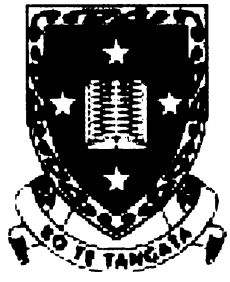
ASPECTS OF THE CHEMISTRY OF SOME PERSISTENT ORGANIC CONTAMINANTS AND THEIR REMOVAL FROM RIVER AND WASTEWATER



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Abstract

Liquid/liquid extraction, glass fibre and 3-0.05 μm filtration and SIM-GC/MS procedures were used to determine the levels of free and particle bound resin acids in Tarawera River water samples collected at the State Highway 30 bridge, downstream of the discharge point of the Tasman and Carter-Holt-Harvey Tissue pulp mills. Typically, 78-80% of the recoverable resin acids and resin neutrals were found to be associated with particulate matter.

Addition of 0.1% sodium azide at the time of collection was found to inhibit the biodegradation of resin acids in Tarawera River water samples for periods of up to 90 days. In the absence of sodium azide the biodegradation of resin acids in Tawawera River water samples stored in glass winchesters at 4°C proceeded with a half-life of ca. 19 days.

Analyses of the upper and lower zones of sodium azide stabilised Tarawera River water samples which were allowed to stand undistributed for 30 days water showed that partial settling of resin acid carrying particulate matter occurred on standing. An experiment performed using a bulk 19.6 L sample of sodium azide stabilised Tarawera River showed, that after the progressive withdrawal of analytical samples over a 30 days period, there was a 300% increase in the level of resin acids remaining in the residual 1.6 L water sample.

Provided that well mixed, sodium azide stabilised Tarawera River water samples were extracted and analysed together, total resin acids levels exhibited a coefficient of variation (CV) (for 5 or 6 replicates) of less than 7%. Prior filtration through sintered glass to remove gross particulate matter further reduced the CV to 4%. These CVs are appreciably smaller than those previously determined for unstabilised Tarawera River water samples.

Filtration experiments performed using Whatman No.1, glass fibre, 0.8, and 0.45 μm filter papers, followed by liquid/liquid extraction of filtrates and Soxhlet extraction of dried filter papers, showed that for Tarawera River water samples, typically 11, 36, 34, and 47% of the recoverable resin acids were associated with particles of size greater than the pore size of Whatman No.1, glass fibre, 0.8 and 0.45 μm filter papers respectively.

Similar results were obtained in sequential filtration experiments performed using glass fibre, 3, 0.8, 0.45, 0.2, and 0.05 μm filter papers and sodium azide stabilised Tarawera River water that had been stored for up to 90 days.

Sequential filtration of water samples from Tasman's clarifier and biological treatment ponds (ponds 1-4) showed that particle bound resin acid levels increased from ca. 5% (clarifier) to 70% (pond 4 outlet) during the passage of effluent water through the treatment system.

During treatment, free pimaric acid and dehydroabietic acid levels fell substantially, while the bound levels were approximately constant. The level of free abietan-18-oic acid remained approximately constant in ponds 2, 3 and 4, while the level of particle bound abietan-18-oic acid in these ponds increased as levels of particle bound abiet-13-enoic acid decreased.

Incubation of clarifier water for 31 days under aerobic conditions at 25°C, showed that very little degradation of resin acids present in the clarifier occurred. This result showed the clarifier water to be largely sterile.

Glass fibre filtration of pond 1 water removed little resin acid and ca. 10% of the initial of 5 day biological oxygen demand (BOD_5). Since filtration removed the component BOD_5 that degraded slowly it was concluded that particulate BOD_5 degrades more slowly than free BOD_5. dehydroabietic acid (DHAA) group resin acids (= secodehydroabeitic acids 1 and 2, dehydroabietic acid, abietic acid and abiet-13-enoic acid), pimaric acid, and abietan-18-oic acid showed similar degradation kinetics irrespective of whether they were free or particle bound. Soluble BOD_5 degraded at approximately the same rate at which resin acids were degraded.

The optimal doses of polyaluminium chloride (PAC) and polyferric sulfate (PFS), followed by Whatman No. 1 filtration, required to remove turbidity, colour and resin acids from Tarawera River water were found to be 60-70 mg/L (for PAC) and 20 mg/L (for PFS) respectively. Filtration of pond 1 water through 0.85 mm pumice reduced colour and resin acids by ca. 54-46%, whereas PFS flocculation followed by pumice

filtration reduced resin acid, colour and BOD_5 levels by 89, 89 and 88% respectively. These reductions are greater than those achieved for pond 1 water in the existing biological treatment system. Flocculation alone using 20 mg/L PFS removed most of the colour, turbidity and resin acids from pond 4 water samples.

The finding that resin acids could be recovered from flocs prompted the hypothesis that it might be possible to design an analytical technique based on pre-concentration by flocculation of the low levels of resin acids in massively diluted receiving water samples. 95-100% of expected resin acids levels were recovered in experiments performed using 5, 10 and 50-fold diluted Tarawera River water.

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List of abbreviations

AA	flame atomic absorption
18Ab	abietan-18-oic acid
Abiet	abietic acid
Σ	sum of
%	percent
% loi FDS	% weight loss on ignition of freeze dried solids
ADT	air-dried tonne
AOX	adsorbed organic halide
BCF	bioconcentration factor
BCMP	bleached chemi-mechanical pulp
BKPME	bleached kraft pulp mill effluent
BOD	biological oxygen demand
BOD_5	5 day biological oxygen demand
ca.	approximately
CCC	critical coagulation concentration
Cls	12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids
cm	centimeter
CO	clarifier outlet
COD	chemical oxygen demand
CV	coefficient of variation
CTMP	chemi-thermomechanical pulp
DDT	*p,p'*-dichlorodiphenyl-trichloroethane
DFA	dissolved air flotation
DHAA	dehydroabietic acid
DNA	Deoxynucleic acid
DO	dissolved oxygen
e.g.	for example
EDX	energy dispersive X-ray analyses
13-ene	abiet-13-enoic acid
EROD	7-ethoxyresorufin-*O*-deethylase activity
et al	and other
FID	flame ionisation detector
g	gram
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
GFFT0	glass fibre filtered at t = 0
h	hour
HCB	hexachlorobenzene
i.e.	as in
ICP	inductively coupled plasma
ISS	inorganic suspended solids
IFDS	Inorganic freeze-dried solids
L	litre
LC_{50}, 96 h	median lethal concentration – concentration required to cause mortality in half a group of organisms
K_D	distribution coefficient
Kow	n-octanol-water partition coefficient
KTB	Kawerau Town Bridge

m	meter
mg	milligram(s)
mL	millilitre
mol/L	mole per litter
min	minute
m/z	mass-to-charge ratio
MS	mass spectrometry/mass spectrum
OSS	organic suspended solids
OFDS	organic freeze-dried solids
P1	pond 1
P2	pond 2
P3	pond 3
P4	pond 4
PAHs	polyaromatic hydrocarbons
PAC	polyaluminium chloride
PDA	*O*-methylpodocarpic acid
PDA-Et	*O*-methylpodocarpic ethyl ester
PCDs	polychlorinated dibenzo-*p*-dioxins
PCDFs	polychlorinated dibenzofurans
PFS	polyferric sulfate
RF	response factor
Pim	pimaric acid
rpm	revolutions per minute
rw	river water
rs	river sediment
ww	mill waste
s	second
Seco	secodehydroabietic acids -1 and 2
SEM	scanning electron microscopy
SH30	state Highway 30
SH 2	state Highway 2
SIM	selected ion mode
stdev	standard deviation
TIC	total ion chromatogram
Tasman	Tasman Pulp and Paper Company Limited
TCDF	2,3,7,8-tetrachlorodibenzofuran
TFDS	total freeze dried solids
TMP	thermomechanical pulp
TSS	total suspended solids
TVSS	total volatile suspended solids
µg/g	micrograms/gram
µg/L	micrograms/litre
µm	micro metre
UFT0	unfiltered samples
UV	ultraviolet

Chapter 1
Introduction

1.1. Introduction

In developed economies the environmental impact of industrial processes is an area of increasing public concern. For example, in New Zealand these pressures have led to the introduction of The Resource Management Act (1991).

A producer of large volumes of wastewater is the pulp and paper industry. Pulp mill effluents are typically highly coloured, toxic, high in biochemical oxygen demand (BOD) and may contain appreciable levels of actions, suspended solids and odorous compounds.

Much of the toxicity of pulp and paper mill effluents is associated with the presence of low molecular weight extractable organic compounds, including chlorophenols and resin acids. Several authors (Kennedy *et al* 1996; Melcer *et al* 1995) have recently reviewed the toxicity of chlorophenols and resin acids. The lethal concentration that kills 50% of the population in 96 h (LC_{50}, 96 h) of resin acids towards rainbow trout and salmon is typically of the order of 1000 μg/L, with sub-lethal physiological responses apparent at 30 μg/L (Okairi *et al* 1984a,b).

In recent years technologies have been applied to reduce the impact of pulp mill effluents. In-plant technology developments include the replacement of chlorine bleaching technologies and improved methods for the treatment of wastewaters.

While these technologies can significantly reduce BOD and chlorinated organic compound levels, there remains a need to develop additional technologies to further reduce effluent impacts. Remaining problems include colour removal and a need for an improved understanding of the processes by which resin acids (often the dominant class of extractable organic compounds present in final discharges) can be attenuated by biological and/or physical process, both in treatment systems and recipient waters. In particular there is a significant gap in the literature concerning the manner in which resin

acid speciation effects influence the extent to which resin acids are degraded during both biological treatment and subsequent contact with natural recipient waters.

1.2. Evolution of the modern pulp and paper industry

Papyrus 'paper' was first produced more than five thousand years ago by the ancient Egyptians who subsequently exported it to many other parts of the ancient world. After AD 640, Arab nations introduced the Chinese method of making paper using fibres derived from rags, plants and plant residues. This method proved to be an easier and more economic process (Turner and Skiold 1983).

Much of the historical development of paper making is conjecture. However, from analyses of pieces of paper, woven cloth, metal moulds and watermark devices, historians have been able to fit together a likely pattern of development. The ages of paper making and fibre beating methods can be distinguished and identified by scientific study (Scott *et al* 1995). It was not until 1634 that the Chinese papermaking craft was described on a series of wood blocks by Sung Ying Hsing (Encyclopaedia of Chemical Technology 1996).

Smook (1997) has described the development of the paper industry in Germany. 'Der papierer' 1568, by Jost Amman is the first record of paper making in Europe. Subsequently, in 1712, Engelbert Kaempfer, a German merchant, informed Europe of the processes used in Japanese paper manufacture. Bryan Donkin developed the first usable paper machine and put it into operation in 1803. In 1820 Thomas Crompton patented a method for drying paper with the help of steam-heated cylinders and drying filters. Ground wood pulping was developed in Germany in 1840, while the kraft pulping process was invented in 1884 by Carl Dahl.

Currently the bulk of modern paper production is derived from cellulose extracted from trees. This typically involves chemical or mechanical treatments (see Section 1.2.3) to extract cellulose fibres which are then reconstituted into paper sheets. The quality of a finished paper can be further enhanced by bleaching which improves the brightness (Kappa number) of pulps.

In 1960, the global production of paper was 70 million tons, 50% of which was produced in the USA. By 1990 annual production was 210 million tons, 30% of which was produced in the USA (McGraw-Hill Encyclopaedia of Science & Technology 1997).
The chemical composition of wood is summarised in Section 1.2.1.

1.2.1. Chemical composition of wood

Wood contains three major classes of macromolecular components, cellulose (42%), hemicellulose (29%) and lignin (26%), together with low molecular weight extractives (3%) (Uprichard and Lloyd 1980).

Lignin is a highly branched aromatic polymer, which gives wood its rigidity. It acts as a macromolecular glue, binding the hemicellulose and cellulose together. The extractives include a wide range of low molecular weight organic compounds such as fatty acids, resin acids, phenolics and monoterpenes (see Table 1.1).

Table 1.1. Classes of extractable compounds (% contribution) typically present in *Pinus radiata* (Uprichard and Lloyd 1980).

compound class	heartwood	sapwood
fatty acids (free)	2	1
fatty acids (esters)	11	41
resin acids	71	41
phenols	6	3
unsaponifiables	10	14

The aim of the pulping process is to liberate the cellulose fibres from the wood tissue matrix. Chemical pulping uses specific chemicals and reaction conditions to remove unwanted lignin, while mechanical pulping liberates the cellulose by physically grinding the wood into fibres and fibre aggregates.

Mechanical pulping

Mechanical pulping involves the separating of wood fibres by physical or mechanical grinding. The oldest method is stone ground wood pulping. Subsequently refiner pulping and the mechanical pulping methods were developed. The latest advance is chemi-thermomechanical pulping (CTMP).

Stone ground wood pulping involves individual fibres being torn off de-barked logs by being ground against a revolving grindstone. Since this tends to damage the fibres and produces relatively weak paper it is not a favoured method of pulping.

Refiner pulping involves de-barked logs being chipped and refined between two parallel discs rotating in opposite directions. Modern refiners usually have discs of 900-1400 mm diameter rotating at 1200-1800 rpm. The grinding forces generate temperatures of up to 100-200°C. This causes the lignin to soften and allows cellulose fibres to be released from the chips. Paper produced by this process is stronger than that produced by the stone ground wood method.

1.2.3. Chemical pulping

The kraft process

In the kraft pulping process wood chips are cooked or digested under pressure with a mix of hot caustic soda and sodium sulfate. The insoluble cellulose fibres are left as a pulp, whilst the lignin and wood extractive are solubilised and removed. The kraft process removes as much as 90-95% of lignin from the wood (Kringstand and Lindstrom 1984). In New Zealand and throughout the world, the kraft process is the dominant chemical wood-pulping method (Sierra-Alverez 1990).

The sulfite process

The sulfite process was once a major contributor to chemical pulp production but its use has since declined. The major factors for this decline have been:

(i) alpine tree species cannot be satisfactorily pulped

(ii) pulp strengths are usually inferior to kraft pulp strengths

(iii) recovery of spent cooking liquors is difficult.

1.2.4. Thermochemical pulping

Thermomechanical pulping (TMP) is a modified refiner pulping method. Prior to pulping, chips are steamed under pressure at around 120°C to soften the lignin. The fibres are not as damaged as they are in refiner pulping. Thus better quality paper is made, however the pulp yield is slightly lower than refiner pulping.

Chemi-thermomechanical pulping

Chemi-thermomechanical pulping is thermomechanical pulping combined with a small amount of sodium sulfite in the steaming process to soften the chips before refining. High yields of pulp and high strength paper are obtained.

Mechanical pulping affords a high yield of pulp (e.g. 80-96%), since a large proportion of the lignin is retained within the fibre (McFarlane *et al* 1993; Cox 1981). During chemical wood pulping soluble organic materials are released from the wood. The principal compounds lost are normally extractives and wood sugars. Mechanical pulps require little or no bleaching. The presence of residual lignin material can cause the paper to develop a yellow colouration when exposed to heat, air or light.

1.2.5. Bleaching

Kraft pulp is usually dark due to the presence of chromophoric groups in residual lignin. Bleaching is used to brighten the pulp. It is often a two-stage process, comprising delignification and brightening stages.

The main function of the delignification stage is to remove remaining lignin, while that of the brightening stage is to increase the brightness of the pulp by chemical modification. A commonly used bleaching sequence (prior to environmental concern in respect of the production of organo-chlorine by products) was successive treatment with chlorine,

sodium hydroxide extraction, chlorine dioxide and sodium hydroxide. Bleaching processes that do not use chlorine-based chemicals have now been developed. A major advantage of these methods, which typically use peroxide, ozone or oxygen treatments, is that they do not produce chlorinated by-products (such as chlorophenols). Table 1.2 lists some common bleaching agents.

Table 1.2. Common bleaching agents.

stage	symbol	description
chlorination	C	chlorine gas or chlorine water
chlorine/chlorine dioxide	CD	chlorine and chlorine dioxide
alkaline extraction	E	sodium hydroxide solution
hypochlorite	H	sodium or calcium hypochlorite
chlorine dioxide	D	aqueous chlorine dioxide
oxygen	O	oxygen gas and alkali
peroxide	P	hydrogen peroxide
sequential chlorine dioxide and chlorine	D/C	chlorine dioxide followed by chlorination without an intermediate washing step

1.3. The origin and nature of pulp and paper effluents

Pulping processes produce different types of effluents depending on the pulp yield and the extent to which pulping chemicals are recovered. Other effluent sources include washing water from de-barking operations, scrubbing operations, bleaching, paper making, final washing and weak black liquor leaks and spills.

More than 250 chemical compounds have been identified in pulp and paper mill effluents (Suntio *et al* 1988). Much of the toxicity of such effluents has been attributed to the presence of low molecular weight organic species (Walden and Howard 1981; Liss *et al* 1997; Leach *et al* 1977). Environmentally sensitive components in pulp and paper mill effluents include chlorinated low molecular weight compounds including chlorophenols and chloro-resin acids.

Resin acids are tricyclic diterpenoids that occur naturally in wood. The structures and names of commonly encountered resin acids are given in Appendix 1. Dehydroabietic acid (DHAA), when exposed to bleaching chemicals can be chlorinated to produce mono- and dichlorinated dehydroabietic acids (Furman and Easty 1984).

Table 1.3 summarises sources of the classes of compounds commonly found in the pulp mill effluents.

Table 1.3. Sources and nature of low molecular weight components from pulp and paper processing (McFarlane *et al* 1993).

source	nature of components
wood partition	tannins, resin acids monoterpenes, carbohydrates
chemical pulping by-products	
tall oil*	resin acids and fatty acids
turpentine*	monoterpenes
black liquor*	degraded lignin products (aromatics) resin acids and fatty acids
mechanical pulping by-products	
refining/paper making	resin acids, fatty acids and monoterpenes

*Present in effluents only due to spills and uncontrollable losses

1.3.1. Effluent treatment: primary, secondary and tertiary

Raw effluent is subjected to combinations of primary, secondary and tertiary treatment to reduce the levels of environmentally sensitive components such as suspended solids, colour, BOD and toxicity. Primary treatment by physical methods such as screening, skimming and sedimentation removes solid debris, floating material and settlable solids. Secondary treatment reduces the organic content of the effluent by biochemical degradation. Colour and non degradable dissolved material can be reduced, or completely eliminated, by tertiary treatment using chemical, biological and physical processes.

In many countries, low cost treatment systems for pulp and paper effluents involve primary sedimentation with a gravity clarifier or a settling basin, followed by secondary treatment in a series of aerated lagoons. This removes most of the toxic compounds and BOD, but has little effect on colour.

Primary treatment

Clarification, using flotation or sedimentation techniques, is the most widely used form of primary treatment (Rimmer 1975; Springer 1993). Clarification has been reported to remove up to 97% of suspended solids from New Zealand pulp effluents (Cox 1981).

Flotation clarifiers use a fine stream of air bubbles to float suspended solid material to the surface, where it is skimmed off by a mechanical scraper.

Circular sedimentation clarifiers consist of a circular basin with rotating bottom scrapers and surface skimmers (see Figure 1.1). Wastewater enters at the centre of the clarifier and overflows at the outer perimeter (edge). Settled solids are raked to the centre where they are pumped out using a solids pump.

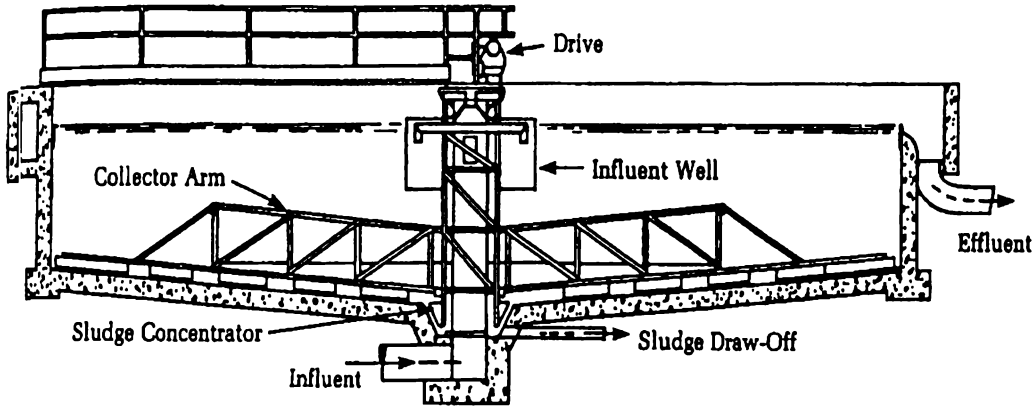

Figure 1.1. Schematic diagram of a circular sedimentation clarifier.

Secondary treatment

Biological treatment of pulp and paper effluents to reduce BOD and toxicity has been used in New Zealand for over 30 years. Scandinavian and North America companies have been slower to adopt secondary treatment system technologies (Simons 1996).

Secondary (or biological) treatment uses organisms to convert dissolved and suspended substrates into organic solid with a lower BOD (Jank 1975; Springer 1993). Bacteria are primarily responsible for this conversion. Treatment systems may also contain a variety of other organisms including algae, fungi, viruses, protozoa and yeast. Over time, bacteria evolve to suit the operating conditions (temperature, dissolved oxygen, wastewater composition, nutrient levels, etc).

Secondary treatment systems are often designed as oxidation basins. The availability of dissolved oxygen in these systems limits their performance. The addition of aerators, to create an aerated stabilisation basin (ASB) increases the dissolved oxygen level and assists in maintaining suspended solids levels, thereby increasing BOD removal to 80-90% over a 3-20 day retention period (Springer 1993; Valtilla 1991) (Figure 1.2) ASB systems have significant operational costs due to the need for mechanical aeration (electricity) and where necessary, the addition of supplementary nutrients.

Variations in BOD removal and suspended solid levels during cooler winter months have been reported for some Scandinavian and North American mills (Saunamaki 1989; Springer 1993). A further difficulty is that process and/or seasonal variations can result in toxic breakthrough events, in which the BOD and/or toxicity of the effluent rises to an unacceptable level. Minimising the impact of these undesirable events, when using biological treatment alone, usually requires the use of additional holding lagoons or basins with long hydraulic retention times and vigorous aeration or oxygenation.basins with long hydraulic retention times and vigorous aeration or oxygenation.

Such facilities require considerable areas of land (which may not be available) and impose additional operating costs (for aeration, etc). ASB systems can reduce resin acids and chlorophenols by more than 90% as well as suspended solids suspended solids (Liss *et al* 1997; Ubay *et al* 1997).

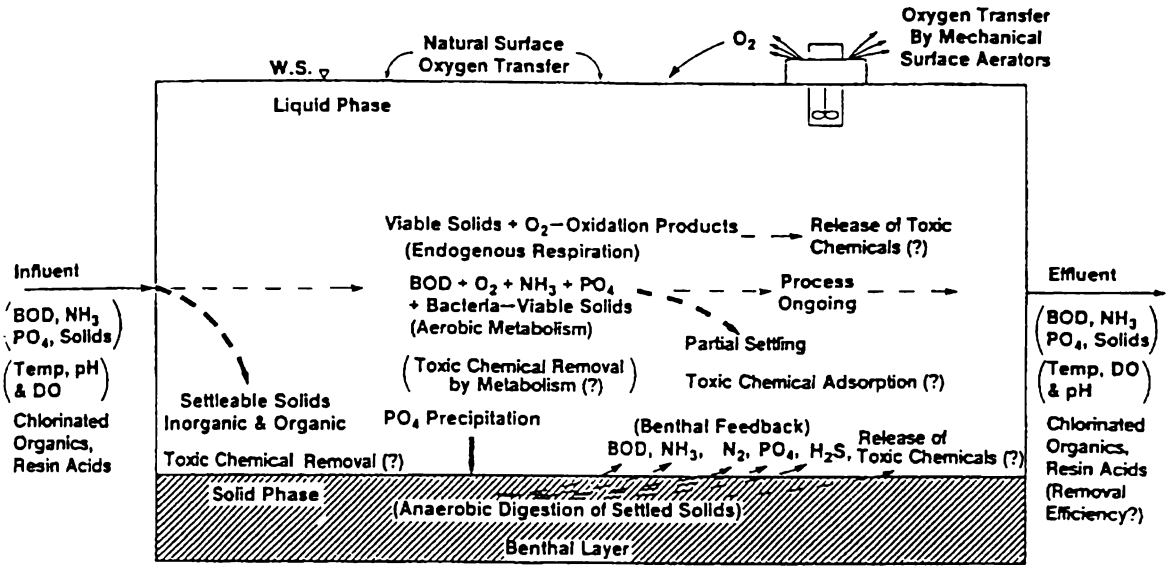

Figure 1.2. Schematic diagram of an ASB system (Bryant *et al* 1988).

Tertiary treatment

Tertiary treatment refers to treatment processes that follow secondary biological treatment. It may involve physical, biological and chemical treatment steps designed to remove constituents such as colour, bacteria, nutrients, residual suspended solids and BOD in order to meet discharge consents.

Gibbons *et al* (1992) demonstrated that even some extensively biotreated CTMP effluents may still show acute lethal and chronic toxicity in the *Ceriodaphnia* test, while Bhattacharyya and Sarma (1997) and Garg and Kanshal (1997) have noted that colour is biologically refractive and is not greatly reduced by secondary treatment. In some circumstances colour may even increase during secondary treatment (Chen and Horan 1998).

Tertiary flocculation has been shown to reduce BOD, colour and adsorbed organic halide (AOX) levels (Hodgson *et al* 1998; Chen and Horn, 1998). Coloured particulate matter can be removed by dissolved air flotation (DAF) followed by skimming or aspiration

(Wilson and Wong 1970). To date however the cost of these technologies has largely precluded their routine use. Other tertiary treatments include ozone treatment, flocculation and filtration, membrane processes, reaction with activated carbon and land treatment.

Ozone treatment

Ozone treatment has been investigated as a technology to improve the quality of secondary treated kraft mill effluents (Dorica and Wong 1979) and to decolourise kraft black liquor (Huriet and Gelly 1970).

Early work showed that ozonolysis can decrease the colour and suspended solid levels of primary and secondary treated effluents. For example, Furgason *et al* (1974) have reported 70-80% and 15% removal of colour and chemical oxygen demand (COD) respectively from primary clarifier effluent, while Melnyk *et al* (1977) have reported that ozone treatment of a primary and secondary treated effluent reduced colour levels by 50% and COD and BOD levels by as much as 90%. Burdarksa (1981) successfully used ozone for the removal of colour from a secondary treated Bulgarian kraft effluent.

More recently, Rob-Arcand and Archibald (1996) have reported the results from the ozone treatment of biologically treated effluents from 18 Canadian TMP, CTMP and bleached chemi-mechanical pulp (BCMP) and kraft pulp mills. Large decreases in BOD, toxicity, colour and the level of resin acid and fatty acids where observed.

Cost is a major impediment to the more widespread use of ozone for colour removal.

Adsorption with activated carbon

There is a long and productive history concerning of the use adsorption processes for water treatment (Copeland and Smithson 1970). Adsorption can deal with compounds that are otherwise difficult to remove by conventional processes. The importance of adsorption processes is apparent from annual world sales of adsorbent (in excess of $US 500 million) (Gupta *et al* 1990).

