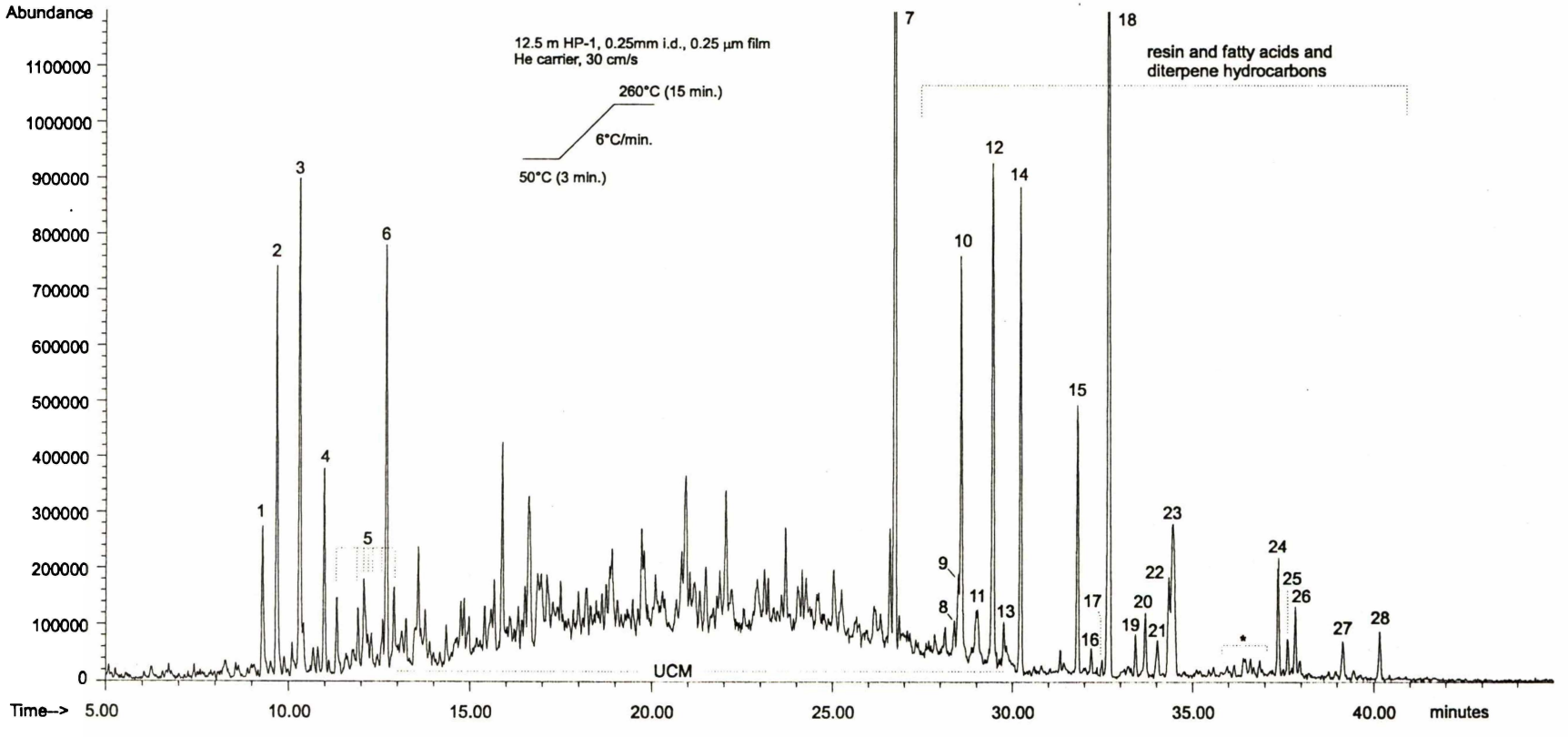
FAs were largely saturated species, FA14:0 to FA24:0 identifiable by GC-MSD. FA16:0 and FA18:0 were the dominant species.

A range of RAs and DTs similar to those present in the sediments (Chapter 5) were present at highly variable concentrations in the ground waters. Transformed species dominated the RAs, parent compounds being limited to dehydroabietic acid *[128]*, and seco-dehydroabietic acids *[103* and *104]*, with very small amounts of chloro- and dichlorodehydroabietic acids *[140* and *143]* identifiable by GC-MSD. The dominant transformed RAs were abietanoic *[127]* and 7-oxokauranoic acids *[126]*, with smaller amounts of pimaranoic *[119]*, 8-pimarenoic *[111]*, and 8-isopimarenoic acids *[112]* also present.

DTs were dominated by retene *[105]*, fichtelite *[87]*, and dehydroabietin *[90]*. Smaller amounts of related species with molecular weights 242, 260, 262, 270, and 272 were also found, as described in Chapter 5 for seepage basin sediments. Also present was another similar DT of molecular weight 258 *[76]*. The DTs were similar in concentration to RAs in bores 11/1 and 11/2, while in bores 12/1 and 16/1 they were quantitatively dominant components of the total RA and DT fraction, producing EO profiles for these waters which were distictively different from other waters sampled.

Several late eluting compounds of highest observed mass 348, 350, 400, and 402 *[146–151]* were present in most samples. These compounds were also found in the degraded Q Basin effluent. Their mass spectra showed some fragment ions similar to those found for RAs.

S_8 was present in variable amounts and was particularly high in water from B15/1. β-sitosterol *[152]* and the related sterol *[153]* were also found as relatively minor components in the bore waters.

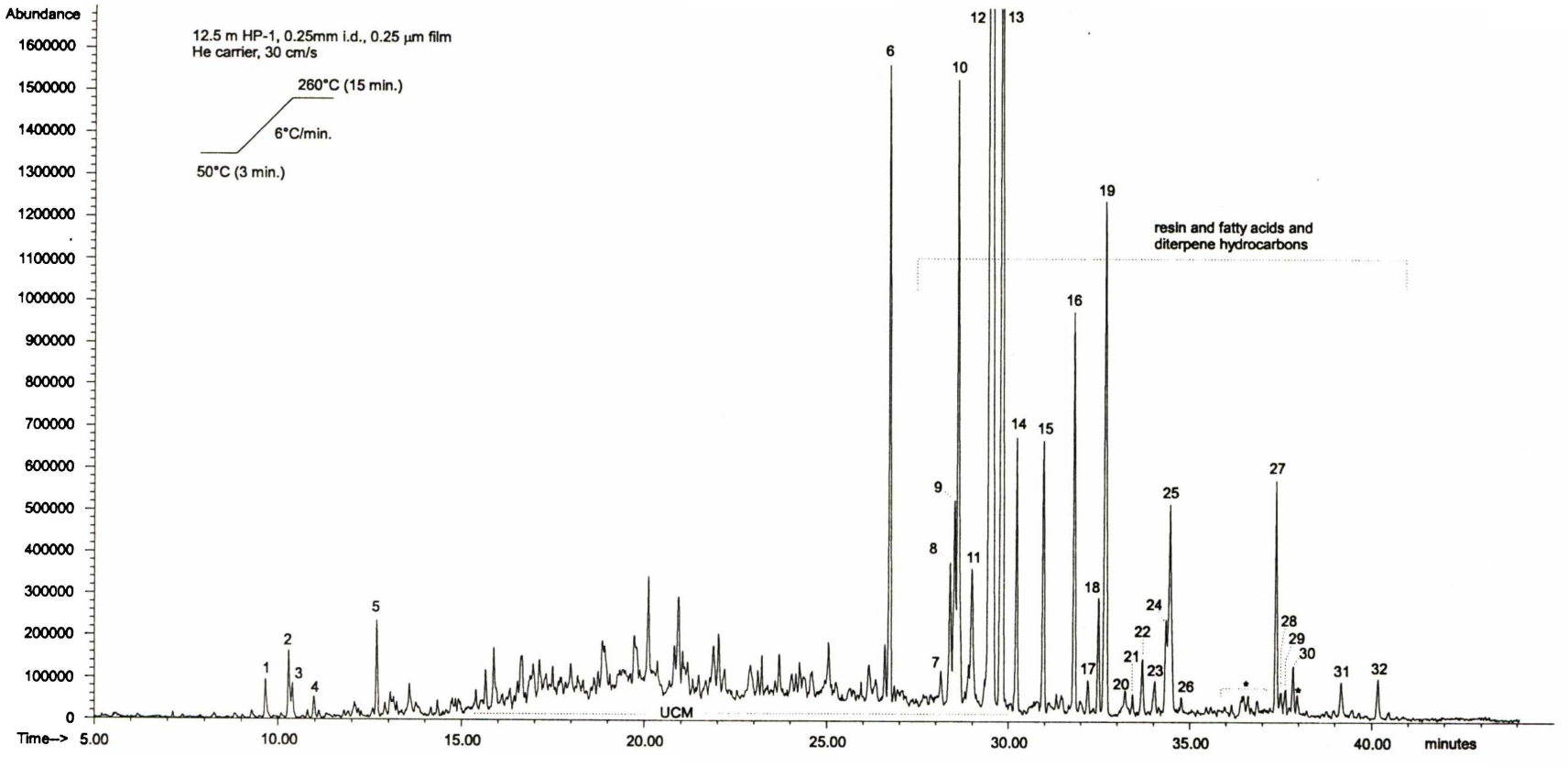


Peaks:

1. 2-ethylhexanol *[19]*
2. 2,3,5-trimethyl-2-cyclopentenone *[21]*
3. 2,3,4-trimethyl-2-cyclopentenone *[26]*
4. tetramethyl-2-cyclopentenone *[30]*
5. tetramethyl-2-cyclopentenones
6. propionylthiophene *[47]*+ phenylacetic acid *[36]*
7. HC18 internal standard
8. DT260P *[77]*
9. DT260I/S *[78]*
10. FA16:0 *[81]* + DT262P *[79]*
11. DT262I *[80]*+ S_8 *[96]*
12. fichtelite *[87]*
13. dehydroabietin *[90]*
14. FA17:0 surrogate standard
15. FA18:0 *[102]*
16. seco-dehydroabietic acid #1 *[103]*
17. seco-dehydroabietic acid #2 *[104]*
18. retene *[105]*
19. 8-pimarenoic acid *[111]*
20. pimaranoic acid *[119]*
21. RA304? *[124]*
22. 7-oxokauranoic acid *[126]*
23. abietanoic *[127]* + dehydroabietic *[128]* acids
24. bis(2-ethylhexyl)phthalate *[145]*
25. RA350? *[146]*
26. RA348? *[147]*
27. RA350? *[148]*
28. RA402? *[151]*

*: contamination (*m/z*=94)
UCM: unresolved complex mixture

Figure 6.13: GC-MSD TIC of a pH2 extract of ground water from bore 11/1



Peaks:

1. 2,3,5-trimethyl-2-cyclopentenone *[21]*
2. 2,3,4-trimethyl-2-cyclopentenone *[26]*
3. 4-methylphenol *[27]*
4. tetramethyl-2-cyclopentenone *[30]*
5. propionylthiophene *[47]* + phenylacetic acid *[36]*
6. HC18 internal standard
7. DT258 *[76]*
8. DT260P *[77]*
9. DT260I/S *[78]*
10. FA16:0 *[81]* + DT262P *[79]*
11. DT262I *[80]* + DT260A *[84]*
12. fichtelite *[87]*
13. dehydroabietin *[90]*
14. FA17:0 surrogate standard
15. tetrahydroretene *[98]*
16. FA18:0 *[102]*
17. seco-dehydroabietic acid #1 *[103]*
18. seco-dehydroabietic acid #2 *[104]*
19. retene *[105]*
20. chlorodehydroabietin *[114]*
21. 8-pimarenoic acid *[111]*
22. pimaranoic acid *[119]*
23. RA304? *[124]* + 13-abietenoic acid *[120]*
24. 7-oxokauranoic acid *[126]*
25. abietanoic *[127]* + dehydroabietic *[128]*acids
26. FA20:0 *[129]*
27. bis-(2-ethylhexyl)phthalate *[145]*
28. FA22:0 *[138]*
29. RA350? *[146]*
30. RA348? *[147]*
31. RA350? *[148]*
32. RA402? *[151]*

*: contamination (*m/z*=94)
UCM: unresolved complex mixture

Figure 6.14: GC-MSD TIC of a pH2 extract of ground water from bore 12/1

The concentrations of identified MCPs, FAs, RAs, and DTs in the ground waters are shown in Figure 6.15, and median concentrations summarised in Table 6.6. EO data are listed in Appendix 2 as Tables 6.12–15.

Table 6.6: Median concentrations (μg L^{-1}) of extractable organics in shallow groundwaters

Well	n	MCPs	FAs	RAs	DTs	ΣRADT[a]
10/1	4	150	42	79	18	97
10/2	3	150	28	52	8	60
11/1	4	140	53	200	330	530
11/2	3	110	31	340	450	810
11/3	1	350	54	160	110	270
12/1	4	130	45	210	2100	2300
13/1	4	35	19	51	2	62
14/1	4	180	20	200	110	300
15/1	4	15	17	48	<1	48
16/1	4	77	60	120	920	1060
all wells	35	110	29	120	110	280

a. sum of identified RAs and DTs

RA concentrations varied markedly between samples, median levels varying between 340 μg L^{-1} in B11/2 to 48 μg L^{-1} in B15/1 (Figure 6.15a). RAs were significantly correlated with sodium levels (Spearman rho=0.636, $p<0.001$, n=35) and with colour (Spearman rho=0.739, $p<0.001$).

DT concentrations were even more variable, medians ranging from 2000 μg L^{-1} in B12/1 to <1 μg L^{-1} in B15/1 (Figure 6.15b). There were no significant correlations between DT concentrations and other measured analytes.

MCP concentrations were similar in all wells except B13/1 and B15/1, which contained lower levels (Figure 6.15c). MCPs were significantly correlated with both sodium (rho=0.448, p=0.094, n=35) and colour (rho=0.655, p=0.002, n=35). FA levels were generally low, variable, and similar in all ground waters (Figure 6.15d).

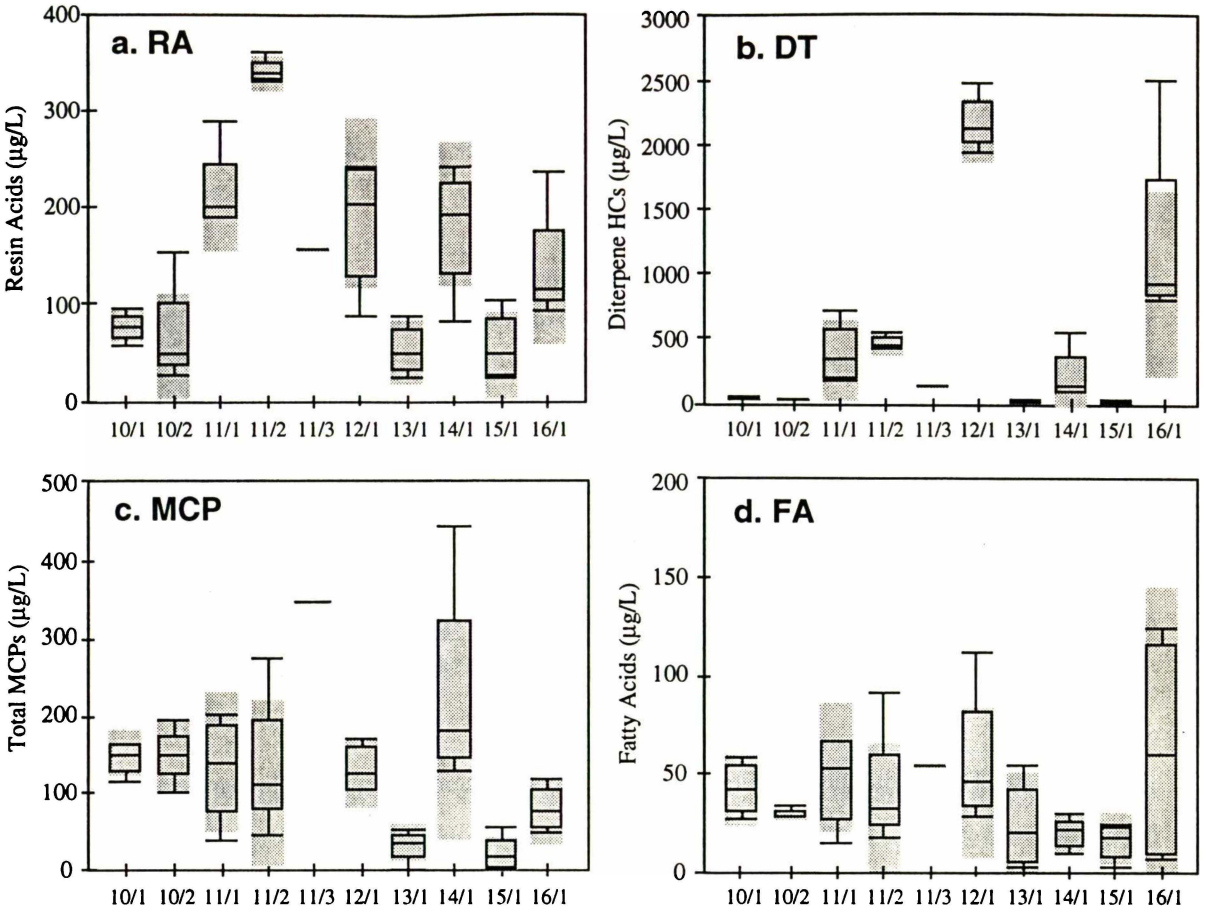


Figure 6.15: Concentrations of major identified EOs in shallow ground waters

The most distinctive feature of the EO chemistry of the ground waters was the DT levels which were spatial variable, and unrelated to other effluent-derived constituents. This was particularly evident in B16/1, which had among the lowest colour, sodium and chloride concentrations of all the ground waters, yet contained elevated DT levels. These spatial differences in EO chemistry were most apparent when the sum of RAs and DTs (RADT) were plotted (Figure 6.16). B12/1 stood out as having the highest RADT levels, followed by B16/1, B11/1 and /2, and B14/1. RADT concentrations in B10/1 and /2, B13/1, and B15/1 were clearly much lower.

Removals of EOs from the effluent during infiltration from the seepage ponds into shallow ground waters were estimated using the same approach used for colour removal calculations (section 6.5.3, eqn. 6.1). This approach was somewhat problematic for EOs because their concentrations varied greatly over time in the seepage ponds (section 4.4.5), whereas colour change in the ponds was much smaller. Choosing source effluent concentrations to use in eqn. 6.1 for removal calculations was therefore somewhat subjective. The Q Basin effluent median RA level (390 µg L^{-1}, section 4.3.5) was chosen because Q Basin was a large, full seepage basin close to the sampling wells, and its composition was determined using the same pH 2 extraction procedure as the ground waters in the preliminary studies. Assuming Q Basin represented a reasonable effluent-source, and sodium to be a conservative tracer, median removals of trimethyl-2-cyclopentenones (tri-MCPs), FAs, total RAs, and ΣRADTs are summarised in Table 6.7.

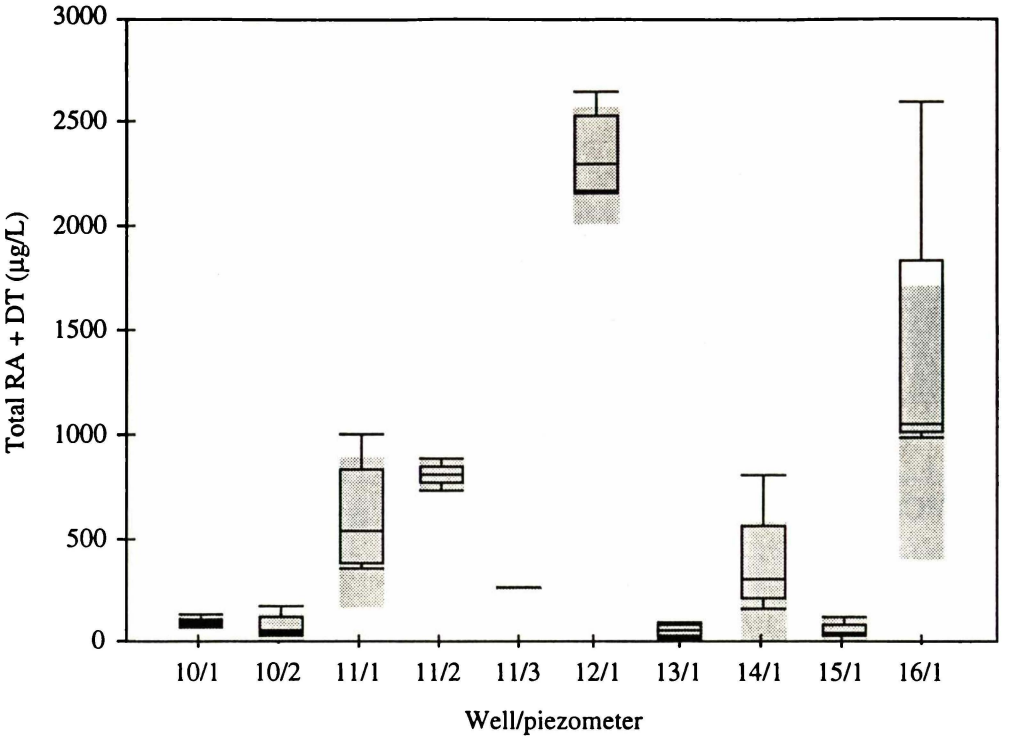


Figure 6.16: Total resin acid plus diterpene hydrocarbon concentrations in shallow ground waters

Table 6.7: Median removals of major extractable organics based on comparison with median Q Basin levels. Underlined values are significantly < or > zero ($p<0.05$).

		Median reductions (%)			
Well	n	tri-MCPs	FAs	RAs	ΣRADTs
10/1	4	-230	-1	51	67
10/2	3	-270	29	66	79
11/1	4	-130	-6	-10	-48
11/2	3	-140	43	-75	-110
11/3	1	-640	-22	7	14
12/1	4	-140	2	-10	-590
13/1	4	30	41	60	74
14/1	4	-270	51	-9	10
15/1	4	71	-56	60	78
16/1	4	-79	-74	12	-360
all wells	35	-140	32	12	14

The % removal estimates were generally highly variable so that many median values were not significantly different from zero. There were also many -ve values, suggesting that increases occurred between seepage basin and underlying ground water. In general, the EO reductions were relatively small (<80%) and were overshadowed by the large increases observed for some constituents.

The least variable data were obtained for RAs, for which significant +ve removals were calculated for B10/1, 10/2, 13/1, and 15/1. A clearly -ve reduction (i.e. an increase) resulted for B11/2 (Figure 6.17a). The sum of RAs and DTs (ΣRADTs) also showed interesting results, B10/1, 10/2, 13/1, and 15/1 again showing +ve removals, but B12/1 and 16/1 giving large increases (Figure 6.17b).

These estimated removals were subject to considerable uncertainty because of the assumptions made about source effluent composition, and because of the limited quantitative accuracy of the pH 2 EO analysis method. The results for the MCPs in particular probably reflected analytical limitations, as these analytes were quantitatively minor in the effluents and quantitation was not considered accurate.

However, the calculations highlighted the distinctly different RA chemistry of B11/2 and RADT chemistry of B12/1 and 16/1. It appeared that B11/2 had RAs which were less degraded than Q Basin, suggesting seepage to this well was more direct than it was to other wells (i.e. a sub-surface pathway of preferential flow). This was consistent with the high colour and sodium content of B11/2.

The very high DT content of B12/1, and to a lesser extent B16/1, was the other major feature of the data. DTs at the levels found in these wells could not have been sourced from degraded seepage basin effluent because high levels of DTs were never accumulated in the ponds. The source of the DTs was unclear. To produce such high DT concentrations in the ground water by effluent seepage, relatively undegraded effluent would had to have penetrated the ground (perhaps via leakage from the adjacent drain) and undergone anaerobic transformation. Such transformations have been proven to occur with RAs incubated under anaerobic conditions (Tavendale 1994). It was therefore conceivable that the DTs in the ground water were effluent-sourced, as assumed for sediments from the seepage basins (Chapter 5). As was found in the sediments, low concentrations of chlorodehydroabietin *[114]* were identifiable in the ground water samples from B12/1, suggesting at least some of the DTs were products of effluent RA transformation. Colour data, however, were not supportive of the presence of high concentrations of effluent in the ground water sampled, colour reductions for B12/1 and B16/1 being among the highest measured (Figure 6.12). It was also possible, but seemed unlikely given the physical setting of the ponds, that the DTs in the ground waters were from natural sources (e.g. decaying buried plant material) rather than from the effluent.

In summary, there was a substantial amount of spatial variation in the EO chemistry of the ground waters beneath the ponds. While effluent-derived compounds were detectable in all the samples, the concentrations of the major EO groups varied widely between wells and, to a lesser extent, between depths within a given well (e.g. B11). RAs and MCPs were significantly, although weakly, correlated with sodium and colour levels. Substantial variations in EOs removals were estimated. Significant removals of RAs were calculated for waters from bores B10/1, 10/2, 13/1, and 15/1, while a significant increase was calculated for B11/2. Distinctly different EO chemistry was found in B12/1 and B16/1 as a result of high levels of DTs.

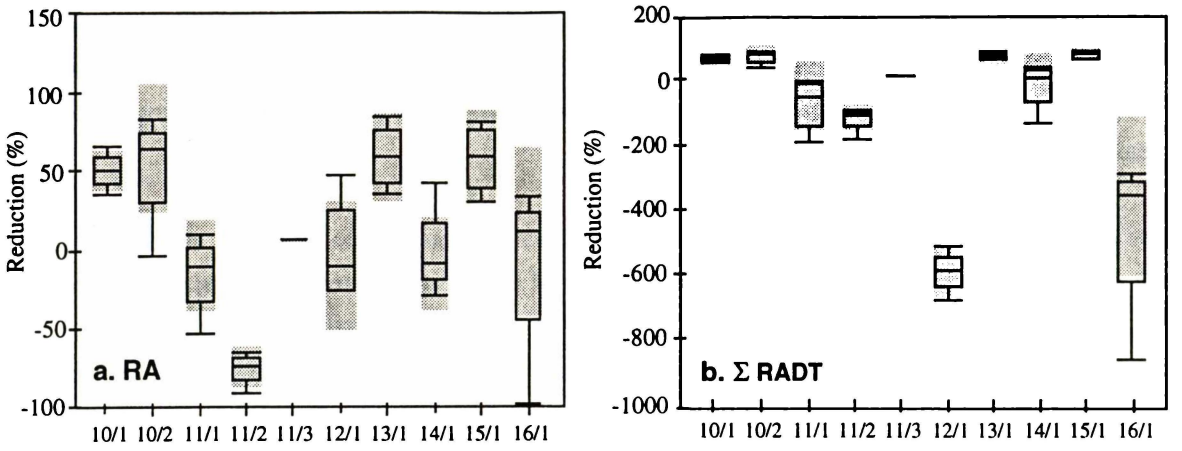


Figure 6.17: Reductions in a) resin acid (RA) and b) resin acid plus diterpene hydrocarbon (ΣRADT) levels based on comparison with median Q Basin concentrations

6.5.5 Summary of results from initial studies

The preliminary assessments of shallow ground water composition found:

- Variable, but generally high, concentrations of sodium and chloride were present in the ground waters, indicating heterogeneous distribution of effluent-sourced water beneath the seepage ponds. Dilution of seepage pond effluent was not great, averaging approximately 30%.

- Ground waters had highly variable colour levels, which were weakly, but statistically significantly, correlated with sodium and RA concentrations. Colour reductions were estimated to be 24–94% (overall median 75%). Infiltration therefore resulted in colour removal ranging from very effective to very ineffective.

- Effluent-derived EOs were present at highly variable levels in all ground waters. Distinct differences in the concentrations of RAs and DTs were found between wells. Based on the RA and DT chemistry, and estimated removals of these constituents, three groups of waters which were quite different in EO chemistry were present: 1) bore 11/2, 2) bores 12/1 and 16/1, and 3) bores 10/1, 10/2, 13/1, 15/1.

- Reliable estimation of EO removals during infiltration was limited by the semi-quantitative characteristics of the pH 2 analytical method, and uncertainty in source effluent EO composition.

- The EO chemistry, colour, and sodium data indicated the possible presence of a preferential effluent flow path to B11/2.

In general, the ground waters contained relatively high concentrations of mobile effluent-derived inorganic constituents (sodium and chloride), variable colour levels, generally low but variable RA levels, and highly variable DT concentrations. The ground water system directly

beneath the pond was therefore spatially heterogeneous, resulting in a complex distribution of effluent-derived constituents. This complexity and high spatial variability in ground water composition prevented reliable estimation of treatment performance.

6.6 Reassessments of Shallow Ground Water Composition

The initial studies were successful in obtaining ground water samples affected by effluent infiltration, and in determining ground water characteristics in terms of key effluent-derived contaminants. The results gave acceptable measures of colour behaviour during infiltration, but were more limited for assessing changes in EOs. Better quantitative measures of EOs' concentrations in ground waters were required to confirm spatial differences in EO chemistry that were observed in the initial study. In addition, obtaining a definitive link between ground water and source effluent was necessary to provide accurate assessment of EO removal occurring during infiltration. A second ground water monitoring exercise was therefore undertaken.

6.6.1 Objectives

The reassessment study aimed to:

1. Refine measures of concentrations and short-term temporal variability in sodium, colour, and EOs by replicate sampling and analysis of ground waters representative of the range of chemistries present beneath the seepage basins;

2. Estimate removals of colour and EOs from effluent during infiltration by comparing the composition of ground water with overlying seepage basin effluent;

3. Obtain preliminary measurements of chlorophenolics' concentrations in shallow ground waters beneath the seepage basins; and

4. Assess EO chemistry, sodium, and colour in samples from the unconsolidated sediments beneath the ponds using porous ceramic cup samplers.

6.6.2 Sampling and analysis

Wells representative of the EO chemistry observed in the initial studies were selected for resampling. Bores 11/1, 11/2, 11/3, 11/4, 12/1, and 15/1 were sampled between 5 (bore 12/1) and 8 (bore 11/4) times over a 7 week period in November/December 1988. During this time the overlying seepage basin P7 was flooded with effluent and its chemistry monitored (section 4.4).

Five water samples were also taken during this period using ceramic cup samplers sited adjacent to bore 11, at depths between 0.65 and 1.0 m beneath the seepage basin. These were used for preliminary assessments of the sampling technique, and for examining the chemistry of ground water from the unconsolidated sediment zone. Sample numbers are summarised in Table 6.8.

Table 6.8: Numbers of samples analysed from each well in the reassessment study

	Analyte			
Sample well	sodium	colour	extractable organics	chlorophenolics
11/1	7	7	7	1
11/2	7	7	6	1
11/3	7	7	7	1
11/4	8	8	8	2
12/1	5	5	5	1
15/1	7	7	7	–
ceramic cups	5	5	5	–

Sodium was analysed by AAS, colour by the NCASI method, EOs by pH 11 extraction and GC-FID/MSD analysis, and chlorophenolics by acetylation, hexane extraction and GC-ECD.

6.6.3 Extractable organic composition of ground waters

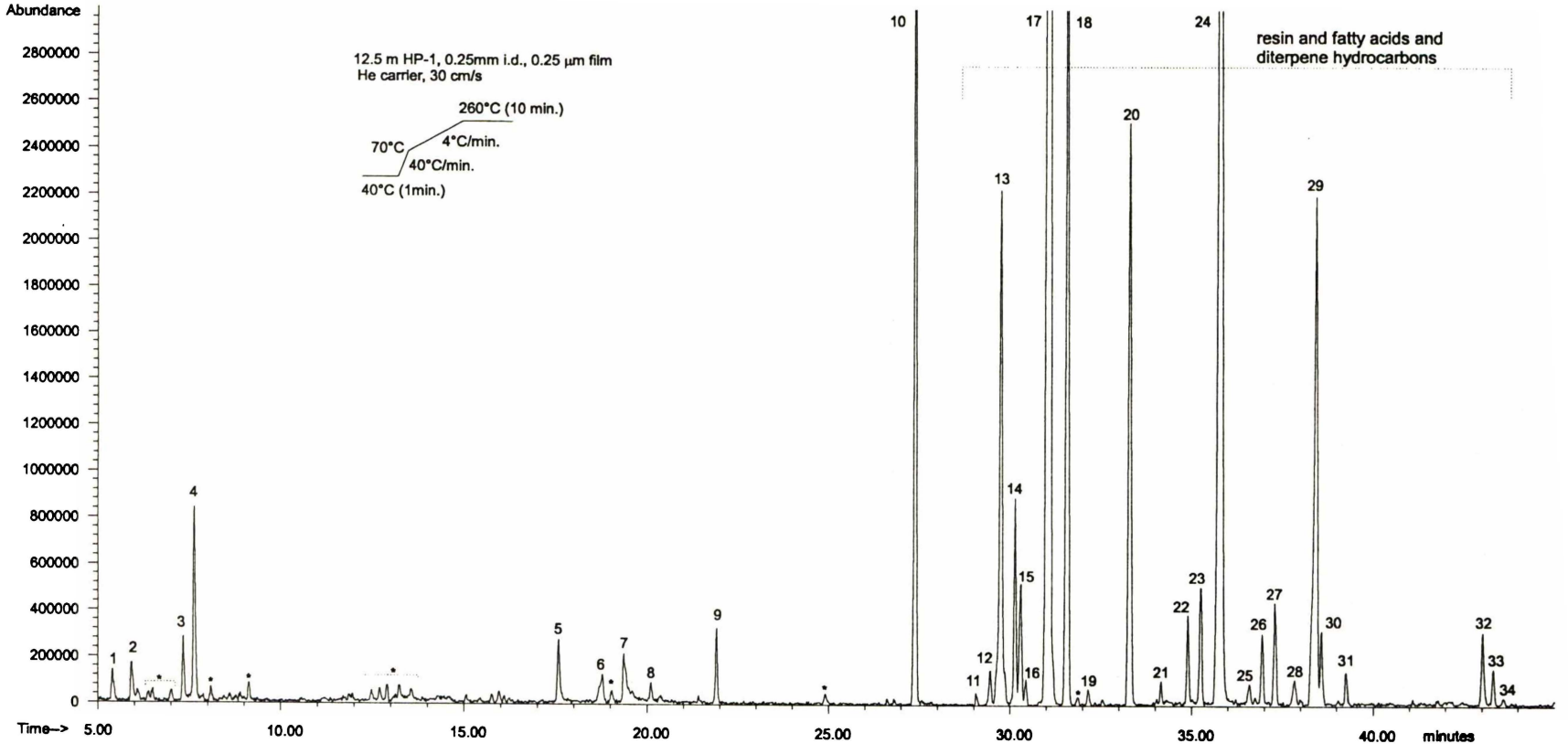
The pH 11 extraction procedure gave extracts which were visibly less coloured than those from the pH 2 procedure, and gave smaller UCMs and less baseline "noise" in GC analyses. Figure 6.18 shows a GC-MSD TIC of bore 12/1 analysed by the pH 11 procedure (compare with the pH 2 extract TIC shown in Figure 6.14).

The qualitative compositon of the EOs found was very similar to that found in the initial studies. Major groups of identifiable compounds were the MCPs, RAs, and DTs. The late eluting compounds of mw=348–402 *[146–151]*, were however, present at much lower concentrations than were previously found in the pH 2 extracts.

6.6.4 Quantitative chemistry

The concentrations of sodium, colour, and EOs are shown in Figure 6.19, and summarised in Table 6.9 (data listed in Table A2.17, Appendix 2). The results from the reassessment period measurements showed some differences in concentrations from the initial studies, but the spatial relationships between wells were essentially the same (e.g. compare Figures 6.19, 6.10, and 6.15). Within-well variability was noticeably lower in the reassessment period, reflecting improved analytical techniques (for EOs) and the shorter time interval over which the measurements were made.

The most obvious feature of the quantitative results was the high variability, and very high maximum concentrations attained, for FAs and RAs from B11/4. This well, the shallowest sampling zone in the bore 11 cluster, intercepted effluent from the overlying seepage pond shortly after monitoring began. This is described further in section 6.6.6.



Peaks:

1. 2,3,5-trimethyl-2-cyclopentenone *[21]*
2. 2,3,4-trimethyl-2-cyclopentenone *[26]*
3. camphor *[34]*
4. dihydro-α-terpineol *[35]*
5. unidentified compound *[61]*
6. unidentified mw=208? *[62]*
7. unidentified compound *[63]*
8. unidentified mw=208? *[64]*
9. HC16 standard
10. HC18 standard
11. DT258 *[76]*
12. DT260P *[77]*
13. DT260I/S *[78]* + DT262P *[79]*
14. FA16:0 *[81]*
15. DT262I *[80]*
16. DT242 *[82]* + DT260A *[84]*
17. fichtelite *[87]*
18. dehydroabietin *[90]*
19. Caxtonellite *[93]*
20. tetrahydroretene *[98]*
21. FA18:1 *[101]*
22. FA18:0 *[102]*
23. seco-dehydroabietic acid #1 *[103]*
24. retene *[105]*+ seco-dehydroabietic acid #2 *[104]*
25. chlorodehydroabietin *[114]*
26. 8-pimarenoic acid *[111]*
27. pimaranoic acid *[119]*
28. isopimaranoic *[122]*+ 13-abietenoic *[120]* acids
29. 7-oxokauranoic *[126]*+ abietanoic acids *[127]*
30. dehydroabietic acid *[128]*
31. FA20:0 *[129]*
32. bis-(2-ethylhexyl)phthalate *[145]*
33. FA22:0 *[138]*
34. RA350? *[146]*

*. peak too small for mass spectral identification

NB. all acids present as methyl esters

Figure 6.18: GC-MSD TIC of a pH11 extract of ground water from bore 12/1

The DT concentrations in bore 11/1 were also somewhat more variable than other bore 11 cluster samples. This variability was attributable to high retene and fichtelite concentrations in the last two samples taken. This increasing trend in DTs in B11/1 apparently continued over the following 18 months, as very high concentrations of these compounds, especially retene, were found when the well was resampled in 1990 (section 6.8). While short-term variability was not great, over longer time periods ground water composition changed considerably.

Table 6.9: Median concentrations of sodium, colour and extractable organics in ground waters (and seepage basin P7; see section 6.6.5) during the reassessment period

Well	sodium	colour	MCP	FA	RA	DT	Σ RADT
	$mg\ L^{-1}$	CPU	.....	.....	$\mu g\ L^{-1}$	.....	.....
11/1	410	1010	84	47	130	150	280
11/2	390	1950	120	40	210	110	310
11/3	260	1410	41	47	160	120	320
11/4	320	960	230	96	350	58	380
12/1	400	1100	130	67	270	2330	2600
15/1	390	240	27	16	18	2	19
seepage basin[a]	205	1020	10	84	270	13	290

a: median concentrations in the overlying seepage basin for the final 13 days of monitoring

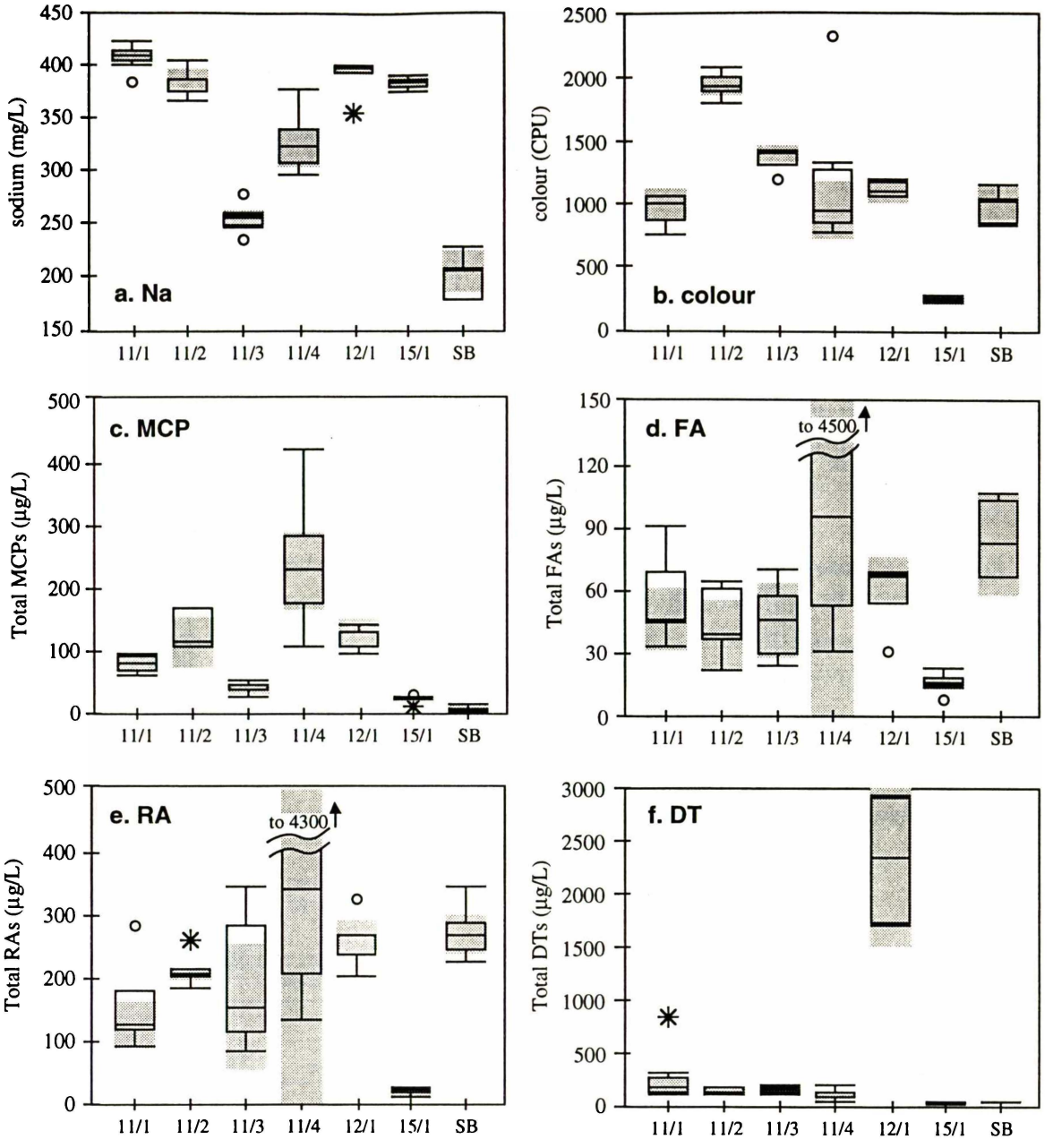


Figure 6.19: Concentrations of sodium, colour, and extractable organics in ground waters during the reassessment period. SB refers to seepage basin P7 (section 6.6.5).

6.6.5 Effluent treatment during infiltration

Reductions in colour and EOs were estimated by comparing the concentrations present in ground water with those present in the overlying seepage basin during the final 13 days of the reassessment period ("SB" data plotted in Figure 6.19). The concentrations of colour and EOs were relatively stable in the seepage basin over this period (Figure 4.17), having undergone large changes in composition in the previous 35 days. Equation 6.1 was used to calculate the removals presented in Figure 6.20 and Table 6.10. Bore 11/4 data was excluded because of the high concentration effluent intercepted in the well (section 6.6.6).

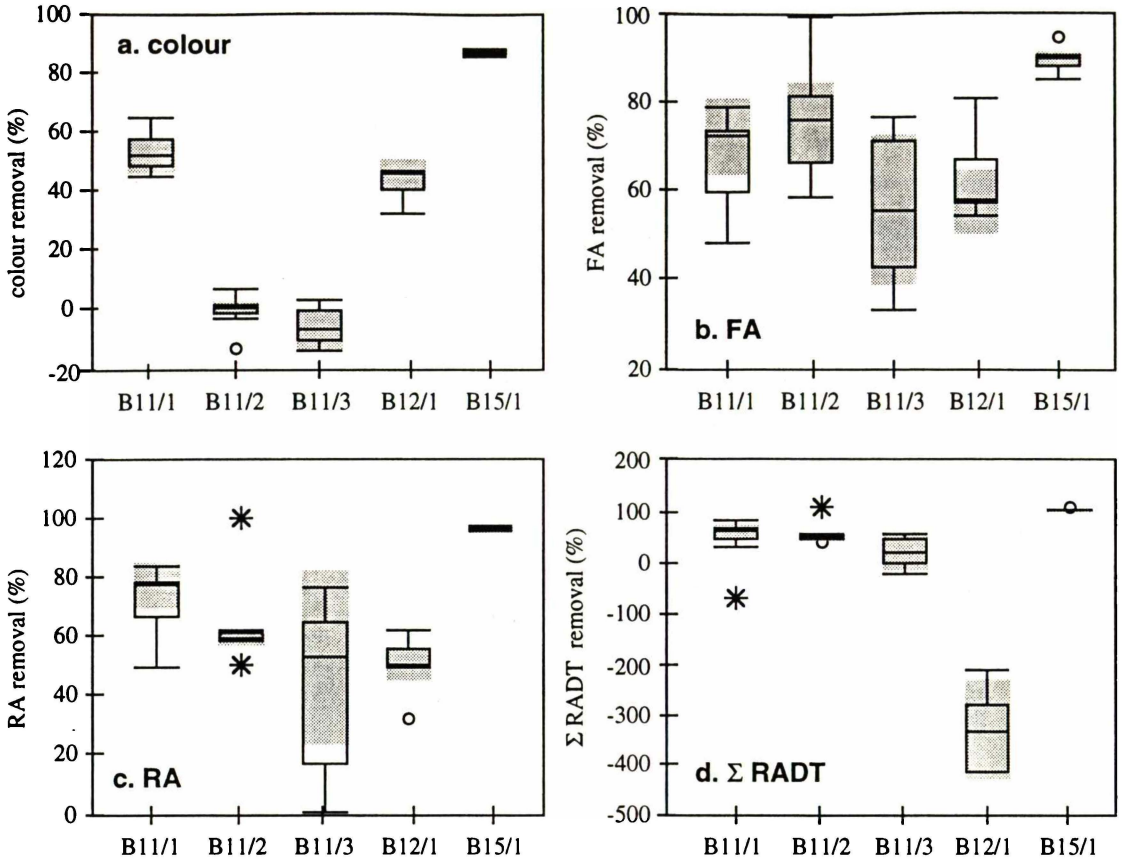


Figure 6.20: Removals of extractable organics and colour during infiltration

Table 6.10: Median calculated removals of extractable organics and colour

		Median reductions (%)				
Well	n	colour	MCPs	FAs	RAs	ΣRADTs
11/1	7	52	-360	72	78	53
11/2	6/7	0.2	-550	76	59	43
11/3	7	-8	-260	56	53	8
12/1	5	46	-600	58	50	-360
15/1	7	88	-52	90	97	97
all wells	32/33	45	-310	73	62	44

As found in the initial studies, the "contaminant removal" data showed marked differences between wells. They also showed some -ve removals, particularly for MCPs and DTs which were present in higher concentrations in the ground water than in the overlying pond at the end of the monitoring. This indicated that the ground water sampled was not sourced directly from degraded effluent of the composition left in the P7 seepage basin. Estimating contaminant removal by this approach was therefore not reliable, particularly for labile constituents such as EOs.

Estimating colour removal in this way was less likely to be affected to the same extent by time-varying source composition, because of the relative stability of colour compared with EOs. The colour removal data shown in Figure 6.20 and Table 6.10 was therefore more reliable. The data showed considerable variation in colour reductions, medians ranging from 88% in B15/1 to -8% in B11/3, the overall ground water median being 45%.

6.6.6 Ground water response to effluent infiltration

The only clear response in ground water chemistry attributable to infiltration of effluent from the overlying seepage pond was observed in bore 11/4, which sampled ground water from the interface between the surficial sediments and consolidated ignimbrite, at 3.1–4.5 m beneath the seepage basin floor. The response occurred within two days of flooding the seepage basin. Changes in ground water chemistry were dramatic and attributed to effluent flow through fractures in the surficial sediments. The changes observed are described below.

Physical response: ground water levels

Changes in ground water levels directly beneath the seepage pond (in bore 11), were neither sufficiently large nor consistent to be definitively related to effluent seepage from the pond above (Figure 6.21). Inspection of the longer term trends in water level (Figure 6.8) revealed that the apparent increase in level observed in bore 11/4 may have been an artifact of the abnormally low level recorded immediately before effluent addition to the pond.

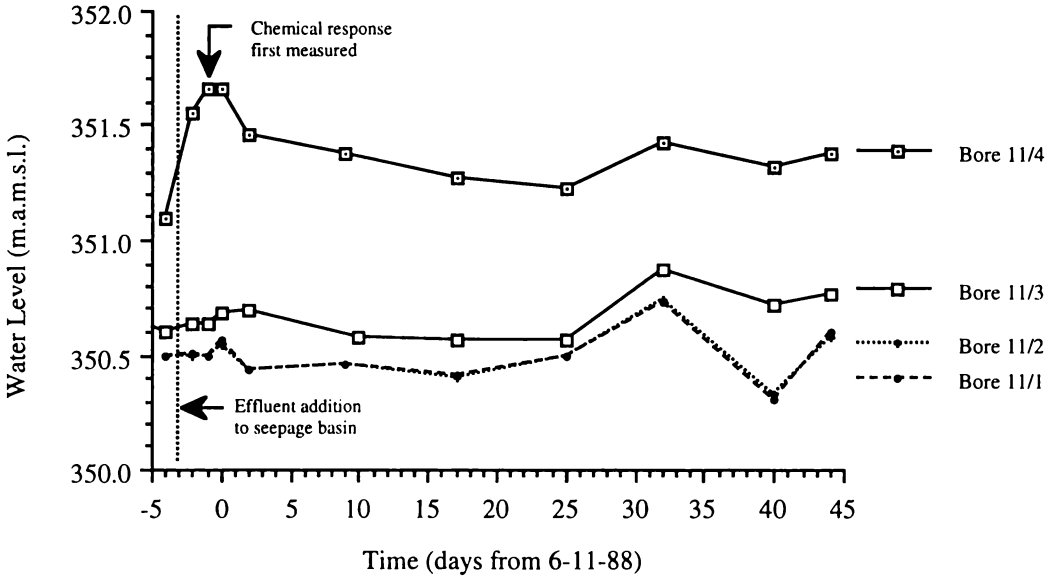


Figure 6.21: Ground water levels in bore 11 during the reassessment period

Chemical responses

Increases in the concentrations of sodium, colour, and EOs were measured in bore 11/4. The changes occurred within two days of the first addition of effluent to the pond, were transient, and isolated to bore 11/4 (Figures 6.22–6.24).

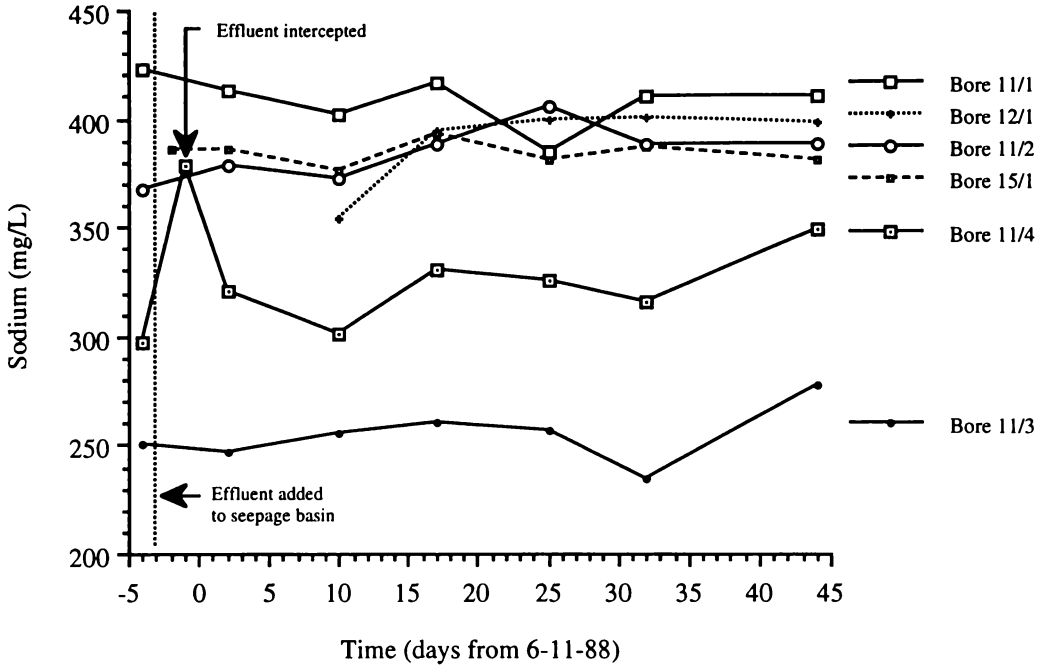


Figure 6.22: Ground water sodium concentrations during the reassessment period

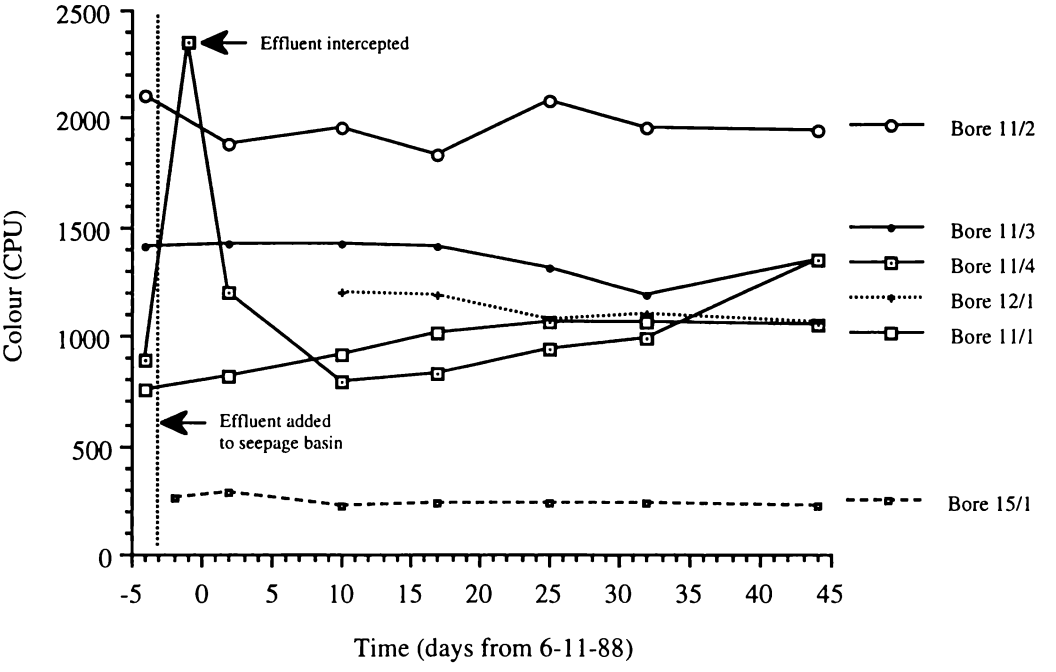


Figure 6.23: Ground water colour during the reassessment period

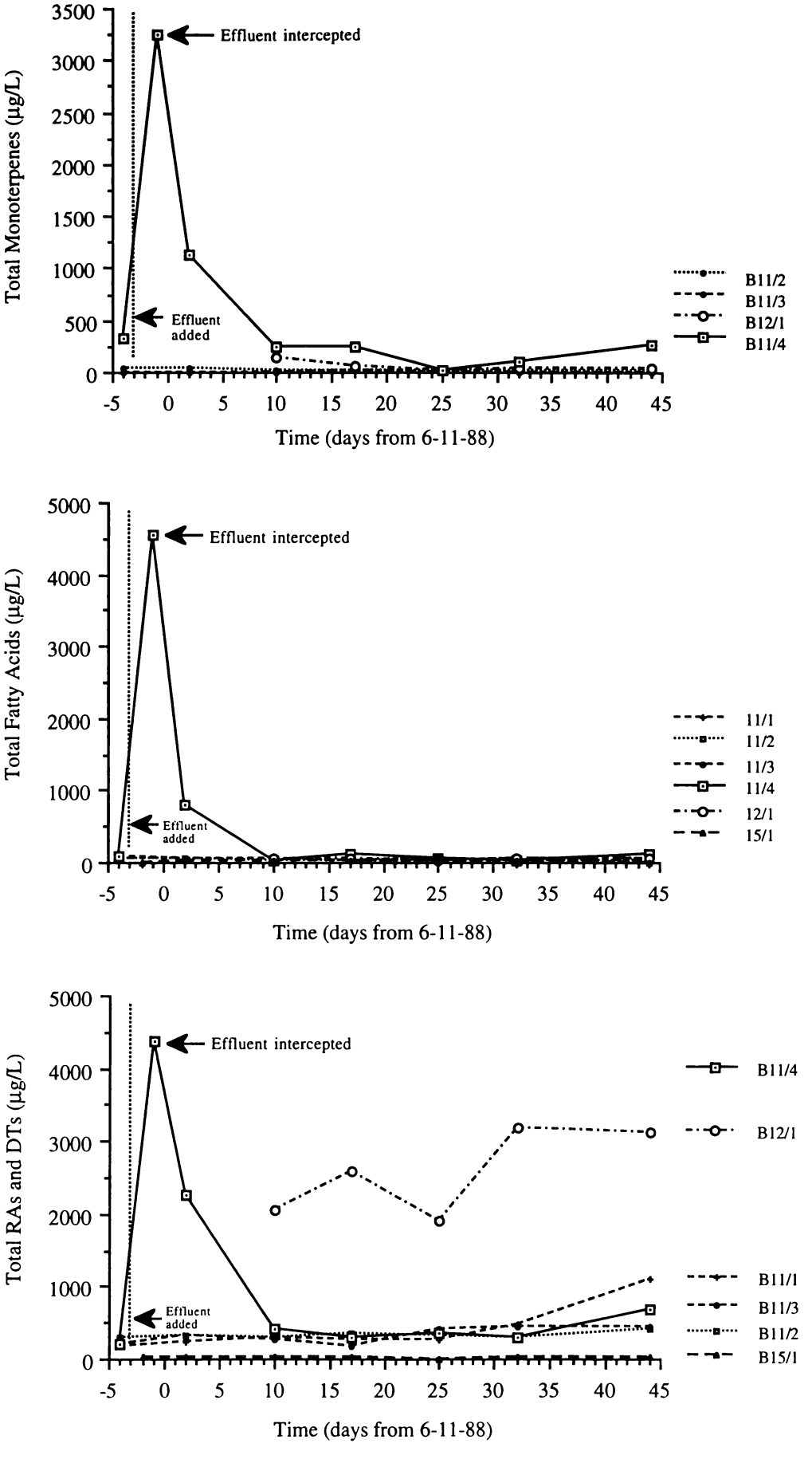


Figure 6.24: Concentrations of extractable organics in ground waters during the reassessment period

The short time (≤ 2 days) between effluent addition to the seepage pond and the response in ground water chemistry was consistent with transport of effluent via highly permeable zones, possibly fractures in the surficial sediments.

The transient nature of the responses was, however, inconsistent with continuous plug flow through fractures. Although additional effluent was added to the pond for another day after the response was first measured, the concentrations of effluent constituents in the ground water decreased. This indicated that the route by which effluent moved to bore 11/4 was blocked after passage of the initial plug. A mechanism which could have accounted for this behaviour was flow through self-sealing fractures, either in the bulk surficial sediments, or between the bore casing and the sediments. Given the quality of the well construction, which included a substantial sealing layer of bentonite above the screened section, the latter possibility seemed less likely.

It was possible that dessication fractures in the sediments were formed when the basin was dried out prior to the experiment. Upon rewetting with effluent, these were sealed, thereby allowing only a "spike" of effluent to be transmitted into the ground water. Soil shrinkage upon drying, and swelling upon rewetting, and the associated changes in transport of liquid waste into the subsurface, are problems which are often overlooked in the management of land application systems (Fuller and Warwick 1985a).

No clear response was observed in the deeper sampling piezometers of the bore 11 well cluster. Water levels in bore 11/4 were approximately 1 m higher than in the bore 11 wells sampling from deeper zones (bores 11/3, /2, and /1; Figure 6.8). This indicated that the hydraulic connection between the unconsolidated sediments and the ground water in the underlying ignimbrite was poor. Horizontal movement of infiltrating effluent along the restrictive layer at the sediment/ignimbrite boundary, rather than vertical transport into the ignimbrites below, was therefore more likely to occur. This was a plausible explanation for the lack of chemical response in the sampling wells sited below bore 11/4.

Changes in ground water chemistry

Water samples taken from bore 11/4 showed marked changes in composition due to interception of effluent sourced from the seepage pond.

The EOs present in the ground water samples taken from bore 11/4 between 2 and 20 days after effluent addition to the pond were markedly different from those found in the sample taken before effluent loading. MTs, which were usually relatively minor constituents of the ground waters influenced by the seepage system, were present in high concentrations. The MT chemistry of the effluent-affected ground water was similar to that observed in J Pond (section 4.3.4), with fenchone, camphor, DHT, and α-terpineol as major components. MT concentrations dropped rapidly over time to pre-dosing levels after 11 days. Unsaturated FAs, in particular oleic acid (FA18:1), which were major constituents of the parent effluent, but which were found at only very low concentrations in the ground water samples taken before effluent application to the pond, were present at high concentrations. As was observed for the

MTs, these compounds had essentially disappeared after 11 days. Dehydroabietic acid was the dominant RA found in the ground water immediately after effluent infiltration. Other RAs not usually present in the ground waters in significant amounts, such as pimaric, sandaracopimaric, and 13β-hydroxyabietanoic acids were also found in the samples.

The composition of the ground waters sampled from wells other than bore 11/4 remained relatively stable over the duration of the experiment. One exception was the DT content of bore 11/1, which increased in the samples taken towards the end of the trial. A marked increase in the concentrations of DTs, retene *[105]* in particular, was primarily responsible for the changes.

Bore 11/1 was resampled 22 months after this experiment (October 1990). The increasing trend in RA and DT concentrations had continued, indicating that slow, but substantial, changes in ground water composition were occurring. Between the start and the end of the land application experiment, the concentrations had increased from 170 to 1100 $\mu g\ L^{-1}$. A further increase to 2400 $\mu g\ L^{-1}$ occurred in the following 22 months. These increases in DTs occurred without corresponding increases in sodium or colour (which dropped over the 22 month period; Table 6.15).

It was unlikely that the changes observed in bore 11/1 were attributable to the seepage experiment conducted in November/December 1988 in basin P7 because they were measured in the deepest well beneath the seepage basin, and no similar changes were observable in the shallower ground waters sampling from zones closer to the seepage pond. The changes more probably reflected long-term fluctuations in the ground water chemistry of the seepage field. Attributing small changes in ground water chemistry due to seepage from a single, relatively small, isolated source within a large seepage field, when changes of potentially greater magnitude were occurring from unidentifiable sources, was therefore unlikely to be successful.

6.6.7 Chlorinated phenolics

Analysis of six ground water samples for chlorophenolics was performed. These preliminary data showed that ground waters which, from their elevated colour levels, were clearly effluent affected, contained relatively low concentrations of chlorophenolics (Table 6.11). Ground water taken from bore 11/4 on 5/11/88 (when the effluent spike was observed) contained clearly elevated concentrations. Total chlorophenolics in this sample were present at about 4% of the concentrations found in the seepage basin effluent at that time. The chlorophenolics concentrations of 1.7–4 $\mu g\ L^{-1}$ found in the other ground water samples were approximately 17–40% of that present in the seepage pond in the final few days of monitoring. These were relatively lower than RAs and DTs, which were present in ground waters at concentrations comparable with those present in the pond (Table 6.9). This suggested that chlorophenolics were being more effectively removed during infiltration than RAs and DTs.

Table 6.11: Concentrations of chlorophenolics found in ground waters beneath the seepage basin

	Bore:	11/1	11/2	11/3	11/4	12/1	11/4	
	Date:	23-11	23-11	23-11	23-11	23-11	5-11	
Constituent		$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	% [a]
Total chlorophenols		0.5	0.4	0.4	0.5	0.6	6.4	11
Total chloroguaiacols		0.6	0.8	0.8	0.5	1.1	13	5
Total chlorovanillins		0.3	0.5	0.6	0.2	0.7	4.5	2
Total chlorocatechols		0.6	0.7	0.8	0.3	0.9	1.8	6
dichlorohydroxybenzaldehyde		0.9	0.6	0.6	0.3	0.7	2.4	5
Total chlorophenolics		2.9	3.0	3.2	1.7	4.0	28	4

a: concentration expressed as percentages of the seepage basin effluent concentrations on 5-11-88.

6.6.8 Waters from the surficial sediments: Ceramic cup samples

Few satisfactory samples were obtained from the ceramic cup samplers sited in the unconsolidated sediments beneath the seepage basin. The results obtained for five such samples are summarised in Tables 6.12 and 6.13 (EO data is listed in Appendix 2, Table A2.18).

Before effluent addition to the seepage basin, samples taken from depths between 0.65 and 1.0 m beneath the floor of the seepage basin contained moderately elevated and similar colour and sodium levels, but very different concentrations of EOs (Table 6.12). The composition of the RAs in the 0.65 m sample was similar to that of degraded seepage basin effluent, with abietanoic acid as the dominant compound. Smaller amounts of dehydroabietic, pimaric, seco-dehydroabietic, abietic, 13-abietenoic, pimaranoic, 8(14)-pimarenoic, 8-isopimarenoic, and 8,15-pimaradienoic and 8,15-isopimaradienoic were also present. MTs were not detectable.

Two samples were taken after effluent addition to the seepage basin (on 5/11/88) from the samplers sited adjacent to bore 11 (location 2). The sample from 0.75 m beneath the basin, contained high concentrations of RAs, MTs, colour, and sodium (Table 6.13).

Table 6.12: Composition of ceramic cup water samples taken from the sediments beneath the seepage basin before effluent application (2/11/88)

		Location 1		Location 2
Constituent	Units	depth=0.65 m	depth=0.95 m	depth=1.0 m
Sodium	$mg\ L^{-1}$	230	220	280
Colour	CPU	1150	730	1130
Total fatty acids	$\mu g\ L^{-1}$	23	7	5
Total resin acids	$\mu g\ L^{-1}$	1520	4	37

Table 6.13: Composition of ceramic cup water samples taken from the sediments beneath the seepage basin after effluent application (5-11-88)

		depth = 1.0 m	depth = 0.75 m	
Constituent	Units	Concentration	Concentration	% of pond value
Sodium	mg L^{-1}	320	440	79
Colour	CPU	1600	3160	136
Total monoterpenes	µg L^{-1}	<20	6100	40
Total fatty acids	µg L^{-1}	22	790	4
Total resin acids	µg L^{-1}	130	22600	43

Effluent was intercepted in the 0.75 m sampler, but not in the 1.0 m sampler. The colour of the effluent contaminated sample was greater than that of the seepage basin effluent above, and had an inky-black/green appearance, rather than the dark brown colour of the effluent. The colour increase observed, and the change in visual appearance of the leachate, were not large, but were consistent with the changes in colour observed in soil column experiments (Chapter 7).