During recent years large numbers of adsorbents have been investigated (Bhattacharyya and Sarma 1997) and a critical review has been presented by Mall *et al* (1996). Mall and Prasad (1998) investigated the use of pyrolysed bagasse char as adsorbent for an Indian pulp and paper effluent. They found a dose of 15 g/L at pH 2-5 achieved colour and COD removals of 64% and 80% respectively.

Bamboo dust carbon, at a dose of 45 g/L achieved 99% colour and 100% mercury removal at pH less than 7 (Bhattacharyya and Sarma 1996).

Chen and Horan (1998) considered procedures for treating kraft pulp mill effluents. Activated carbon treatment was rejected because of the large amount of carbon that would be needed to decolourise highly coloured effluent water and the likely high cost of regeneration of activated carbon or any other sorbent. Chen and Horan (1998) therefore concluded that chemical precipitation was the only economically viable means of pulp mill effluent treatment.

Dissolved air flotation

In flotation systems, air bubbles are introduced by a sparger, a pump, or by stirring. The air bubbles attach themselves to the hydrophobic aggregates and carry them to the surface of the liquid. If the colloidal particles are hydrophilic, as is the case with paper mill effluent, the hydrophilic particles are first rendered hydrophobic by coating them with appropriate coagulants and coagulant aids. Once the surfaces of the particles are hydrophobic, they can be induced to coalesce and form aggregates of the correct size and density for flotation. Flotation can be easily adapted to function as a continuous flow process and it can be used to treat large volumes of water (Lemlich 1968; Hayes and Munroe 1974; Herschmiller and Branion 1973; Pinho *et al* 2000).

Flotation has been used successfully in South Africa and Sweden for the tertiary treatment of paper mill effluents (Whiting and Hayes 1985). The principle advantages of adsorptive bubble separation processes are that they are fast and require simple, small scale and inexpensive equipment.

Flocculation and filtration

Coagulation and flocculation are processes whereby compounds such as metal salts are added to effluents in order to destabilise colloidal material and cause the aggregation of small particles into larger, more easily removed flocs. The effectiveness of the process is influenced by the coagulation agent, the dose of the coagulant, the pH and ionic strength of the effluent solution and the concentration and nature of the organic compounds (Randtke 1988).

Stephenson and Duff (1996) have investigated flocculation as a procedure for the removal of organic compounds, especially compounds which are responsible for colour and turbidity, from mechanical pulping effluents. They investigated the efficiency of $FeCl_3$, $AlCl_3$, $Al_2(SO_4)_3$ and $FeSO_4$ as flocculation agents, the optimum doses of these flocculants and the pH required to achieve maximum removal of colour, turbidity and total carbon (TC). They also performed dilution experiments to establish the lowest practical dose of the flocculent. It was found that flocculation (for undiluted effluent and doses of 2.5, 5.0, 3.4 and 4.5 g/L of ferric chloride, ferrous sulfate, aluminium chloride and aluminium sulfate respectively) reduced colour, TC and turbidity, by up to 88, 90 and 98% respectively. Precipitation of the flocculated material yielded virtually colourless effluent water.

Hodgson *et al* (1998) have reported tertiary flocculation and flotation of a ClO_2 bleached kraft pulp mill effluent using a combination of a quaternary polyamine, polyacrylamide coagulants and flocculent. This treatment reduced colour, COD, AOX, 2,3,7,8-tetrachlorodibenzofuran (TCDF) and mixed-function oxygenase induction by 61%, 24%, 23%, 80% and 18% respectively.

Early work on flocculation and filtration was reported by Hayes and Munro (1974). They concluded that that while successful, the method was too expensive to be adopted at the time.

More recently, Chen and Horan (1998) have assessed the technical and economic viability of a variety of tertiary treatment processes for removal of colour and COD. Included in the study were investigations of ozonisation, adsorption by activated carbon

and a combination of flocculation dissolved air flotation and multi-media filtration. They concluded that the combination of flocculation, DAF and filtration was the best option.

Water quality, suitable for in house reuse was obtained using 90 mg/L alum at pH 5.3-5.5. 70% COD and 90% colour removal was achieved producing a treated effluent containing 50 mg/L COD and 40 Pt-Co units of colour. The operational cost of this process was estimated as 0.1 £/m^3. This included landfill and sludge disposal costs. In contrast, ozone dosed at 60 mg/L removed 90% colour and 20% COD, at a cost in the range 0.08 to 0.1 £/m^3 effluent, while activated carbon achieved 95% colour removal at a carbon dosage of 2000 mg/L and operation costs of 1.8 £/m^3.

Membrane filtration

Colour levels can be reduced by microfiltration, nanofiltration (Clair *et al* 1997), ultrafiltration and reverse osmosis techniques (Leitner 1972), or a combination of these techniques (Sierka *et al* 1997). Ultrafiltration has become a more significant technology in recent years (Gerbasi *et al* 1993; Salovius *et al* 1993).

Membrane filtration technology offers several advantages (Sierka *et al* 1997; Dal-Cin *et al* 1996) including:

(i) good wastewater quality
(ii) compact treatment facility
(iii) easy process control
(iv) low chemical requirements
(v) reduced sludge production.

However, in spite of these advantages, the utilisation of membrane filtration technologies is still limited due to the low flow rate and difficulties associated with membrane fouling.

Membrane fouling is a phenomenon whereby substances in the wastewater, such as suspended solids, bacteria and organic molecules, may be either adsorbed into membrane pores or deposited onto the membrane surface (Johnson and Wimmersted 1985). Deposition eventually leads to the formation of a gel or cake-like layer on the outer surface of the membrane. Fouling can be controlled using cross flow membrane filtration

technologies (Kothe and Schroth 1999). Such technologies, which were first developed in the 1930s (Morgan 1930), have now been applied to effluents from several Scandinavian mills (Jonsson and Wimmersted 1985).

Land treatment

Land treatment involves application of treated wastewater to land surface by irrigation, ponded systems, or over-land flow. Constructed wetlands may also be used. Treatment occurs by a combination of adsorption, filtration and biological activity (USEPA 1981; Hutchins *et al* 1985; Crites 1984).

Land treatment has been used successfully as a tertiary treatment in the USA and in India (Narum *et al* 1979; Rajesh and Kulkarmi 1985). While it was effective in removing toxicity and suspended solids, there were however changes in the soil chemistry.

In 1965, 30 pulp and paper companies in the USA used land disposal of effluents. This number had declined to 17 by 1985 (NCASI 1985). Reasons for reduced usage are (William and Maurice 1992):

a) mill closure
b) improved wastewater treatment removing the need for land application
c) problems associated with reduced soil permeability, uncontrolled runoff, or ground water contamination
d) possible liability issues associated with ground water remediation.

In New Zealand, Mills (1997) has studied the persistence of a variety of organic compounds including monoterpenes, fatty acids, resin acids, chlorophenols and coloured compounds in sediments and ground water samples recovered from bores adjacent to a land treatment system. The system comprised 44 unlined seepage ponds totalling 86 ha in area, into which approximately 10 000 m^3/d effluent was loaded for approximately 8 months of each year.

Mills (1997) found that ground water in the vicinity to the seepage ponds was affected by infiltration in a highly variable manner, depending on the direction of aquifer flows. In general, bores which intersected aquifers influenced by seepage outflows exhibited

elevated sodium and colour levels and moderate to low concentrations of extractable organic substances.

Disposal to sea

Effluents discharged to natural water ways (rivers, lakes, etc) ultimately enter the sea. In some circumstances, the direct discharge of pulp and paper effluents to the sea may be deemed to be an environmentally reasonable or acceptable option.

Many authors have discussed the impact of pulp and mill effluent discharged directly, or indirectly (via rivers, etc) to the sea. For example, Ubey *et al* (1997) have concluded that the coloured effluent from a Dalaman pulp and paper mill could be discharged directly (via an outfall pipe) to Mediterranean bottom waters provided a sufficient initial dilution was achieved using a multiport diffuser system. Toxicity tests showed that no toxic effects from the mill's effluent wastewater in the marine environment was expected.

Ozturk *et al* (1992) have reported the impact of marine outfall from several Turkish municipal and pulp mill discharges to the Black Sea. Bioassay assessments performed using *Lepistes reticuloris* indicated that provided a minimum 40 fold initial dilution was achieved, no toxic effects (LC_{50}, 96 h) were expected.

Because of the wide spread distribution of organochlorine compounds throughout the Baltic Sea (which has a narrow outlet to the North Sea), steps have been taken since the 1970s to reduce the level of these and other pulp mill source compounds reaching the Baltic sea (Lagergren 1996). In the 1970s it was estimated that Swedish pulp mills released 8-10 kg AOX/tonne pulp. With the introduction of new bleaching technologies this has now dropped to < 1 kg/tonne pulp. It is believed that additional changes (best available technology) could reduce this to < 0.1-0.1 kg/tonne pulp (Lagergren 1996).

Balk *et al* (1993) have reported the results of an investigation which measured the hepatic 7-ethoxyresorufin-*O*-deethylase activity (EROD) of perch captured at stations along the Swedish coast. Their results showed that bleached kraft mill effluents affected fish populations over distances of more than 20-40 km from the discharge point.

Deoxynucleic acid (DNA) adducts in perch living in the receiving waters of bleached kraft mill at Nmorrsundet, Sweden, on the coast of the Bothanian Sea have recently been investigated by Ericson and Larsson (2000). It was noted that while levels had reduced since the introduction of modified bleaching technologies in 1984/85, perch captured close to the mill (2 km) had significantly elevated levels of aromatic (hydrophobic) DNA adducts in both liver and intestines compared to perch captured 8 km away and from reference areas.

Nyholm *et al* (1991) has investigated the environmental impact of effluents from a mill producing unbleached mechanical sulfite pulp. Prior to discharge to the ocean, effluent waters were subjected to anaerobic and aerobic treatment. Parameters evaluated included the degradability of the effluent, persistence of colour and the impact of the effluent on transplanted organisms positioned in cages around the diffuser area. Repeated oxygenated calculation showed that the discharged wastewater caused only marginal oxygen depletion. For an initial 1:100 dilution at source and 1:10000 dilution at 1 km, it was concluded that the effluent would not exhibit acute, lethal effects after initial dilution, nor were chronic effects on fish and invertebrates found at distances 50-100 m from the outlet.

Other results indicated that colour would not be visible if it was retained in bottom waters, but there may be circumstances in which buoyant effluent water might be periodically visible 200-1000 m from the outlet (visibility criterion 10 Pt-Co units/L). Fibres were detected in sediments within only 50 m of the diffuser.

In the USA, the Marine Protection, Research and Sanctuaries Act governs all discharges of waste to ocean waters by vessels, citizens or local authorities. The only permitted ocean dumping activity of any significance is the disposal of dredged spoil. In general, ocean dumping of industrial waste, sewage sludges, chemical and biological warfare agents, radiological and high-level radioactive wastes is not permitted. An exception may be made in exigent circumstances such as for the New York city area, where certain acid and alkaline industrial wastes and sewage sludge are disposed of to a deep water site (site 106) located in the New York Bight, just off the New Jersey continental slope. This dumpsite has been in operation since 1961 and is anticipated that its use will shortly be terminated.

Wastes disposed of in the sea are complex mixtures varying widely in composition and concentrations. In the marine environment waste mixtures undergo dispersion and advection and are modified by physical, geochemical and biological processes. The ultimate fate of a particular waste is dependent on the integration of these short and long term processes. Waste material is initially dispersed by physical processes, which continuously act to dilute as it reaches the seafloor, where other processes serve to concentrate it. Chemical and biological processes are for the most part; short term in nature, until the waste reaches the seafloor where these processes are then more long term in nature. Once the waste reaches the seafloor, sedimentological processes (i.e., settling, sedimentation and bioaccumulation) also serve to concentrate it, although geochemical processes can affect the mobility of some wastes (Berger 1974).

Deep well injection

Deep wells can be used to dispose of wastewater into a subsurface stratum. Injection wells must be designed in a manner to protect all formations containing useable waters. Several methods have been devised based upon land formation and waste type.

An injection well typically consists of a series of concentric pipes. The outermost piping, referred to as surface casing, usually extends below the deepest useable water aquifer. Two strings of piping extend to the injection zone: the outer long string and inner production (injection) tubing. The outermost and long strings of pipes are cemented back to the surface casing. The inner production tubing is used to deliver the fluid to be injected under pressure or by gravity flow. Injected fluids may also be injected through perforations at the bottom of the long string.

A packer is usually set at the bottom of the well between the production tubing and long string casing (annular space) to prevent waste from backing up into the annulus. The annulus is then filled with an inert fluid and maintained under pressure slightly higher than the waste injection pressure to prevent leaks into the annular space. The wellhead is capped and equipped with an automatic shut-off valve and gauges to monitor injection pressure, injection rate and annulus pressures (Wraner 1968).

Commercial underground injection disposal facilities have been used to inject about 300 different varieties of waste including oil-field brines generated during the production of oil and gas; inorganic and organic industrial liquid wastes and radioactive wastes.

Problems encountered with the injection of brine solutions include precipitation of salts and hydroxides, concentration and inadequate filtration of suspended solids. Problems associated with the injection of radioactive waste include confinement, dissipation of heat that is generated, system corrosion and radiation protection (Roxburgh 1987).

Geochemical concerns regarding the injection of hazardous and toxic waste evolves around the mobility of waste once injected and the interactions that take place between the waste and the formation material or water within the injection zone. Its diffusion rate, degree of sorption, interaction with the formation material and distance the injected waste travels in the formation water govern mobility of the waste.

During injection, diffusion is considered negligible since the ground water velocity during injection (i.e. radial ground water flow) is greater (a few meters per day) than that during non-injection periods (a few cm per day).

Sorption results in retardation of waste constituents relative to the advancing waterfront. Sorption can occur via several means. Heavy metals can be significantly retarded (i.e. migrate up to ten times slower than the advancing water front), primarily by ion exchange with clay minerals, whereas organic waste constituents are retarded by sorption to the formation material. The latter case is not desirable since the end result is a decrease in permeability, thus the need for higher injection pressures to achieve the desired injection rate.

Geochemical interactions may be beneficial, neutral, or detrimental. Potential problems associated with waste and formation interaction include changes in pH and ionic strength, bond destruction of clay particles, chemical solution of various clays, dissolution, precipitation and adsorption or exchange. These reactions can result in pore blockage, changes in waste character and reduced rates of movement of certain waste components, or formation of aluminium and ferric oxide gels, which can reduce the permeability of the injection zone formation.

Disposal to surface water

A common method of disposal of pulp and paper effluent is discharge to surface water. The main problems caused by such disposal include turbidity, colour, odour and depletion of dissolved oxygen and the presence of toxic compounds. In extreme cases fish kills can occur. Reduction in biodiversity and avoidance are common. The presence of effluent species may also impact upon downstream users of the water.

Santos and Duarto (1998) found that sediments collected downstream of a pulp and paper discharge contained higher levels of humic acid and fulvic acid components with high levels of phenolic and methoxyl groups.

Van Loon *et al* (1991) investigated the fate of aromatic and aliphatic chlorolignins using pyrolysis-GC/MS. Monochloroguaiacol was the most abundant structure specific aromatic chlorolignin pyrolysis product. Cibulic *et al* (1990) studied COD, BOD, phenol, oil and grease levels in the River Sava, Yugoslavia, which was contaminated by wastewater from a pulp and paper mill. COD, BOD and toxic compound concentrations were greater during the summer at low river water levels.

Wigilus *et al* (1988) have reported that treated municipal water taken from surface water into which pulp and paper effluents have been discharged contained residual effluent species and chlorinated products formed during the disinfection step of water treatment.

Early in 1990 changes from chlorine to chlorine dioxide were made to the bleaching processes of a Canadian pulp and paper mill. These changes greatly altered the chemical and physical properties of the effluent discharges (Martel *et al* 1996). Changes in resident fish and wildlife population in the aquatic receiving environments of the new discharges were monitored over the period of the mill upgrade (Munkittrick *et a*l 1992). Several investigators reported a reduction in toxic constituents, such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Swanson *et al* 1996). Others author noted that nutrient enrichment due to phosphorus additions to secondary effluent treatment basins, had increased (Bothwell 1992; Podemski and Culp 1996).

Dube *et al* (1997) investigated the effects of nutrient enrichment from bleached kraft pulp mills on the water chemistry, nutrient limitation status, periphyton biomass and orthocladinae communities in the Thompson River, Canada, 1991-1994. Spatial differences in phosphorus concentrations were two fold higher at the near–field site compared to a far-field site, resulting in a doubling of mean periphyton accrual at near-field site (25 $\mu g/cm^2$). In the winter, individual orthoclads were 1-2 $\mu g/cm^2$ heavier at the near-field site compared to the far-field site. This suggested that nutrient enrichment from bleached kraft pulp mill effluent (BKPME) affected biomass at multiple trophic levels. Nutrient diffusing substrata deployed at the near-field site showed that periphyton, chironomid biomass and chironomid density were not limited by phosphorus availability in the winter when BKPME concentrations were high, but were phosphorus limited in the autumn when effluent concentrations were low.

The impact of pulp and paper discharges to surface water can be minimised by discharge through diffusers designed to ensure rapid mixing. For example Vlastelicia and Ross (1990) reported the design basis for a diffuser outfall to maintain compliance with Washington State's water quality standards for temperature and dissolved oxygen (DO) beyond the authorised dilution zone for pulp and paper discharge into the Columbia River. The new diffuser maintained dissolve oxygen at the dilution zone boundary and downstream through the potential oxygen-sag region at 8.8 mg/L.

The problem of reduced DO caused by pulp and paper discharges has been addressed by oxygen injection. Marr *et al* (1993) studied four oxygen injection systems:

a) jet aeration with a blower system to introduce air into water pumped from the river
b) diffused oxygenation using the vaporisation pressure of liquid oxygen to force pure gas through a disk diffuser as fine bubbles
c) side-stream oxygenation by injection of oxygen gas into a high–pressure stream of water pumped from the river
d) diffused aeration using a system similar to the diffused oxygenation system, except that air was used to supply the oxygen rather than liquid oxygen.

An independent assessment (Marr *et al* 1993) of the best means by which the dissolved oxygen requirements at Gulf Island pond could be attained, taking into consideration environmental and economic factors and technical feasibility, recommended system b) (a diffused oxygenation system). This system had the lowest capital cost, the shortest schedule to start up and the best system flexibility.

1.4. Environmental impact of pulp mill effluents

The pulp paper industry produces large quantities of organic and chlorinated organic wastes. Those compounds may be toxic and/or mutagenic, difficult to degrade, have a propensity to bioaccumulate and pose a potential hazard to human health.

This section describes impact due to colour, toxicity, suspended solid, bioaccumulation, and speciation of inorganic and organic compounds and distribution between organic and aqueous phases.

1.4.1. Impacts due to colour, toxicity, BOD and suspended solids

The impact of pulp and paper discharges on the environment varies with the quantity and composition of the effluent and the assimilative capacity of ecosystem. Previously emphasis has been placed upon three attributes of pulp mill discharges:

a) fibre and suspended solid levels
b) organic and nutrient loads
c) colour and turbidity.

Factors a) and b) can increase bacterial activity in the recipient waters and deplete the available oxygen supply in the water, thus decreasing dissolved oxygen (DO) and increasing BOD having potentially disastrous effects on aquatic biota, in particular fish. High BOD can generally be avoided by biological treatment. Colour can restrict photosynthetic organism and diminish visual clues necessary for organisms to feed or reproduce (Owens *et al* 1991).

A large number of publications (Canaria *et al* 1999; Francois and Christain 1993) have concentrated on the toxicity and the fate of pulp mill effluents in receiving water. Much of the acute toxicity of these discharges is attributed to the presence of resin and fatty acids, chlorinated phenols and to a lesser extent, a broad group of neutral compounds. (McLeay and Associates 1987, Liss *et al* 1997; Owens *et al* 1991). Resin acids are acutely toxic towards fish in the 300 to 1500 ng/mL range (Swanson 1993).

The toxicity of chlorinated phenols and related compounds has been related to a number of factors including the extent of chlorination and the pH of the recipient water. Acute toxicity to fish occurred in the range of 20 to 2800 ng/mL with higher toxicity observed at more acidic pHs (Swanson 1993).

Long term exposure of aquatic biota to pulp mill discharges can result in the accumulation of chlorinated and non-chlorinated compounds in their tissues. Chronic effects such as liver dysfunction can occur in trout as a result of the bioaccumulation of these compounds (Oikari *et al* 1982). Less profound effects included enlarged livers, increased blood bilirubin levels, vacuolisation of liver tissue and induction of specific enzymes. Furthermore, food chain transfer may also occur resulting in higher and higher concentrations at each level in the food chain (Owens *et al* 1994).

1.4.2. Accumulation effects

The accumulation of xenobiotic compounds in fish or other aquatic species can result from either the direct uptake of contaminants from the waste, or through the food chain. Many factors can affect the rate and extent of bioconcentration, including the duration and condition of exposure (e.g. pH, temperature, dissolved oxygen), chemical concentration and speciation, the species of the organism, its overall state of health and its metabolic rate (McLeay and Associates 1987).

Resin acids and chlorophenolics are moderately hydrophobic (lipophilic) compounds and therefore have the potential to accumulate in the fatty tissue of fish exposed to mill effluents (Barron 1990).

Laboratory studies have been used to establish the fate environmental pollutants have in biological systems. Oikari *et al* (1984a). Wachtmeister *et al* (1991) and Nimi and Lee (1992) have demonstrated that the liver detoxifies resin acids. Resin acids are rapidly metabolised to polar, water soluble conjugates, which are passed into the bile before being extracted by the body. Between 90 and 100% of resin acids found in the bile are conjugated and present almost exclusively as glucuronides.

Several studies have measured the uptake of resin acids in tissues. Table 1.4 presents a summary of the tissue concentration of resin acids in various organs. Oikari *et al* (1984b) found that the distribution of resin acids varied between tissues e.g. abietic and pimaric acid accumulated to a greater extent in brain tissue, whereas higher concentrations of dehydroabietic acid were found in plasma and bile.

Table 1.4. Uptake of resin acids (μg/g wet weight) in various tissues (reproduced from McLeay and Associates 1987).

compound	organism	tissue	concentration	reference(s)
DHAA [a]	sockeye	whole body	19	Kruzynski 1987
	salmon	bile	647	
		brain	620	
		kidney	278	
		liver	263	
		carcass	8	
DHAA [a]	rainbow	plasma	237	Oikari *et al* 1982
	trout	liver	101	
		kidney	83	
		brain	16	
		muscle	24	
resin acid	rainbow	liver	273	Oikari *et al* 1982
mixture	trout	kidney	88	
		brain	82	
		muscle	24	
resin acid	rainbow	gills	9	Oikari *et al* 1984a
mixture	trout	plasma	33	
		bile	28	

[a] DHAA = dehydroabietic acid

1.4.3. Speciation of inorganic effluent components

The term chemical speciation (Duffield and Williams 1989) may be used to encompass both functionally defined speciation, that is, the determination of species that are available in food or present as exchangeable forms and operationally defined speciation which refers to the determination of extractable forms of an element. Speciation is the form in which the analyte is present in the sample. It can be either actual chemical speciation (e.g. variation in oxidation state) or phase-associated speciation, as is often the case for organic substances.

There is a number of important environmental factors which may affect the speciation of metals in the environmental. One of the most important of these is prevailing redox conditions which not only determine the oxidation state of some metals but may also influence the bioavailability and toxicity of the element. For example, Fe(II) and Mn(II) are soluble in natural waters deficient in oxygen, but will precipitate out at higher oxygen levels (Peters *et al* 1992). In other cases photoreduction may be important. Changes in pH may shift the acid-base equilibrium and redox conditions.

Individual physico-chemical forms may include particulate matter, dissolved simple inorganic species, organic complexes and the elements adsorbed on a variety of colloidal particles. All these species can coexist and may not be in thermodynamic equilibrium with one another. An ionic metal spike added to an unfiltered natural water sample may take time, ranging from hours to months, to equilibrate with the natural pool of metal species (Florence 1989; Demora 1983).

When studying speciation of elements in waters it is important to understand both the biological and geochemical cycling. Biological cycling includes bioaccumulation, bioconcentration, bioavailability and toxicity (Morrison *et al* 1989), while geochemical cycling involves the transport, adsorption and precipitation of the element in the water system. (Latouche *et al* 1993).

It is now well established that no meaningful interpretation of either biological or geochemical cycling can be made without speciation information (Turner 1984). Each of the different physico-chemical forms of an element may have a different toxicity so

analysis of a water sample for total metal concentration alone does not provide sufficient information to predict toxicity. For example, two rivers may contain the same concentration of total dissolved Cu. If the first has most of the copper adsorbed on colloidal particles there will be little or no effect on aquatic life, but if the second river has free Cu(II) as the main species, few organisms would survive. Lipid soluble metal complexes are particularly toxic forms of heavy metals because they can diffuse rapidly through biomembranes and carry both metal and ligand into the cell (Stauber and Florence 1987).

Inorganic speciation measurements have been performed using a variety of techniques including electroanalysis (Esteban *et al* 1993), ion exchange, dialysis, ultrafiltration (Castilho 1991), sequential filtration (Shkinev *et al* 1996), solvent extraction (Pickering 1986) and sequential extraction (Raksasatya *et al* 1997). Speciation effects have also been evaluated using computer modelling (Powell 1999).

1.4.4. Speciation of organic effluent components

Little information is available in respect of the speciation of resin acids in polluted waterways. Since the toxicity of resin acids toward fish and other aquatic species is likely to depend on their physio-chemical form, a knowledge of resin acids speciation in recipient water is essential to an understanding of toxicity and bioaccumulation. Speciation effects are brought about by the partitioning of resin acids between water and particulate matter.

The process by which chemicals become associated with a solid phase is generally referred to as sorption (either adsorption onto two-dimensional surfaces, or absorption into a three-dimensional matrix). In the case of comparatively volatile organic molecules, phase transfer to particulate matter by absorption processes may involve a combination of van der Waals forces and hydrogen-bonding. For non-volatile, polar resin acids, liquid-solid interactions are likely to include the above interaction and in addition may include ionic interaction between carboxyl groups and specific binding sites on the surface of the solid material.

Hall and Liver (1996a,b) have reported the results of experiments in which the interaction of resin acids with aerobic and anaerobic biomass were determined for a Canadian CTMP effluent. An analysis of the kinetics of resin acid partitioning onto sodium azide inactivated biomass, previously not exposed to resin acids, showed that there was an initial very rapid sorption of most of resin acids (which occurred in less than 10 minutes), followed by a slower, second sorption process which occurred over a 12 h to 9 day period (depending on biomass level) to afford a final equilibrium in which ca. 90% of resin acids were associated with biomass. The rates of both the first and second sorption steps were faster for aerobic systems, than was the case for anaerobic systems. It also appeared that the rate of resin acid partitioning onto aerobic biomass was governed by the availability of particulate surface. Typical biomass equilibrium levels were 90, 89, 89, 86 and 77% for pimaric acid, isopimaric acid, abietic acid, palustric acid and dehydroabietic acid respectively.

It was proposed that partitioning of resin acids into activated aerobic biomass could be described by a linear partitioning model according to the equation:

$K_d = Y/C$ where:

Y = amount (mg/g total suspended solid (TSS) of resin acid partitioned onto biomass)

C = concentration in mg/L of resin acids in the liquid phase.

Assuming the suspended solid has a density of 1000 g/L, multiplication of Hall and Livers K_d values, expressed as L/g TSS by 1000 g/L affords an estimate of the more common dimensionless value of the distribution coefficient (K_D in Table 1.5). It is apparent from the data presented in Table 1.5, that DHAA is less strongly partitioned into biomass than is the case for isopimaric acid, abietic acid, pimaric acid and palustric acid.

Table1.5. K_d and estimated K_D values for resin acid partitioning into aerobic biomass (Hall and Liver, 1996b).

resin acid	K_d (L/g TSS)	estimated K_D
isopimaric acid	1.14	1140
abietic acid	1.03	1030
pimaric acid	0.978	978
palustric acid	0.737	737
dehydroabeitic acid	0.31	310

The constant fractions (ca 85-90%) of each of the resin acids found in anaerobic biomass experiments using different biomass to resin acids ratios showed that adsorption was not a reversible process.

Hoel and Aarsand (1995) have investigated the acute toxicity of colloidal and dissolved material in biologically treated secondary effluents from a Norwegian TMP mill. Resin acids were the found to be the major toxic component class in effluents. In a series of experiments resin acid speciation effects were evaluated and the acute toxicity of glass fibre and membrane filtered TMP effluent samples towards *Daphnia magna* were determined. Resin acids were found to be predominantly particulate associated and it was shown that removal of resin acid particulates by filtration rendered the filtrates non-toxic.

Hoel and Aarsand's (1995) conclusion that resin acids were primarily responsible for the toxicity of the CTMP effluent which they investigated is consistent with the finding of Dethlefs *et al* (1995). Reverse phase C18 filtration of a toxic alkali-oxygen-peroxide (EOP) bleach effluent afforded extracts that had little or no effect on *Daphia magna* in growth inhibition and lumininescence tests. The extracts contained 66% of resin acids.

1.4.5. Distribution effects

The distribution of organic compounds between water and natural solids (e.g., soils, sediments and suspended particles) or organisms can, in many cases, be viewed as a partition process between the aqueous phase and the bulk organic matter present in natural solids or in biota. As early as 1899 (Overton 1899), investigators studying the

uptake of nonpolar drugs by organisms found that they could use water-immiscible organic solvents such as *n*-octanol as a surrogate for organisms, or parts of organisms.

Since *n*-octanol is a reasonable surrogate for many kinds of environmental and physiological organic matter, it has become the most popular reference phase for assessing the organic phase water partitioning behaviour of organic solutes.

Traditionally, direct measurements of *n*-octanol-water partition coefficient (K_{ow}) have used the conventional "shake flask" (partition) method (Leo *et al* 1971; OECD 1981). This experimental approach is restricted, however, to compounds for which K_{ow} is less than about 10^5 (i.e., log $K_{ow} < 5$), since for more hydrophobic compounds the concentration in the aqueous phase becomes too low to be accurately determined.

Support beds coupled with solid sorbent cartridges can be used to determine K_{ow} (Tewari *et al* 1982, Woodburn *et al* 1984). An inert support bed packed in a small column is coated with an *n*-octanol solution (typically 10 mL) of the target compound and a large volume of *n*-octanol–saturated water (up to 10 L) is passed through the support. As the water passes through the column an equilibrium is established between the water and *n*-octanol. Retrieval of the chemical of interest from the elutant water, by passing it through a sorbent cartridge, can afford enough material to allow quantification of the water load. This result, along with knowledge of the volume of water extracted and the concentration of the compound in the *n*-octanol, ultimately provides the K_{ow} value.

The partition process is determined by the relative fugacity of the compound in each phase and at equilibrium, assuming ideal behaviour:

$$K_{ow} = C_o / C_w$$

where C_o is the concentration of the compound in *n*-octanol phase and C_w is the concentration in the water phase.

The data available for highly hydrophobic compounds (i.e., polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) indicates that as molecular size of the molecule increases, the incompatibility of the compound with water-saturated *n*-octanol increases and hence the deviation from ideality also increases.

There are however some exceptions. For example, Chiou *et al* (1982, 1983) have demonstrated that for hexachlorobenzene (HCB) and *p,p'*-dichlorodiphenyl-trichloroethane (DDT), part of the deviation in the experimental data from ideal behaviour is due to the highly hydrophobic nature of these compounds in the aqueous phase. Chiou *et al* (1982, 1983) found that the solubilities of HCB and DDT were 1.9 and 2.8 times higher respectively in *n*-octanol-saturated water, as compared with pure water, demonstrating the increasing significance of the organic co-solute (*n*-octanol) effect with increasing hydrophobicity of compound. The lower-chlorinated PCBs, which have higher water solubilities and vapour pressures, are more susceptible to biodegradation.

The uptake of PCBs and PAHs by plants from compost (and generally soil) can be envisaged as a series of consecutive partition steps which are directly related to the K_{ow} of the substrate (MacBerthouex and Gan, 1991). Thus substrates with high log K_{ow} values, such as PCBs and PAHs (and resin acids: see Table 1.6) are more likely to be absorbed from soil and or groundwater by plant roots.

The degree of accumulation of contaminants by biota (plants), or by aquatic species (e.g. mussels) from water, is often expressed as a bioconcentration factor (BCF). For mussels in field and experimental situations the BCF of a range of organic compounds has been related to physicochemical characteristics of the compounds such as aqueous solubility, or the octanol-water partition coefficient (Donkin and Widdows 1990; Geyer *et al* 1982). Such relationships indicate that the uptake of organic compounds is generally a passive process, with compounds diffusing across external membranes of mussels until a steady state between rates of uptake and depuration is attained (Widdows and Donkin 1992). The time required to achieve a steady state can range from hours for more soluble organic compounds (e.g., toluene log $K_{ow} < 3$, Hansen and Jensen 1978) to weeks or months for hydrophobic molecules (e.g. hexachlorobiphenyl, log $K_{ow} > 7$, Hawker and Connell 1986).

Although hydrophobicity driven partitioning satisfactorily explains the bioaccumulation characteristic of molluscs, there are anomalies (Widdows and Donkin 1992). For example Pruell *et al* (1986) noted that the BCFs of PCBs for mussels were always higher than those of hydrocarbons of equivalent K_{ow}.

Since the log K_{ow} values of resin acids and degraded resin neutral compounds (Tavendale, 1994) (Table 1.6), are comparable to those of PCBs, it is reasonable to expect the BCFs of resin acids to be similar to those reported for PCBs.

Table 1.6. Log K_{ow} and aqueous solubility K_s of resin acids and resin neutrals (Tavendale 1994, Weiss 2000).

compound	K_s mol/L	log K_{ow}
dehydroabietic acid	2.2×10^{-5}	-
abietic acid	1.4×10^{-5}	5.8
abietan-18-oic acid	-	7.2
dehydroabietin	-	8.1
phenanthrene	6.62×10^{-6}	4.57
PCB 28	0.61×10^{-6}	5.80
PCB 52	0.14×10^{-6}	6.10
PCB153	0.28×10^{-8}	6.90

It can be anticipated that the log K_{ow} values for retene and tetrahydroretene (two of the more persistent resin neutral compounds encountered in Tarawera River water samples (Wilkins *et al* 1996a)), will be greater than those for abietic acid and abietan-18-oic acid. Retene and tetrahydroretene do not contain a carboxyl group and so will therefore be more hydrophobic. Log K_{ow} of dehydroabeitic acid would be expected to be less than 5.8 since it is more soluble than abietic acid.

1.5. The New Zealand pulp and paper industry

During the 1930s (the depression era) *P. radiata* trees were plant on marginal land in the Central North Island of New Zealand.

In 1951 the New Zealand Government offered a permanent annual log supply of 651,600 cubic tons, from the Kaingaroa State Forest, to an enterprise commanding the technical resources to establish a newsprint industry.

A join venture Company, with shareholdings from the Fletcher Construction Company Ltd, Merritt-Chapman and Scott Overseas Incorporated, New York (USA) and the Raymond Concrete Pile Company, Delaware (USA) began building a pulp and paper mill for Bayswater Incorporated (an English Company) on the Tasman site close to Kawerau in July 1953. Fletchers subsequently acquired full ownership of the Tasman mill. A major expansion of the mill occurred in 1969.

Permission to discharge effluent to the Tarawera River was allowed by the Tasman Enabling Act. This Act remains in place, but in recent years a series of voluntary modifications to permitted discharges have been negotiated with Environment Bay of Plenty. These initiatives have arisen, in part, from enactment in 1991 of the Resource Management Act.

Table 1.7. Production and effluent treatment in the New Zealand pulp and paper industry (PPI 1999; Nicol 1997).

Company	mill type	process	pulp ADT/y	paper ADT/y	effluent treatment
Pan Pacific Forest Industries (N.Z.) Ltd., Napier	pulp	TMP	240 000		screening, ocean outfall
Carter Holt Harvey Tissue Ltd., Caxton Mill	pulp, paper	BCTMP	75 000	45 000	anaerobic
Carter Holt Harvey Ltd., Kinleith Mill	pulp, paper	kraft, NSSC	420 000	250 000	screening, primary clarification, ASB
Carter Holt Harvey Ltd., Mataura Mill	recycled paper		24 000		screening and clarification
Carter Holt Harvey Ltd., Penrose Mill	recycled paper		67 000		municipal sewer
Carter Holt Harvey Ltd., Whakatane Mill	pulp paperboard, recycled fibre	GW, NSSC,	55 000	85 000	primary clarification
Tasman Pulp and Paper, Co. Ltd., Kawerau	pulp, paper	GW, kraft, TMP	63 000	400 000	primary clarification, ASB
Winstone Pulp International, Ohakune	pulp	CTMP, BCTMP	135 000		primary clarification

ADT/y = air dried tonne/year; BCTMP = bleached chemi-thermomechanical pulp; CTMP = chemi-thermomechanical pulp; GW = ground wood; NSSC = neutral sulfite semi-chemical pulp; TMP = thermomechanical pulp; ASB = aerated stabilisation basin

The manufacture of pulp and paper is now a major industry in New Zealand, employing approximately 3000 people and exporting pulp and paper products valued at over $NZ

800 million in 1999 (NZFOA, 1999). The country presently has eight pulping and/or paper making facilities in operation, which in total produce over 1.5 million air dried tonnes (ADT) of pulp per year (Table 1.7).

1.5.1. Pulping technologies used by Tasman and Caxton

The Carter Holt Harvey (Caxton) Tissue mill uses a sulfonated CMTP process to produce 45 000 ADT/y of toilet and towel tissue, lightweight paper grades and speciality papers.

The Tasman mill produces mechanical and kraft pulps. Mechanical (ground wood) pulp and some of the mill's kraft production (in semi-bleached form) is fed to three paper machines. The remainder of the kraft pulp production, in a variety of unbleached, bleached and specialist grades, is sold on the world market.

Two continuous digesters convert wood chips to pulp at the rate up to 1000 tonnes a day. The digesters utilise isothermal cooking technology to improve pulp quality and reduce the level of bleaching required to achieve the brightness required for some markets. Total newsprint production is 1000 tonnes/day, total kraft pulp production is 700 ADT/day of which approx. 200-250 tonnes is unbleached (Donald 2000).

The No. 1 bleach plant uses two hypochlorite stages for brightening of kraft pulp (ca. 100 tonnes/day) and bleaching of mechanical pulp (newsprint). The No. 2 bleach plant uses chlorine dioxide followed by an oxygen and peroxide assisted extraction stage and two chlorine dioxide stages (i.e. a DEODnD sequence). Production from this plant is ca. 450 tonnes/day.

1.5.2. Effluent treatment

Wastewater from the Tasman mill is initially fed into a primary clarifier, which removes settlable material. It then passes through a 1.6 m internal diameter pipe into Tasman's lagoon system. Total effluent flow was 199 ML/day as of December 1999.

Tasman's lagoon system comprises four connected ponds, the last three of which are aerated (aeration capacity is 1900 kW). The first pond acts primarily as a settling area for

remaining solids. The system occupies an area of 45 hectares and has a total volume of 1.3 x 10^6 m^3 leading to a retention time of just under 5 days (120 h). Table 1.8 shows the results of a mid-1999 tracer study to determine pond residence times.

Table 1.8. Characteristics of Tasman's treatment lagoons.

pond	inflow m^3/s	outflow m^3/s	volume m^3	active volume m^3	design residence time (h)	actual residence time (h)
1	3.2	-	> 26 000	34 000	2.3	3.0
2	2.7	2.7	230 000	220 000	24	23
3	2.7	2.5	580 000	490 000	61	51
4	2.6	2.8	450 000	356 000	48	38
Total	2.7	2.8	128 600	1 100 000	135	115

The foam contains higher levels of resin acids and chlorinated organic substances than is case for the effluent water (Judd 1991). It is desirable that the foam does not become air borne, particularly in hot windy weather. The sprinklers are fed by 150 kW pumps. After treatment in the ASB, brown coloured (due to residual lignin) effluent is discharged into the Tarawera River at a rate of 199 ML/day.

1.5.3. Previous Tarawera River investigations

Since 1985 a number of investigations concerning aspects of the organic and inorganic chemistry of pulp mill effluents discharged to the Tarawera River has been performed at the University of Waikato. In particular Panadam (1988), Fitzgerald (1989), Osborne (1991), Singh-Thandi (1993), Davidson (1996) and Wang (1997) have previously studied aspects of the chemistry of the Tarawera River and the adjacent Western Drain. Environment Bay of Plenty (formerly the Bay of Plenty Regional Council) has also presented several water quality assessments (McIntosh 1995).

Organic substances

Panadam (1988) reported concentrations of total resin acids in State Highway 30 (SH30) and State Highway 2 (SH2) Tarawera River water samples in the range 248-2615 µg/L (Wilkins and Panadam 1987). Significant aspects of Panadam's investigations were the

identification of abietan-18-oic acid as the dominant resin acid constituent of the extracts and the detection of significant levels of the four degraded resin neutrals; fichtelite, dehydroabietin, tetrahydroretene and retene. It was also found that resin acid levels in sediments taken from the river banks were appreciably higher (ca. 100 fold) compared to those taken from the river bed. The high adsorptive capacity of bank clays, compared to that of the river-bed pumice was suggested as a possible explanation.

Panadam (1988) also investigated river resin acid levels during a period of extended mill shutdown, when discharges first slowed, then ceased altogether. Despite this, residual levels of resin acids were still detected in the river. Panadam suggested that this may be the result of desorption of species from the river bed, although the possibility that resin acids may also have originated from Caxton's discharge can not be discounted.

Fitzgerald (1989) subsequently reported resin acid data for river water and sediment samples collected from four sampling sites, namely Kawerau Town Park (above mill discharges), SH30, SH2 and the lower (coastal) bridge. River water resin acids levels, which were typically in the range 400-1000 μg/L, were generally lower than those determined by Panadam (1988) for water samples collected during 1984 and 1987-88. Resin acids were not detected in the Town Park site water samples, collected upstream of the mill discharges. Total fatty acids varied between 100 μg/L (Town Park) and 460 μg/L (SH30), with levels dropping downstream of the SH30 site.

Fitzgerald's sediment results supported the finding of Panadam (1988) that bank sediments contained levels of organics ca. 100 times greater than river bed pumice and gravel samples.

Fitzgerald (1989) reported two other significant findings. Firstly, an elevated level of total resin acids of 1544 μg/g were found in dark coloured sludge-like samples collected from under the SH2 bridge. Secondly, extraction of river bed pumice material revealed only very low levels of adsorbed resin acids which seemed to preclude adsorbed resin acids as being the source of resin acids detected by Panadam (1988) in river water sampled during the period of mill closure.

Osborne (1991) analysed water and sediment samples collected between 1989 and 1991. Table 1.9 shows the levels of fatty acids and resin acids present in water and sediment samples.

Table 1.9. Total fatty and resin acids levels detected in some 1989-91 Tarawera River water and sediment samples analysed by Osborne (1991).

Site	water samples (μg/L)		sediment samples (μg/g)	
	fatty acids	resin acids	fatty acids	resin acids
Town Park	38	11	40-62	0.6-2
Tasman discharge	1860	1860		
SH30	96	263	66	55
Lower bridge	93	59	52	159
Bridge by sea	75	186	33-149	49-354

[a] Lower Bridge and Bridge by sea are ca. 14.8 km and 16 km downstream of Tasman's discharge

Palmitic acid and stearic acids were the dominant saturated fatty acids while palmitoleic and oleic acids were the dominant unsaturated fatty acids. As was the case for the samples analysed by Panadam (1988) and Fitzgerald (1989), DHAA and abietan-18-oic acid were the dominant resin acids in the samples examined by Osborne (1991).

Other resin acids detected included pimaric acid, secodehydroabietic acid-1 (seco-1), secodehydroabietic acid-2 (seco-2), abietic acid, 12-chlorodehydroabietic acid (12-Cl-DHAA), 14-chlorodehydroabietic acid (14-Cl-DHAA) and 12,14-dichlorodehydroabietic acid (12,14-diCl-DHAA). Low levels of resin neutrals such as fichtelite and dehydroabietin were also detected.

Filtration of water samples before extraction showed 14-57% removal of resin acids using a 3 μm filter and almost 100% removal by ultra filtration (2000 amu particle retention). This suggested that the bulk of the extractable resin acids were associated with suspended solids (particulates) in the water samples.

Singh-Thandi (1993) investigated the levels of chlorophenols, fatty acids, resin acids and resin neutrals present in 24 hour composite Tarawera River water samples and Caxton

and Tasman final effluents, collected during two 21 day synoptic surveys undertaken between November 1991 and February 1992.

Table 1.10 lists the range of total of resin acids, resins neutrals and chlorophenolic compounds found in the Tasman and Caxton mill effluents during the two synoptic surveys.

Table 1.10. Total resin acids, resin neutral and chlorophenols levels (µg/L) found in Tasman and Caxton final discharges, Tarawera River water SH30 samples, during two synoptic surveys (Nov 1991 and Feb 1992; Wilkins *et al* 1996a).

compound class	Tasman	Caxton	SH30
resin acids	383-1023	4588-7204	34-121
resin neutrals	20-32	-	4.0-8.0
chlorophenols	5.2-8.0	0.1-0.2	0.3-0.8

Synoptic survey samples collected downstream of Tasman's discharge showed resin acid levels between 34 and 121 µg/L. Dominant resin acids were dehydroabietic acid and abietan-18-oic acid with lesser quantities of pimaric acid, abietic acid, secodehydroabietic acid-1, secodehydroabietic acid-2 and sandaracopimaric acid. Lower concentration of resin neutrals and chlorophenolics were also detected in the ranges 4 to 8 µg/L and < 1 µg/L respectively (Wilkins *et al* 1996a).

Caged mussels placed below the Tasman discharge for six months, during a period which partly overlapped with synoptic survey, were shown to accumulate resin acids (864 to 1980 µg/L), chlorophenols (4 to 52 µg/L) and resin neutrals. Fichtelite, a resin neutral, was shown to accumulate 23.6 times more strongly than resin acids (Singh-Thandi 1993).

Davidson (1996) has reported the levels of extractable organic substance in some Western Drain water samples and in ground water which seeped into a series of shallow bore holes (1-3 m) drilled adjacent the Tarawera River, in the vicinity of Otakiri-Soldiers Rd. (see Table 1.11).

Table1.11. SIM GC/MS determined levels of resin acids (μg/L) identified in some Otakiri-Soldiers Road bore hole water samples collected 28/10/1995 (Wilkins *et al* 1996b).

compound	River	Hole 1 (2 m)[a]	Hole 2 (47 m)	Hole 3 (87 m)	Western Drain
seco-1	4.0	0.6	0.1	nd	nd
seco-2	1.6	0.3	tr	nd.	nd
pimaric acid	3.0	2.9	0.5	tr	tr
abietan-18-oic acid	67	19	1.9	0.1	0.2
DHAA	32	10	1.8	0.2	0.2
12-Cl-DHAA	0.3	nd	nd	nd	nd
14-Cl-DHAA	1.2	0.4	0.3	0.1	nd
12,14-diCl-DHAA	1.7	0.9	0.1	nd	nd

[a]distance in meters from the river bank

The results which Davidson obtained for water samples taken from bore holes 1 to 87 m distance from the river bank (Table 1.11) demonstrated that, under some circumstances, ground water may be influenced by seepage from the Tarawera River.

Table 1.12. Resin acid levels (μg/L) identified in water and sediment samples collected from the Tarawera River, at Johnsons Road, on 5/2/96 (Wang 1997).

Compound	water samples (μg/L)		sediment samples (mg/kg)	
	KTB	SH30	KTB	SH30
seco-1	_	2.2	0.09	1.7
seco-2	_	1	0.07	0.8
pimaric acid	_	5.7	0.39	19
abietan-18-oic acid	_	55	3.0	33
abietic acid	_	2	0.14	1.3
DHAA	_	7	1.6	21
12-Cl-DHAA	_	0.3	0.04	5.7
14-Cl-DHAA	_	1.8	0.09	6.1
12,14-diCl-DHAA	_	2.4	0.06	14
Total resin acids		88	5.5	102

Wang (1997) analysed water and sediment samples collected between Feb-June 1996. Data for some SH30 and KTB water and sediment samples appear in Table 1.12. Levels identified were consistent with those reported by Davidson (1996).

Inorganic and colour analyses

The Tarawera River is known to be influenced by cation and anion contributions from natural geothermal sources and from paper mill discharges (Pang 1994; McIntosh 1995). Upstream of the township of Kawerau, the Tarawera River receives Na, Cl, Fe, Mg, B and Al contributions from geothermal water sources within the Tarawera Forest and from natural geological leaching processes.

The section of the river between Kawerau and Tasman's discharge point receives inflows from an adjacent geothermal field. The geothermal field, which is used to supply steam to the Tasman plant, typically discharges to the Tarawera River at a rate of 0.24 m^3/s. Below Tasman's discharge pipe, mill effluent is the principle source of inorganic species. Data determined by McIntosh (1995) and Wilkins *et al* (1998) are presented in Table 1.13.

Table 1.13. Cation levels (µg/L) identified in March 1995 and Feb. 1996 Tarawera River water samples (McIntosh 1995 and Wilkins *et al* 1998).

	1995 results		1996 results	
	KTB	SH30	KTB	SH30
calcium	7.4	11.8	1.5	2.3
potassium	5.8	8.2	7.6	9.8
magnesium	7.4	6.6	3.3	3.3
sodium	54	78	41	72
silica	-	21	-	-
aluminium	0.01	0.05	0.04	0.10
iron	0.12	0.23	0.16	0.36
boron	0.31	0.85	0.58	0.96

KTB = Kawerau town bridge; SH30 = State Highway 30 bridge

Colour data (McIntosh 1993) (see Table 1.14) clearly showed that downstream of Tasman's discharge point, colour is greatly increased.

Table 1.14. Absorption coefficients of some Tarawera River water samples, collected 19/3/93 (McIntosh 1993).

	KTB	Upstream Ruruanga*	SH30	SH2
270 nm (UF)	2.2	3.8	32.5	29.6
270 nm (F)	1.4	2.7	26.3	25.6
340 mm (UF)	1.49	1.8	21.0	21.0
340 nm (F)	1.38	2.33	20.6	19.7

(F) = filtered sample; (UF) = unfiltered samples; * upstream of geothermal discharge point

Odour

In 1991 NECAL (Graham 1991) carried out odour testing on behalf of the Bay of Plenty Regional Council, which confirmed that odorous substances were present in Tarawera River water samples and that Tasman was a contributor to this odour. Head space analyses identified a range of volatile organic substances such as hexane, benzene and toluene, in all except the Kawerau Bridge control site sample. Since none of the detected compounds were expected to give the observed odour it was suggested that the odour might be due to reduced sulfur compounds such as methanethiol, dimethylsulfide and dimethyldisulfide. Sulfur compounds have very low odour thresholds (sub-μg/L) and may have been present in the downstream water samples at levels below instrumental detection limits.

1.5.4. Environmental impact of discharges to the Tarawera River

In 1997 the Ministry for the Environment reported on the state of the New Zealand environment (Smith, 1997). The report noted that the Tarawera River was not a typical example of New Zealand's rivers. In addition to discharges from dairy farms, stormwater and sewage from the town of Edgecumbe, the lower part of the river receives effluent from the two pulp and paper mills and a geothermal plant which adds sulfates and heavy metals. Below the mill discharge points water is significantly coloured (Table 1.14) and gives off an odour typical of chemical pulp and paper mill discharges.

Compared with its upper reaches, the lower part of the river has low concentrations of dissolved oxygen, elevated temperature, more chemical and microbial contaminants, little or no submerged vegetation, a restricted range of fish and invertebrates and a highly mobile pumice river bed seething with oxygen-sapping micro-organisms (McIntosh,

1995). Trout reportedly vanished from the lower Tarawera River within months of the Tasman mill's opening.

For four decades, the Tasman mill was subject to legislation (The Tasman Pulp and Paper Enabling Act 1954), which gave it immunity from water and soil legislation and the Health Act. The requirements of the Enabling Act are being progressively replaced by terms and conditions defined by The Resource Management Act (1991).

Originally effluent was discharged untreated, however during the 1970s effluent quality was improved by secondary treatment in an oxidation pond system. In recent years Tasman has spent millions of dollars to reduce colour and organochlorine discharges (Tasman 1997). The geothermal discharges have also been reduced.

As a result, water clarity has improved (Bay of Plenty Regional Council 1995), however, organic matter discharges from both of the mills have increased during the past decade, particularly since Caxton opened a new treatment plant in 1992. Dissolved oxygen is now lower than it was in 1985. As a result, the river's ability to support balanced invertebrate populations has fallen in recent years, with (for example) mayfly and caddisfly species declining both downstream and upstream of the discharges (McIntosh 1995).

1.5.5. Possible options for Tasman

It is Tasman's stated policy to achieve minimum environmental impact by using state of the art equipment, processes and procedures, which balance environmental protection with economic development (Tasman 1997).

As a consequence of this policy, the quality of Tasman's wastewater discharges has steadily improved in recent years, through reductions in contaminants, fibre loss reduction, process improvements, investments in new control systems, the adoption of more rigorous procedures to manage spills and improved training of employees and contractors to ensure they have a greater awareness of their ability to impact upon mill operations and mill effluents.

Recent environmental initiatives include a voluntary greenhouse gas agreement and plan of improvements which have, or in the near future will have:

a) reduced solid wastes

b) reduced AOX discharges to less than 0.4 kg/tonne of bleached kraft pulp

c) reduced odorous sulfur emissions

d) reduced water use from an average of 150 ML/day to less than 120 ML/day

e) reduced wastewater colour by 20% compared with 1996-97 levels

Minimisation of solids disposal

Tasman operates its own landfill. During the past decade steps have been taken to maximise landfill utilisation and efficiency. In 1995 Tasman commissioned a $4.9 million primary solids dewatering plant and recently commissioned a new solid waste compactor at a cost of $478,000. Recovered waste solids from the dewatering process are transported to the landfill.

Previously run-off from the landfill area drained into the primary solids lagoon, where a build-up over a period of more than 20 years contributed to a reduction in lagoon efficiency. As a result, a significant amount of oxygen consuming material was carried into the effluent treatment plant putting an additional ten per cent load on that treatment system.

Kraft pulping involves the operation of a lime circuit within the process. Lime mud is currently disposed of by specialised dumping in specific forest areas. Recently, waste lime mud has been investigated as a pasture supplement, with encouraging results.

Reduction of sulfur emissions

A Tasman commissioned odour assessment programme (Tasman 1997), carried out during 1996 by a division of Lincoln University, saw local residents participating as members of testing panels to evaluate levels of mill odour emissions and their impact upon the community.