The composition of EOs in the 0.75 m sample showed that significant transformations had occurred in the sediment zone. Dehydroabietic and 13β-hydroxyabietanoic acids were the major RAs present, together making up over 70% of this fraction. 8,15-isopimaradienoic, pimaric, 13-abietenoic, and abietanoic acids were also present in substantial amounts. Leachates from continually flooded soil-columns (Chapter 7) were also dominated by dehydroabietic and 13β-hydroxyabietanoic acids.

The MT fraction was composed predominantly of α-terpineol, but also contained *p*-cymene, fenchone, camphor, and DHT as significant components. A similar composition was found in J Pond (section 4.3.4) and in the initial phases of the laboratory soil-column experiments (Chapter 7). Fatty acid concentrations were relatively low, indicating that they were readily degradable and/or sorbed to the sediments. Again, this result was consistent with the laboratory experiments where degradative removal occurred.

A compound tentatively identified from its mass spectrum as 1,2,4-trithiolane *[31]* was found at a concentration of about 580 µg L^{-1} (assuming a response factor equal to that of camphor). This compound, which may have have contributed to the highly sulphurous odour of the sample, has been tentatively identified in effluent treatment system sludge from another New Zealand kraft mill (Panadam-Twigley 1988) and was found in Kinleith J Pond effluents.

While only a single sample, the composition of the leachate at 0.75 m depth showed that infiltration through the seepage basin sediments was, with the exception of FAs, not providing adequate treatment of any of the effluent components analysed. Transformation of the MTs and RAs had occurred during passage through the sediments, but total concentrations were reduced by, at maximum, about 60%. Colour reductions were negligible, and may even have increased, as was found to occur in laboratory trials (Chapter 7).

The integrity of the sample was, however, questionable. Interception of pond effluent at 0.75 m depth within two days of effluent application to the pond indicated a rapid rate of effluent infiltration to the sampler. Compared with NZFP's estimated seepage rates of 10 mm d^{-1} (Chapter 1), the ≥370 mm d^{-1} necessary to reach the sampler within two days suggested that preferential flow through highly permeable sediment, possibly the material repacked around the sampler during placement, must have occurred. This was one of the concerns identified with the use of the ceramic cup samplers beneath the flooded pond. Alternatively, more rapid effluent transport through the upper sediments may have been due to the effects of seepage basin discing, which was carried out annually to promote infiltration. If so, the result may then have reflected changes which would be typical of the seepage field.

Although the chemistry observed was consistent with that in the pond, and with soil-column experiments, sample integrity was questionable. Further experiments aimed at optimising placement and sampling procedures for these shallow sediment zone samplers would therefore be required to obtain reliable information on changes in effluent composition in the surficial sediments.

6.6.9 Summary of results from the reassessment period

Sodium, colour and EOs in ground waters from the wells beneath seepage basin P7 were measured 5–8 times over a seven week period, giving a data set from which reliable estimates of contaminant levels were made. The ground water chemistry was similar to that measured in the initial studies, confirming the spatial patterns initially observed. Short-term temporal variability in ground water chemistry was not great, but there was evidence from DT chemistry of bore 11/1 that large, longer-term changes, were occurring.

Comparison of ground water composition with that of the overlying seepage pond gave variable estimates of contaminant removals. The most reliable estimates were those for colour because of the relative stability of colour in the pond system. Median calculated removals ranged between -8% and 88%. RA removals were 50–97%, while changes in total RADT levels ranged from a 97% reduction to a 360% increase. MCPs were substantially higher in the ground water than in the seepage basin effluent. The data indicated that it was unlikely that the ground water sampled was sourced from effluent of the composition present in seepage basin P7 at the end of the monitorng period (as was assumed in the removal calculations).

Samples taken from one well, bore 11/4, and one sample from a sediment zone sampler at 0.75 m beneath the floor of the seepage basin, were the only ground waters which definitely contained effluent sourced directly from the seepage pond. The response time, duration, and chemistry of the ground water response to effluent loading indicated that transport to bore 11/4 was probably via fracture flow. Effluent percolating through the sediments to the ground water sampling wells by non-fracture flow was not intercepted. Possible reasons were insufficient experimental duration, or siting of wells in zones which were not receiving effluent directly from the overlying seepage basin.

Extractable organic chemistry of the ceramic cup sample taken from the sediment zone shortly after effluent addition to the pond was consistent with that of leachates from soil column

experiments, suggesting that it represented effluent percolating through bulk sediment. However, the rapid rate of effluent infiltration to the sampling zone indicated that at least some fracture flow to the sampler had also occurred.

In summary, the reassessment study improved the ground water chemistry database but was unable to provide definitive data on contaminant removals during effluent infiltration. To do so would have required a long-term programme, in which the chemistry of a number of seepage basins was monitored over several flooding cycles while also monitoring ground waters beneath the ponds. Adding a unique conservative tracer (e.g. dye or radioisotopic species such as ^3H_2O) to the effluent would be required to confirm the link between ground water and pond samples and hence validate removal calculations. Alternatively, properly installed and tested ceramic cup samplers sited in the unconsolidated surficial sediments could provide the samples required to determine contaminant removals during infiltration.

Despite the problems associated with estimating contaminant removal on a field scale, the results from the monitoring showed that levels of effluent-sourced contaminants in the shallow ground waters were comparable, or in some cases (e.g. MCPs, DTs) higher than in degraded seepage basin effluent. This suggested that much of the treatment activity of the LA system occurred in the seepage ponds rather than in the underlying sediments and shallow ground waters.

6.7 Off-site Migration of Effluent

Elevated concentrations of sodium, colour, and EOs were found in most shallow ground waters beneath the seepage ponds. The movement of these contaminants away from the seepage system therefore needed to be determined. Of particular interest were:

1. effluent distribution between the major ignimbrite aquifers;

2. contaminant attenuation with distance from the seepage ponds; and

3. extractable organic chemistry of off-site ground waters.

The wells depicted in Figures 6.5 and 6.6 were drilled to examine distribution of effluent in the ground water system on an approximate North–South transect away from the seepage ponds towards Tokoroa. This was the direction of ground water flow, and hence effluent migration, away from the seepage area. Information on effluent migration and attenuation was obtained by examining concentrations of effluent constituents (e.g. chloride, sodium, colour, RAs) in each major ignimbrite unit along this transect.

Data used for these assessments were:

- sodium data from NZFP's monthly monitoring programme. Wells B73, 74, 89, and 90 were monitored by NZFP at approximately monthly intervals between April 1987 and July 1988. After a break of about a year, monthly monitoring recommenced in July 1989. Wells B86 and 94 were installed later in the programme (June 1988 and January 1989 respectively) and

therefore a more limited data set for these wells was obtained. Data from this monitoring, for the period April 1987 to December 1989, and with limited resampling data collected in October 1990, were used to evaluate the spatial distribution of effluent in the ignimbrite aquifers, and to check temporal trends in sodium concentrations.

- a single set of chloride data for wells B73, 74, 89, and 90 sampled September 1987. These were used to assess contaminant attenuation by comparing relative concentrations of chloride (an unreactive tracer), sodium, colour, A270, and EOs with distance from the seepage area.

- three sets of EO, colour, and A270 data for wells 73, 74, 89, 90 from samplings conducted in September 1987, November 1987, and April 1989, and one set from well 86 in April 1989.

- EO, colour, sodium, and A270 data from replicate sampling of well B74/1 in July 1989 (also used for sampling and analysis precision assessments; section 3.5 and 6.2.1); and

- EO, colour, sodium, and A270 data from a single sampling of well B74/2 in October 1990, which was used to check for longer term changes in ground water chemistry (section 6.8).

These data are summarised as median concentrations in Table 6.14 and appended in Tables A2.19 and A2.20 (Appendix 2).

6.7.1 Effluent distribution in the ignimbrite units

Sodium concentrations varied markedly both within, and between, ignimbrite units at the same location (i.e. within the same well cluster). Concentrations were highest in the densely welded, high permeability, zones of the Marshall A ignimbrite (Figure 6.24). Well 74 was the exception, as sodium concentrations in the Marshall B were as high as, or higher than, those present in the Marshall A. The large differences in sodium concentrations between, and within, the ignimbrite units meant that each unit had to be treated separately when examinating effluent attenuation with distance from the ponds, or temporal trends in contaminant levels. The within-unit differences highlighted the effects of ground water and effluent movement through densely welded, fractured ignimbrite zones.

Concentrations of colour, A270, and EOs (RAs and DTs) were consistent with the effluent distribution given from sodium levels, highest levels being present in the welded zones of the Marshall A unit and, in bore 74, in the Marshall B unit. Elevated colour, A270, and RADT levels were found in wells 73/1 and 2, B74/1 and 2, and at lower levels in B74/3, B89/2, and B90/2 (Figure 6.26). A270 and colour were well correlated in effluent-affected waters (e.g. in B74, R^2=0.990; for all wells R^2=0.975). A270 was a more sensitive measure of organic colour, and was therefore more suitable for off-site ground waters, as colour levels in some wells approached detection limits for the NCASI colour measurement procedure (section 3.2). A270 was therefore plotted in Figure 6.26 as a measure of colour. RADTs were significantly ($p<0.001$) correlated with colour (R^2=0.852), A270 (R^2=0.864), and sodium (R^2=0.625).

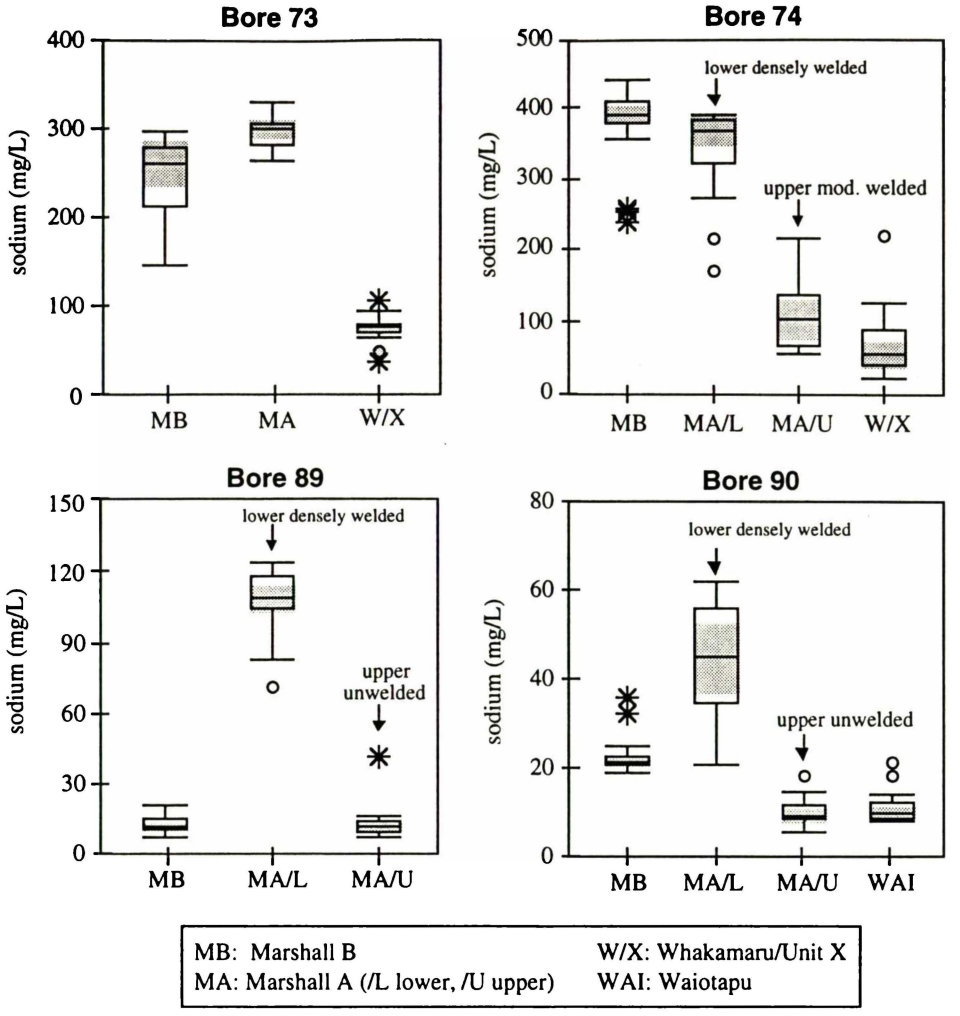


Figure 6.25: Sodium concentrations in the major ignimbrite units in off-site ground waters.

The variation observed in the data plotted in Figures 6.25 and 6.26 was attributable partly to analytical and sampling variation but, more importantly, to temporal changes in analyte concentrations. Concentrations in the most clearly effluent-affected wells dropped over time (discussed in section 6.8). This was most apparent for EO data for B90/2, in which RAs and DTs were found in both September and November 1987, but had dropped to undetectable levels in April 1989 (data points indicated in Figure 6.26).

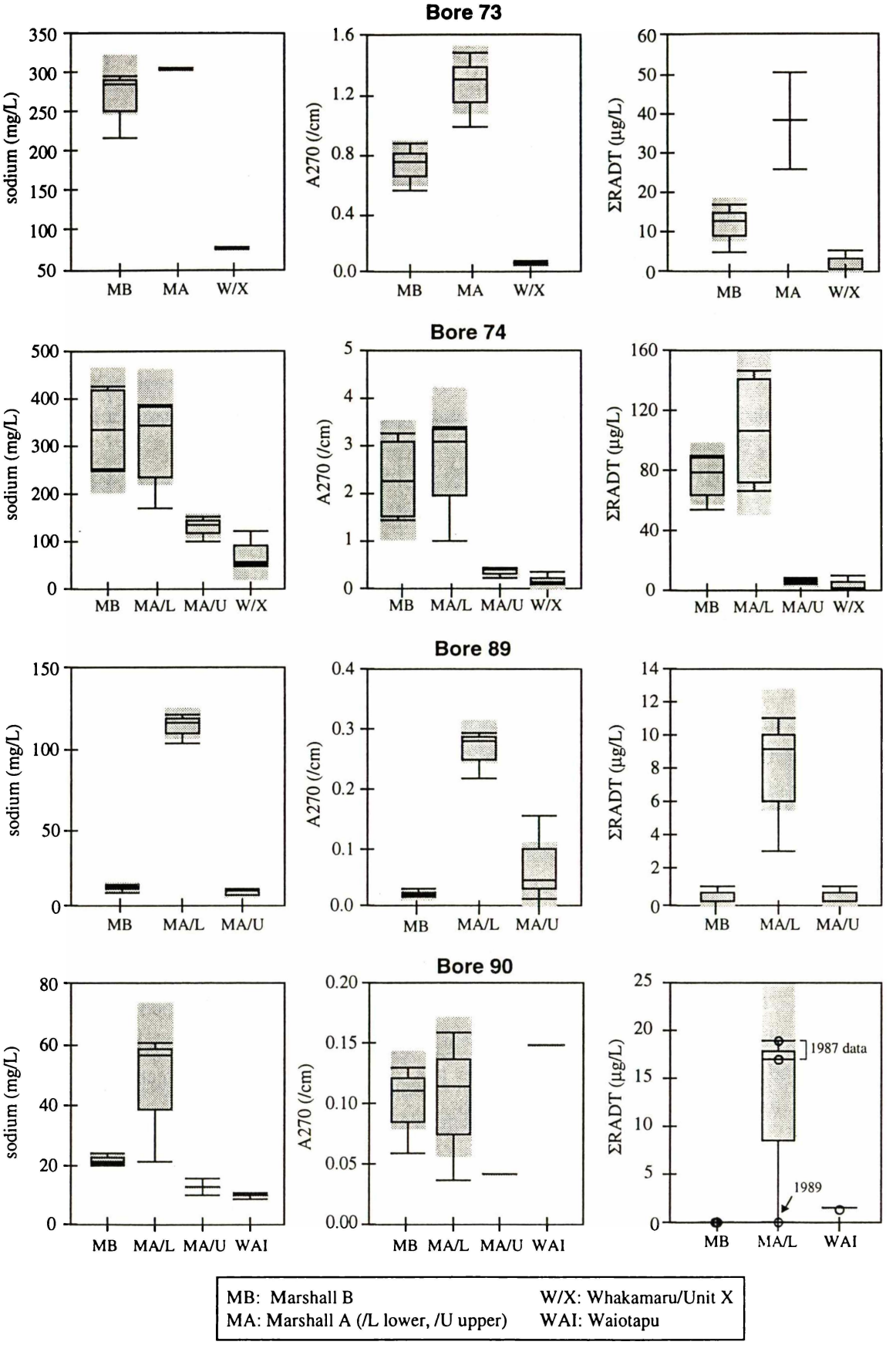


Figure 6.26: Sodium, A270, and total resin acid plus diterpene hydrocarbon (ΣRADT) concentrations in off-site ground waters

Table 6.14: Median concentrations of sodium, colour, and A270 in off-site ground waters

Well	Ignimbrite Unit	Sodium[a]	Sodium[b]	Colour	A270	Σ RADT[c]
		mg L^{-1}	mg L^{-1}	CPU	cm^{-1}	µg L^{-1}
73/1	Marshall B	263	286	89	0.75	13
73/2	Marshall A	302	304	256	1.31	39
73/3	Whakamaru/Unit X	74	74	10	0.06	<1
74/1	Marshall B	396	336	683	2.30	79
74/2	Marshall A	373	345	881	3.11	107
74/3	Marshall A	103	135	42	0.36	4
74/4	Whakamaru	50	54	12	0.09	<1
89/1	Marshall B	12	15	4	0.03	ND
89/2	Marshall A	110	117	29	0.25	9
89/3	Marshall B	12	10	28	0.05	ND
94/1	Marshall B	25	–	–	–	–
94/2	Marshall A	29	–	–	–	–
94/3	Marshall A	44	–	–	–	–
90/1	Marshall B	22	21	12	0.11	ND
90/2	Marshall A	45	56	20	0.12	17
90/3	Marshall A	10	12	5	0.04	–
90/4	Waiotapu	10	9	35	0.15	1
86/1	Marshall A	30	13	16	0.03	ND
86/2	Waiotapu	16	16	18	0.04	ND

a: median of all sodium data from NZFP files; b: median of sodium data from only those samplings where colour and EOs were measured; c: sum of identified resin acids and diterpene hydrocarbons – "<1" indicates RADTs found at concentrations totalling less than 1 µg L^{-1}, "ND" indicates RADTs not detected (detection limits approximately 0.2–0.5 µg L^{-1} per component).

6.7.2 Changes in contaminant concentrations with distance from the seepage area

Highest sodium concentrations were present in ground waters immediately adjacent to the seepage area (bores 73 and 74). These levels were comparable with those measured in the shallow ground waters directly beneath seepage basin P7. Concentrations decreased rapidly with distance away from the seepage area (Figure 6.27).

Compared with the highest sodium concentrations measured near the ponds (median Na^+=373 mg L^{-1} in B74/2), median sodium concentrations in the Marshall A aquifer fell to 29% at approximately 100 m distance (B89/2, median 110 mg L^{-1}), then to 12% by 800 m (B94/3, median 44 mg L^{-1}). At 1400 m (B90/2), median sodium was 12% of the B74 value, and fell to 8% by 2700 m (B86/1, median 30 mg L^{-1}). Although concentrations dropped markedly with distance from the seepage area, they did not reach background levels (6–10 mg L^{-1}) in the wells monitored.

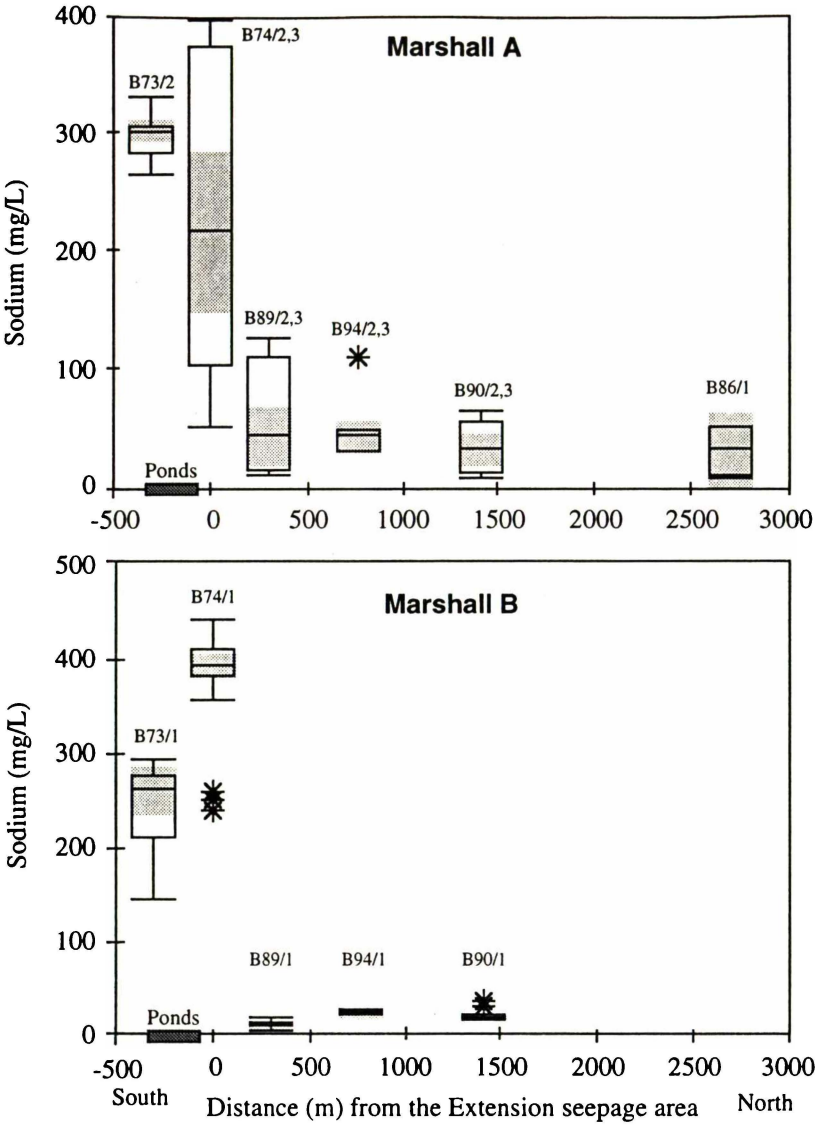


Figure 6.27: Changes in sodium concentrations in Marshall A and B ignimbrite aquifers with distance from the Extension Area seepage ponds

To assess the relative attenuation of effluent constituents in the ground water system, changes in relative concentrations with distance were compared with those for chloride (which was assumed to be an unreactive tracer). Concentrations were expressed as % of those in B74/2, the well sampling the welded Marshall A unit at the edge of the seepage field. This comparison, shown in Figure 6.28, showed relative attenuation (in increasing order) sodium < A270 ≤ RADT < colour. The B90/2 result for RADT was surprising, as concentrations were higher in this well in both September and November 1987 than found in B89/2, which was sited much closer to the seepage area. The reason for the elevated RADT levels was not determined, but they were consistent with elevated sodium and A270 concentrations measured on these occasions.

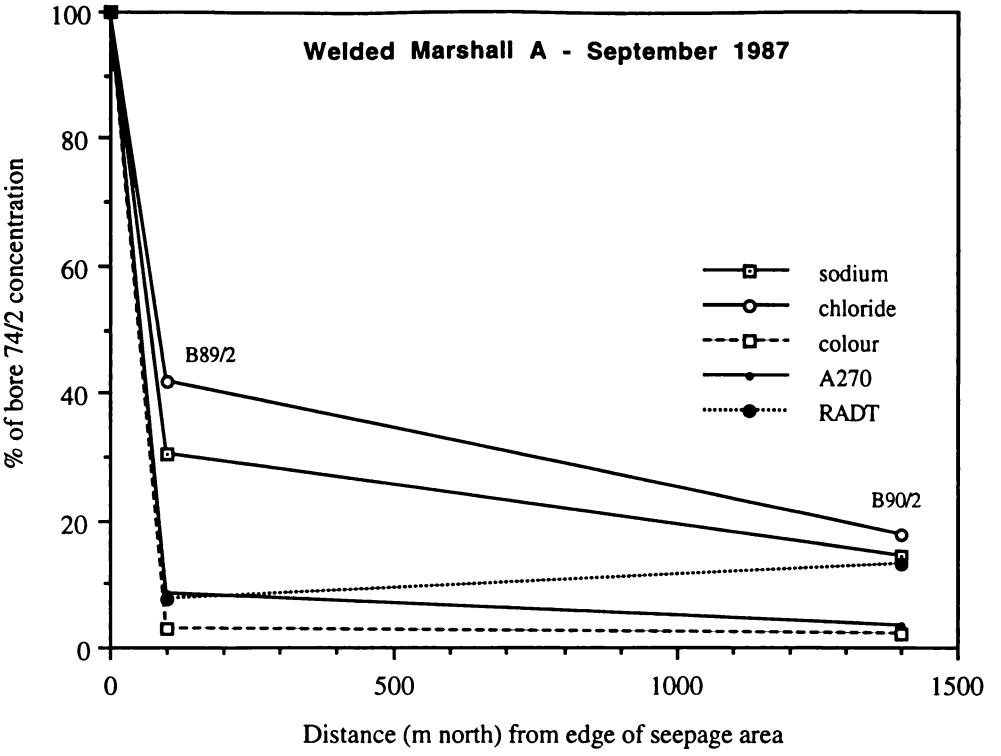


Figure 6.28: Changes in relative concentrations of chloride, sodium, colour, A270, and resin acids plus diterpene hydrocarbons (RADT) with distance from the seepage area September 1987.

Colour and A270 were high in the welded Marshall A and Marshall B units in the wells immediately adjacent to the seepage area (B73/1, 2 and B74/1, 2). While high, they were somewhat lower than those measured in most shallow ground waters beneath seepage pond P7 (e.g. Table 6.9). Colour and A270 dropped rapidly with distance from the ponds, median concentrations falling to 4% and 8% respectively of the B74/2 medians within approximately 100 m, and to 2% and 1% by 2700 m. RADTs were also strongly attenuated, median concentrations dropping to 9% of the B74/2 level by 100 m, but rising to 16% at 1400 m, and falling to <1% at 2700 m.

April 1989 data showed similar trends to the 1987 data, except that RADTs were not detected in B90/2. Attenuation of organics was rapid, RADTs dropping to 2% of the B74/2 levels by 100m, after which they were undetectable (<1% of the B74/2 level). Colour and A270 also decreased rapidly, A270 dropping to 7.6% in 100 m, then to 1.3% and 1.1% after 1400m and 2700 m respectively. These data are plotted in Figure 6.29.

Colour, A270, and RADTs decreased more rapidly with distance than sodium, indicating that organics were being more actively attenuated than sodium in the ground water system. This was consistent with the lower colour, but comparable sodium levels, in B73 and B74 compared with the shallow ground waters beneath pond P7.

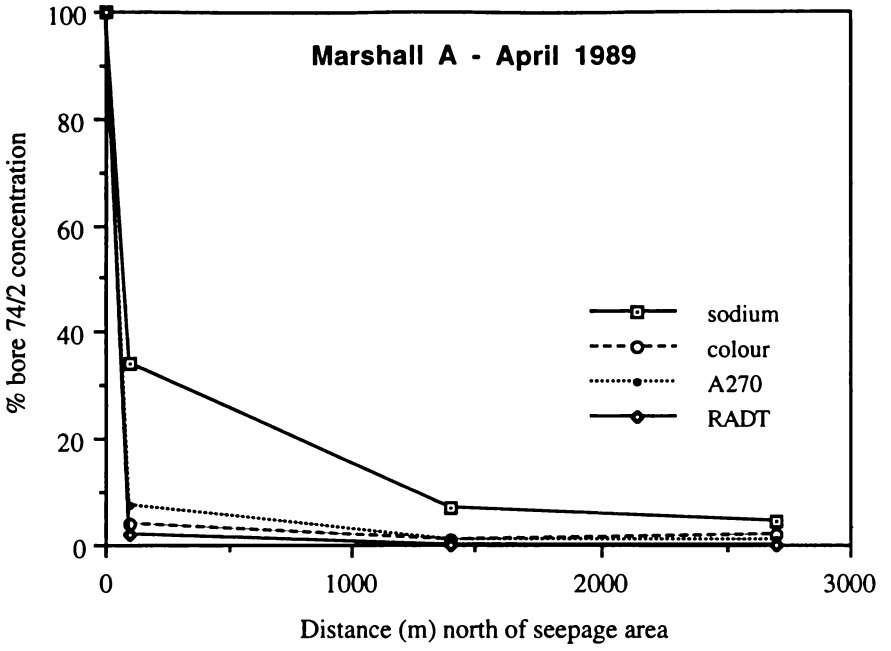


Figure 6.29: Decreases in relative sodium, colour, A270, and resin acid and diterpene (RADT) levels with distance in the Marshall A aquifer. April 1989 data.

6.7.3 Extractable organics in off-site ground waters

Off-site ground waters were extracted by the pH 2 procedure in September and November 1987, and by the pH 11 procedure in samples taken April 1989, July 1989, and October 1990. As observed for the shallow ground waters, these procedures recovered a similar range of compounds, but UCMs were greater with the pH 2 method. Late eluting, unidentified compounds of m/z 350–402 were also present at higher levels in the pH 2 extracts.

Extracts from effluent-affected ground waters were dominated by UCM, above which effluent-derived compounds similar to those found in the shallow ground waters beneath the seepage ponds were identifiable. MCPs, largely trimethyl- and tetramethyl- substituted species, were present but not reliably quantifiable as extracts were concentrated to small volumes prior to GC analysis, during which these compounds could be lost in variable amounts by volatilisation.

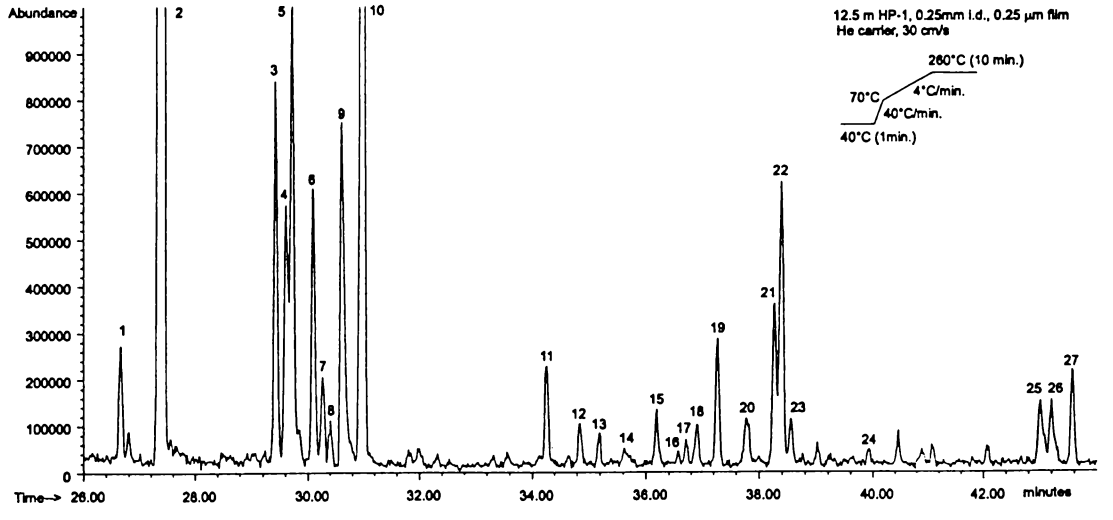
A range of RAs and DTs, most of which were also found in seepage basin sediments and shallow ground waters, were also present. The RA chemistry was similar to that of the shallow ground waters, a diverse range of monoenic and saturated RAs being identifiable. The major RAs were abietanoic acid and 7-oxokauranoic acid. DT chemistry was generally not so diverse as that observed in the shallow ground waters, although bore 74/1, and to a lesser degree B74/2 and B90/2 in 1987, were exceptions. These waters contained fichtelite and DT260 compounds in relatively large amounts, collectively making up approximately half the total RADT concentration. Late eluting compounds of m/z 348–402 were prominent components in some samples.

Also present in highly variable amounts were a number of compounds which were not effluent-sourced. These included phthalic acid esters (mainly DEHP, but also other methyl- and ethyl-

substituted phthalates in smaller amounts), benzothiazole *[53]*, 2-(methylthio)benzothiazole *[70]*, 2-(4-morpholinyl)-benzothiazole *[85]*, and several compunds with mass spectra simialr to suubstituted morpholines (e.g. *[43]*). These species were not present in analytical blanks, and were therefore assumed to be introduced during sampling. Benzothiazoles have been found in estuarine sediments and linked to their use as curing agents and anti-oxidants in rubber manufacture (Spies *et al.* 1987). They have also been found in ground waters receiving infiltration from municipal sewage disposal (Hutchins *et al.* 1985), and are associated with a range of fungicidal and industrial products (Brownlee *et al.* 1992; Reemtsma *et al.* 1995). In the Kinleith ground waters, they were possibly sourced from rubber hosing used in the air-lift sampling equipment.

Figure 6.30 shows a representative GC-MSD TIC of the RAs and DTs present in off-site ground water close to the seepage area. Quantitative data are listed in Tables A2.20 (Appendix 2).

Comparisons of the concentrations of total RAs and DTs in the shallow ground waters beneath seepage pond P7 with RA+DT levels in bores 74/2 and 89/2 (the most contaminated wells close to the seepage area) indicated that there was attenuation of the EOs occurring in the ignimbrites beneath the ponds. Using the approach described in equation 6.1 to correct for dilution (using Na^+ as tracer and median concentrations from the reassessment period for shallow gruond waters, section 6.6), provided estimates of RA+DT reductions of 61% at B74/2, and 90% at B89/2. Colour reductions calculated in the same way were 10% at B74/2 and 91% at B89/2.



Peaks: 1. Unidentified mw=248 *[74]*; 2. HC18 internal standard; 3. DT260P *[77]*; 4. DT260I/S *[78]*; 5. DT262I *[80]*; 6. FA16:0 *[81]*; 7. DT262P *[79]*; 8. DT242 *[82]*; 9. 2-(4-morpholinyl)benzothiazole *[85]*; 10. fichtelite *[87]*; 11. FA18:1 *[101]*; 12. FA18:0 *[102]*; 13. seco-dehydroabietic acid #1 *[103]*; 14. seco-dehydroabietic acid #2 *[104]*; 15. contamination (*m/z*=56); 16. pimaric acid *[110]*; 17. 8-pimarenoic acid *[111]*; 18. 8-isopimarenoic acid *[112]*; 19. pimaranoic acid *[119]*; 20. isopimaranoic *[122]* + 13-abietenoic *[120]* acids; 21. 7-oxokauranoic acid *[126]*; 22. abietanoic acid *[127]*; 23. dehydroabietic acid *[128]*; 24. RA348? *[132]*; 25. bis(2-ethylhexyl)phthalate *[145]*; 26. RA350? *[146]*; 27. RA348? *[147]*. Resin and fatty acids present in extract as methyl esters.

Figure 6.30: GC-MSD TIC of resin acids and diterpene hydrocarbons in B74/1 (pH 11 extract)

6.8 Ground Water Response to Seepage System Retirement

Use of the seepage system was reduced markedly from mid-1988, and from late 1988 it was no longer used for effluent disposal. The response in ground water chemistry to the seepage system retirement was of interest. A limited set of ground waters from beneath seepage pond P7, and bore 74/2, were taken in October 1990 to assess whether major changes in ground water chemistry had occurred over the preceding two years. In addition, sodium data collected by NZFP from off-site wells between 1988 and 1990 were also used to investigate trends in ground water sodium levels that would reflect reduced effluent contamination.

6.8.1 Shallow ground waters beneath pond P7

Bores 11/1, 11/2, and 16/1 were sampled in October 1990. Results are summarised in Table 6.15. EO data are appended in Table A2.21 (Appendix 2). Compared with previously measured concentrations, 1990 ground waters had:

- lower sodium for all wells
- lower colour in B11/1 and B16/1, but similar in B11/2
- lower RAs in B16/1, similar in B11/2, but higher in B11/1
- lower DTs for B16/1, but higher in B11/2, and much higher in B11/1.

Table 6.15: Contaminant concentrations in ground waters sampled October 1990

Bore	sodium	colour	AOX	MCP	FA	RA	DT
	mg L^{-1}	CPU	mg L^{-1}	.....	.....	µg L^{-1}	.....
B11/1	330	800	6.9	42	30	410	1980
B11/2	180	1920	7.4	33	23	240	190
B16/1	150	39	1.5	3	27	26	69
B74/2	170	250	1.7	13	20	29	38

It was clear that marked changes in ground water chemistry had occurred in the 22 months between measurements. While some analytes had decreased in concentration, as was anticipated to occur after effluent seepage had stopped, others had increased markedly.

The relationship between colour and AOX data was interesting. The coloured component of BKME has usually been associated with high molecular weight chlorolignin. Correlation between colour and AOX might therefore be expected. The AOX and colour levels in B11/1 and 11/2 were not consistent with such a relationship, colour levels in B11/2 being much higher than might have been expected from either AOX or sodium levels. Possible explanations for the relatively higher colour than AOX were AOX mineralisation (which would reduce AOX levels but not necessarily colour), or colour increase due to interaction with sediments (as observed in soil column experiments, Chapter 7). These data highlighted the complexity of effluent behaviour in the ground water system.

6.8.2 Off-site ground waters

Based on sodium distribution between the ignimbrite units, wells sited close to the ponds, in the most permeable zones of the Marshall A unit (e.g. B73/2, 74/2 and possibly 89/2), were most likely to show earliest and strongest response to changes in effluent loading. Sodium data from each ignimbrite unit were plotted and visually examined for the presence of changes in sodium concentrations that could have been associated with seepage system retirement. These plots are shown in Figure 6.31 (Marshall B), 6.32 (Whakamaru/Unit X), and 6.33 (Marshall A). The line fitted through the data is a LOWESS smooth (Systat Inc.), a robust smoothing method which does not require the shape of the function being fitted to be known.

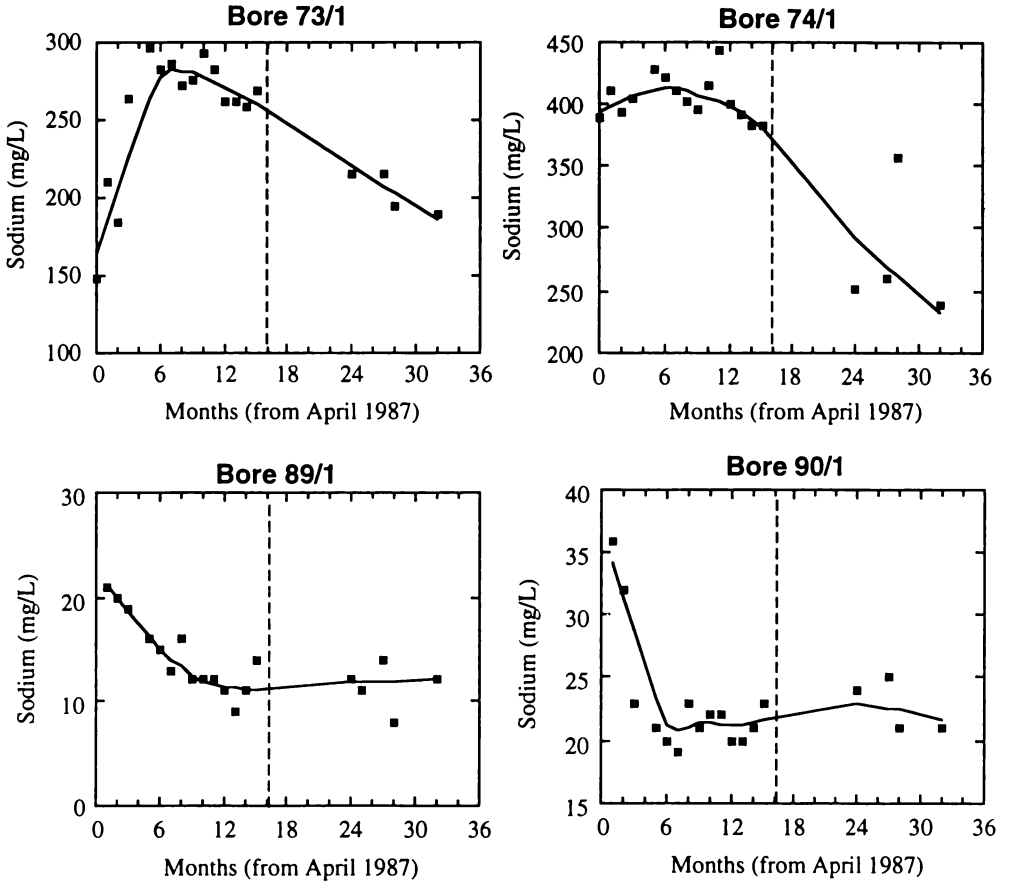


Figure 6.31: Temporal trends in sodium concentrations in Marshall B aquifer. Dashed line denotes approximate time of seepage system retirement (mid-late 1988).

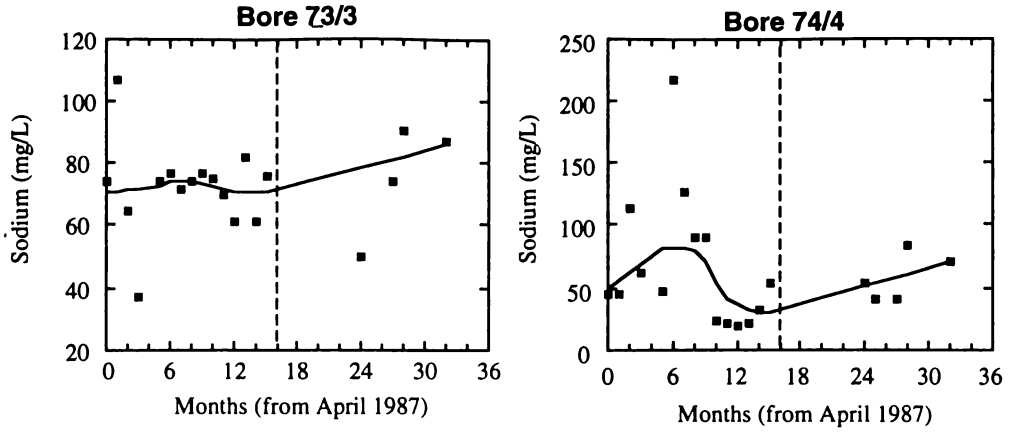


Figure 6.32: Temporal trends in sodium concentrations in Whakamaru/Unit X aquifer. Dashed line denotes approximate time of seepage system retirement (mid-late 1988).

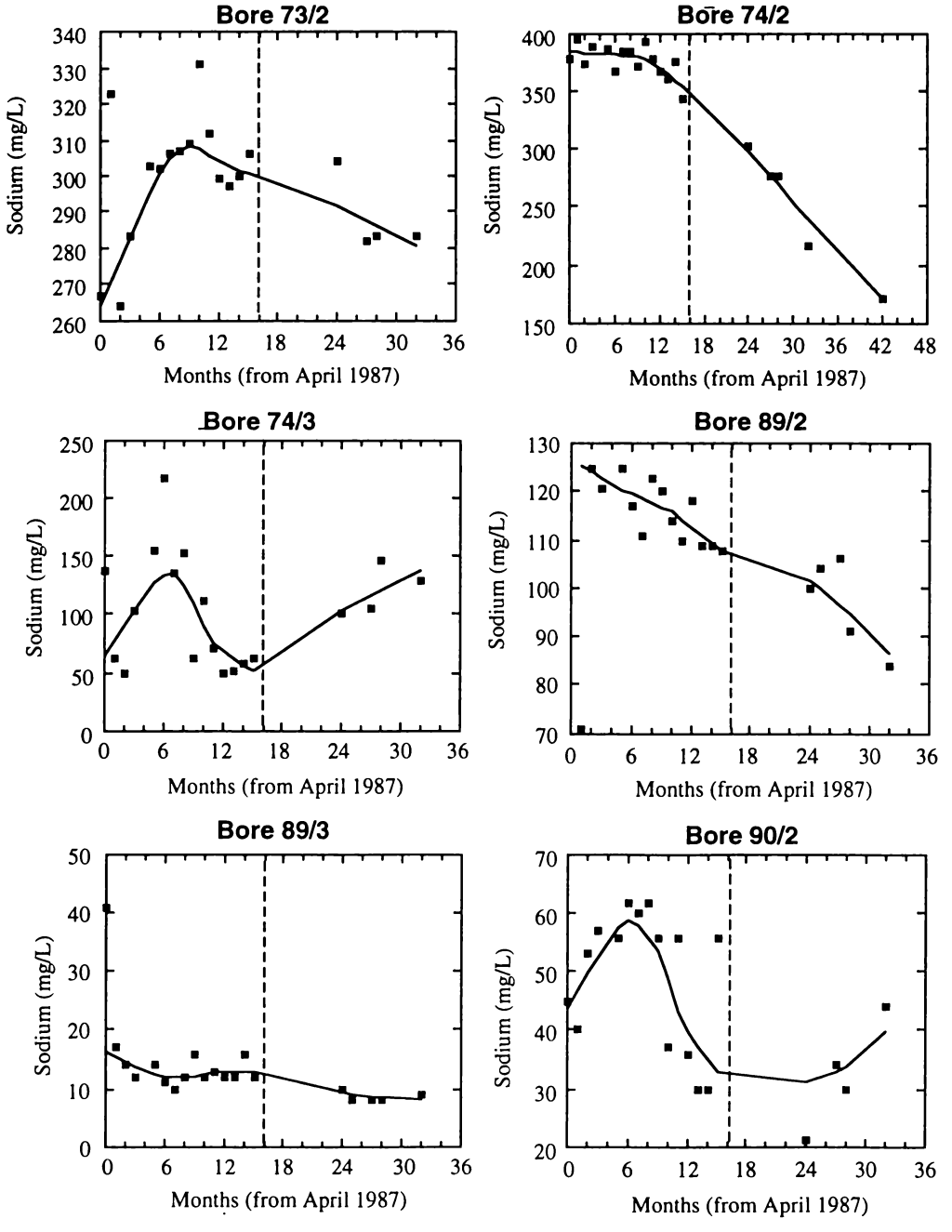


Figure 6.33: Temporal trends in sodium concentrations in Marshall A aquifer. Dashed line denotes approximate time of seepage system retirement (mid-late 1988).

The plotted data showed definite decreasing trends in sodium after mid-1988 for wells 73/1 and 74/1 in the Marshall B, and in wells 73/2, 74/2, and 89/2 in the Marshall A aquifer (the high permeability zones). Trends in wells 74/3 and 89/3, which sampled the less welded, lower permeability zones of the Marshall A were weaker, or not apparent due to data variability. No changes coinciding with seepage system retirement were observed in the Whakamaru/Unit X wells 73/3 and 74/4.

Insufficient data was collected for colour, A270, or RADTs to reliably assess trends in most wells. However, large decreases in the concentrations of these constituents were observed in B74/2, the well with the longest data record (having been resampled in October 1990).

Changes in sodium concentrations consistent with declining use, then retirement, of the Extension Area seepage system in mid-late 1988 were therefore apparent from data records from both Marshall B, and more particularly, from the high flow zones of the Marshall A ignimbrite.

6.9 Summary of the Ground Water Investigations

Ground waters from beneath the seepage basins and from off-site wells were analysed for sodium, chloride, colour, A270, and EOs. The shallow ground waters beneath the seepage ponds contained generally high sodium concentrations, indicating the presence of a substantial proportion of effluent-sourced water. Colour, A270, and EOs' concentrations were much more spatially variable than sodium, indicating variable degrees of organic component attenuation in the ground. The marked differences in the chemistry of the ground waters means that any generalisation about the composition of a "typical" shallow ground water will be subject to considerable uncertainty. Off-site ground waters were also variable in their composition. The spatial variation was consistent with the hydrogeology of the ignimbrites sampled by each well, highest concentrations at each location generally being found in the highly welded, high flow zones.

EOs in effluent-affected ground waters were dominated by UCM, above which MCPs, FAs, RAs, and DTs were identifiable. A wide range of transformed RAs and DTs, similar to the suite of compounds found in seepage basin sediments, were present in the ground waters.

Estimating effluent treatment during infiltration by comparing ground water composition with overlying seepage basin effluent was not successful. Large changes in EO concentrations of the seepage basin effluent during the period of monitoring prevented reliable definition of source effluent composition. In addition, no definitive link between ground water sampled from the wells and overlying effluent was established. The only ground water response to effluent seepage that was recorded was a transient response which was attributed to fracture flow through the surficial sediments.

Off-site migration of effluent was assessed by sampling ground waters from discrete ignimbrite units along a ground water gradient away from the seepage area. Elevated concentrations of sodium, chloride, colour, A270, and RADTs were found in the Marshall A and B ignimbrites

immediately adjacent to the seepage ponds. Concentrations decreased with distance from the ponds, the organic components being more strongly attenuated than sodium or chloride.

In summary, the ground water investigations were successful in assessing the composition and concentrations of effluent-sourced contaminants in ground waters affected by effluent infiltration, and in evaluating their movement off-site. Obtaining measures of treatment afforded by effluent infiltration through the surficial sediments beneath the seepage basins was less successful. Laboratory-scale simulations were therefore carried out to address this aspect of the study. These experiments are described in Chapter 7.

Chapter Seven

Soil-Column Simulations

7.1 Introduction

The field studies of effluents, sediments and ground waters showed that a considerable degree of effluent modification was occurring in the LA system. However, the practical difficulty of intercepting infiltrating effluent of well defined origin and composition in shallow ground water monitoring wells within a reasonable time frame meant that a direct measure of changes in effluent composition occurring during infiltration through seepage basin sediments was not obtained from the field studies. Laboratory experiments were therefore carried out to examine these changes.

Passing effluent through soil-columns is one way of simulating the processes occurring in the shallow sediments beneath a LA site. This approach has been widely used in determining the behaviour of inorganic and organic waste constituents in disposal situations (e.g. Rao and Davidson 1979; Bouwer *et al.* 1981; Fuller and Warwick 1985b; Hutchins *et al.* 1985). Comparison of influent ("feed") and effluent ("leachate") chemistries provides a direct measure of treatment or modification occurring during infiltration. Analysis of accumulated residues in the soil enables the contribution of deposition and sorption mechanisms for observed treatment to be quantified. Relative mobilities of effluent constituents can also be measured by monitoring leachate chemistry over time.

Compared with field studies, column experiments in the laboratory allow influent and leachate compositions to be more readily compared and permit better control over variables affecting the fate of effluent constituents. While they have these advantages, soil-columns are relatively simple models of usually complex real systems. As such, they may not be able to reproduce all the important environmental factors which influence contaminant fate. Extrapolation of results to operational systems must therefore be made with caution (Fuller and Warwick 1985b).

7.1.1 Objectives

The soil-column experiments were carried out to gain a better understanding of effluent modification occurring during passage through seepage site ash sediments, and hence possible effects of the Kinleith LA process on shallow ground water chemistry by:

1) determining the relative mobilities of effluent-sourced colour, sodium, chloride, RAs, FAs, and MTs in ash sediment;

2) analysing the EO chemistry of soil-column leachates and sediments;

3) measuring treatment of effluent-sourced colour, RAs, FAs, and MTs in soil-columns; and

4) comparing effluent treatability under two effluent application regimes representing the range of probable conditions operating at Kinleith.

7.2 Experimental Approach

7.2.1 Effluent application regime

The soil-column experiments were designed to simulate the range of effluent application regimes operating at Kinleith. In the Kinleith system, effluent was applied to the basins for several months of the year. The effluent remained ponded in some infiltration basins for periods of several weeks or more. Over the summer months the basins were dried and the surficial sediment aerated by discing. The system therefore operated on a cycle of long term flooding (during which underlying sediments would be anaerobic), and drying/resting (during which surficial sediments would have regained aerobic state).

To simulate the range of possible processes occurring in this system, both continually flooded and flood-dry application regimes needed to be modelled. Two sets of column experiments were therefore conducted; one in which effluent remained ponded above the soil for the entire duration of the experiment, and a second in which effluent was allowed to infiltrate into the soil profile, thereby exposing the soil surface between applications.

The continually flooded (CF) regime simulated the "worst case" conditions of continuous effluent exposure and limited oxygen transfer into the sediments. Under these conditions, transformation and partial degradation of effluent organics were anticipated, possibly producing products such as the RAs and DTs observed in sediments and ground waters beneath the seepage basins. Accumulation of organic sludge at the effluent–sediment interface was another possible consequence of this application method.

The flood-dry (FD) regime modelled the other extreme; i.e. a situation where effluent was applied in a way that allowed air to be drawn into the upper sediment profile after each effluent application. This is the recommended approach for operating a LA system as it promotes aerobic decomposition of organic matter and preserves the infiltrative characteristics of the soil (Hutchins *et al.* 1985).

Using these two simulations, the effect of application regime was assessed, and the potential treatability of the effluent by LA measured.

For each of the CF and FD regimes, two columns were operated. One was fed with No. 2 effluent (coded as the "FD-E" and "CF-E" columns), and the other was dosed by the same procedures with distilled water as controls (the "FD-DW" and "CF-DW" columns). Table 7.1 summarises the column codes and operational regimes used.

Table 7.1: Summary of columns used

Column Number	Code	Feed Applied	Loading Regime
1	FD-DW	distilled water	flood-dry cycle
2	FD-E	effluent	flood-dry cycle
3	CF-DW	distilled water	continuously flooded
4	CF-E	effluent	continuously flooded

7.2.2 Column construction

Columns (150 cm long x 10 cm internal diameter) were made from Class E PVC tubing. Large columns were made so that at realistic loading rates, sufficient volumes of leachate would be generated for EOs' analysis. A polypropylene base plate, into which a glass exit tube was sealed with a drilled rubber bung, was cemented on the bottom of each column. The exit tube was packed with glass wool, and fitted with a 5 cm length of plastic tubing and stopcock. Glass beads (200 mL, 40 mesh) were added to the column and covered with a layer of glass wool. A close-fitting plastic bag was placed over each column between applications to limit effluent evaporation. Figure 7.1 shows the column construction.

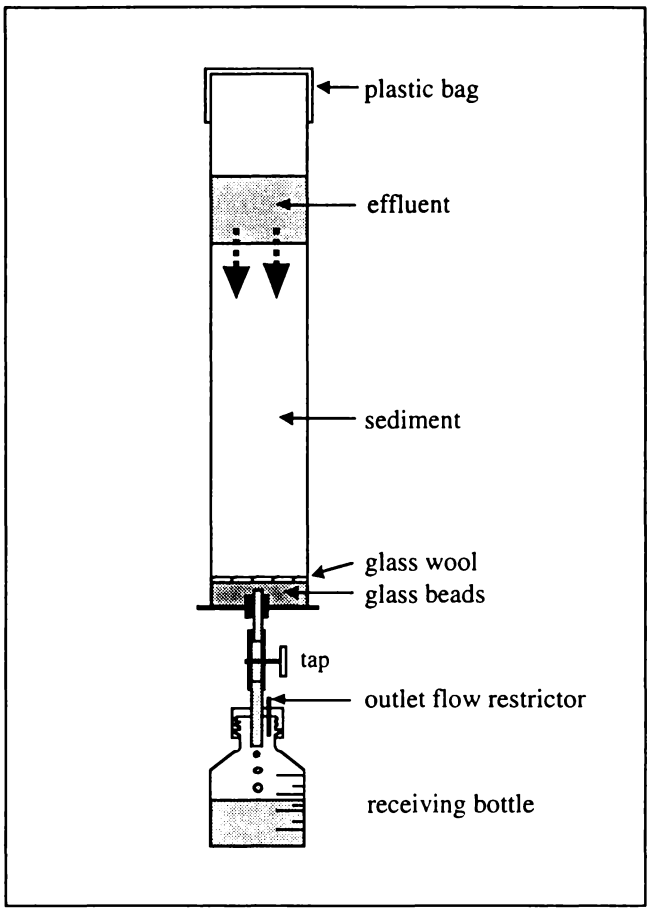


Figure 7.1: Column construction (not to scale)

Surface soil (0–0.5 m depth) which had no known previous contact with effluent was collected from a site adjacent to seepage basin P7 and stored in plastic bags at 4 °C until use. Prior to packing into the columns, the soil was sieved (2 mm) to remove coarse debris (twigs, root matter, pumice stones) and thoroughly mixed. Moisture content (mean ± s) of the sieved soil was 19 ± 3% as determined by drying eight subsamples overnight at 105 °C.

Soil was packed into the columns in approximately 1 cm increments, tamping firmly with a wooden rod between additions until 100 ± 0.5 cm had been added. The mass of soil added to each column was recorded. Based on the masses and volume packed, bulk densities of the four columns were 0.85, 0.91, 0.87, and 0.79 g cm^{-3}.

Prior to effluent addition, approximately 10 L of distilled water were passed through each column and the soil allowed to reach field capacity by leaving the columns to drain completely until no further leachate was collected overnight. Effluent or distilled water application was then started.

7.2.3 Effluent loading and leachate collection

The effluent loading rates employed were intended to approximate those of the Kinleith system. To dispose of all the No. 2 effluent produced (10,000 m^3 d^{-1}) over the area of the EA basins (56 ha), an application rate of 179 m^3 ha d^{-1}, or 18 mm d^{-1} was required. The increased production resulting from the mill modernisation was expected to cause marked changes in effluent composition. While the exact nature of these changes was unknown at the time, sodium concentrations were expected to increase by up to about 40% above the levels already produced. Application was therefore aimed at between 18 and 25 mm d^{-1}.

The FD regime columns were dosed with 600 mL of effluent (or distilled water) twice a week, giving an average application rate of 22 mm d^{-1}. The outlet taps of these columns were left open, allowing unrestricted drainage from these columns into the receiving bottles.

Application to the CF columns was determined by the amount drained in each collection. 3 L of effluent (or water) was initially added to the top of each column. The outlet taps were then opened and the columns allowed to drain into the receiving bottles until at least 500 mL from each was collected.. The volume recovered was measured, and the ponded effluent at the top of the column replenished with the same amount of effluent as the leachate collected. Variable volumes, which were generally greater than 600 mL (mean = 780 mL, range = 420–1200 mL), were collected from these columns using this approach. Over the period when these columns were in operation (320 days), 67 L were percolated through the effluent fed column, giving an average loading rate of 27 mm d^{-1}.

At the end of the experiment, low vacuum (water pump) was applied to the column outlets to remove the final remnants of effluent retained in the columns.

The "plug flow" application and collection method gave long term average loading rates which approximated those required to simulate the Kinleith situation. However, upon effluent addition/collection, the method gave much higher short-term loading rates. Assuming effluent drainage occurred over 16 hours (typical overnight collection period), loading rate for the FD columns was approximately 110 mm d^{-1}, and the CF columns ranged between 80 and 230 mm d^{-1} over the duration of effluent loading/collection. These were much higher than the long term average rates, and could have reduced treatment efficiency compared with a system using lower and/or more uniform application rates.

Using estimated pore volumes for the columns (section 7.3) and twice weekly application/collection frequency, effluent residence times in the columns were calculated to be 3.8 weeks for the FD-E column and 1.3–3.8 weeks for the CF-E column (depending on volumes collected). Therefore, despite high loading rates during effluent addition, effluent spent considerable periods in contact with sediment.

Feed effluents were grab sampled from the No. 2 effluent flow metering station (No. 2 drain site in Figure 4.4), and stored in plastic containers at 4 °C until use. Ten batches of feed effluents were used during the experiment. The composition of these effluents was variable, especially with regard to the concentrations of EOs (Table 7.2). This variability, in combination with the effects of mixing, retardation, and degradation in the columns, precluded straightforward comparison of leachate and feed concentrations after the initial batches of effluent had been added. While this was a disadvantage with regard to interpretation of the breakthrough curves, it more realistically simulated the Kinleith system where No. 2 effluents with markedly variable EO levels were applied directly to the seepage ponds. Assessment of treatment efficiency was therefore carried out by a mass balance of the entire experiment.

Table 7.2: Composition of the effluents applied to the soil columns

Batch No.	Sodium mg L^{-1}	Chloride mg L^{-1}	Colour CPU	Total MT mg L^{-1}	Total FA mg L^{-1}	Total RA mg L^{-1}
1	750	720	2200	110	3.4	4.6
2	770	720	2300	58	1.8	4.2
3	780	670	2300	61	2.1	3.8
4	820	410	6000	9.4	5.2	18
5	930	n.a.	5900	25	5.6	11
6	980	n.a.	3500	13	17	66
7	1010	n.a.	3800	12	17	66
8	530	n.a.	1800	28	0.3	27
9	530	n.a.	2000	24	<0.2	59
10	560	n.a.	2700	28	63	87

n.a. – not analysed (effluent tracer used only in the initial stages of the experiment)

Feed effluent stability during storage was assessed for batches 9 and 10. The composition remained stable over the 28 and 35 days respectively that these effluents were in use, with variability in MT, FA and RA totals (cv ±%, n=4) of ±2–8%.

7.2.4 Experimental duration

It was envisaged that the experiment would need to be carried out over a relatively long time to simulate the major operating features of the Kinleith system. These features included an effluent application period of at least several months, followed by a rest phase of a few months, then another cycle of effluent application. The rates at which effluent constituents moved through the sediment profile were not known at the start of the trial, nor were the rates of chemical transformations that were hypothesised to occur in the sediment zone of the LA system. It was anticipated that chemical processes were likely to be slow under a CF regime, as oxidation reactions would be inhibited. The exact duration of an ideal trial was therefore not reliably predictable at the start of the experiment, so it was run in a way which accommodated both the essential process features of interest and the practicality of conducting a long term laboratory trial.

The experiment was conducted in two phases. Phase 1, which lasted 38 weeks, simulated the several month initial application period. Columns were then rested for 52 weeks, during which no additional effluent was added. The CF columns remained flooded and the FD-E columns allowed to dry. The rest phase was longer than would have occurred in most of the Kinleith LA system seepage basins, but was used in the laboratory trial to investigate the long-term behaviour of EOs and colour in effluent-flooded sediments. The processes which produced the EO composition observed in sediment and ground water under the seepage basins were thought to be slow, anaerobic transformations. The columns were therefore left for as long as possible to provide the best possible opportunity for these processes to occur.

Phase 2 was then carried out, and lasted a further 8 weeks. This simulated continued effluent application following a rest period. The composition of the initial leachates, which originated from fluid stored in the columns for the 52 week rest period, gave information on the long-term behaviour of the EOs and colour under the anaerobic conditions of the flooded soil column. After the 8 week period, the columns were drained, sectioned, and the soils analysed for EOs.

7.2.5 Mass balance calculation

EOs, sodium, colour, and iron were analysed in feed effluents and leachates from each column. At the end of the experiment, the columns were cut open, and the sediments divided into ten sections and analysed for EOs. Analysis of EOs in the feeds, leachates, and sediments of the effluent fed columns enabled a mass balance to be calculated, to provide an estimate of EO removal in the soil column system:

$$\text{Input} = \text{Output} + \text{Accumulation} + \text{Removal}$$

$$F = L + S + R$$

or;

$$R = F - L - S$$

where F = mass added in the feed effluents
L = mass recovered in the leachates
S = mass recovered from the sediments, and
R = removal.

The magnitude of R provides a measure of the sustainability of the treatment process, since only mechanisms which remove the effluent constituents from the soil-water system provide truly sustainable waste treatment and protection of both soil and ground water quality. Major removal processes in a LA system are volatilisation and microbial/chemical degradation.

Under the experimental conditions employed, volatilisation was likely to be a minor removal process. The columns were covered (although not sealed), ponded fluid underwent minimal physical disturbance, and the majority of the compounds analysed were relatively involatile. Room temperature remained constant at about 20 °C throughout the experiment, but upon effluent application, temperatures at the effluent-sediment interface would have dropped due to the addition of the cold-stored effluent (4 °C). MT hydrocarbons, with boiling points of 156–178 °C, were the compounds most susceptible to volatilisation. Even for these compounds, volatilisation was probably minor, as indicated by the results from the seepage pond trial

(section 4.4.7). Apparent removals for EO compounds observed in these experiments were therefore largely due to chemical and microbial degradation.

7.2.6 Analytes and analytical procedures

The effluent constituents monitored and the procedures used in each phase of the experiment are summarised in Table 7.3. Chloride was used as a tracer to estimate column pore volumes and the relative mobilities of the other constituents in the initial stages of the experiment. The behaviour of sodium as a tracer in the soil water system was of interest because of its application to effluent plume monitoring in the ground water system. Its analysis was also more convenient than chloride, and was therefore monitored throughout the experiment. Iron was implicated in the unusual colour behaviour observed (section 7.4.2), and was therefore measured in all leachates and feed effluents. Analytical data are summarised in Tables A2.22–A2.24 (Appendix 2).

Table 7.3: Analytical procedures used in the soil column experiments

Constituent	Compartment	Procedure	Section
chloride	feeds, leachates	ferricyanide (APHA 407D)	3.2.2
sodium	feeds, leachates	AAS at 330.3 nm	3.2.1
colour	feeds, leachates	absorbance at 465 nm (NCASI 1971)	3.2.3
iron	feeds, leachates	AAS at 248.3 nm	3.2.4
extractable organics	feeds, leachates	Phase 1: pH 2 extraction, GC-FID/MSD	3.4.2
		Phase 2: pH 11 extraction, GC-FID/MSD	3.4.3
extractable organics	sediments	AALL extraction	3.6.4

7.3 Effluent mobility

The mobility of an effluent constituent in a soil-column can be assessed by examination of a breakthrough curve (BTC). A BTC is a plot of relative concentration (C/C_0) of the column leachate (C) compared with the feed concentration (C_0) versus the number of column pore volumes displaced (V/V_0), where V=volume of leachate eluted and V_0=volume of fluid held in the column. In the ideal miscible displacement experiment, the BTC of an unreactive solute is a symmetrical sigmoid curve which passes through $C/C_0=0.5$ at V_w, the volumetric water capacity (or one pore volume) of the column (Nielson and Biggar 1961). Breakthrough is defined to occur at the point where $C/C_0=0.5$, while complete breakthrough occurs when $C/C_0=1$.

For components whose transport through the column is affected by sorption, precipitation, or exchange, breakthrough occurs at greater volumes eluted from the column. The ratio of the average velocity of water (v_w) to that of the component (v_c), is a measure of the degree of component retardation (expressed as the "retardation factor", R_f):

$$R_f = \frac{v_w}{v_c}$$

R_f can be assessed from the BTC as the number of soil-column pore volumes at which analyte breakthrough occurs. The shape and position of the BTCs of sorbed components is affected by sorption isotherm shape, concentration, relative rate of sorption compared with advective and dispersive transport, and relative rates and degrees of sorption and desorption. The causes and effects of such "non-ideal" behaviour of organic solutes during transport through porous media have been reviewed in detail by Brusseau and Rao (1989).