Survey results were supplemented by more than 12 months of meteorological data and a computer modelling study designed to predict how airborne emissions from the mill were dispersed under varying weather and atmospheric conditions. This work provided the basis for predicting the potential impact of possible options for future mill improvements.

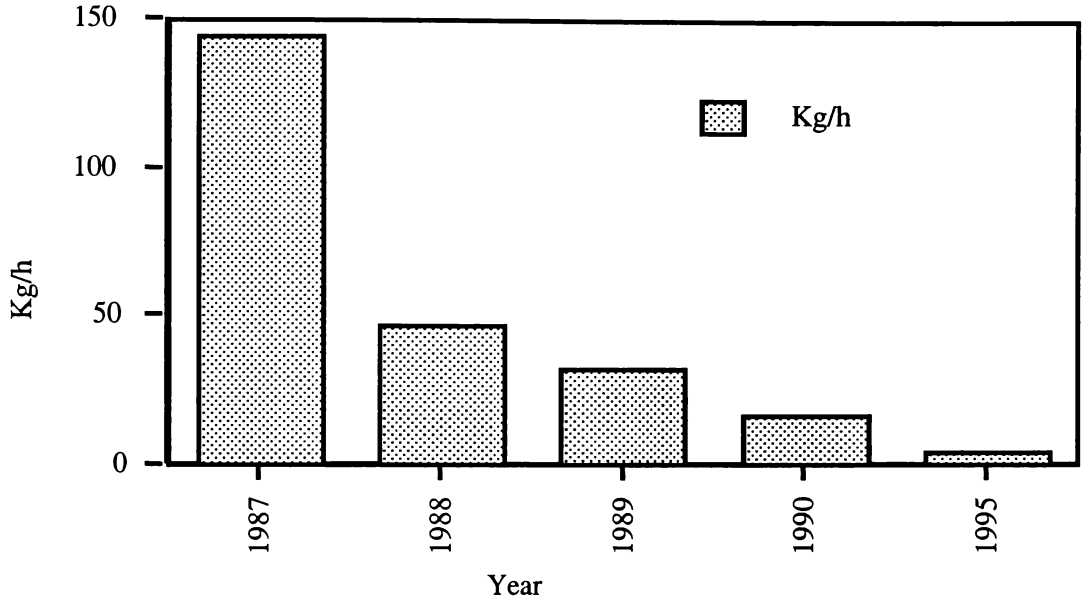

Figure 1.3. Total reduced sulfur emission for the Tasman mill (Tasman 1997)

River dissolved oxygen

During recent years, especially the summers of 1993-1996, dissolved oxygen levels in the lower reaches of the Tarawera River have fallen below the guideline level of 6 mg/L (see Figure 1.4).

The situation has been closely monitored by Tasman and Environment Bay of Plenty and where necessary, to protect river life, DO levels have been boosted by direct injection of oxygen. Maintenance of DO levels is seen as an environmental priority.

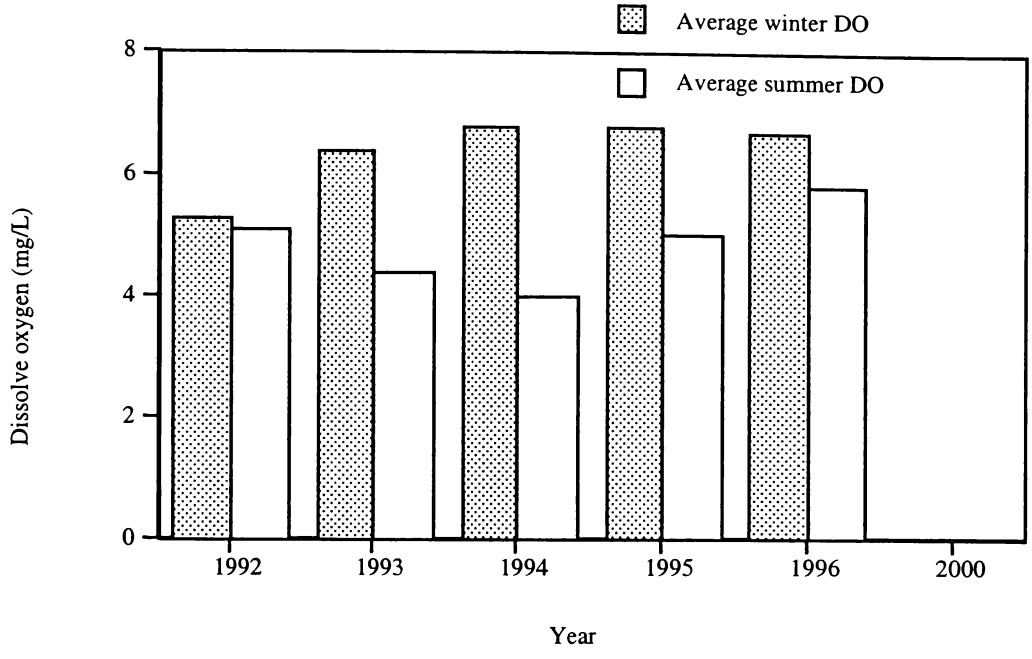

Figure 1.4. Downstream Tarawera River dissolved oxygen levels - average winter and summer values (Tasman 1997).

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Reduced water usage

Water conservation projects have resulted in mill water use dropping by more than 27% between 1994 and 1997. As a result of these reductions the loading on the wastewater treatment system has reduced, allowing treatment efficiency to increase.

Reduced AOX and organochlorine discharges

Following the introduction of elementary chlorine free (ECF) chlorine dioxide bleaching in mid-1998, chlorine discharges, expressed as kg AOX/tonne of bleached pulp, have been reduced by 60% from the 1994 level of 0.9 kg/tonne to less than 0.4 kg/tonne.

In 1997, the Total Equivalent Toxicity (TEF) of dioxins in Tasman's wastewater, prior to discharge and river dilution, was 1.1 parts per quadrillion. Following the introduction of ECF bleaching in 1998 the potential for the generation of dioxins as a by-product of mill bleaching processes was effectively eliminated.

Colour reduction

It is widely recognised that the colour of the lower reaches of the Tarawera River is the factor that most strongly influences people's perceptions about river quality. As a consequence of plant improvements and the commissioning of technologies designed to minimise the production of coloured species (mainly chromophoric polyphenolic lignin molecules), river colour has fallen by more than 50% since 1985 (see Figure 1.5). However viewed from above the river still appears dark and ominous.

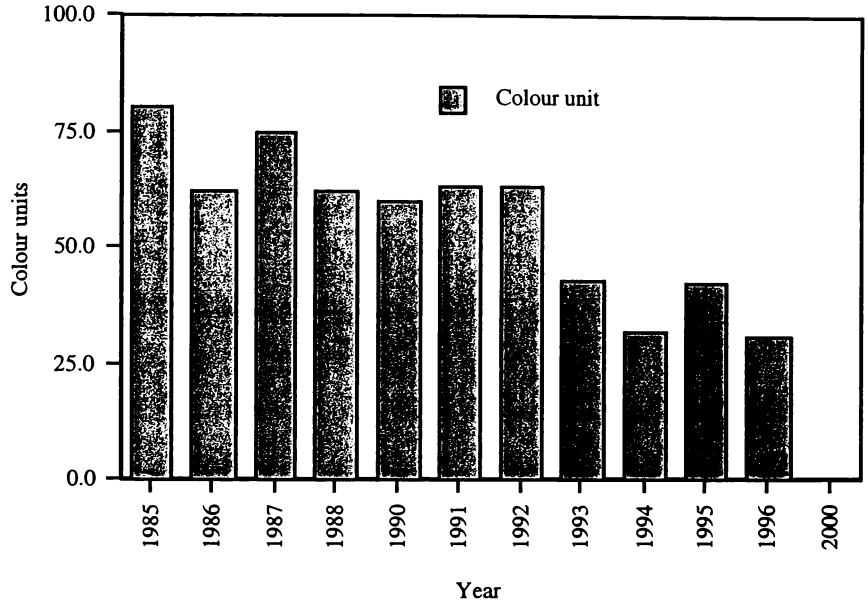


Figure 1.5. Tarawera River colour below Tasman's discharge point. Colour levels were measured relative to Pt-Co units (Tasman 1997).

Efforts to reduce colour discharges by further improvements to mill technologies and operating practises are continuing. Currently a further 20% reduction colour is being sought.

Possible alternative colour reduction strategies

While continuing small incremental decreases in colour levels can be expected, a major reduction in colour levels is likely to be achieved only by commissioning new tertiary treatment plant or by major changes in effluent disposal strategies.

Possible tertiary treatment options could include flocculation-filtration, ozone treatment, absorption onto activated carbon, or membrane filtration. Presently none of these technologies are considered to be economically viable.

Possible alternative disposal strategies for all or part of treated mill wastewaters include:

a) deep well injection

b) ocean disposal via a pipe line from the mill to the sea

c) land disposal (irrigation)

Deep well injection

Deep well injection, especially in the fragile Tarawera Plains aquifer system, is unlikely to be able to handle the volume of effluent (currently ca. 150 ML/day)

Pipeline to sea

The merits of discharging Tasman's biological treated effluents directly to the sea (via a 20 km pipeline), rather than via the Tarawera River, have been periodically considered. The cost of constructing a ca. 1.6 m diameter pipeline to the sea (estimated to be $11 million (Humes 2000)), excluding possible land purchase costs, render this option unattractive economically. It is also questionable from an environmental point of view.

Land based disposal

Land disposal is currently being utilised as a procedure to dispose of denatured primary solids and waste lime mud (Tasman 1997).

During 1987-1990, the possibility that biologically treated effluent could be disposed of by irrigation was investigated (Sligh 1993). In a three year trial, effluent was irrigated on Tasman Forestry's tree orchard, Onepu Springs Road, next to the Tarawera River. Trial results suggested that the best irrigation rate to be 60 to 80 mm per week and showed that 2000 hectares would be required to accept all of Tasman's effluent.

Positive aspects of the trial included enhanced pasture growth, increased earth worm population, declined grass grub population, a neutral effect on livestock, 60 to 90% removal of colour and reduced river BOD.

Negative aspects were a flow of coloured ground water towards the Tarawera River and increased soil pH and sodium soil levels. Sometimes the soil became impervious. It was concluded (Sligh 1993) that land irrigation with the total effluent streams would be too expensive and not acceptable during wet weather periods.

Wang *et al* (1999) have recently reported the results of a 16 month trial in which primary treatment effluent from a New Zealand TMP pulp mill was applied to 500 mm dia by 750 mm deep barrel lysimeters containing two types of intact soil cores. Irrigation was scheduled on a weekly basis and effluent was applied at a loading rate of 30 mm/week. Parameters analysed included conductivity, turbidity, BOD, COD, TOC, cations (Na, Ca, Zn, B, Fe, Al, As, Cr, Cu, Mn, Mo, Ni and Pb), pH, colour and organic species (resin acids, phenols and phytosterols).

Removal rates through the soil cores were greater than 90% for TOC, COD, BOD, turbidity, resin acids, phytosterols and phenols. No excessive nutrient and heavy metal leaching was observed during the experiment. Compared with controls, higher levels of cations were detected in leachates.

For example Na, K and Fe levels for soil 1 (a tephric type soil) were in the range 4.5-11.5, 5.2-11.0 and 0.15-12 mg/L respectively, compared with 0.7-1.2, 1.2-5.4 and 0.004-0.04 mg/L respectively for a control soil. Therefore, Wang *et al* (1999) concluded that land application was only a viable option to treat TMP effluent from selected pulp mill streams with little or no sodium added during processing.

Since kraft effluent streams typically contain elevated sodium levels, land disposal is not likely to be an acceptable option for Tasman, or other New Zealand pulp mills.

1. 6. Objectives of present study

From the literature reviewed above, it is clear that significant progress has been made in understanding the environmental impact of pulp and paper discharges and the development of improved technologies to minimise this impact. Much however remains to be done. The Tarawera River is an obvious choice for the study of pulp and paper effluent impacts from the New Zealand industry. The relatively low dilution factor achieved upon discharge to this recipient means that effluent species are present at easily detectable levels.

The research described in this thesis starts with an investigation of aspects of the environmental chemistry of resin acids in the Tarawera River and then includes aspects of the treatment system. Specific objectives include:

1. Development of procedures to allow improved accuracy and precision of resin acid analysis. Much of the data reported in literature is semi-quantitative. CVs of 20% and greater are common. In order to carry out prolonged experiments and to monitor subtle changes, stabilised samples and analytical precision better than 10% are required. Much of the initial work was directed toward achieving this goal.

2. Investigation of the speciation of resin acids and coloured species in Tarawera River water. It was envisaged that a sequential filtration experiment would allow the size distribution of particles to be determined. There is some evidence that resin acids are particle bound. The sequential filtration experiment will allow this possibility to be investigated and provide information about the size distribution of the particles, which have absorbed resin acids. The chemical composition of such particulates is also of interest.

3. Effective treatment of the effluent requires an understanding of the chemical and physical form of the species that need to be removed. Included in this is the effect of interactions with particulate matter on degradation pathways.

4. The finding that the majority of the resin acids in the Tarawera River and in the final discharge water samples were particle bound indicated that filtration and flocculation/filtration studies would be of benefit. The possibility that primary filtration, with or without flocculation, may provide a cost effective treatment strategy needs to be also explored.

Chapter 2

Materials and methods

2.1. Sampling

River water samples

River water samples were collected on 14 occasions between 16 June 1998 and 22 June 2000 in glass winchesters (2.5 L) and plastic containers (20 L) which had previously been soaked with Decon 90 for 24 h, rinsed with 1 mol/L HCl, washed with tap water and finally distilled water. Sampling sites and collection dates are listed in Table 2.1. In the field, care was taken not to collect stagnant or slow flowing water by a bank. Winchesters or plastic containers were rinsed with river water then filled leaving no air gap in the bottle. Water samples were transported to the laboratory within 4 h of collection and stored at 4°C until required for analyses.

Sodium azide was added, with shaking, at the rate of 2.5 g per 2.5 L (equivalent to 0.1% w/v) to some of the Tarawera River and treatment pond water samples collected on 14/1/99, 25/2/99, 8/7/99, 1/11/99, 27/1/00, 11/3/00, 4/4/00, 27/4/00, 15/4/00 and 22/6/00.

Sediment samples

Sediment samples (marked with sample identification codes) were collected in plastic bags on 16/6/98 from the banks of the Tarawera River at the Kawerau town bridge, SH30 and SH2 bridge (Table 2.1). Sediment samples were air dried for four days and then oven dried at 45°C for 3 h and stored at room temperature until required for Soxhlet extraction.

Mill wastewater samples

Water samples were collected in 2.5 L glass winchesters and 20 L plastic containers (pre-rinsed as described for river water samples) from Tasman Pulp and Paper Mill's clarifier and effluent treatment ponds (see Table 2.1) on 1/11/99. The average retention time of water in treatment ponds 1, 2, 3 and 4 at the time of collection was 2.5 h, 1 day, 2.5 days and 2 days respectively.

Table 2.1. Tarawera River and Tasman Pulp and Paper Mill sampling sites and sample types.

site	code	distance from sea (km)	sample type(s)*
Kawerau Town Bridge	KTB	28.5	rw, rs
State Highway 30 Bridge	SH30	18.5	rw, rs
State Highway 2 Bridge	SH2	0.7	rw
Clarifier outlet	CO	-	ww
Treatment pond 1 (outlet)	P1	-	ww
Treatment pond 2 (outlet)	P2	-	ww
Treatment pond 3 (outlet)	P3	-	ww
Treatment pond 4 (outlet)	P4	-	ww

*rw = river water, rs = river sediment, ww = mill wastewater

2.2. Extraction protocols

2.2.1. Liquid/liquid extraction of water samples

Water samples (1 L, 500 mL or 100 mL) were liquid/liquid extracted for 17 h with redistilled dichloromethane (ca.170 mL). *O*-Methylpodocarpic acid (PDA) (typically 500 µL of a 0.022 mg/mL solution in dichloromethane) was added to the water phase as surrogate (recovery) standard immediately before extraction commenced. After extraction *O*-methylpodocarpic acid ethyl ester (PDA-Et) (typically 500 µL of a 0.023 mg/mL solution in dichloromethane) was added to the dichloromethane extractive solution as primary (quantification) standard and the extraction solvent was removed using a rotary evaporator. Residual material was dissolved in dichloromethane (ca. 2 mL). Any water

present in the solution was removed by addition of anhydrous Na_2SO_4 and filtration of the dried solution through glass wool packed in a Pasteur pipette.

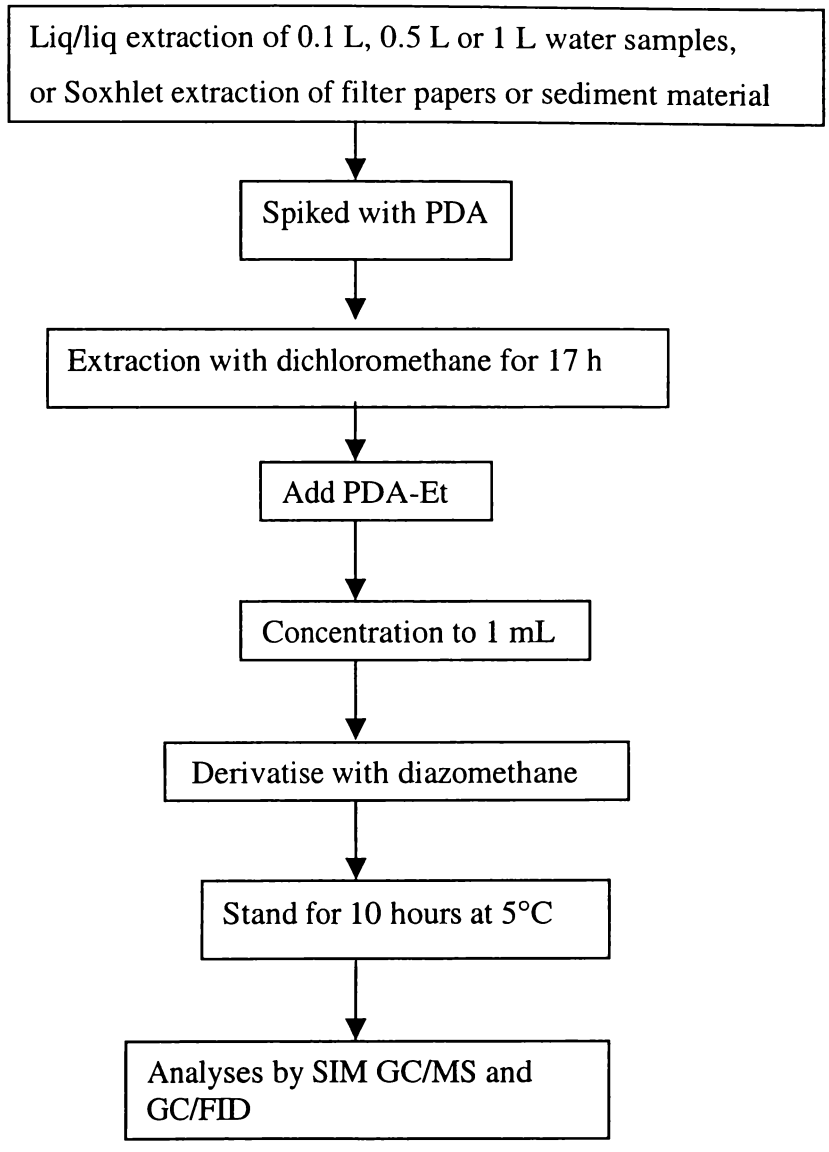


Figure 2.1. Flow diagram for the organic analyses protocol.

An ethereal solution of diazomethane (CH_2N_2) was added to the filtrate and the mixture was allowed to stand for 10 h at 5°C. The derivatised extractive solution was concentrated to ca. 0.5 mL and transferred to a GC/MS vial, which was capped and stored at 5°C prior to SIM GC/MS analysis. (Caution: diazomethane is a hazardous substance)

The liquid/liquid extraction and derivatisation protocols are depicted, in block diagram format, in Figure 2.1.

2.2.2. Soxhlet extraction of sediment samples

Accurately weighed, dried, sediment material (ca. 0.1 to 0.3 g) was placed in a glass extraction thimble and extracted with redistilled dichloromethane for 16 h using a Soxhlet apparatus. *O*-Methylpodocarpic acid (PDA) (typically 500 μL of a 0.022 mg/mL solution in dichloromethane) was introduced onto the sediment material in the extraction thimble as surrogate (recovery) standard immediately before extraction commenced. After extraction *O*-methylpodocarpic acid ethyl ester (PDA-Et) (typically 500 μL of a 0.023 mg/mL solution in dichloromethane) was added to the dichloromethane extractive solution as primary (quantification) standard and the extraction solvent was removed using a rotary evaporator. Residual material was dissolved in dichloromethane (ca. 2 mL). Any water present in the solution was removed by addition of anhydrous Na_2SO_4 and filtration of the dried solution through glass wool packed in a Pasteur pipette. An ethereal solution of diazomethane (CH_2N_2) was added to the resulting solution and the mixture was allowed to stand for 10 h at 5°C. The derivatised extractive solution was concentrated to ca. 0.5 mL and transferred to a GC/MS vial, which was capped and stored at 5°C prior to SIM GC/MS analysis.

2.3. Organic component analyses

A flame ionisation detector (FID) is one of the most widely used gas chromatography (GC) detectors for organic compound analyses. When an organic compound is burnt in a hydrogen and air flame, a low level of positive ions and electrons is produced. The ion current from each separated compound in the sample mixture can be detected via a Wheatstone bridge circuit and amplified. The concentration of each component in a mixture, separated using a capillary column, can be assessed by comparing its peak area with that for a known amount of a target species.

Mass spectrometry (MS), a technique which uses a high-energy electron beam to ionise molecules, is a very sensitive technique for the identification of organic compounds. In

the quadrupole MS instrument used in the present investigation, positive ions (generated by electron impact) are accelerated by a potential field and are focused on to the detector to give a mass spectrum.

The capillary columns used in GC-FID or GC/MS analyses are typically 25 to 50 m in length and have an internal diameter (id) in the range 0.22 to 0.53 mm (standard and mega-bore types respectively). The flow rate of standard bore capillary columns (< 1 mL/min) are generally such that the column output can be fed directly into the ionisation chamber of the MS. Each component eluting from the GC column, can be identified by both its retention time and by its mass spectral fragmentation pattern.

2.3.1. GC/FID

GC analyses of derivatised water and sediment extract were performed using a 25 m HP-1 capillary column installed in a HP5980 GC. Typical GC/FID acquistion conditions are given in Table 2.2.

Resin acids and resin neutrals were identified by comparison with retention times determined for authentic samples of the target compounds. Identifications were also confirmed in subsequent total ion chromatogram (TIC) mode GC/MS analyses. Typically, for a 1 L water sample, the GC/FID detection limit was 2 μg/L.

Table 2.2. Typical GC/FID parameters.

GC instrument	HP5980 series 2
auto injector	HP7363A
column	25 mx 0.22 mm id HP-1
injector	split/splitless
injection volume	2 μL
splitless time	0.5 min
carrier gas	hydrogen
initial temperature	125°C
initial time	0.5 min
temperature programme rate 1	35°C/min (to 170°C)
temperature programme rate 2	3°C/min (to 295°C)
final hold time	5 min (at 295°C)

Figure 2.2 and 2.3 are typical GC/FID profiles determined for a SH30 Tarawera River water sample and a Tasman pond 1 sample respectively.

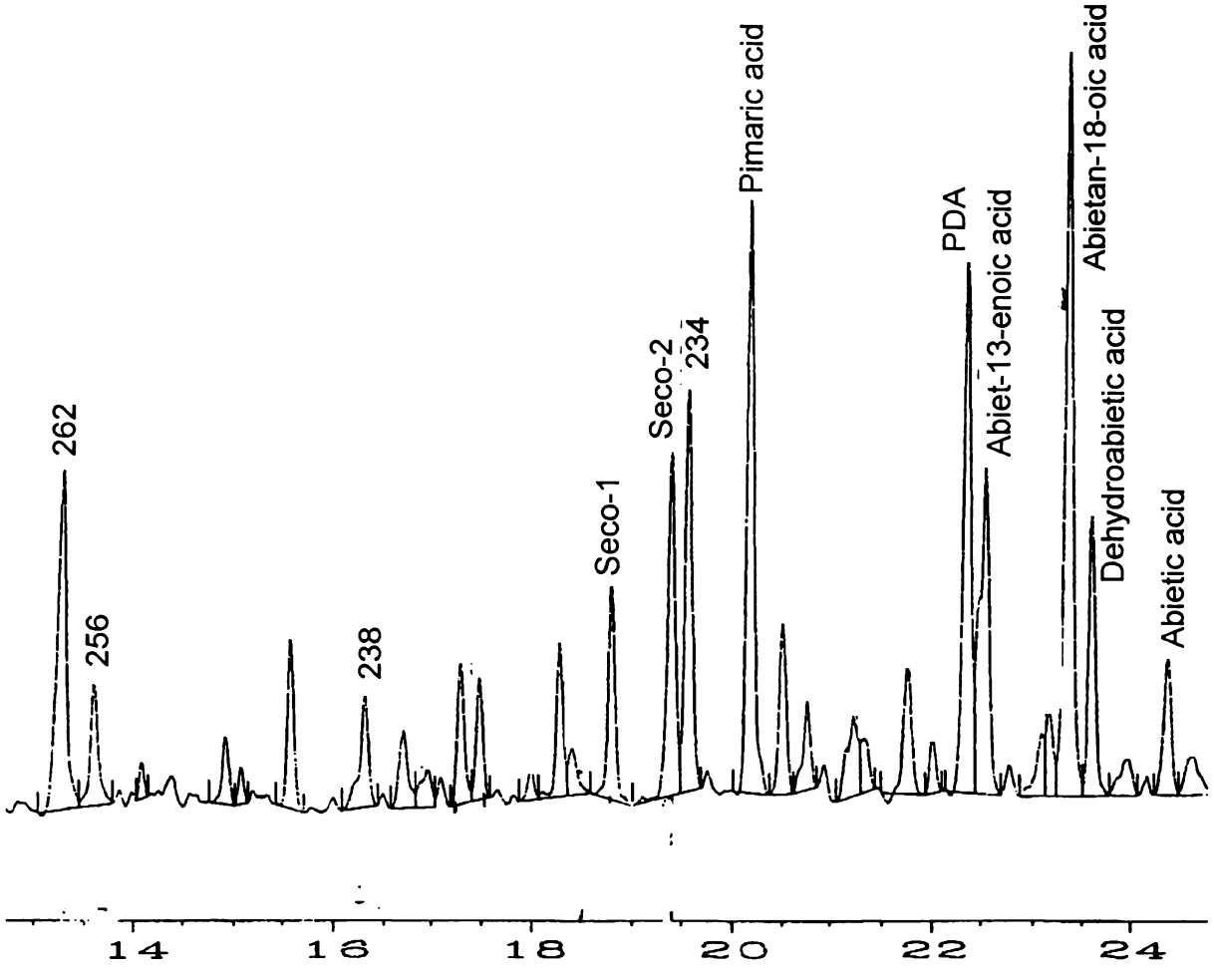


Figure 2.2. GG/FID chromatogram of a SH30 Tarawera River water sample collected 16/6/98.