For components which undergo loss from the column by degradation or volatilisation, or are irreversibly retained by sorption or precipitation, $C/C_0=0.5$ may never be reached. Other constituents may be produced by reactive processes within the column, giving BTCs which exceed $C/C_0=1$. For either of these situations, the point at which breakthrough occurs cannot be determined by the conventional approach, and an arbitrary definition of breakthrough points and R_f values must be made.

The organic constituents monitored in the experiments described in this chapter, displayed reactive characteristics; colour exceeded $C/C_0=1$, some EOs failed to reach $C/C_0=0.5$, and others not initially present in the effluents were produced. The highly variable concentrations of the effluent feeds used (Table 7.2) also complicated the interpretation of BTCs.

7.3.1 Chloride and sodium

Chloride, which was present in the effluent at high concentrations, was used as a conservative tracer to determine column pore volumes. Breakthrough curves for chloride and sodium are shown in Figure 7.2

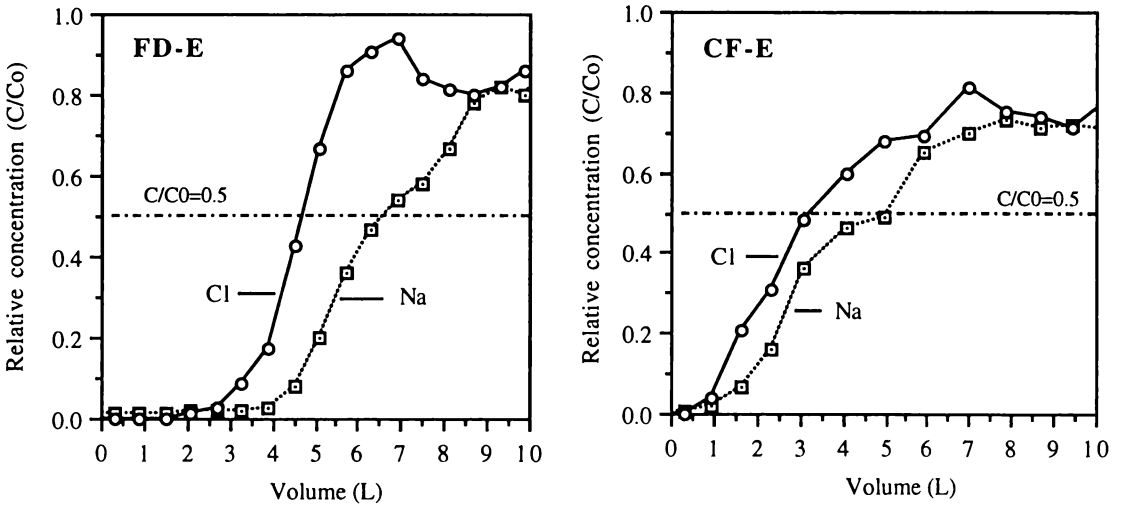


Figure 7.2: Breakthrough curves for sodium and chloride in continuously flooded (CF-E) and flood-dry (FD-E) effluent-fed columns

These BTCs showed that:

- the two columns had different hydrodynamic characteristics, as shown by the different curve shapes. The CF-E column BTC was broader than that for the FD-E column, and both sodium and chloride eluted at lower volumes. The major difference between the columns was the method of effluent dosing. It seemed, therefore, that dosing method affected fluid flow through the columns. Neither column showed the ideal symmetrical BTC shape. This was not unexpected, as the column materials were fairly coarse and not necessarily uniformly packed, and flows were discontinuous. Ideal behaviour is usually only approached in columns packed with uniform sized particles of limited size range and operated at constant flow rate.

- pore volumes of the two columns were different, the CF-E column being lower (3.0 L) than the FD-E column (4.6 L). The broader BTC and earlier elution from the CF-E column was consistent with channeling or flow through soil macropores.

- sodium was retarded, presumably by ion exchange, giving R_f values of 1.5 and 1.4 for the CF-E and FD-E columns respectively.

- relative concentrations (C/C_0) of chloride did not reach 1.0 in either column. Even allowing for analytical error (approximately ±10%), the results were low. This suggested that some chloride was retained in the columns, and that chloride may not have been behaving as an unreactive tracer. However, the approximate pore volumes obtained from the chloride BTC were adequate for the purposes of the experiment.

Assuming that chloride breakthrough gave a reasonable estimate of the column pore volumes, the BTCs of other constituents were plotted as C/C_0 versus pore volumes (Figures 7.3 to 7.6) to allow direct comparison of the effect of effluent application regime on constituent mobility.

7.3.2 Colour

The colour of the leachates from both CF-E and FD-E columns exceeded that of the feed effluents, giving BTCs in which C/C_0 exceeded 1.0. This indicated that colour increases were occurring during effluent transport through the sediments. Leachate colour reached $C/C_0 = 0.5$ at 4.5 L for the CF-E column ($R_f = 1.5$) and at approximately 9 L for the FD-E column ($R_f = 2.0$). The initial stages of colour BTCs are shown in Figure 7.3. Longer term changes in colour in the columns is discussed in section 7.4.2.

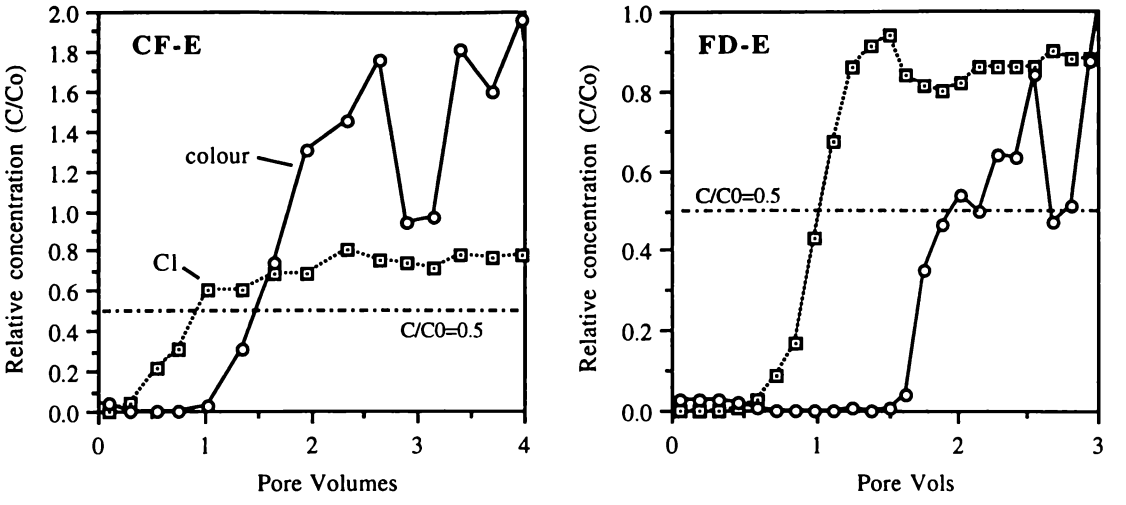


Figure 7.3: Colour breakthrough curves for continuously flooded (CF-E) and flood-dry (FD-E) columns

7.3.3 Extractable organics

The behaviour of EOs in the columns was complex due to retardation, degradation, and variability in concentrations in the feed effluents. Because of extensive EO transformation and disappearance from the aqueous phase in the columns, breakthrough could not be assessed in terms of C/C_0=0.5, as it can for unreactive constituents. Very clear differences between the two application regimes were, however, observed.

MTs were highly mobile, eluting from both columns in substantial concentrations at about 1 pore volume (R≈1). This result was consistent with the relatively low molecular weights of the MTs, and the hydrophilicity of the MT alcohols, which were the dominant species eluting in the initial leachates. While C/C_0 in the initial leachates rose to only about 0.2, this amounted to concentrations of over 20 mg L^{-1}, since the feed effluent concentration at this stage was >100 mg L^{-1} (Table 7.2).

After the initial breakthrough, MT behaviour in the CF-E and FD-E columns was markedly different. High concentrations persisted under the CF-E regime, while in the FD-E system, the MT concentrations declined rapidly after breakthrough to barely detectable levels in most samples. Low levels of MTs appeared in a few later leachates, but relative concentrations, C/C_0, remained <0.01. Effective removal of MTs was therefore occurring in the FD-E column, but much less effectively under the CF-E regime. The MT chemistry, which showed considerable differences from the feed effluents, is discussed in section 7.4.3. Figure 7.4 shows the MT breakthrough from both columns.

Fatty acids were present in the leachates from both columns in highly variable amounts, and no clear breakthrough behaviour was apparent from the BTCs (Figure 7.5).

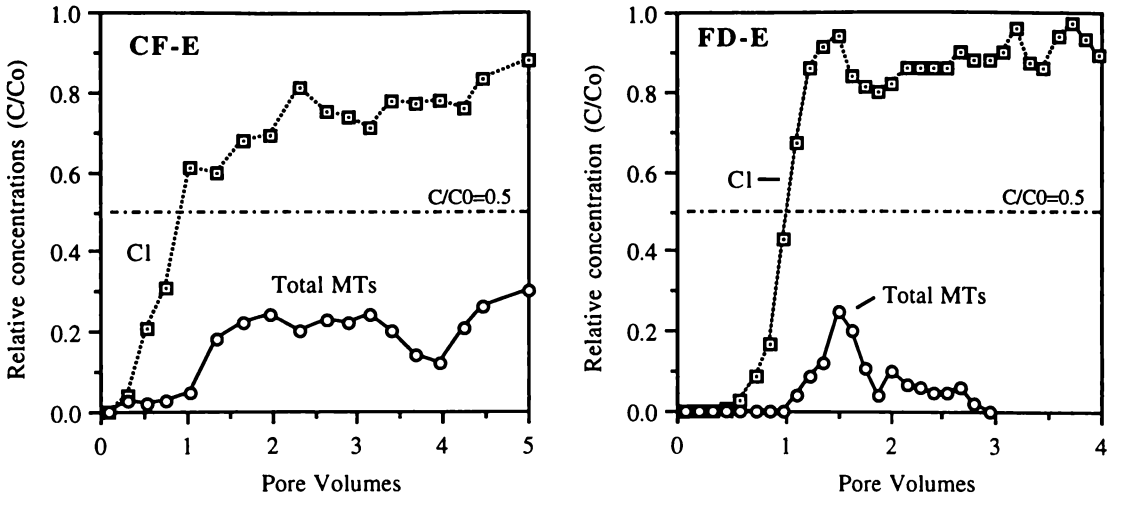


Figure 7.4: Monoterpene breakthrough curves for continuously flooded (CF-E) and flood-dry (FD-E) columns

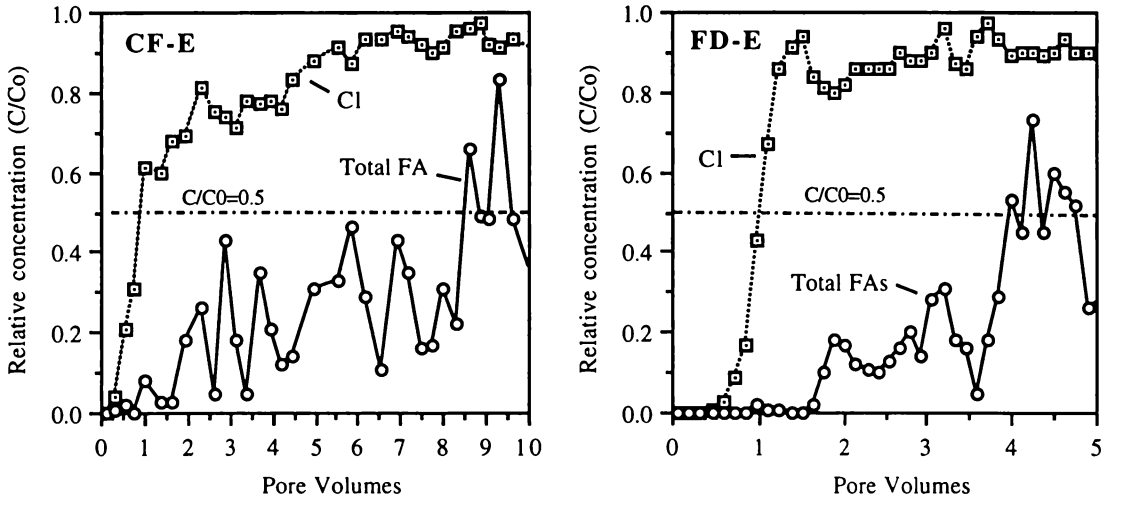


Figure 7.5: Fatty acid breakthrough curves for continuously flooded (CF-E) and flood-dry (FD-E) columns

Resin acid behaviour differed under the two application regimes. In the CF-E column, breakthrough was gradual and reached C/C_0=0.5 after approximately 8.5 pore volumes (Figure 7.6). RA movement through the sediments was therefore strongly retarded. This was consistent with high octanol-water partition (log K_{ow}) values for RAs and DTs (Holmbolm 1991; Hynning *et. al.* 1993), and field observations in which RAs and DTs were found in high concentrations in seepage basin sediments (Chapter 5). The soil-column sediments were also found to have accumulated RAs (section 7.5). Substantial modification of the RA fraction occurred in the CF-E column, indicating transformation (presumably microbially mediated) was occurring. RA chemistry is described in section 7.4.5.

In the FD-E column, clear breakthrough of RAs did not occur. Low levels of RAs, mainly transformed species (section 7.4.5), were found in most leachate samples eluting after about 2

pore volumes. Relative concentrations were $C/C_0 \leq 0.02$ for all leachates except four later eluting samples (7.5–8 pore volumes) when relative concentrations rose to reach $C/C_0=0.07$. These low levels were difficult to quantify reliably as the GC-FID chromatograms were dominated by UCM in the RA elution region (e.g. Figure 7.16). Concentrations may have been overestimates due to the difficulty in integrating the very small RA peaks above a large, noisy, UCM. However, it was clear from these results that a considerable degree of RA removal occurred in the FD-E column. This was confirmed in phase 2 of the experiment, and in sediment residue analyses (section 7.5).

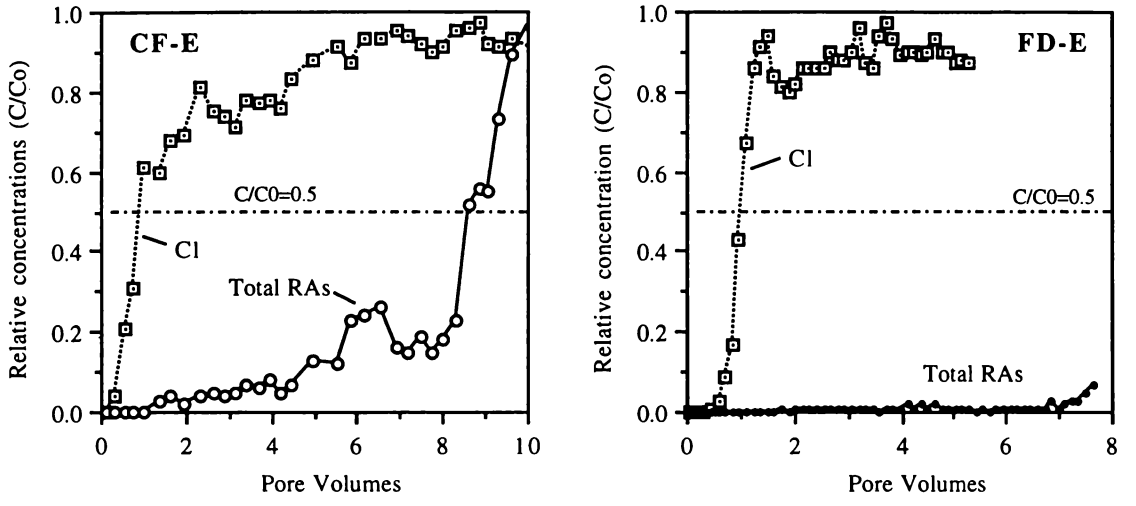


Figure 7.6: Resin acid breakthrough curves for continuously flooded (CF-E) and flood-dry (FD-E) columns

7.3.4 Summary of contaminant mobility

The mobility data, summarised in Table 7.4, indicated that RAs were the least mobile constituents monitored. MTs and colour were far more mobile. Extrapolating these results to the field situation indicated that in a CF regime, MTs, colour, sodium, and chloride would be expected to move readily through the sediments into ground water. RAs would eventually break through the sediments, but would lag behind MTs and colour. In a FD system, EOs were effectively removed, and therefore mobility was not assessable.

Table 7.4: Mobilities of the effluent constituents in the soil-columns

	Retardation Factor (R_f)		
Constituent	Continuous Flooding	Flood-Dry	Mobility
Chloride	1.0	1.0	assumed unretained
Sodium	1.5	1.4	high
Colour	1.5	2.0	high
Total monoterpenes	ca. 1	ca. 1	high
Total fatty acids	n.a.	n.a.	n.a.
Total resin acids	ca. 8.5	no breakthrough	low

n.a.: not assessable from data collected

7.4 Leachate Chemistry

7.4.1 Sodium

Sodium concentrations were high in both CF-E and FD-E leachates, reaching levels similar to the feeds (Figure 7.7).

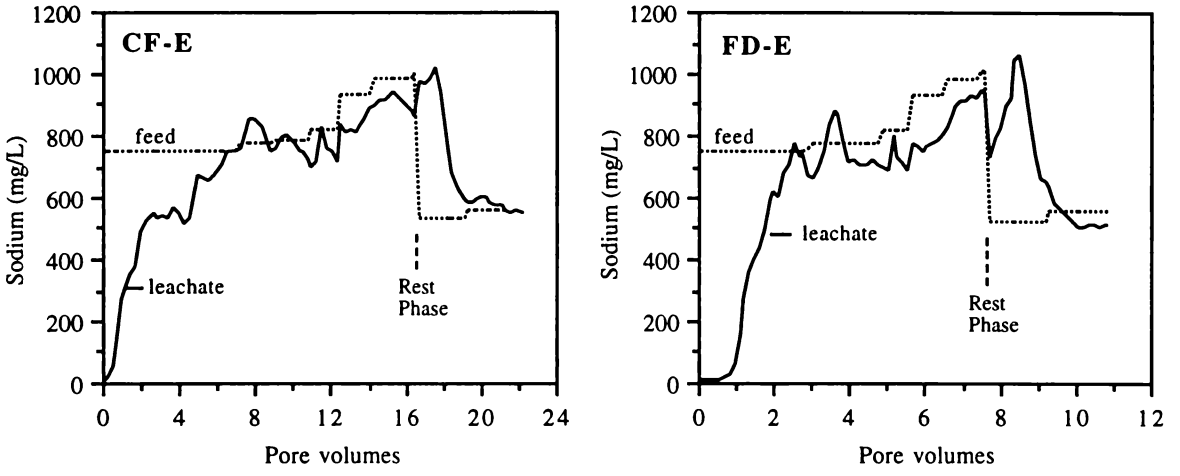


Figure 7.7: Sodium concentrations in CF-E and FD-E columns

7.4.2 Colour

Leachate colour from both CF-E and FD-E columns was high, often exceeding the feed effluent colour (Figure 7.8). The most notable increase in colour occurred in the CF-E column when leachate emerged after the one year rest phase. By the end of the trial, leachate colour was similar to that in the feed effluent.

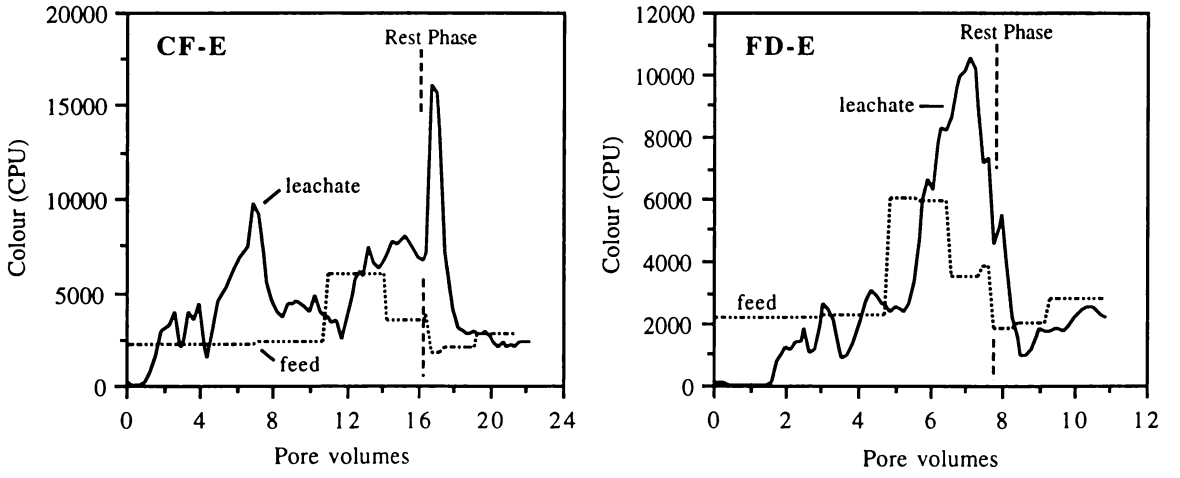


Figure 7.8: Colour levels in CF-E and FD-E column leachates

The colour enhancement observed was unexpected, but such increases have been previously reported for leachates from soils dosed with sulphite liquors, and with water after kraft effluent application (Blosser and Owens 1963). Colour increases have also been reported in activated sludge treatment of kraft mill effluent, and attributed to the biochemical demethylation and

oxidation of lignin to form highly chromophoric quinonoid structures (Larrera *et al.* 1989; Davis *et al.* 1978; Cecen *et al.* 1992).

Increases in the colour of mechanical mill pulps have been attributed to the formation of highly coloured complexes between ferric ions and phenolic (particularly catecholic) structures within the lignin (Jansen and Forsskahl 1989). Ferric and ferrous ions also increased the sensitivity of the pulp to colour reversion on exposure to light. It was therefore possible that interactions between iron in the soil column sediments and effluent lignin may have been responsible for the colour increases observed in the column simulations.

In a qualitative experiment, dropwise addition of aqueous Fe^{3+} to No. 2 effluent resulted in a marked increase in visible colour, producing an inky-black solution similar in appearance to the soil-column leachates. Leachates were analysed for iron and revealed that very high concentrations were eluted from the effluent fed columns (Figure 7.9). Iron was therefore being solubilised and leached from the sediments. Complex formation with effluent lignin may have contributed to iron stabilisation and transport from the columns. Iron levels in the leachates from the columns receiving only distilled water were much lower; concentrations (mean ± s) in the FD-DW and CF-DW leachates were 0.8 ± 0.6 mg L^{-1}, and 1.7 ± 0.6 mg L^{-1} respectively, indicating that effluent was involved in iron mobilisation from the CF-E and FD-E columns.

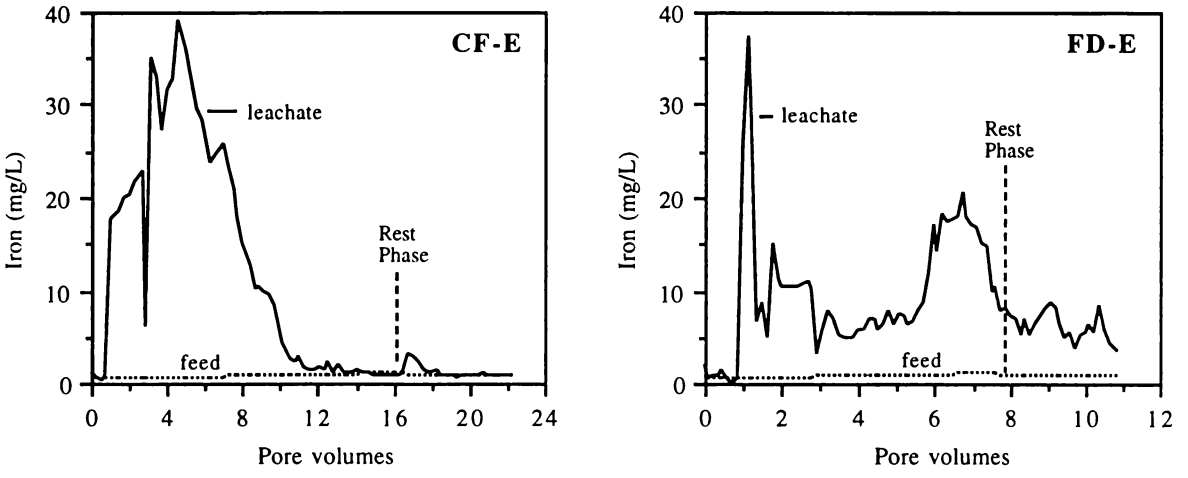


Figure 7.9: Iron levels in CF-E and FD-E column leachates

No correlation between iron and colour concentrations was found, indicating that while iron may have played a part in colour intensification, it was not the sole factor involved. This was demonstrated by the relatively small increase in iron, but large increase in colour, observed in the CF-E column during the one year rest phase (Figures 7.8 and 7.9).

The iron present in the leachates remained in solution over periods of more than a year without acidification. Precipitation of iron hydroxide occurs readily in aerobic environments, suggesting the iron released from the soil columns was in organically-bound form. Complexation by organics is a documented mechanism for stabilisation of iron in aqueous systems (Stumm and Morgan 1981).

The presence of high concentrations of iron in the leachates was also consistent with the composition of ground waters contaminated by wood waste disposal (Sweet and Fetrow 1975). Elevated levels of iron were also found in ground waters from five of the six wells beneath the P7 seepage basin. The highly coloured waters from bores 11/1–4 and bore 12/1 had mean concentrations (n = 5–8) of 8–20 mg L^{-1}, while the much lower coloured waters from bore 15/1 contained 2.5 mg L^{-1}. However, as was found for the column leachates, there was no significant correlation between colour and iron concentrations.

7.4.3 Monoterpenes

MTs appeared in the CF-E leachates very soon after effluent addition commenced, and remained at relatively high concentrations throughout the duration of the trial (Figure 7.10). MTs also eluted rapidly from the FD-E column, but then reduced in concentration, appearing only at low levels in a few phase 1 leachate samples. After the rest phase, MT levels again peaked in the FD-E column, and were present at variable levels throughout phase 2 (Figure 7.10).

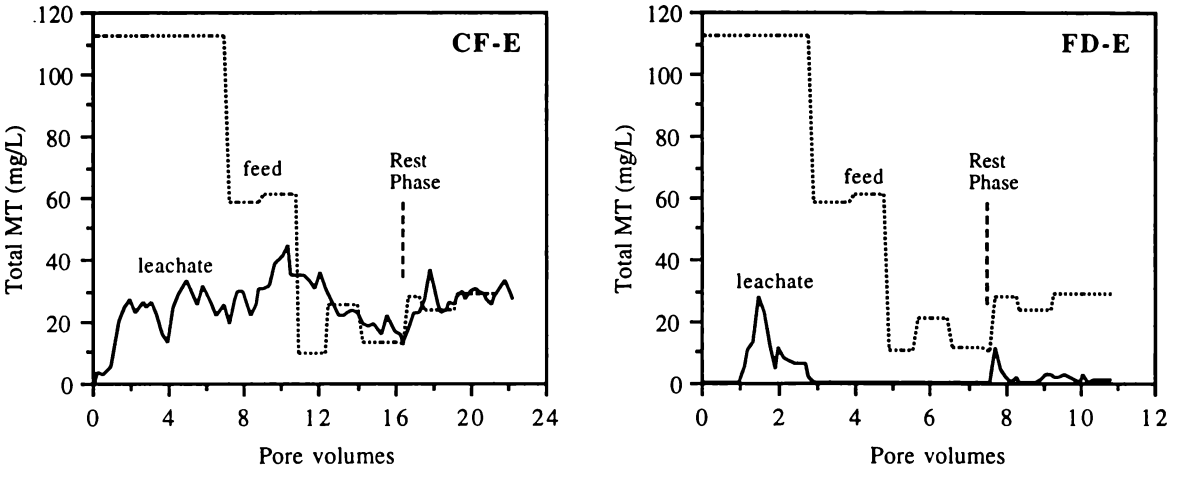


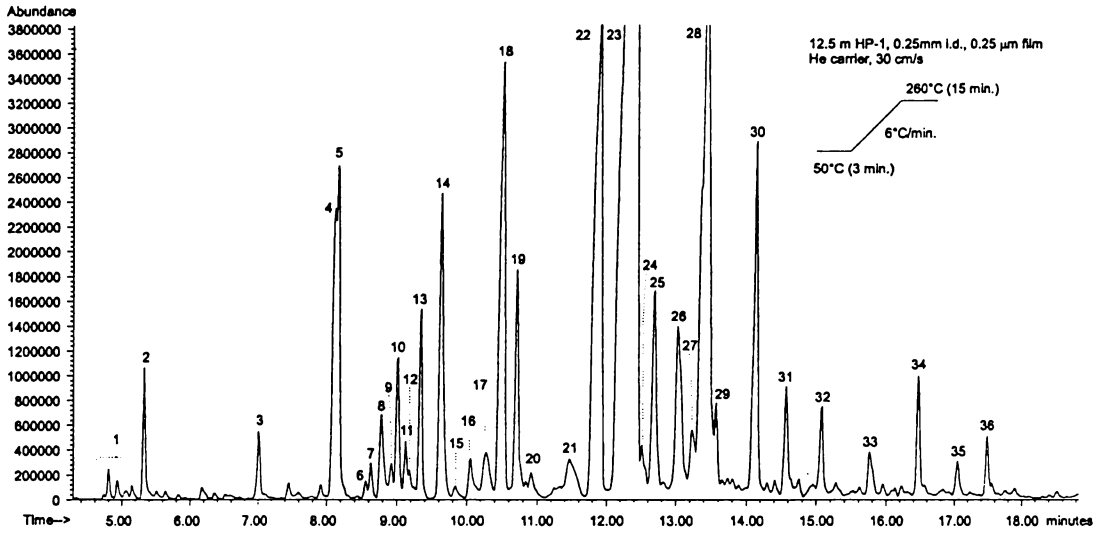
Figure 7.10: Monoterpene levels in CF-E and FD-E column leachates

The appearance, then disappearance, of the MTs in the FD-E column was consistent with an initial acclimation phase (during which MTs passed through the column) followed by degradative removal. Their appearance in phase 2 was almost certainly attributable to effluent flow between the column walls and the sediment due to sediment dehydration and shrinkage during the 52 week rest phase. Effluent elution was very rapid at this time, leachate appearing almost immediately after addition, and the leachate composition was very similar to the feed. When the columns were cut open at the end of the experiment, the top 35 cm of the sediment core was found to have contracted away from the walls of the tubing.

Apart from during the acclimation phase at the start of the experiment, and the channel flow observed in phase 2, MTs were effectively removed from the effluent in the FD-E column. The following discussion of leachate MT chemistry is therefore that observed from the CF-E column.

The composition of the MT fraction initially eluted from the CF-E (and FD-E) column was similar to that of the parent feed effluent, although the MT hydrocarbons, largely α- and β-pinene *[5* and *9]*, were absent. The alchohols α-terpineol *[48]*, 4-terpineol *[45]*, borneol *[44]*, and fenchol *[32]* were the dominant compounds in the early leachates. The abundance of these compounds declined over time, and fenchone *[29]*, camphor *[34]*, and DHT *[35]* became the major identifiable MTs. After a relatively long time interval (about 22 weeks), the relative amounts of *p*-cymene *[15]* increased (Figure 7.12).

As effluent transformation proceeded, the relative concentrations of parent MTs decreased, leaving a suite of transformation products, some of which were poorly resolved in GC chromatograms and remained unidentified. A typical GC-MSD chromatogram of the MT region of a CF-E column leachate is shown in Figure 7.11.



Peaks:

1. dimethylcyclopentanones *[1]*; 2. 4-methylpentanoic acid *[2]*; 3. camphene *[7]*; 4. MT138 *[10]*; 5. MT138 *[11]*; 6. MT136 *[12]*; 7. MT138 *[13]*; 8. 2,5-dimethyl-2-cyclopentenone *[6]*; 9. MT136 *[14]*; 10. *p*-cymene *[15]*; 11. MT138 *[16]*; 12. MT136, ms as for *[14]*; 13. MT138 *[22]*; 14. 2-ethylhexanoic acid *[20]* + 2,3,5-trimethyl-2-cyclopentenone *[21]*; 15. 3-acetylthiophene *[23]*; 16. MT136 + 2-acetylthiophene *[25]*; 17. 2,3,4 trimethyl-2-cyclopentenone *[26]*+ MT152; 18. fenchone *[29]*; 19. α,*p*-dimethylstyrene *[28]*; 20. tetramethyl-2-cyclopentenone *[30]*; 21. fenchol *[32]* + unidentified MT?; 22. camphor *[34]*; 23. dihydro-α-terpineol (isomer 1) *[35]*; 24. dihydroterpin-4-ol *[39]* + MT154 *[40]*; 25. dihydro-α-terpineol (isomer 2) *[41]*; 26. terpin-4-ol *[45]*; 27. MT154 *[46]*; 28. unresolved mix of MT152 + MT154 *[49]* + methylthiophene-2-carboxylate *[50]*; 29. MT152 + MT156 *[51]*; 30. HC12 standard; 31. unidentified mw=182 *[55]*; 32 phenylpropanoic acid *[56]*; 33. unidentified mw=184 + 170 *[57]*; 34. unidentified mw=184 *[58]*; 35. unidentified mw=184? *[59]*; 36. 4-(1-methylethyl)benzoic acid *[60]*. All acids detected as methyl esters.

Figure 7.11: Typical GC-MSD total ion chromatogram of MTs in CF-E column leachate

Some MT transformation products eluted at the same GC retention times as the parent compounds. This meant that GC-FID analysis of transformation sequences was possible only for major constituents. Even for these compounds, only the large initial changes were able to be reliably monitored by GC-FID before the amounts of unidentified compounds coeluting with

identifiable peaks of interest became significant. At later stages of effluent transformation, the GC-FID signal was often made up of a mixture of components rather than that of the single compound initially present.

When transformation or degradation sequences were monitored by GC-FID under these circumstances, the concentrations of parent compounds dropped, then appeared to stabilise at relatively high levels. When analysed by GC-MSD, the relatively stable residuals were found to be made up of transformation products rather than the parent compounds. This interference in the GC-FID signal of a monitored compound by coeluting peaks was termed "coeluting interference" (c.i.). Figure 7.12 shows the disappearance of major MT compounds and appearance of transformation products in the CF-E column leachates during phase 1 of the experiment. The regions where "coeluting interference" was apparent are labelled.

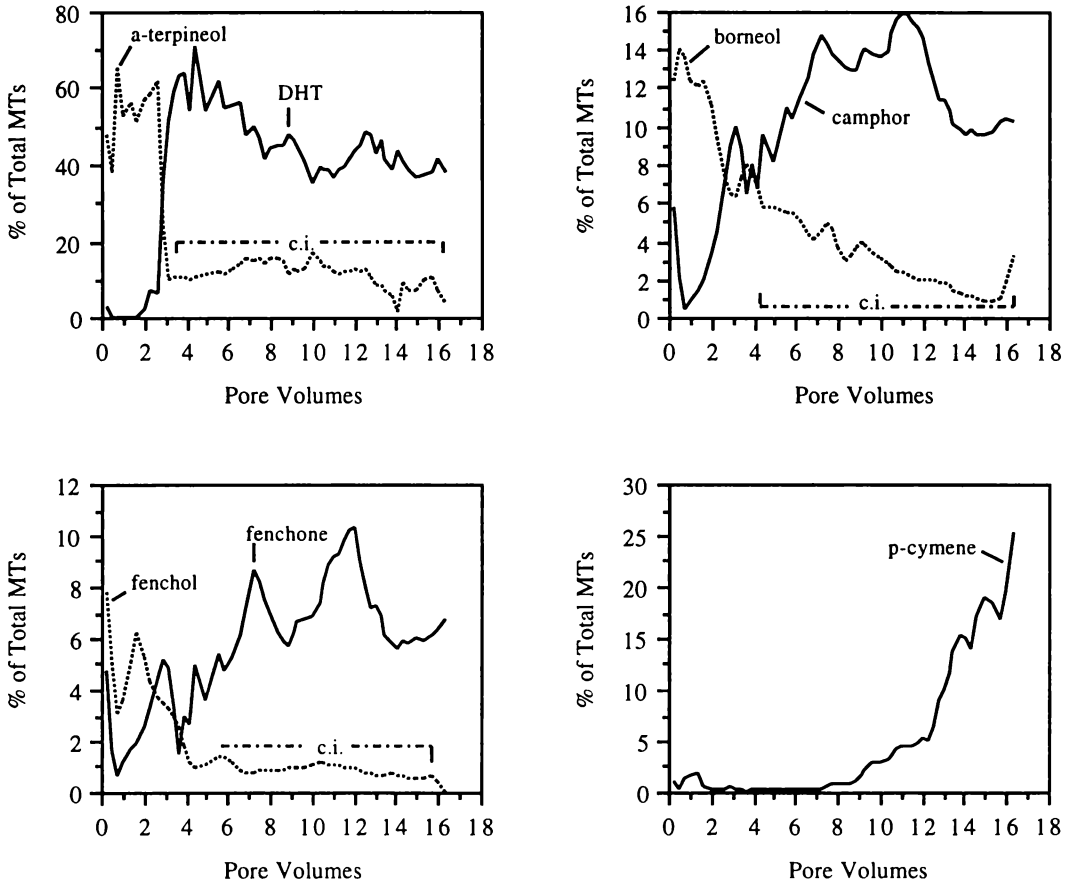


Figure 7.12: Disappearance and appearance of major MTs and transformation products in the CF-E column during phase 1 (c.i. – coeluting interferences with GC-FID signal of parent compound)

In addition to the major compounds, several minor compounds were detected and tentatively identified: α,*p*-dimethylstyrene *[28]*, a compound with a mass spectrum identical to that of DHT *[41]*, 4-(1-methylethyl)benzoic acid *[60]*, carvomenthone *[46]*, and camphene *[7]*.

Others which remained unidentified included several compounds of mw=138, an unresolved mixture of at least two compounds of mw=154 and 152 eluting at the same retention time as α-

terpineol, and several later eluting unidentified compounds of apparent molecular weight 156, 170, 182, and 184. Compounds of mw=138 gave MS library matches (>90% match quality) for 1-methyl-4-(1-methylethenyl)-cyclohexane or the double bond isomer 1-methyl-4-(1-methylethyl)-cyclohexene. Figure 7.11 and Appendix 1 show the GC profile and mass spectra of these compounds.

The MT composition of the leachate eluting immediately after the rest phase (i.e. in the initial stage of phase 2) was similar to that observed in the phase 1 leachates. Dominant compounds were *p*-cymene (30% of the total MTs), fenchone (5%), camphor (10%), and DHT (40%). As additional effluent was applied to the column, the composition of the leachate changed to approach the composition of feed effluent. This was best illustrated by changes in the two major components, DHT and *p*-cymene. DHT concentration decreased, α-terpineol increasing correspondingly to become the major MT compound,and *p*-cymene concentration slowly dropped (Figure 7.13).

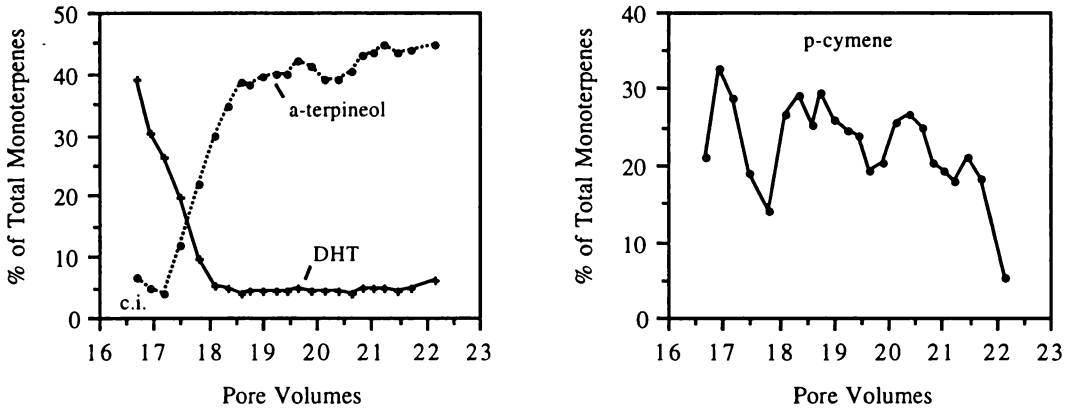


Figure 7.13: Changes in the relative concentrations of major MTs in the CF-E column during phase 2 of the soil-column experiments (c.i.- coeluting interference in GC-FID chromatogram)

The CF-E column MT chemistry in phase 2 was different from that observed in phase 1. Borneol and fenchol were oxidised to camphor and fenchone (consistent with the chemistry observed in phase 1), but α-terpineol was persistent, and was not reduced to form DHT, the major component present in the phase 1 leachates. The prolonged ponding without addition of fresh feed effluent had presumably depleted the microbiological population responsible for α-terpineol reduction.

The qualitative changes in effluent MT composition which occurred in the CF-E column were consistent with those observed in the effluent studies (Chapter 4). The formation of both saturated and aromatic compounds also occurs during fossilisation of turpentine oil in wood stumps, where *p*-cymene and *p*-menthane are major end products (Streibl and Herout 1969). Similar processes also apparently occur beneath landfills; fenchone, camphor, menthone, and 1-isopropyl-4-methylcyclohexanol (a plausible product of 4-terpineol reduction) were major monoterpenes identified in anaerobic ground waters contaminated by landfill leachates (Reinhard *et al.* 1984).

FD-E column leachates in phase 2 contained a similar suite of MTs to that present in the feed effluents, although fenchone and camphor were present in relatively larger amounts in the leachate than in the feed, and α- and β-pinene were absent in the leachate. Even with limited contact with the sediment (due to channel flow in the column in phase 2), some MT modification was therefore occurring.

7.4.4 Fatty acids

Concentrations of FAs in the leachates were low and variable and showed no relationship with levels in the feed effluent (Figure 7.14).

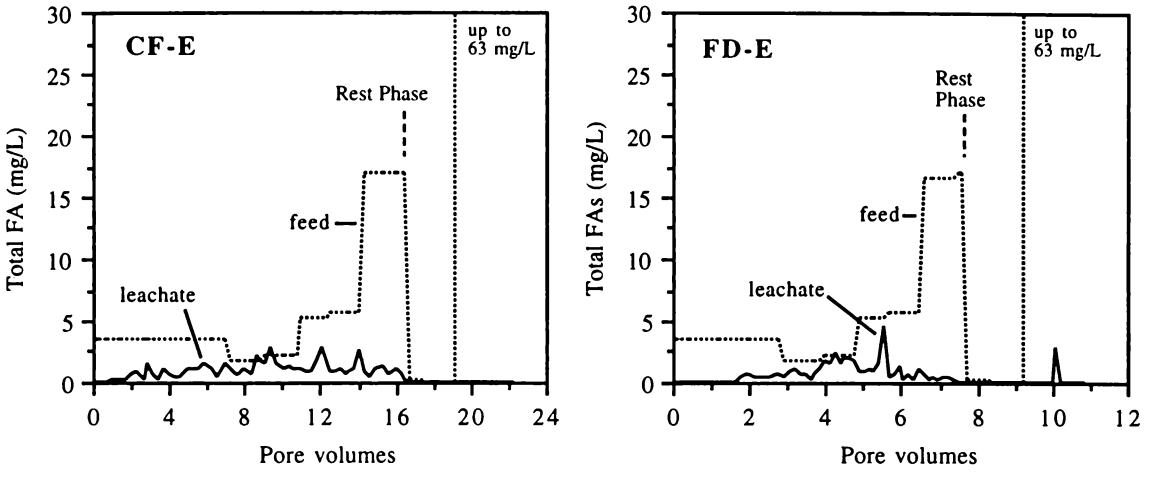


Figure 7.14: Fatty acid levels in CF-E and FD-E column leachates

Saturated species, dominated by even carbon numbered FA14:0 to FA24:0 compounds, were the dominant FAs present in the leachates. FA16:0 was the major compound. FA6:0 (possibly 4-methylpentanoic acid *[2]* from MS library match), and 2-ethylhexanoic acid *[20]* were also found in the CF-E column leachates. These have been reported in landfill leachate (Reinhard *et al.* 1984; Sawhney and Kozloski 1984). FA6:0 has been identified as an intermediate in the anaerobic degradation of lignin fragments and model compounds (Colberg and Young 1985; Grbic-Galic and Young 1985). Unsaturated compounds were limited to FA18:1 species.

7.4.5 Resin acids

RAs were present in the CF-E column leachates in relatively high concentrations for much of the experiment, but appeared at appreciable levels only in transient "spikes" in phase 2 from the FD-E column (Figure 7.15). The appearance of RAs in the FD-E column leachate was attributable to column channelling (as was found for MTs, section 7.4.3).

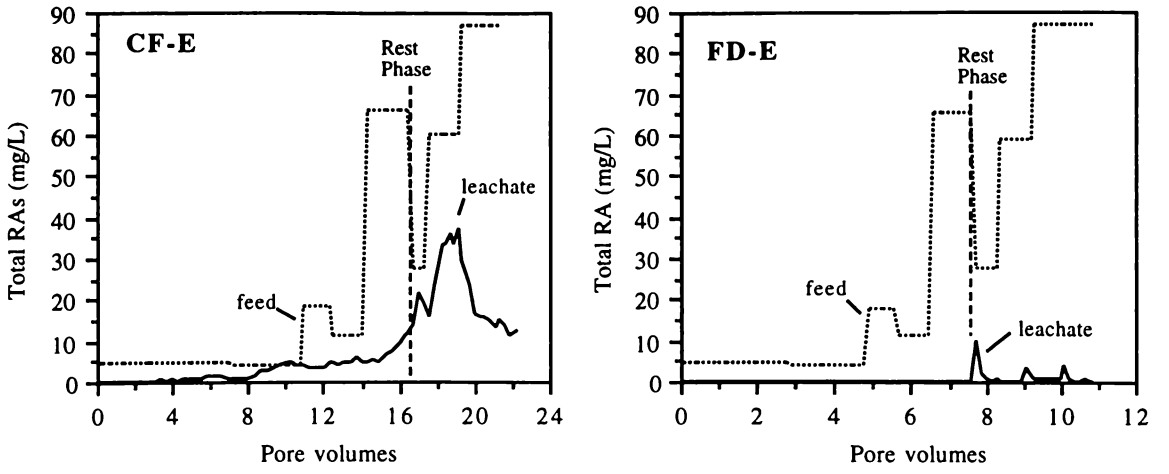
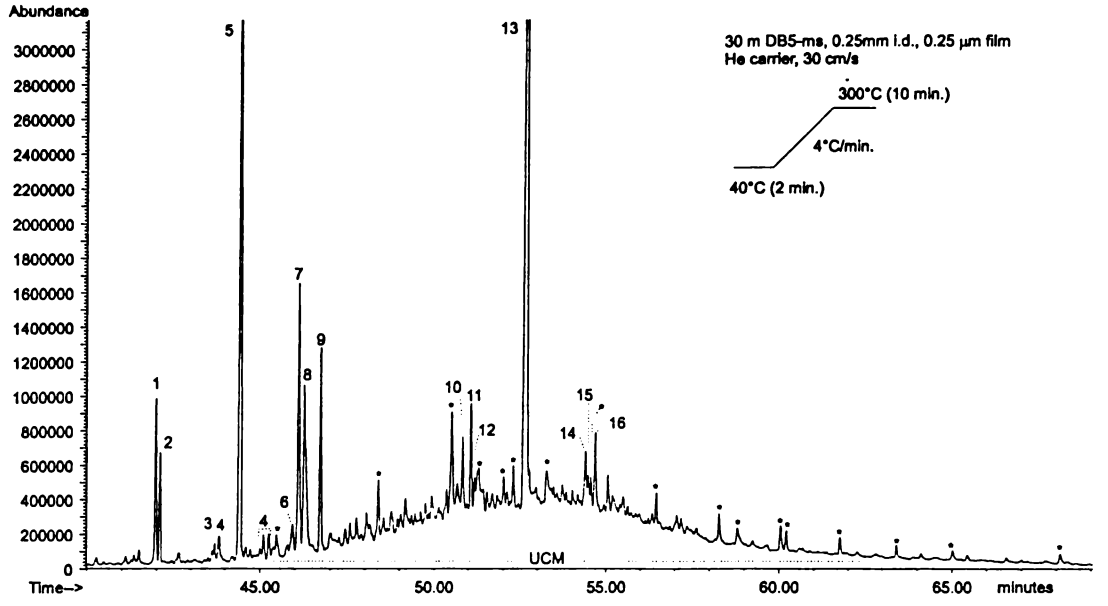


Figure 7.15: Resin acid concentrations in CF-E and FD-E column leachates

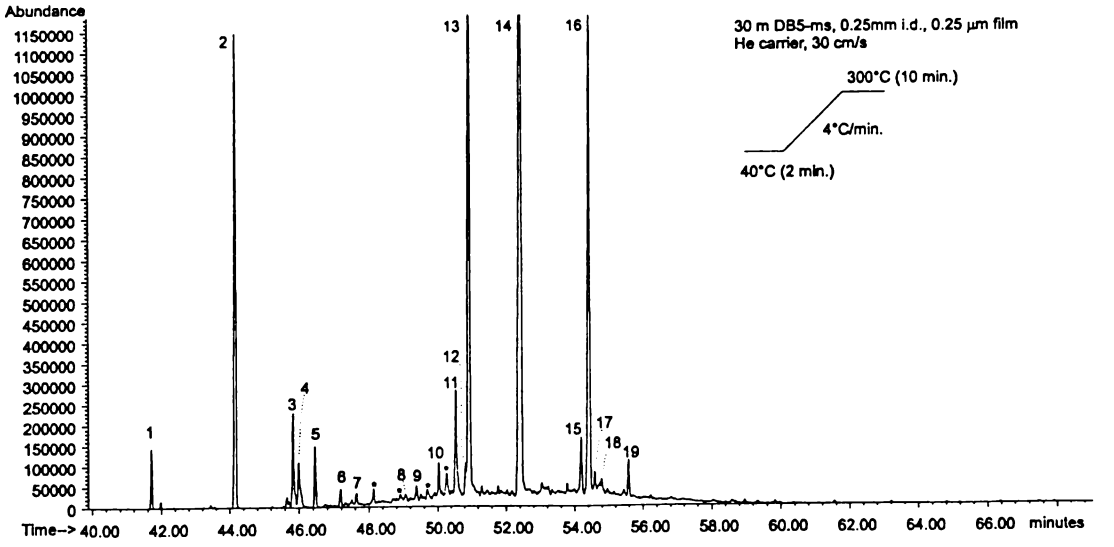
The RA region of GC-FID chromatograms of FD-E and CF-E column phase 1 leachate extracts was dominated by a UCM (Figures 7.16 and 7.17). In the CF-E leachates, four major RAs, 13-abietenoic *[120]*, abietanoic *[127]*, dehydroabietic *[128]*, and 13β-hydroxyabietanoic *[136]* acids, were clearly identifiable above the UCM. Other parent RAs including seco-dehydroabietic acids *[103* and *104]*, pimaric *[110]*, and sandaracopimaric *[113]* acids, as well as degradation products including pimaranoic *[119]*, and 7-oxodehydroabietic *[139]* acids, became identifiable as leachate RA concentrations increased. Unidentified species included two compounds of mw=334 *[135* and *137]*, which eluted immediately before and after 13β-hydroxyabietanoic acid. These were assumed to be hydroxylated RA monoenes. Dehydroabietic and 13β-hydroxyabietanoic acids were the major compounds present in the CF-E leachates, together constituting (on average) 68% of the total RA fraction.



Peaks:

1. FA16:0 *[81]*; 2. unidentified DT260 + mw=292? *[83]*; 3. *anteiso*-F17:0 *[91]*; 4. methyl-(2-ethylhexyl)phthalates *[92]*; 5. FA17:0 surrogate standard; 6. FA18:2; 7. FA18:1 *[101]*; 8. FA18:1; 9. FA18:0 *[102]*; 10. abietanoic acid *[127]*; 11. FA20:0 *[129]*; 12. dehydroabietic acid *[128]*; 13. HC24 standard; 14. 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-ethylphenol *[134]*; 15. RA334? *[135]* 16. Kinleithic acid *[136]*; *. saturated and unsaturated hydrocarbons; UCM. unresolved complex mixture; all acids detected as methyl esters.

Figure 7.16: GC-MSD total ion chromatogram of resin and fatty acids in FD-E column leachate



Peaks:

1. FA16:0 *[81]*; 2. FA17:0 surrogate standard; 3. FA18:1 *[101]*; 4. FA18:1; 5. FA18:0 *[102]*; 6. seco-dehydroabietic acid #1 *[103]*; 7. seco-dehydroabietic acid #2 *[104]*; 8. 8-pimarenoic acid *[111]*; 9. pimaranoic acid *[119]*; 10. 13-abietenoic acid *[120]*; 11. abietanoic acid *[127]*; 12. FA20:0 *[129]*; 13. dehydroabietic acid *[128]*; 14. HC24 standard; 15. RA334? *[135]*; 16. Kinleithic acid *[136]*; 17. RA334? *[137]*; 18. FA22:0 *[138]*; 19. 7-oxodehydroabietic acid *[139]*; *. hydrocarbons; all acids detected as methyl esters.

Figure 7.17: GC-MSD total ion chromatogram of resin and fatty acids in CF-E column leachate

The RA profile of the initial phase 2 leachate from the CF-E column was somewhat different from that of the phase 1 leachates. Abietanoic acid *[127]* and dehydroabietic acid *[128]* were the major compounds, making up about 25% and 50% of the total RAs respectively (initial points in Figure 7.18). As was found for the MTs, RA transformation by aromatisation and saturation was occurring over the rest phase. 13β-hydroxyabietanoic acid *[136]* was present in only very small amounts, indicating that it was degradable in the flooded soil column. Several minor RAs, probably hydroxylated and/or oxidised species were also present in the leachate.

As effluent dosing continued, the RA composition of the CF-E leachate changed markedly. The concentration of 13β-hydroxyabietanoic acid *[136]* increased when the dosing cycle began, but then, in contrast to phase 1 (where it remained a dominant component of the leachate), it slowly decreased in relative concentration (Figure 7.18). Dehydroabietic acid remained the dominant constituent, making up about 60% of the RA fraction. The relative levels of abietanoic acid *[127]* decreased, then rose during phase 2 (Figure 7.18). The metabolism of RAs was therefore markedly affected by the 52 week rest period. Presumably, without fresh effluent supply, the microbial populations responsible for the transformations observed in phase 1 were unable to sustain themselves.

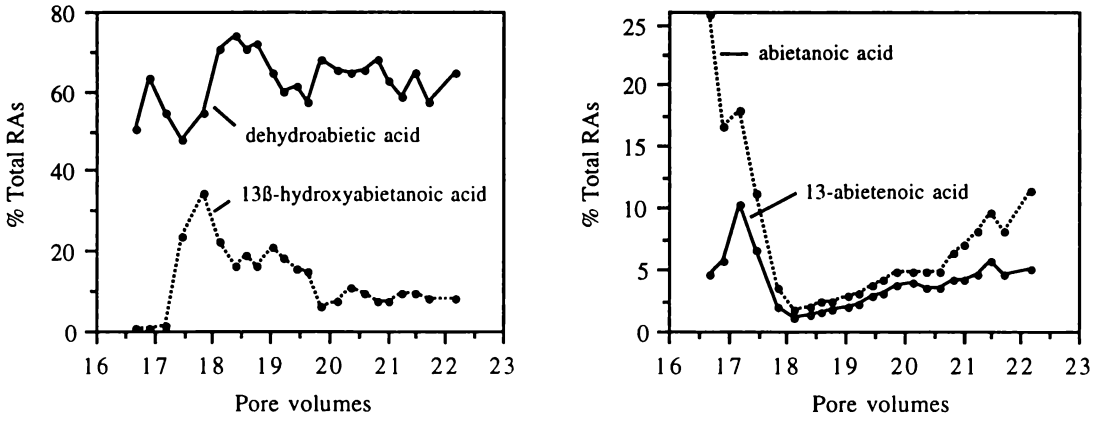


Figure 7.18: Changes in the relative concentrations of major resin acids in the CF-E column leachate during phase 2

The RA composition of the FD-E column leachates in phase 2 was similar to that of the feed effluent. Abietic acid *[131]*, which was not found in appreciable concentrations in the CF-E leachates, was found in the FD-E leachates. The passage of effluent through the column with little modification was consistent with channel flow.

7.4.6 Other compounds in CF-E leachates

Phenylacetic acid *[36]* and phenylpropanoic acid *[56]* were found in the CF-E leachates. Reinhard *et al.* (1984) found these compounds in anaerobic landfill leachates, and hypothesised that they were intermediates in the anaerobic degradation of lignin or lignin fragments, as implied by their formation during the anaerobic degradation of ferulic acid, a lignin model compound (Healy *et al.* 1980). They were also present in the anaerobic sludge of a New Zealand kraft mill effluent treatment system (Panadam-Twigley 1988). Trace amounts of

cyclohexanone and methylcyclohexanone were also found by GC-MSD. These compounds have been identified in the microbial degradation pathway of lignin model compounds (Grbic-Galic and Young 1985).

Di-and tri-methyl-2-cyclopentenones, and acetylthiophene was also identifiable at low concentrations. Consistent with the documented degradability of non-chlorinated, non-alkylated, monomeric phenolics (Sierra-Alvarez *et al.* 1990), guaiacol was not found in the leachates. *Bis*-(2-ethylhexyl)phthalate was also found at relatively high concentrations in most samples, presumably due to leaching from the PVC column.

In the phase 2 leachates, methyl substituted 2-cyclopentenones were present at relatively stable concentrations similar to those present in the feed effluents. This suggested that these compounds were relatively stable under the flooded soil conditions, and was consistent with their presence in shallow ground waters from beneath the seepage ponds (Chapter 6). As was found in phase 1, guaiacol was absent from the leachates, confirming the readily degradable nature of the monomeric phenolics.

7.5 Extractable Organics in Column Sediments

The nature and concentrations of EOs associated with the sediments in the CF-E and FD-E columns were very different. The sediments in the CF-E column contained elevated levels of effluent derived compounds, while the concentrations and composition of extractives in the FD-E column sediments were similar to those found in the soil used to prepare the columns.

7.5.1 CF-E column sediments

RAs and MTs were the major sediment phase EOs. The levels of total RAs, MTs, and FAs varied with depth in the soil column as shown in Figure 7.19. Figure 7.20 shows a GC-MSD TIC of surficial CF-E column sediment. Analytical data are summarised in Appendix 2, Table A2.24.

MTs were dominated by *p*-cymene, with minor amounts of a MT138 (probably 1-methyl-4-(1-methylethenyl)-cyclohexane or double bond isomer), α-terpineol, 4-terpineol, α- and β-pinenes, and camphor making up the remainder.

The composition of the RA fraction was similar to that found in the phase 2 leachates. An exception was pimaric acid, which was a minor species in the leachates, but a major constituent of the upper sediments. Plausible transformation products of pimaric acid in the sediments and leachates were quantitatively relatively minor monoenic species. It therefore appeared that partitioning to the sediments was the primary mechanism for the removal of pimaric acid. Dehydroabietic, abietanoic, 13-abietenoic, and isopimaric acids were the other major compounds present. 13β-hydroxyabietanoic acid, the major RA degradation product in the leachates, was a minor sediment phase constituent. DTs, largely dehydroabietin, were also found as relatively minor constituents as shown in Figure 7.20.

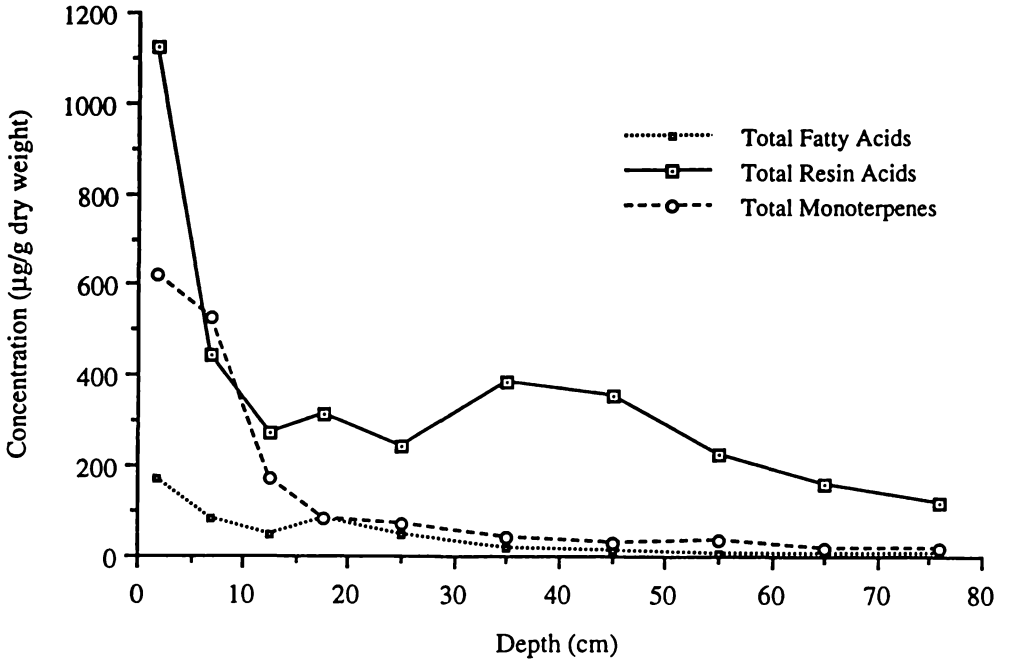
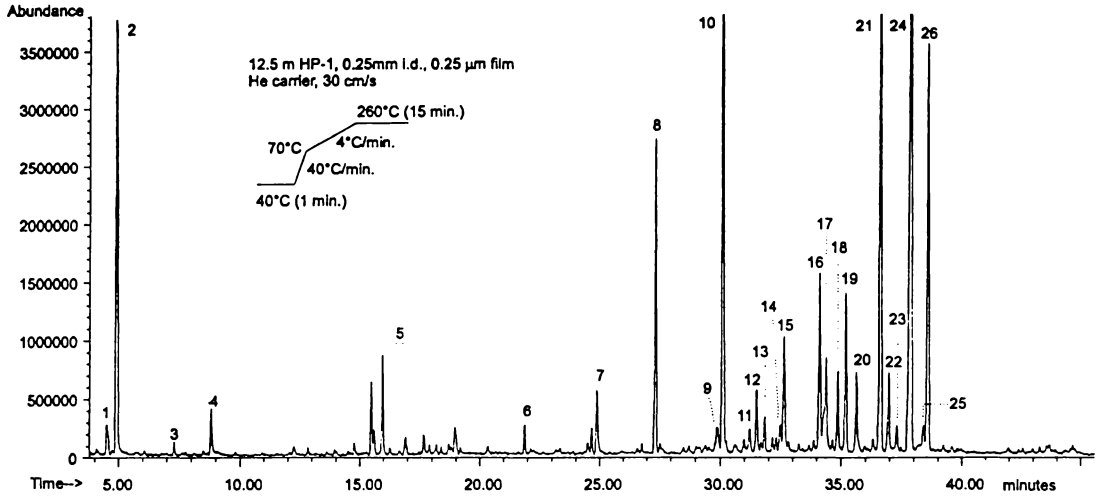


Figure 7.19: Concentration–depth profiles of total resin acids, fatty acids and monoterpenes in the CF-E column sediments



Peaks:

1. MT138 *[11]*; 2. *p*-cymene *[15]*; 3. camphor *[34]*; 4. α-terpineol *[48]*; 5. mw=204 compounds, mass spectra similar to *[71]*; 6. HC16 standard; 7. FA14:0 *[75]*; 8. HC18 standard; 9. HC + DT272; 10. FA16:0 *[81]*; 11. DT272; 12. dehydroabietin *[90]*; 13. *anteiso*-FA17:0 *[91]*; 14. DT270 *[95]*; 15. DT272 + DT290 unresolved; 16. FA18:1; 17. FA18:1; 18. FA18:0; 19. seco-dehydroabietic acid #1 *[103]*; 20. seco-dehydroabietic acid #2 *[104]*; 21. pimaric acid *[110]*; 22. sandaracopimaric acid *[113]*; 23. 8(14)-pimarenoic acid *[118]*; 24. isopimaric acid *[121]* + 13-abietenoic acid *[120]*; 25. RA318 + abietanoic acid *[127]*; 26. dehydroabietic acid *[128]*. Fatty and resin acids detected as methyl esters.

Figure 7.20: GC-MSD TIC of surficial CF-E column sediment

The concentrations of RAs did not all vary with depth in the same way. Profiles for five of the major compounds are shown in Figure 7.21. The DTs, represented in Figure 7.21 by the major DT272 compound, were concentrated in the surface layers of the sediment, while the acids penetrated more deeply into the sediment profile. The formation of these compounds in the soil

column was a possible contributing factor, leading to the unusual total RA concentration versus depth profile (Figure 7.19).

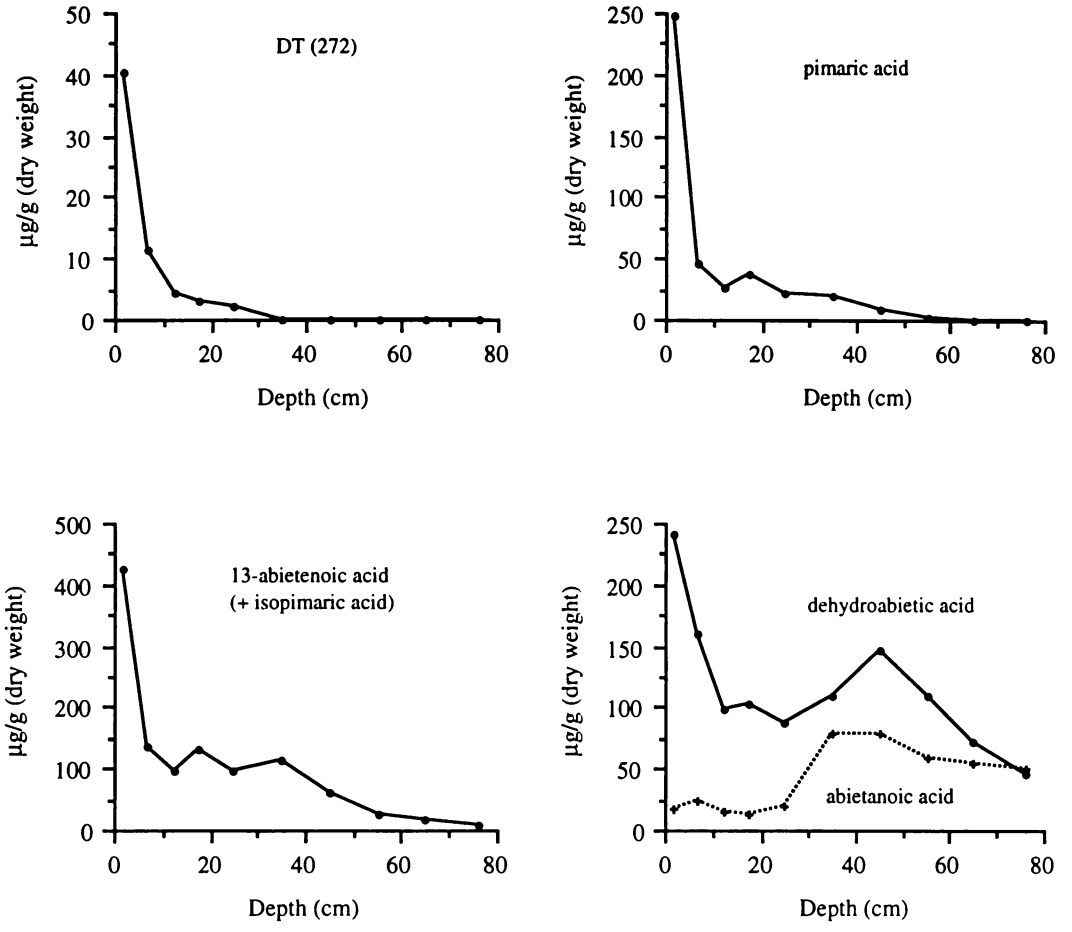


Figure 7.21: Depth profiles of major resin acids and diterpene hydrocarbons in CF-E column sediments

The composition of the FA fraction was similar to that found in the leachates, being predominately saturated species. FAs were quantitatively relatively minor components of the sediment phase extractives.

Other minor components were several compounds of mw=204, which were confined to the upper sediment zones. Sesquiterpenes, bicyclic $C_{15}H_{24}$ compounds (e.g. longifolene), have mass spectrum similar to those of the mw=204 compounds present in the column sediments e.g. *[71]*. They have been found in marine sediments contaminated by pulp mill effluent (Kinae *et al.* 1981; Yamaoka 1979), in the effluent treatment system of another New Zealand kraft mill (Panadam-Twigley 1988), and in the activated sludge plant effluent from an Australian thermomechanical pulp mill (Richardson and Bloom 1983). The accumulation of these compounds, at the top of the sediment column was consistent with the behaviour of the mono- and diterpene hydrocarbons.

7.5.2 FD-E column sediments

Concentrations of EOs in the FD-E column sediments were very low. MTs were undetectable in all but two samples (at 40–60 cm depth) in which low concentrations (0.4 and 0.9 $\mu g\ g^{-1}$) of 4-terpineol were detected. RA levels were not significantly different from those found in the soil used to pack the columns (Figure 7.22). FA concentrations were variable, and after blank correction were not appreciably different from "background" levels.

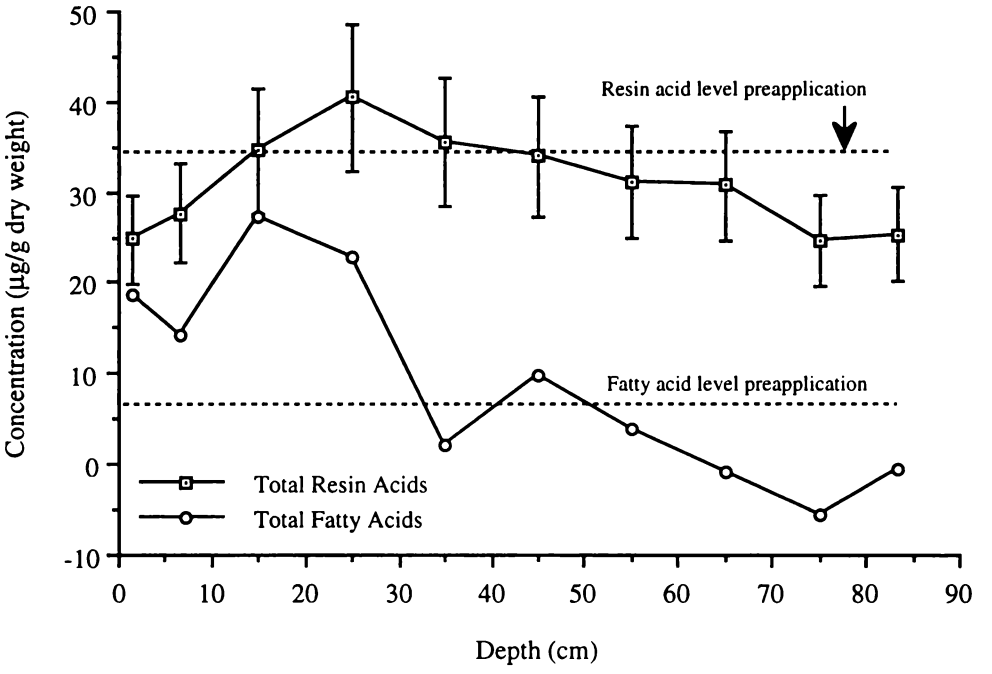


Figure 7.22: Concentrations of sediment phase resin and fatty acids in the FD-E column (resin acid error bars are approximate analytical 95% confidence intervals). Negative FA concentrations due to blank correction.

The RAs found in the sediments were similar to those found in the soil before effluent application commenced. Abietanoic acid was the dominant compound, and increased in concentration with depth, while other RAs all followed a trend of an initial increase followed by a decrease. Figure 7.23 plots these changes for the major species. The FAs present in the CF-E column sediments were also found in the sediments from the FD-E column.

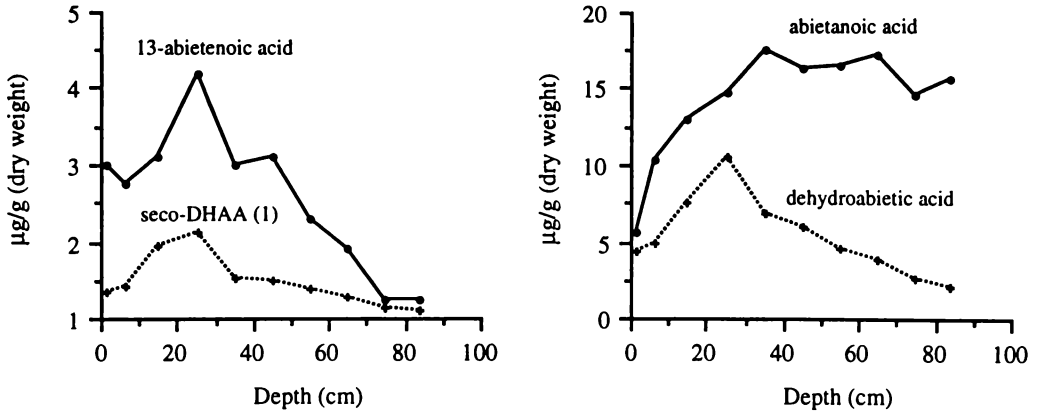


Figure 7.23: Depth profiles of major resin acids in the FD-E column sediments

7.6 Effluent Treatment Efficiency

Mass balance for the experiment was carried out as described in section 7.2.5. Tables 7.5 and 7.6 summarise the mass balances obtained for each column.

Table 7.5: Mass balance for the CF-E column

	Mass	Mass recovered in:			% recovered in:			Removal
Constituent	Added	Leachate	Sediment	Total	Leachate	Sediment	Total	(%)
Sodium (g)	53.1	46.5	3.4 [(a)]	49.9	88	6	94	6
Colour (g)	208	313	n.a.	313	151	–	151	-51
Iron (mg)	55	660	n.a.	660	1200	–	1200	–
Monoterpenes (mg)	4190	1710	170	1880	41	4	45	55
Fatty Acids (mg)	800	49	27	76	6	3	9	91
Resin Acids (mg)	1990	495	1430	1930	25	72	97	3

a: estimated from the mass retained before breakthrough; n.a. not analysed

Table 7.6: Mass balance for the FD-E column

	Mass	Mass recovered in:			% recovered in:			Removal
Constituent	Added	Leachate	Sediment	Total	Leachate	Sediment	Total	(%)
Sodium (g)	37.1	32.3	4.8 [a]	37.1	87	13	100	0
Colour (g)	151	148	n.a.	148	98	–	98	2
Iron (mg)	40	453	n.a.	453	1133	–	1133	–
Monoterpenes (mg)	2600	123	1	124	5	<1	5	95
Fatty Acids (mg)	688	26	7	33	4	1	5	95
Resin Acids (mg)	1560	18	-15 [b]	3	1	<1	1	99

a: estimated from the mass retained before breakthrough; b: Negative value arises from slightly lower concentrations in the FD-E sediment than in the "preapplication soil": Total mass in FD-E column sediment after effluent dosing = 184 mg, but from preapplication soil concentration (34 µg g^{-1}), the FD-E column contained 199 mg before effluent dosing (see Figure 7.22).

The mass balances showed:

- no colour removal occurred under either application regime. Colour intensification occurred in the CF-E column, more colour leaving the column in the leachate than was added in the feed effluents;

- treatment efficiencies of EOs were dependent on the application regime. In the FD-E column essentially all the EOs were removed, resulting in little leaching from the column or accumulation in the sediments. The 5% total MTs that left the column in the leachate did so in the initial acclimation phase or in the channelling observed in phase 2. Channelling was responsible for almost all the RAs leaving the column.

- MTs and RAs were poorly removed in the CF-E column. MT removal was approximately 55%, and most of this occurred in the earlier part of the experiment. In phase 2, essentially all (94%) of the MTs added were recovered in the leachate, indicating that after prolonged flooding, little removal could be expected to occur. While a variety of RA transformation products were formed in the CF-E column, little overall removal of these compounds resulted.

- FAs were effectively treated (>90% removals) by both FD and CF application methods.

- association with the sediments was a major mechanism for RA removal from the effluent in the CF-E column. Essentially all the RAs not recovered in the leachate were accumulated in the sediments, where most (72%) of that added was found. Figure 7.24 summarises the fate of the EOs in the CF-E column.

- more iron was leached from the columns than was added in the feed effluents.

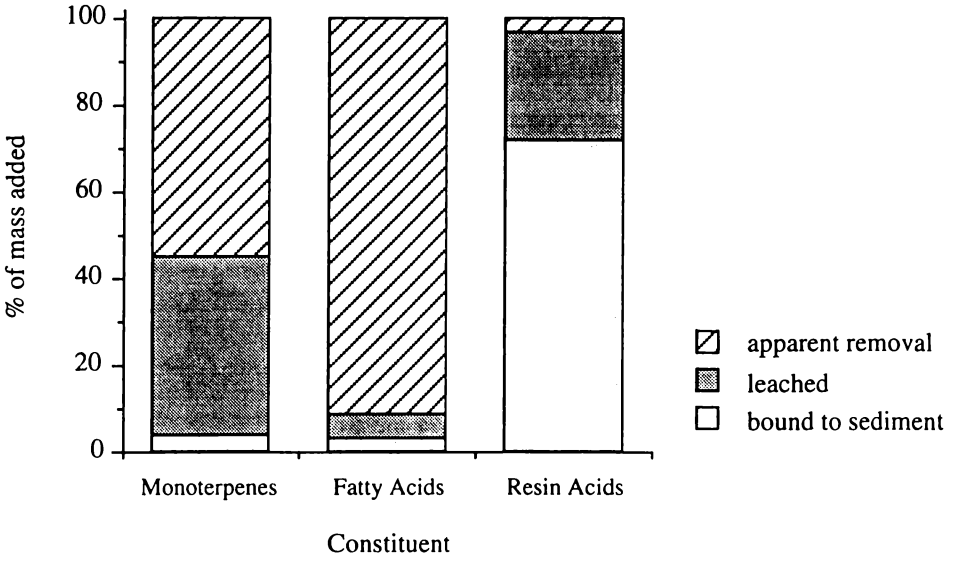


Figure 7.24: Fate of extractable organics in the CF-E column

7.7 Summary and Conclusions

7.7.1 Mobilities of effluent constituents

Breakthrough behaviour of EOs and colour was "non-ideal" due to transformation, degradation, and interaction with the sediments in the columns. Breakthrough for these components could not, therefore, be assessed from the traditional method ($C/C_0=0.5$). Instead, the trial allowed the relative mobilities to be assessed. Colour, MT alchohols and ketones, sodium, and chloride were all relatively mobile ($R_f<2$). RAs were substantially retarded ($R\approx8.5$) by association with the sediments.

7.7.2 Extractable organic chemistry of leachates

The EO composition of leachates was dependent on the application regime. After an initial acclimation phase, when MTs were found in the leachate, the FD-E regime effectively removed EOs from the effluent. Channelling, caused by drying during the rest period, allowed relatively unmodified effluent to pass through the soil during phase 2.

Leachates from the CF-E column contained a suite of transformed EOs, which changed in composition over time. Parent effluent MT alcohols dominated the initial leachates, but were rapidly transformed by oxidation or reduction to their corresponding ketones or saturated alcohol analogues. DHT was the major MT present in CF-E leachates. Over time, *p*-cymene was produced, indicating that aromatisation was also occurring in the column. The transformation products appeared resistant to further degradation under the experimental conditions, and remained present as major constituents in phase 1 leachates.

RAs were also substantially modified. 13β-hydroxyabietanoic acid was the major single transformation product in the leachates. FAs, largely saturated compounds, were present in low and variable quantities. Methyl-substituted 2-cyclopentenones were consistently present. Other EOs in the leachates included phenylpropanoic, phenylacetic, and caproic (FA6:0) acids, which may have been sourced from lignin degradation.

The prolonged period of flooding without application of fresh feed effluent altered the nature of the transformations occurring in the column. The proportions of saturated MTs and RAs decreased, so that DHT and abietanoic acid became relatively minor constituents in the leachate. The major single compound in the MT fraction was then α-terpineol. Concentrations of 13β-hydroxyabietanoic acid decreased, leaving dehydroabietic acid as the most abundant RA. *P*-cymene remained a significant MT.

7.7.3 Extractable organic chemistry of sediments

The CF-E column sediment accumulated RAs and MTs, whereas the FD-E column sediment did not. CF-E column sediment RAs were a mixture of parent and transformed species including dehydroabietic, abietanoic, 13-abietenoic, and pimaric acids as major components. DT hydrocarbons were also present at lower levels. MTs were dominated by *p*-cymene, with smaller amounts of other species including an unidentified MT138 species, α–terpineol, and camphor, also present.

7.7.4 Treatment efficiency

Effluent treatment differed markedly between the two application regimes. The FD-E regime effectively removed EOs from the effluent. No EO residues accumulated in the column sediments. This indicated that the FD-E regime gave essentially complete degradative removal of EOs.

The CF-E application method gave relatively poor treatment of EOs. MTs and RAs were present at appreciable concentrations in most CF-E leachates and were accumulated in column sediments. Removals of MTs and RAs from the soil columns were estimated to be 55% and 3% respectively. Most of the unremoved MTs exited the columns in the leachate, while most of the RAs was retained in column sediments. FAs were effectively removed from the CF-E column.

Colour was not removed under either the FD-E or CF-E conditions. Large increases in colour were observed after the 52 week rest period in the CF-E column, resulting in nett increase in colour for the CF-E application regime. Qualitative evidence for interaction between effluent and sediment iron being involved in the observed colour intensification was obtained.

7.7.5 Comparison of soil-column and seepage system chemistry

The soil-columns were intended to simulate the range of conditions existing in the Kinleith seepage system. It was therefore of interest to compare the chemistries of column leachates with shallow ground waters, and soil-column sediments with those from beneath the seepage ponds.

The CF-E column leachates contained RAs that were also major constituents of seepage basin effluents, and to a lesser extent, some shallow ground waters from the Kinleith LA system. The major characteristic of the RA chemistry of the leachates was the presence of 13β-hydroxyabietanoic acid. This was a transient intermediate observed during effluent degradation in a seepage basin (section 4.4.6) and was a major RA in J Pond effluent (section 4.3.4). However, it was not present at significant levels in the ground waters.

In the seepage basins, effluent was fed batch-wise, so that transformations continued through intermediates until no further degradation occurred. In J Pond, effluent addition was continuous, so that steady state was approached and transformed intermediates were maintained at elevated levels. The latter situation was analogous to the CF-E regime. It was therefore reasonable that J pond effluent and CF-E column leachates had similar EO chemistry. MTs in the CF-E column leachates and J pond effluents were also similar, although a greater degree of MT saturation (α-terpineol to DHT) was observed in the soil column.

The composition of the shallow ground waters differed from the leachates in that MTs were not major EOs in the ground waters, and RAs were dominated by saturated species (e.g. abietanoic acid) or DTs (e.g. fichtelite, dehydroabietin, retene) rather than by dehydroabietic acid or 13β-hydroxyabietanoic acid, as was found in the CF-E leachates. This was probably due to a combination of aerobic degradation of EOs in the seepage ponds (section 4.4) which would have removed the majority of the MTs and RA intermediates before effluent penetrated deeply

into the underlying sediments, and slow, anaerobic transformation of RAs in the ground waters, producing DTs.

The sediments from the CF-E column and the seepage system at Kinleith contained a number of compounds in common, but they differed in the relative abundances of parent RAs, transformed RAs, and DTs. The seepage system sediments contained relatively small amounts of parent RAs, and were dominated by saturated RAs and DTs (Chapter 5). In contrast, the sediment extractives from the column experiment were dominated by RAs that were present in the feed effluents, and monoenic degradation products. Abietanoic acid was the only major saturated compound present. DTs were minor, and lacked the diversity that was present in the seepage system sediments. The reasons for these differences were unclear. The CF-E soil-column model did, however, show that association with sediments was a significant process for RA retention during LA. This was consistent with the presence of high concentrations of RAs and DTs in sediments in the seepage system.

Colour in the soil-column leachates was high, as it was in most of the shallow ground waters beneath the seepage basins. There was some evidence for small and variable colour reductions in the ground waters, whereas no such reductions were observed in the soil-column experiments.

7.7.6 Conclusion

In general, the soil-columns were useful models for investigating changes in effluent composition resulting from soil percolation. They demonstrated that many of the EOs present in the effluent would be only partially degraded under a CF application regime, and that the residuals would leach and/or accumulate in sediments. The trials also showed that EOs were completely removed under an aerobic FD application regime. The EO chemistry of the CF-E soil-column sediments and leachates was similar to that of J pond effluent, but was somewhat different from that of ground waters. These differences demonstrated the limitations of model systems in predicting detailed effects of full-scale operations where different physical, chemical, and microbiological conditions may be found, and where processes may occur at different rates from those simulated in the laboratory.

Chapter Eight

Summary and Conclusions

8.1 Introduction

This chapter summarises the major findings of the study and relates these findings to the aims and objectives proposed at the beginning of the work (Chapter 1). The results are also used to discuss the significance of some of the operational variables identified in the conceptual model of the LA system (Figure 1.7). Some recommendations for future study are also made.

The overall aim of the project was to determine whether the Kinleith LA system was suitable for sustainable treatment of effluent colour and EOs. To achieve this aim, studies of effluent behaviour in LA system seepage ponds, sediments, aquifer materials and ground waters were undertaken. Observations made in these investigations were complemented by laboratory-based simulations. Conclusions drawn from these studies, as they relate to each of the objectives defined in Chapter 1, were as follows.

8.2 Summary of Major Results

8.2.1 Treatment of effluent colour and extractable organics in the seepage ponds

Treatment of effluent colour in the seepage ponds was minimal. The greatest reduction measured in the study was approximately 25%, after 45 days in seepage pond P7. Some circumstantial evidence for small increases in colour were also obtained from other parts of the system. Colour removal of practical significance for effluent treatment was therefore not occurring.

Extractable organics underwent substantial modification and removal in the seepage ponds. The rates of the removal processes differed between the classes of compounds monitored. Disappearance rates, given from the time required to reduce initial concentrations by 90%, decreased in the order FAs>CPs≈MTs>RAs. The concentrations of all the classes of low molecular weight extractable organics analysed were reduced by 98–99.9% (≥95% by processes other than dilution) after approximately 30 days in the seepage pond.

EOs underwent both oxidative and reductive transformations in the seepage ponds, producing a range of transient intermediates and more stable end products. RA behaviour was distinctly different from the other compound classes, largely due to an initial period of transformation (rather than removal) during which major intermediates were formed. Important intermediates were 13β-hydroxyabietanoic acid *[136]*, 13-abietenoic acid *[120]*, and dehydroabietic acid *[128]*. RAs were the most persistent class of compounds analysed, and were present, largely as a suite of transformed species, at a total concentration of approximately 300 $\mu g\ L^{-1}$ at the end of the monitoring period. This concentration was comparable with concentrations found in some shallow ground waters beneath the ponds.

In summary, it was concluded that the seepage ponds were active treatment zones, resulting in removal of at least 95% of the EOs, but little treatment of effluent colour.

8.2.2 Penetration of organic contaminants into sediments and aquifer materials

The suite of EOs found in sediments and aquifer materials beneath the seepage ponds was different from that present in drain or pond effluents. Transformed RAs, largely the saturated compound abietanoic acid *[127]*, and DTs, largely fichtelite *[87]*, dehydroabietin *[90]*, and retene *[105]*, were the major compounds present in the sediments. The concentrations of these species was very high (up to 10,000 mg kg^{-1}) in surficial, and in some deeper, sediments.

Depth profiles of EOs measured in shallow cores, excavated pits, and borehole cores showed that while accumulation of EOs at the surface was occurring, there were also discrete zones beneath the surface where contamination by high levels of EOs was present. The deepest contaminated zone was found at 5 m beneath the seepage basin. The high concentrations of effluent-derived EOs in some of these zones indicated that relatively untreated effluent was moving through the sediments to zones where transformation and accumulation were occurring. The use of EOs as markers of effluent contact with sediments enabled such zones to be readily identified.

The results indicated that some effluent transport was occurring via fractures and permeable conduits rather than by uniform infiltration into the sediments. This was consistent with the geology of the surficial ash deposits and underlying ignimbrites of the area. The result of this undesirable feature was penetration of EOs to depths beneath the water table.

8.2.3 Ground water contamination by extractable organics and colour

Extractable organics, colour, sodium, and chloride concentrations were determined in shallow wells (2–15 m depth) beneath the seepage ponds, and in deeper (9–110 m) off-site wells.

Shallow ground waters

Shallow ground water chemistry was spatially variable, reflecting the heterogeneous nature of the geology beneath the seepage basins. Concentrations of sodium and chloride were high (e.g. 200–480 mg L^{-1} Na^{+}) and indicated the water sampled was approximately 70–80% seepage basin effluent.

Colour levels were more variable than sodium or chloride and ranged from visually very pale yellow (<100 CPU) to very dark brown/black (2100 CPU). The high spatial variability in colour was further evidence for non-uniform effluent movement in the ground water system.

Effluent-related EOs were found in all shallow ground waters, but with great variability in chemistries and concentrations. Resin acids and diterpene hydrocarbons were generally dominant compounds. Best estimates of the range of median concentrations of these compounds found in each well were: 1) RAs 18–350 μg L^{-1} and 2) DTs 2–2300 μg L^{-1}. Total RA+DT median concentrations were 19–2600 μg L^{-1}, the overall median level being 300 μg L^{-1}. The concentrations of some compounds, particularly DTs, were higher in ground water than in degraded seepage pond effluent. Other compounds found in ground waters included methyl-substituted 2-cyclopentenones and fatty acids.

A preliminary set of analyses indicated that the concentrations of chlorophenolics in shallow ground waters were low, totalling approximately 2–4 μg L^{-1}.

Off-site ground waters

The chemistry of off-site ground waters was also highly variable and was strongly influenced by the zone from which water was sampled. Ground waters from the fractured, high flow, zones of the Marshall A and Marshall B ignimbrites contained elevated levels of effluent-sourced Na^+, colour, and RAs and DTs. Samples taken from less welded zones of the Marshall unit, and from the Whakamaru and Waiotapu ignimbrites contained much lower conentrations.

Median sodium concentrations in wells immediately adjacent to the seepage area were as high as 400 mg L^{-1}. Colour levels were also high in these zones, median concentrations of up to 900 CPU being found. Elevated concentrations of RAs and DTs (median totals of up to 110 μg L^{-1}) were also found in wells close to the seepage area.

Na^+ and colour concentrations in the most contaminated deep wells immediately adjacent to the seepage area were similar to the median concentrations found in the shallow wells directly beneath the seepage basins. RAs and DTs were present at substantially lower concentrations in the deep wells than in the shallow wells. After correcting for dilution (using Na^+ as tracer), colour and RA+DTs concentrations were estimated to be reduced by approximately 10% and 60% respectively between the shallow ground waters and the most contaminated ground water in the Marshall A ignimbrite immediately adjacent to the seepage area.

Sodium and chloride concentrations were diluted rapidly with distance from the seepage area. Compared with Na^+ or Cl^-, organic contaminants (colour and RA+DTs) were attenuated in the off-site ground water system, falling to levels of <10% those present at the edge of the seepage field after approximately 100 m. After correcting for dilution (using Na^+ as tracer), concentrations of colour and RA+DT were reduced by approximately 90% between shallow ground water beneath the seepage ponds and bore 89/2 (high flow Marshall A ignimbrite, approximately 100 m from edge of seepage area).

Some evidence for decreases in ground water contaminant levels in response to retirement of the seepage system was obtained from changes in Na^+ concentrations over time in high flow zones of the Marshall A and B units.

8.2.4 Effluent treatment occurring through infiltration

Effluent treatment was estimated in two ways:1) from comparisons of field measurements of seepage pond effluent and ground water chemistry; and 2) from soil-column simulations carried out in the laboratory. The field assessments gave data which reflected the real-world variability present in the system, but were unable to provide reliable estimates of removals of labile components, in particular EOs, because of their reactivity in the seepage ponds.

Colour removals during effluent infiltration estimated from field data ranged from very small (8% increase) to large (94% removal). Median colour removals of approximately 75% (range 24%–94%) and 45% (-8%–88%) were estimated in two studies. Such "averages" are of limited

value, however, due to the high variability present, and potential for bias (depending on which wells were sampled). Ground water concentrations of RAs and DTs were highly variable and were not well related to concentrations or chemistries found in the seepage ponds. Assessing removals of EOs from field data was therefore not possible.

Laboratory simulations showed that effluent treatment was dependent on the application regime, especially for EOs. Under a continuously flooded regime, in which the sediment surface was always covered with effluent, removal of MTs, FAs, and RAs from the effluent aqueous phase were 59%, 94%, and 75% respectively. Analysis of soils revealed 72% of the RAs added to the column were associated with the sediments, but only 4% of the MTs and 3% of the FAs. Total removals from the system were 55% MTs, 91% FAs, and 3% RAs. These results showed that sorption to sediments was a significant process for RAs, but was less so for MTs which were highly mobile in the soil. They also showed that degradative removal from an infiltration system under flooded conditions was minimal for RAs, incomplete for MTs, but highly efficient for FAs.

Under an application regime incorporating a flood–dry cycle, in which the sediment surface was exposed to the air between effluent applications, >95% of the EOs were removed from the system. No significant residuals remained in the soil. The small quantities of EOs released from this system were leached during the initial start-up phase (acclimation) and after a long rest period (artifacts of soil shrinkage in the columns). LA using this type of application regime would therefore be expected to give effective, sustainable, treatment of EOs.

Treatment of colour was poor under both application regimes. Large increases in colour were observed during the simulations, some leachates being more coloured than the feed effluent. Colour removal over the duration of the experiments was -51% for the continuously flooded trial, and 2% for the flood-dry simulation. Interaction between the effluent and sediment-phase iron was implicated in the colour increases observed. It was concluded that effluent infiltration through the seepage area soils would not provide adequate treatment of colour.

8.3 Significance of Operational Variables Identified in System Model

The conceptual model of the Kinleith LA system presented in Figure 1.7 identified several system variables which were potentially important in determining the performance of the LA system for sustainable effluent treatment. The results obtained from the study allowed some qualitative assessment of the relative importance of some of these processes and features.

Potentially significant removal processes identified in the model were biodegradation, sedimentation, sorption, photodegradation, and volatilisation. The collective evidence from the study indicated that biodegradation was an important process for EO treatment. The seepage ponds appeared to be active treatment zones, in which disappearance of >95% of the EOs was measured. The transformation chemistry observed in the pond study was evidence that degradation was at least partially responsible for the observed disappearances. Volatilisation was implicated in the loss of some MTs in the drain and pond system, but its quantitative contribution to the disappearance of MTs could not be determined.

Sorption and sedimentation were found to be important processes for removing RAs from effluent during infiltration. In column studies, 72% of added RAs remained associated with soils. Sediments and aquifer materials from beneath the seepage ponds contained high concentrations of RAs and DTs. In the absence of fracture flow, RAs and DTs were found at highest concentrations in surficial sediments (e.g. in Pond E core), an observation consistent with accumulation in sediments and associated organic matter. In contrast, MTs were found to be highly mobile in seepage area sediments, as evidenced by rapid leaching and little accumulation in soil-column trials. Colour was also found to be highly mobile in sediments in soil-columns.

The relative concentrations of colour, RAs and DTs, sodium, and chloride in off-site ground waters indicated that sorption to ignimbrite aquifer materials was attenuating transport of organics away from the seepage area.

Dilution by rainfall and runoff, and by dispersion in ground water, was a potentially important process affecting effluent fate. In one pond study, an approximately 60% reduction in Na^+ concentration occurred which coincided with periods of rainfall. Rainfall and runoff were therefore significant under some circumstances, the magnitude of the effect depending on factors such as weather conditions (season), volumes of effluent in the seepage basins, and soil saturation. Conversely, concentration by evaporation could be important, especially in summer when evaporation exceeds precipitation.

Dilution in ground water was found to be important in off-site situations, but in the shallow ground waters beneath the ponds, dilution was relatively small (on average approximately 30%, depending on assumed effluent source). There appeared to be a zone directly beneath the seepage area in which dilution factors were small, as evidenced by high Na^+ concentrations in both shallow and deep wells. This "vertical plume" of effluent was rapidly diluted by regional ground water outside the boundaries of the seepage area.

Also identified in the conceptual model was the fractured, heterogeneous, geology of the system. This was found to be a major factor influencing the distribution of effluent in the ground water system, both in the shallow zones beneath the ponds, and in off-site ignimbrite units. Concentrations of effluent-derived contaminants were spatially highly variable in ground waters, consistent with ground water (and effluent) movement through fractured, high flow, zones. The spatial distribution of EOs in sediments was also sufficiently variable to implicate fracture-flow in transport of effluent through the shallow ground water system.

In summary, the study results indicated that the dominant processes affecting the treatment and transport of effluent in the LA system and associated sediments and ground waters were 1) removal of EOs, probably by biodegradation, in the seepage ponds, 2) sorption of RAs and DTs by sediments and ignimbrites, and 3) effluent and ground water transport through fractures. The recalcitrance of colour, and its relatively high mobility in surficial sediments was another major feature.

8.4 Land Application as a Sustainable Treatment Option

The original aim of the study was related to examining the sustainability of the Kinleith LA system for effluent treatment. Accumulation of EO residues in the sediments beneath the seepage ponds, and contamination of ground water by Na^+, Cl^-, colour, and some EOs (in particular RAs, DTs, and MCPs) was evidence that the system had insufficient treatment capacity to sustainably process the loads of contaminants delivered to seepage.

While not a sustainable treatment system, the overall reductions in the concentrations of key contaminants in the system were large, partly due to dilution, but largely due to other processes (as described above). These reductions can be seen by examining concentrations of sodium, colour, and RAs (plus DTs) in the No. 2 effluent, in shallow ground water beneath the seepage basins, and in deeper ground water below and adjacent to the seepage area. These data are summarised in Table 8.1.

Table 8.1: Comparison of contaminant concentrations in the LA system

Constituent	Location through the land application system				
	No. 2 effluent[a]	seepage pond[b]	shallow GW[c]	deep GW d=0[d]	deep GW d=100[e]
sodium (mg L^{-1})	840	205	380	345	120
colour (CPU)	4600	1020	1070	880	29
RA+DT (µg L^{-1})	121,000	290	300	107	9
CP (µg L^{-1})	1030	12	3	n.a.	n.a.

a: mean data from Stuthridge (1991); b: degraded pond P7, median of last 13 days (Chapter 4); c: median data for shallow ground waters beneath seepage pond P7 from reassessment period (section 6.6); d: median data for B74/2, distance = 0 from seepage area; e: median data for B89/2, distance =100 m from seepage area; n.a. not assessed due to low levels

This comparison highlights the large changes in chemistry occurring in the seepage ponds, and relatively minor change occurring between ponds and shallow ground water. It also shows that colour reduction between the ponds and shallow ground water system was small, and that significant attenuation of colour was apparently occurring during ground water migration away from the seepage area.

If the LA system was defined to have boundaries at the edge of the seepage field, the degree of treatment (as judged by disappearance of effluent components from the aqueous phase) was large for the EO constituents. Resin acids, the most recalcitrant EOs monitored reduced from over 100,000 µg L^{-1} in the No. 2 effluent to approximately 100 µg L^{-1} in the most impacted deep ground water on the edge of the seepage field, a reduction of 99.9%. Colour change from 4600 CPU to 880 CPU is an approximately 80% reduction, of which about 60% occured through dilution (from Na^+ concentration change).

While in theory it was not sustainable (because of inadequate treatment of colour and contamination of sediments and ground waters), the LA system reduced the concentrations of EOs by large amounts, mostly in the seepage ponds. On this basis, the treatment efficiency of the system for EOs was high, and prevented gross contamination of ground water by organics.

8.5 Conclusion

The study determined that LA, as used on the Kinleith site, was not a sustainable treatment method. This was principally because of the resistance of colour to treatment, and because of the fractured geology of the site which channeled effluent through the ground water system. The study also showed that EOs could be treated effectively by LA provided an aerobic, flood-dry, application regime was used. Even under these conditions, however, colour removal did not occur. These results were consistent with the generally accepted view that colour is the "land limiting constituent" for treatment of pulp mill effluents by LA.

8.6 Recommendations for Further Work

Land treatment has many potential benefits but, as demonstrated in the present study, it also has limitations which must be understood to prevent soil and ground water contamination. The work carried out on the Kinleith system highlighted the major limitation of LA for treatment of BKME i.e. colour removal. This aspect therefore remains the key area requiring further study.

Some of the shallow ground waters beneath the seepage ponds at Kinleith contained relatively low levels of colour. This suggests that there was a colour removal process operating in some localised zones. Conversely colour increases were observed in laboratory simulations of effluent movement through the pumice ash sediments typical of the Kinleith area. There is clearly a need to better understand the processes involved in colour formation and removal. If the mechanisms of these processes could be understood, it may be possible to design treatment systems in which such processes are optimised and used as bases for colour removal. Further study on the interactions between effluent colour and geological materials (sediments, ignimbrites) is therefore warranted.

In studies of the seepage ponds, the processes responsible for the disappearance of EOs were not determined. Since this part of the system was the most active zone for effluent treatment, optimising its performance would be worthwhile. To do so, the roles of potentially important processes such as biodegradation and sedimentation in contaminant removal need to be determined.

The sediments of the LA site were found to contain high levels of EOs. The distribution, long-term fate, and potential environmental effects of these residuals need to be established to ensure future uses of the site are not compromised.

Ground water beneath and adjacent to the Extension Area seepage system were found to be contaminated with Na^+, Cl^-, colour, and EOs. Further studies of the fate of these contaminants in the ground water system are required. In particular, trend monitoring should be established to measure changes in contaminant levels over time. To achieve this, careful calibration of each monitoring well will be required to ensure sampling is carried out consistently, and variance minimised. To accurately quantify the EOs present in these waters, modern analytical techniques based on GC-MSD in selected ion mode (SIM) should be used. Such techniques will require a wider range of resin acids, in particular transformed species, diterpene hydrocarbons,

and methyl-substituted 2-cyclopentenones for use as analytical standards. Isolation and/or synthesis of these compounds should be a priority.

The present study investigated the performance of a segregated effluent stream containing very high levels of contaminants, in particular colour and EOs. Modern mills produce effluents of considerably lower colour and organic content, which may be more amenable to treatment than the No. 2 effluent stream. Despite the problems identified in this study, an aerobically operated LA system may still play a useful role in effluent treatment of lower coloured effluents, particularly if EO (e.g. resin acid) removal is required. Further investigation of the performance of LA for treating such wastes would be worthwhile.

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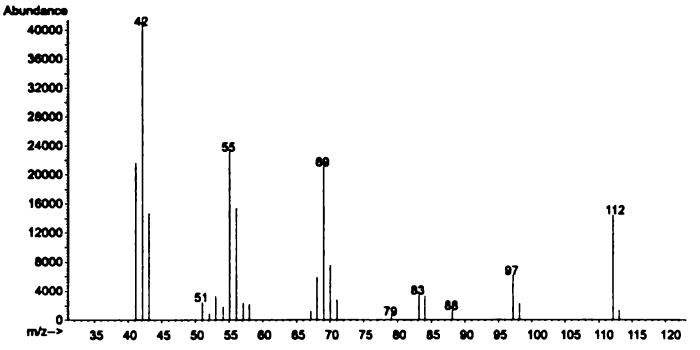
Appendix 1

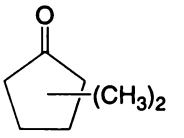
Structures and Mass Spectra

Format:

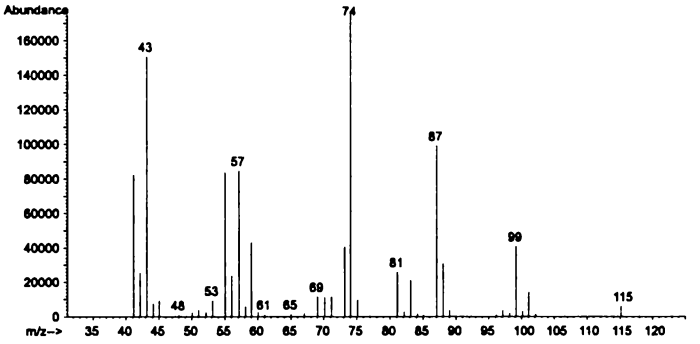
No. Compound Name [identification method (e.g. mass spectral library, % match) or reference]	
Mass Spectrum	**Structure**

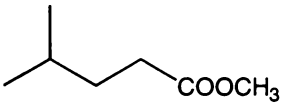
1. dimethylcyclopentanone [NBS library #63965, 94%; all isomers have similar mass spectra]



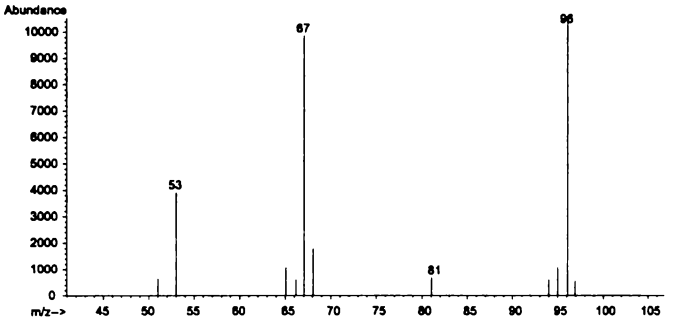


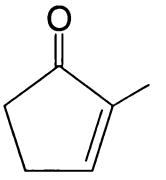
2. 4-methylpentanoic acid (methyl ester) [NBS library #65207, 90%]



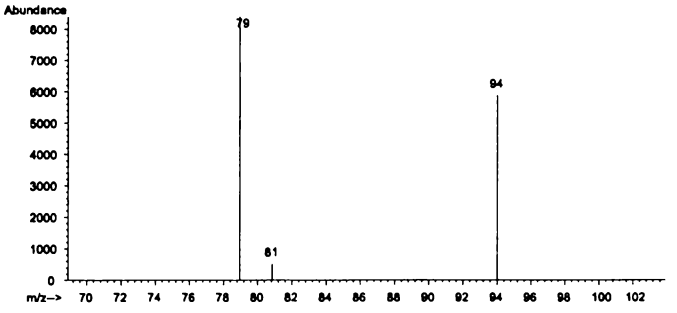


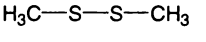
3. 2-methyl-2-cyclopenten-1-one [NBS library #1093, 80%]



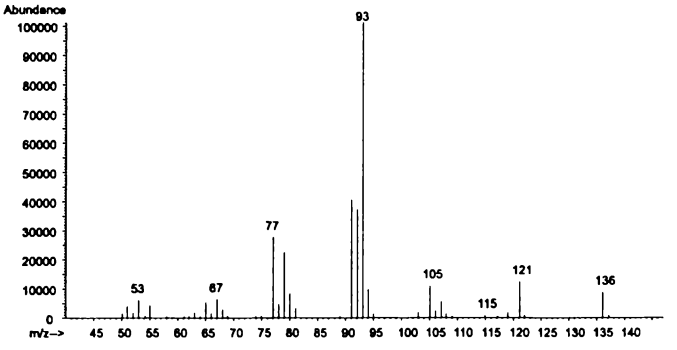


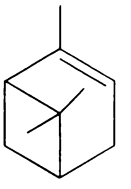
4. dimethyldisulphide [NBS library #988, 70%]



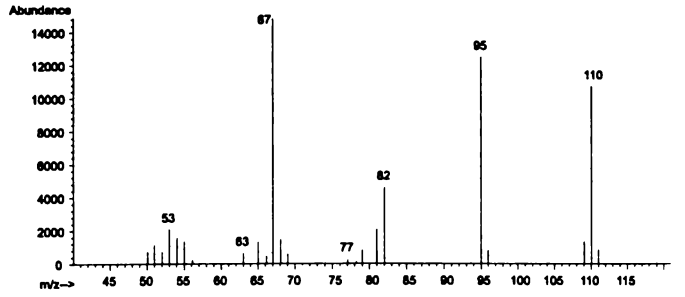


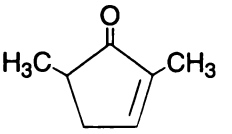
5. α-pinene [standard match]



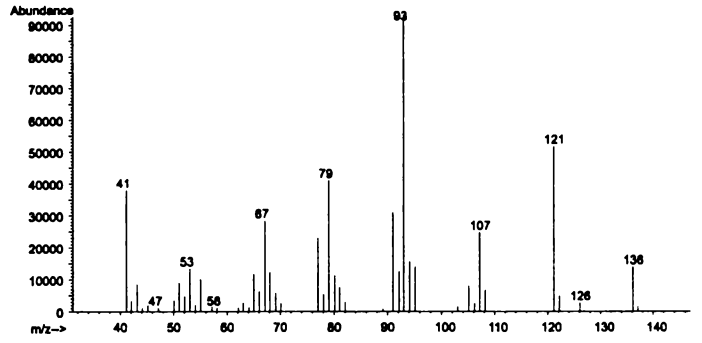


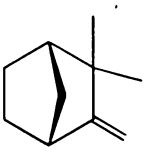
6. 2,5-dimethyl-2-cyclopenten-1-one [NBS library #2285; Voss 1984]



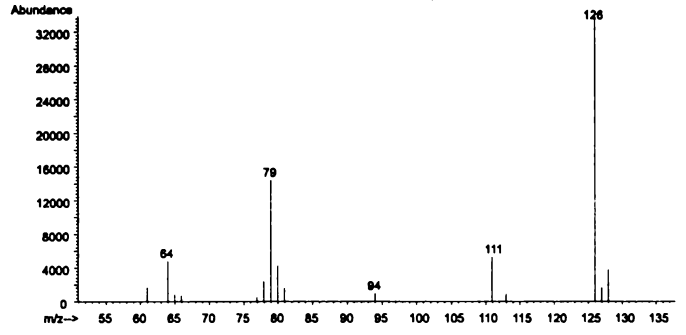


7. camphene [NBS library #65764, 98%]



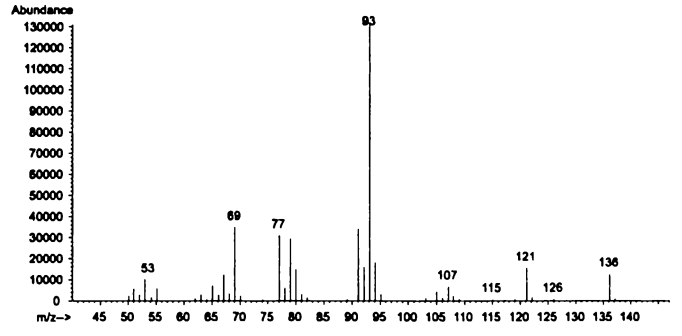


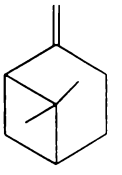
8. dimethyltrisulphide [NBS library #64839, 91%]



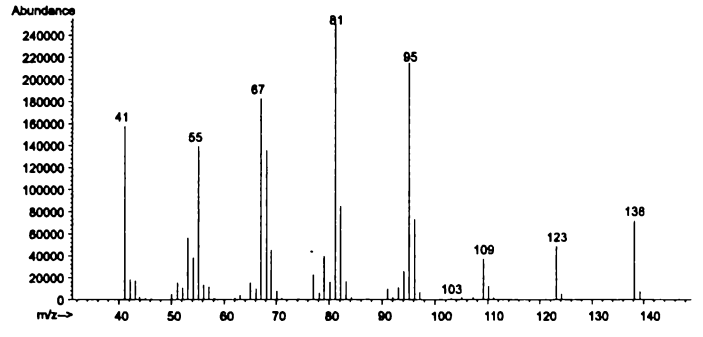
H_3C-S-S-S-CH_3

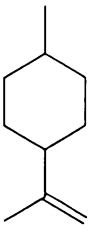
9. β-pinene [standard match]



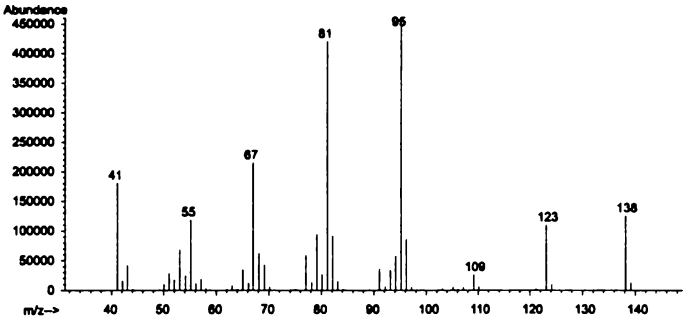


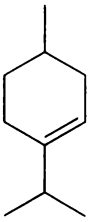
10. 1-methyl-4-(1-methylethenyl)cyclohexane [NBS library #7039, 96%]



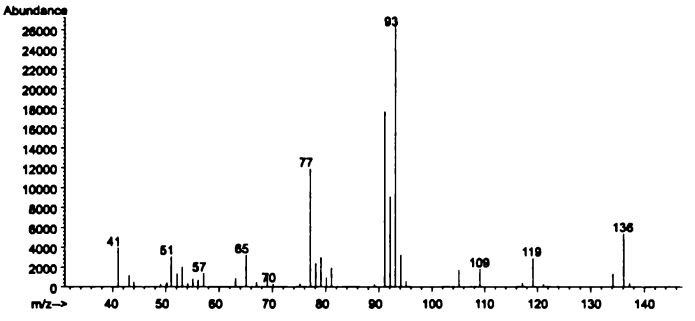


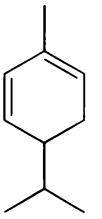
11. 4-methyl-4-(1-methylethenyl)cyclohexane [NBS library #65928, 98%]



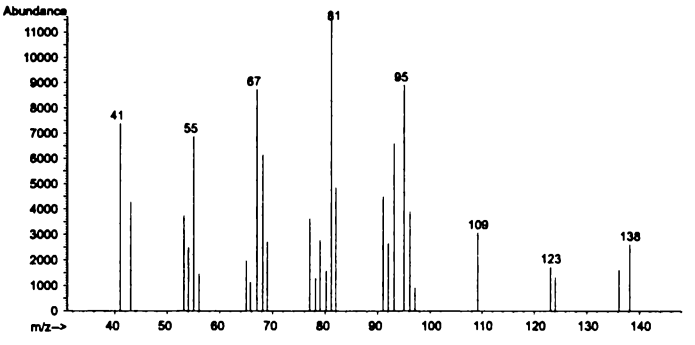


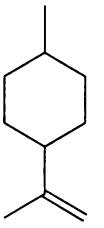
12. MT136 [possibly α-phellandrene; NBS library #65816, 90%]



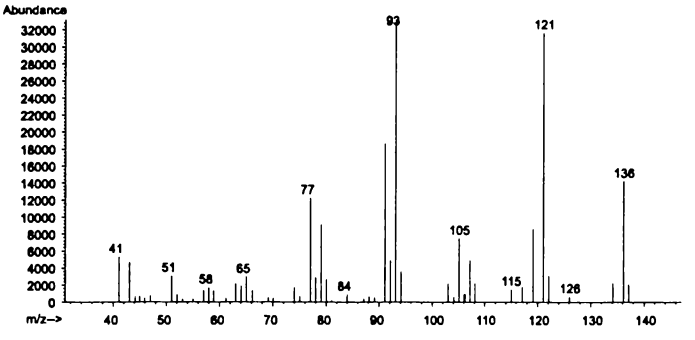


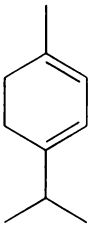
13. 1-methyl-4-(1-methylethenyl)cyclohexane [similar to compound 10; NBS library #7039, 90%]



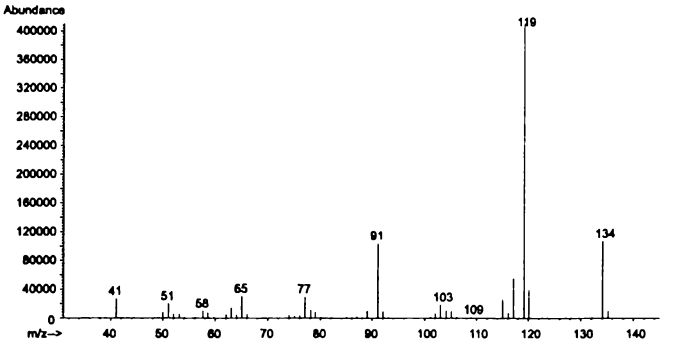


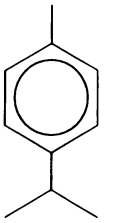
14. 1-methyl-4-(1-methylethyl)-1,3-cyclohexadiene [NBS library #65757, 97%]



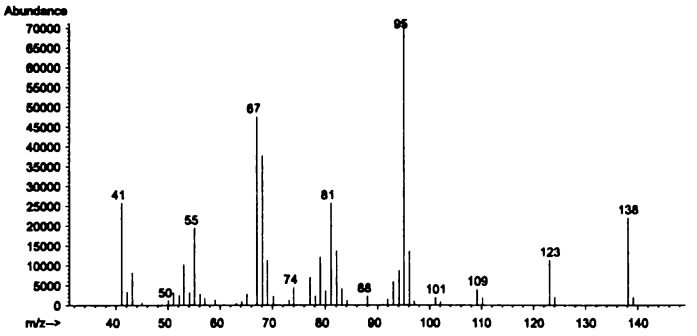


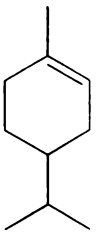
15. *p*-cymene [standard match]



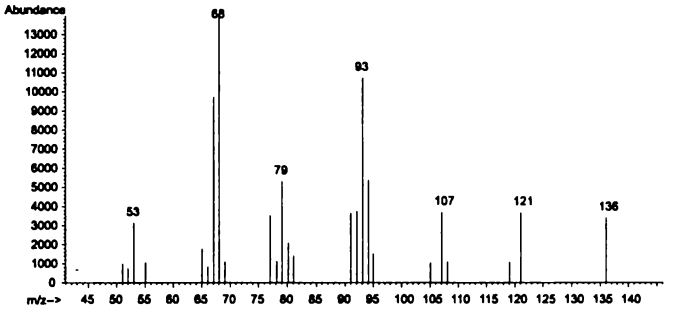


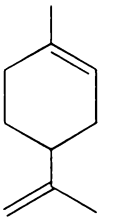
16. 1-methyl-4-(1-methylethyl)cyclohexene [NBS library #65936, 96%]



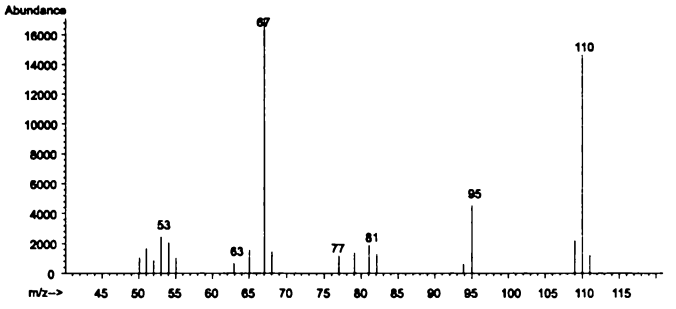


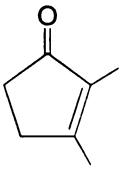
17. limonene [standard match]



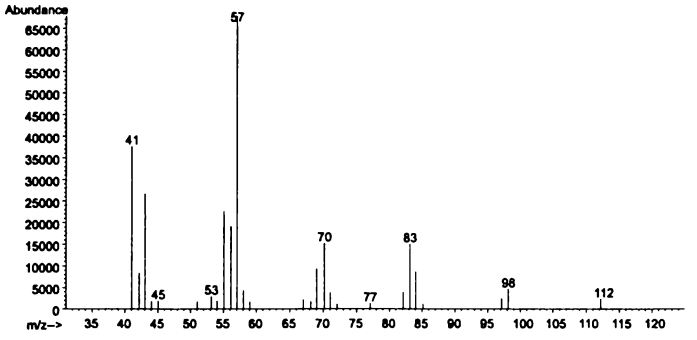


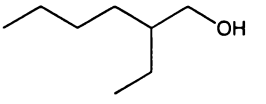
18. 2,3-dimethyl-2-cyclopenten-1-one [NBS library #2285, 94%; Voss 1984]



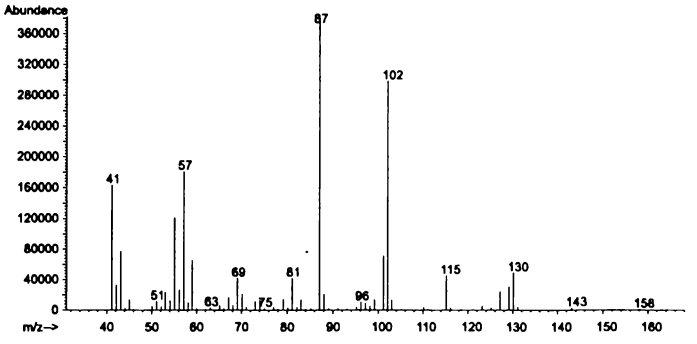


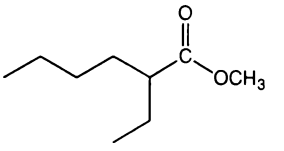
19. 2-ethylhexanol [NBS library #65293, 90%]



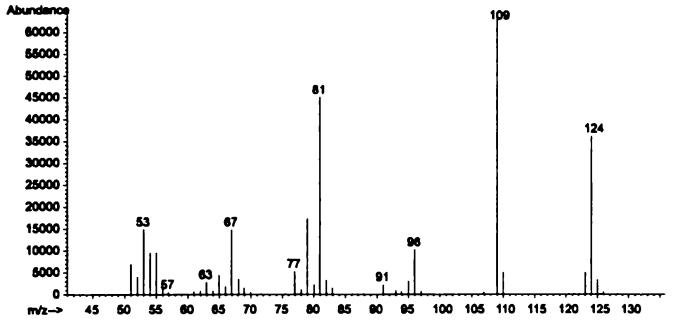


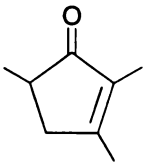
20. 2-ethylhexanoic acid (methyl ester) [NBS library #67421, 75%]



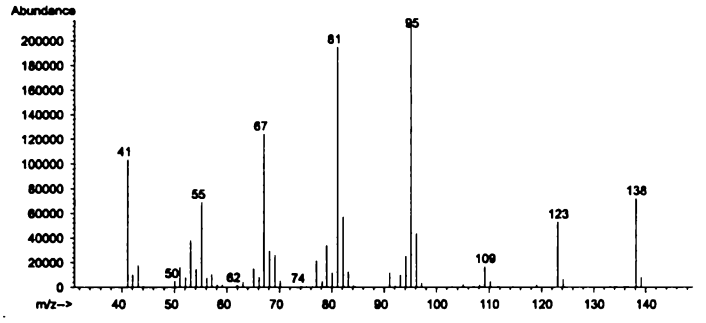


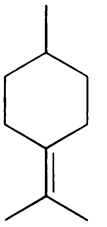
21. 2,3,5-trimethyl-2-cyclopenten-1-one [Voss 1984]



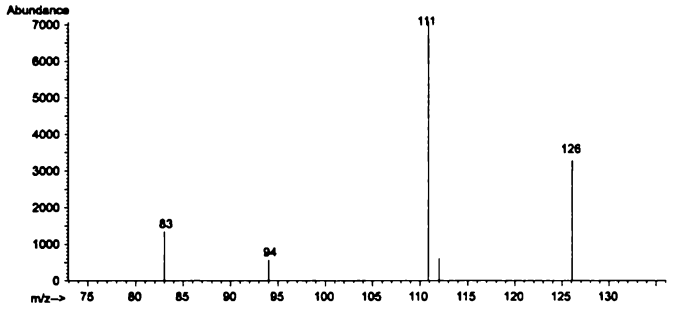


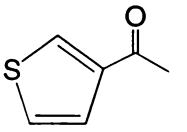
22. 1-methyl-4-(1-methylethylidene)-cyclohexane [NBS library #64946, 97%]



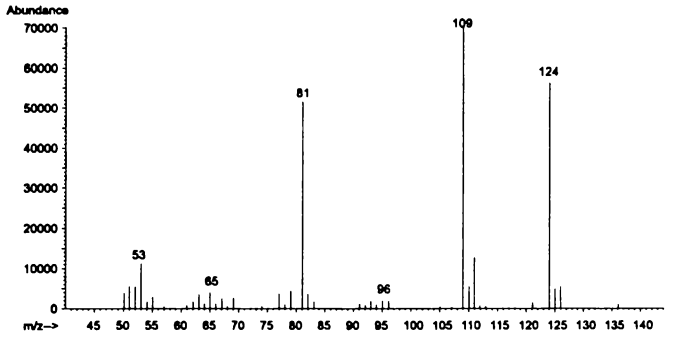


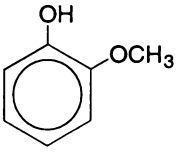
23. 3-acetylthiophene [NBS library #64856, 74%]



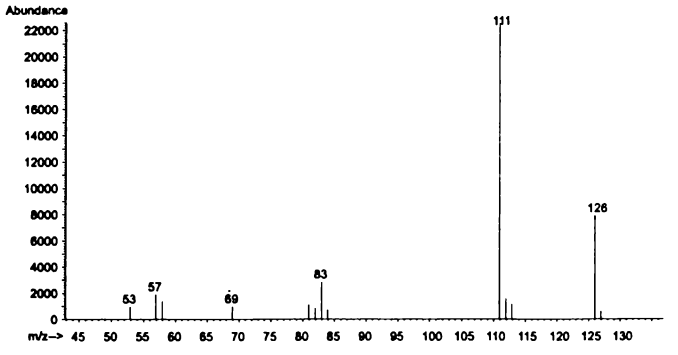


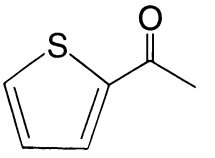
24. guaiacol [standard match]



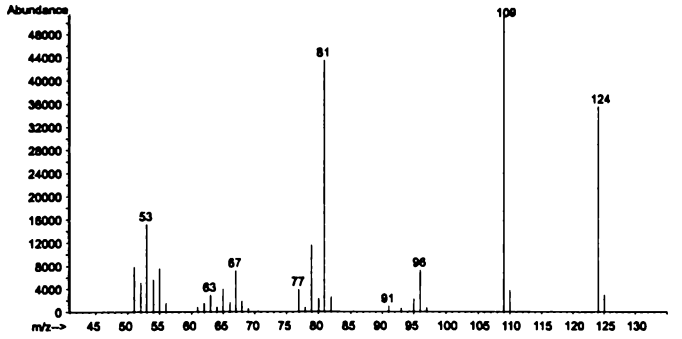


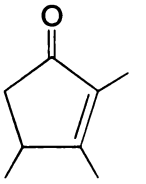
25. 2-acetylthiophene [NBS library #64853, 90%]



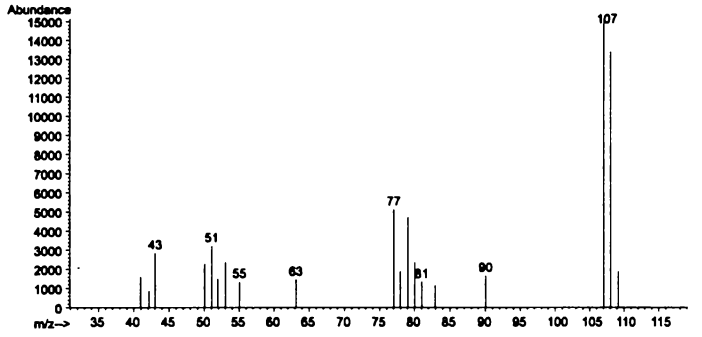


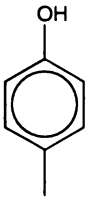
26. 2,3,4-trimethyl-2-cyclopenten-1-one [NBS library #4173, 91%; Voss 1984]



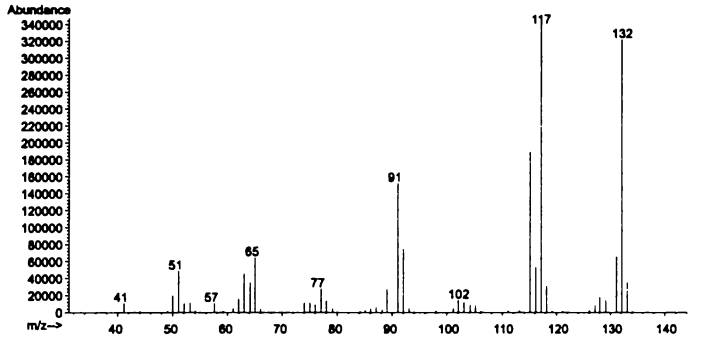


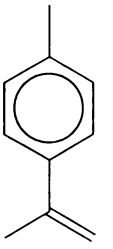
27. 4(?)-methylphenol [NBS library #63786, 93%]



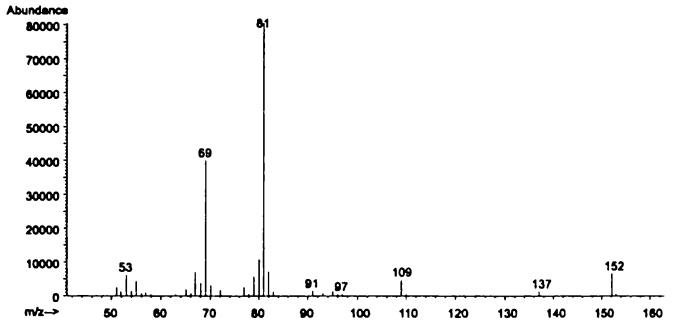


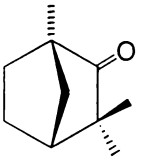
28. 1-methyl-4-(1-methylethenyl)benzene (α, *p*-dimethylstyrene) [NBS library #5874, 97%]



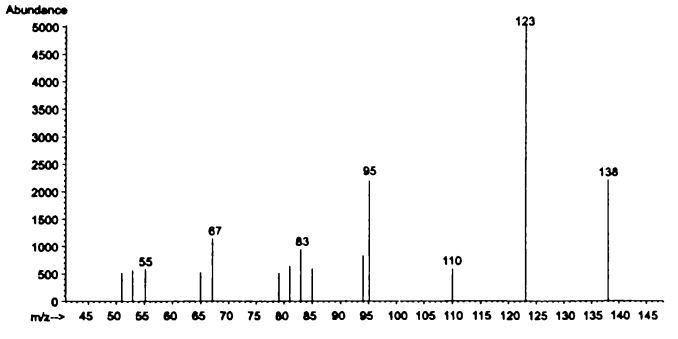


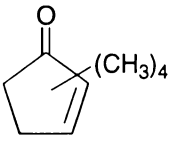
29. fenchone [NBS library #66953, 95%; Swigar and Silverstein 1981]



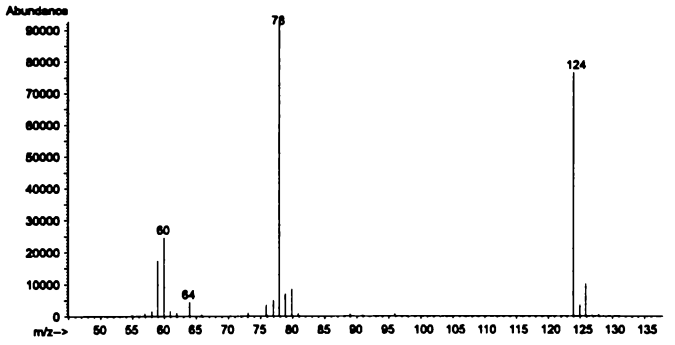


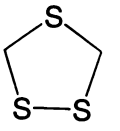
30. tetramethyl-2-cyclopentenone [Voss 1984]



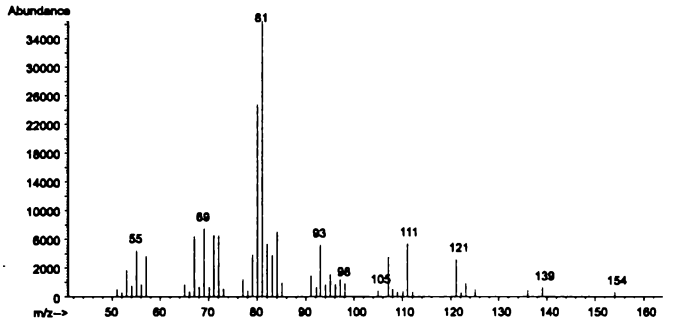


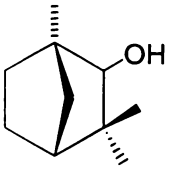
31. 1,2,4-trithiolane [NBS library #64744, 90%]



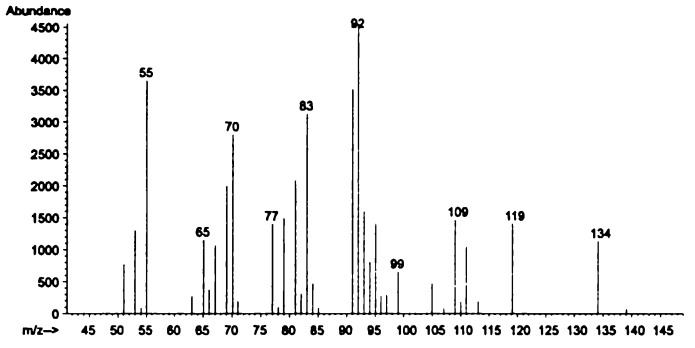


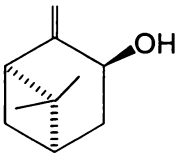
32. fenchol [standard match]



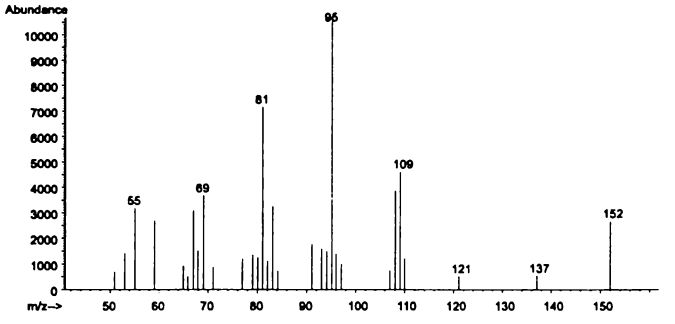


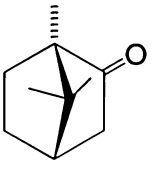
33. unidentified monoterpene (pinocarveol?) [NBS library #10311, 65%]



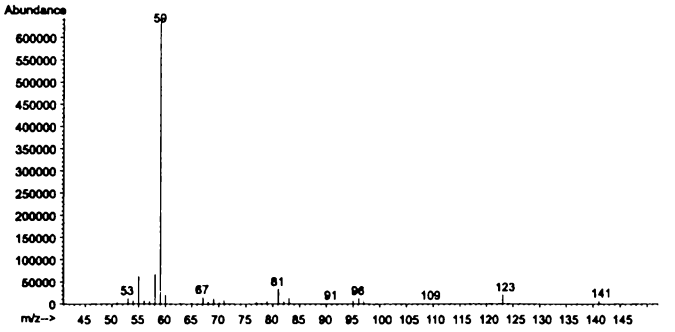


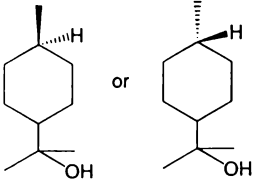
34. camphor [standard match]



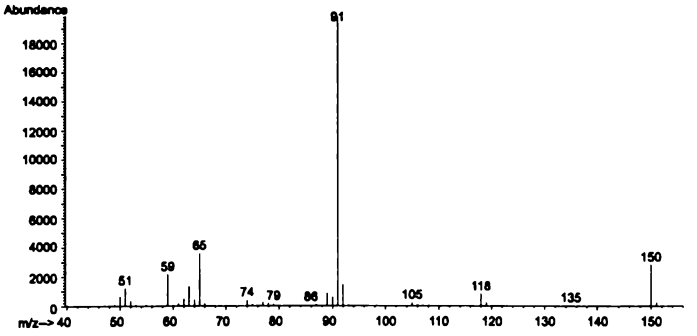


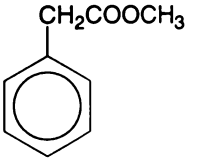
35. dihydro-α-terpineol (α,α-4-trimethylcyclohexanemethanol) [NBS library #11564, 80%]



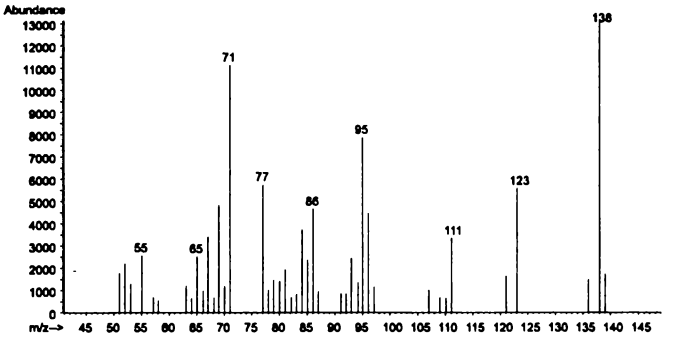


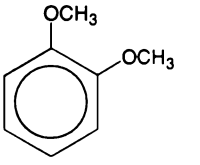
36. phenylacetic acid (methyl ester) [NBS library #9693, 89%]



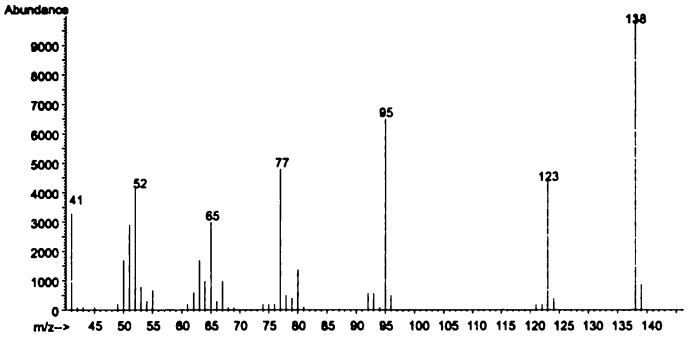


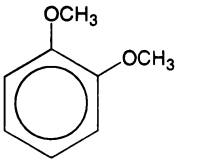
37. dimethoxybenzene (*m/z* 77,95,123,138) + unidentified MT (71, 111, 121, 136, 154?)