Abbreviations: 262 = fichtelite; 256 = dehydroabietin; 238 = tetrahydroretene; 234 = retene; seco-1 = secodehydroabietic acid-1; seco-2 = secodehydroabietic acid-2; PDA = *O*-methylpodocarpic acid; PDA-Et = *O*-methylpodocarpic acid ethyl ester

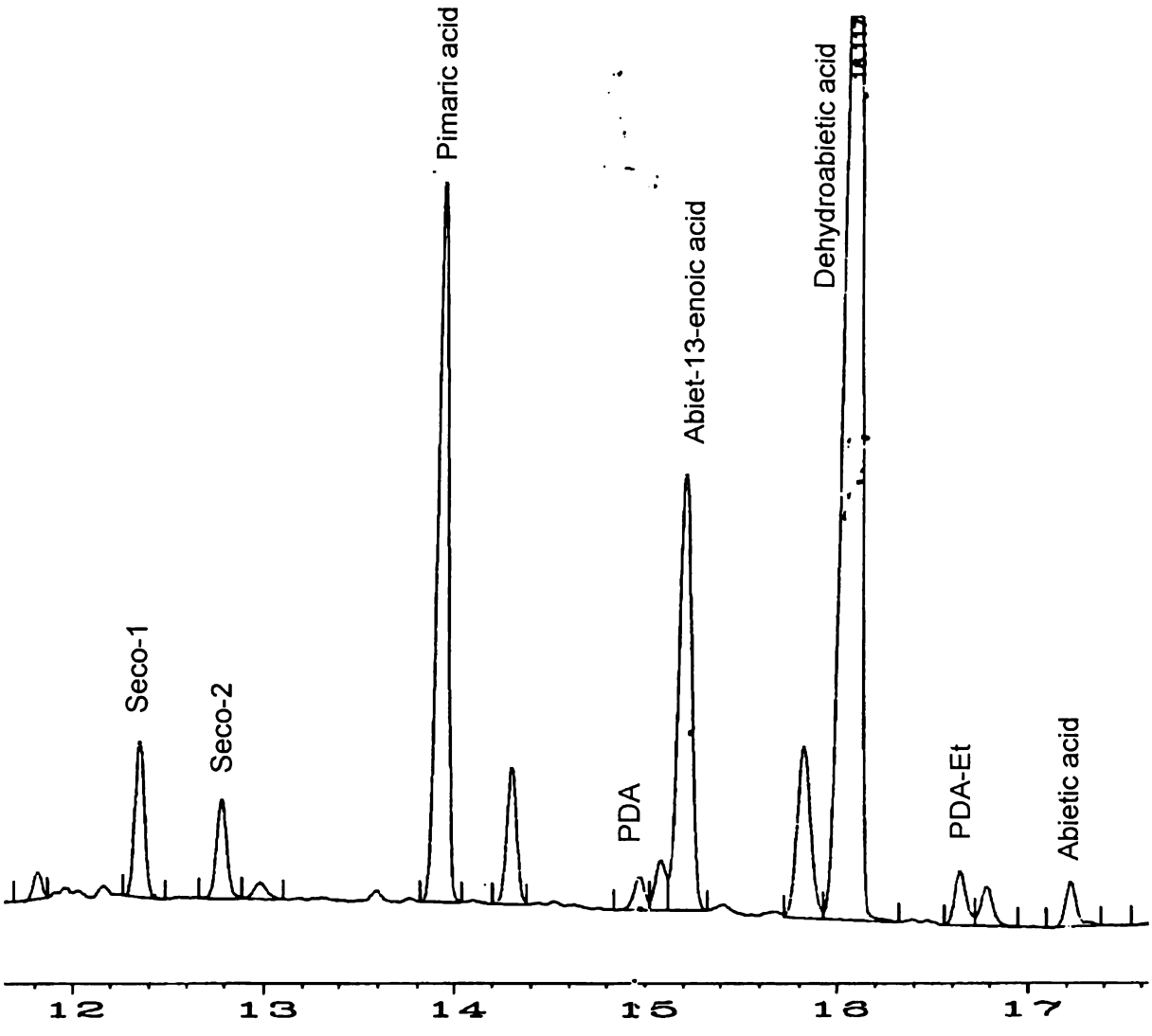


Figure 2.3. GG/FID chromatogram of a Tasman pond 1 water sample collected on 1/11/99.

Abbreviations: seco-1 = secodehydroabietic acid-1; seco-2 = secodehydroabietic acid-2; PDA= *O*-methyl-podocarpic acid ; PDA-Et = *O*-methylpodocarpic acid ethyl ester

2.3.2. Total ion chromatogram (TIC) mode GC/MS

The sum of all of the detected ions detected in a GC/MS analyses gives the total ion chromatogram (TIC) of the sample. In general a TIC GC/MS profile of a sample is very similar to its GC/FID chromatogram. The TIC GC/MS responses of individual compounds may however vary to a greater extent than is the case for GC/FID analyses.

Typical TIC GC/MS acquisition parameters are given in Table 2.3.

Table 2.3. Typical TIC GC/MS parameters.

GC instrument	HP5980 series 1
MS	HP5970B
MS scan range	*m/z* 40-400
auto injector	HP7363A
column	25 m x 0.22 mm id HP-1
injector	split/splitless
injection volume	2 μL
splitless time	0.25 min
carrier gas	helium
initial temperature	125°C
initial time	0.25 min
temperature programme rate 1	35°C/min (to 170°C)
temperature programme rate 2	5°C/min (to 285°C)
final hold time	5 min (at 285°C)

2.3.3. Selected ion monitoring (SIM) GC/MS

The sensitivity of GC/MS analyses can be greatly increased by acquiring the MS ion current in selected ion mointoring (SIM) mode. The SIM technique differs from the TIC technique in that only a few preselected ions are focussed on the detector. This can result in ca. 100 fold increase in sensitivity, compared with TIC GC/MS analysis, largely because the bulk of the time is spent monitoring high intensity fragment ions.

The ions used in SIM GC/MS analyses are given in Table 2.4. Ions shown in bold were used for quantification. Other ions were utilised as confirmation ions (eg: to calculate ion ratios). Extracted ion chromatograms of each quantitation ion were plotted and integrated to determine the peak area contributions of individual resin acids, or resin neutrals.

Table 2.4. Ions used for SIM GC/MS analyses.

compound	ions used (*m/z*)	compound	ions used (*m/z*)
resin acids[a]		standards	
abietic acid	**256**[b], 241, 316	*O*-methylpodocarpic acid	**227**
abiet-13-enoic acid	**275**, 318	*O*-methylpodocarpic acid	
abietan-18-oic acid	**163**, 261, 320	ethyl ester	**227**
DHAA	**239**, 299, 314		
12-Cl-DHAA	**273 + 275**	resin neutrals	
14-Cl-DHAA	**273 + 275**	fichtelite	**262**, 109,191
12,14-diCl-DHAA	**307+ 309**	dehydroabietin	**256**, 159, 241
seco-DHAA-1	**146**, 187, 316	tetrahydroretene	**238**, 181, 223
seco-DHAA-2	**146**, 316	retene	**234**, 204, 219
pimaric acid	**121**, 316, 180		

[a] acids detected as the corresponding methyl esters, [b] Quantification ions are given in bold type

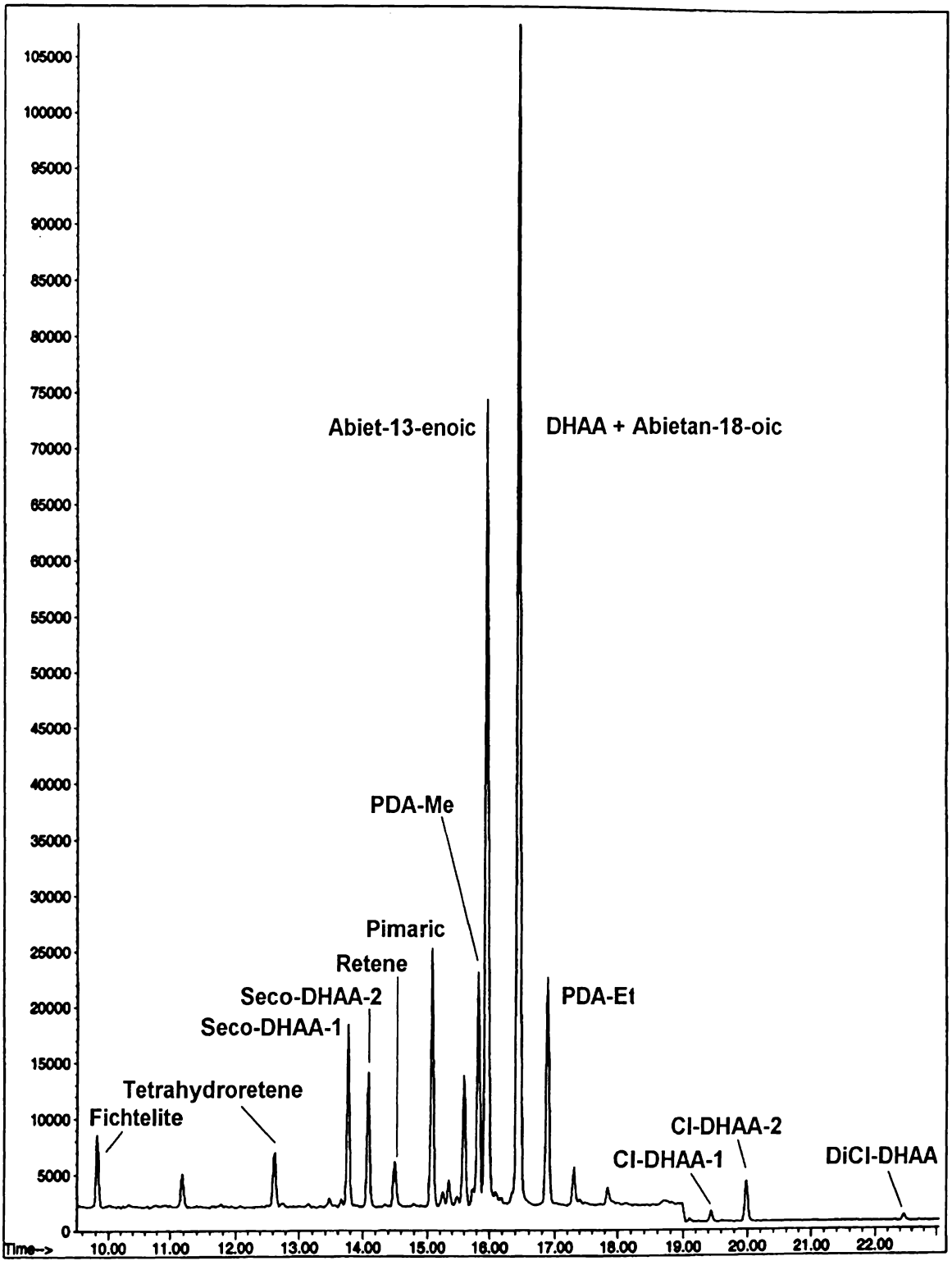


Figure 2.4. SIM GC/MS chromatogram of a SH30 Tarawera River water sample, collected 16/9/98.

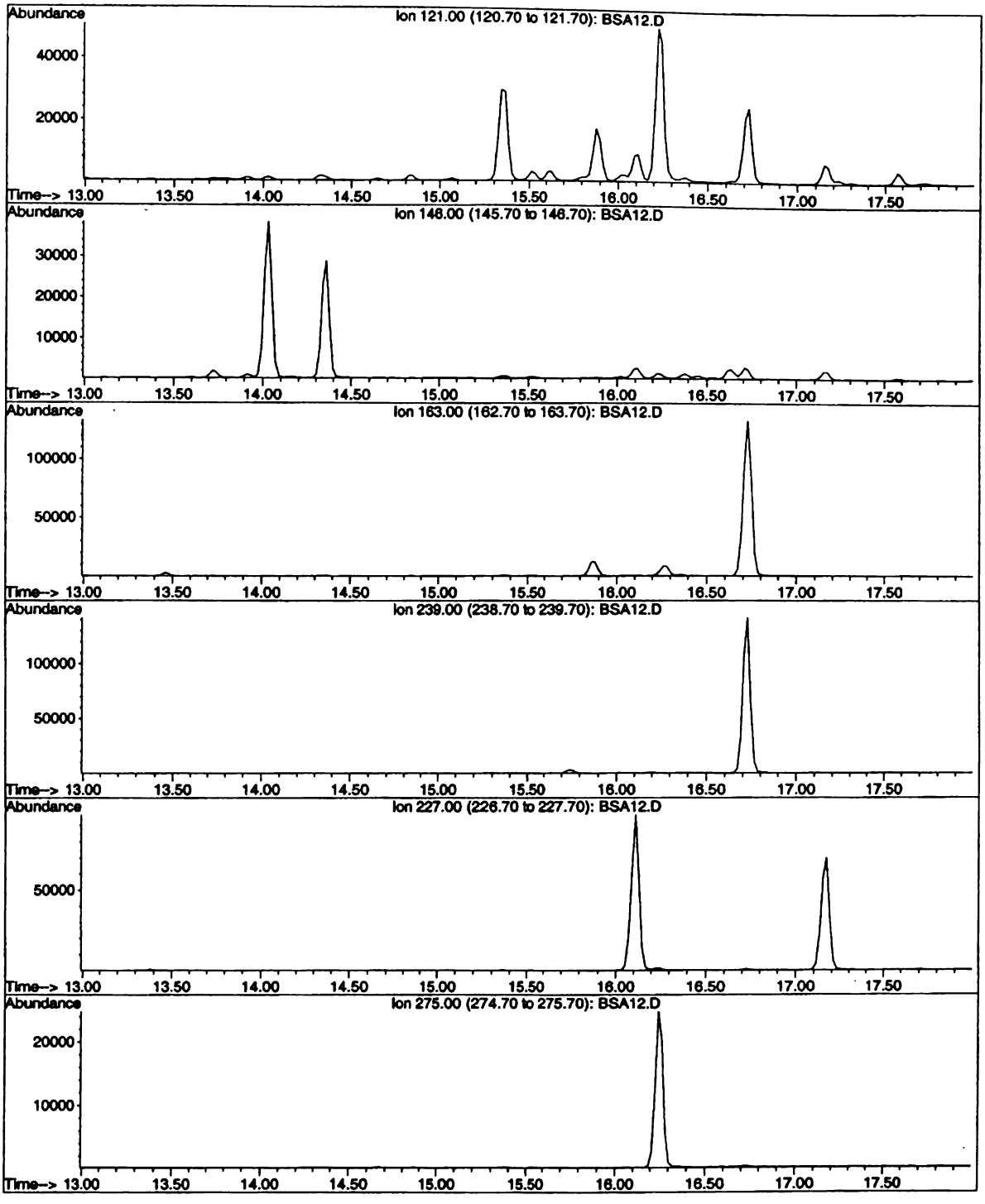


Figure 2.5. *M/z* 121 (pimaric acid), 146 (secodehydroabietic acids-1 and 2), 163 (abietan-18-oic acid), 239 (dehydroabietic acid) and 275 (abiet-13-enoic acid) SIM GC/MS ion profiles determined for a SH30 Tarawera River water sample, collected 16/9/98.

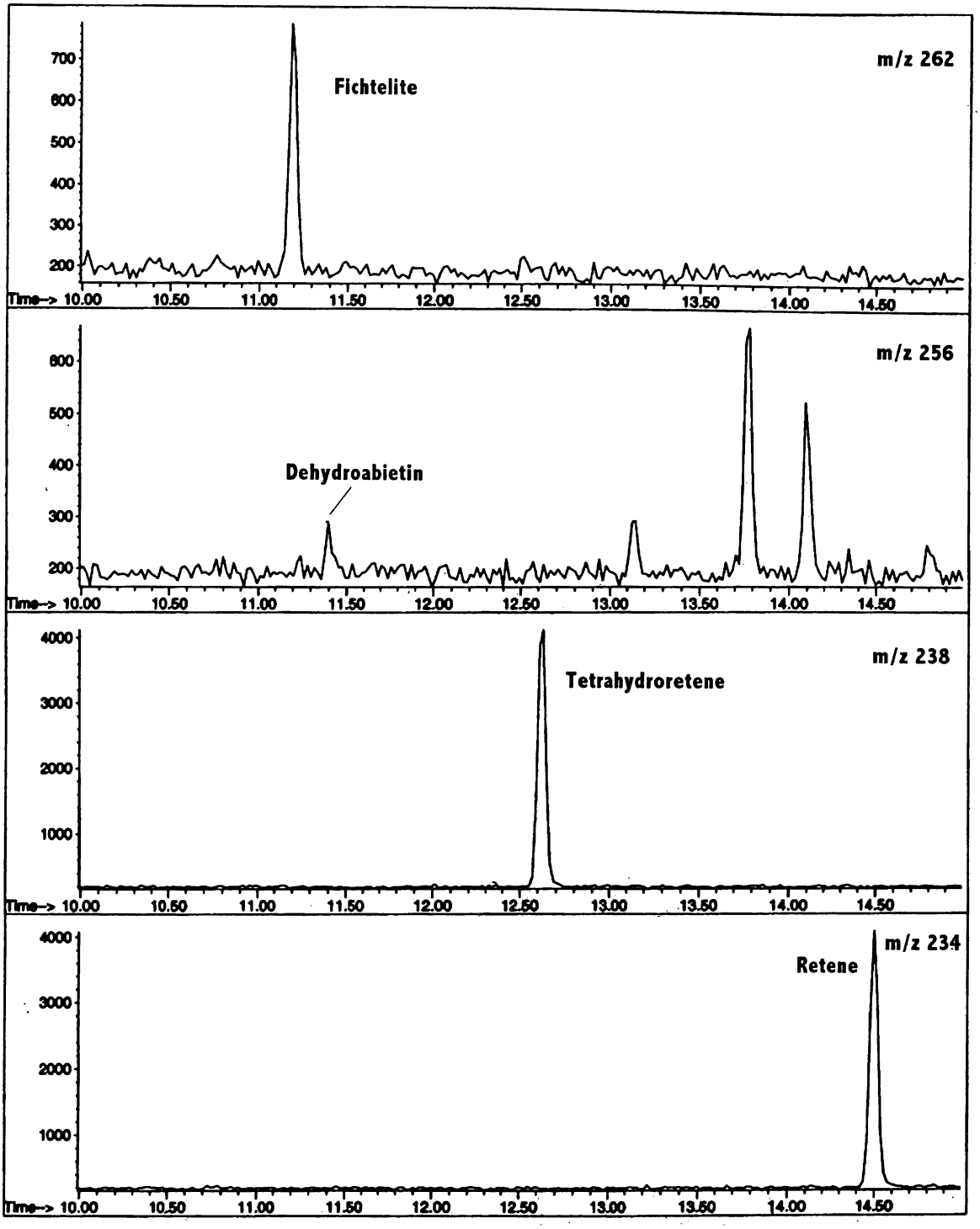


Figure 2.6. *M/z* 262 (fichtelite), 256 (dehydroabietin), 238 (tetrahydroretene) and 234 (retene) SIM GC/MS ion profiles determined for a SH30 Tarawera River water sample, collected date 16/9/98.

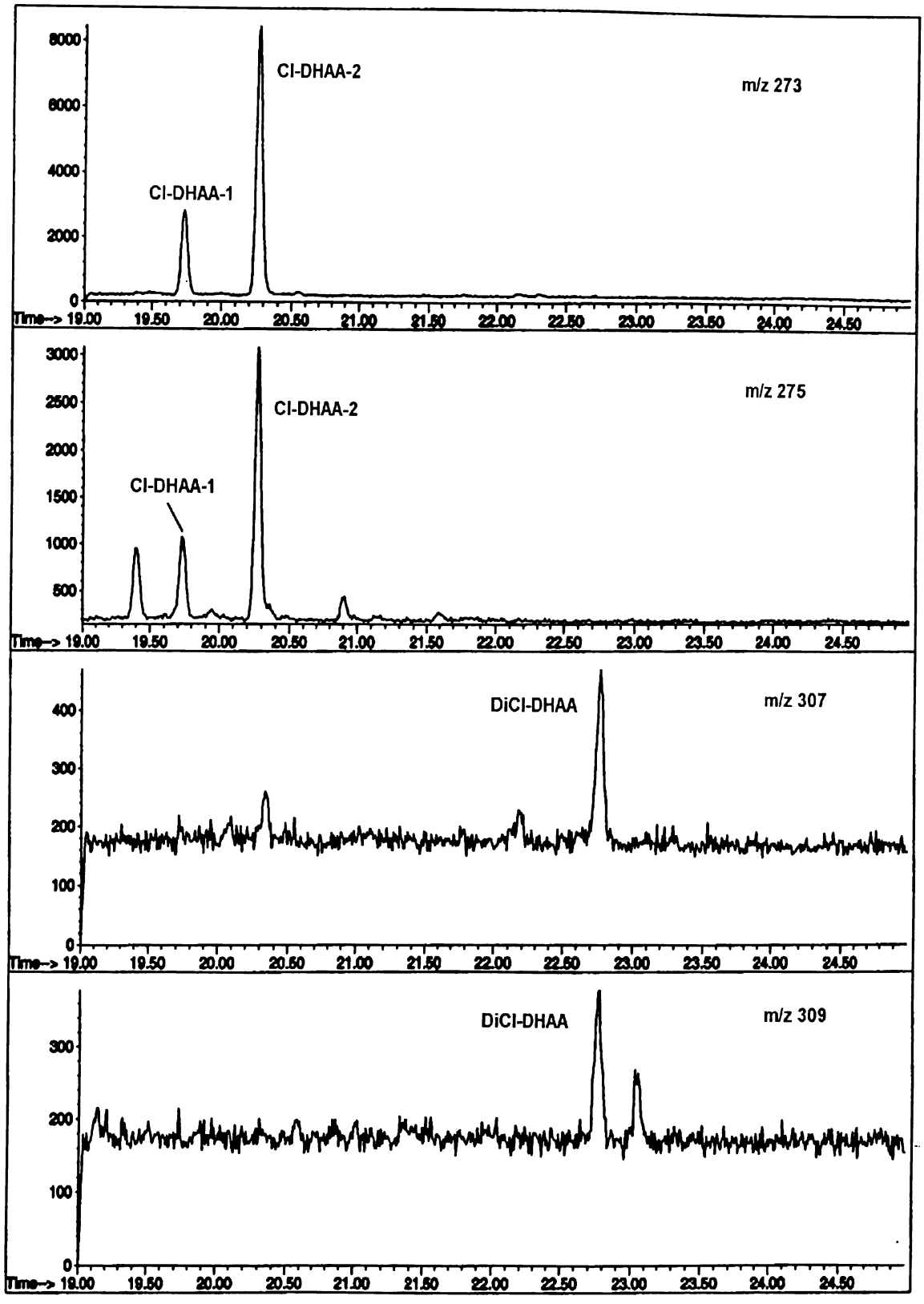


Figure 2.7. *M/z* 273 and 275 (chloro-DHAA isomers), and 307 and 309 (dichloro-DHAA) SIM GC/MS ion profiles determined for a SH30 Tarawera River water sample, collected 16/9/98.

2.3.4. Response factors

Response factors vary with the structure of the compound and the detector used. Compounds with similar structure generally have similar GC/FID response factors. For example Zinkel *et al* (1971) has reported GC/FID response factors for a wide variety of resin acids. Response factors, relative to pimaric acid, were typically in the range 0.95-1.05.

In this investigation response factors were calculated relative to *O*-methylpodocarpic acid ethyl ester (PDA-Et). Response factors were determined in one of two ways. When authentic specimens were available, as was the case for pimaric acid, DHAA, 12-Cl-DHAA, 14-Cl-DHAA, 12,14-diCl-DHAA and PDA, GC/FID, TIC GC/MS and SIM GC/MS response factors were determined using a standard solution containing known amounts of individual compounds.

Alternatively when authentic specimens of target compounds were not available, the concentration of target compounds (e.g. seco-DHAA isomers and abietan-18-oic acid) in a reference solution was determined using GC/FID and a unit response factor relative to DHAA. In light of the observations of Zinkel *et al* (1971) (see above), the use of a unit response factor introduces an uncertainty of not more than 5-10% in the concentration of the target resin acids. The reference solution was then used to drive the TIC GC/MS and SIM GC/MS response factors for some target substance based on the GC/FID determined concentration of these compounds in the reference solution.

Response factors for seco-DHAA-1, seco-DHAA-2, abietan-18-oic acid, abiet-13-enoic acid and abietic acid were determined using the GC/FID reference solution technique described above. The mathematical expression used to derive SIM GC/MS response factors for authentic specimens or via the reference GC/FID solution technique, relative to DHAA are given below. Since the GC/FID and SIM GC/MS determined concentration of species in the reference solution are identical, these terms mutually cancel in the expression, which derives the SIM GC/MS RF.

RF (*authentic specimen*) =

$$\frac{\text{(peak area of the target compound) x (concentration of PDA-Et)}}{\text{(peak area of PDA-Et) x (concentration of the target compound)}}$$

RF (*species in reference solution*) =

$$\frac{\text{(peak area (X) in SIM) x (peak area DHAA in FID) x (RF DHAA in SIM)}}{\text{(peak area (X) in FID) x (peak area DHAA in SIM)}}$$

Table 2.5. Typical SIM GC/MS response factors determined for resin acids and resin neutrals relative to the *m/z* 227 ion response of PDA-Et.

compound	ion (*m/z*)	typical RF
pimaric acid	121	0.693
abiet-13-enoic acid	275	0.095
abietan-18-oic acid	163	1.261
dehydroabetic acid (DHAA	239	1.555
O-methylpodocarpic acid (PDA-Me)	227	0.982
12-chlorodehydroabietic acid (12-Cl-DHAA)	273+275	1.109
14-dichlorodehydroabietic acid (14-Cl-DHAA)	273+275	1.109
12,14-dichlorodehydroabietic acid (diCl-DHAA)	307+309	1.250
fichtelite	262	
tetrahydroretene	238	
retene	234	

2.3.5. SIM GC/MS detector linearity

Linearity and reproducibility of detector response in SIM GC/MS mode were demonstrated using solutions containing a fixed amount of PDA-Et (200 µL of a 0.023 mg/ mL solution in dichloromethane) and variable amounts of a 0.022 mg/mL solution of PDA-Me in dichloromethane (50, 100, 200, 300, 400 and 500 µL). The slope of the least squares fitted lines defines the response factor of PDA-Me relative to PDA-Et.

Detector linearity can be conveniently assessed by plotting the ratio of PDA-Me peak area divided by the PDA-Et peak area, against the volume of PDA-Me added to each solution. The reproducibility of the detector system was routinely evaluated by single, or multiple, injections (e.g. n = 4) of each of the reference solutions.

A typical detector linearity and reproducibility profile determined for four replicate injections of each of the reference solutions is depicted in Table 2.6. These results can be compared (for example) with those determined 30 days previously for sub-samples of the same reference solutions. The close correspondence between the respective RF and linearity profiles (illustrated in Figure 2.8 for analyses conducted 30 days apart) was typical of that observed over the 36 month duration of the present investigation.

Table 2.6. Ratio of peak area of PDA-Me/PDA-Et determined for mixtures of PDA-Me and PDA-Et[a].