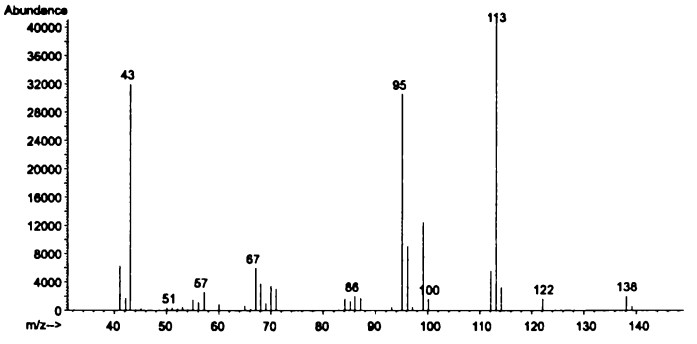


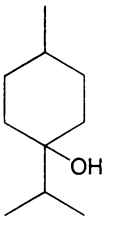
38. dimethoxybenzene (veratrole) [NBS library #6904, 90%]



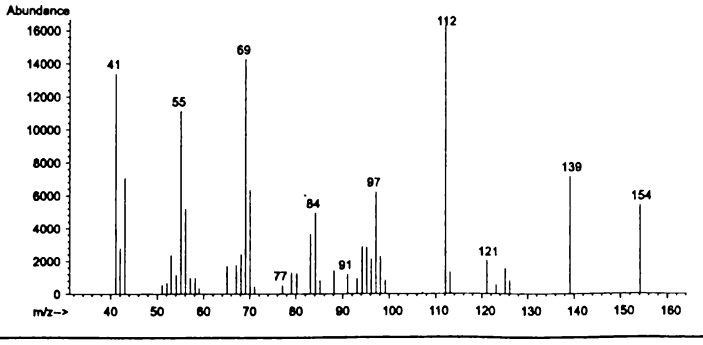


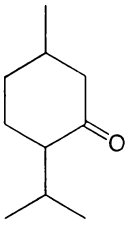
39. dihydroterpin-4-ol [NBS library #67293, 77%. mw=156]



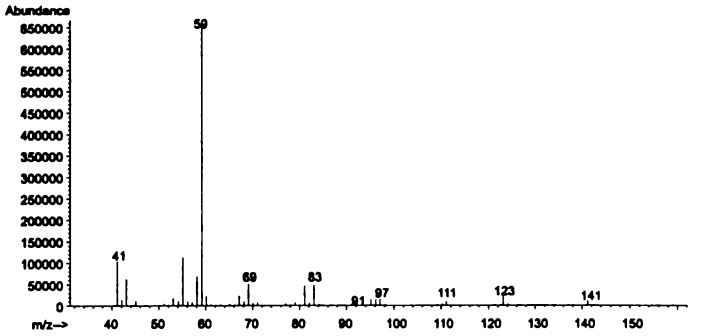


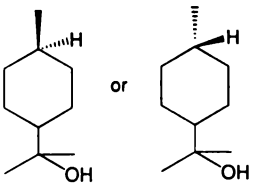
40. 5-methyl-2-(1-methylethyl)cyclohexanone..[NBS library #67110, 95%]



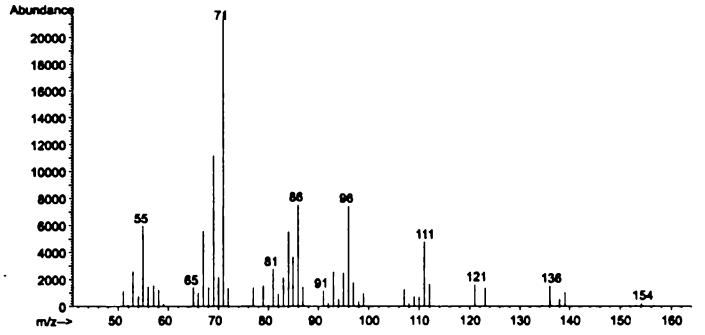


41. dihydro-α-terpineol isomer 2 (α,α-4-trimethylcyclohexanemethanol)

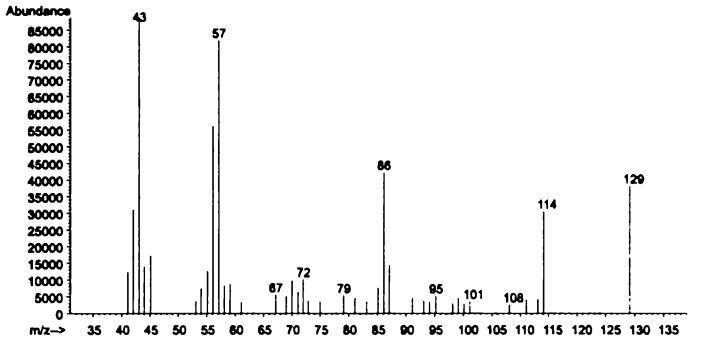


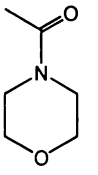


42. unidentified MT154

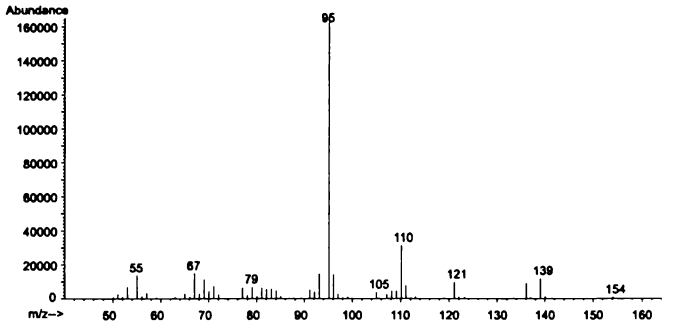


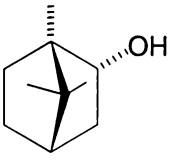
43. acetylmorpholine? [NBS library #5223, 80%]



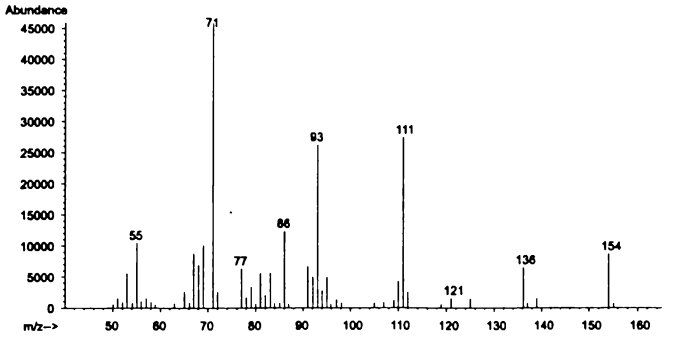


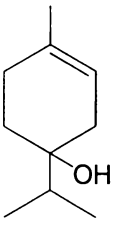
44. borneol [standard match; NBS library #67100, 90%)



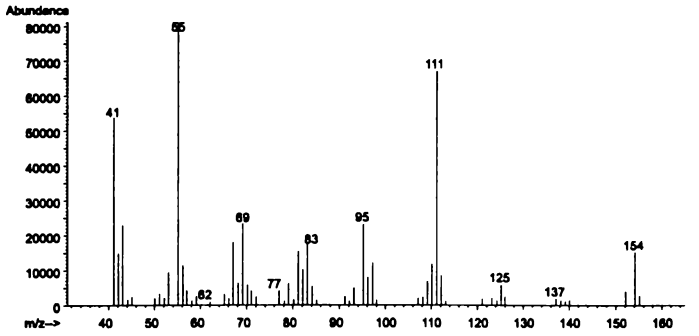


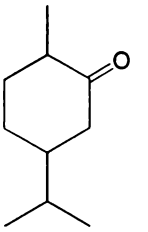
45. terpin-4-ol [standard match; NBS #67093, 97%]



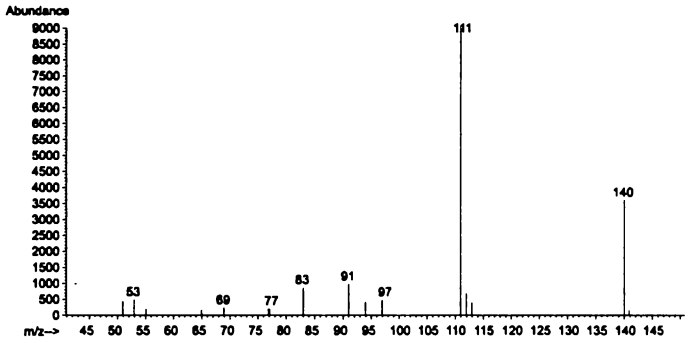


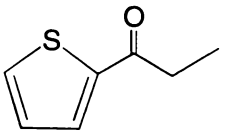
46. 2-methyl-5-(1-methylethyl)cyclohexanone [carvomenthone?; NBS library #11025, 81%]



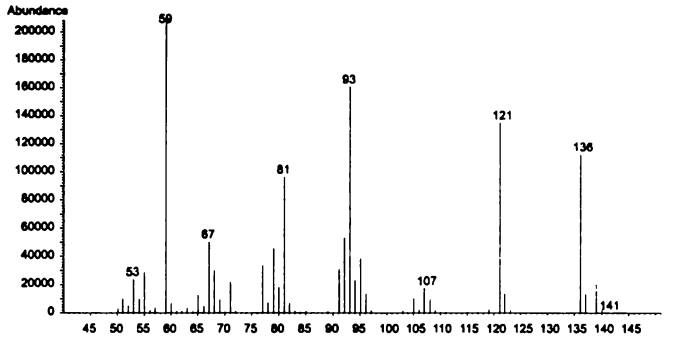


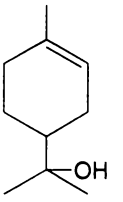
47. propionylthiophene [NBS library, 75%; Voss 1984]



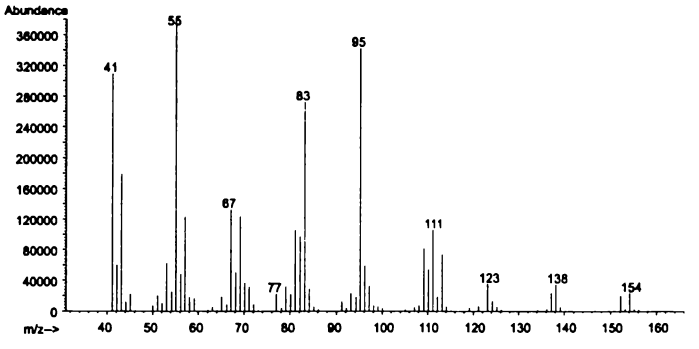


48. α-terpineol [standard match]

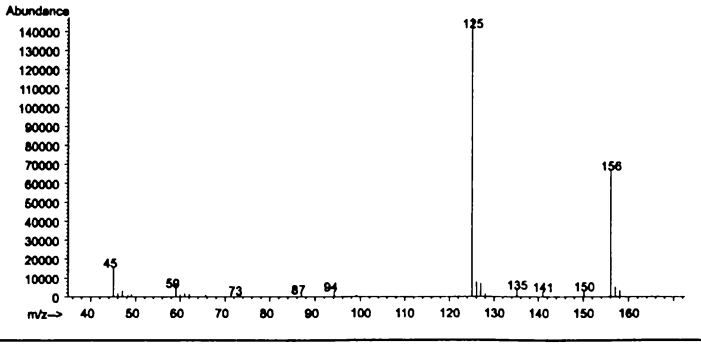


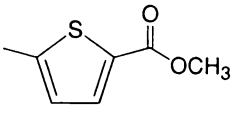


49. MT152 plus MT154 (unresolved)

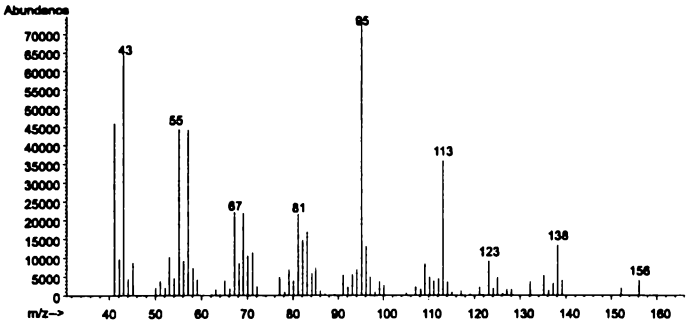


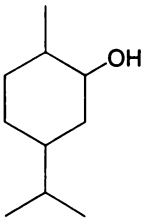
50. unidentified compound [possibly 5-methyl-thiophene-2-carboxylate, NBS library #11311, 86%]



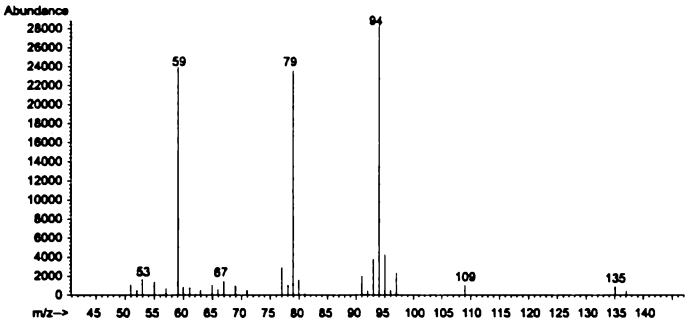


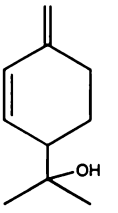
51. 2-methyl-5-(1-methylethyl)cyclohexanol [NBS library #11519, 96%] **plus MT152**



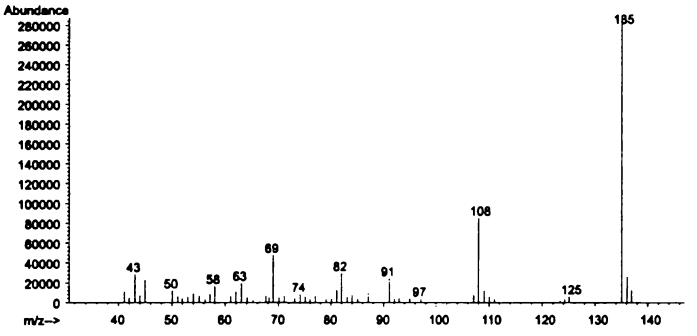


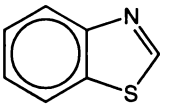
52. unidentified monoterpene [possibly *p*-mentha-1(7),2-dien-8-ol, NBS library #10312, 78%]



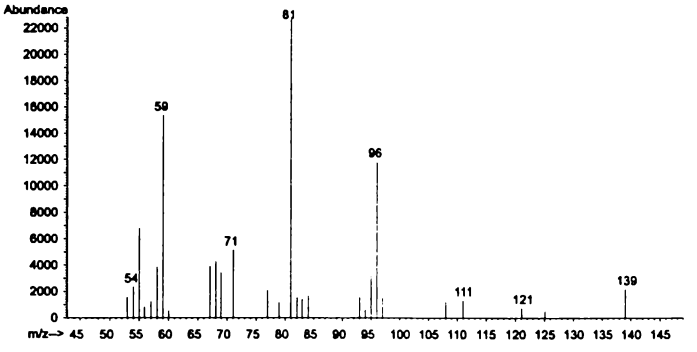


53. benzothiazole [NBS library #6263, 94%]

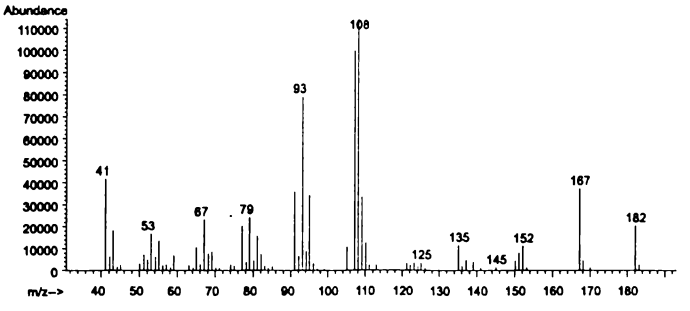




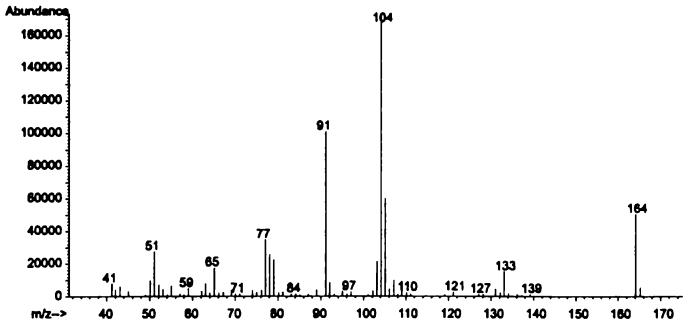
54. unidentified monoterpene derivative?

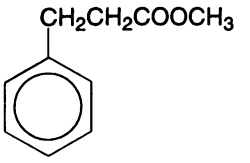


55. unidentified mw=182

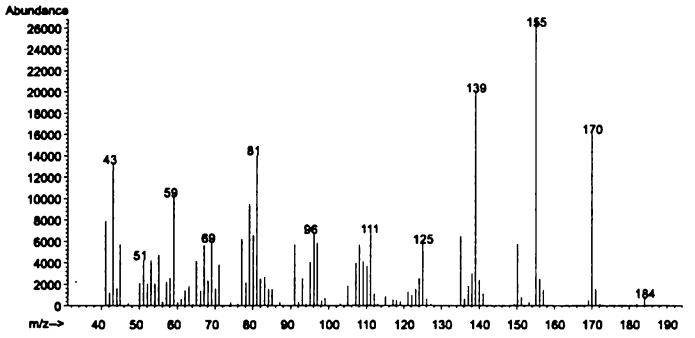


56. phenylpropanoic acid (methyl ester) [NBS library #67829, 97%]

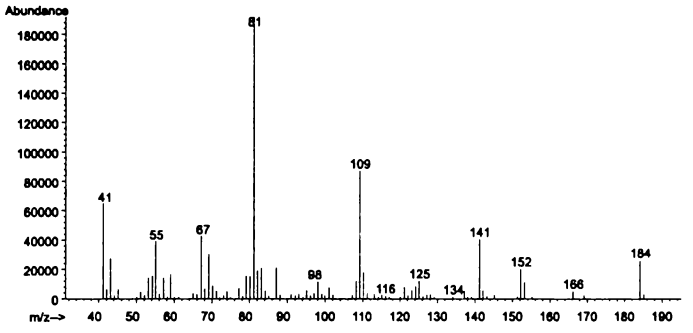




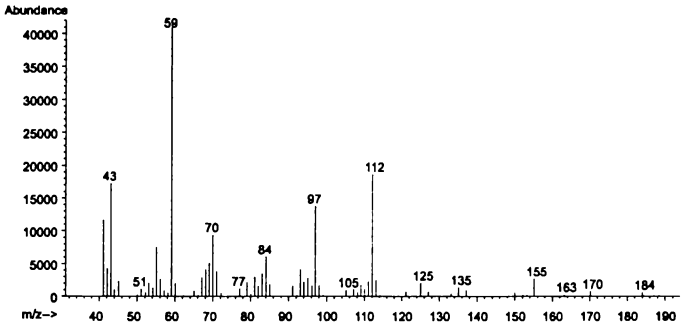
57. unidentified mw=184 plus mw=170



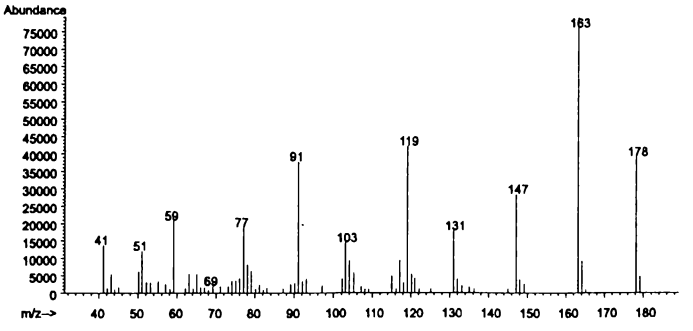
58. unidentified mw=184

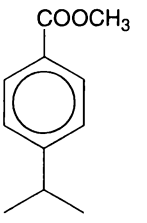


59. unidentified mw=184?

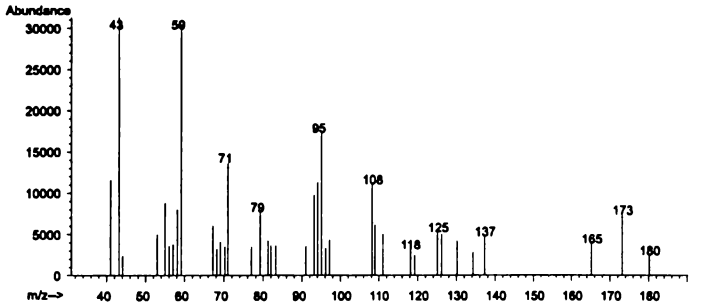


60. 4-(1-methylethyl)benzoic acid [NBS library #17248, 95%]

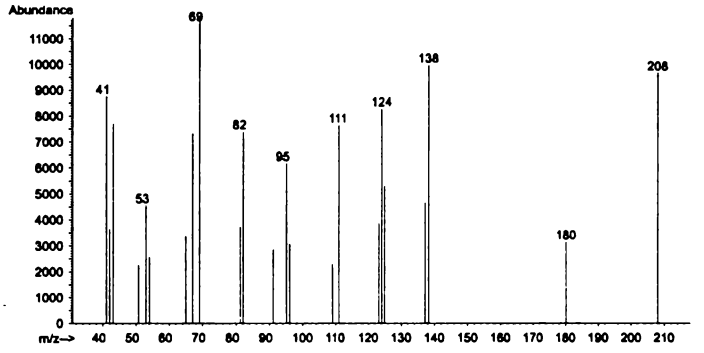




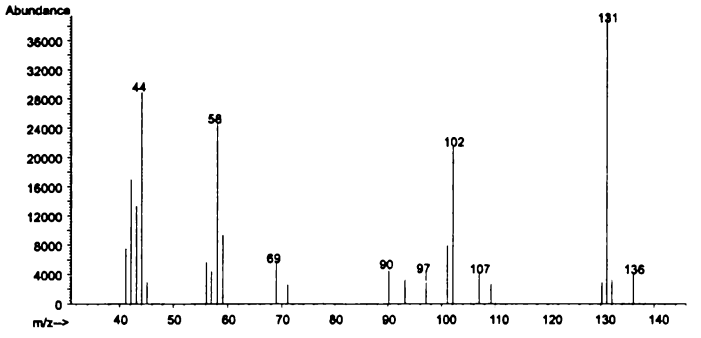
61. unidentified compound



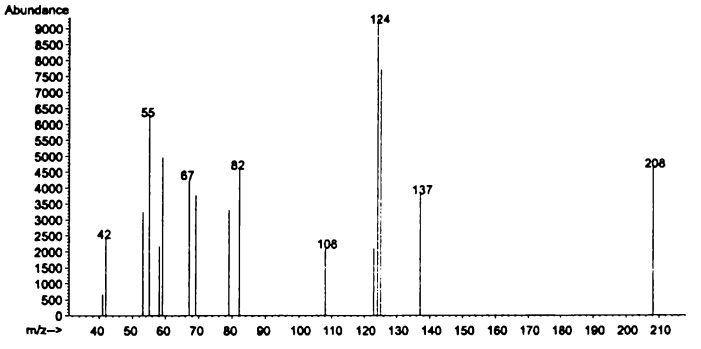
62. unidentified compound



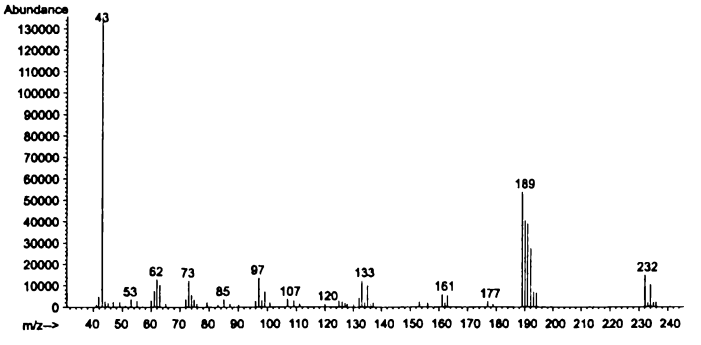
63. unidentified compound

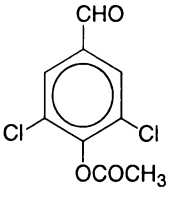


64. unidentified compound

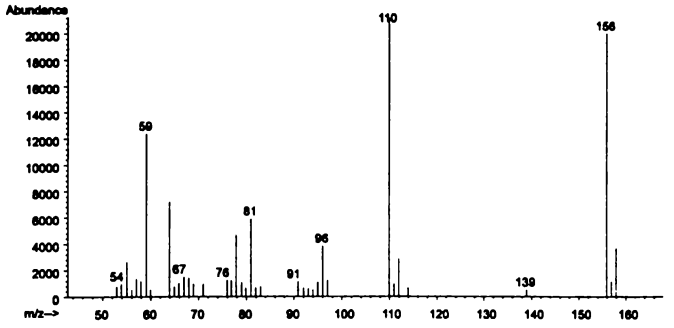


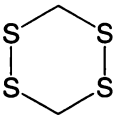
65. 3,5-dichloro-4-hydroxybenzaldehyde (acetate) [Wallis et al. 1993]



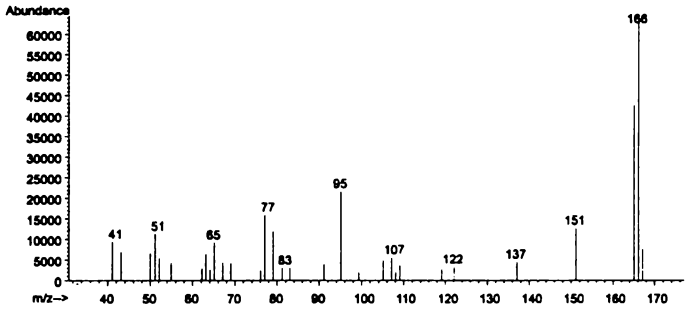


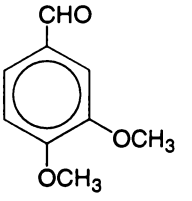
66. 1,2,4,5-tetrathiolane [NBS library #11244, 75%]



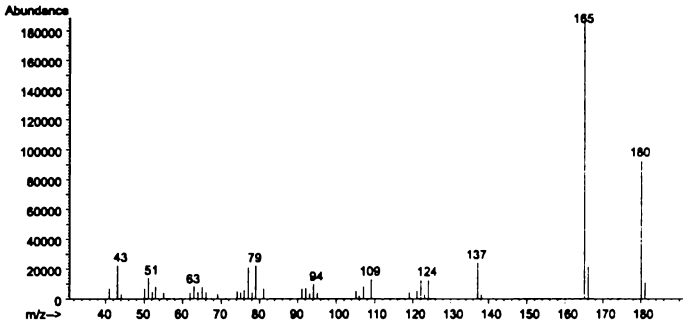


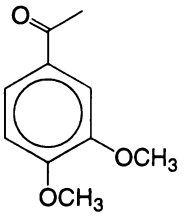
67. 3,4-dimethoxybenzaldehyde [NBS library #13935, 92%]



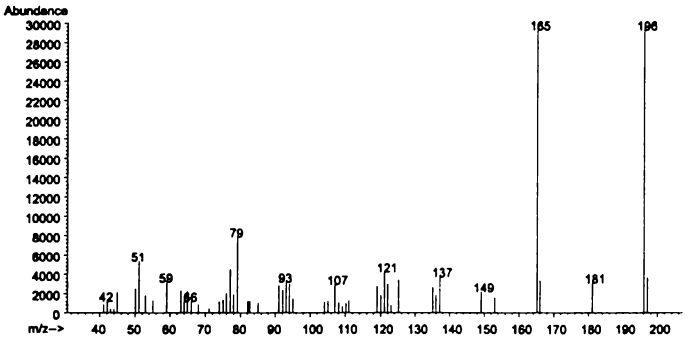


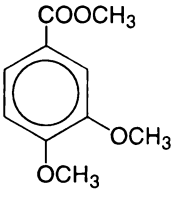
68. 3,4-dimethoxyacetophenone [NBS library #68734, 95%]



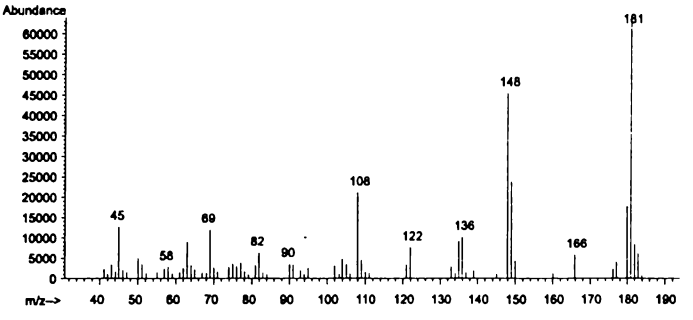


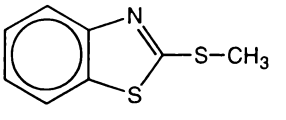
69. 3,4-dimethoxybenzoic acid (methyl ester) [NBS library #64967, 99%]



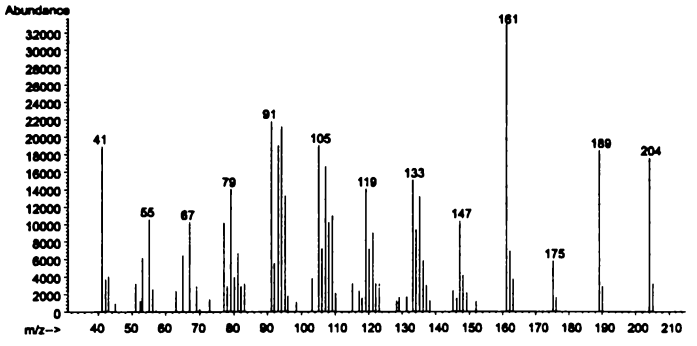


70. 2-(methylthio)benzothiazole [NBS library #68790, 97%]

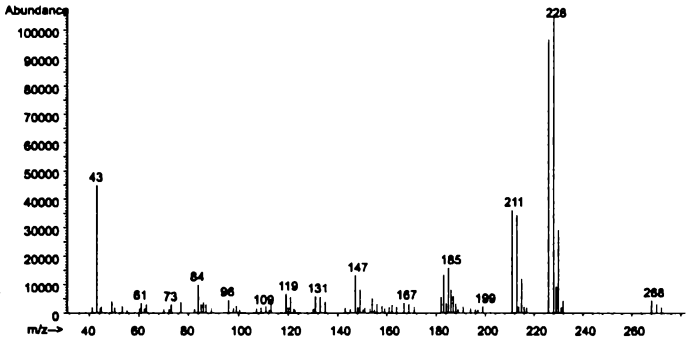


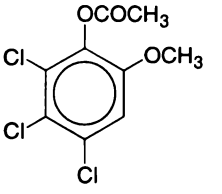


71. unidentified mw=204 compounds [typical mass spectrum; possibly sesquiterpenes]

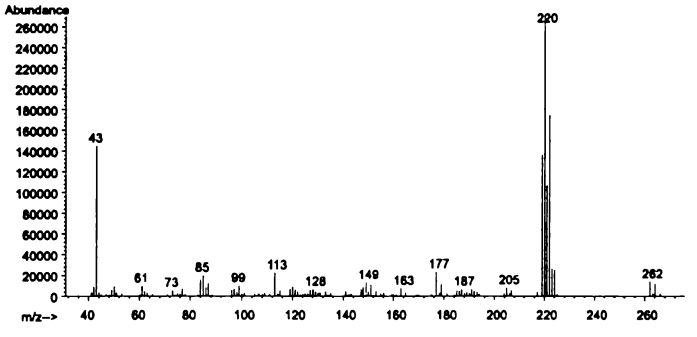


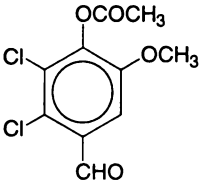
72. 4,5,6-trichloroguaiacol (acetate) [standard match; Wallis et al. 1993]



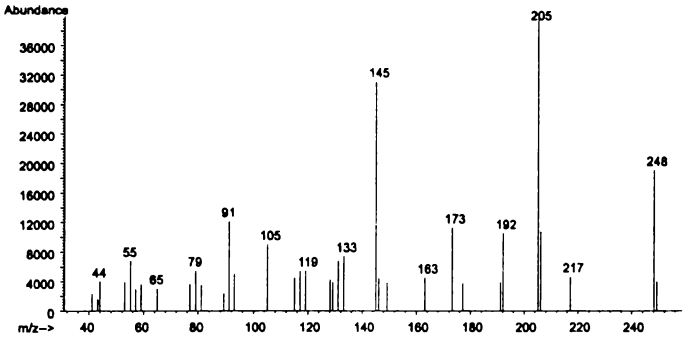


73. 5,6-dichlorovanillin (acetate) [Wallis et al. 1993]

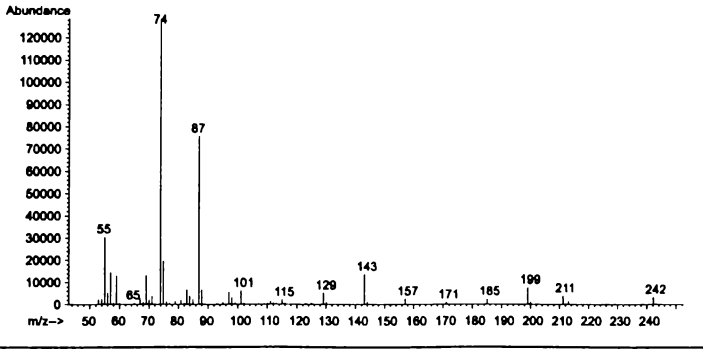




74. unidentified compound mw=248 [DT248A?]

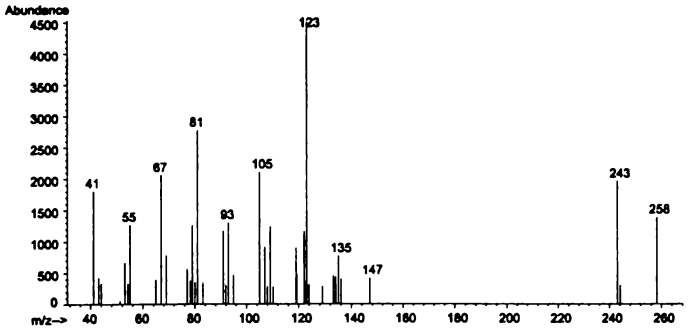


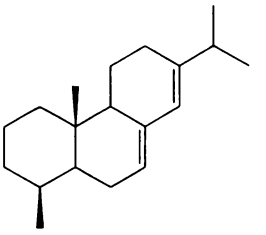
75. tetradecanoic acid (methyl ester) [FA14:0; standard match]



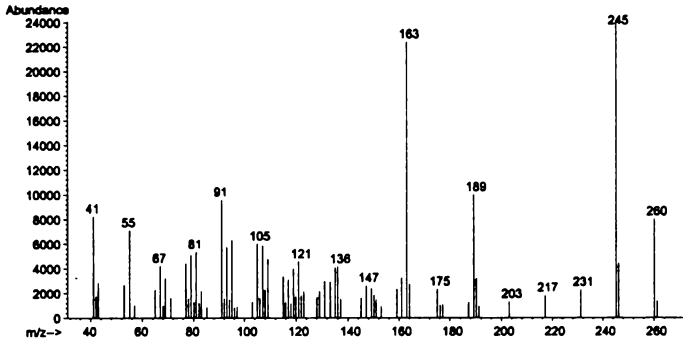
$H_3C{-}(CH_2)_{12}COOCH_3$

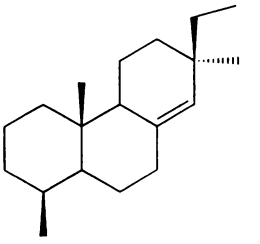
76. DT258 [diterpene hydrocarbon, 2 double bonds, possibly abietadiene?]



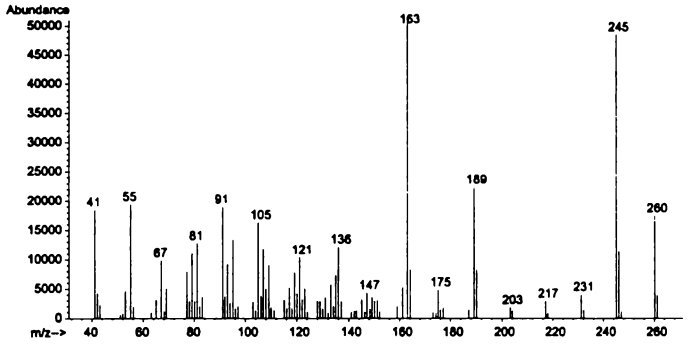


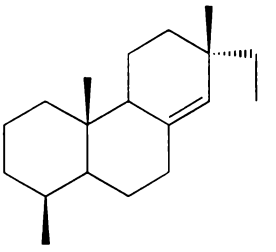
77. DT260P [diterpene hydrocarbon, 1 double bond, possibly pimarene?]



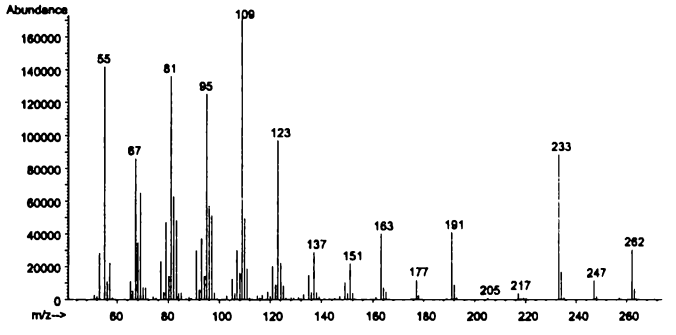


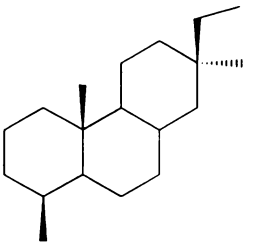
78. DT260I/S [diterpene hydrocarbon, 1 double bond, possibly sandaraco- or isopimarene?]



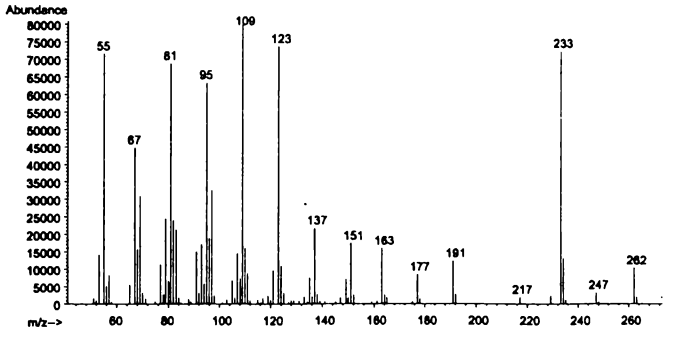


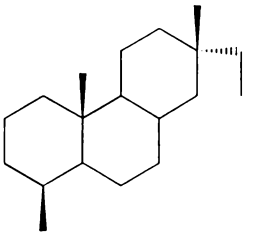
79. DT262P [Barrick and Hedges 1981]



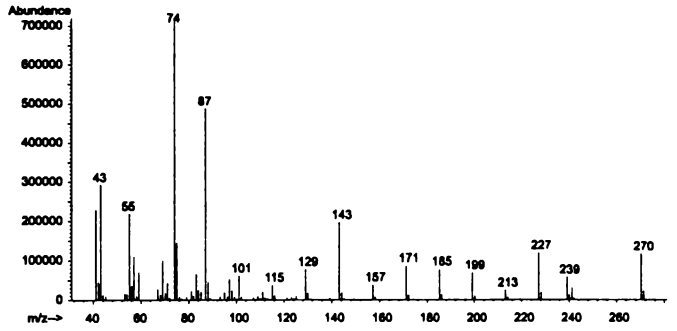


80. DT262I [Barrick and Hedges 1981]



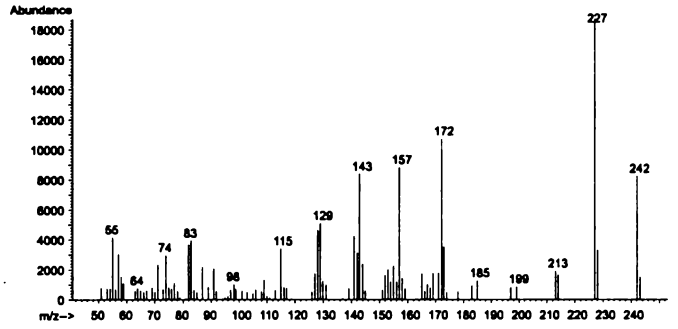


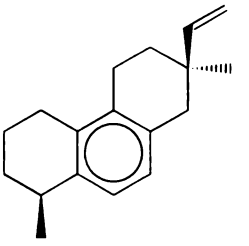
81. hexadecanoic acid (methyl ester) [FA16:0; palmitic acid; standard match]



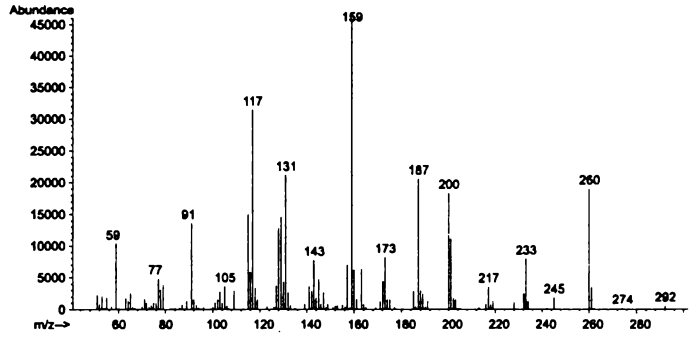
$H_3C{-}(CH_2)_{14}COOCH_3$

82. DT242P? [Singh-Thandi 1993]

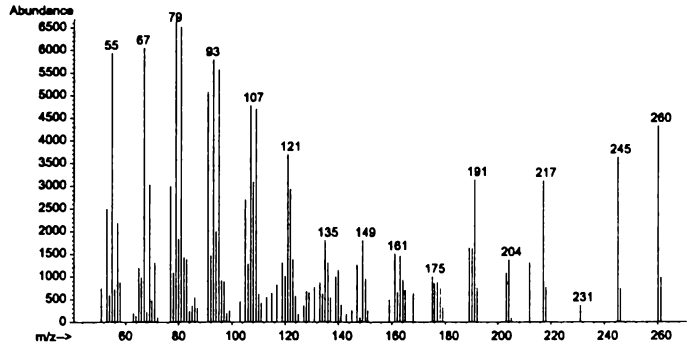


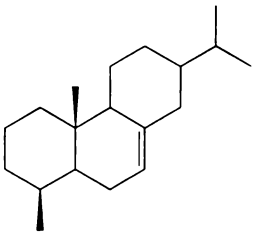


83. unidentified DT260 plus mw=292?

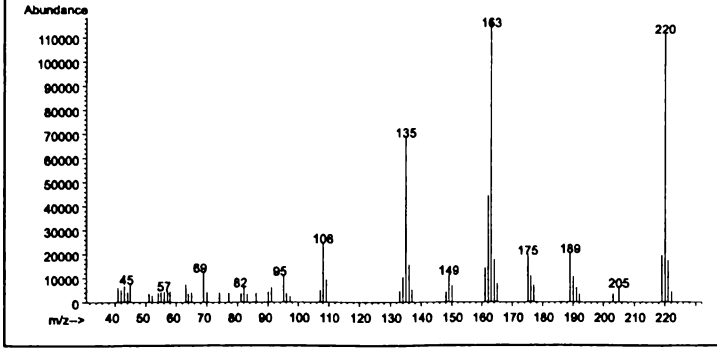


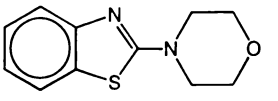
84. DT260A [diterpene hydrocarbon, 1 double bond, possibly abietene?]



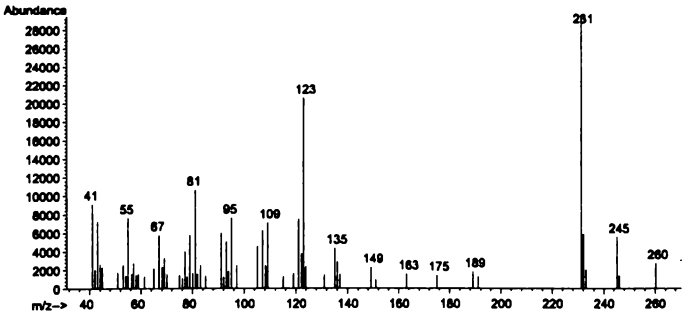


85. 2-(4-morpholinyl)-benzothiazole [Spies et al. 1987]

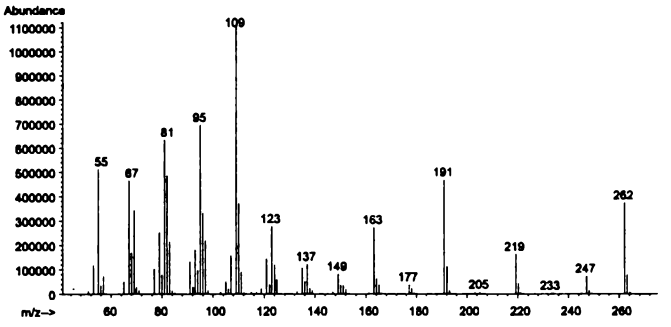


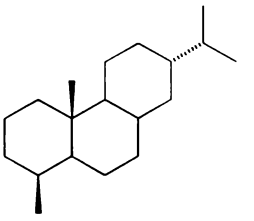


86. DT260 [diterpene hydrocarbon, 1 double bond, possibly a pimarene?]

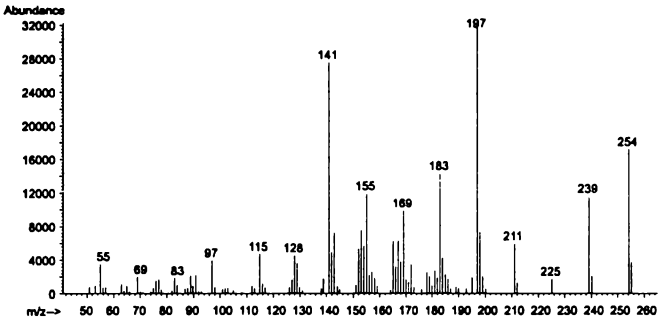


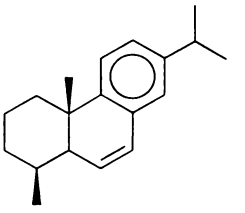
87. fichtelite [18-norabietane; Barrick and Hedges 1981]



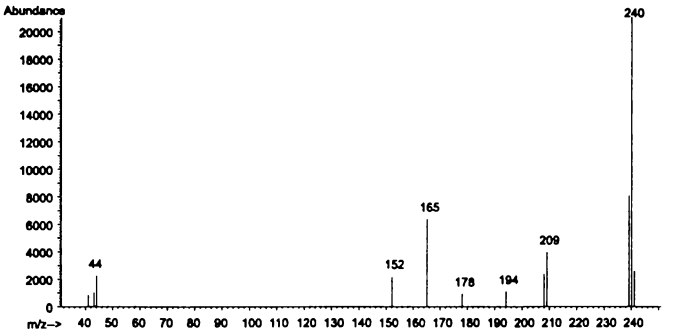


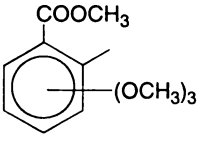
88. DT254 (possibly structure given in Fig.4 of La Fleur 1983?)



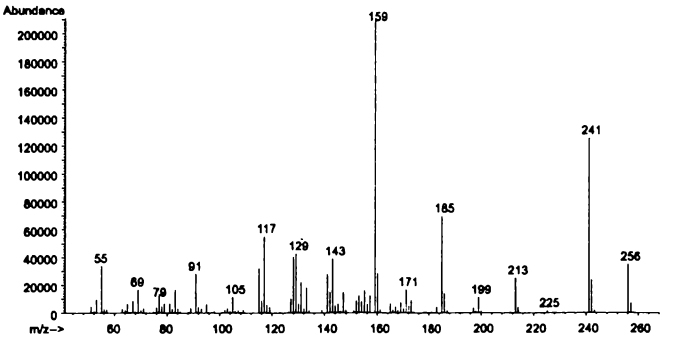


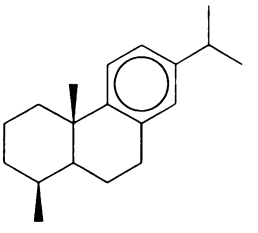
89. trimethoxy-2-methylbenzoic acid (methyl ester)..[NBS library #31890, 47%]



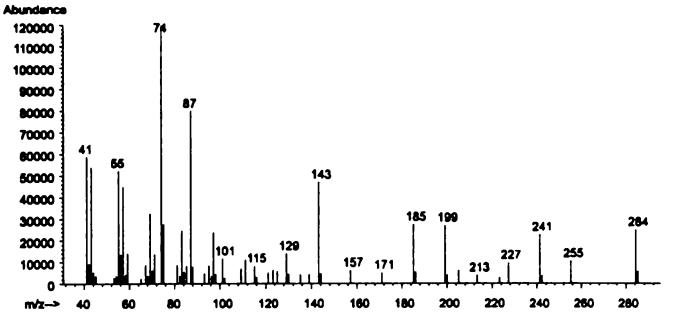


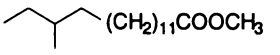
90. dehydroabietin [18-norabieta-8,11,13-triene; NMR; Simoneit 1977]



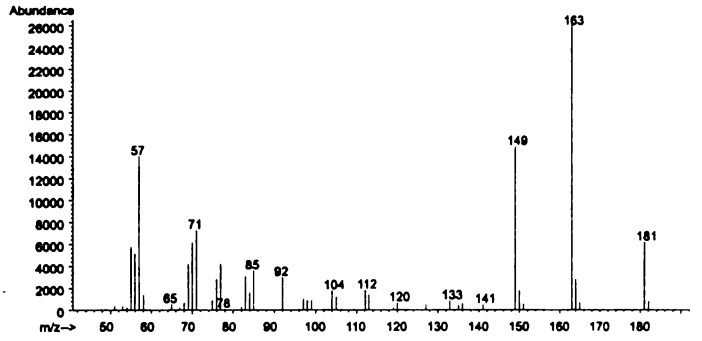


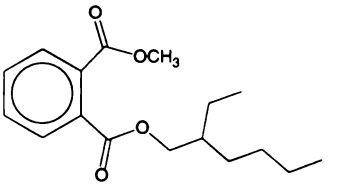
91. 14-methylhexadecanoic acid (methyl ester) [*anteiso*-FA17:0; NBS library #72371, 97%]



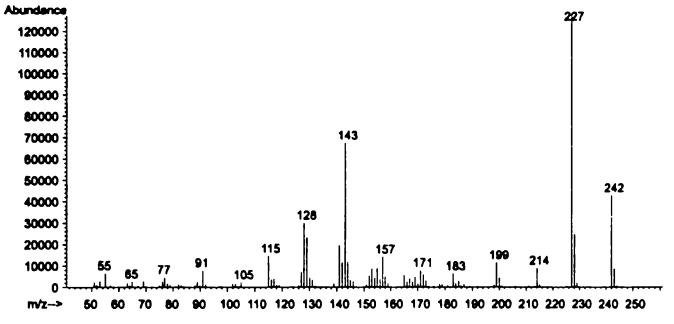


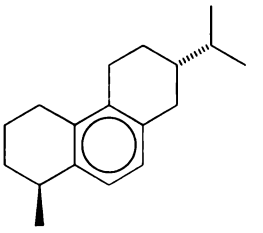
92. methyl-(2-ethylhexyl)phthalate [NBS library #41491, 56%]



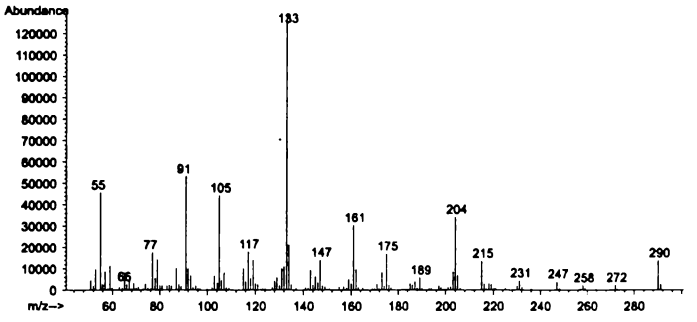


93. Caxtonellite (DT242A) [Singh-Thandi 1993]

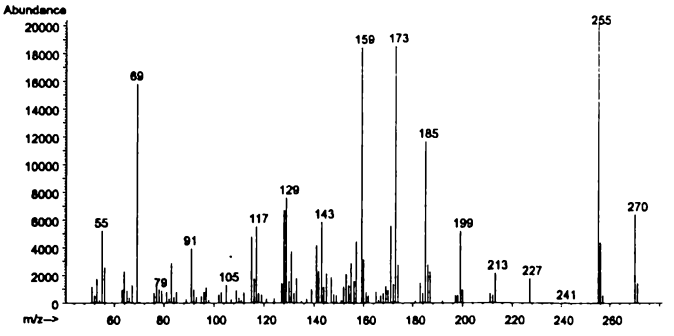


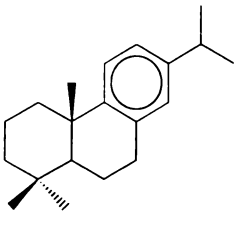


94. unidentified compound mw=290

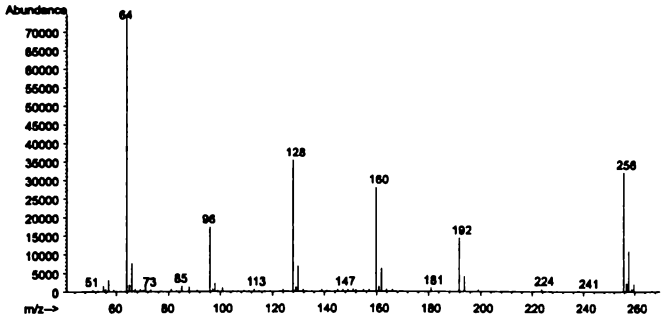


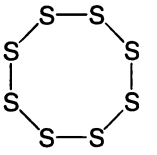
95. dehydroabietane (DT270A) [Simoneit 1977; Kitadani et al. 1970; Tan & Heit 1981]



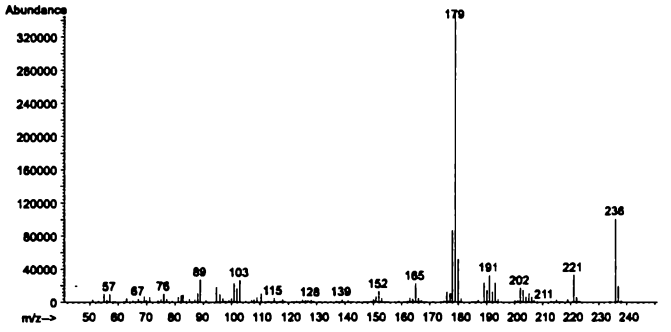


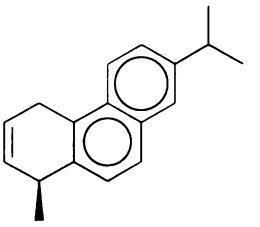
96. S_8 [standard match]



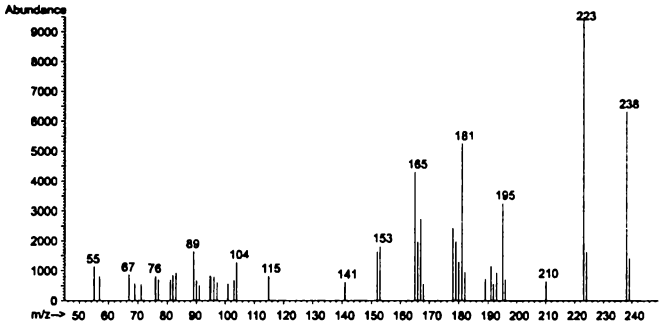


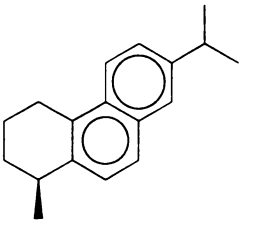
97. DT236 [possible structure depicted]



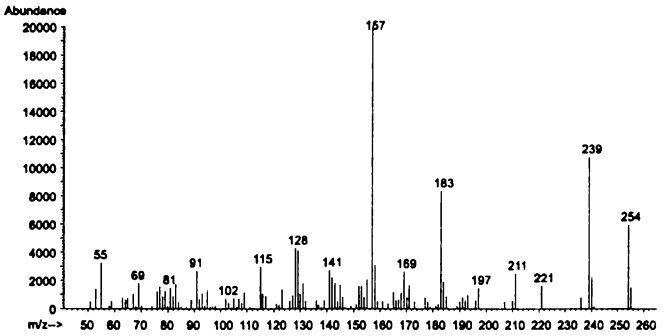


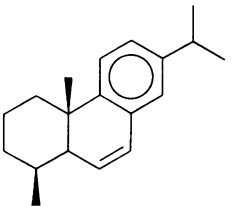
98. 1,2,3,4-tetrahydroretene [partial NMR; Wakeham et al. 1980; Hynning et al. 1993]



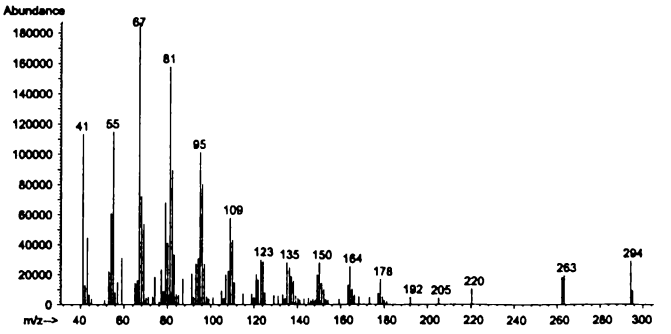


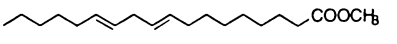
99. DT254 [structurally related to compound 88, double bond in ring A or ring B]



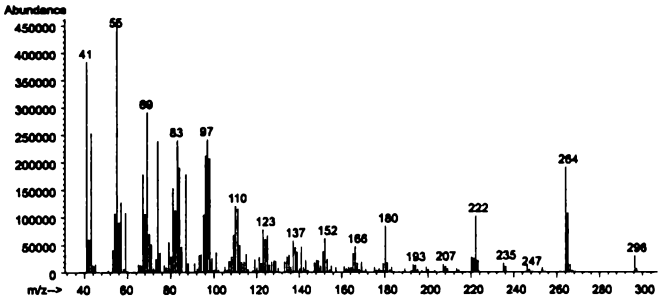


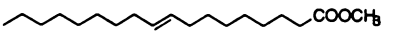
100. *cis*-9, *cis*-12-octadecadienoic acid (methyl ester) [FA18:2; linoleic acid; standard match]



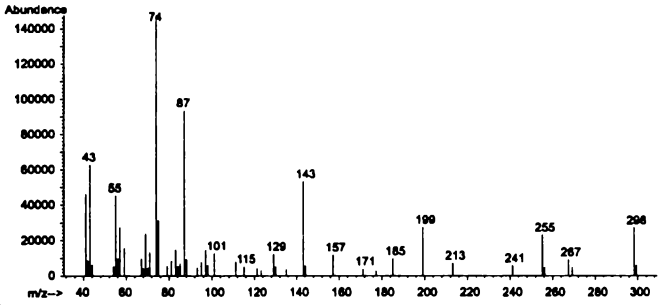


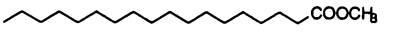
101. *cis*-9-octadecenoic acid (methyl ester) [FA18:1; oleic acid; standard match]



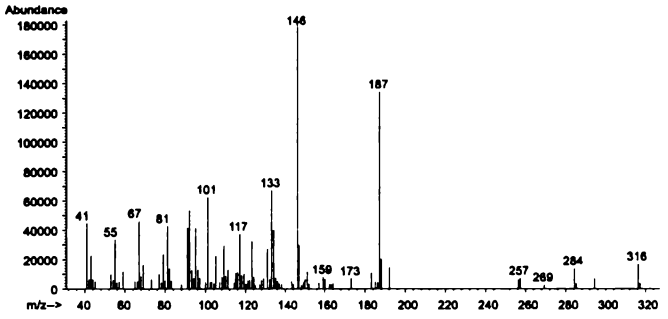


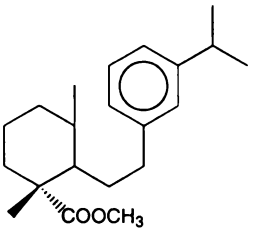
102. octadecanoic acid (methyl ester) [FA18:0; stearic acid; standard match]



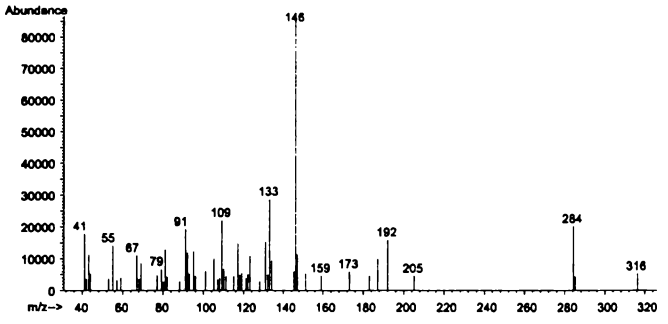


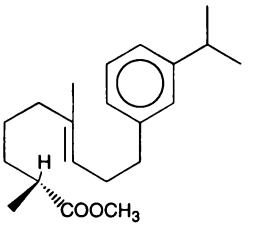
103. seco-dehydroabietic acid isomer #1 [Panadam 1988]