PDA	Run 1[b]							
vol (μL)	A	B	C	D	Mean	stdev	CV	Run 2[c]
50	0.241	0.231	0.208	0.208	0.222	0.017	7%	0.250
100	0.427	0.422	0.404	0.409	0.416	0.011	3%	0.443
200	0.875	0.775	0.748	0.762	0.790	0.058	7%	0.807
300	1.209	1.272	1.206	1.283	1.243	0.041	3%	1.247
400	1.577	1.677	1.720	1.615	1.647	0.064	4%	1.612
500	2.008	2.024	2.039	1.988	2.015	0.022	1%	2.094

[a] 250 μL of PDA–Et added to all mixtures. [b] Run 1, samples A-D are four replicates.
[c] Run 2 analyses performed 30 days after run 1 analyses.

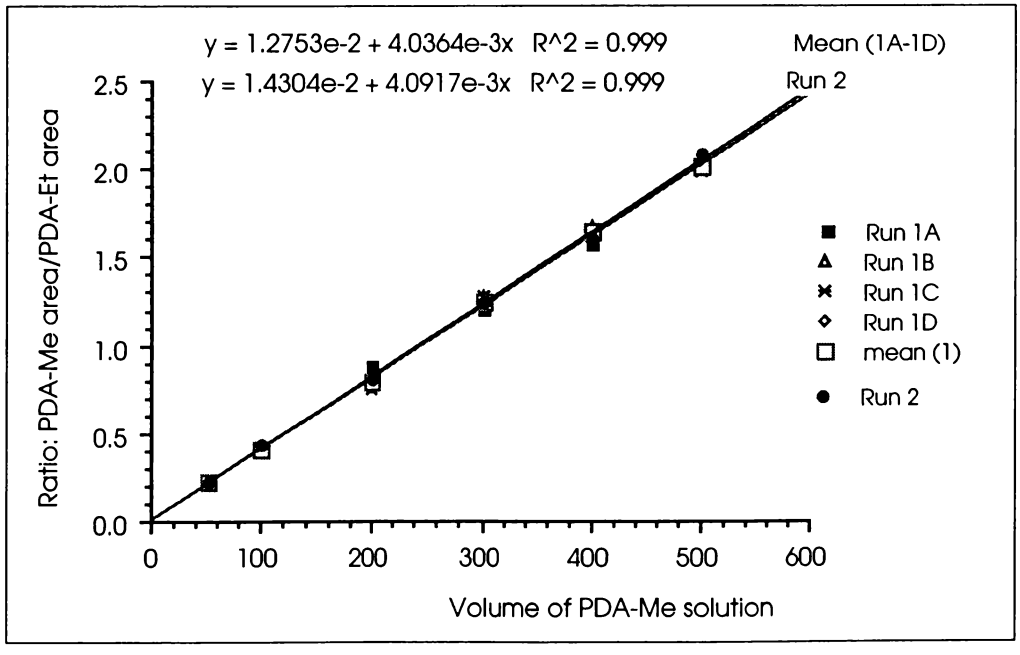


Figure 2.8. Detector linearity profile determined for PDA-Me relative to PDA-Et. (Ratio PDA-Me area/PDA-Et area versus volume (μL) of PDA solution.

2.3.5. Quantification

Concentrations of resin acids and resin neutrals were calculated from peak areas determined for appropriate ion chromatograms (e.g. *m/z* 239 for DHAA: see Table 2.5), acquired using SIM GC/MS detection and PDA-Et as primary standard. Concentrations were calculated using the following equation:

concentration of compound (X) (μg/L) =

$$\frac{\text{peak area of (X) x concentration (μg/L) of PDA-Et in sample}}{\text{peak area of PDA-Et x response factor for compound (X)}}$$

All calculations were performed using purpose written Excel spreadsheets.

Quantification results were accepted if the recovery of PDA-Me was in the range 85-110%.

2.3.6. Reproducibility

The reproducibility of the GC/MS system was routinely evaluated by multiple injections of a selected sample. Typical results, determined for four injections of a SH30 Tarawera River water sample collected on 25/2/99, are presented in Table 2.7.

Table 2.7. SIM GC/MS determined resin acid levels (μg/L) (mean of replicate analyses) identified for a Tarawera River SH30 water sample injected four times, collected 25/2/99.

sample	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total
1	17.9	6.5	31.2	17.8	34.7	2.5	110.6
2	17.7	6.4	30.7	17.7	34.2	2.4	109.1
3	17.9	6.3	30.3	17.9	35.4	2.4	110.2
4	17.7	6.4	30.3	18.0	35.2	2.5	110.1
mean	17.8	6.4	30.6	17.9	34.9	2.4	110.0
stdev	0.12	0.08	0.43	0.13	0.54	0.06	0.64
CV	1%	1%	1%	1%	2%	1%	1%

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichlorodehydroabietic acids; total = total resin acids

The overall reproducibility and standard deviation of the extraction and analytical protocol (see Section 2.5) was assessed using a 20 L bulk sample of well mixed river water. Quantification was performed using SIM GC/MS detection (see Table 2.8)

Table 2.8. SIM GC/MS determined resin acid levels (μg/L) (mean of replicate analyses) identified in Tarawera River SH30 water samples, collected 14/12/98.

Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	% recv	
SH30 A	8.3	6.7	17.8	10.9	15.8	2.4	61.9	100.0
SH30 B	8.2	6.5	18	11.1	15.2	2.7	61.6	96.2
SH30 C	9.0	7.0	17.0	11.0	15.5	2.5	62.0	98.6
SH30 D	9.2	7.1	17.9	11.6	16	2.3	64.0	100.6
SH30 E	8.1	6.8	17.7	11.5	15.7	2.5	62.2	101.1
average	8.5	6.8	17.7	11.2	15.6	2.5	62.3	99.3
stdev	1.21	0.20	0.35	0.28	0.28	0.13	0.87	
CV	14.2%	2.9%	1.9%	2.5%	1.8%	5.2%	1.4%	

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichlorodehydroabietic acids; total = total resin acids; % recv = % recovery of PDA

2.4.Filtration experiments

2.4.1. Single stage filtration experiments

Samples of Tarawera River water (1.0 L) collected at the SH30 Bridge or wastewater collected from the Tasman Pulp and Paper Mill's treatment ponds were filtered (at 18°C) through glass fibre (GF), filter paper (Whatman No. 1) or Millipore or Whatman membrane filters (3.0, 0.8, 0.45, 0.2, 0.05 or 0.025 μm pore size) using water pump pressure and a 47 mm Millipore filter system. The filtrate was retained (Table 2.9) for liquid/liquid extraction (Section 2.2.1) and inorganic analyses.

Prior to the filtration of water samples, glass fibre and Millipore filter papers were washed with distilled water (ca. 1 L) until such time as UV analyses at 270, 340 and 440 nm afforded blank (zero) absorbances and resin acids could not be detected in the filtrate. Filter papers were dried (15 min) and Soxhlet extracted using the protocol described in Section 2.2.2.

Typical reproducibility data determined for replicate liquid/liquid and Soxhlet extractions after glass fibre or Whatman No. 1 filtration are presented in Tables 2.9 and 2.10 respectively.

Table 2.9. Resin acid levels (μg/L) determined for replicate extractions of filtrates and glass fibre filter papers recovered from a bulk SH30 Tarawera River water sample collected 14/12/98.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	% recv
glass fibre filtered A	6.5	5.2	11.5	12.6	8.8	1.8	46.4	97.2
glass fibre filtered B	6.2	4.9	10.8	9.4	8.1	1.6	41.0	92.4
glass fibre filtered C	6.0	4.9	10.8	7.4	8.4	1.7	39.2	96.3
glass fibre filtered D	5.5	4.5	10.1	7.7	7.8	1.7	37.3	87.4
glass fibre filtered E	6.0	4.8	10.7	7.6	8.1	1.6	38.8	97.9
glass fibre filtered F	5.8	4.6	9.6	7.2	7.1	1.6	35.9	74.1
average	6.0	4.8	10.6	8.7	8.1	1.7	39.8	90.9
stdev	0.31	0.23	0.6	1.9	0.53	0.07	3.4	9.1
CV	5.2%	4.7%	5.7%	22.0%	6.5%	4.5%	8.5%	10%
glass fibre Soxhlet A	1.5	1.3	4.5	3.1	3.4	0.51	14.3	90.1
glass fibre Soxhlet B	1.6	1.4	4.3	3.4	3.0	0.52	14.2	86.7
glass fibre Soxhlet C	1.8	1.9	5.5	3.3	4.8	0.66	18.0	90.0
glass fibre Soxhlet D	1.5	1.4	4.1	2.8	3.5	0.52	13.8	71.1
glass fibre Soxhlet E	1.7	1.7	5.1	2.9	4.4	0.56	16.4	90.2
glass fibre Soxhlet F	1.4	1.1	3.8	2	2.7	0.42	11.4	83.1
average	1.6	1.5	4.6	2.9	3.6	0.5	14.7	85.2
stdev	0.13	0.26	0.58	0.46	0.74	0.07	2.1	7.5
CV	8.4%	18%	13%	16%	21%	15%	14%	8.7%

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichlorodehydroabietic acids; Total = total resin acids; % recv = % recovery of PDA

Table 2.10. Resin acid levels (µg/L) determined for replicate extractions of filtrates and Whatman No. 1 filter papers recovered from a bulk SH30 Tarawera River water sample collected 14/12/98.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	% recv
Whatman No. 1 filt. A[c]	5.8	5.8	12.3	8.4	10.8	1.9	45.0	94.3
Whatman No. 1 filt. B	5.9	6.2	13.3	8.5	11.7	2.2	47.8	94.1
Whatman No. 1 filt. C	5.9	6.1	12.6	8.8	11.2	1.9	46.5	94.8
Whatman No. 1 filt. D	4.3	4.6	9.9	7.1	8.9	1.4	36.2	75.7
Whatman No. 1 filt. E	5.3	5.7	12.1	8.1	10.7	1.9	43.8	89.9
Whatman No. 1 filt. F	4.0	4.2	9.1	9.0	8.3	1.4	36.0	102.0
average	5.2	5.4	11.6	8.3	10.3	1.8	42.6	91.8
stdev	0.77	0.76	1.5	0.61	1.23	0.29	4.7	8.8
CV	15%	14%	13%	7.4%	12%	16%	11%	9.6%
Whatman No. 1 Sox. A	0.73	0.8	2.4	1.45	2.2	0.24	7.8	92.4
Whatman No. 1 Sox. B	0.49	0.53	1.3	0.93	1.3	0.27	4.8	87.8
Whatman No. 1 Sox. C	0.42	0.47	1.2	0.74	1	0.23	4.1	87.3
Whatman No. 1 Sox. D	0.37	0.4	1.1	0.68	0.8	0.12	3.5	81.7
Whatman No. 1 Sox. E	0.42	0.32	0.9	0.6	0.7	0.28	3.2	86.2
Whatman No. 1 Sox. F	0.54	0.60	1.4	0.83	1.2	0.04	3.2	86.5
average (n = 6)	0.45	0.52	1.4	0.81	1.2	0.20	4.6	87.0
stdev	0.13	0.17	0.53	0.28	0.54	0.09	1.7	3.4
CV	26%	32%	39%	35%	46%	48%	36%	3.9%

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichlorodehydroabietic acids; total = total resin acids; % recv = % recovery of PDA.

2.4.2. Sequential filtration experiments

Tarawera River water was sequentially filtered at 18°C through glass fibre (7.5 L) and 3 µm (6.4 L), 0.8 µm (5.3 L), 0.45 µm (4.2 L), 0.2 µm (3.1 L), 0.05 µm (2 L) and 0.025 µm (0.8 L) filter papers. After each filtration step, 1 L (or 0.7 L for 0.025 µm) filtered water and the corresponding filter paper were liquid-liquid extracted, or Soxhlet extracted, respectively. Sequentially filtered water solutions were prepared and liquid/ liquid, or Soxhlet extracted (filter papers) on the same day. Cation, colour, conductivity and turbidity levels were typically also determined for each of the filtered river water samples.

The sequential filtration experiment, in flow diagram format is depicted in Figure 2.9.

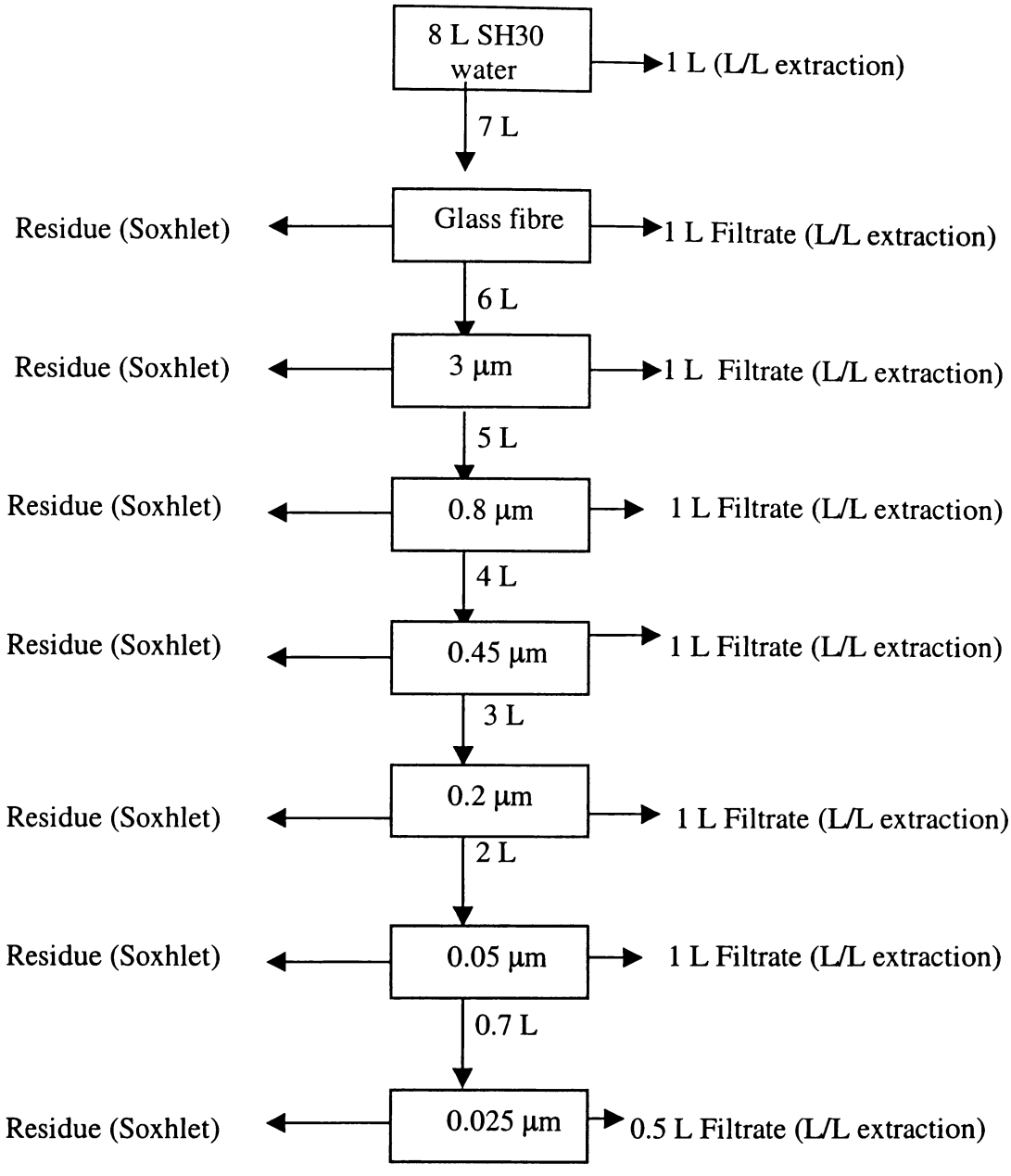


Figure 2.9. Schematic of the sequential filtration protocol.

2.5 Inorganic analyses

2.5.1. Atomic absorption

The technique of atomic absorption (AA) was developed in the mid 1950s and until recently, flame atomic absorption spectroscopy was the most widely used of all atomic spectral methods due to its simplicity, effectiveness and relatively low cost. The light absorption of each atomised cation at its characteristic wavelength is proportional to its

concentration, provided the cation concentration is within the linear response range limits of the instrument.

A series of standard solutions was prepared for each cation and calibration curves were constructed. Where appropriate river samples were diluted to bring them into the range of the standard solutions. Tarawera River water samples were not filtered prior to AA analyses. The levels of Na, K (diluted 5 fold) and Ca present in the water samples were determined using a GBC 909 flame atomic absorption (AA) spectrometer.

Typical instrument parameters used for Na, K and Ca analyses are given in Table 2.11. Calibration curves for Na, K and Ca are given in Appendix 2.

2.5.2. Carbon furnace atomic absorption

Carbon furnace atomisation atomic absorption systems, which first appeared on the market about 1970, generally provide enhanced sensitivity, because the entire sample is atomised in a short period and the average residence time of the optical path is a second or more. Furnace atomisation offers the advantage of unusually high sensitivity for small sample volumes (typically 0.5 to 10 μL) with absolute detection limits in the range of 10^{-6} to 10^{-9} g of analyte.

A disadvantage of non flame methods such as furnace atomisation is that their relative precision is generally in the range of 5 to 10% compared with the flame or plasma atomisation systems. Furthermore furnace methods are slow, typically requiring several minutes per element. Another disadvantage is that the linear analytical range is low, often less than two orders of magnitude. Consequently, non-flame atomisation is ordinarily applied only when flame or plasma atomisation provides inadequate detection.

The Al and Fe levels in Tarawera River water samples (typically in the μg/L range) were such that they could not be satisfactorily determined using flame AA. They were therefore determined using furnace AA (GBC 905).

Typical parameters used for Al and Fe analyses are given in Table 2.11. Calibration curves for Al and Fe are given in Appendix 2.

Table 2.11. Parameter settings used for Na, K, Ca, Al and Fe analyses.

parameter	Na	K	Ca	Al	Fe
system type	flame	flame	flame	furnace	furnace
lamp current (mA)	5.0	10.0	6.0	10.0	7.0
wavelength (nm)	589.0	766.5	422.7	396.2	248.3
slit width (nm)	0.5	0.5	0.5	0.5	0.2
flame type	air-acetylene	air-acetylene	air-acetylene	air-acetylene	air-acetylene
acetylene flow (L/min)	5.0	5.0	5.0	0.5	5.0
air flow L/min)	5.0	5.0	5.0	5.0	5.0
replicates	3	3	3	3	3
sampling mode	manual	manual	manual	auto	auto

2.5.3. Inductively coupled plasma optical emission spectrometry (ICP-OES)

Plasma methods offer several benefits compared with the flame and furnace methods. Among their advantages is lower inter-element interference, which is a direct consequence of the higher temperature. Secondly, spectra can be obtained for most elements under a single set of excitation conditions, consequently spectra of many elements can be recorded simultaneously. This property is of particular importance for multi-element analysis of small samples. Flame sources are less satisfactory in this regard because optimum excitation conditions vary widely from element to element; a high temperature is needed for some elements and a low temperature for other elements. Also, the region of the flame that gives rise to optimum line intensities varies from element to element.

Another advantage of more energetic (higher temperature) sources is that they permit the determination of low concentrations of elements that tend to form refractory compounds (i.e. compounds that are highly resistant to decomposition by heat or other treatments).

Despite these advantages, it is unlikely that emission methods, based upon high-energy sources, will ever totally displace flame and furnace atomic absorption. Rather, plasma emission and flame or furnace absorption methods are more appropriately viewed as complementary methods.

Included among the advantages of atomic absorption procedure are simpler and less expensive equipment requirements, lower operating costs, somewhat greater precision (presently at least) and procedures that require fewer operator skills to yield satisfactory results.

In this investigation levels of Na, Ca, K, Si, S, Al, B, As and Hg were determined using a GBC Integra XL ICP system. Typical ICP parameters are given in Table 2.12. Wavelength and other parameter for determined elements are given in Table 2.13.

Table 2.12. Parameter settings used for cation ICP analyses.

parameter	value
height plasma (mm)	6.0
nebuliser flow (L/min)	0.5
pump (rpm)	10.0
PMT (volts)	600
power (W)	1200
auxiliary gas flow (L/min)	0.5
plasma gas (L/min)	10.0
replicates	3

Table 2.13. Element wavelengths and scanning functions used for ICP analyses.

element	wavelength	monochromator function	resolution order[a]
Na	588.995	1st	2nd
Ca	422.673	2nd	2nd
K	766.49	1st	2nd
Si	251.612	2nd	2nd
S	180.731	2nd	2nd
Al	309.271	2nd	1st
Fe	259.94	1st	2nd
B	249.773	1st	2nd
As	188.979	2nd	1st
Hg	194.164	2nd	2nd

[a] Resolution functions: 1st order = 0.018 nm, 2nd order = 0.009 nm.

2.6. Physical characterisation procedures

2.6.1. Light scattering methods for determination of particle sizes

Particle size can be determined by light scattering. A Mastersizer-S instrument (Malvern Instruments Ltd., England, was used to determine particle size(s). The essential components of the instrument are depicted in Figure 2.10.

Laser diffraction size analysis is based on the principle that particles of a given size diffract through a given angle, with the diffraction angle increasing with decreasing particle size. A narrow beam of monochromatic light (the laser beam) is passed through suspension and the diffracted light is focused onto a multi-element ring detector. The particles (or aqueous suspension of particles) to be measured are added to the sample dispersion unit (Figure 2.10), containing about 1 L of water which is circulated through the flow cell which is illuminated by the laser light beam. The particles dispersed in the solvent scatter light to produce a unique scattered light pattern. The detector senses the angular distribution of the scattered light. (Singer *et al* 1988) and a computer (which manages the measurement) analyses the diffracted light pattern and intensities and presents the results.

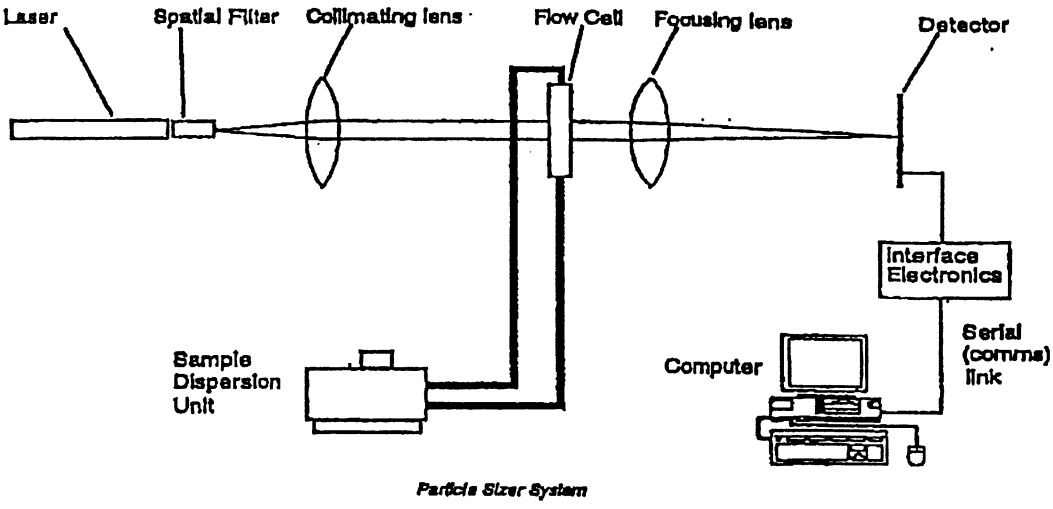


Figure 2.10. Particle size system (Source: Mastersizer-S instrument manual, Malvern Instrument Ltd., 1996).

The standard procedure for the use of the instrument was as follows. Tap water (1 L) was added to the dispersion unit and circulated through the flow cell. The obscuration (related to turbidity) was recorded (normally close zero). The tap water was drained and replaced by the sample and diluted with tap water until obscuration was typically between 18 and 28 arbitrary units. The instrument subtracts the tap water background and calculates particle sizes from the scattered intensities recorded.

2.6.2. Colour and turbidity

Colour is the effect in the human eye of reflected light energy. Dissolved organic species contribute to colour.

The colour of Tarawera River and Tasman Pulp and Paper Mill treatment pond wastewater samples was assessed by determination of their absorbances at 270, 340 and 440 nm using a 1 cm quartz cell and a Hitachi 150-20 spectrophotometer which had been zeroed using distilled water.

Turbidity is a measure of the light scattering effect within a water sample and is principally due to the presence of suspended and/or dissolved substances. Turbidity, expressed in nephaloturbidimetric units (NTU), was determined at 20°C using a Hach 2100 turbidimeter.

2.6.3. pH and conductivity

The pH of water samples was determined at 20°C using a Philips PHM61 pH meter that had been calibrated against pH 9.18 and pH 4.00 buffer solutions. The conductivity of water samples was determined at 25°C using a Philip PR 9501 instrument that had been calibrated against a 0.01 mol/L KCl solution.

2.7. 5 Day biochemical oxygen demand (BOD_5)

The 5 day biochemical oxygen demand (BOD_5) test is widely used to assess organic pollution in aquatic systems. Dissolved oxygen (DO) is measured initially and after incubation in the dark for 5 days at 20°C the BOD_5 is computed from the difference between initial and the DO_5 determinations.

A disadvantage of the BOD_5 methodology is that it takes at least five days to obtain results. The possibility therefore exists that there can be a delay of up to 4-5 days in identifying highly polluted discharges entering a water way.

DO determinations of Tasman pulp and paper mill wastewater samples (ponds 1 and 4) were performed using the iodometric (or Winkler) method, as described in Standard Methods for Determination of Water and Wastewater, (APHA, 1985).

BOD_5 methodology:

Wastewater (V mL) (8 to 100 mL depending BOD_5 level) was pipetted into two 300 mL glass bottles which were then filled to overflowing with dilution water prepared by mixing 1 mL of each of reagents 1-4 diluted to 1 L by the addition of distilled water.

Reagent 1: A phosphate solution was prepared by dissolving 8.5 g of KH_2PO_4, 21.75 g of K_2HPO_4, 33.4 g of $Na_2HPO_4.7H_2O$ and 1.7 g of NH_4Cl in 1 L of distilled water.

Reagent 2: A magnesium sulfate solution was prepared by dissolving 22.5 g

of $MgSO_4.7H_2O$ in 1 L of distilled water.

Reagent 3: A calcium chloride solution was prepared by dissolving 7.5 g of $CaCl_2$ in 1 L of distilled water.

Reagent 4: A ferric chloride solution was prepared by dissolving 0.25 g of $FeCl_3$ in 1 L of distilled water

One of the 300 mL sample bottles was carefully stoppered (excluding air bubbles) pending the initial DO_0 analyses. The second bottle was stoppered, sealed with parafilm to prevent the loss of water and kept for 5 days in the dark in a thermostatically controlled water bath at 20±1°C, after which DO_5 was measured.

DO analyses were performed by adding $MnSO_4$ (1 mL of a 480 g/L $MnSO_4.4H_2O$ solution in distilled water) and alkaline-iodide-azide reagent (1 mL of a solution containing 500 g NaOH, 135 g NaI and 10 g NaN_3 in 1040 mL of distilled water) to the water sample in the BOD bottle. When the resulting precipitate had settled to ca. half the bottle volume, conc. H_2SO_4 (1 mL) was added and the bottle was restoppered and shaken several times. The solution was then allowed to stand for 5 min and a 200 mL portion of the incubated sample was titrated against sodium thiosulfate using starch solution (5 drops) as indicator to determine the DO concentration.

For titration of the 200 mL sample, 1 mL of 0.025 mol/L $Na_2S_2O_3$ is equivalent to 1 mg DO/L The 0.025 mole/L sodium thiosulfate solution was standardised using potassium bi-iodate $KH(IO_3)_2$ (812.4 g of $KH(IO_3)_2$ in 1 L of distilled water). Relevant equations are given below:

1. Oxygen reaction: $Mn^{2+} + 2OH^- + 1/2O_2 \rightarrow MnO_2 + H_2O$
2. Iodine liberation: $MnO_2 + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O$
3. Iodine titration: $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

BOD_5 (mg/L) was calculated using the following equation:

$$BOD_5 = \frac{(DO_0 - DO_5) \times 300}{V}$$

where DO_0 = DO (mg/L) of diluted sample immediately after preparation

DO_5 = DO (mg/L) of diluted sample after 5 days incubation at 20°C

V = original sample volume (8-100 mL) added to the BOD bottle

The experiment was repeated with several dilutions of the prepared sample to obtain final DO within the range of 2 to 6 mg/L for a particular sample.

2.8. Total volatile suspended solids (TVSS)

A gravimetric method was used to indirectly determine the mass of total volatile suspended solids (TVSS) (ie combustible organic suspended solids). 0.45 μm Whatman filter papers were exhaustively washed using distilled water (ca.1 L) and dried overnight in a vacuum desiccator (water pump pressure) and furnaced at 550°C overnight. This afforded a zero (blank) result (typically 0.000-0.001 g).

The weight of volatile organic suspended solids in water samples were determined by collecting suspended solid material on pre weighed 0.45 μm (Whatman) filter papers which were then dried overnight in a vacuum desiccator and reweighed to give the total weight of total suspended solids (TSS) where TSS = [(weight of TSS + filter paper) - (weight of the filter paper)]. Dried filter papers were then furnaced overnight at 550°C. This afforded a residue which was presumed to arise from inorganic suspended solids (ISS). TVSS was calculated as TVSS = (TSS-ISS) and expressed as mg/L of filtered water.

2.9. Scanning electron microscopy (SEM)

The SEM forms an image by scanning the surface of the sample with a final focused electron beam (about 10^{-2} μm diameter). The high energy beam stimulates the emission of secondary electrons, back-scattered electrons, X rays and some times light photons from the sample surfaces. The electrical signal derived from the collected secondary, or back-

scattered electrons, is used to form a television-type image of the surface under examination (Lee, 1993). In this investigation SEM analyses were performed using a Hitachi S4000 instrument.

2.9.1. SEM sample preparation

The inability to view the solution phase is a major limitation of the SEM technique when applied to the study of suspended solids. Freeze drying has been recommended (Smart and Tovey, 1982) as a method for recovering suspended solid material and preparing it for SEM analyses. Tarawera River and mill wastewater samples (500 mL) were filtered through Whatman 0.45 μm filter paper and the filter paper and residue was freeze dried (DYNAVAC Freeze Drier Model FD12). This was achieved by plunging the sample into liquid nitrogen and removing the water under vacuum at -40°C.

A portion of the residual solid material (ca. 2 mg) was applied to double sided conductive carbon sellotape (Shintron, Japan), which was then mounted on an SEM stub and coated with 200 to 500°A of platinum-palladium using a diode sputtering system (Hitachi E1030). The coating serves to prevent a build up of charge on the surface of the specimen.

2.9.2. Energy dispersive X-ray analysis

Energy dispersive X-ray (EDX) analysis was performed using a Kevex microanalyser attached to the scanning electron microscope (SEM) system. Sample preparation is described in Section 2.9.1. Distribution maps were used to identify the dispersive nature of identified elements within the samples.

When the sample material is irradiated with an electron beam of suitable energy, X-rays characteristic of the atoms in the sample will be emitted. SEM EDX results can be interpreted both qualitatively and quantitatively.

Energy dispersive X-ray analysis (EDX) is the quantitative variant of SEM. EDX analyses, realistically speaking, give only a semi-quantitative estimate of the composition

of the sample material. EDX results should always be compared with the results of analyses determined using more reliable methods such as atomic absorption or inductively coupled optical emission spectroscopy.

While EDX analysis is a useful procedure for determining variations in the ratio of elements, it is a less satisfactory procedure for the determination of absolute amounts or oxidation states of elements.

2.10. Coagulation studies

The critical coagulation concentration (CCC) for river water and wastewater samples were determined by conventional jar tests, using a six–place jar tester (BOLTAC) equipped with multi-speed stirrers. The jar test protocol consisted of a 3 min high shear mixing of coagulant(s), followed by 10 min of slow mixing and a 30 min standing period. The CCC was then determined as the least amount of coagulant required to produce a clear solution.

The removal of resin acids and BOD_5 by coagulation was determined by adding the CCC under normal coagulation conditions, followed by allowing the sample to settle for a further 2 h, prior to withdrawal from the jar of appropriate sub-sample for resin acid and BOD_5 analyses. Precipitated material was removed by gravity filtration (Whatman No. 1) or centrifugation. The experiment was repeated at different pHs.

2.11. Hydraulic conductivity of granular media

When water flows through a porous medium, the medium provides a resistance to flow and a pressure gradient forms in the bed. For a constant head (pressure difference) and a given cross section area, the water flux depends on the properties of the medium. Darcy's Law can be used (Andersland *et al* 1996) to determine the hydraulic conductivity where:

$$Q = A K \Delta H / L$$

Q = Flux of water (m^3/s)

A = Bed section area (m^2)

K = Hydraulic conductivity (m/s)

L = Bed depth or distance between two pressure measurement points (m)

$\Delta H = H_1 - H_2$ = Head loss across the bed depth (m)

Flux of the water was determined by measuring the time (s) required for the passage of a given volume of water between the marks A and B (Figure 2.11),

i.e. Q = A d / t, where

t = time (s)

d = distance (m) between A and B,

therefore $K = d L / (H_1 - H_2) t$

Methodology:

A 500 x 35 mm glass column was filled to less than one third of its height with the filter media and water was applied to the column which was fitted with constant head device. Head loss across the bed was determined using manometer tubes separated by the bed depth L. The apparatus used is shown in Figure 2.11.

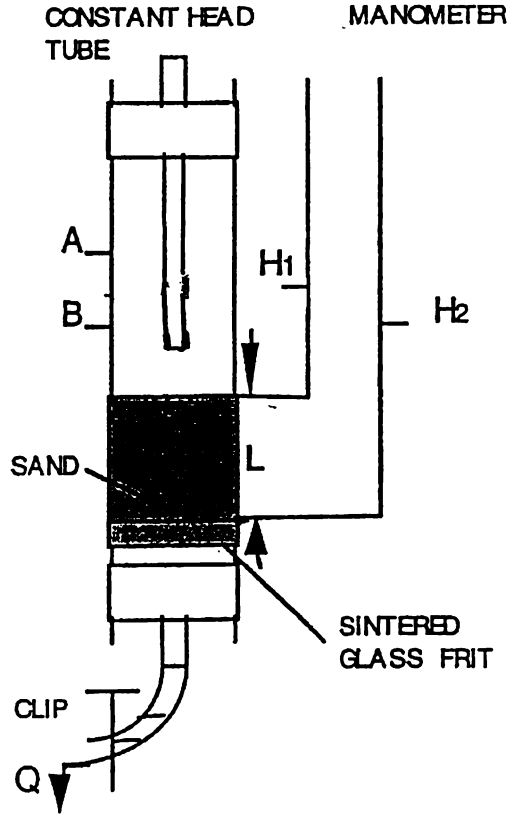


Figure 2.11. The experimental apparatus used for measurement of the hydraulic conductivity of filter media.

2.12. Surface area of granular media

The surface area of granular media was determined using a Nova 1000 high-speed gas sorption-analyzer (Quantachrome Corporation, USA). Analyses were carried-out by measuring a 3 point isotherm for the sorption of N_2 at liquid nitrogen temperature. Sample cells 2 and 3 (volume = 5.23 and 5.63 cm^3 respectively) were used for this work. Approximately 0.6-0.9 g of pumice, dried overnight at 100°C, was used to fill the cell. The sample solutions were outgassed at 120°C overnight by flushing with N_2 under reduced pressure. After degassing the sample was weighed and a teflon rod was placed in the neck of the cell and the cell was connected to the analyser station. Liquid N_2 was used to maintain the temperature of the cell and the experiment was programmed for a 45 min adsorption. Data for specific surface area, pore volume and pore size distribution were computer generated using system software.

2.13. Granular filtration experiments

Granular filtration studies were performed using the apparatus shown in Figure 2.12. It consisted of a 425 x 44 mm glass column, fitted with a No. 1 glass sinter at the base of the column to support the media and a 370 mm collection tube (side arm). Care was taken to ensure the collection tube (side arm) was maintained in saturated state to avoid the possibility of channeling due to air penetration.

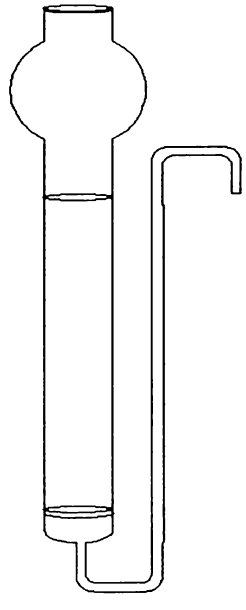


Figure 2.12. Illustration of the glass column design.

Filtration experiments were performed using a known weight of granular material, sufficient to give a 310 mm bed. The void volume of the media was determined in a separate experiment by measuring the amount of water required to fill the void-volumes. Before use, the medium bed was back washed and flushed with between 10 and 15 bed void-volumes of tap water until the turbidity and absorbances at 270, 340 and 440 nm were less than 0.25 NTU and 0.002 respectively.

Samples to be filtered were applied to the column and tap water was added as the experiment proceeded to maintain constant head pressure. Typically, the first three bed void-volumes from the column were discarded. Filtration trials were continued until 3 L of untreated effluent, or 1 L of flocculated effluent, had been collected. Absorbance and turbidity measurements were made of each successive 100 mL of column eluent. Results are expressed as the mean for the experiment. In general variation in data after the initial flushing of system was within the range 7-10%.

Chapter 3

Resin acid speciation in Tarawera River water

3.1. Introduction

Pulp and mill effluents are complex matrices where small amounts of lipophilic resin acids co-exist with abundant lignin residues, humic acids and many other materials e.g. suspended solids. It is probable that these materials interact with resin acids through processes such as covalent bonding, charge transfer, van der Waals forces and hydrogen bonding.

While much is known about the levels of resin acids, cations and anions and absorbance of Tarawera River water, adjacent ground water and river sediment, (Wilkins and Panadam 1987; Wilkins *et al* 1996a, 1996b, 1998; Judd *et al* 1998; Singh-Thandi 1993) only a preliminary account of resin acid speciation effects in this natural recipient water has appeared (Osborne 1991).

Osborne (1991) compared the levels of resin acids present in (i) unfiltered, (ii) 3 μm filtered and (iii) ultra-filtered Tarawera River water samples and observed that resin acid concentrations in the filtrate decreased as the pore size of the filtering membrane decreased. This observation led to the conclusion that removal of suspended solids reduced the levels of recoverable resin and fatty acids, possibly indicating that some of the resin and fatty acids were associated with particulate matter. Osborne (1991) also noted that as the distance between the mill outfalls and the sampling sites increased, the fraction of total resin acids removed by 3 μm filtration increased (Table 3.1).

Table 3.1. Removal of resin acids by 3 μm filtration (Obsorne 1991).

Site	total resin acids (μg/L) non-filtered sample	% resin acids removed by 3 μm filtration
SH30	203	14%
Edgecumbe-Matata Rd	127	30%
Lower bridge	23	57%

This chapter reports an assessment of the significance of extraction pH and the levels of extractable resin acids recovered from Whatman No. 1, glass fibre and 3, 0.8, 0.45, 0.2, 0.05 and 0.025 μm filtered SH30 Tarawera River water samples.

3.2. Experimental

Water samples were collected from the Tarawera River, at the SH30 bridge on 16 June and 14th December, 1998 and transported to the laboratory in 2.5 L glass winchesters on the day of collection. Water samples were stored at 5^{o}C until required for extraction.

Unfiltered, filtered and sequentially filtered river water samples were prepared as reported in Sections 2.1, 2.5 and 2.6. Total free (liquid-liquid extracted) and bound (Soxhlet extracted) resin acid levels were determined using the extraction protocols and SIM GC/MS methodologies reported in Sections 2.2.1, 2.2.2 and 2.3.

Cation and colour levels were determined using filtered (Whatman No. 1 or 0.45 μm) solutions prepared as described in Sections 2.8.2 and 2.7 respectively. Conductivity, pH and turbidity were determined as described in Sections 2.8.3 and 2.8.2.

3.3. Results and discussion

3.3.1. Initial experiments

Significance of extraction pH

In recent years a number of extraction protocols has been proposed for the recovery of resin acids from recipient waters. For example pHs ranging from 2 to 12 have been used in liquid-liquid extractions of resin acids from pulp mill effluents (Turner and Wallin 1985; Voss and Rapsomatiotis 1986).

Some researchers have advocated extraction using an acidic medium to ensure minimal dissociation of resin acids, while other worker have recommended extraction using an alkaline medium to minimise isomerisation (Li *et al* 1996; Richardson *et al* 1992).

Resin acid levels identified in duplicate pH 4, pH 7.6 (natural river pH) and pH 10 liquid/liquid extractions of Tarawera River water samples collected at the SH30 bridge on 6/6/98, ca. 3.4 km downstream of the discharge points of two pulp and paper mills are presented in Table 3.2.

Table 3.2. SIM GC/MS determined resin acid levels (µg/L, average of duplicate analyses) identified in pH adjusted SH30 Tarawera River water samples, collected 16/6/1998.

	Seco	Pim	18-Ab	DHAA	Abiet	13-ene	Cls	total	%
pH 7.6 (as collected)	11.6	3.8	23.4	8.5	2.4	16.1	3.6	69.4	
pH 4	9.6	3.1	17.8	8.4	1.7	12.0	2.2	54.8	79%
pH 10	10.8	3.6	22.0	8.5	2.2	15.6	2.7	65.4	94%
pH 7.6 0.45 µm filtered	3.7	1.7	10.6	4.2	0.5	7.1	1.1	28.9	42%
pH 4 0.45 µm filtered	4.5	1.8	8.9	5.4	0.5	6.7	1.0	28.8	41%
pH 10 0.45 µm filtered	3.4	1.5	9.3	4.0	0.5	6.4	1.0	26.1	38%

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid; Abiet = abietic acid, 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichlorodehydroabietic acids; total = total resin acids; % = % resin acids relative to unfiltered SH30 water, pH 7.6 (as collected).

The results represented in Table 3.2 show that for highly coloured Tarawera River water samples, extraction at pH 10, offers no advantage over extraction at pH 7.6, while extraction at pH 4 results in a lesser recovery of resin acids (79% of that recoverable at pH 7.6).

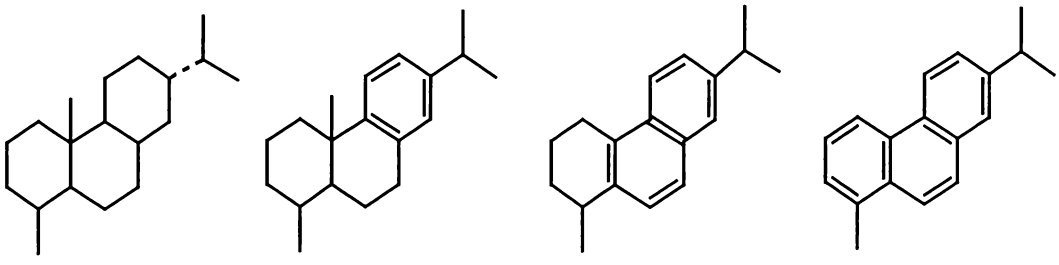
<u>0.45 µm filtered samples.</u>

The reduced resin acid levels present after filtration through 0.45 µm filter paper (38-42% of initial levels) (see Table 3.2) are consistent with the hypothesis that a portion of the recoverable resin acids in the Tarawera River water samples are bound to suspended solid materials (sediment particles, macromolecular aggregates of lignins, etc).

It is also apparent that pH adjustment over the range 4 to 10 does not greatly affect the relative levels of free and bound resin acids in the 0.45 µm filtered samples.

Resin neutrals

In addition to resin acids, degraded resin neutrals may be present in Tarawera River water samples (Wilkins and Panadam, 1987). Resin neutrals were more efficiently recovered from duplicate unfiltered water samples, without pH adjustment, than was the case at pH 4 and pH 10. Filtration (0. 45 μm) prior to liquid extraction substantially reduced the recoverability of resin neutrals. The greater the aromaticity of the substrate (3, 2, 1 and 0 aromatic rings are present in retene, tetrahydroretene, dehydroabietin and fichtelite respectively), the greater the removal by 0.45 μm filtration.



fichtelite dehydroabietin tetrahydroretene retene

It is apparent that resin neutrals, which because of their hydrocarbon nature and absence of a carboxyl group are less hydrophilic than resin acids, are more extensively surface absorbed to suspended solid particles than are resin acids (Table 3.3).

Table 3.3. SIM GC/MS determined resin neutral levels (μg/L) identified in SH30 Tarawera River water samples collected 16/6/98. % recoveries relative to natural, unfiltered, river water are given in brackets.

	fichtelite	dehydro-abietin	tetrahydro-retene	retene	total resin neutrals
SH30	5.7	0.70	4.2	11.0	21.6
SH30 pH 4	4.8 (84%)	0.42 (61%)	2.9 (68%)	7.1 (64%)	15.2 (70%)
SH30 pH 10	4.5 (79%)	0.50 (71%)	3.0 (72%)	7.7 (70%)	15.8 (73%)
SH30 0.45 μm	2.2 (38%)	0.16 (23%)	0.44 (10%)	0.8 (7%)	3.6 (7%)
SH30 pH 4 0.45 μm	2.6 (45%)	0.17 (25%)	0.66 (15%)	1.1 (10%)	4.5 (21%)
SH30 pH 10 0.8 μm	2.1 (36%)	0.10 (14%)	0.41 (10%)	0.8 (7%)	3.3 (15%)

Biodegradation of resin acids in stored river water samples

Resin acid analyses were complicated by the continuing biodegradation of organic substances after sample collection. The possibility that biodegradation could be arrested by the addition of sodium azide or mercuric salts (Hall and Liver 1996b), was considered and is explored in Chapter 4, however in the initial (preliminary investigations) reported in this chapter, sodium azide, or mercuric salts were not added since it was anticipated that these species would interfere with cation analyses and may function as resin acid flocculation agents (e.g. by formation of mercuric resin acid salts).

Results for replicate resin acid analyses, performed 1, 5 and 22 days after collection (see Table 3.4), showed that for river water stored at 5°C in screw capped glass winchesters, total resin acid levels decayed exponentially with a half-life of about 19 days (Figure 3.1) and that over a 5 day period resin acid levels typically decayed by ca. 20%. This decrease is in the order of, or in most cases less than, the standard deviation subsequently established for replicate extractions at this stage of the investigation (see Section 3.3 2).

Table 3.4. SIM GC/MS determined resin acid levels (μg/L) (average of duplicate analyses) identified in SH30 Tarawera River water samples, collected 14/12/1998 and extracted 15/12/1998, 20/12/1998 and 5/1/1999.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total
1 day	8.5	6.8	17.7	11.2	15.6	2.5	62.3
5 days	6.0	4.2	17.1	9.7	12.8	1.9	51.6
22 days	1.9	1.0	9.7	9.3	6.3	2.3	30.5

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichlorodehydroabietic acids; total = total resin acids.

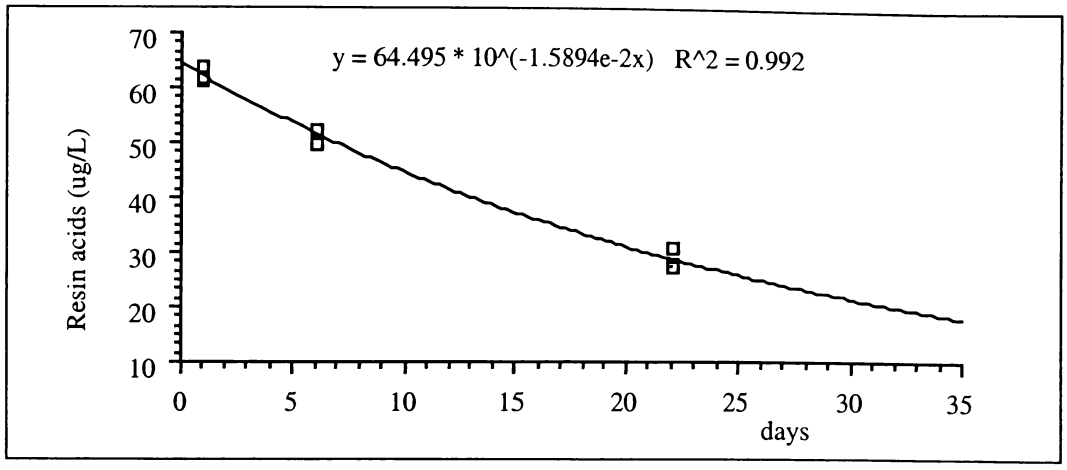


Figure 3.1. Decay profile for total resin acids present in a SH30 Tarawera River water sample collected 14/12/98.

3.3.2. Single stage filtration experiments

A series of single stage and sequential (see Section 3.3.3) filtration experiments were performed on Tarawera River water samples collected on 14/12/98. Multiple analyses of filtered samples were performed in order that the precision and reliability of filtration experiments and therefore of speciation effects could be determined. Equipment limitations necessitated that groups of filtration and extraction experiments were typically carried out in batches over 2-3 day periods, commencing at times 1-21 days after collection.

The results presented in Tables 3.5 and 3.6 should be interpreted accordingly. In particular allowance must be made for post-collection biodegradation of with resin acids (estimated to proceed with a half-life of 19 days: see above) prior to the extraction of a particular batch of samples.

The issue of biodegradation prior to extraction was addressed by comparing resin acid levels present in groups of unfiltered and filtered samples that had been stored for identical times.

0.45 μm filtered river water samples

Replicate extractions of 0.45 μm filtered river water samples, collected on 14/12/98 and extracted 20/12/98, resulted in an average resin acid recovery of 34% (see Table 3.5) of the level of resin acids present at the time of the experiments (6 days after collection).

Table 3.5. SIM GC/MS determined resin acid levels (μg/L) (average of replicate analyses) identified in SH30 Tarawera River and 0.45 μm filtered river water samples, collected 14/12/1998 and extracted 20/12/1998.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%[b]
SH30 A[a]	6.0	4.1	17.2	9.6	13.1	2.0	52.0	
SH30 B	6.4	4.3	16.8	9.4	12.7	2.0	51.6	
SH30 C	5.6	4.1	16.8	9.3	12.4	1.8	50.0	
SH30 D	5.8	4.1	17.5	10.4	13.0	1.9	52.7	
average	6.0	4.2	17.1	9.7	12.8	1.9	51.6	
stdev	0.34	0.10	0.34	0.50	0.32	0.10	1.14	
CV	5.7%	2.4%	2.0%	5.2%	2.5%	5.0%	2.2%	
SH30 E/24 h[a]	4.1	3.5	13.5	7.8	10.6	2.1	41.6	
SH30 F/24 h[a]	4.8	3.7	14.3	8.1	11.1	2.2	44.2	
average	4.5	3.6	13.9	8.0	10.9	2.2	42.9	83%
0.45 μm filtered A	2.3	1.5	5.0	5.2	2.9	0.64	17.5	
0.45 μm filtered B	2.2	1.6	5.4	5.1	3.1	0.76	18.2	
0.45 μm filtered C	2.7	1.4	7.8	4.5	3.8	0.81	21.0	
0.45 μm filtered D	2.2	1.1	3.6	4.8	2.1	0.55	14.4	
0.45 μm filtered E	2.3	1.5	5.3	4.5	3.1	0.72	13.1	
0.45 μm filtered F	3.0	1.7	5.8	5.9	3.5	0.78	20.7	
average	2.5	1.5	5.5	5.0	3.1	0.71	17.5	34%
stdev	0.33	0.21	1.36	0.53	0.58	0.10	3.2	
CV	13%	14%	25%	11%	19%	14%	18%	
0.45 μm Soxhlet A	1.9	1.3	6.7	4.7	4.6	0.62	19.8	
0.45 μm Soxhlet B	3.1	2.2	10.3	7.1	7.8	1.24	31.7	
0.45 μm Soxhlet C	2.6	2.0	9.1	4.9	7.6	0.87	27.1	
0.45 μm Soxhlet D	2.0	1.2	6.6	3.8	4.1	0.53	18.2	
0.45 μm Soxhlet E	3.1	2.2	9.6	6.9	7.2	0.90	29.9	
0.45 μm Soxhlet F	2.3	1.4	7.0	4.5	4.7	0.71	20.6	
average	2.5	1.7	8.2	5.3	6.0	0.81	24.6	47%
stdev	0.53	0.47	1.64	1.36	1.70	0.25	5.7	
CV	21%	27%	20%	26%	28%	31%	23%	

[a] After additional overnight storage in a beaker at room temperature, [b] average % recovery relative to unfiltered SH30 river water. Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichlorodehydroabietic acids; total = total resin acids.

Because of equipment limitations, two of the reference unfiltered river water samples (samples E and F, see Table 3.5), were allowed to stand in beakers, at room temperature for an additional 24 h period, prior to liquid/liquid extraction. These samples exhibited resin acid levels 79-83% of those determined for replicate (n = 4) samples extracted the preceding day.

Soxhlet extraction of the air-dried 0.45 μm filter papers resulted in the recovery of average level of resin acids which was 47% of the average level present in unfiltered river water samples. The combined levels of free (liquid-liquid extraction of filtrates) and bound (Soxhlet extraction of filter papers) resin acids was 81% of that determined for unfiltered samples.

The standard deviations and CV determined for free and bound resin acids (filtered samples) (typically in the range 11-31%) were substantially greater than those determined for unfiltered river water samples (typically 2 to 5.7%) (see Table 3.5). The greater uncertainty in filtered and Soxhlet extracted resin acid levels, can in part, be attributed to the greater % uncertainty in the smaller levels of resin acids present in these samples.

<u>0.8 μm filtered river water samples.</u>

Replicate extractions of 0.8 μm filtered river water samples, collected on 16/6/98 and extracted 6/1/99, resulted in resin acid recoveries of 33-43% of that obtained for unfiltered pH 7.6 (natural) river water (see Table 3.6). The greater CV (ca. 11%) in resin acid levels determined for SH30 Tarawera River water extracted 22-23 days after collection (see Table 3.6) can in part, be attributed to the smaller levels of resin acids present in these samples (due to biodegradation prior to extraction).