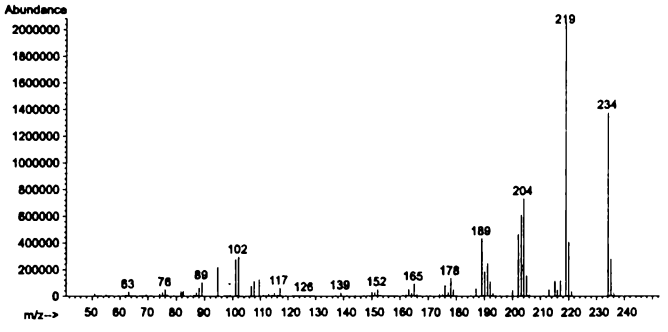


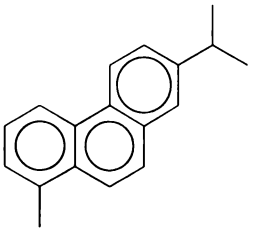
104. seco-dehydroabietic acid isomer #2 [Panadam 1988]



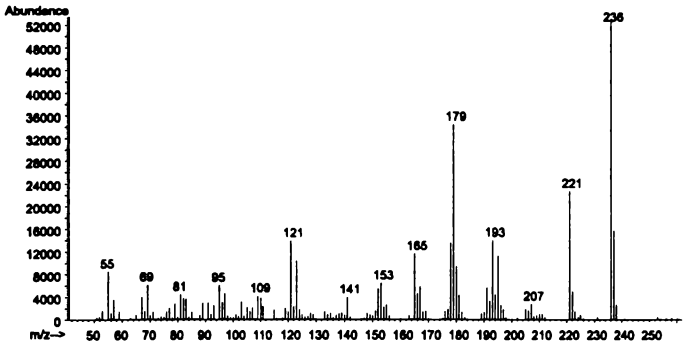


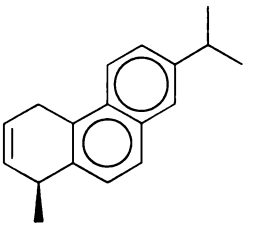
105. retene [standard match]



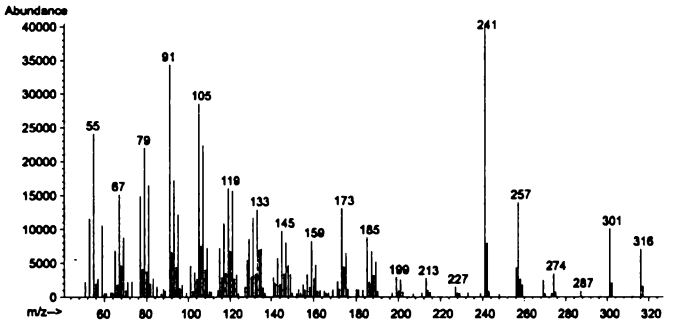


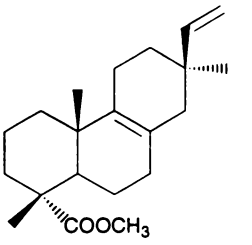
106. DT236 [possible structure similar to that shown]



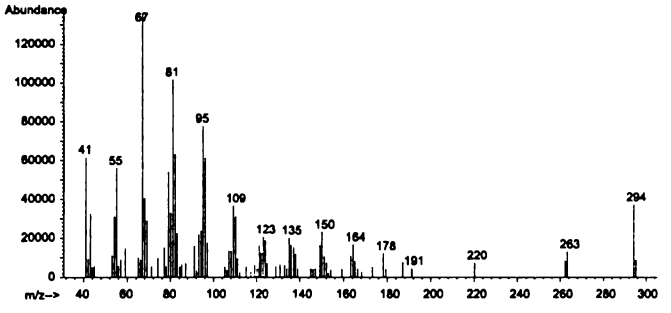


107. 8,15-pimaradien-18-oic acid (methyl ester)..[Zinkel et al. 1971]



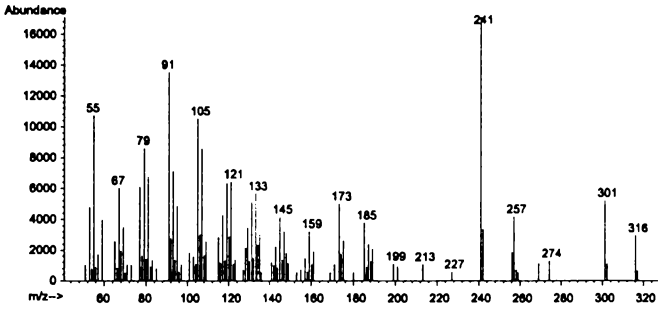


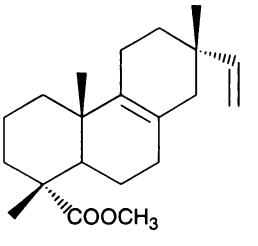
108. octadienoic acid (methyl ester) [FA18:2]



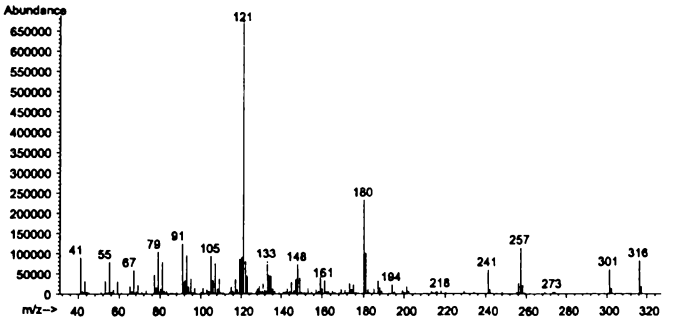
$CH_3(CH_2)_{12}(CH)_4COOCH_3$

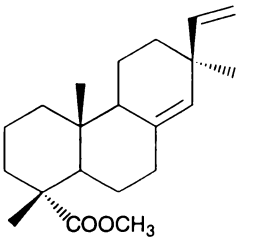
109. 8,15-isopimaradien-18-oic acid (methyl ester) [Zinkel et al. 1971]



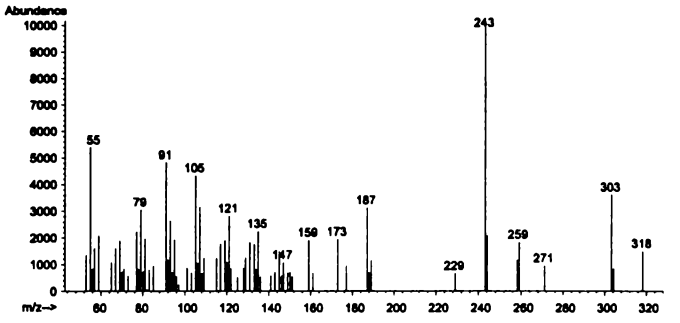


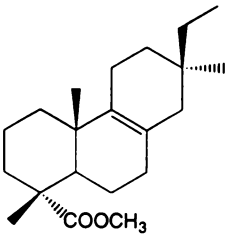
110. pimaric acid (methyl ester) [Zinkel et al. 1971]



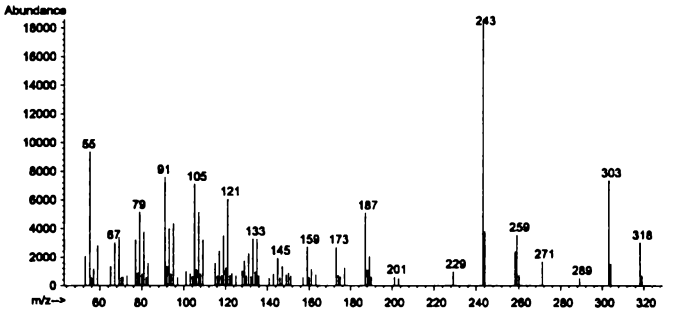


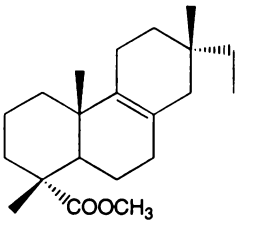
111. 8-pimaren-18-oic acid (methyl ester) [Zinkel et al. 1971; Chang et al. 1971]



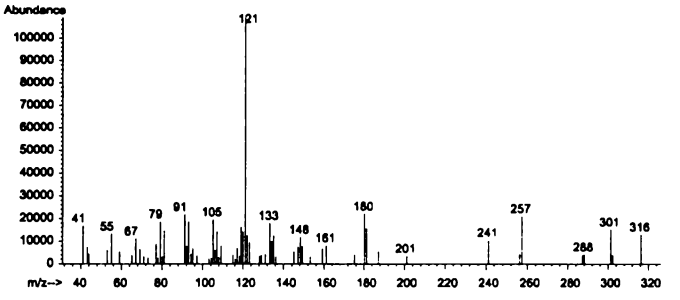


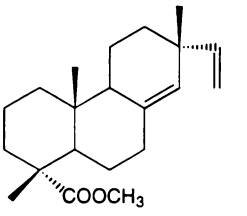
112. 8-isopimaren-18-oic acid (methyl ester) [Zinkel et al. 1971; Chang et al. 1971]



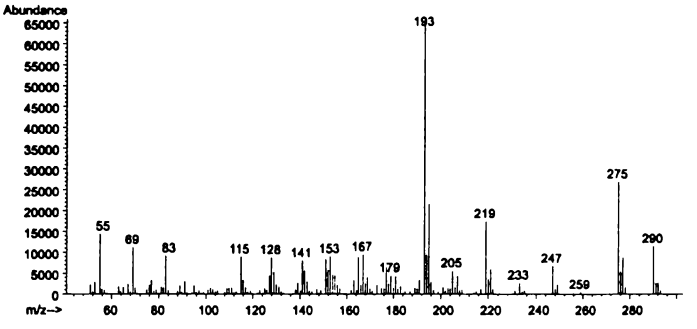


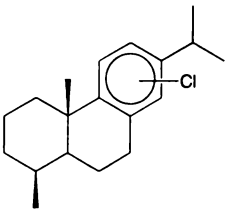
113. sandaracopimaric acid (methyl ester) [Zinkel et al. 1971; Chang et al. 1971]



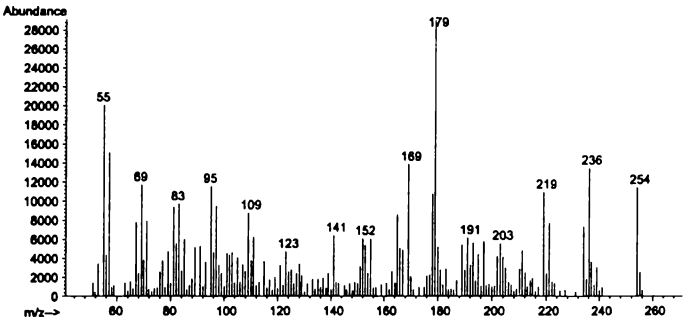


114. chlorodehydroabietin [12- or 14-chloro isomer; Hynning et al. 1993]

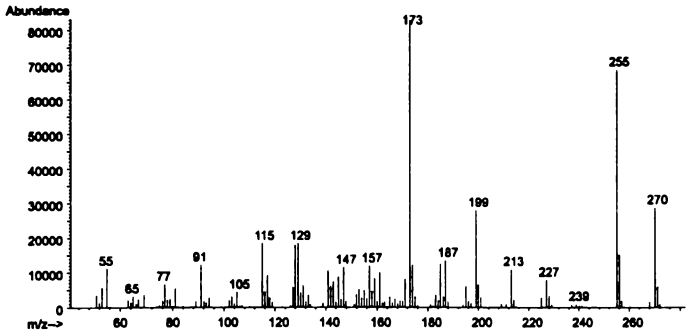




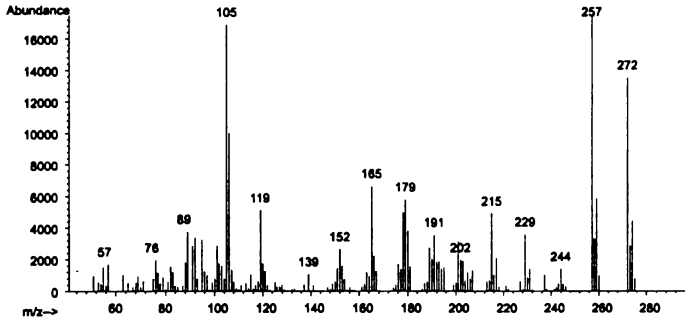
115. DT254 [unknown structure, poorly resolved]

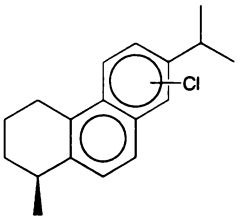


116. DT270 [structure unknown]

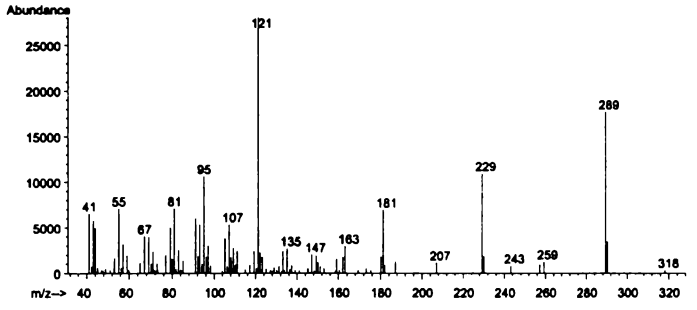


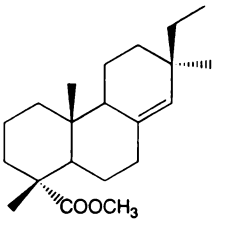
117. chlorotetrahydroretene?



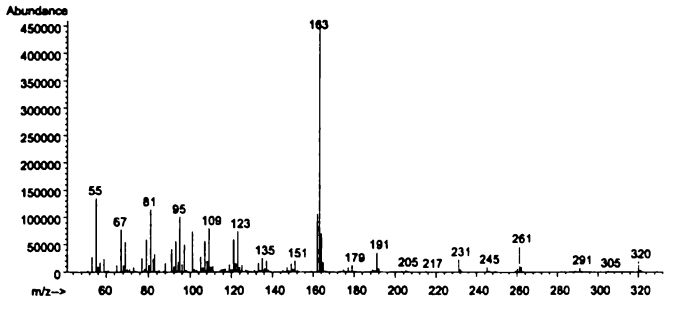


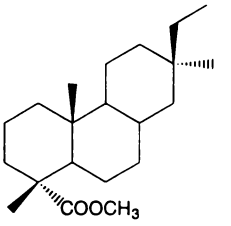
118. 8(14)-pimaren-18-oic acid [Zinkel et al. 1971; Chang et al. 1971]



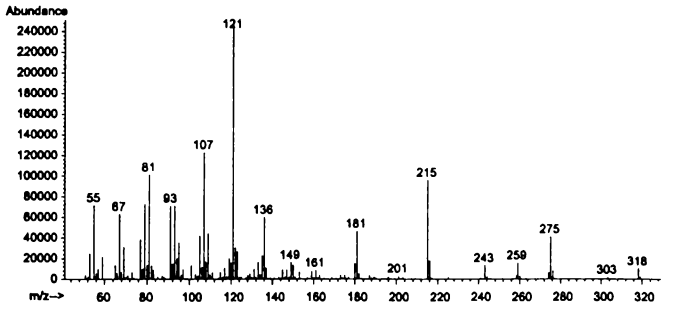


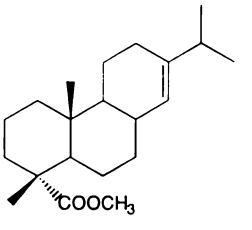
119. pimaran-18-oic acid (methyl ester) [Zinkel et al. 1971; Chang et al. 1971]



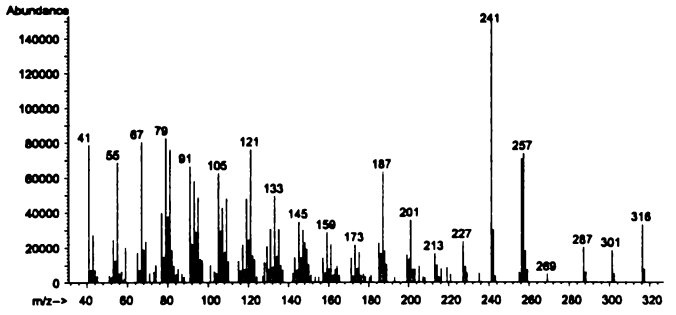


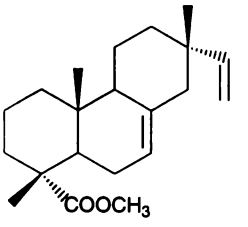
120. 13-abieten-18-oic acid (methyl ester) [Zinkel et al. 1971; Chang et al. 1971]



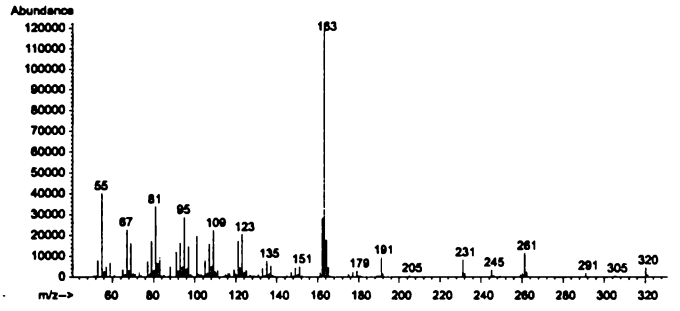


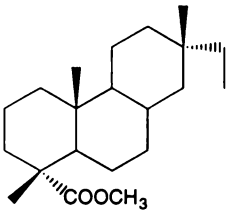
121. isopimaric acid (methyl ester) [Zinkel et al. 1971; Chang et al. 1971]



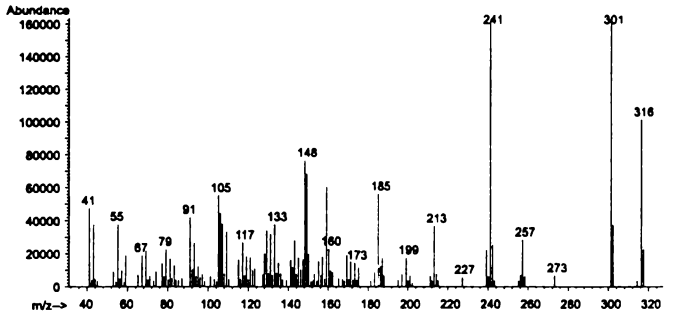


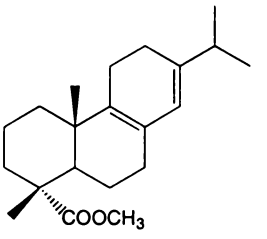
122. isopimaran-18-oic acid (methyl ester) [Zinkel et al. 1971; Chang et al. 1971]



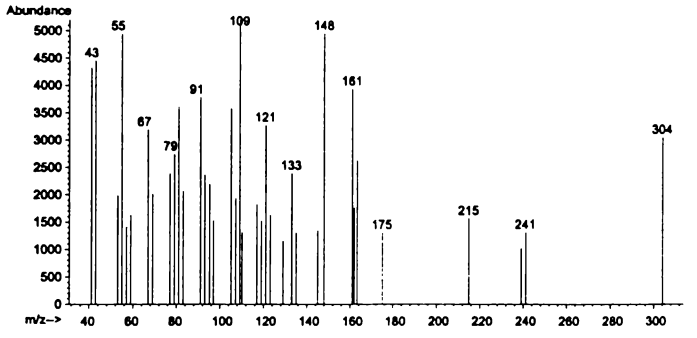


123. palustric acid (methyl ester) [Zinkel et al. 1971]

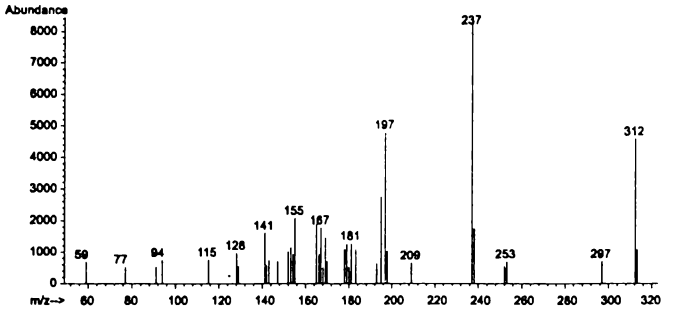


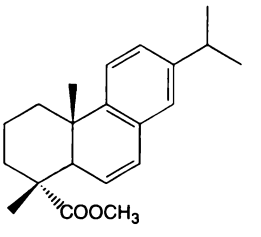


124. unidentified RA304? [possibly underivatised resin acid residue?]

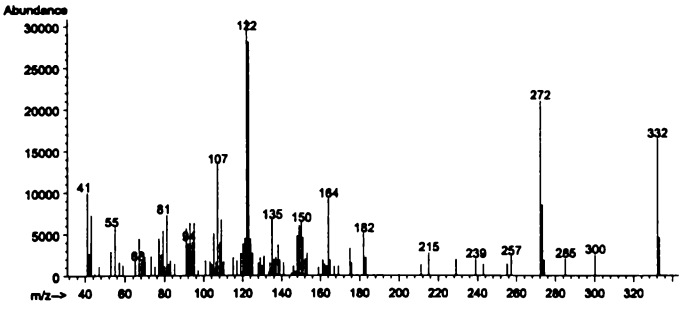


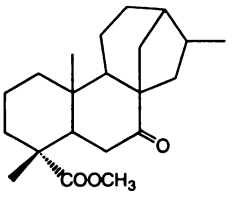
125. 6,8,11,13-abietatetraen-18-oic acid (methyl ester) [Zinkel et al. 1971; Chang et al. 1971]



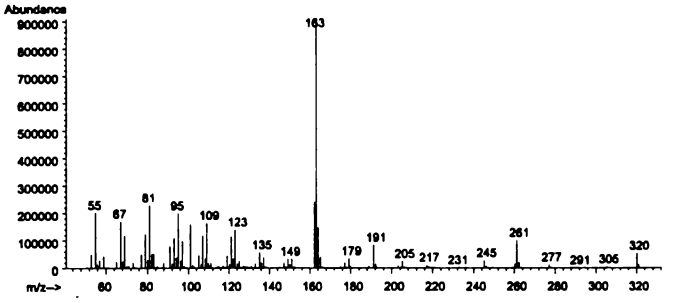


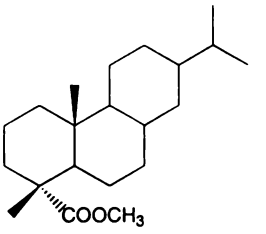
126. 7-oxokauran-18-oic acid (methyl ester) [tentative identification, NBS library #47209, 70%]



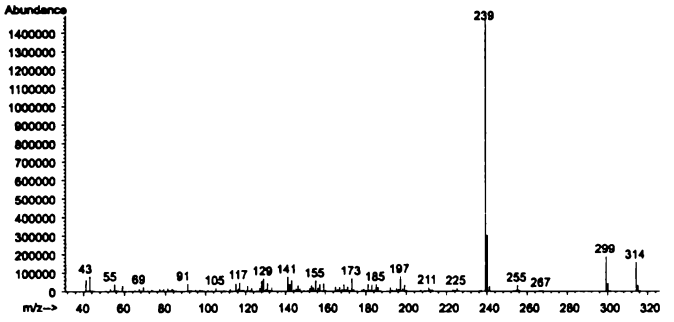


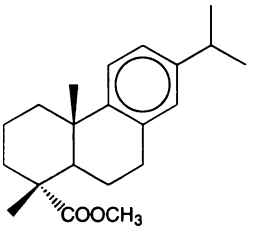
127. abietan-18-oic acid (methyl ester) [NMR; Zinkel et al. 1971; Chang et al. 1971]



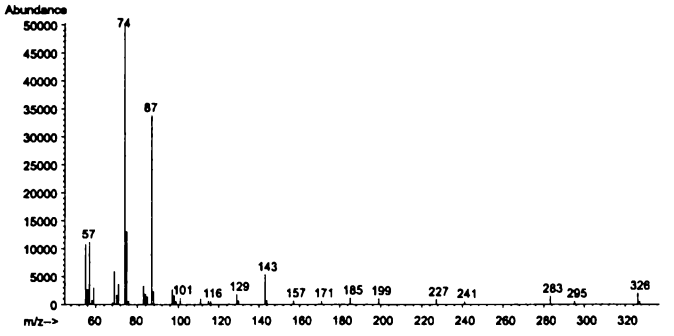


128. dehydroabietic acid (methyl ester) [standard match]



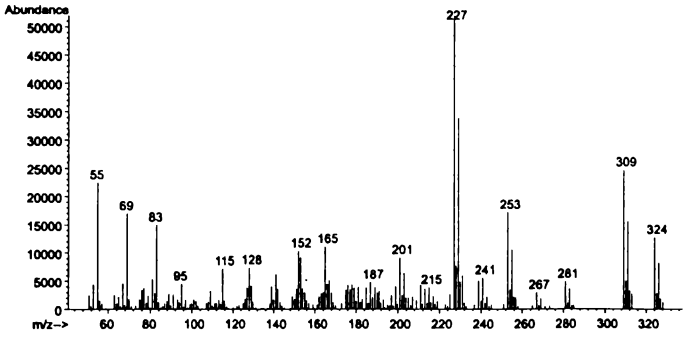


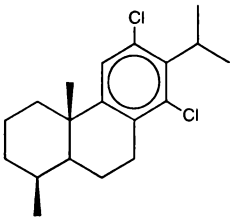
129. eicosanoic acid [FA20:0; NBS library #73342, 94%]



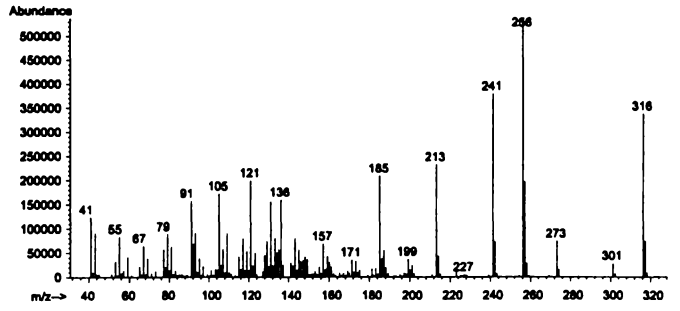
$CH_3(CH_2)_{18}COOCH_3$

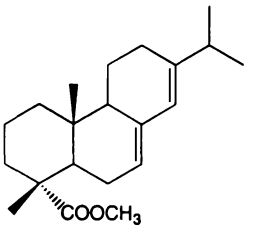
130. 12,14-dichlorodehydroabietin [Hynning et al. 1993]



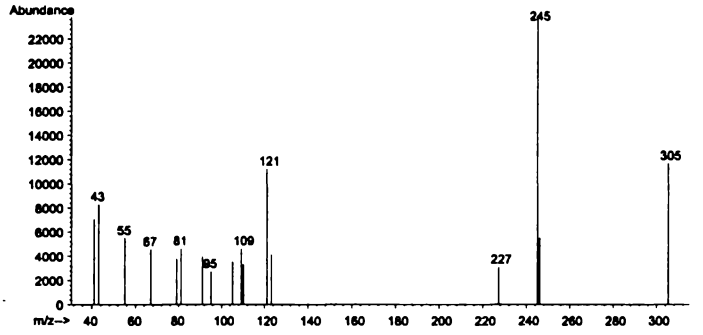


131. abietic acid (methyl ester) [standard match]

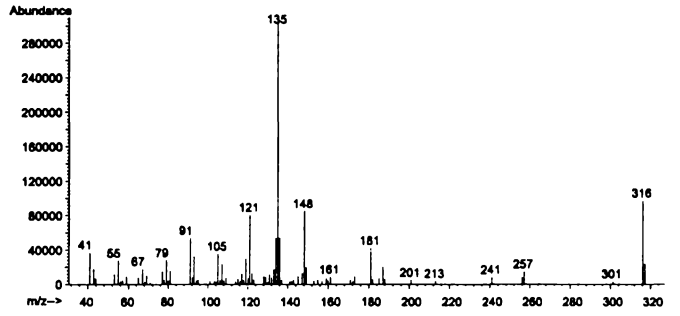


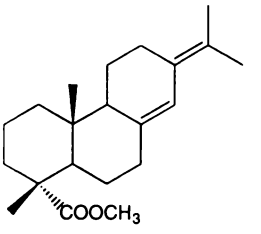


132. unidentified resin acid [mw=348?, dihydroxylated resin acid, Singh Thandi 1993]

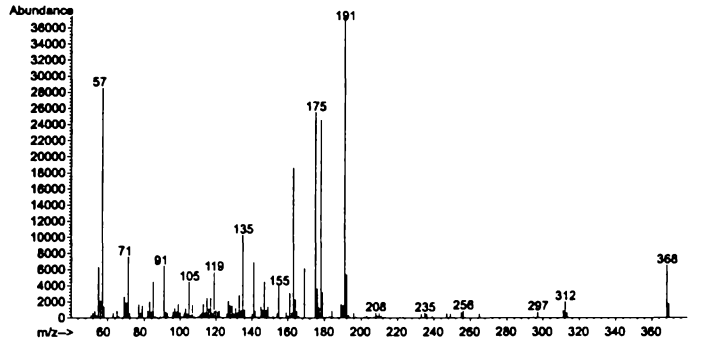


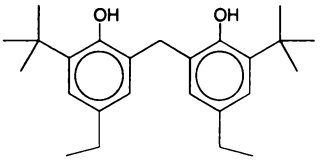
133. neoabietic acid (methyl ester) [Zinkel et al. 1971]



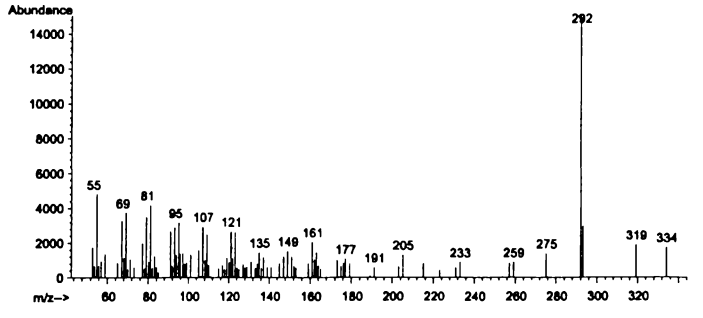


134. 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-ethylphenol [NBS library #51188, 91%]

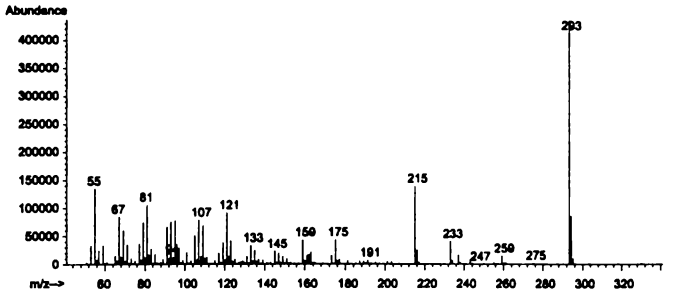


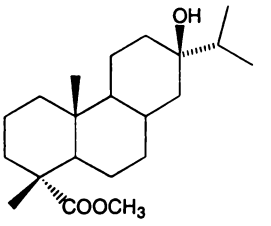


135. unidentified RA334?

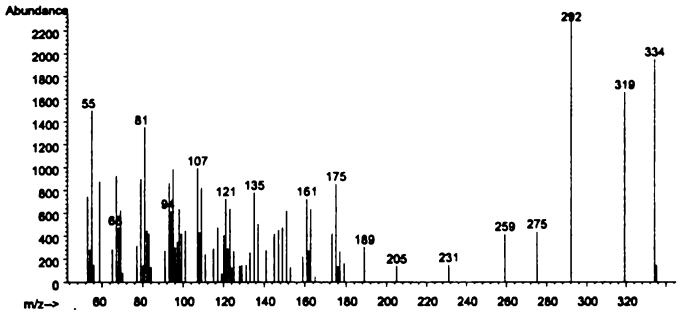


136. Kinleithic acid (13β-hydroxyabietan-18-oic acid, methyl ester) [std match, Wilkins et al. 1987]

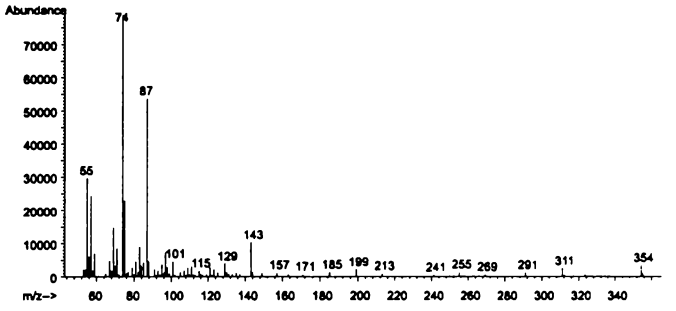




137. unidentified RA334?

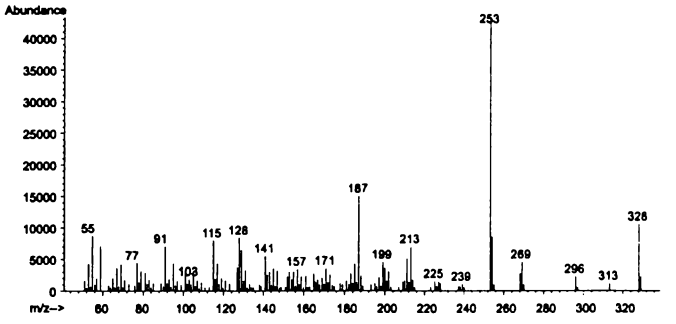


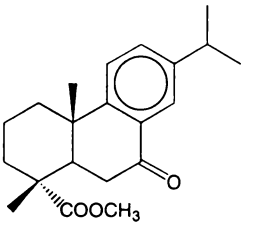
138. docosanoic acid (methyl ester) [FA22:0; Behenic acid; standard match]



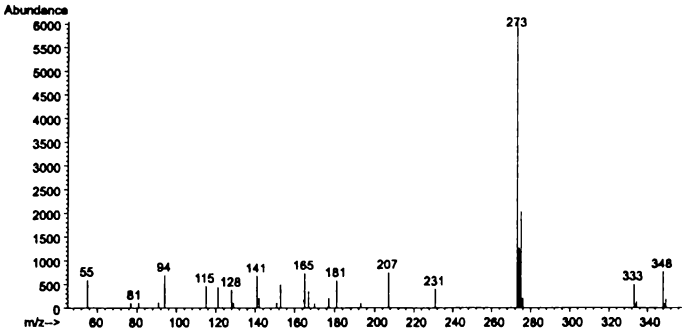
$CH_3(CH_2)_{20}COOCH_3$

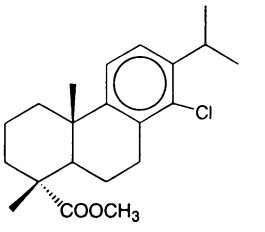
139. 7-oxodehydroabietic acid (methyl ester) [Brownlee and Strachan 1977]



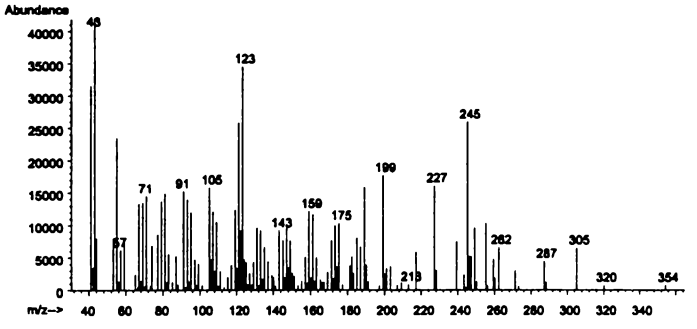


140. 14-chlorodehydroabietic acid (methyl ester) [Remberger et al. 1990]

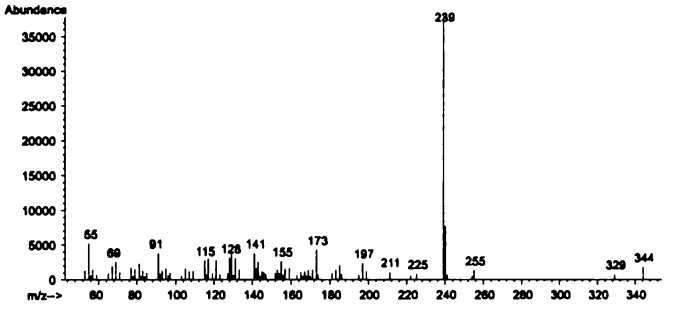




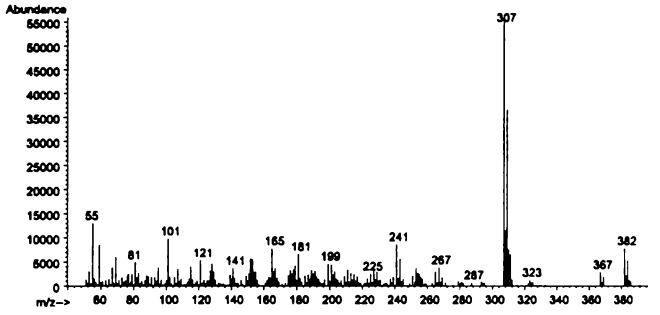
141. unidentified resin acid derivatives (unresolved)

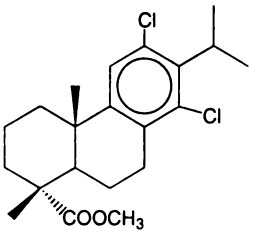


142. unidentified resin acid derivative

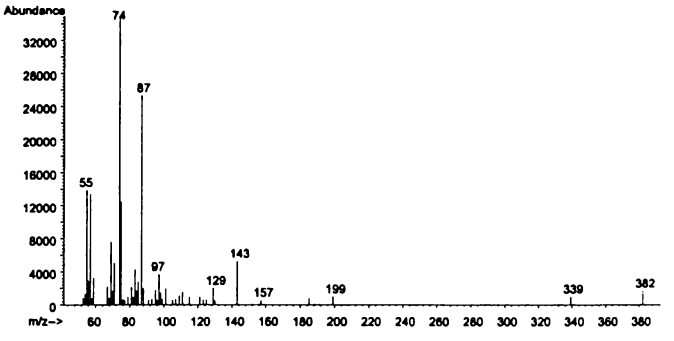


143. 12,14-dichlorodehydroabietic acid (methyl ester) [Remberger et al. 1990]



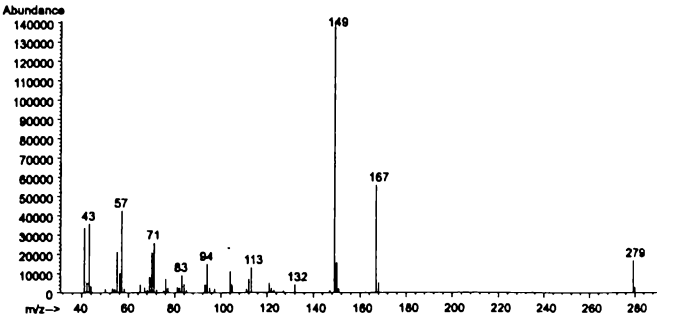


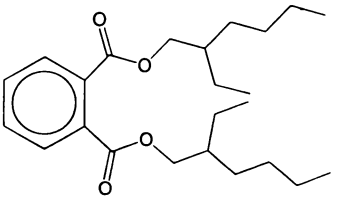
144. tetracosanoic acid (methyl ester) [FA24:0; lignoceric acid; standard match]



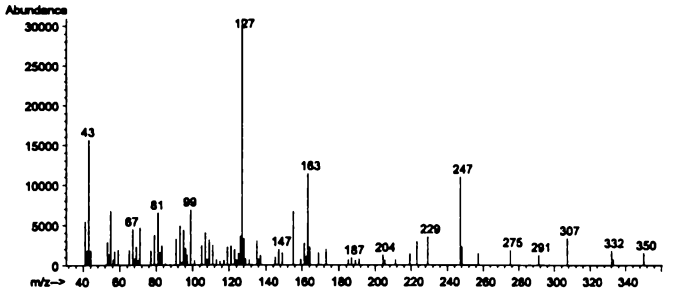
$CH_3(CH_2)_{22}COOCH_3$

145. bis(2-ethylhexyl)phthalate [standard match]

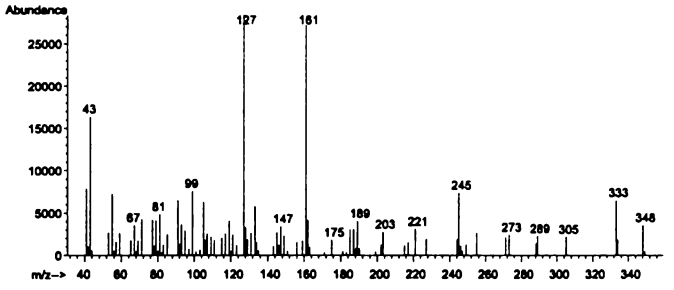




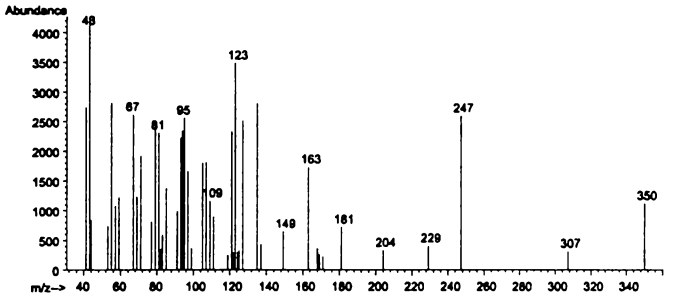
146. resin acid derivative mw=350? [possibly saturated hydroxyketone or dihydroxymonoene?]



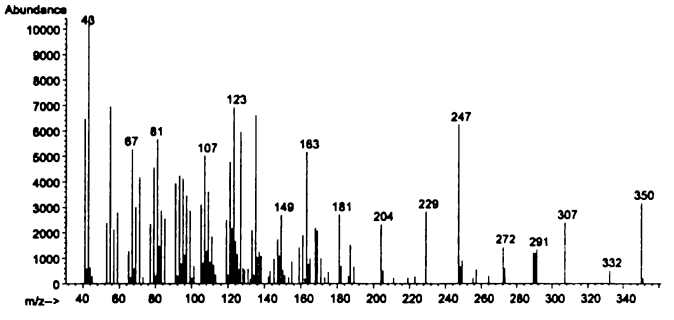
147. RA derivative mw=348? [saturated diketone, monoenic hydroxyketone, or dihydroxydiene?]



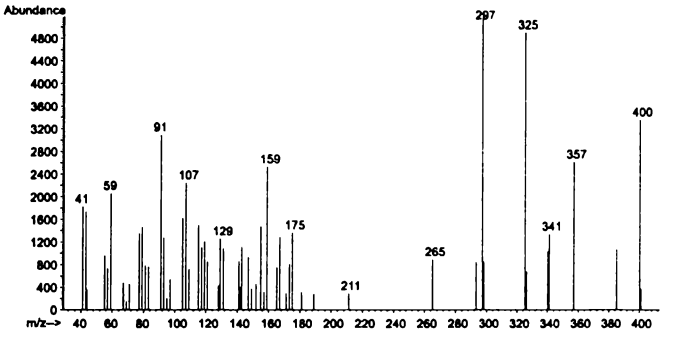
148. resin acid derivative mw=350? [possibly saturated hydroxyketone or dihydroxymonoene?]



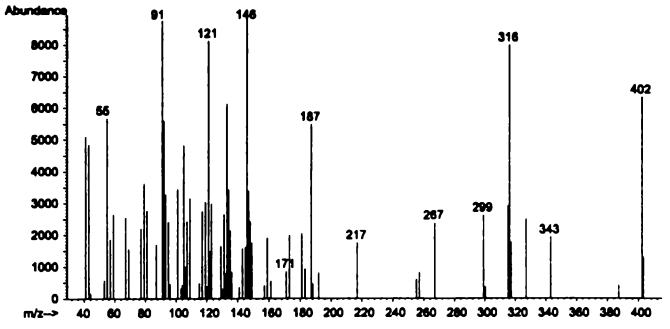
149. resin acid derivative mw=350? [possibly saturated hydroxyketone or dihydroxymonoene?]



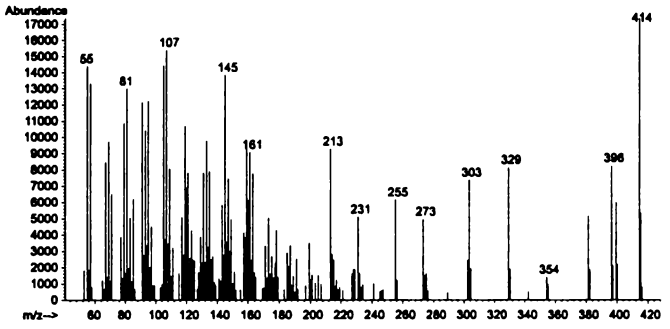
150. resin acid derivative mw=400? [structure unknown]

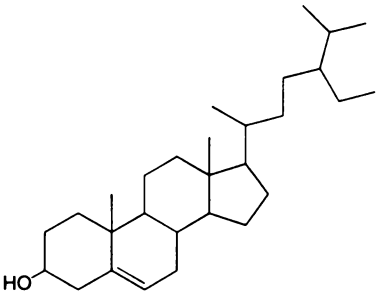


151. resin acid derivative mw=402? [structure unknown]

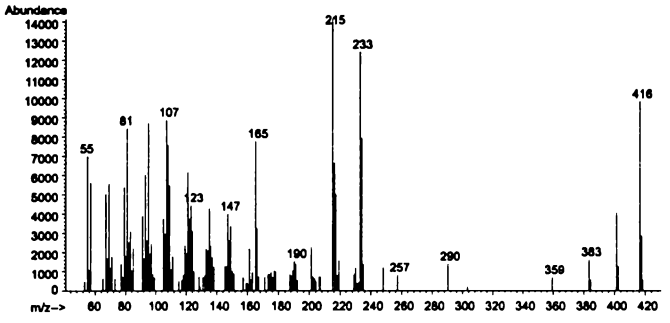


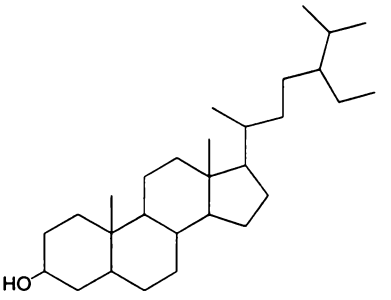
152. β-sitosterol [NBS library #74349, 93%]





153. unidentified sterol [possibly saturated sitosterol analogue?]





Appendix 2

Data Tables

Table A2.1: No. 2 Drain data from preliminary study

Sample Code	K21	K22	K23	K24	K25*	K26	K27	K28	K29	K210	K211	K212	K213	K214	K215	K216*	K217*
Date	27/1/87	3/2/87	11/2/87	18/2/87	3/10/87	25/3/87	9/4/87	15/4/87	22/4/87	28/4/87	6/5/87	4/6/87	12/6/87	15/6/87	2/7/87	9/7/87	15/7/87
Extractable organics (ug/L):																	
a-pinene	3097	13861	3856	16021	1739	20252	941	1798	15275	913	513	47110	8764	4239	18870	377	520
b-pinene	142	20974	5147	26520	1374	5818	NQ	NQ	24050	NQ	NQ	42730	6729	NQ	16003	139	189
limonene	647	1943	1419	1927	274	1572	130	657	1735	106	73	3787	793	314	2359	113	255
fenchol	1677	2268	3566	3086	994	1928	489	1946	1841	1386	767	6026	2115	2469	5861	3330	1742
MT154+138 (unresolved)	505	818	1244	1069	349	814	151	603	695	520	273	1656	742	811	1449	955	557
borneol	2361	2897	5198	4196	1714	3431	474	2845	2341	2361	1447	7179	3550	3634	6790	4724	2629
4-terpineol	760	1271	1835	1932	699	1651	196	1098	1250	1016	547	3449	1205	1335	2687	2000	897
a-terpineol	16858	15437	32111	29884	8817	17621	3530	21221	17385	12409	8018	39282	17619	20011	54381	22528	9706
Total Monoterpenes	26048	59469	54376	84635	15960	53086	5911	30169	64572	18710	11638	151218	41517	32813	108401	34166	16495
2,5-dimethyl-2-cyclopentenone	185	182	300	495	176	457	50	451	538	385	356	570	297	677	577	175	80
dimethyltrisulphide	1449	1054	1019	1530	394	2168	49	701	676	2706	1261	1943	1470	1336	1790	335	127
2,3,4-trimethyl-2-cyclopentenone	364	377	763	972	288	393	58	632	416	568	468	874	505	806	753	633	417
guaiacol	774	1108	2063	7648	1705	2750	NQ	7264	1629	2722	2152	3688	1764	15975	2066	1737	557
Total Miscellaneous Compounds	2772	2721	4144	10645	2563	5768	157	9048	3259	6382	4236	7075	4036	18794	5186	2880	1181
FA16:0 (palmitic)	310	292	412	7343	336	538	105	358	227	532	556	1006	685	1075	977	151	1904
anteiso-FA17:0	45	43	63	969	55	92	15	64	32	72	80	96	79	214	107	NQ	293
FA18:3 (pinolenic)	NQ	NQ	NQ	763	55	76	NQ	45	NQ	NQ	128	155	75	541	78	NQ	NQ
FA18:2 (linolenic)	NQ	NQ	NQ	513	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	415	NQ	NQ	NQ
FA18:2 (linoleic)	54	89	120	17171	712	930	35	677	35	108	632	534	254	3021	240	NQ	870
FA18:1 (oleic)	94	136	214	28010	1211	1691	82	1387	71	183	1032	840	386	4169	390	43	3081
FA18:0 (stearic)	88	178	154	1319	227	356	56	292	140	142	188	492	291	1123	272	66	1116
Total Fatty Acids	590	738	963	56088	2596	3683	293	2823	505	1037	2616	3123	1770	10558	2064	261	7264
seco-dehydroabietic acid (isomer 1)	NQ	51	NQ	2640	220	233	32	139	NQ	77	266	85	104	863	NQ	94	545
seco-dehydroabietic acid (isomer 2)	NQ	30	NQ	685	200	101	19	70	NQ	53	175	70	64	462	NQ	52	557
pimaric acid	61	103	184	4322	560	654	198	485	68	376	1096	425	178	2095	290	311	5039
sandaracopimaric acid	17	20	NQ	1058	263	125	38	90	NQ	72	228	120	64	509	162	60	956
isopimaric acid	39	146	78	2058	374	139	48	120	66	110	367	512	227	865	130	78	384
palustric acid	NQ	271	184	2807	538	540	73	373	296	165	550	266	60	1298	194	116	3120
6,8,11,13-abietatetraeneoic acid	NQ	NQ	NQ	534	197	160	34	174	NQ	122	651	167	108	876	68	75	582
dehydroabietic acid	135	279	193	10716	1383	1759	726	1346	212	1440	2782	1237	607	4493	710	837	9576
abietic acid	403	206	107	16548	1109	1196	NQ	139	143	513	1244	1003	160	8118	836	481	5740
neoabietic acid	NQ	NQ	NQ	1560	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
Total Resin Acids	655	1106	746	42928	4844	4907	1169	2936	785	2928	7359	3885	1572	19579	2390	2103	26499
Sodium (mg/L)		736	786	795	649	793	457	292		1030	640	660	325	710	614	383	596
Chloride (mg/L)		553	568	670	547	803	440	168		696	537	544	346	379	486	356	545
Colour (CPU)		2742	3155	3036	2177	1613	1149	1391		3786	2786	2286	1000	3964	2571	2036	2250

*: Samples did not have HC18 internal standard added, therefore monoterpenes and miscellaneous compounds not included in quantitative data analysis
NQ: not quantified (peak areas less than detection threshold)

Table A2.1 (cont.): No. 2 effluent drain data from preliminary study

Sample Code	K218*	K219	K220	K221	K222	K223	K224	K225	K226	K227*	K228*	K229*	K230	K231
Date	23/7/87	10/9/87	17/9/87	1/10/87	8/10/87	13/10/87	21/10/87	27/10/87	2/11/87	9/11/87	16/11/87	23/11/87	30/11/87	14/12/87
a-pinene	503				3064		113807	14084		560	6974	10125	2192	320
b-pinene	52				937		141936	5653		550	4744	13099	NQ	705
limonene	447				328		683	2836		600	2600	3000	2113	921
fenchol	4277				1727		3885	3750		2021	5497	7926	3594	2219
MT154+138 (unresolved)	1220				874		1455	360		250	1214	900	360	270
borneol	6848				3202		4596	5550		3524	8999	13568	5243	4573
4-terpineol	1757				1230		2113	2008		934	3395	5718	2235	2140
a-terpineol	22937				18044		28599	21001		10182	38169	56359	23191	16925
Total Monoterpenes	38041				29406		297073	55243		18621	71592	110695	38928	28073
2,5-dimethyl-2-cyclopentenone	236				443		379	136		857	1550	1025	916	672
dimethyltrisulphide	359				660		4043	3164		338	1761	5463	3345	676
2,3,4-trimethyl-2-cyclopentenone	928				785		509	957		789	1865	1717	951	769
guaiacol	1354				2128		1875	4305		4107	11577	11534	4201	4072
Total Miscellaneous Compounds	2877				4015		6806	8563		6091	16753	19739	9413	6189
FA16:0 (palmitic)	79				3310		806	1588		400	325	2206	3916	622
anteiso-FA17:0	NQ				785		198	208		77	65	461	847	83
FA18:3 (pinolenic)	NQ				1420		NQ	NQ		NQ	NQ	374	217	33
FA18:2 (linolenic)	NQ				862		NQ	NQ		NQ	NQ	175	NQ	NQ
FA18:2 (linoleic)	NQ				4808		280	371		27	163	3834	3000	348
FA18:1 (oleic)	NQ				6463		280	618		154	239	6584	8058	561
FA18:0 (stearic)	101				944		NQ	420		99	73	413	626	72
Total Fatty Acids	180				18592		1564	3205		757	865	14047	16664	1719
seco-dehydroabietic acid (isomer 1)	107				951		1046	200		122	104	1126	616	146
seco-dehydroabietic acid (isomer 2)	49				786		347	200		78	63	668	347	98
pimaric acid	397				3394		303	959		553	355	3440	2669	446
sandaracopimaric acid	101				1230		471	283		89	66	695	462	106
isopimaric acid	96				1553		457	294		150	127	2330	840	346
palustric acid	144				2690		286	441		226	190	586	1260	46
6,8,11,13-abietatetraeneoic acid	123				1113		NQ	763		312	288	586	1939	370
dehydroabietic acid	856				6855		563	2831		1812	1108	10015	8021	1224
abietic acid	190				7493		285	844		208	389	8559	507	552
neoabietic acid	NQ				NQ		NQ	NQ		NQ	NQ	774	NQ	71
Total Resin Acids	2063				26065		3758	6815		3550	2690	28779	16661	3405
Sodium (mg/L)	746	1100	408	909	793	519	376	558	390	472	403	500	820	786
Chloride (mg/L)	749	595	314	680	655	449	364	380	254	414	311	548	396	424
Colour (CPU)	2107	2589	1694	3992	5081	2143	1746	4536	968	2857	1920	2589	2899	3351

*: Samples did not have HC18 internal standard added, therefore monoterpenes and miscellaneous compounds not included in quantitative data analysis
NQ: not quantified (peak areas less than detection threshold)

Table A2.2: J Pond data from preliminary study

Sample	KJ1	KJ2	KJ3*	KJ4*	KJ5*	KJ6	KJ8	KJ9	KJ10	KJ11	KJ12	KJ13	KJ14*	KJ15*	KJ16	KJ17	KJ18
Date	18/6/87	2/7/87	9/7/87	15/7/87	23/7/87	10/9/87	1/10/87	8/10/87	13/10/87	21/10/87	27/10/87	2/11/87	9/11/87	16/11/87	23/11/87	30/11/87	14/12/87
Extractable Organics (ug/L):																	
a-pinene	286	95	22	28	22	NQ	NQ	NQ				NQ	NQ	NQ	NQ	NQ	NQ
b-pinene	NQ	28	88	93	NQ	NQ	NQ	NQ				NQ	NQ	NQ	NQ	NQ	NQ
fenchone	652	487	564	231	551	276	341	290				NQ	100	515	450	555	303
fenchol	70	106	113	55	68	62	77	77				NQ	NQ	NQ	NQ	NQ	NQ
camphor	1581	1332	789	756	1533	715	883	811				234	681	1472	1440	1503	1838
DHT (+ MT154)	1330	972	454	442	893	356	440	505				393	515	717	915	523	591
borneol (+ phenylacetic acid)	249	148	175	77	102	62	77	63				69	223	404	431	435	513
terpen-4-ol	679	743	304	314	711	301	577	557				401	453	782	869	593	527
a-terpineol	4856	5665	2123	1930	4363	2800	4649	5226				5876	5773	6901	7761	5154	4159
Total Monoterpenes	9703	9576	4632	3926	8244	4572	7044	7528				6973	7746	10791	11865	8763	7931
2,5-dimethyl-2-cyclopentenone	102	99	42	55	150	84	91	86				NQ	NQ	NQ	NQ	NQ	NQ
dimethyltrisulphide	54	57	128	100	85	NQ	NQ	NQ				NQ	NQ	NQ	NQ	NQ	NQ
DMCP (+ p-cymene)	372	339	182	171	319	209	257	283				72	139	81	338	659	121
2,3,5-trimethyl-2-cyclopentenone	557	345	202	178	447	245	303	379				102	182	193	597	1016	224
2,3,4-trimethyl-2-cyclopentenone	223	160	104	110	169	95	117	157				69	156	185	334	229	138
Total Miscellaneous Compounds	1308	999	657	614	1170	633	769	905				243	477	459	1269	1904	483
FA16:0	NQ	180	88	85	79	178	288	337				111	135	87	100	100	100
FA18:0	NQ	NQ	62	87	88	156	257	331				NQ	NQ	NQ	NQ	NQ	NQ
Total Fatty Acids	NQ	180	150	171	166	334	545	668				111	135	87	100	100	100
fichtelite	NQ	NQ	NQ	69	71	NQ	131	106				NQ	NQ	NQ	NQ	NQ	NQ
dehydroabietin	260	517	131	127	103	311	342	480				371	1185	867	746	948	152
seco-dehydroabietic acid (isomer 1)	400	841	560	663	393	599	698	759				852	1237	1021	390	223	500
seco-dehydroabietic acid (isomer 2)	186	404	286	320	196	301	396	494				532	629	562	181	430	302
8,15-isopimaradienoic acid	210	526	277	309	228	402	557	599				744	1158	1086	460	314	422
8,15-pimaradienoic acid	138	349	144	179	129	197	320	449				392	372	511	249	279	293
pimaric + 8-pimarenoic acids	1372	3144	1925	2012	1297	2103	2103	2404				3490	4820	4199	1736	1633	1316
sandaracopimaric acid	124	374	244	253	169	293	364	446				475	414	370	100	219	137
8(14)-pimarenoic acid	119	200	94	126	79	134	446	459				414	200	180	100	100	100
13-abietenoic acid	668	1487	1314	1442	711	1366	1686	1802				2720	1138	4595	1139	1602	2657
abietanoic acid + 6,8,11,13-abietatetraenoic acid	1162	1711	1145	1037	898	1475	NQ	NQ				NQ	2304	8141	2204	3139	4113
dehydroabietic acid	9755	13615	5099	5081	3579	8085	9156	9629				22227	18529	23912	8553	8255	9468
abietic acid	146	876	208	270	118	NQ	NQ	492				NQ	NQ	2832	793	1367	1586
Kinleithic acid	1823	2009	1044	1235	1482	1780	3116	3434				4024	3609	2508	911	944	804
7-oxodehydroabietic acid	338	823	614	604	463	578	840	1400				727	438	627	368	759	161
Total Resin Acid + Diterpene Hydrocarbons	16701	26877	13085	13726	9916	17624	20155	22953				36968	36033	51412	17931	20212	22011
Sodium (mg/L)	766	747	749	746	748	734	823	826	792	767	718	661	643	627	630	599	655
Chloride (mg/L)	629	651	652	621	620	661	722	675	667	636	602	600	511	737	460	446	442
Colour (CPU)	3609	3496	3460	3145	3508	4230	4350	4380	4350	4030	3890	3510	3190	2857	3170	3035	3080

*: Samples did not have HC18 internal standard added, therefore monoterpenes and miscellaneous compounds not included in quantitative data analysis
NQ: not quantified (peak areas less than detection threshold)

Table A2.3: Q Basin data from preliminary study.

Sample	ES1	ES2	ES3	ES4	ES5	ES6	ES7
Date	10/3/87	25/3/87	1/4/87	8/4/87	15/4/87	22/4/87	28/4/87
Extractable Organics (ug/L):							
2,3,5-trimethyl-2-cyclopentenone	NQ	20	32	15	NQ	NQ	NQ
2,3,4-trimethyl-2-cyclopentenone	NQ	22	23	17	NQ	NQ	NQ
Total Miscellaneous Compounds	NQ	42	55	32	NQ	NQ	NQ
FA16:0	33	35	37	13	22	44	45
FA18:0	13	20	32	7	12	13	26
FA20:0	36	25	61	23	17	22	24
FA22:0	62	69	77	26	49	35	35
FA24:0	32	39	52	14	29	16	18
Total Fatty Acids	176	188	259	83	129	131	148
DT252	195	NQ	NQ	NQ	NQ	NQ	NQ
DT262P	49	24	6	6	10	45	21
fichtelite	87	222	124	33	76	62	84
dehydroabietin	199	347	23	NQ	12	15	48
DT242	NQ	NQ	NQ	NQ	38	43	37
tetrahydroretene	20	19	15	NQ	10	4	NQ
seco-dehydroabietic acid (isomer 1)	138	19	37	6	8	5	NQ
seco-dehydroabietic acid (isomer 2)	81	7	23	3	5	3	NQ
pimaric + 8-pimarenoic acids	38	25	46	11	18	13	17
sandaracopimaric acid	21	5	20	3	NQ	4	5
13-abietenoic acid	48	24	40	9	19	9	15
RA320A + RA312A + RA332K**	104	169	139	58	110	85	119
dehydroabietic acid	55	54	54	24	49	36	46
Total Resin Acids + Diterpene Hydrocarbons	1034	915	527	154	355	324	392
Sodium (mg/L)		501	469	524	476		443
Chloride (mg/L)		425	398	448	418		374
Colour (CPU)		2885	2820	3070	2830		2500

** abietanoic (RA320A), 6,8,11,13-abietatetraenoic (RA312A), and 7-oxokauranoic (RA332K) acids coeluting
NQ: not quantified (peaks less than detection threshold)

Table A2.4: EOs, CPs, sodium, and colour in No. 2 drain at source and P7 seepage pond inlet. 24 hr composite samples.

	No.2 drain at source					No.2 drain at inlet to basin P7			
Date (day-month of1988)	02-11	03-11	04-11	05-11	06-11	03-11	04-11	05-11	06-11
sodium (mg/L)	660	989	884	1000	914	317	683	852	901
colour (CPU)	2420	3784	4602	6545	5080	3068	3102	4364	5863
Extractable Organics (ug/L):									
2-methyl-2-cyclopentenone	445	66	116	91	182				
2,3-dimethyl-2-cyclopentenone	624	99	116	46	373		88	28	37
2,5-dimethyl-2-cyclopentenone	739	682	453	324	463	109	357	363	370
2,3,4-trimethyl-2-cyclopentenone	871	759	686	718	621	262	443	539	618
2,3,5-trimethyl-2-cyclopentenone	298	224	183	233	231	76	166	193	218
Total Methyl-2-cyclopentenones	2977	1829	1553	1411	1870	447	1055	1123	1243
dimethyltrisulphide	549	1123	1242	210	814	98	98	162	269
guaiacol	1674	1271	1167	1519	1703	148	1049	812	1228
a-pinene	3614	4735	5059	1660	4311	55	862	1732	993
b-pinene	6863	9627	9823	3682	8126	44	1356	2819	1491
p-cymene						65	493	515	336
limonene	648	679	693	213	658	65	277	350	227
fenchol	2076	1466	1666	1805	1887	290	774	949	1021
camphor (veratrole coelutes)	394	189	207	318	288	297	297	239	244
MT154	824	699	598	515	661	68	440	400	510
MT154	1071	726	806	983	904	669	849	829	918
borneol	3815	2551	2936	3604	3332	819	1970	2254	2834
4-terpineol	2364	1579	1682	1990	1917	569	1305	1301	1605
a-terpineol	21942	13784	15702	20120	18425	5487	11910	13196	16174
Total Monoterpenes	43611	36036	39172	34891	40508	8427	20533	24583	26351
palmitic acid (FA16:0)	1161	7514	7642	2822	6183	322	4436	6683	2546
anteiso-heptadecanoic acid (a.i.- FA17:(	204	1166	1194	504	1032	117	692	1172	408
n-heptadecanoic acid (FA17:0)		184	197	76	170		115	158	63
FA18:3	113	1450	1372	266	1730		648	1196	210
FA18:2	68	656	648	179	715		284	543	105
linoleic acid (FA18:2)	1423	16697	15785	1817	16067		7224	13145	2397
oleic acid (FA18:1)	2657	28133	27347	6114	25568		12766	23345	5352
stearic acid (FA18:0)	242	889	928	237	983	58	497	783	244
FA18:2	402	5071	4736	1535	4109		3035	4745	1302
epoxystearic acid	241	2537	2510	874	2548		1137	2156	618
Total Fatty Acids	6510	64297	62360	14423	59106	497	30833	53925	13243
seco-dehydroabietic acid #1	588	3490	3275	1348	4862	243	2159	3284	1258
seco-dehydroabietic acid #2	309	1929	1818	767	2925	246	1176	2023	686
pimaric acid	2500	12018	11528	5486	15320	916	7756	11719	4675
sandaracopimaric acid	440	2019	1992	958	2653	74	1413	2100	817
isopimaric acid	1572	8414	9197	1027	9759	563	1387	11594	6447
palustric acid	476	10471	3443	3376	18744		6896	4173	
6,8,11,13-abietatetraeneoic acid		656	711	300	847	869	2896	2876	1529
dehydroabietic acid	3700	17619	18838	8761	26520	3775	15896	21211	11022
abietic acid	6065	42305	39307	18747	57405	250	23211	36974	10489
neoabietic acid		7176	3557	2458	13430			4795	
Total Resin Acids	15650	106097	93666	43230	152466	6936	62791	100748	36924
Chlorophenolics (ug/L):									
2,4-dichlorophenol	33.7	43.4	48.8	71.4	58.4	13.4	31.7	42.1	51.1
2,4,6-trichlorophenol	42.6	71.4	66.2	100.3	80.4	14.5	47.0	64.3	76.0
2,3,4,6-tetrachlorophenol	7.2	10.4	10.9	13.4	11.8	1.2	7.5	8.9	11.8
pentachlorophenol	2.1	4.5	4.6	4.3	3.8	0.5	2.8	3.4	3.3
Total Chlorophenols	85.6	129.8	130.4	189.3	154.3	29.6	89.0	118.7	142.3
4,5-dichloroguaiacol	113.6	178.9	214.4	259.8	296.1	42.2	96.0	157.3	193.0
3,4,5-trichloroguaiacol	240.1	362.5	341.4	549.4	409.3	57.1	184.1	233.0	382.0
4,5,6-trichloroguaiacol	33.6	63.1	68.7	91.6	74.3	9.6	31.3	50.1	65.3
tetrachloroguaiacol	89.5	145.5	109.9	192.6	116.0	23.2	80.9	78.6	138.2
Total Chloroguaiacols	476.8	750.0	734.4	1093.4	895.8	132.2	392.3	519.0	778.5
5-chlorovanillin	14.6	21.0	21.9	26.9	23.7	2.3	15.1	17.9	23.8
6-chlorovanillin	198.7	264.3	291.0	306.0	337.3	76.1	143.9	240.3	290.7
5,6-dichlorovanillin	128.1	209.2	212.0	242.6	223.8	51.0	114.3	187.2	222.1
Total Chlorovanillins	341.4	494.6	525.0	575.5	584.9	129.5	273.3	445.3	536.7
3,4,5-trichlorocatechol	4.9	7.5	10.2	7.7	6.9	14.8	9.0	12.1	32.2
tetrachlorocatechol	21.5	32.6	44.4	50.0	32.4	11.0	21.7	32.0	46.9
Total Chlorocatechols	26.4	40.1	54.5	57.7	39.3	25.8	30.7	44.1	79.1
dichlorohydroxybenzaldehyde	67.2	90.5	87.7	125.2	105.8	21.3	58.6	86.2	106.6
Total Chlorophenolics	997.5	1504.9	1532.0	2041.2	1780.1	338.3	843.9	1213.4	1643.1

Table A2.5: EOs, CPs, sodium, and colour in P7 seepage basin monitoring trial

Date (day-month of1988)	02-11	04-11	05-11	06-11	07-11	08-11	09-11	10-11	12-11	16-11	19-11	20-11	21-11	22-11
sodium (mg/L)	190	296	564	661	614	641	636	644	448	494	445	340	337	343
colour (mg/L)	764	n.a.	2327	4338	3892	3851	3938	4050	2813	3000	2700	1913	1800	1973
Extractable Organics (ug/L):														
2,5-dimethyl-2-cyclopentenone		38	46	14	31	15	15							7
2,3-dimethyl-2-cyclopentenone		85	220	231	213	228	217	148	91	34	89	29	33	90
2,3,5-trimethyl-2-cyclopentenone		193	303	356	287	305	301	190	155	60	81	39	33	63
2,3,4-trimethyl-2-cyclopentenone		97	117	136	99	109	139	100	82	34	50	29	25	41
Total Methyl-2-cyclopentenones	0	414	686	737	630	657	673	438	328	128	220	97	92	201
dimethyltrisulphide		23	46	51	31	29	45		47	43	83	19	33	31
guaiacol		218	626	433	347	286	178	63	82	17	13			
a-pinene		231	941	629	491	425	498	127	142	51	31	19		14
b-pinene		308	1486	1005	647	582	665	154	148	51	21	20		29
p-cymene		61	315	221	77	65	70							
limonene		73	228	194	88	155	154	54	37	17				
fenchol		289	478	486	362	347	338	154	129	26	8			
camphor		223	229	190	162	176	196	123	142	170	93	77	63	57
unid. MT154		64	227	248	162	208	169	47	30					
unid. MT154		151	225	282	181	222	236	99	90	53	29	19	18	17
DHT		286	367	313	307	319	385	262	319	420	374	281	216	247
borneol		799	1316	1468	1233	1239	1217	593	517	211	109	58	29	29
4-terpineol		543	874	880	777	788	779	415	351	215	126	79	50	59
a-terpineol		5250	8417	9267	8392	8693	8594	5423	4386	3069	1845	1196	874	800
Total Monoterpenes	0	8278	15102	15182	12879	13219	13300	7452	6292	4283	2636	1749	1250	1253
palmitoleic acid (FA16:1)														
palmitic acid (FA16:0)	44	1538	3964	3848	3176	3143	3021	2393	1448	707	273	172	131	143
anteiso-heptadecanoic acid (FA17:0)		216	691	564	489	464	475	391	235	64				
FA18:3			224	332	240									
FA18:2			625	182	120									
linoleic acid (FA18:2)	25	734	2364	3414	2620	1231	986	694	370					
oleic acid (FA18:1)		3574	11994	9322	7491	7532	6723	4083	2135	429	102	76		64
FA18:1														78
stearic acid (FA18:0)		433	369	604	281	240	342	164	277	185	131	87	26	82
FA18:2		1013	2301	1806	1575	1827	1685	1054	511					
epoxystearic acid		167	158	762	633	263	210	318	191					
Total Fatty Acids	69	7676	22691	20833	16624	14699	13442	9097	5166	1385	506	335	157	366
fichtelite														
dehydroabietin													36	36
seco-dehydroabietic acid #1		637	1865	1681	1477	1567	1559	1311	907	868	760	561	539	572
seco-dehydroabietic acid #2		357	1083	928	806	871	841	737	521	466	390	276	278	292
8,15-isopimaradienoic acid			597	553	379	478	369	443	267	404	237	166	163	169
8,15-pimaradienoic acid			199	184	126	159	123	148	89	88	97	43	63	77
pimaric acid		2154	6595	5937	5144	5651	5327	4590	3307	3174	2776	1978	1939	1984
sandaracopimaric acid		385	1252	1071	877	974	962	812	577	503	446	321	302	302
8(14)-pimarenoic acid														45
isopimaric acid		2238	6032	6682	5869	7578	7787	7797	5511	5972	5236	3651	3405	3411
palustric acid			1133			301	220							
RA312A + RA320A + RA332K**	169	1008	2049	1782	1555	1682	1429	1209	861	764	737	624	491	571
dehydroabietic acid	27	5978	14567	13796	12303	14901	14565	14683	10764	11840	11015	7892	7826	8085
abietic acid		3634	17429	12019	10871	11768	9846	5486	3097	1258	774	429	286	170
13ß-hydroxyabietanoic acid						518	603	721	486	814	1244	911	1005	1306
7-oxodehydroabietic acid											89	68	84	133
Total Resin Acids + Diterpenes	196	16392	52802	44633	39408	46448	43629	37938	26385	26153	23801	16921	16417	17153

** abietanoic (RA320A), 6,8,11,13-abietatetraenoic (RA312A), and 7-oxokauranoic (RA332K; very minor) acids coeluting

Chlorophenolics (ug/L):													
2,4-dichlorophenol	11.7	20.3	29.4	24.5	22.6	24.2	15.1	12.8	10.0	3.5	2.3	1.8	1.8
2,4,6-trichlorophenol	11.3	31.4	45.5	34.9	33.2	35.7	23.5	18.9	14.1	8.5	5.6	3.7	3.8
2,3,4,6-tetrachlorophenol*	1.2	4.5	7.2	4.9	4.8	4.9	3.7	3.4	3.0	0.2	0.4	0.3	0.3
pentachlorophenol	0.3	2.1	2.1	0.4	0.4	0.4	0.4	0.4	0.2	0.2	0.1	0.1	0.1
Total Chlorophenols	24	58	84	65	61	65	43	36	27	12	8.4	6.0	6.0
4,5-dichloroguaiacol	31.1	71.2	106.7	81.0	59.5	60.4	14.4	26.8	6.4	2.4	1.5	1.9	1.8
3,4,5-trichloroguaiacol	48.1	115.0	175.9	133.7	106.9	103.7	43.1	42.9	17.6	5.8	3.2	2.8	3.1
4,5,6-trichloroguaiacol	7.7	23.9	32.9	24.6	19.2	19.0	4.7	7.0	2.5	0.5	0.3	0.2	0.3
tetrachloroguaiacol	22.9	50.4	65.0	50.4	47.8	46.5	23.6	21.1	9.8	3.2	1.8	1.2	1.2
Total Chloroguaiacols	110	261	380	290	233	230	86	98	36	12	6.7	6.0	6.4
5-chlorovanillin*	2.4	9.0	14.6	9.9	9.6	9.8	7.5	6.9	6.0	0.4	0.7	0.6	0.5
6-chlorovanillin	47.0	121.4	182.8	162.7	129.1	127.2	79.2	79.9	49.4	5.9	3.6	3.4	2.7
5,6-dichlorovanillin	34.0	106.0	133.3	121.7	100.9	95.6	57.2	52.6	24.8	4.0	3.8	3.5	3.2
Total Chlorovanillins	83	236	331	294	240	233	144	139	80	10	8.1	7.5	6.4
3,4,5-trichlorocatechol	9.1	13.7	20.1	20.8	27.8	30.3	41.7	30.8	40.1	34.4	27.0	23.8	23.2
tetrachlorocatechol	9.5	18.4	24.4	23.4	12.7	10.4	13.6	14.1	10.0	7.4	7.9	6.8	6.1
Total Chlorocatechols	19	32	44	44	40	41	55	45	50	42	35	31	29
dichlorohydroxybenzaldehyde	17.1	46.0	64.2	55.6	51.3	49.6	36.5	30.5	24.8	7.2	5.1	4.4	3.6
Total chlorophenolics	253	634	904	748	626	618	364	348	219	84	63	54	52

*: 3 compounds coeluting - use peak area/3 for each of TetCP and 5-CV

Table A2.5 (cont.): EOs, CPs, sodium, and colour in P7 seepage basin monitoring trial

Date (day-month of1988)	23-11	24-11	25-11	26-11	27-11	29-11	01-12	05-12	07-12	08-12	12-12	14-12	16-12	20-12
sodium (mg/L)	358	376	377	393	392	202	199	181	177	177	206	208	204	229
colour (mg/L)	2089	2104	2160	2122	2180	1087	1103	878	845	856	1017	1043	1028	1160
Extractable Organics (ug/L):														
2,5-dimethyl-2-cyclopentenone	5	8	5	4	4									
2,3-dimethyl-2-cyclopentenone	92	57	77	66	74	5	4							
2,3,5-trimethyl-2-cyclopentenone	53	44	42	40	38	8	9	2	2	6	5	5	4	1
2,3,4-trimethyl-2-cyclopentenone	41	37	36	36	35	5	10	4	4	9	6	5	5	2
Total Methyl-2-cyclopentenones	192	146	159	146	152	19	23	6	5	16	11	10	9	4
dimethyltrisulphide	43	10	10	21	29	4	3							
guaiacol														
a-pinene	4													
b-pinene	18													
p-cymene														
limonene														
fenchol														
camphor	38	28	30	25	22	0	0	0	0	0	0	0	0	0
unid. MT154														
unid. MT154	13	8	7											
DHT	183	151	131	13	11									
borneol	21	32	17	30	37	13	17	2						
4-terpineol	33	16	15	15	13									
a-terpineol	374	133	22											
Total Monoterpenes	684	368	221	83	84	13	17	2	0	0	0	0	0	0
palmitoleic acid (FA16:1)								8	7	5	4	3	5	5
palmitic acid (FA16:0)	90	104	90	84	84	39	35	42	29	37	39	66	49	69
anteiso-heptadecanoic acid (FA17:0)														
FA18:3														
FA18:2														
linoleic acid (FA18:2)							61	7	5	8	4	5	4	9
oleic acid (FA18:1)	35	27	17	17	29	65	15	14	15	18	9	13	8	9
FA18:1	74	54	32	34	42	30								
stearic acid (FA18:0)	47	48	32	36	40	11	14	23	12	17	12	20	16	13
FA18:2														
epoxystearic acid														
Total Fatty Acids	246	233	171	170	194	145	125	94	68	84	68	108	83	104
fichtelite								14	14	9	12	13	16	15
dehydroabietin	69	19	20	58	32									
seco-dehydroabietic acid #1	583	502	529	552	518	208	209	190	64	59	14	16	15	9
seco-dehydroabietic acid #2	297	269	270	276	264	88	93	95	35	32	9	9	10	3
8,15-isopimaradienoic acid	167	152	168	180	192	33	33							
8,15-pimaradienoic acid	75	75	89	99	97	26	25							
pimaric acid	1932	1701	1684	1669	1569	379	379	27	18	16	20	19	21	25
sandaracopimaric acid	285	233	218	209	190	28	19	9	6	7	5	5	5	6
8(14)-pimarenoic acid	41	42	43	44	43	13	13	7	2	5	8	8	8	11
isopimaric acid	3066	2546	2369	2118	1573	80	82	16	11	13	12	14	10	17
palustric acid														
RA312A + RA320A + RA332K**	494	491	498	468	423	68	77	105	97	84	177	191	183	275
dehydroabietic acid	7585	6594	6416	5960	4653			15	13	12	24	28	24	
abietic acid	135		37	70	86	124	130	11						
13ß-hydroxyabietanoic acid	1616	1778	2137	2207	498									
7-oxodehydroabietic acid	193	201	246	247	64									
Total Resin Acids + Diterpenes	16537	14604	14725	14156	10205	1047	1059	489	260	238	281	304	292	361
Chlorophenolics (ug/L):														
2,4-dichlorophenol	1.3	0.9	0.9	1.0	1.0	0.2	0.2	0.2	0.0	0.1	0.0	0.1	0.1	0.2
2,4,6-trichlorophenol	2.3	1.8	1.9	1.5	1.5	0.4	0.4	0.3	0.2	0.1	0.2	0.2	0.2	0.2
2,3,4,6-tetrachlorophenol*	0.2	0.1	0.1	0.2	0.2	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.2
pentachlorophenol	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Chlorophenols	3.9	3.0	3.0	2.8	2.8	0.7	0.6	0.5	0.2	0.2	0.4	0.4	0.3	0.6
4,5-dichloroguaiacol	2.4	0.6	0.9	1.1	1.2	1.3	1.0	0.3	0.1	0.1	0.5	0.6	0.7	0.4
3,4,5-trichloroguaiacol	3.0	2.6	2.6	2.8	2.9	1.9	1.8	1.4	1.1	1.2	1.2	1.5	1.4	0.9
4,5,6-trichloroguaiacol	0.2	0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
tetrachloroguaiacol	0.8	0.9	0.8	0.7	0.7	0.5	0.4	0.3	0.3	0.2	0.3	0.3	0.3	0.2
Total Chloroguaiacols	6.4	4.2	4.5	4.7	4.9	3.8	3.4	2.1	1.6	1.6	2.1	2.5	2.5	1.6
5-chlorovanillin*	0.4	0.3	0.2	0.3	0.4	0.1	0.1	0.0	0.0	0.1	0.2	0.2	0.1	0.1
6-chlorovanillin	2.8	0.7	0.2	0.1	0.3	0.4	0.4	0.1	0.1	0.1	0.2	0.3	0.3	0.1
5,6-dichlorovanillin	3.1	3.7	3.4	3.3	3.8	0.2	0.2	0.1	0.1	0.1	0.1	0.2	0.1	0.1
Total Chlorovanillins	6.3	4.6	3.9	3.8	4.5	0.7	0.7	0.2	0.2	0.2	0.5	0.7	0.5	0.3
3,4,5-trichlorocatechol	17.3	23.9	23.0	21.7	23.4	5.6	5.4	2.7	3.0	3.0	5.8	5.6	4.8	5.6
tetrachlorocatechol	4.9	6.0	6.1	5.9	6.5	2.5	2.6	1.8	1.8	1.8	3.1	3.4	2.8	3.4
Total Chlorocatechols	22	30	29	28	30	8	8.0	4.5	4.8	4.8	8.9	8.9	7.6	9.0
dichlorohydroxybenzaldehyde	3.2	0.8	0.6	1.0	1.8	0.9	0.9	0.7	0.3	0.4	0.8	0.6	0.7	0.7
Total chlorophenolics	42	42	41	40	44	14	14	7.9	7.1	7.3	13	13	12	12

** abietanoic (RA320A), 6,8,11,13-abietatetraenoic (RA312A), and 7-oxokauranoic (RA332K; very minor) acids coeluting

*: 3 compounds coeluting - use peak area/3 for each of TetCP and 5-CV

Table A2.6: Extractable organics in sediments from beneath seepage basin P6. Concentrations are mg/kg dry sediment.

Depth (mm)	0-100	100-200	200-300	300-400	400-500	500-600	600-700	700-800	800-900	900-1000	1300-1400	background
FA16:0	53.0	12.0	1.5	1.3	0.3	0.7	2.3	1.8	1.7	2.8	2.4	0.9
FA18:1	9.0	NQ	0.7	0.5	0.1	0.4	0.7	0.4	0.6	0.4	0.8	0.6
FA18:0	30.0	5.0	0.6	0.4	0.1	0.3	0.9	0.7	0.6	0.9	1.0	0.5
FA20:0	63.0	10.0	0.5	0.2	0.1	0.2	0.9	0.3	0.6	0.6	0.8	0.9
FA22:0	144.0	32.0	2.4	0.7	0.3	0.4	2.8	1.1	2.3	1.8	3.0	2.2
FA24:0	79.0	15.0	1.6	NQ	0.2	NQ	1.4	0.9	2.3	1.1	2.6	2.1
Total Fatty Acids	378.0	74.0	7.3	3.1	1.1	2.0	9.0	5.2	8.1	7.6	10.6	7.2
fichtelite	51.0	30.0	1.5	0.5	0.1	0.2	0.8	4.1	2.7	3.6	1.6	0.1
dehydroabietin	372.0	367.0	0.9	0.2	0.1	2.5	0.4	2.3	4.8	15.1	2.0	0.1
tetrahydroretene	60.0	35.0	NQ	NQ	NQ	NQ	NQ	NQ	0.5	1.4	0.1	NQ
retene	74.0	10.0	1.6	0.3	0.1	0.1	0.8	13.0	35.5	4.3	0.8	NQ
Total Diterpene Hydrocarbons	557.0	442.0	4.0	1.0	0.3	2.8	2.0	19.4	43.5	24.4	4.5	0.2
seco-dehydroabietic acid #1	127.0	26.0	2.4	0.8	0.2	0.3	3.7	1.8	2.9	5.2	2.2	NQ
seco-dehydroabietic acid #2	87.0	12.0	1.0	0.3	0.1	0.1	1.8	NQ	1.0	1.7	0.9	NQ
8,15-pimarenoic acid	43.0	10.0	0.9	0.2	0.1	0.1	1.4	0.3	0.5	1.2	0.5	NQ
pimaric acid	216.0	45.0	3.3	1.1	0.3	0.6	5.3	1.1	2.7	7.3	2.7	0.3
8-isopimarenoic acid	NQ	NQ	0.9	0.3	0.1	0.1	0.6	0.3	0.5	0.8	0.7	NQ
8-pimarenoic acid	94.0	22.0	2.4	0.9	0.3	0.4	2.5	1.2	2.9	4.0	1.9	0.4
pimaranoic acid	130.0	36.0	4.8	1.3	0.4	0.3	3.3	3.6	2.6	5.3	1.9	NQ
13-abietenoic acid	219.0	55.0	4.6	1.5	0.5	0.7	5.7	1.8	3.5	7.5	3.3	0.4
isopimaranoic acid	NQ	NQ	NQ	0.1	NQ	0.2	0.6	NQ	NQ	NQ	0.3	0.1
abietanoic acid	2034.0	1023.0	64.5	19.2	20.6	7.3	67.8	26.4	59.1	106.6	54.1	1.0
dehydroabietic acid	508.0	253.0	14.7	4.5	5.0	2.0	21.0	4.8	13.1	22.3	13.7	4.2
Total Resin Acids	3458.0	1482.0	99.5	30.2	27.6	12.1	113.7	41.3	88.8	161.9	82.2	6.4

NQ: not quantified (below peak detection threshold).

Table A2.7: Extractable organics in sediments from Pit C3. Concentrations in mg/kg dry sediment.

Depth (m)	0.0	0.7	0.8	0.8	0.9	1.8	2.5
F14:0	3.7	0.8	0.5	2.4	0.7	0.6	0.3
F15:0	NQ	0.4	0.5	1.5	0.5	0.5	0.3
F16:1	NQ	0.2	0.2	2.3	0.5	NQ	0.2
F16:0	37.6	5.1	3.2	10.7	4.1	4.2	2.1
F18:1	NQ	1.8	0.8	5.1	1.0	0.8	0.4
F18:0	14.9	3.0	1.7	5.2	1.5	2.2	0.7
F20:0	4.0	1.3	0.4	0.4	NQ	0.4	NQ
F22:0	14.2	3.2	1.0	1.1	0.3	2.3	0.3
F24:0	3.9	2.0	0.4	1.4	0.4	1.1	0.3
Total Fatty Acids	78.3	17.7	8.8	30.0	9.0	12.0	4.6
fichtelite	19.7	13.6	6.2	8.8	3.5	81.8	NQ
dehydroabietin	977.5	371.3	99.3	51.2	4.3	15.9	1.3
tetrahydroretene	23.0	6.9	2.5	2.3	NQ	5.7	NQ
retene	NQ	1.0	0.0	4.4	1.9	75.7	NQ
Total Diterpene Hydrocarbons	1020.2	392.9	108.1	66.7	9.7	179.0	1.3
seco-dehydroabietic acid #1	33.2	22.8	9.7	10.3	0.8	7.7	1.0
seco-dehydroabietic acid #2	13.1	10.4	3.9	6.8	0.8	5.4	0.8
pimaric + 8-isopimarenoic acids	33.3	13.6	6.1	1.7	0.3	5.6	0.7
sandaracopimaric + 8-pimarenoic acids	NQ	9.0	5.1	2.1	0.3	4.6	0.5
pimaranoic acid	44.7	56.6	38.0	16.8	1.9	22.0	2.1
13-abietenoic + isopimaranoic acids	19.9	16.5	10.8	8.3	1.4	10.5	0.8
abietanoic + dehydroabietic acids	696.0	151.1	94.2	54.7	11.2	75.7	17.6
Total Resin Acids	840.2	280.1	167.8	100.7	16.7	131.4	23.5

NQ: not quantified (below peak detection threshold).

Table A2.8: Extractable organics in Pond E sediment core. Concentrations in mg/kg dry sediment (<0.25 mm fraction)

Sample Code	A1	A5	B1	B5	B9	B13	B17	B21	B25	C1	C5	D1	D5
Depth Interval (mm)	5 - 18	18-31	31-47	47-64	64-80	92-108	123-142	155-175	175-197	198-215	215-236	240-248	248-260
FA14:0	18.1	45.2	15.3	19.5	13.9	6.7	8.4	6.4	4.9	6.6	7.7	8.1	2.0
FA15:0	NQ	NQ	4.3	5.9	4.6	2.2	1.8	1.6	NQ	1.6	1.7	2.2	7.3
FA16:0	46.6	83.8	42.9	61.2	21.9	24.5	19.2	15.3	11.5	15.7	17.8	23.9	65.6
FA18:1	41.0	61.6	47.3	45.1	8.3	31.8	22.0	4.7	6.9	18.2	6.7	21.7	13.3
FA18:0	18.0	36.1	14.7	19.7	14.1	10.9	7.6	5.5	3.8	5.7	5.3	11.6	22.1
FA22:0	123.7	27.7	13.2	4.9	7.2	7.7	1.9	1.1	NQ	1.2	NQ	10.4	7.6
FA24:0	122.0	23.9	10.6	NQ	8.2	7.9	NQ	1.9	1.7	2.3	NQ	11.8	9.4
Total Fatty Acids	369.4	278.3	148.3	156.3	78.2	91.7	60.9	36.5	28.8	51.3	39.2	89.7	127.3
DT262P	104.7	61.0	25.9	13.5	18.2	3.4	3.8	2.6	2.6	2.0	2.4	3.0	NQ
DT260P	47.9	24.3	12.2	8.0	44.1	2.4	2.3	1.7	1.9	1.4	2.1	2.6	NQ
DT260I	26.1	NQ	4.1	NQ	1.8	0.9	NQ	0.6	NQ	0.5	NQ	4.8	7.3
fichtelite	1368.0	741.3	305.8	142.5	177.7	46.3	45.4	38.5	54.8	38.9	50.3	86.0	113.0
dehydroabietin	1166.0	288.0	39.0	10.3	9.0	2.6	1.4	1.1	1.2	1.5	1.5	45.0	250.6
caxtonellite	51.0	26.2	7.6	NQ	2.0	1.1	0.8	0.5	1.1	0.6	1.2	10.1	16.7
tetrahydroretene	1314.0	287.6	55.6	37.9	41.1	8.0	1.7	NQ	1.1	0.8	1.2	62.3	97.0
retene	3337.8	1023.1	290.7	33.2	173.0	160.6	128.1	30.9	49.8	41.0	42.6	154.9	151.0
Total Diterpene Hydrocarbons	7415.5	2451.5	740.9	245.4	466.9	225.3	183.5	75.9	112.5	86.7	101.3	368.7	635.6
seco-dehydroabietic acid #1	228.9	131.7	41.2	19.3	17.3	9.6	6.6	5.6	7.8	6.6	6.8	21.1	36.6
seco-dehydroabietic acid #2	57.2	32.9	10.3	4.8	4.3	2.4	1.7	1.4	2.0	1.7	1.7	5.3	9.2
pimaric acid	35.0	NQ	NQ	NQ	3.4	1.1	0.6	0.5	NQ	1.9	NQ	NQ	5.6
8-isopimarenoic acid	88.5	27.0	9.1	5.9	1.6	1.5	NQ	NQ	NQ	1.0	NQ	NQ	7.4
8-pimarenoic acid	129.3	62.6	25.1	10.0	7.9	4.4	3.1	3.6	5.0	3.8	3.6	13.3	23.4
pimaranoic acid	343.2	163.7	59.5	27.0	29.2	7.9	5.1	4.0	4.0	3.5	3.5	11.2	12.2
13-abietenoic acid + isopimaranoic acid	194.5	57.8	20.2	7.8	14.9	1.9	1.7	2.5	2.2	1.9	NQ	12.6	5.7
isopimaranoic acid	NQ	NQ	18.5	9.9	NQ	7.9	2.8	1.7	1.3	2.5	2.1	NQ	NQ
abietanoic acid	2207.0	968.0	381.2	112.0	99.5	52.8	24.1	20.6	27.0	23.3	18.6	86.7	156.3
dehydroabietic acid	205.1	131.2	44.6	23.0	12.2	10.0	4.9	3.4	4.8	5.6	2.6	13.5	13.6
Total Resin Acids	3488.7	1574.9	609.7	219.7	190.3	99.5	50.6	43.3	54.1	51.8	38.9	163.7	270.0
ß-sitosterol	1061.0	89.7	128.0	36.5	64.3	39.1	NQ	23.0	12.0	25.8	6.6	66.4	85.4
sitostanol	294.1	26.7	34.8	10.7	19.1	14.7	NQ	21.0	11.7	25.6	5.7	34.3	NQ
Total Sterols	1355.1	116.4	162.8	47.2	83.4	53.8	NQ	44.0	23.7	51.4	12.3	100.7	85.4

Table A2.8 (cont.): Extractable organics in Pond E sediment core. Concentrations in mg/kg dry sediment (<0.25 mm fraction)

Sample Code	D9	D13	D17	D21	D25	E1	E5	E9	E17	E21	E25	E29	F5
Depth Interval (mm)	272-289	303-321	339-355	373-395	413-437	442-467	467-485	503-522	630-658	696-721	788-810	854-884	902-923
FA14:0	12.8	7.3	6.2	7.7	8.6	3.3	3.3	3.1	2.6	5.6	1.9	1.6	0.7
FA15:0	2.9	1.6	1.5	2.0	NQ	0.7	0.9	0.8	0.4	0.9	0.8	0.5	0.4
FA16:0	32.9	21.9	19.4	25.1	23.3	8.2	9.3	7.2	6.0	14.0	10.9	4.2	1.1
FA18:1	13.3	4.9	3.9	4.6	4.5	1.1	1.3	0.9	0.8	1.2	1.8	1.3	1.1
FA18:0	10.6	9.5	7.6	9.6	8.1	3	3.2	2.4	1.9	4.2	5.0	1.8	2.8
FA22:0	1.9	3.1	2.2	4.8	2.1	0.4	NQ	NQ	NQ	NQ	NQ	NQ	NQ
FA24:0	NQ	1.9	1.8	5.4	NQ	0.5	0.2	0.2	NQ	NQ	NQ	NQ	NQ
Total Fatty Acids	74.4	50.2	42.6	59.2	46.6	17.2	18.2	14.6	11.7	25.9	20.4	9.4	6.1
DT262P	NQ	0.4	NQ	NQ	NQ	0.1	NQ	NQ	NQ	NQ	NQ	NQ	NQ
DT260P	NQ	0.4	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
DT260I	NQ	NQ	NQ	NQ	NQ	0.1	NQ	NQ	NQ	NQ	NQ	NQ	NQ
fichtelite	10.9	8.9	10.4	14.3	11.0	3.0	2.0	1.9	0.6	0.4	NQ	NQ	NQ
dehydroabietin	5.1	2.1	1.0	0.8	1.9	0.2	NQ	NQ	NQ	NQ	NQ	NQ	NQ
caxtonellite	2.0	1.5	1.3	2.1	2.1	0.4	0.4	0.4	NQ	NQ	NQ	NQ	NQ
1,2,3,4-tetrahydroretene	15.2	26.8	17.1	27.8	17.4	2.9	1.9	1.6	NQ	NQ	NQ	NQ	NQ
retene	11.8	29.1	16.6	43.5	25.1	10.6	10.9	11.2	2.5	0.7	1.0	3.0	0.0
Total Diterpene Hydrocarbons	45.0	69.2	46.4	88.5	57.5	17.3	15.2	15.1	3.1	1.1	1.0	3.0	0.0
seco-dehydroabietic acid #1	1.7	3.5	3.2	6.3	4.0	1.3	0.9	0.7	NQ	NQ	NQ	NQ	NQ
seco-dehydroabietic acid #2	0.4	0.9	0.8	1.6	1.0	0.3	0.2	0.2	NQ	NQ	NQ	NQ	NQ
pimaric acid	NQ	0.6	1.6	NQ	NQ	0.8	0.5	NQ	NQ	NQ	1.0	NQ	NQ
8-isopimarenoic acid	NQ	2.6	1.3	NQ	NQ	0.7	0.5	NQ	NQ	NQ	0.5	NQ	NQ
8-pimarenoic acid	NQ	2.5	1.9	3.0	2.7	0.8	NQ	NQ	NQ	NQ	NQ	NQ	NQ
pimaranoic acid	NQ	3.3	1.3	7.3	1.3	0.7	NQ	NQ	NQ	NQ	NQ	NQ	NQ
13-abietenoic acid + isopimaranoic acid	NQ	3.1	2.0	3.8	1.5	0.9	NQ	NQ	NQ	NQ	NQ	NQ	NQ
isopimaranoic acid	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
abietanoic acid	9.6	12.7	12.2	49.3	13.5	4.2	3.2	2.1	0.7	NQ	0.7	NQ	1.9
dehydroabietic acid	2.7	6.0	4.3	7.7	3.4	2.0	1.4	1.4	0.3	NQ	NQ	NQ	NQ
Total Resin Acids	14.4	35.2	28.6	79.0	27.4	11.7	6.7	4.4	1.0	NQ	2.2	NQ	1.9
ß-sitosterol	NQ	6.0	2.8	3.0	10.5	4.1	2.4	2.8	NQ	NQ	NQ	NQ	NQ
sitostanol	NQ	3.5	NQ	NQ	5.0	2.9	1.7	2.4	NQ	NQ	NQ	NQ	NQ
Total Sterols	NQ	9.5	2.8	3.0	15.5	7.0	4.1	5.2	NQ	NQ	NQ	NQ	NQ

NQ: not quantified (below peak detection threshold).

Table A2.9: Extractable organics in core from bore 10. Concentrations in mg/kg dry sediment.

Depth (m)	0	0.5	1	1.5	2	3	4	5	6	7	8	9.5	12
F14:0	0.8	1.2	10.4	2.1	3.7	1.7	3.2	2.0	1.5	1.6	1.9	0.3	0.2
F15:0	0.7	1.1	NQ	1.4	2.7	1.4	2.6	1.3	1.4	1.0	1.4	0.5	0.2
F16:1	NQ	NQ	NQ	1.6	6.0	2.8	1.5	2.4	2.4	1.0	2.7	0.3	0.3
F16:0	13.6	6.3	185.1	20.7	14.1	7.5	16.1	7.8	7.6	5.1	7.6	2.5	1.5
F18:1	NQ	NQ	29.5	2.2	6.2	2.7	1.6	2.8	2.1	1.0	2.3	0.4	0.3
F18:0	5.0	1.8	76.5	6.8	3.8	2.3	4.1	2.0	1.9	1.4	2.0	0.8	0.4
F20:0	6.0	0.4	8.0	2.9	0.8	0.3	0.3	NQ	0.1	NQ	0.1	NQ	NQ
F22:0	14.6	0.9	44.4	4.5	2.4	0.3	1.0	NQ	0.3	NQ	0.2	NQ	NQ
F24:0	5.8	0.5	12.2	1.5	1.5	0.3	0.3	NQ	0.1	NQ	0.2	NQ	NQ
Total Fatty Acids	46.5	12.4	366.1	43.7	41.1	19.3	30.6	18.2	17.5	11.2	18.5	4.8	3.0
fichtelite	5.9	1.1	13.7	2.9	3.7	0.0	0.8	1.8	0.7	0.5	0.7	NQ	NQ
dehydroabietin	2.9	0.9	602.1	16.1	3.9	1.8	0.8	1.1	0.9	0.4	0.9	NQ	NQ
tetrahydroretene	0.0	NQ	32.4	0.9	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
retene	0.0	0.6	613.4	12.9	51.3	127.3	5.6	8.8	1.7	NQ	NQ	NQ	NQ
Total Diterpene Hydrocarbons	8.8	2.7	1261.5	32.8	58.9	129.1	7.2	11.7	3.3	0.9	1.6	NQ	NQ
seco-dehydroabietic acid #1	26.4	1.4	177.1	12.2	5.0	NQ	2.2	0.3	0.3	NQ	NQ	NQ	NQ
seco-dehydroabietic acid #2	9.5	0.7	116.6	7.0	2.5	NQ	1.0	NQ	0.2	NQ	NQ	NQ	NQ
pimaric + 8-isopimarenoic acids	38.5	1.0	341.3	23.7	7.7	NQ	2.4	0.6	0.1	NQ	0.2	NQ	0.2
sandaracopimaric + 8-pimarenoic acids	3.8	NQ	48.8	2.5	5.8	1.5	0.5	0.6	0.4	NQ	0.3	0.2	NQ
pimaranoic acid	16.3	1.9	25.1	1.4	5.5	NQ	1.3	NQ	NQ	NQ	NQ	0.2	NQ
isopimaric + 13-abietenoic + isopimaranoic acids	14.2	1.8	338.1	29.6	8.4	0.5	1.9	0.7	0.1	NQ	NQ	0.2	0.2
abietanoic + dehydroabietic acids	548.8	26.7	1733.8	166.3	57.9	9.5	36.8	13.6	1.8	1.0	0.8	1.2	1.9
Total Resin Acids	657.5	33.6	2780.7	242.7	92.7	11.6	46.1	15.8	2.9	1.0	1.4	1.7	2.3

Table A2.10: Extractable organicsin core from bore 11. Concentrations in mg/kg dry sediment.

Depth (m)	0	0.5	1	2	3	4	5	6	7	8	9
F14:0	NQ	0.6	0.6	0.7	0.9	1.0	1.1	0.8	0.5	0.5	0.8
F15:0	NQ	0.6	0.5	0.6	0.7	0.8	0.7	0.6	0.5	0.4	0.5
F16:1	NQ	0.9	0.9	1.0	1.3	1.8	4.3	1.0	0.9	0.7	1.0
F16:0	32.5	2.4	2.7	3.4	4.9	4.2	30.5	3.6	3.0	2.1	2.6
F18:1	NQ	1.0	1.2	1.6	2.2	1.9	2.0	1.1	1.0	0.7	1.0
F18:0	14.2	0.8	0.8	1.1	2.0	1.3	2.5	1.3	1.0	0.6	1.1
F20:0	18.1	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
F22:0	57.6	1.3	1.5	0.4	2.0	0.3	3.3	0.2	NQ	NQ	NQ
F24:0	26.9	1.1	1.4	0.4	1.6	0.3	2.2	0.1	NQ	NQ	NQ
Total Fatty Acids	149.2	8.6	9.4	9.2	15.7	11.6	46.7	8.6	7.0	4.9	6.9
DT260	NQ	NQ	NQ	NQ	4.9	NQ	12.5	NQ	NQ	NQ	NQ
fichtelite	13.5	0.7	NQ	0.5	118.4	5.3	555.8	1.8	1.3	0.4	0.2
dehydroabietin	NQ	NQ	NQ	2.6	1.4	0.4	NQ	0.3	0.3	0.2	0.3
tetrahydroretene	NQ	NQ	NQ	0.2	0.6	NQ	NQ	NQ	NQ	NQ	NQ
retene	NQ	NQ	NQ	0.4	32.0	16.2	782.8	NQ	0.2	NQ	NQ
Total Diterpene Hydrocarbons	13.5	0.7	NQ	3.7	157.3	21.9	1351.0	2.0	1.7	0.7	0.5
seco-dehydroabietic acid #1	76.8	3.1	1.5	0.7	1.3	NQ	3.3	0.2	NQ	NQ	NQ
seco-dehydroabietic acid #2	28.3	1.2	0.8	0.3	1.4	NQ	NQ	0.1	NQ	NQ	NQ
pimaric + 8-isopimarenoic acids	100.9	3.0	2.1	0.8	2.8	0.4	4.9	0.5	0.1	0.1	NQ
sandaracopimaric + 8-pimarenoic acids	24.8	4.2	1.0	1.5	5.4	0.4	3.1	0.3	0.1	0.1	NQ
pimaranoic acid	37.2	3.9	1.1	0.9	7.1	0.2	16.1	0.3	0.1	0.1	NQ
isopimaric + 13-abietenoic + isopimaranoic acids	127.2	3.5	2.6	0.8	3.5	0.2	5.1	0.3	0.1	0.1	NQ
abietanoic + dehydroabietic acids	1395.2	50.1	24.3	12.2	28.5	1.9	19.2	4.6	1.3	0.4	NQ
Total Resin Acids	1790.4	69.0	33.5	17.1	50.1	3.2	51.7	6.3	1.7	0.8	NQ

Table A2.11: Extractable organics in core from bore 16. Concentrations in mg/kg dry sediment.

Depth (m)	0	0.5	1.5	2	3	4	5	6	7	8	11
F14:0	0.3	0.9	0.7	1.6	0.9	0.6	1.0	0.8	0.8	0.5	0.3
F15:0	0.2	0.4	0.6	1.2	0.7	0.5	1.0	0.5	0.7	0.4	0.2
F16:1	0.4	1.0	0.6	1.2	0.8	0.6	0.0	0.5	0.8	0.5	0.3
F16:0	1.6	1.9	3.8	6.6	3.9	2.6	5.4	2.1	3.3	2.6	1.2
F18:1	0.4	0.6	0.6	1.8	0.8	0.7	0.4	0.8	1.2	0.6	0.4
F18:0	0.5	0.5	1.3	1.8	1.1	0.8	1.4	0.7	1.1	0.7	0.5
F20:0	0.1	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
F22:0	0.2	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
F24:0	0.2	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
Total Fatty Acids	4.0	5.3	7.5	14.2	8.2	5.7	9.1	5.4	7.9	5.3	2.8
fichtelite	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
dehydroabietin	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
tetrahydroretene	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
retene	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
Total Diterpene Hydrocarbons	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
seco-dehydroabietic acid #1	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
seco-dehydroabietic acid #2	0.1	NQ	NQ	NQ	0.5	NQ	NQ	NQ	NQ	NQ	NQ
pimaric + 8-isopimarenoic acids	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
sandaracopimaric + 8-pimarenoic acids	NQ	1.1	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
pimaranoic acid	0.1	0.6	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
isopimaric + 13-abietenoic + isopimaranoic acids	1.0	0.6	NQ	3.6	2.5	NQ	NQ	NQ	NQ	NQ	NQ
abietanoic + dehydroabietic acids	1.2	2.3	NQ	3.6	2.9	NQ	NQ	NQ	NQ	NQ	NQ
Total Resin Acids	2.3	4.6	NQ	7.2	5.8	NQ	NQ	NQ	NQ	NQ	NQ

NQ: not quantified (below peak detection threshold).

Table A2.12: Shallow ground water EO chemistry - October 1987 sampling. Concentrations in ug/L.

Bore	B10/1	B10/2**	B11/1	B11/2	B11/3**	B12/1	B13/1**	B14/1	B15/1	B16/1**
2,3,5-TMCP (+ 2-ethylhexanoic acid)	53.8	36.5	93.4	9.1	174.4	72.8	6.7	61.4	7.5	20.8
2,3,4-TMCP	37.7	35.3	59.6	11.2	75.3	53.9	11.9	55.1	29.0	37.7
TetMCP (isomer unknown)	19.7	17.2	19.7	6.1	35.1	19.6	5.9	18.9	0.0	13.6
TetMCP (isomer unknown)	23.6	4.7	6.4	5.1	10.9	5.3	2.0	5.9	16.0	5.2
TetMCP (isomer unknown)	11.7	6.7	26.0	13.2	53.3	21.4	4.2	19.7	2.6	12.4
Total methyl-2-cyclopentenones	146.4	100.4	205.1	44.7	349.0	173.0	30.6	160.9	55.1	89.8
FA16:0	17.4	15.6	9.9	11.2	27.6	28.3	0.7	13.0	6.0	0.0
FA18:0	17.3	16.7	4.4	4.5	26.5	23.2	0.7	8.4	4.9	4.7
Total Fatty Acids	34.8	32.3	14.4	15.7	54.2	51.4	1.4	21.4	11.0	4.7
DT260P	0.0	0.9	17.3	20.8	5.1	5.4	0.0	6.9	0.0	26.8
DT260I	0.0	0.9	15.8	11.7	19.3	0.0	0.0	16.2	0.0	0.0
DT260A	0.0	0.0	0.0	0.0	0.0	131.7	0.0	7.2	0.0	213.2
DT262P	0.0	0.0	0.0	0.0	0.0	26.3	0.0	0.0	0.0	0.0
fichtelite	3.1	1.9	140.3	158.2	74.8	929.3	0.0	50.2	0.0	1104.4
dehydroabietin	2.4	0.0	6.5	5.8	0.0	1112.7	0.0	0.0	0.0	901.8
tetrahydroretene	0.0	0.0	0.0	0.0	0.0	100.1	0.0	0.0	0.0	200.6
seco-dehydroabietic acid #1	1.7	0.0	5.6	9.2	5.8	29.4	0.0	2.7	0.0	14.6
retene	8.7	1.1	34.5	200.5	13.7	183.3	0.0	57.4	0.0	65.8
seco-dehydroabietic acid #2	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
unid. mw=290?	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8-pimarenoic acid	2.6	1.1	9.3	19.6	4.2	28.8	0.0	3.9	0.0	13.4
8-isopimarenoic acid	0.0	1.2	13.1	26.7	11.0	7.8	0.0	10.6	0.0	3.1
pimaranoic acid	3.5	2.0	17.3	31.2	19.2	16.9	0.0	7.9	0.0	4.7
unid. RA304?	4.8	4.0	9.3	20.0	13.8	13.3	1.8	11.3	4.3	2.0
unid. RA316?	3.3	2.4	9.3	14.3	4.6	5.0	3.3	15.0	4.6	2.0
abietanoic + 7-oxokauranoic acids	34.3	19.7	109.4	196.9	90.7	73.7	19.2	129.4	20.8	48.3
dehydroabietic acid	12.7	4.4	34.7	56.2	26.7	16.9	4.4	27.9	5.6	10.6
unid. RA330?	0.0	2.0	0.0	0.0	0.0	4.2	1.4	3.6	0.0	3.9
unid. RA273?	3.5	0.0	7.7	9.1	4.2	3.7	0.0	11.9	2.4	1.6
unid. RA332 ?	8.4	7.6	15.3	9.1	6.6	9.2	5.7	21.8	7.6	4.3
unid. RA350?	0.0	0.0	22.6	61.4	0.0	0.0	11.7	0.0	0.0	11.4
unid. RA348?	0.0	0.0	46.2	80.5	0.0	0.0	9.3	0.0	0.0	13.4
unid. RA350?	10.1	21.4	47.6	44.3	23.9	14.1	11.2	16.0	12.3	14.7
unid. RA350?	7.8	8.1	19.9	27.6	4.5	5.3	4.0	9.6	4.4	3.9
unid. mw=400?	9.4	7.4	19.3	27.8	9.8	8.3	5.0	24.5	6.4	12.8
unid. mw=402?	35.5	19.3	43.1	49.7	28.9	36.6	11.4	81.0	21.0	32.0
unid. mw=400?	4.4	5.0	11.6	25.1	4.1	3.3	2.3	12.5	3.4	6.2
Total DTs	14.2	4.9	214.3	397.0	113.0	2488.8	0.0	137.9	0.0	2512.7
Total identified RAs	57.4	28.4	189.4	339.8	157.7	173.6	23.6	182.4	26.4	94.7
Total identified RAs+DTs	71.6	33.3	403.7	736.7	270.6	2662.5	23.6	320.3	26.4	2607.4
Total DT + RA + RA330-350?	109.5	78.7	581.6	1003.1	328.3	2717.3	72.0	409.7	62.0	2664.7

** FA17:0 surrogate not added. Concns are not recovery corrected.

Table A2.13: Shallow ground water EO chemistry - November 1987 sampling. Concentrations in ug/L.

Bore	B10/1	B10/2**	B11/1**	B11/2	B12/1	B13/1	B14/1	B15/1	B16/1
2,3,5-TMCP + 2-ethylhexanoic acid	67.0	52.7	55.7	133.2	38.6	0.0	80.4	0.0	12.2
2,3,4-TMCP	52.7	63.8	53.0	66.3	35.8	0.0	71.2	0.0	30.6
TetMCP (isomer unknown)	23.7	41.4	21.4	25.3	13.9	0.0	22.1	0.0	10.6
TetMCP (isomer unknown)	6.5	13.1	6.1	13.7	4.6	0.0	8.0	0.0	2.9
TetMCP (isomer unknown)	17.0	26.4	38.4	39.6	13.9	0.0	24.4	0.0	7.7
Total Methyl-2-cyclopentenones	167.0	197.6	174.7	278.1	106.8	0.0	206.1	0.0	64.0
FA16:0	29.8	15.4	19.6	17.7	27.9	3.5	3.6	1.2	5.7
FA18:0	29.1	12.4	18.7	13.0	0.0	4.1	3.4	1.2	4.6
Total Fatty Acids	58.9	27.8	38.2	30.7	27.9	7.6	7.1	2.3	10.3
DT260P	3.6	2.9	7.6	14.4	31.5	0.0	0.0	0.0	13.6
DT260I	0.0	0.0	73.9	66.0	166.5	0.0	0.0	0.0	125.0
DT260A	0.0	0.0	11.2	17.5	9.5	0.0	0.0	0.0	0.0
DT262P	0.0	0.0	12.1	6.4	0.0	0.0	0.0	0.0	31.1
fichtelite	2.5	2.9	312.0	227.7	954.4	0.0	40.7	0.0	648.5
dehydroabietin	0.0	3.6	16.5	4.8	511.2	0.0	0.0	0.0	19.2
tetrahydroretene	0.0	0.0	2.7	4.6	33.6	0.0	0.0	0.0	3.8
seco-dehydroabietic acid #1	5.5	10.0	10.4	14.0	43.7	0.0	6.2	1.5	34.4
retene	10.3	10.5	281.8	106.9	246.7	0.0	28.3	0.8	26.8
seco-dehydroabietic acid #2	2.8	6.5	5.2	7.0	21.9	0.0	3.1	0.8	17.2
unidentified m/z 290?	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8-pimaren-18-oic acid	1.5	3.3	8.7	10.1	14.2	0.0	0.0	0.0	3.8
8-isopimaren-18-oic acid	6.7	13.1	24.4	37.6	10.0	0.0	7.1	0.0	0.0
pimaranoic acid	3.0	3.8	40.6	44.4	22.7	0.0	8.2	0.0	3.4
unid. RA304?	6.1	12.0	22.2	24.2	11.5	3.0	10.7	4.6	4.8
unid. RA316?	5.1	13.0	12.2	14.1	16.0	7.0	13.8	5.0	3.8
abietanoic + 7-oxokauranoic acids	40.8	91.8	154.9	197.3	102.6	33.9	159.6	23.6	49.0
dehydroabietic acid	19.5	27.6	45.2	52.5	27.5	8.6	23.8	6.8	12.2
unid. RA330?	2.1	6.1	3.8	3.4	0.0	2.9	4.8	1.2	0.0
unid. RA273?	10.9	8.5	9.8	3.6	6.0	3.5	8.0	1.7	0.0
unid. RA332 ?	11.0	22.4	9.4	10.7	18.4	7.3	17.5	5.3	10.5
unid. RA350?	19.4	48.5	37.7	0.0	29.9	17.5	39.5	16.6	16.4
unid. RA348?	18.9	46.8	30.8	32.8	33.5	15.1	34.4	16.1	23.8
unid. RA350?	16.5	44.3	23.6	0.0	32.3	15.3	35.0	15.7	31.8
unid. RA350?	5.6	13.9	7.0	4.2	11.1	5.5	10.9	4.9	10.6
unid. mw=400?	9.4	26.1	13.3	11.7	23.2	7.7	28.7	7.1	19.6
unid. mw=402?	39.6	105.3	45.0	49.0	70.0	17.6	88.8	25.1	56.4
unid. mw=400?	4.2	12.3	23.4	22.1	8.9	3.3	13.7	3.7	9.9
Total DTs	16.4	19.9	717.8	448.3	1953.3	0.0	69.1	0.8	868.1
Total identified RAs	79.7	156.0	289.5	362.8	242.6	42.5	208.0	32.6	120.0
Total identified RAs+DTs	96.1	175.9	1007.3	811.2	2195.9	42.5	277.0	33.4	988.1
Total DT + RA + RA330-350?	191.8	391.4	1163.7	904.1	2354.6	119.8	451.4	104.4	1089.8

** FA17:0 surrogate not added to B10/2 and B11/1. Concns are not recovery corrected.

Table A2.14: Shallow ground water EO chemistry - December 1987 sampling. Concentrations in ug/L.

Bore	B10/1	B10/2	B11/1	B12/1	B13/1	B14/1	B15/1	B16/1
2,3,5-TMCP (+ 2-ethylhexanoic acid)	71.7	64.4	8.9	52.3	15.5	46.2	0.0	4.2
2,3,4-TMCP	47.5	47.5	18.4	52.0	11.2	46.2	6.0	24.6
TetMCP (isomer unknown)	27.3	22.6	6.4	19.4	7.4	16.3	2.5	11.1
TetMCP (isomer unknown)	6.5	7.1	1.8	6.0	2.0	5.3	0.0	2.7
TetMCP (isomer unknown)	9.2	10.1	4.6	18.4	2.7	16.9	0.0	3.3
Total methyl-2-cyclopentenones	162.2	151.6	40.1	148.0	38.8	130.9	8.5	45.9
FA16:0	15.0	14.0	34.0	31.1	25.3	14.3	10.1	35.3
FA18:0	11.2	13.4	34.4	81.8	28.7	14.7	11.8	74.3
Total Fatty Acids	26.2	27.4	68.4	112.9	53.9	29.0	21.9	109.7
DT260P	0.0	0.0	0.0	32.2	0.0	19.1	0.0	13.3
DT260I	0.0	0.0	11.2	176.4	0.0	19.4	0.0	137.1
DT260A	0.0	0.0	0.0	12.4	0.0	0.0	0.0	0.0
DT262P	0.0	0.0	0.0	54.0	0.0	0.0	0.0	42.7
fichtelite	4.1	2.0	72.7	1058.1	3.7	97.3	0.0	706.0
dehydroabietin	0.0	0.0	4.3	460.2	0.0	0.0	0.0	27.6
tetrahydroretene	0.0	0.0	0.0	93.8	0.0	0.0	0.0	12.0
seco-dehydroabietic acid #1	0.0	0.0	0.0	18.1	0.0	0.0	0.0	15.3
retene	15.1	5.7	364.9	286.2	0.0	427.5	0.0	23.8
seco-dehydroabietic acid #2	0.0	0.0	0.0	9.1	0.0	0.0	0.0	7.7
unid. mw=290?	9.7	0.0	0.0	13.6	0.0	0.0	0.0	0.0
8-pimarenoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.3
8-isopimarenoic acid	9.5	0.0	14.0	8.1	0.0	0.0	3.3	0.0
pimaranoic acid	3.2	1.7	19.9	20.4	0.0	16.8	0.0	13.0
unid. RA304?	7.2	3.6	25.6	21.7	0.0	22.6	13.2	6.1
unid. RA316?	8.0	1.7	7.7	0.0	0.0	20.4	0.0	6.1
abietanoic + 7-oxokauranoic acids	47.2	35.0	122.6	130.0	57.6	183.1	50.2	36.8
dehydroabietic acid	17.9	15.7	48.8	52.7	32.1	44.6	9.1	34.2
unid. RA330?	3.6	3.0	9.6	0.0	3.7	0.0	4.0	0.0
unid. RA273?	9.2	11.4	15.5	0.0	7.5	14.2	10.6	0.0
unid. RA332 ?	13.9	14.8	26.3	18.6	10.7	39.6	20.5	0.0
unid. RA350?	25.1	21.1	56.3	41.8	26.9	71.1	44.4	0.0
unid. RA348?	23.0	19.0	74.5	39.5	45.3	87.1	49.1	20.6
unid. RA350?	25.1	20.4	65.8	44.5	33.9	104.0	53.2	14.4
unid. RA350?	7.6	6.3	26.3	20.0	31.8	43.6	26.9	0.0
unid. mw=400?	15.4	11.4	29.9	30.1	12.3	58.7	23.2	9.4
unid. mw=402?	54.5	43.1	85.3	62.3	33.4	119.8	75.1	34.5
unid. mw=400?	8.8	6.8	20.6	13.9	8.5	30.1	13.1	0.0
Total DTs	19.2	7.8	453.1	2173.3	3.7	563.4	0.0	962.6
Total identified RAs	77.8	52.4	205.3	238.4	89.7	244.5	62.6	115.3
Total identified RAs+DTs	97.0	60.1	658.4	2411.7	93.5	807.9	62.6	1077.9
Total DT + RA + RA330-350?	229.4	161.5	966.1	2611.5	253.2	1210.4	284.5	1125.2

* seco-2 calculated as 0.5 x seco-1 (some coelution with retene)

Table A2.15: Shallow ground water EO chemistry - July 1988 sampling. Concentrations in ug/L.

Bore	B10/1	B11/1	B11/2	B12/1	B13/1	B14/1	B15/1	16/1
2,3,5-TMCP (+ 2-ethylhexanoic acid)	47.9	22.6	56.7	26.3	7.6	90.8	0.0	32.3
2,3,4-TMCP	37.6	36.3	25.4	33.1	10.5	64.0	10.3	43.6
TetMCP (isomer unknown)	16.6	27.5	11.1	28.6	12.0	196.3	7.8	16.7
TetMCP (isomer unknown)	6.8	8.5	4.8	6.9	4.1	74.5	1.4	7.0
TetMCP (isomer unknown)	6.8	14.1	15.8	12.2	16.6	22.8	0.0	22.5
Total methyl-2-cyclopentenones	115.7	109.1	113.8	107.0	50.7	448.4	19.6	122.1
FA16:0	27.6	45.2	55.3	18.7	16.6	10.1	4.7	60.0
FA18:0	21.5	23.2	36.0	20.7	12.1	8.1	18.4	64.3
Total Fatty Acids	49.2	68.4	91.2	39.4	28.8	18.2	23.1	124.3
DT260P	0.0	6.1	30.4	25.3	0.0	10.4	0.0	35.6
DT262P	4.5	20.9	84.1	207.2	2.5	8.0	2.5	79.3
DT260I	7.5	6.3	17.7	76.1	5.0	0.0	0.0	0.0
DT262I	0.0	0.0	0.0	0.0	0.0	0.0	0.0	33.9
fichtelite	8.5	42.1	175.4	900.1	5.8	12.6	0.0	292.3
dehydroabietin	0.0	8.4	25.8	92.3	0.0	0.0	0.0	82.9
tetrahydroretene	0.0	0.0	18.5	403.5	3.2	2.4	0.0	107.2
seco-dehydroabietic acid #1	5.8	11.4	30.7	0.0	2.5	2.7	15.6	0.0
retene	14.2	78.4	206.9	378.5	5.7	42.6	8.2	168.7
seco-dehydroabietic acid #2*	2.9	5.7	15.4	0.0	1.2	1.4	7.8	0.0
unid. mw=290? (not found)								
8-pimaren-18-oic acid	5.6	7.1	18.8	11.1	1.7	2.0	20.1	0.0
8-isopimaren-18-oic acid	7.2	21.7	38.0	0.0	6.5	4.8	0.0	40.4
pimaranoic acid	7.8	20.7	39.2	20.2	3.4	4.0	0.0	29.2
unid. RA304?	13.6	25.1	45.6	10.6	11.1	6.9	31.0	52.9
unid. RA316?	6.4	4.6	14.6	0.0	0.0	0.0	0.0	0.0
abietanoic + 7-oxokauranoic acids	49.8	93.1	136.5	41.4	29.5	55.0	47.5	128.2
dehydroabietic acid	17.8	36.8	51.2	15.3	12.8	12.0	14.8	38.8
unid. RA330?	7.1	14.9	0.0	14.5	3.3	3.8	19.2	18.4
unid. RA273?	18.7	0.0	23.2	10.8	5.6	9.1	18.0	48.1
unid. RA332 ?	39.4	42.6	25.6	11.4	10.7	15.5	29.8	67.1
unid. RA350?	35.8	44.8	31.3	12.1	14.5	16.7	32.6	63.5
unid. RA348?	63.2	63.2	43.2	26.9	14.4	20.4	35.8	101.5
unid. RA350?	48.3	41.7	34.7	26.4	20.5	26.6	38.9	84.3
unid. RA350?	17.7	26.8	0.0	11.5	6.7	8.7	16.9	33.5
unid. mw=400?	17.9	19.3	16.0	14.9	6.0	10.9	25.7	51.9
unid. mw=402?	53.2	72.6	36.5	42.9	20.4	34.2	68.0	113.9
unid. mw=400?	9.4	12.2	29.6	8.3	5.8	6.1	22.8	45.5
Total DTs	23.4	89.5	367.3	1704.4	17.7	34.8	10.3	631.3
Total identified RAs	108.1	269.2	521.3	466.5	62.0	123.2	106.2	405.2
Total identified RAs+DTs	131.6	358.8	888.6	2171.0	79.7	157.9	116.5	1036.6
Total DT + RA + RA330-350?	381.8	622.5	1106.8	2295.2	166.5	265.8	338.8	1505.8

* seco-2 calculated as 0.5 x seco-1 (some coelution with retene)

Table A2.16: Summary of shallow ground water data October 1987-July 1988

Well	Date	sodium	chloride	colour	MCP	FA	DT	RA	RA+DT
10/1	28/9/87	393	332	903	146	35	14	57	72
10/2	30/9/87	393	320	163	100	32	5	28	33
11/1	23/9/87	481	348	1379	205	14	214	189	404
11/2	23/9/87	468	342	1785	45	16	397	340	737
11/3	4/10/87	388	341	1169	349	54	113	158	271
12/1	4/10/87	422	365	615	173	51	2489	174	2662
13/1	4/10/87	350	281	67	31	1	0	24	24
14/1	1/10/87	383	376	585	161	21	138	182	320
15/1	30/9/87	317	198	118	55	11	0	26	26
16/1	23/9/87	334	185	105	90	5	2513	95	2607
10/1	3/11/87	375	332	502	167	59	16	80	96
10/2	3/11/87	344	320	530	198	28	20	156	176
11/1	3/11/87	430	348	1532	175	38	718	289	1007
11/2	3/11/87	474	343	2140	278	31	448	363	811
12/1	3/11/87	440	336	660	107	28	1953	243	2196
13/1	3/11/87	326	281	259	0	8	0	43	43
14/1	3/11/87	440	404	730	206	7	69	208	277
15/1	3/11/87	268	199	85	0	2	1	33	33
16/1	4/11/87	315	260	206	64	10	868	120	988
10/1	18/12/87	357	338	760	162	26	19	78	97
10/2	18/12/87	352	325	326	152	27	8	52	60
11/1	18/12/87	443	389	1087	40	68	453	205	658
11/2	18/12/87	481	357	1870					
12/1	18/12/87	433	352	641	148	113	2173	238	2412
13/1	18/12/87	321	292	105	39	54	4	90	93
14/1	18/12/87	433	405	543	131	29	563	244	808
15/1	18/12/87	283	192	83	9	22	0	63	63
16/1	18/12/87	303	225	130	46	110	963	115	1078
10/1	22/3/88	373	335	779					
10/2	22/3/88	374	347	465					
11/1	22/3/88	420	378	636					
11/2	22/3/88	411	359	1571					
12/1	22/3/88	445	373	607					
13/1	22/3/88	370	304	129					
14/1	22/3/88	360	364	566					
15/1	22/3/88	328	190	128					
16/1	22/3/88	260	221	126					
10/1	19/7/88	348			116	49	35	97	132
11/1	19/7/88	396			109	68	162	197	359
11/2	19/7/88	393			114	91	559	330	889
12/1	19/7/88	385			107	39	2083	88	2171
13/1	19/7/88	263			51	29	22	58	80
14/1	19/7/88	331			448	18	76	82	158
15/1	19/7/88	355			20	23	11	106	117
16/1	19/7/88	273			122	124	800	237	1037

MCP: methyl-substituted 2-cyclopentenones; FA: fatty acids; DT: diterpene hydrocarbons; RA: resin acids (identified)

RA+DT: resin acids plus diterpene hydrocarbons; RADT + mw(330-350): resin acids plus diterpene hydrocarbons plus unidenti

Table A2.17: Shallow ground water chemistry, November/December 1988

Bore	B11/1	B11/1	B11/1	B11/1	B11/1	B11/1	B11/1	B11/2	B11/2	B11/2	B11/2	B11/2	B11/2	B11/2	B11/3	B11/3	B11/3	B11/3	B11/3	B11/3	B11/3
Date (day/month of 1988)	2/11	8/11	16/11	23/11	1/12	8/12	20/12	2/11	8/11	16/11	23/11	1/12	8/12	20/12	2/11	8/11	16/11	23/11	1/12	8/12	20/12
sodium (mg/L)	423	413	402	417	385	410	410	368	378	372	388	406	388	388	251	247	256	260	257	234	277
colour (mg/L)	754	820	911	1013	1065	1061	1057	2108	1875	1954	1826	2081	1961	1943	1407	1425	1425	1410	1309	1185	1343
Extractable organics (ug/L):																					
2,5-DMCP																					
2,3-DMCP																					
2,3,5-TMCP	27.4	21.5	19.0	18.2	42.4	29.9	26.1	91.8	87.1	64.2	56.8		65.3	58.8	24.0	18.1	14.2	21.3	5.5	15.3	19.9
2,3,4-TMCP	2.1	28.5	21.7	20.5	20.3	34.0	34.2	41.5	39.7	28.7	26.2		31.7	30.1	17.4	11.2	11.5	12.5	10.2	11.3	12.9
TetMCP	21.8	26.9	12.5	12.0	7.1	17.0	16.9	15.7	18.7	13.0	10.1		12.1	11.4	7.3	5.1	5.7	5.7	8.2	3.8	5.5
TetMCP	8.2	7.7	4.9	4.1	1.5	6.1	5.7	14.7	17.9	6.5	12.7		5.4	4.0							
TetMCP	11.9	14.1	11.5	8.0	12.7	10.2	8.7	7.0	7.8	7.0	5.0		3.9	3.6	7.7	6.8	9.2	10.8	5.0	7.3	10.2
Total MCP	71.4	98.7	69.6	62.8	83.9	97.2	91.6	170.6	171.1	119.4	110.9		118.4	108.0	56.4	41.1	40.8	50.3	28.9	37.6	48.4
a-pinene																					
b-pinene																					
p-cymene																					
fenchone																					
fenchol																					
camphor																					
MT154								32.0	34.1	26.5	22.0		18.9	16.6	7.7	6.8	9.2	10.8	5.0	7.3	10.2
DHT																					
borneol																					
terpen-4-ol																					
a-terpineol																					
Total Monoterpenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	32.0	34.1	26.5	22.0		18.9	16.6	7.7	6.8	9.2	10.8	5.0	7.3	10.2
FA14:0	10.3	5.8	5.0	4.4	2.6	4.4	10.0	6.6	4.9	3.1	2.9		3.1		5.9	3.6	3.3		2.6		2.2
FA16:1	24.2	17.1	17.2	9.1	12.4	8.2	7.2	8.9	10.2	9.5	6.2		7.3	2.0	9.4	5.1	19.8	5.3	4.8	3.9	5.9
FA16:0	36.2	24.8	14.2	19.0	10.2	21.1	33.3	27.2	23.9	13.4	14.2		14.0	9.5	28.6	25.2	13.8	10.9	28.4	12.9	14.6
anteiso F17:0																					
FA18:2																					
FA18:1	4.7	5.2	0.0	2.5	1.7	3.2	8.9	4.8	15.8	2.2	6.0		9.0	3.1	3.2	5.2	2.3	2.5	19.2	4.3	3.9
FA18:0	16.0	11.7	9.2	9.5	6.9	10.1	14.7	14.5	10.2	9.2	8.5		8.5	7.6	16.3	14.7	7.6	6.1	16.1	5.7	7.3
FA18:2																					
Total Fatty Acids	91.5	64.6	45.5	44.5	33.9	47.0	74.1	62.1	65.1	37.3	37.8		42.0	22.2	63.3	53.8	46.7	24.9	71.2	26.8	33.9
DT260P/I/A (ur)+ DT262P	13.3	19.1	22.4	15.9	11.8	28.0	58.4	13.5	6.1	20.8	20.0		18.1	22.5	15.5	31.7	36.2	17.3	18.1	22.4	25.6
DT262I	2.2	3.0	6.1	4.6	3.3	8.6	18.9	2.6		3.9	3.3		3.7	4.6	3.5	5.5	4.4	4.0	2.4	5.5	7.0
fichtelite	42.6	69.3	91.2	67.3	45.8	111.2	213.9	42.8	44.9	55.5	47.4		43.6	68.3	68.0	114.0	76.1	73.4	51.7	102.5	132.0
dehydroabietin	3.0	1.0	2.9	1.9	1.8	5.6	22.0	1.7	1.2	2.4	3.9			2.1							
tetrahydroretene																					
seco-dehydroabietic acid #1	2.5	3.0	3.7	4.1	5.9	5.0	6.4	6.0	6.8	6.6	6.5		6.9	8.0	2.9	6.9	3.7	3.9	82.4	28.1	8.4
seco-dehydroabietic acid #2	1.7	1.5	2.1	2.5	5.0	3.1	2.0	4.0	3.1	4.8	4.3		5.5	5.4	1.4	3.8	3.5	1.7	40.8	17.0	6.4
retene	15.8	39.6	51.2	60.2	9.4	135.7	496.9	47.4	61.7	16.2	78.9		16.0	51.8	6.9	14.4	6.2	12.7	5.1	15.1	14.1
8,15-pimaradienoic acid																					
8,15-isopimaradienoic acid																					
pimaric acid																					
sandaracopimaric acid																					
8-isopimarenoic acid	4.9	6.3	6.2	6.8	5.7	6.7	13.9	8.4	12.8	9.4	8.3		6.3	8.2	4.9	12.8	9.4	5.4	57.2	13.7	9.0
8-pimarenoic acid	5.1	5.6	4.3	5.8	10.9	9.5	8.9	11.9	12.5	12.9	17.9		15.5	19.4	3.3	4.6	6.3	4.5	5.3	7.9	14.8
pimaranoic acid	8.4	15.8	18.9	18.0	29.3	30.4	56.6	30.4	31.8	33.0	32.4		37.6	46.3	20.0	23.6	22.0	27.1	19.4	29.5	58.0
isopimaranoic + 13-abietenoic acids	8.0	11.4	11.0	12.4	15.4	15.5	28.4	14.2	18.9	17.8	19.0		17.9	21.6	7.1	13.1	8.8	10.7	19.6	18.1	21.4
abietanoic + 7-oxokauranoic acids	50.3	60.1	64.7	65.0	111.4	107.9	166.7	113.4	99.2	14.8	121.6		17.9	19.4	56.1	67.2	11.6	17.6	117.8	184.3	16.0
dehydroabietic acid	7.9	13.5	10.6	13.1					25.6	106.3			111.5	134.4	9.0	23.1	67.0	10.3	4.3		137.5
kinkelthic acid																					
Total RAs + DTs	165.8	249.2	295.5	277.6	255.7	467.2	1093.0	296.3	324.5	304.1	363.4		300.7	412.2	198.7	320.8	255.1	188.6	424.1	444.3	450.1
Total Resin Acids	88.9	117.3	121.7	127.7	183.6	178.1	282.9	188.4	210.6	205.5	209.9	0.0	219.2	262.9	104.7	155.2	132.3	81.3	346.9	298.7	271.4
Total Diterpene Hydrocarbons	76.9	132.0	173.8	149.9	72.1	289.2	810.1	107.9	113.8	98.7	153.5	0.0	81.4	149.3	93.9	165.6	122.8	107.3	77.3	145.6	178.7

Table A2.17 (cont.): Shallow ground water chemistry, November/December 1988

Bore	B11/4	B11/4	B11/4	B11/4	B11/4	B11/4	B11/4	B11/4	B12/1	B12/1	B12/1	B12/1	B12/1	B15/1	B15/1	B15/1	B15/1	B15/1	B15/1	B15/1
Date (day/month of 1988)	2/11	5/11	8/11	16/11	23/11	1/12	8/12	20/12	16/11	23/11	1/12	8/12	20/12	4/11	8/11	16/11	23/11	1/12	8/12	20/12
sodium (mg/L)	297	378	321	301	330	325	316	349	354	394	400	401	398	386	386	376	393	381	387	381
colour (mg/L)	896	2351	1200	788	825	938	984	1343	1204	1182	1072	1101	1065	260	280	218	236	240	240	221
Extractable organics (ug/L):																				
2,5-DMCP	26.3	38.3	28.6	14.5	16.3	6.0	10.0	11.4												
2,3-DMCP	66.2	111.8	67.7	56.6	61.1	30.2	39.3	88.6	19.6	15.3	8.3	12.6	11.2							
2,3,5-TMCP	81.4	157.3	108.8	74.2	78.5	43.2	59.9	113.1	56.9	46.0	44.4	61.1	55.6							
2,3,4-TMCP	53.4	74.9	54.8	42.4	48.9	24.3	39.8	64.8	41.6	35.5	36.3	53.1	49.2	15.9	16.7	18.3	6.9	14.4	15.8	14.9
TetMCP									16.4	11.8	10.4	17.4	16.7	11.8	10.7	12.3	4.6	11.1	12.6	12.5
TetMCP																				
TetMCP	16.9	42.1	20.1	12.6	14.3	5.6	11.2	14.9												
Total MCP	244.2	424.4	280.0	200.4	219.1	109.4	160.3	292.8	134.5	108.6	99.4	144.1	132.6	27.7	27.4	30.6	11.5	25.6	28.5	27.4
a-pinene																				
b-pinene																				
p-cymene		24.1	15.5																	
fenchone	86.7	99.6	95.9	71.0	73.2	10.6	36.5	84.4	20.9	9.5	6.4	9.4	10.0							
fenchol		121.1	24.1																	
camphor	168.9	199.3	166.4	119.3	120.6	18.9	44.9	129.4	45.0	20.3	4.7	4.5	8.8							
MT154	53.7	167.8	63.1	48.9	48.1		30.2	58.0	21.7	19.6	15.8	21.9	20.5							
DHT	14.8	216.3	125.2	18.1	9.5				48.4	10.5										
borneol		322.8	81.1																	
terpen-4-ol		216.4	64.7																	
a-terpineol		1877.9	496.6																	
Total Monoterpenes	324.2	3245.3	1132.6	257.4	251.4	29.5	111.6	271.8	136.1	59.9	26.9	35.8	39.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
FA14:0	6.4	49.7	13.8		9.7	13.4	2.2	8.1	3.5	5.1			4.8							
FA16:1	11.3	114.8	30.7	4.5	12.6	10.3	2.1	13.7	5.5	9.2	6.1	10.1	10.9	4.8	3.5	2.2	5.6	4.7	3.5	
FA16:0	37.0	1169.2	297.2	17.7	53.4	20.3	17.9	47.0	31.1	31.3	15.7	24.8	31.3	5.7	9.0	8.5	7.0	12.9	9.6	5.3
anteiso F17:0		160.9	35.0																	
FA18:2		497.2	32.6																	
FA18:1	3.2	2177.4	300.6	7.1	14.5	13.5	1.5	11.4	9.3	5.2	2.7	5.6	5.3	0.8	2.1		1.0			
FA18:0	27.1	150.2	68.4	9.6	24.0	11.8	8.3	27.3	17.5	18.4	6.9	14.2	18.0	3.6	5.6	5.2	2.7	5.9	4.5	3.0
FA18:2		221.0	29.3																	
Total Fatty Acids	85.1	4540.3	807.6	38.9	114.2	69.3	32.1	107.5	67.0	69.2	31.4	54.7	70.2	14.8	20.2	16.0	16.4	23.5	17.6	8.3
DT260P/I/A (ur)+ DT262P	11.1				7.3	14.8	21.2	24.1	144.4	225.5	36.1	279.8	273.1							
DT262I	3.3				1.7	2.5	4.4	6.6	27.2	43.1	36.5	52.8	54.3							
fichtelite	69.7	54.1	56.6	20.2	39.8	39.7	66.3	122.6	723.8	1133.6	969.2	1367.5	1364.1							
dehydroabietin					3.4	2.0	1.4	6.2	208.1	210.8	143.2	193.6	211.6							
tetrahydroretene									129.8	130.0	12.0	213.6	251.1							
seco-dehydroabietic acid #1	4.5	181.9	74.0	26.4	7.6	52.4	14.0	21.1	31.7	19.6	8.5	12.1	9.7	1.7	2.1	2.8	2.3	2.0	2.3	2.6
seco-dehydroabietic acid #2	3.9	120.3	45.4	16.2	5.6	27.3	7.8	12.6	19.8	13.9	7.1	10.0	8.5	0.8	2.5	2.4	1.0		1.9	
retene							23.4		488.0	590.1	502.9	802.3	735.0	3.1	2.2	1.7	2.5			1.5
8,15-pimaradienoic acid				6.8																
8,15-isopimaradienoic acid				3.4																
pimaric acid		501.1	168.2	19.0	14.2															
sandaracopimaric acid		109.0	36.5																	
8-isopimarenoic acid	5.1			5.4		53.8	8.0	30.5	23.0	21.6	15.0	26.0	17.2							
8-pimarenoic acid	4.0				5.4	7.1	5.8	8.3	24.0	22.5	13.8	20.5	16.1							
pimaranoic acid	17.7			9.8	11.8	15.5	17.4	37.8	25.4	25.7	25.0	34.5	33.0							
isopimaranoic + 13-abietenoic acids	10.0	402.3	318.1	17.9	21.2	25.8	12.4	45.7	19.3	16.5	13.4	17.3	16.1	3.3	2.9	3.1	3.2	2.5	3.7	6.1
abietanoic + 7-oxokauranoic acids	78.1	632.6	236.4	61.9	69.2	87.4	14.1	364.5	182.4	151.1	24.5	149.8	138.8	6.4	9.6	8.8	7.9	6.3	7.3	9.8
dehydroabietic acid	13.1	2220.3	1277.4	194.9	83.7	15.4	105.8				99.4			2.5	2.4	2.3	2.1		2.4	4.9
kinkelithic acid		144.8	42.0	44.9	15.6															
Total RAs + DTs	220.7	4366.2	2254.7	426.9	286.6	343.7	302.0	679.9	2047.1	2604.0	1906.4	3179.7	3128.7	17.8	21.6	21.1	19.0	10.8	17.6	24.9
Total Resin Acids	136.5	4312.1	2198.1	406.7	234.5	284.7	185.3	520.5	325.7	271.0	206.6	270.1	239.3	14.7	19.5	19.4	16.5	10.8	17.6	23.3
Total Diterpene Hydrocarbons	84.2	54.1	56.6	20.2	52.2	59.0	116.8	159.4	1721.4	2333.0	1699.8	2909.6	2889.4	3.1	2.2	1.7	2.5	0.0	0.0	1.5

Table A2.18: Ceramic cup water sample chemistry from beneath seepage basin P7

Sample	PP1/2	PP1/1	PP2/1	PPB	PPB
Date	2/11/88	2/11/88	2/11/88	5/11/88	5/11/88
Depth	0.65 m	0.95 m	1.0 m	1.0 m	0.75 m
sodium (mg/L)	230	220	280	320	440
colour (mg/L)	1150	730	1130	1600	3160
Extractable organics (ug/L):					
2,3-DMCP					99.9
2,3,5-TMCP					149.1
2,3,4-TMCP					134.3
Total MCPs					383.3
p-cymene					235.8
fenchone					294.4
camphor					689.6
DHT					473.6
pinocamphone (?)					70.9
borneol					70.9
4-terpineol					382.6
a-terpineol					3896.5
Total Monoterpenes					6114.4
trithiolane					578.6
palmitoleic acid		0.7	1.0		
palmitic acid	16.0	3.6	2.2	8.1	375.4
oleic acid		1.6	0.7	6.3	322.0
stearic acid	7.3	1.0	0.8	7.4	91.7
Total Fatty Acids	23.2	6.9	4.7	21.8	789.1
seco-dehydroabietic acid (1)	51.6		1.6	5.6	588.7
seco-dehydroabietic acid (2)	21.0		0.6	2.6	306.6
8,15-pimaradienoic acid	8.0			2.2	201.5
8,15-isopimaradienoic acid	18.3			2.1	1038.7
pimaric acid	108.0				1059.8
8-isopimarenoic acid	36.4		3.2	13.0	
8-pimarenoic acid			0.8	2.6	37.8
pimaranoic acid + 8,14-pimarenoic acid	36.8		1.0	2.1	50.5
isopimaranoic acid + 13-abietenoic acic	167.9	0.5	4.7	14.9	1227.6
abietanoic acid + 7-oxokauranoic acid	835.9	2.2	13.8	39.1	1291.4
dehydroabietic acid	199.6	1.4	9.3	30.9	12129.1
abietic acid	35.9		1.7	16.2	399.6
13ß-hydroxyabietanoic acid					4309.1
Total Resin Acids + Diterpenes	1519.4	4.0	36.6	131.5	22640.4

Table A2.19: Sodium (mg/L), colour (CPU), A270 (/cm) in off-site wells

	Bore 73/1			Bore 73/2			Bore 73/3		
Date	Na	colour	A270	Na	colour	A270	Na	colour	A270
Apr-87	148			267			74		
May-87	211			323			107		
Jun-87	184			264			65		
Jul-87	264			283			37		
Sep-87	297	89	0.748	303	170	0.993	74	13	0.061
Oct-87	283			302			77		
Nov-87	286	127	0.870	306	313	1.480	72	10	0.052
Dec-87	272			307			74		
Jan-88	276			309			77		
Feb-88	293			331			75		
Mar-88	283			312			70		
Apr-88	263			299			61		
May-88	262			297			82		
Jun-88	258			300			61		
Jul-88	270			306					
Apr-89	216	84	0.557	304	256	1.306	76	8	0.069
May-89							50		
Jul-89	216			282			74		
Aug-89	195			283			91		
Dec-89	189			283			87		

	Bore 74/1			Bore 74/2			Bore 74/3			Bore 74/4		
Date	Na	colour	A270	Na	colour	A270	Na	colour	A270	Na	colour	A270
Apr-87	389			379			138			44		
May-87	412			396			62			44		
Jun-87	394			374			50			113		
Jul-87	404			390			103			63		
Sep-87	429	956	2.960	387	1032	3.420	155	42	0.362	46	7	0.061
Oct-87	422			369			219			219		
Nov-87	412	1036	3.300	386	944	3.340	135	20	0.208	126	23	0.308
Dec-87	402			386			154			91		
Jan-88	396			372			63			90		
Feb-88	415			393			111			23		
Mar-88	443			379			70			22		
Apr-88	400			369			50			18		
May-88	391			362			51			21		
Jun-88	384			377			57			31		
Jul-88	383			345			63			54		
Apr-89	252	343	1.463	303	818	2.879	101	92	0.429	54	12	0.089
May-89										40		
Jul-89	259	410	1.640	277			106			40		
Aug-89	358			276			146			84		
Dec-89	239			216			129			71		
Oct-90				170	246	1.035						

	Bore 89/1			Bore 89/2			Bore 89/3		
Date	Na	colour	A270	Na	colour	A270	Na	colour	A270
Apr-87	21			71			41		
May-87	20			125			17		
Jun-87	19			121			14		
Jul-87	16			125			12		
Sep-87	15	4	0.027	117	29	0.295	14	45	0.156
Oct-87	13			111			11		
Nov-87	16	2	0.035	123	26	0.280	10	<5	0.020
Dec-87	12			120			12		
Jan-88	12			114			16		
Feb-88	12			110			12		
Mar-88	11			118			13		
Apr-88	9			109			12		
May-88	11			109			12		
Jun-88	14			108			16		
Jul-88	12			100			12		
Apr-89	11	12	0.021	104	32	0.218	10	28	0.049
May-89							8		
Jul-89	14	16	0.030	106	24	0.215	8		
Aug-89	8			91			8		
Dec-89	12			84			9		

Table A2.19 (cont.): Sodium (mg/L), colour (CPU), A270 (/cm) in off-site wells

	Bore 90/1			Bore 90/2			Bore 90/3			Bore 90/4		
Date	Na	colour	A270	Na	colour	A270	Na	colour	A270	Na	colour	A270
Apr-87				45			8			21		
May-87	36			40			18			18		
Jun-87	32			53						14		
Jul-87	23			57			13			10		
Sep-87	21	12	0.060	56	20	0.115	15	5	0.040	10	35	0.150
Oct-87	20			62			9			9		
Nov-87	19	18	0.131	60	31	0.160	9			8		
Dec-87	23			62			12			11		
Jan-88	21			56			10			10		
Feb-88	22			37			10			13		
Mar-88	22			56			9			12		
Apr-88	20			36			6			11		
May-88	20			30			9			9		
Jun-88	21			30			11					
Jul-88	23			56			7			9		
Apr-89	24	12	0.112	21	8	0.036						
May-89										8		
Jul-89	25			34	8	0.040				8		
Aug-89	21			30								
Dec-89	21			44								

	Bore 94/1			Bore 94/2			Bore 94/3		
Date	Na	colour	A270	Na	colour	A270	Na	colour	A270
Dec-88	30			109			47		
Jul-89	23			28			41		
Aug-89	25			29					

	Bore 86/1			Bore 86/2		
Date	Na	colour	A270	Na	colour	A270
Sep-88	49			15		
Apr-89	13	16	0.032	16	12	0.032
Aug-89	5			18		
Dec-89	47			16		
Oct-90				16	23	0.052

Table A2.20: Extractable organics in off-site wells

September 1987 sampling:

Well	73/1	73/3	74/1	74/2	74/3	74/4	89/1	89/2	89/3	90/1	90/2	90/4
FA16:0	1.3	1.2	1.4	5.4	9.6	3.4	4.6	2.8	4.6	3.0	2.3	1.2
FA18:0	0.4	0.7	1.4	4.1	21.5	2.1	2.3	2.3	2.7	2.5	1.0	0.6
Total Fatty Acids	1.7	1.9	2.8	9.5	31.0	5.5	6.9	5.1	7.3	5.4	3.2	1.9
DT262P	0.0	0.0	5.2	12.7	0.0	0.0	0.0	0.0	0.0	0.0	5.2	0.0
DT262I	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
fichtelite	0.0	0.0	19.0	38.8	0.0	0.0	0.0	0.0	0.0	0.0	6.6	0.0
tetrahydroretene	0.0	0.0	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
seco-dehydroabietic acid #1	0.0	0.0	1.7	4.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
seco-dehydroabietic acid #2 + retene	0.0	0.0	6.7	5.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8-isopimarenoic acid	0.0	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
pimaranoic acid	0.0	0.0	3.6	11.8	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0
isopimaranoic acid (+ RA314?)	0.0	0.0	7.0	3.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
unid. RA316?	0.0	0.0	5.3	2.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
unid. RA318 (8-abietenoic?)	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
abietanoic + 7-oxokauranoic acids	3.8	0.5	28.0	57.9	2.2	0.4	0.0	7.2	0.5	0.0	5.6	0.9
dehydroabietic acid	5.0	0.0	10.1	9.4	2.2	0.0	0.0	3.5	0.3	0.0	1.3	0.4
unid. RA330?	0.0	0.0	0.0	4.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
unid. RA350? (+ 7-oxodehydroabietic acid)	12.4	0.0	14.3	0.0	0.0	0.0	0.0	4.5	0.0	0.0	0.0	0.0
unid. RA348?	9.4	0.0	13.7	0.0	0.0	0.0	0.0	4.9	0.0	0.0	0.0	0.0
unid. RA350?	13.2	0.0	18.1	0.0	0.0	0.0	0.0	6.1	0.0	0.0	0.0	0.0
unid. RA350?	8.3	0.0	8.8	0.0	0.0	0.0	0.0	3.2	0.0	0.0	0.0	0.0
unid. mw=400?	3.2	0.0	10.5	7.4	0.0	0.0	0.0	2.2	0.0	0.0	0.0	0.0
unid. mw=402?	20.6	0.0	45.2	0.0	0.0	0.0	0.0	9.0	0.0	0.0	5.3	0.0
unid. mw=400?	0.0	0.0	1.8	0.0	0.0	0.0	0.0	2.1	0.0	0.0	0.0	0.0
Total DTs	0.0	0.0	32.3	54.6	0.0	0.0	0.0	0.0	0.0	0.0	11.8	0.0
Total RAs (i.d.)	12.9	0.5	58.4	91.9	4.4	0.4	0.0	10.7	0.8	0.0	7.4	1.4
Total identified RAs+DTs	12.9	0.5	90.6	146.5	4.4	0.4	0.0	10.7	0.8	0.0	19.2	1.4
Total DT + RA + mw 330-350	56.3	0.5	145.5	151.1	4.4	0.4	0.0	29.4	0.8	0.0	19.2	1.4

November 1987 sampling:

Well	73/1	73/2	73/3	74/1	74/2	74/3	74/4	89/1	89/2	89/3	90/1	90/2	90/3
FA16:0	1.7	1.7	1.5	3.0	2.6	2.3	5.1	1.3	1.5	2.6	4.7	1.9	0.8
FA18:0	1.1	0.5	0.8	0.7	0.6	0.9	5.4	0.8	0.6	2.9	2.2	0.8	0.5
Total Fatty Acids	2.8	2.2	2.3	3.7	3.1	3.2	10.6	2.1	2.1	5.5	6.9	2.7	1.3
DT262P	0.0	0.0	0.0	12.7	10.6	0.0	0.0	0.0	0.0	0.0	0.0	3.5	0.0
fichtelite	0.0	1.8	0.0	53.9	43.8	0.0	0.0	0.0	0.0	0.0	0.0	5.1	0.0
tetrahydroretene	0.0	0.0	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
seco-dehydroabietic acid #1	0.0	2.5	0.0	0.6	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0
seco-dehydroabietic acid #2 + retene	0.0	2.6	0.0	4.9	1.9	0.8	0.0	0.0	1.9	0.0	0.0	0.4	0.0
pimaranoic acid	0.0	0.0	0.0	1.4	1.6	0.8	0.0	0.0	0.0	0.0	0.0	1.1	0.0
unid. RA304? + 13-abietenoic acid	0.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	1.6	0.0	0.0	1.2	0.0
isopimaranoic acid (+ RA314?)	0.0	0.0	0.0	0.9	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
unid. RA316?	0.0	2.4	0.0	0.4	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0
abietanoic + 7-oxokauranoic acids	3.2	31.4	0.3	7.4	15.6	1.1	6.1	0.8	2.5	0.0	0.0	3.7	0.0
dehydroabietic acid	1.5	7.1	0.1	2.1	2.6	1.3	2.7	0.0	2.6	0.0	0.0	1.6	0.0
unid. RA350? (+ 7-oxodehydroabietic acid)	0.0	0.0	0.0	1.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.8	0.0
unid. RA348?	0.0	0.0	0.0	1.4	0.0	0.0	0.0	0.0	2.8	0.0	0.0	1.7	0.0
unid. RA350?	0.0	0.0	0.0	2.6	1.1	0.0	0.0	0.0	6.2	0.0	0.0	0.0	0.0
unid. RA350?	0.0	0.0	0.0	1.0	1.1	0.0	0.0	0.0	2.6	0.0	0.0	0.0	0.0
unid. mw=400?	0.0	0.0	0.0	2.0	1.1	0.0	0.0	0.0	2.2	0.0	0.0	1.2	0.0
unid. mw=402?	0.0	0.0	0.0	1.5	1.1	0.0	0.0	0.0	16.2	0.0	0.0	7.7	0.0
unid. mw=400?	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0	0.0	2.2	0.0
Total DTs	0.0	3.2	0.0	73.1	55.9	0.8	0.0	0.0	1.9	0.0	0.0	8.8	0.0
Total RAs (i.d.)	4.7	47.7	0.4	13.2	21.9	3.2	8.8	0.8	7.3	0.0	0.0	8.1	0.0
Total identified RAs+DTs	4.7	50.8	0.4	86.3	77.8	4.0	8.8	0.8	9.2	0.0	0.0	16.9	0.0
Total DT + RA + mw 330-350	4.7	50.8	0.4	93.0	79.9	4.0	8.8	0.8	20.9	0.0	0.0	20.4	0.0

April 1989 and July 1989 sampling:

Well	73/1	73/2	73/3	74/1	74/2	74/3	74/4	89/1	89/2	89/3	90/1	90/2	86/1	86/2	74/1
Date	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Jul-89
FA16:1	0.8	0.6	8.0	4.4	1.4	0.4	10.1	4.0	1.9	9.2	6.0	1.9	3.2	1.8	7.5
FA16:0	3.4	1.1	8.9	3.4	2.3	0.8	17.5	2.2	1.4	40.1	9.2	1.6	1.9	1.1	4.7
FA18:1	1.8	0.6	10.0	2.2	0.5	0.3	4.8	1.3	0.7	3.3	3.3	1.8	0.7	0.5	2.7
FA18:0	1.2	0.5	6.2	0.7	1.5	0.3	14.5	0.7	0.4	34.0	4.2	0.6	0.6	0.2	1.0
Total Fatty Acids	7.3	2.8	33.1	10.7	5.7	1.7	46.9	8.2	4.5	86.6	22.6	5.9	6.4	3.7	15.9
DT260P				2.4	2.7	0.2									8.2
DT260I				5.2	5.7	0.6									
DT262P				8.1	7.5	0.7									
DT262I				2.9	3.8	0.1									1.5
fichtelite		0.8		25.6	25.8	1.8			0.5						19.4
seco-dehydroabietic acid #1	0.7	0.9		1.0	2.4	0.2			0.6						1.0
seco-dehydroabietic acid #2	0.8	0.9		1.5	3.0	0.2			0.5						1.9
retene				1.3	7.2	0.2			0.3						
8,15-pimaradienoic acid	0.8				2.6										
8-pimarenoic acid	1.1	0.8	0.5	2.4	2.0	0.2									2.6
8-isopimarenoic acid	1.4	2.4	0.3	1.7	6.3	0.4									
pimaranoic acid				2.9	14.1	0.8									3.2
unid. RA304? + 13-abietenoic acid	1.5	1.5													
isopimaranoic acid (+ 13-abietenoic acid)				2.4	7.5	0.7			0.6						3.2
unid. RA318 (8-abietenoic?)	1.0														
abietanoic + 7-oxokauranoic acids	4.2	16.2	3.7	12.6	43.4	1.9	0.2		0.8						12.4
dehydroabietic acid	5.8	2.6	0.7	1.5	1.4	0.5			0.2						2.1
unid. RA330?	1.1	1.2		2.2	1.2	0.7			0.9						
unid. RA350? (+ 7-oxodehydroabietic acid)	1.1	2.9		2.3	5.0	0.7									6.4
unid. RA348?	1.4	2.5		2.9	6.3	0.8			0.4						3.1
unid. RA350?															1.7
unid. RA350?															
unid. mw=400?															0.6
unid. mw=402?															0.2
unid. mw=400?															1.0
Total DTs	0.0	0.8	0.0	45.6	52.6	3.5	0.0	0.0	0.8	0.0	0.0	0.0	0.0	0.0	29.2
Total RAs (i.d.)	17.3	25.2	5.2	26.0	82.6	4.7	0.2	0.0	2.6	0.0	0.0	0.0	0.0	0.0	26.3
Total identified RAs+DTs	17.3	26.0	5.2	71.6	135.2	8.3	0.2	0.0	3.4	0.0	0.0	0.0	0.0	0.0	55.5
Total DT + RA + m/z 330-350	20.8	32.6	5.2	79.0	147.6	10.5	0.2	0.0	4.8	0.0	0.0	0.0	0.0	0.0	66.7

Table A2.20: Extractable organics in off-site wells

September 1987 sampling:

Well	73/1	73/3	74/1	74/2	74/3	74/4	89/1	89/2	89/3	90/1	90/2	90/4
FA16:0	1.3	1.2	1.4	5.4	9.6	3.4	4.6	2.8	4.6	3.0	2.3	1.2
FA18:0	0.4	0.7	1.4	4.1	21.5	2.1	2.3	2.3	2.7	2.5	1.0	0.6
Total Fatty Acids	1.7	1.9	2.8	9.5	31.0	5.5	6.9	5.1	7.3	5.4	3.2	1.9
DT262P	0.0	0.0	5.2	12.7	0.0	0.0	0.0	0.0	0.0	0.0	5.2	0.0
DT262I	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
fichtelite	0.0	0.0	19.0	38.8	0.0	0.0	0.0	0.0	0.0	0.0	6.6	0.0
tetrahydroretene	0.0	0.0	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
seco-dehydroabietic acid #1	0.0	0.0	1.7	4.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
seco-dehydroabietic acid #2 + retene	0.0	0.0	6.7	5.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8-isopimarenoic acid	0.0	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
pimaranoic acid	0.0	0.0	3.6	11.8	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0
isopimaranoic acid (+ RA314?)	0.0	0.0	7.0	3.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
unid. RA316?	0.0	0.0	5.3	2.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
unid. RA318 (8-abietenoic?)	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
abietanoic + 7-oxokauranoic acids	3.8	0.5	28.0	57.9	2.2	0.4	0.0	7.2	0.5	0.0	5.6	0.9
dehydroabietic acid	5.0	0.0	10.1	9.4	2.2	0.0	0.0	3.5	0.3	0.0	1.3	0.4
unid. RA330?	0.0	0.0	0.0	4.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
unid. RA350? (+ 7-oxodehydroabietic acid)	12.4	0.0	14.3	0.0	0.0	0.0	0.0	4.5	0.0	0.0	0.0	0.0
unid. RA348?	9.4	0.0	13.7	0.0	0.0	0.0	0.0	4.9	0.0	0.0	0.0	0.0
unid. RA350?	13.2	0.0	18.1	0.0	0.0	0.0	0.0	6.1	0.0	0.0	0.0	0.0
unid. RA350?	8.3	0.0	8.8	0.0	0.0	0.0	0.0	3.2	0.0	0.0	0.0	0.0
unid. mw=400?	3.2	0.0	10.5	7.4	0.0	0.0	0.0	2.2	0.0	0.0	0.0	0.0
unid. mw=402?	20.6	0.0	45.2	0.0	0.0	0.0	0.0	9.0	0.0	0.0	5.3	0.0
unid. mw=400?	0.0	0.0	1.8	0.0	0.0	0.0	0.0	2.1	0.0	0.0	0.0	0.0
Total DTs	0.0	0.0	32.3	54.6	0.0	0.0	0.0	0.0	0.0	0.0	11.8	0.0
Total RAs (i.d.)	12.9	0.5	58.4	91.9	4.4	0.4	0.0	10.7	0.8	0.0	7.4	1.4
Total identified RAs+DTs	12.9	0.5	90.6	146.5	4.4	0.4	0.0	10.7	0.8	0.0	19.2	1.4
Total DT + RA + mw 330-350	56.3	0.5	145.5	151.1	4.4	0.4	0.0	29.4	0.8	0.0	19.2	1.4

Table A2.20 (cont.): Extractable organics in off-site wells

November 1987 sampling:

Well	73/1	73/2	73/3	74/1	74/2	74/3	74/4	89/1	89/2	89/3	90/1	90/2	90/3
FA16:0	1.7	1.7	1.5	3.0	2.6	2.3	5.1	1.3	1.5	2.6	4.7	1.9	0.8
FA18:0	1.1	0.5	0.8	0.7	0.6	0.9	5.4	0.8	0.6	2.9	2.2	0.8	0.5
Total Fatty Acids	2.8	2.2	2.3	3.7	3.1	3.2	10.6	2.1	2.1	5.5	6.9	2.7	1.3
DT262P	0.0	0.0	0.0	12.7	10.6	0.0	0.0	0.0	0.0	0.0	0.0	3.5	0.0
fichtelite	0.0	1.8	0.0	53.9	43.8	0.0	0.0	0.0	0.0	0.0	0.0	5.1	0.0
tetrahydroretene	0.0	0.0	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
seco-dehydroabietic acid #1	0.0	2.5	0.0	0.6	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0
seco-dehydroabietic acid #2 + retene	0.0	2.6	0.0	4.9	1.9	0.8	0.0	0.0	1.9	0.0	0.0	0.4	0.0
pimaranoic acid	0.0	0.0	0.0	1.4	1.6	0.8	0.0	0.0	0.0	0.0	0.0	1.1	0.0
unid. RA304? + 13-abietenoic acid	0.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	1.6	0.0	0.0	1.2	0.0
isopimaranoic acid (+ RA314?)	0.0	0.0	0.0	0.9	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
unid. RA316?	0.0	2.4	0.0	0.4	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0
abietanoic + 7-oxokauranoic acids	3.2	31.4	0.3	7.4	15.6	1.1	6.1	0.8	2.5	0.0	0.0	3.7	0.0
dehydroabietic acid	1.5	7.1	0.1	2.1	2.6	1.3	2.7	0.0	2.6	0.0	0.0	1.6	0.0
unid. RA350? (+ 7-oxodehydroabietic acid)	0.0	0.0	0.0	1.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.8	0.0
unid. RA348?	0.0	0.0	0.0	1.4	0.0	0.0	0.0	0.0	2.8	0.0	0.0	1.7	0.0
unid. RA350?	0.0	0.0	0.0	2.6	1.1	0.0	0.0	0.0	6.2	0.0	0.0	0.0	0.0
unid. RA350?	0.0	0.0	0.0	1.0	1.1	0.0	0.0	0.0	2.6	0.0	0.0	0.0	0.0
unid. mw=400?	0.0	0.0	0.0	2.0	1.1	0.0	0.0	0.0	2.2	0.0	0.0	1.2	0.0
unid. mw=402?	0.0	0.0	0.0	1.5	1.1	0.0	0.0	0.0	16.2	0.0	0.0	7.7	0.0
unid. mw=400?	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0	0.0	2.2	0.0
Total DTs	0.0	3.2	0.0	73.1	55.9	0.8	0.0	0.0	1.9	0.0	0.0	8.8	0.0
Total RAs (i.d.)	4.7	47.7	0.4	13.2	21.9	3.2	8.8	0.8	7.3	0.0	0.0	8.1	0.0
Total identified RAs+DTs	4.7	50.8	0.4	86.3	77.8	4.0	8.8	0.8	9.2	0.0	0.0	16.9	0.0
Total DT + RA + mw 330-350	4.7	50.8	0.4	93.0	79.9	4.0	8.8	0.8	20.9	0.0	0.0	20.4	0.0

Table A2.20 (cont.): Extractable organics in off-site wells

April 1989 and July 1989 sampling:

Well	73/1	73/2	73/3	74/1	74/2	74/3	74/4	89/1	89/2	89/3	90/1	90/2	86/1	86/2	74/1
Date	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Apr-89	Jul-89
FA16:1	0.8	0.6	8.0	4.4	1.4	0.4	10.1	4.0	1.9	9.2	6.0	1.9	3.2	1.8	7.5
FA16:0	3.4	1.1	8.9	3.4	2.3	0.8	17.5	2.2	1.4	40.1	9.2	1.6	1.9	1.1	4.7
FA18:1	1.8	0.6	10.0	2.2	0.5	0.3	4.8	1.3	0.7	3.3	3.3	1.8	0.7	0.5	2.7
FA18:0	1.2	0.5	6.2	0.7	1.5	0.3	14.5	0.7	0.4	34.0	4.2	0.6	0.6	0.2	1.0
Total Fatty Acids	7.3	2.8	33.1	10.7	5.7	1.7	46.9	8.2	4.5	86.6	22.6	5.9	6.4	3.7	15.9
DT260P				2.4	2.7	0.2									8.2
DT260I				5.2	5.7	0.6									
DT262P				8.1	7.5	0.7									
DT262I				2.9	3.8	0.1									1.5
fichtelite		0.8		25.6	25.8	1.8			0.5						19.4
seco-dehydroabietic acid #1	0.7	0.9		1.0	2.4	0.2			0.6						1.0
seco-dehydroabietic acid #2	0.8	0.9		1.5	3.0	0.2			0.5						1.9
retene				1.3	7.2	0.2			0.3						
8,15-pimaradienoic acid	0.8				2.6										
8-pimarenoic acid	1.1	0.8	0.5	2.4	2.0	0.2									2.6
8-isopimarenoic acid	1.4	2.4	0.3	1.7	6.3	0.4									
pimaranoic acid				2.9	14.1	0.8									3.2
unid. RA304? + 13-abietenoic acid	1.5	1.5													
isopimaranoic acid (+ 13-abietenoic acid)				2.4	7.5	0.7			0.6						3.2
unid. RA318 (8-abietenoic?)	1.0														
abietanoic + 7-oxokauranoic acids	4.2	16.2	3.7	12.6	43.4	1.9	0.2		0.8						12.4
dehydroabietic acid	5.8	2.6	0.7	1.5	1.4	0.5			0.2						2.1
unid. RA330?	1.1	1.2		2.2	1.2	0.7			0.9						
unid. RA350? (+ 7-oxodehydroabietic acid)	1.1	2.9		2.3	5.0	0.7									6.4
unid. RA348?	1.4	2.5		2.9	6.3	0.8			0.4						3.1
unid. RA350?															1.7
unid. RA350?															
unid. mw=400?															0.6
unid. mw=402?															0.2
unid. mw=400?															1.0
Total DTs	0.0	0.8	0.0	45.6	52.6	3.5	0.0	0.0	0.8	0.0	0.0	0.0	0.0	0.0	29.2
Total RAs (i.d.)	17.3	25.2	5.2	26.0	82.6	4.7	0.2	0.0	2.6	0.0	0.0	0.0	0.0	0.0	26.3
Total identified RAs+DTs	17.3	26.0	5.2	71.6	135.2	8.3	0.2	0.0	3.4	0.0	0.0	0.0	0.0	0.0	55.5
Total DT + RA + m/z 330-350	20.8	32.6	5.2	79.0	147.6	10.5	0.2	0.0	4.8	0.0	0.0	0.0	0.0	0.0	66.7

Table A2.21: Ground waters sampled October 1990

Sample	B11/1	B11/2	B16/1	B74/2
sodium (mg/L)	329	183	150	170
colour (CPU)	801	1918	39	246
AOX (mg/L)	6.9	7.4	1.5	1.7

Extractable organics (ug/L)	B11/1	B11/2	B16/1	B74/2
2,3,5-TMCP	13.3	16.4	0.0	4.8
2,3,4-TMCP	15.8	7.9	0.0	5.4
TetMCP	7.5	3.5	2.4	0.0
TetMCP	0.0	0.0	0.8	0.0
TetMCP	0.0	0.0	0.0	0.0
TetMCP	5.0	4.9	0.0	3.1
Total methy-2-cyclopentenones	41.6	32.8	3.2	13.3
FA14:0	0.0	0.0	1.1	1.4
FA16:0	12.6	11.5	15.9	13.4
anteiso FA17:0	0.0	0.0	0.0	0.0
FA18:2	0.0	0.0	0.0	2.5
FA18:1	10.3	7.0	2.0	1.8
FA18:0	7.2	5.0	7.7	1.3
FA18:2	0.0	0.0	0.0	0.0
Total Fatty Acids	30	23	27	20
DT260P/I/A + 262P (ur)	256.1	55.6	44.7	22.3
DT262I	50.0	0.0	0.0	0.9
fichtelite	383.0	68.1	19.8	16.3
dehydroabietin	43.5	3.0	0.0	0.0
tetrahydroretene	7.5	0.0	0.0	0.0
seco-dehydroabietic acid #1	18.6	10.2	7.5	4.9
seco-dehydroabietic acid #2 + retene	1251.7	71.1	8.0	1.0
8-isopimarenoic acid	17.7	6.0	1.2	1.2
unid. mw=290?	9.6	5.9	0.0	0.0
8-pimarenoic acid	37.8	26.2	0.6	1.8
pimaranoic acid	95.7	41.4	4.2	4.0
isopimaranoic + 13-abietenoic acids	49.6	17.8	2.0	1.9
abietanoic + 7-oxokauranoic acids	148.8	108.1	5.4	10.2
dehydroabietic acid	23.4	20.5	1.3	2.4
Total RAs plus DTs	2393	434	95	67
Total Resin Acids	410.4	241.3	25.9	28.8
Total Diterpene Hydrocarbons	1982.6	192.8	68.8	38.1

Table A2.22: Summary data for FD-E column leachate

Sample FD-E/	Feed Effluent	Volume Collected mL	Cumulative Volume mL	Pore Volumes	Mean Volume L	Ave Pore Volumes	Na+ mg/L	Cl- mg/L	colour CPU	Fe mg/L	pH	Tot MT µg/L	Tot FA µg/L	Tot RA µg/L
1	DW	600					10	1	126	2.2	n.a.			
2	DW	600	0	0.00	0	0	9	1	90	2.0	n.a.			
3	Batch 1	600	600	0.13	0.30	0.07	10	2	63	0.5	7.6			
4	Batch 1	600	1200	0.26	0.90	0.20	10	1	61	1.0	7.6			
5	Batch 1	600	1800	0.39	1.50	0.33	10	1	73	0.8	7.5			
6	Batch 1	600	2400	0.52	2.10	0.46	11	4	39	1.4	6.7			
7	Batch 1	600	3000	0.65	2.70	0.59	12	24	24	0.5	6.7			
8	Batch 1	600	3600	0.78	3.30	0.72	18	66	1	0.1	6.6			
9	Batch 1	600	4200	0.91	3.90	0.85	23	124	2	0.7	6.5			
10	Batch 1	600	4800	1.04	4.50	0.98	63	313	0	25.4	6.6	346	67	
11	Batch 1	600	5400	1.17	5.10	1.11	153	485	2	37.5	6.4	5039	19	
12	Batch 1	600	6000	1.30	5.70	1.24	270	616	13	29.1	6.5	10032	17	
13	Batch 1	600	6600	1.43	6.30	1.37	354	656	8	6.6	6.7	12969		
14	Batch 1	600	7200	1.57	6.90	1.50	402	674	24	8.6	6.3	28245	10	
15	Batch 1	600	7800	1.70	7.50	1.63	434	602	77	5.0	7.0	22237	64	
16	Batch 1	600	8400	1.83	8.10	1.76	499	583	764	15.2	8.2	12431	337	31
17	Batch 1	600	9000	1.96	8.70	1.89	587	577	1020	11.4	8.6	4250	624	11
18	Batch 1	600	9600	2.09	9.30	2.02	618	591	1186	10.5	7.1	11514	567	37
19	Batch 1	600	10200	2.22	9.90	2.15	600	621	1097	10.3	8.0	8169	423	27
20	Batch 1	600	10800	2.35	10.50	2.28	674	617	1415	10.4	8.7	6967	381	28
21	Batch 1	600	11400	2.48	11.10	2.41	706	616	1384	10.4	7.8	5764	339	29
22	Batch 1	600	12000	2.61	11.70	2.54	773	622	1840	10.6	8.1	6089	450	47
23	Batch 1	600	12600	2.74	12.30	2.67	734	648	1040	11.0	6.8	6414	560	66
24	Batch 1	600	13200	2.87	12.90	2.80	738	630	1120	10.1	7.4	2040	663	39
25	Batch 2	600	13800	3.00	13.50	2.93	669	635	1923	3.3	7.8	39	462	43
26	Batch 2	600	14400	3.13	14.10	3.07	659	649	2577	5.7	7.3	38	961	62
27	Batch 2	600	15000	3.26	14.70	3.20	697	690	2464	7.7	7.0		1051	30
28	Batch 2	600	15600	3.39	15.30	3.33	745	626	2071	6.9	7.3		623	33
29	Batch 2	600	16200	3.52	15.90	3.46	836	621	1186	5.3	7.7		554	31
30	Batch 2	600	16800	3.65	16.50	3.59	880	675	893	4.9	7.4		154	12
31	Batch 2	600	17400	3.78	17.10	3.72	873	697	929	4.9	7.4		614	33
32	Batch 2	600	18000	3.91	17.70	3.85	780	671	1321	4.9	7.7		990	27
33	Batch 3	600	18600	4.04	18.30	3.98	716	642	1786	5.9	7.2		1815	48
34	Batch 3	600	19200	4.17	18.90	4.11	719	651	2079	5.9	7.3		1543	109
35	Batch 3	600	19800	4.30	19.50	4.24	706	646	2731	7.1	8.1		2467	69
36	Batch 3	600	20400	4.43	20.10	4.37	706	643	3042	7.0	7.2		1546	89
37	Batch 3	600	21000	4.57	20.70	4.50	706	647	2875	5.7	7.2		2028	59
38	Batch 3	600	21600	4.70	21.30	4.63	718	666	2571	6.3	7.2		1868	101
39	Batch 3	600	22200	4.83	21.90	4.76	707	651	2652	7.9	8.6		1755	49
40	Batch 4	600	22800	4.96	22.50	4.89	698	648	2333	6.5	7.2		871	39
41	Batch 4	600	23400	5.09	23.10	5.02	685	624	2500	7.4	8.5		959	66
42	Batch 4	600	24000	5.22	23.70	5.15	798	632	2462	7.2	7.3		1060	36
43	Batch 4	600	24600	5.35	24.30	5.28	730	628	2308	6.3	8.7		849	36
44	Batch 4	600	25200	5.48	24.90	5.41	717	612	2643	6.8	8.9		1489	20
45	Batch 4	600	25800	5.61	25.50	5.54	685	605	3267	7.8	7.7		4651	40
46	Batch 5	600	26400	5.74	26.10	5.67	778	564	4714	8.7	8.7		522	18
47	Batch 5	600	27000	5.87	26.70	5.80	762	483	5893	12.0	8.8		673	46
48	Batch 5	600	27600	6.00	27.30	5.93	748	441	6633	17.0	9.0		1199	45
49	Batch 5	600	28200	6.13	27.90	6.07	761	413	6285	14.2	8.8		325	25
50	Batch 5	600	28800	6.26	28.50	6.20	772	n.a.	7821	18.4	8.4		591	32
51	Batch 5	600	29400	6.39	29.10	6.33	783	n.a.	8286	17.3	9.0		298	29
52	Batch 5	600	30000	6.52	29.70	6.46	800	n.a.	8143	17.70	8.1		1006	37
53	Batch 6	600	30600	6.65	30.30	6.59	822	n.a.	8643	18.1	8.5		605	67
54	Batch 6	600	31200	6.78	30.90	6.72	871	n.a.	9602	20.5	8.1	51	173	59
55	Batch 6	600	31800	6.91	31.50	6.85	899	n.a.	9893	18.1	8.8	430	426	132
56	Batch 6	600	32400	7.04	32.10	6.98	915	n.a.	10059	17.2	9.0	198	319	65
57	Batch 6	600	33000	7.17	32.70	7.11	915	n.a.	10555	16.7	8.8		343	109
58	Batch 6	600	33600	7.30	33.30	7.24	931	n.a.	10133	15.0	9.0	368	471	142
59	Batch 6	600	34200	7.43	33.90	7.37	926	n.a.	8965	14.9	8.8	174	323	117
60	Batch 7	600	34800	7.57	34.50	7.50	944	n.a.	7098	10.0	7.5			210
61	Batch 7	600	35400	7.70	35.10	7.63	940	n.a.	7316	10.4	7.3			303
1'	Batch 8	600	36000	7.83	35.70	7.76	733	n.a.	4524	7.7	7.6	11151		9535
2'	Batch 8	600	36600	7.96	36.30	7.89	792	n.a.	5004	8.0	7.5	4252		2158
3'	Batch 8	600	37200	8.09	36.90	8.02	825	n.a.	5451	7.1	7.9	1477		605
4'	Batch 8	600	37800	8.22	37.50	8.15	897	n.a.	3760	7.0	7.6	218		216
5'	Batch 8	600	38400	8.35	38.10	8.28	926	n.a.	2150	5.1	7.4	1546		382
6'	Batch 9	600	39000	8.48	38.70	8.41	1040	n.a.	1584	7.0	7.5	124		79
7'	Batch 9	600	39600	8.61	39.30	8.54	1060	n.a.	988	5.3	7.5	121		80
8'	Batch 9	600	40200	8.74	39.90	8.67	970	n.a.	968	6.4	7.5	251		32
9'	Batch 9	600	40800	8.87	40.50	8.80	849	n.a.	1171	7.2	7.4	402		45
10'	Batch 9	600	41400	9.00	41.10	8.93	736	n.a.	1571	8.2	7.3	855		166
11'	Batch 9	600	42000	9.13	41.70	9.07	665	n.a.	1798	8.8	7.1	2992		3068
12'	Batch 9	600	42600	9.26	42.30	9.20	656	n.a.	1708	8.0	7.1	2302		1169
13'	Batch 10	600	43200	9.39	42.90	9.33	636	n.a.	1736	6.6	7.2	1459		520
14'	Batch 10	600	43800	9.52	43.50	9.46	580	n.a.	1844	4.9	7.3	1759		812
15'	Batch 10	600	44400	9.65	44.10	9.59	563	n.a.	1844	5.6	7.2	2237		381
16'	Batch 10	600	45000	9.78	44.70	9.72	549	n.a.	1728	3.8	7.2	1568		584
17'	Batch 10	600	45600	9.91	45.30	9.85	531	n.a.	1916	5.1	7.3	743		559
18'	Batch 10	600	46200	10.04	45.90	9.98	512	n.a.	2168	5.6	7.2	395		415
19'	Batch 10	600	46800	10.17	46.50	10.11	502	n.a.	2286	6.5	7.2	2839	2833	4227
20'	Batch 10	600	47400	10.30	47.10	10.24	505	n.a.	2393	5.4	7.3	370	27	345
21'	Batch 10	600	48000	10.43	47.70	10.37	510	n.a.	2484	8.5	7.3	556	18	238
22'	Batch 10	600	48600	10.57	48.30	10.50	512	n.a.	2496	5.7	7.8	615	19	273
23'	Batch 10	600	49200	10.70	48.90	10.63	508	n.a.	2345	4.5	7.4	719	63	519
24'	Batch 10	600	49800	10.83	49.50	10.76	515	n.a.	2282	3.9	7.3	600	12	256
25'	Batch 10	600	50400	10.96	50.10	10.89	510	n.a.	2206	3.6	7.3	759	14	221

n.a. not analysed
blank entries indicate concentrations below quantifiable levels

Table A2.23: Summary data for CF-E column leachate

Sample CF-E/	Feed Effluent	Volume Collected mL	Cumulative Volume mL	Pore Volumes	Mean Volume L	Mean Pore Volumes	Na+ mg/L	Cl- mg/L	colour CPU	Fe mg/L	pH	Tot MT µg/L	Tot FA µg/L	Tot RA µg/L
1	DW	1000					7.7	1.1	160	1.3	7.1			
2	DW	1000	0	0.00	0	0	7.7	1.3	117	1.3	7.0			
3	Batch 1	600	600	0.20	0.30	0.10	8.4	2.5	86	0.9	7.2			
4	Batch 1	650	1250	0.42	0.93	0.31	17	26	10	0.6	6.5	3221	23	14
5	Batch 1	750	2000	0.67	1.63	0.54	54	149	8	0.3	6.5	2263	73	
6	Batch 1	600	2600	0.87	2.30	0.77	120	226	4	1.0	6.1	3914	3	
7	Batch 1	1000	3600	1.20	3.10	1.03	272	388	74	17.8	5.8	5335	281	
8	Batch 1	1000	4600	1.53	4.10	1.37	346	433	684	18.5	6.2	20028	118	136
9	Batch 1	750	5350	1.78	4.98	1.66	371	489	1633	20.0	6.4	24541	116	200
10	Batch 1	1100	6450	2.15	5.90	1.97	491	495	2860	20.2	6.6	26903	608	113
11	Batch 1	1100	7550	2.52	7.00	2.33	523	583	3200	21.8	6.3	22879	899	184
12	Batch 1	670	8220	2.74	7.89	2.63	545	543	3880	22.9	6.5	25800	171	249
13	Batch 1	870	9090	3.03	8.66	2.89	531	535	2065	6.0	6.1	24546	1471	204
14	Batch 1	700	9790	3.26	9.44	3.15	538	514	2133	35.0	5.9	26400	606	212
15	Batch 1	780	10570	3.52	10.18	3.39	529	558	3982	32.9	6.0	21936	185	331
16	Batch 1	1000	11570	3.86	11.07	3.69	569	554	3510	27.3	6.2	15647	1191	270
17	Batch 1	720	12290	4.10	11.93	3.98	548	561	4315	31.7	6.0	12948	717	352
18	Batch 1	800	13090	4.36	12.69	4.23	516	547	2000	32.8	5.8	23987	416	229
19	Batch 1	680	13770	4.59	13.43	4.48	533	595	1512	39.2	7.3	28639	471	339
20	Batch 1	2400	16170	5.39	14.97	4.99	672	637	4556	35.8	7.6	33291	1058	600
21	Batch 1	770	16940	5.65	16.56	5.52	653	657	5179	29.6	7.2	25385	1119	547
22	Batch 1	1050	17990	6.00	17.47	5.82	666	627	6205	28.3	6.1	30993	1575	1035
23	Batch 1	1100	19090	6.36	18.54	6.18	704	670	6786	23.9	6.4	26493	977	1112
24	Batch 1	1150	20240	6.75	19.67	6.56	751	672	7411	24.6	6.3	21993	379	1188
25	Batch 1	900	21140	7.05	20.69	6.90	746	683	9692	25.9	7.6	24809	1462	725
26	Batch 2	830	21970	7.32	21.56	7.19	757	675	9115	23.3	7.8	19026	1189	669
27	Batch 2	820	22790	7.60	22.38	7.46	815	659	6929	21.0	6.8	26941	561	893
28	Batch 2	780	23570	7.86	23.18	7.73	853	646	5500	17.9	7.2	29333	571	687
29	Batch 2	780	24350	8.12	23.96	7.99	852	652	4465	15.2	7.4	29673	1048	807
30	Batch 2	1150	25500	8.50	24.93	8.31	824	681	3893	12.7	7.2	21993	732	1079
31	Batch 2	680	26180	8.73	25.84	8.61	774	690	3643	10.2	8.9	25020	2229	2392
32	Batch 2	650	26830	8.94	26.51	8.84	751	700	4286	10.4	8.4	30109	1678	2558
33	Batch 3	740	27570	9.19	27.20	9.07	755	662	4390	9.9	7.5	30488	1624	2552
34	Batch 3	740	28310	9.44	27.94	9.31	795	654	4500	9.5	7.4	30990	2825	3339
35	Batch 3	1300	29610	9.87	28.96	9.65	796	668	4269	8.3	7.7	38269	1616	4105
36	Batch 3	1100	30710	10.24	30.16	10.05	774	653	3917	4.4	8.0	41204	1161	4491
37	Batch 3	630	31340	10.45	31.03	10.34	746	671	4792	3.1	7.7	44718	1237	4545
38	Batch 3	630	31970	10.66	31.66	10.55	747	592	3964	2.7	7.8	34706	1187	3985
39	Batch 3	700	32670	10.89	32.32	10.77	720	664	3799	2.3	8.1	35073	1188	4073
40	Batch 4	670	33340	11.11	33.01	11.00	698	669	3633	2.9	7.6	34715	1053	3704
41	Batch 4	820	34160	11.39	33.75	11.25	710	630	3393	1.6	8.4	34357	918	3334
42	Batch 4	720	34880	11.63	34.52	11.51	825	644	3538	1.5	7.6	32669	957	3191
43	Batch 4	630	35510	11.84	35.20	11.73	755	651	2429	1.5	8.7	30221	1711	3325
44	Batch 4	1100	36610	12.20	36.06	12.02	744	585	3600	1.6	8.9	35493	2889	3357
45	Batch 4	630	37240	12.41	36.93	12.31	715	539	4733	1.5	8.2	30742	1468	4265
46	Batch 5	800	38040	12.68	37.64	12.55	831	505	5679	2.2	8.6	28995	915	4502
47	Batch 5	670	38710	12.90	38.38	12.79	813	460	6142	1.1	8.5	25198	922	3728
48	Batch 5	770	39480	13.16	39.10	13.03	820	447	5800	2.0	8.6	22102	1048	4482
49	Batch 5	690	40170	13.39	39.83	13.28	806	429	7321	1.2	8.6	21950	637	4518
50	Batch 5	650	40820	13.61	40.50	13.50	827	n.a.	6536	1.1	7.7	22908	841	4845
51	Batch 5	1200	42020	14.01	41.42	13.81	856	n.a.	6179	1.2	8.9	23300	986	5809
52	Batch 5	630	42650	14.22	42.34	14.11	890	n.a.	6607	1.4	8.2	22371	2609	4663
53	Batch 6	630	43280	14.43	42.97	14.32	892	n.a.	7000	1.1	8.0	19049	844	4604
54	Batch 6	1000	44280	14.76	43.78	14.59	913	n.a.	7714	1.3	8.3	18299	503	5384
55	Batch 6	1100	45380	15.13	44.83	14.94	912	n.a.	7500	0.8	8.4	19154	1045	4868
56	Batch 6	1100	46480	15.49	45.93	15.31	940	n.a.	7926	0.8	8.5	15869	1257	6714
57	Batch 6	1100	47580	15.86	47.03	15.68	922	n.a.	7598	0.8	8.3	22065	737	7078
58	Batch 6	1000	48580	16.19	48.08	16.03	896	n.a.	6774	1.0	8.9	16472	1093	8927
59	Batch 6	700	49280	16.43	48.93	16.31	876	n.a.	6637	0.8	8.3	15301	692	11256
60	Batch 7	680	49960	16.65	49.62	16.54	865	n.a.	7059	1.1	7.9	12715	212	11548
1'	None	800	800	0.27	0.4	0.13	974	n.a.	16138	3.3	7.9	17618		13587
2'	Batch 8	700	1500	0.50	1.15	0.38	964	n.a.	15590	2.8	7.9	22550		21801
3'	Batch 8	850	2350	0.78	1.93	0.64	982	n.a.	13550	2.4	7.9	22202		18869
4'	Batch 8	900	3250	1.08	2.80	0.93	1020	n.a.	7078	1.5	8.0	26882		15747
5'	Batch 9	1200	4450	1.48	3.85	1.28	940	n.a.	4110	1.2	8.0	36448		23605
6'	Batch 9	700	5150	1.72	4.80	1.60	737	n.a	3104	1.4	7.9	25421		33143
7'	Batch 9	800	5950	1.98	5.55	1.85	676	n.a.	2908	0.8	8.2	22935		33436
8'	Batch 9	420	6370	2.12	6.16	2.05	638	n.a.	2792	0.8	8.2	23172		35608
9'	Batch 9	720	7090	2.36	6.73	2.24	616	n.a.	2810	0.8	7.8	26267		33030
10'	Batch 9	700	7790	2.60	7.44	2.48	594	n.a.	2877	0.8	8.0	25635		36935
11'	Batch 9	620	8410	2.80	8.10	2.70	586	n.a.	2774	0.7	8.1	27576		29617
12'	Batch 10	690	9100	3.03	8.76	2.92	585	n.a.	2696	0.9	8.0	29573		25426
13'	Batch 10	520	9620	3.21	9.36	3.12	594	n.a.	2828	1.0	8.1	26566		23390
14'	Batch 10	800	10420	3.47	10.02	3.34	603	n.a.	2644	1.0	8.4	29770		16317
15'	Batch 10	670	11090	3.70	10.76	3.59	598	n.a.	2272	1.0	7.9	30543		15464
16'	Batch 10	800	11890	3.96	11.49	3.83	586	n.a.	2096	0.8	8.1	29423		15926
17'	Batch 10	700	12590	4.20	12.24	4.08	574	n.a.	2328	1.3	8.2	29130		14805
18'	Batch 10	500	13090	4.36	12.84	4.28	577	n.a.	1976	1.0	7.9	27005		14043
19'	Batch 10	700	13790	4.60	13.44	4.48	570	n.a.	2119	1.0	7.3	25381		13128
20'	Batch 10	620	14410	4.80	14.10	4.70	559	n.a.	2091	1.0	7.9	27921		14823
21'	Batch 10	800	15210	5.07	14.81	4.94	546	n.a.	2345	0.9	7.7	30588		13498
22'	none	710	15920	5.31	15.57	5.19	559	n.a.	2329	1.0	7.7	33242		10800
23'	none	1900	17820	5.94	16.87	5.62	550	n.a.	2250	1.0	8.1	26603		12293

n.a. not analysed

blank entries indicate concentrations below quantifiable levels

Table A2.24: Extractable organics (mg/kg) in column sediments

CF-E column sediments:

Sample (CF-E/)	1	2	3	4	5	6	7	8	9	10	Blank	Soil pre-
Depth (mid-section, mm)	17.5	67.5	125	175	250	350	450	550	650	757.5		effluent addn
2,3-dimethyl-2-cyclopentenone	6.6	6.0	1.7	0.8	0.8	0.5	0.0	0	0	0	0	0.0
Total Methyl-2-cyclopentenones	6.6	6.0	1.7	0.8	0.8	0.5	0.0	0	0	0	0	0.0
a-pinene	7.2	1.8	1.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ß-pinene	6.6	2.6	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MT138	50.4	51.0	12.5	7.9	7.3	3.6	2.1	0.0	0.0	0.0	0.0	0.0
p-cymene	547	467	150	67	56	32	22	27	13	16	4	0.0
limonene			2.9	3.1	2.9	1.0	0.0					
camphor	3.9	1.7	1.6	1.4	1.6	1.4	1.3	1.6	1.2	1.4	0.0	0.0
4-terpineol	1.4	0.9	1.0	1.8	2.0	3.5	3.9	4.1	2.2	2.4	0.0	0.0
a-terpineol	8.8	6.4	5.0	3.7	3.8	3.3	2.7	3.7	2.5	3.1	0.0	0.0
Total Monoterpenes	625	531	175	85	74	44	32	37	19	23	4	0.0
unid. mw=204 (#2)	9.7	3.3	1.0	0.8	0.7	0.7	0.0	0.0	0.0	0.0	0.0	0.0
unid. mw=204 (#4)	12.4	4.4	1.3	1.0	1.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0
FA14:0	7.2	7.0	2.0	2.9	2.8	1.7	1.4	0.7	1.0	0.5	2.0	0.9
FA16:0	81.1	32.5	39.6	54.1	34.4	22.8	16.2	6.7	7.4	6.0	6.5	3.4
anteiso-FA17:0	5.6	4.2	2.0	2.9	2.1	1.5	1.1	0.6	0.7	0.5		
FA 18:1 (oleic acid)	37.5	26.2	8.5	13.3	9.3	5.6	6.1	11.2	10.7	13.5	7.8	0.7
FA 18:1	41.3	25.3	13.3	21.3	13.0	6.7	5.1	5.1	5.9	5.5	5.3	0.6
FA18:0	17.6	10.9	5.2	7.8	6.2	4.0	3.2	1.8	2.3	1.6	0.0	1.1
Total Fatty Acids	190	106	71	102	68	42	33	26	28	28	22	6.8
DT272	5.0	1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
dehydroabietin	14.2	3.9	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DT270	9.0	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DT272	40.1	11.6	4.6	3.0	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
seco-dehydroabietic acid #1	44.5	12.0	6.8	7.8	4.3	8.2	10.8	6.4	5.3	4.0	0.0	1.0
seco-dehydroabietic acid #2	25.0	7.7	3.8	4.3	2.1	3.3	4.8	2.9	2.3	1.8	0.0	0.4
pimaric acid	247.0	45.7	26.6	38.0	21.6	20.1	9.5	1.5	0.9	0.5	0.0	0.6
8-isopimarenoic acid						1.2	2.4	1.3	0.6	0.4		0.3
sandaracopimaric acid	32.3	6.6	3.9	5.8	3.4	5.1	5.7	2.7	1.8	1.6	0.0	1.6
8(14)-pimarenoic acid	3.2	23.7	8.9	2.5	3.9	33.2	32.1	8.8	2.9	3.4	0.0	2.5
8(14)-isopimarenoic acid		3.5	1.6	0.0		4.1	3.5	0.0	0.0	0.0		
13-abietenoic acid (+ isopimaric acid)	426.1	134.7	96.8	130.7	95.0	116.2	60.5	27.3	17.2	9.9	0.0	1.9
abietanoic acid	17.3	24.1	15.0	12.8	19.9	78.4	78.9	59.4	55.5	51.4	0.0	23.5
dehydroabietic acid	241.1	159.9	98.2	103.9	87.5	109.8	147.6	109.6	72.0	45.5	0.0	2.4
unid. RA318 (8-abietenoic?)								1.7	1.1	1.3		
abietic acid	8.4	0.0	1.5	2.7	2.4	1.8	0.0	0.0	0.0	0.0	0.0	0.0
13ß-hydroxyabietanoic acid	7.4	5.4	3.9	1.9	2.2	1.7	1.4	0.7	0.0	0.0	0.0	0.0
Total Resin Acids	1121	442	272	313	244	383	357	222	160	120	0	34.4

FD-E column sediments:

Sample (FD-E/)	1	2	3	4	5	6	7	8	9	10	Blank	Soil pre-
Depth (mid-section, mm)	15	65	150	250	350	450	550	650	750	835		effluent addn
4-terpineol	0.0	0.0	0.0	0.0	0.0	0.4	0.9	0.0	0.0	0.0		
Total Monoterpenes	0.0	0.0	0.0	0.0	0.0	0.4	0.9	0.0	0.0	0.0		
FA14:0	1.3	1.3	1.8	1.4	1.0	1.2	1.1	0.8	0.8	0.8	2.0	0.9
FA16:0	8.8	8.8	11.3	10.5	7.5	8.4	8.1	7.0	6.3	6.4	6.5	3.4
anteiso-FA17:0	1.0	1.0	1.3	1.2	0.7	0.9	0.8	0.6	0.6	0.6		
FA 18:1	1.6	0.6	0.7	0.8	0.0	0.5	0.0	0.0	0.0	0.4		0.0
FA 18:1 (oleic acid)	15.1	12.5	19.0	17.1	6.8	10.4	7.4	5.3	3.6	6.2	7.8	0.7
FA 18:1	9.9	10.0	12.7	11.2	6.2	8.0	6.6	5.2	4.6	5.6	5.3	0.6
FA18:0	2.8	2.1	2.6	2.6	1.9	2.3	1.9	2.0	0.5	1.6	3.5	1.1
Total Fatty Acids	41	36	49	45	24	32	26	21	16	22	22.0	6.8
seco-dehydroabietic acid #1	1.3	1.4	2.0	2.1	1.5	1.5	1.4	1.3	1.1	1.1	0.0	1.0
seco-dehydroabietic acid #2	0.4	0.4	0.6	0.7	0.5	0.5	0.4	0.4	0.3	0.3	0.0	0.4
pimaric acid	2.7	2.1	2.9	3.5	1.5	1.8	1.1	0.8	0.5	0.6	0.0	0.6
8-isopimarenoic acid						0.0	0.2	0.3	0.2	0.2	0.0	0.3
sandaracopimaric acid	0.7	1.0	1.3	1.6	1.3	1.4	1.3	1.3	1.1	1.2	0.0	1.6
8(14)-pimarenoic acid	0.7	1.1	1.4	1.5	1.7	1.8	1.9	2.0	1.7	1.8	0.0	2.5
8(14)-isopimarenoic acid		0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	
13-abietenoic acid (+ isopimaric acid)	3.0	2.7	3.1	4.2	3.0	3.1	2.3	1.9	1.3	1.3	0.0	1.9
abietanoic acid	5.7	10.3	13.0	14.8	17.5	16.3	16.4	17.2	14.5	15.7	0.0	23.5
dehydroabietic acid	4.3	4.9	7.6	10.6	6.9	5.9	4.5	3.8	2.6	2.1	0.0	2.4
unid. RA318 (8-abietenoic?)	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
abietic acid	3.1	1.9	1.4	0.0	0.0	0.0	0.0	0.0	0.6	0.4	0.0	
unid. RA305?	2.1	1.8	1.3	1.5	1.6	1.6	1.4	1.4	0.6	0.6	0.0	
Total Resin Acids	25	28	35	41	36	34	31	31	25	25	0.0	34.4