Table 3.6. SIM GC/MS determined resin acid levels (μg/L) (average of replicate analyses) identified in SH30 Tarawera River and 0.8 μm filtered river water samples, collected 14/12/1998 and extracted 5/1/1999.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%[c]
SH30 A[a]	2.1	1.2	11.2	10.3	7.7	2.7	35.3	
SH30 B	1.7	0.9	9.2	8.8	5.3	2.2	28.2	
SH30 C	1.9	1.0	9.7	9.4	6.6	2.2	30.8	
SH30 D	1.7	0.9	8.9	8.8	5.3	2.2	27.7	
average	1.9	1.0	9.7	9.3	6.3	2.3	30.5	100%
stdev	0.21	0.15	1.03	0.74	1.15	0.25	3.5	
CV	11%	15%	11%	8%	18%	11%	11%	
0.8 μm A[b] liq/liq	1.0	0.3	2.6	4.8	1.5	0.8	10.9	
0.8 μm B liq/liq	0.9	0.2	2.2	3.9	1.5	0.5	9.1	
0.8 μm C liq/liq	0.9	0.3	2.7	3.5	1.7	0.8	10.0	
average	0.9	0.3	2.5	4.1	1.6	0.7	10.0	33%
stdev	0.09	0.06	0.30	0.66	0.12	0.20	0.90	
CV	10%	19%	12%	16%	8%	29%	9%	
0.8 μm A Soxhlet	0.7	0.4	4.4	2.9	3.6	1.2	13.2	
0.8 μm B Soxhlet	0.8	0.5	4.5	3.5	3.6	1.3	14.2	
0.8 μm C Soxhlet	0.6	0.4	3.7	3.7	2.8	1.1	12.3	
average	0.7	0.4	4.2	3.4	3.3	1.2	13.2	43%
stdev	0.09	0.04	0.44	0.40	0.45	0.12	0.95	
CV	13%	8%	11%	12%	13%	10%	7%	

[a]extracted 5/1/99, [b]extracted 6/1/99, [c]average% recovery relative to unfiltered SH30 river water. Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichlorodehydroabietic acids; total = total resin acids.

Glass fibre and Whatman No. 1 filtration

Filtration through glass fibre and Whatman No.1 filter paper (Tables 2.9 and 2.10) reduced total resin acid levels to 64 and 68% respectively of the average level determined for SH30 water samples extracted 24-48 hours previously (Table 2.8). Detailed analytical data for these samples are included in Chapter 2.

3.3.3. Colour, conductivity and cation analyses.

Colour, conductivity and selected cation (Na K, Ca and Fe) levels were determined in replicate (n = 3 to 6) for the filtered river water samples (see Table 3.7). In general highly reproducible values were determined for these parameters.

0.45 μm filtered samples

Replicate extractions of 0.45 μm filtered river water samples, collected on 16/6/98 and extracted 20/12/1998, reduced absorbances at 270, 340 and 440 nm to 82, 78 and 68% of values obtained for unfiltered, pH 7.6, natural receiving water. Conductivity was not affected by 0.45 μm filtration.

Table 3.7. Colour (absorbance), conductivity and Na, K, Ca and Fe levels (mg/L) determined for 0.45 μm filtered SH30 Tarawera River water samples collected 14/12/98.

	270 nm	340 nm	440 nm	cond. x 10^3 S cm^{-1}	Na mg/L	Fe mg/L	Ca mg/L	K mg/L
SH30 A (20/12/98)[a]	0.165	0.061	0.020	0.41	63.9	0.13	0.79	8.9
SH30 B	0.162	0.061	0.018	0.41	63.2		0.83	8.0
SH30 C	0.163	0.061	0.018	0.41	62.4	0.11	0.80	8.8
SH30 D	0.159	0.058	0.018	0.41	58.0		0.82	8.1
SH30 E	0.163	0.060	0.020	0.41	63.7		0.84	8.3
SH30 F	0.165	0.061	0.020	0.41	59.3		0.81	8.8
average	0.163	0.060	0.019	0.41	61.8	0.12	0.82	8.5
stdev	0.002	0.001	0.001	-	2.5	0.01	0.02	0.4
0.45 μm filtered A	0.140	0.048	0.014	0.40	57.0	0.10	0.89	8.8
0.45 μm filtered B	0.138	0.047	0.013	0.40	55.2	0.13	0.91	8.9
0.45 μm filtered C	0.134	0.047	0.013	0.40	57.5		0.84	8.0
0.45 μm filtered D	0.138	0.047	0.013	0.40	56.7		0.81	8.4
0.45 μm filtered E	0.140	0.048	0.014	0.40	57.6		0.92	8.6
0.45 μm filtered F	0.134	0.047	0.013	0.40	57.5		0.79	8.5
average	0.137	0.047	0.013	0.40	56.9	0.11	0.86	8.5
stdev	0.003	0.001	0.001	-	0.9	0.02	0.05	0.3
recovery[b]	82%	78%	68%	99%	93%	91%	97%	100%

[a]extraction date, [b] average% recovery relative to unfiltered SH30 river water.

0.8 μm filtered samples

Filtration through 0.8 μm filter paper (Table 3.8) reduced absorbances at 270, 340 and 440 to 81, 77 and 58% respectively of the average level determined for SH30 Tarawera River water samples extracted at 5/1/98. Cation levels were not effected by filtration (Table 3.8).

Table 3.8. Colour and cation levels determined for replicate 0.8 μm filtered SH30 Tarawera River water samples, collected 14/12/98 and filtered 5/1/98.

	270 nm	340 nm	440 nm	Na mg/L	Fe mg/L	Ca mg/L	K mg/L
SH30 A	0.160	0.059	0.019	67.0	0.154	0.71	8.1
SH30 B	0.161	0.061	0.019	63.4	0.127	0.79	7.8
SH30 C	0.162	0.061	0.020	67.0	0.115	0.91	7.8
SH30 D	0.160	0.060	0.019	63.6		0.79	8.5
average	0.161	0.060	0.019	65.3	0.132	0.80	8.05
stdev	0.001	0.001	0.0005	2.0	0.020	0.08	0.33
CV	0.6%	1.6%	2.6%	3.1%	15%	10%	4.1%
0.8 μm filtered A	0.133	0.047	0.012	65.3	0.115	0.78	8.2
0.8 μm filtered B	0.132	0.047	0.012	61.6	0.126	0.94	8.3
0.8 μm filtered C	0.129	0.046	0.011	67.7	0.115	0.81	8.3
average	0.130	0.046	0.011	64.9	0.121	0.84	8.25
stdev	0.003	0.001	0.001	2.5	0.006	0.07	0.06
CV	2.4%	2.1%	8.5%	3.9%	5.3%	8.6%	0.7%
% recovery[a]	81%	77%	58%	99%	99%	104%	102%

[a] average % recovery relative to unfiltered SH30 river water.

Whatman No. 1 and glass fibre filtered samples

Filtration through Whatman No. 1 (Table 3.9) did not alter cation, conductivity or colour levels. Glass fibre filter paper (Table 3.9) reduced absorbances at 270, 340 and 440 nm to 91, 81 and 70 % respectively of the average level determined for unfiltered SH30 Tarawera River water samples. Cation levels were not effected by filtration (Table 3.9).

Table 3.9. Colour and cation levels determined for replicate Whatman No. 1 and glass fibre filtered SH30 Tarawera River water samples, collected 14/12/98 and filtered 16/12/98.

	270 nm	340 nm	440 nm	cond. x 10^3 S cm^{-1}	Na mg/L	Fe mg/L	Ca mg/L	K mg/L
SH30 A	0.184	0.074	0.026	0.41	67.6	0.19	0.75	8.6
SH30 B	0.188	0.074	0.028	0.41	65.9	0.13	0.91	8.1
SH30 C	0.188	0.075	0.028	0.41	66.4	-	0.89	8.1
SH30 D	0.186	0.074	0.026	0.41	69.0	-	0.68	8.0
SH30 E	0.184	0.074	0.026	0.41	66.4	0.22	0.70	8.3
SH30 F	0.188	0.076	0.028	0.41	69.5	-	0.87	8.4
average	0.186	0.075	0.027	0.41	67.5	0.18	0.80	8.2
stdev	0.002	0.001	0.001	-	1.50	0.05	0.10	0.23
Whatman No. 1 A	0.183	0.073	0.025	0.41	69.6	0.17	0.88	8.05
Whatman No. 1 B	0.178	0.072	0.024	0.41	65.8	0.20	0.73	8.20
Whatman No. 1 C	0.179	0.071	0.024	0.41	66.2	-	0.93	7.85
Whatman No. 1 D	0.176	0.070	0.022	0.41	65.6	-	0.79	7.90
Whatman No. 1 E	0.178	0.070	0.020	0.41	68.0	0.19	0.86	8.00
Whatman No. 1 F	0.179	0.072	0.022	0.41	64.0	0.17	0.87	7.95
average	0.179	0.071	0.023	0.41	66.5	0.18	0.84	7.99
stdev	0.002	0.0012	0.0018	-	1.95	0.01	0.07	0.12
recovery	96%	96%	85%	100%	99%	99%	105%	97%
glass fibre A	0.168	0.059	0.019	0.41	65.2	0.25	0.77	7.65
glass fibre B	0.164	0.057	0.015	0.41	65.7	0.26	0.52	7.85
glass fibre C	0.171	0.061	0.020	0.41	67.8	-	0.66	7.65
glass fibre D	0.171	0.063	0.020	0.41	65.8	-	0.74	8.10
glass fibre E	0.172	0.063	0.021	0.41	67.1	0.15	0.61	7.75
glass fibre F	0.168	0.059	0.019	0.41	65.5	0.22	0.59	8.15
average	0.169	0.060	0.019	0.41	66.2	0.22	0.65	7.86
stdev	0.003	0.002	0.002	-	1.007	0.05	0.10	0.22
recovery [a]	91%	81%	70%	100%	98%	121%	81%	95%

[a] average % recovery relative to unfiltered SH30 river water.

Summary

Filtration through Whatman No. 1, glass fibre, 0.45 and 0.8 μm filter papers did not alter cation or conductivity levels (Tables 3.7, 3.8 and 3.9). Colour levels were however attenuated, especially so at 340 and 440 nm. The downward trend in colour levels exhibited by unfiltered SH30 Tarawera River water samples (e.g. absorbances of 0.186, 0.075 and 0.027 at 270, 340 and 440 nm respectively when first collected (Table 3.9 compared to absorbances of 0.161, 0.060 and 0.019 respectively after 22 days) (Table 3.8) could be due to the gradual flocculation (precipitation) of lignins and other chromophoric polyphenols during storage at 5°C.

3.3.4. Sequential filtration experiments

The design of the sequential filtration experiment is such that for a particular pore size, the sum of the liquid/liquid and Soxhlet extracted resin acid levels should equal the liquid/liquid determined level of resin acids in the preceding filtered water sample (see Figure 3.2).

The levels of resin acids detected in Tarawera River water samples which had been stored at 5°C for 10 days prior to sequential filtration through glass fibre, 3, 0.8, 0.45, 0.2. 0.05 and 0.025 μm filter papers, followed by liquid-liquid, or Soxhlet extraction, are presented in Table 3.10. Resin acid recoveries were consistent with results reported in Table 3.5 for the corresponding single step filtration experiments.

Table 3.10. SIM GC/MS determined resin acid levels (µg/L) identified sequentially filtered Tarawera River SH30 water samples, collected 14/12/98 and extracted 24/12/98.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	% [a]
SH30 A	3.1	3.8	12.9	8.3	11.0	1.8	40.9	
SH30 B	3.0	2.9	11.4	8.2	10.5	1.8	37.8	
average	3.1	3.4	12.2	8.3	10.8	1.8	39.6	100%
glass fibre (liq/liq)	1.8	1.4	9.5	8.1	5.7	1.5	28.1	71%
3 µm (liq/liq)	1.4	1.4	5.1	4.9	3.8	0.9	17.5	44%
0.8 µm (liq/liq)	1.3	0.9	2.8	4.8	2.2	0.5	12.5	32%
0.45 µm (liq/liq)	1.2	1.0	3.4	4.0	2.5	0.6	12.7	32%
0.2 µm (liq/liq)	1.0	0.7	2.5	1.8	2.1	0.6	8.7	22%
0.05 µm (liq/liq)	0.9	0.5	1.1	3.2	-	0.3	6.0	15%
0.025 µm (liq/liq)	0.5	0.4	0.2	2.4	-	-	3.5	9%
glass fibre (Soxhlet)	0.5	0.4	2.7	2.0	2.1	0.4	8.1	23%
3 µm (Soxhlet)	0.23	0.4	1.3	1.1	1.7	0.2	4.9	13%
0.8 µm (Soxhlet)	0.08	0.1	0.5	0.4	0.6	0.1	1.8	5%
0.45 µm (Soxhlet)	0.06	0.1	0.2	0.3	0.3	tr	1.0	3%
0.2 µm (Soxhlet)	0.1	0.2	0.6	0.6	0.7	0.1	2.3	6%
0.05 µm (Soxhlet)	0.3	0.6	1.5	1.7	1.3	0.2	5.6	14%
0.025 µm (Soxhlet)	-	-	0.2	0.9	-	0.1	1.2	3%

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichloro-dehydroabietic acids; total = total resin acids. [a] % recovery relative to unfiltered SH30 river water.

Within the expected precision of the experiment (ca. 20% for both free and bound resin acid levels: see Section 3.3.2) the sum of free and bound resin acids identified in a pair of extracts corresponded to that present in the preceding filtered extract (see Table 3.10 and Figure 3.2). There appeared to be a logarithmic relationship between filter pore size and resin acid level (Figure 3.3).

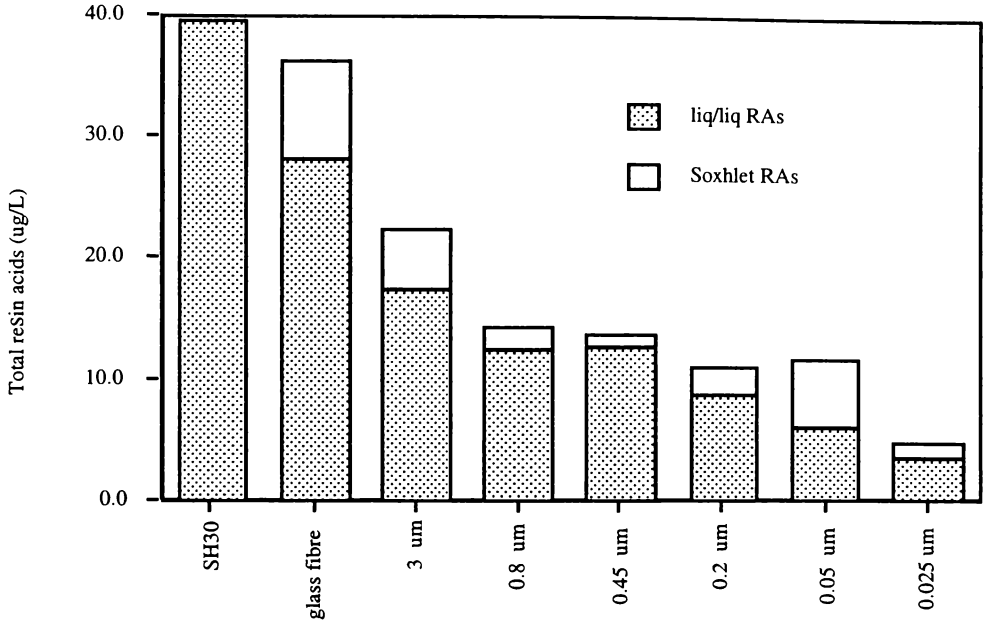


Figure 3.2. Plot of free and bound resin acid levels determined for a sequentially filtered SH30 Tarawera River water sample collected 14/12/98 and extracted 24/12/98.

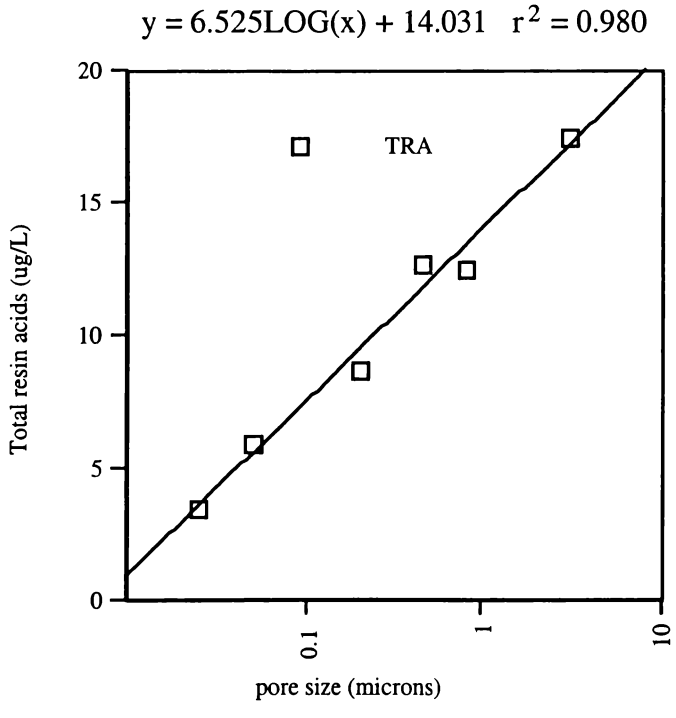


Figure 3.3. Plot of pore size and resin acid levels determined for a filtered SH30 Tarawera River water sample.

The sequential filtration experiment was repeated after a further 4 days (i.e. 14 days storage) (see Table 3.11 and Figure 3.4).

The second set of results, presented in Table 3.11, are consistent with the results presented in Table 3.10, other than that some biodegradation (ca. 25% of the initial level of resin acids - see Table 3.4) appeared to have occurred. It is likely that the poor reproducibility in previously reported literature resin acid data results, at least in part, from resin acid biodegradation between sampling and analysis, even when samples are stored at 5°C.

Table 3.11. SIM GC/MS determined resin acid levels (µg/L) identified in sequentially filtered SH30 Tarawera River SH30 water collected 14/12/98 and filtered 28/12/98.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30 A	2.0	1.1	9.6	7.1	7.4	2.3	29.4	
SH30 B	1.9	1.0	9.8	7.3	7.7	2.3	30.0	
average	2.0	1.0	9.7	7.2	7.5	2.3	29.7	100%
glass fibre (liq/liq)	1.7	1.9	6.6	5.5	5.4	1.1	22.2	75%
3 µm (liq/liq)	1.4	1.1	6.5	6.3	3.4	1.1	19.8	59%
0.8 µm (liq/liq)	1.2	0.6	3.5	4.5	1.7	0.7	13.1	42%
0.45 µm (liq/liq)	1.0	0.6	3.3	5.8	1.6	0.5	12.6	43%
0.2 µm (liq/liq)	1.0	0.5	2.8	5.1	1.5	0.6	11.4	29%
0.05 µm (liq/liq)	0.8	0.2	1.3	3.7	0.7	0.3	7.o	20%
0.025 µm (liq/liq)	1.6	0.3	0.1	1.2	-	-	3.3	12%
glass fibre (Soxhlet)	0.5	0.6	2.6	1.8	3.2	0.4	9.1	31%
3 µm (Soxhlet)	0.3	0.2	1.6	1.3	1.2	0.3	4.9	16%
0.8 µm (Soxhlet)	0.1	0.1	0.8	0.7	0.6	0.1	2.4	6%
0.45 µm (Soxhlet)	0.1	0.1	0.4	0.4	0.2	0.1	1.2	3%
0.2 µm (Soxhlet)	0.2	0.2	0.9	0.9	0.7	0.2	3.0	8%
0.05 µm (Soxhlet)	0.2	0.9	1.2	1.4	0.6	0.2	4.5	19%
0.025 µm (Soxhlet)	-	-	-	0.7	-	-	0.7	4%

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichloro-dehydroabietic acids; total = total resin acids, % recovery relative to unfiltered SH30 river water

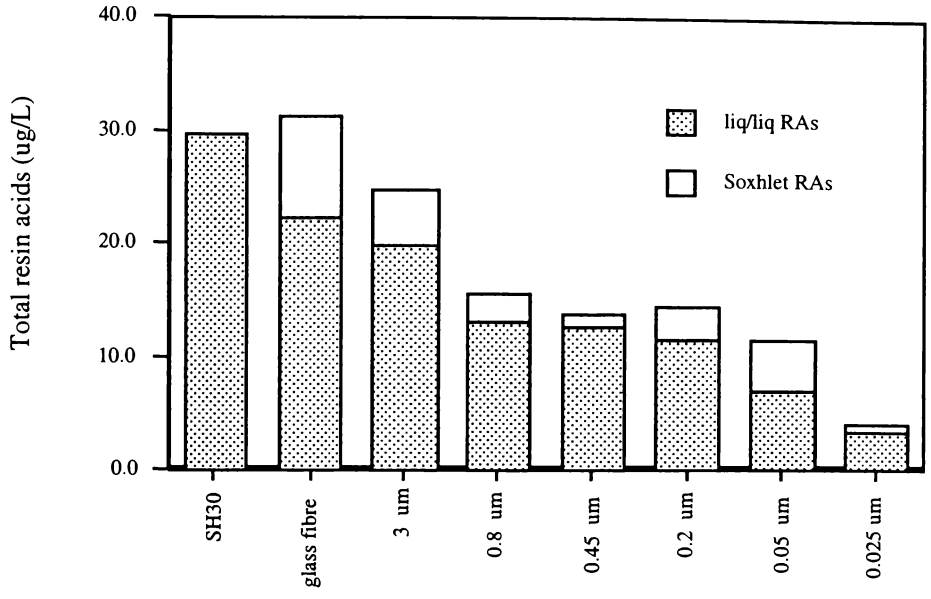


Figure 3.4. Plot of free and bound resin acid levels determined for sequentially filtered SH30 Tarawera River water samples, collected 14/12/98 and filtered 28/12/98.

Colour, turbidity, conductivity and cation levels

Colour, turbidity, conductivity and cation levels determined for sequentially filtered river water samples, which had been stored for 10 days prior to filtration, are presented in Table 3.12

Table 3.12. Colour, turbidity, conductivity and cation levels (mg/L) determined for a SH30 Tarawera River water sample, collected 14/12/98 and filtered 24/12/98.

	270 nm	340 nm	440 nm	tubidity NTU	cond.x 10^3 S cm^{-1}	Na mg/L	K mg/L	Ca mg/L	Fe mg/L
SH30	0.147	0.051	0.016	2.94	0.410	65.2	9.0	0.86	0.24
glass fibre filtered	0.145	0.048	0.013	1.50	0.406	6.3	7.9	0.70	0.22
3 μm filtered	0.136	0.044	0.011	1.14	0.406	69.1	8.2	0.84	0.21
0.8 μm filtered	0.132	0.042	0.007	1.20	0.406	63.9	8.0	0.72	0.26
0.45 μm filtered	0.126	0.037	0.006	1.20	0.406	68.0	8.3	0.77	0.20
0.2 μm filtered	0.117	0.034	0.006	0.97	0.404	66.3	8.3	0.68	0.22
0.05 μm filtered	0.117	0.033	0.005	0.87	0.404	66.3	8.7	0.71	0.02
0.025 μm filtered	0.111	0.030	0.004	0.80	0.404	68.9	8.0	0.74	0.02

A downward trend was apparent in colour levels with the greatest change (% reduction) in colour occurring at 440 nm. A similar downward trend was apparent in turbidity levels.

Conductivity, Na, K and Ca levels were not affected by filtration. On the other hand, Fe levels were substantially attenuated by 0.05 μm filtration. This suggests the presence in Tarawera River water samples of fine Fe oxide, with particle sizes in the range 0.05-0.2 μm. Resin acid levels did not correlate with Fe levels.

Generally similar results were obtained for sequentially filtered samples prepared after 14 days storage (Table 3.13).

Table 3.13. Colour, turbidity, conductivity and cation levels (mg/L) determined for a sequentially filtered SH30 Tarawera River water sample, collected 14/12/98 and filtered 28/12/98.

	270 nm	340 nm	440 nm	turbidity NTU	cond. x 10^3 S cm^{-1}	Na mg/L	K mg/L	Ca mg/L	Fe mg/L
SH30	0.145	0.052	0.015	2.08	0.410	63.0	8.4	0.69	0.27
glass fibre filtered	0.145	0.480	0.013	1.90	0.406	69.3	8.2	0.74	0.29
3 μm filtered	0.136	0.044	0.010	1.32	0.406	66.8	8.2	0.62	0.27
0.8 μm filtered	0.132	0.042	0.009	1.08	0.406	64.5	7.9	0.63	0.26
0.45 μm filtered	0.133	0.042	0.009	1.04	0.404	68.4	7.7	0.75	0.27
0.2 μm filtered	0.126	0.037	0.006	0.93	0.404	69.2	8.2	0.72	0.24
0.05 μm filtered	0.117	0.034	0.005	0.81	0.404	67.8	8.1	0.69	0.02
0.025 μm filtered	0.111	0.030	0.004	0.80	0.404	66.9	8.0	0.75	0.02

Resin neutrals

Results similar to those for the preliminary 0.45 μm experiment (Section 3.3.1) were obtained for resin neutrals. About 50% of resin neutrals was removed by glass fibre filtration and most of resin neutrals were removed by 0.45 μm filtration.

Table 3.14. SIM GC/MS determined resin neutral levels (µg/L) identified in SH30 Tarawera River water samples collected 14/12/98.

	fichtelite	tetrahydro-retene	retene	total resin neutrals	%
SH30 A	2.9	0.1	0.1	3.1	
SH30 B	2.8	0.1	0.1	3.0	
average	2.8	0.1	0.1	3.1	100%
glass fibre (liq/liq)	1.4	0.1	-	1.5	48%
3 µm (liq/liq)	1.0	-	-	1.0	34%
0.8 µm (liq/liq)	0.8	-	-	0.8	26%
0.45 µm (liq/liq)	-	-	-	0.0	0%
glass fibre (Soxhlet)	1.3	-	-	1.4	45%
3 µm (Soxhlet)	0.4	-	-	0.4	13%
0.8 µm (Soxhlet)	0.1	-	-	0.1	5%
0.45 µm (Soxhlet)	0.7	-	-	0.7	23%

The results presented in this chapter have implications in respect of the ability of some extraction protocols to recover both free and particle bound resin acids and resin neutrals. In particular, there have appears to be a need to critically assess if solid phase methods (e.g. those using Bond-elut type C8 or C18 cartridges) recover resin acids and resin neutrals by a combination of absorption (from the aqueous phase to the C8 or C18 phase) and by filtration (trapping of particulates, which may or may not release absorbed resin acids when flushed with methanol or other eluents).

Comparison with Osborne's results

Duplicate samples of 0.45 µm filtered river water samples at SH30 and SH2, collected on 16/6/98, were extracted on 17/6/98 and 19/6/98 respectively. Results are summarised Table 3.15. The average recovery of resin acids from the 0.45 µm filtered Tarawera River samples were 41% (SH30) and 52% (SH2) respectively of the levels recovered from unfiltered river samples. A small but consistent decrease in resin acid levels appears to have occurred over the 2 days the samples were stored at 5°C between the first and second extractions. This is consistent with the earlier observed biodegradation of stored samples.

Table 3.15. SIM GC/MS determined resin acid levels (μg/L, average of duplicate analyses) identified in SH30 and SH2 Tarawera River and 0.45 μm filtered water samples, collected 16/6/1998.

	Seco	Pim	18-Ab	DHAA	18-Ab	13-ene	Cls	total	%
SH30 A[a]	10.7	3.5	21.3	7.9	2.5	15.0	3.1	64.0	
SH30 B	12.6	4.1	25.5	9.0	2.4	17.2	4.1	75.0	
average	11.6	3.8	23.4	8.5	2.4	16.1	3.6	69.5	100%
SH2 A[b]	2.0	2.1	14.0	5.3	1.0	9.0	1.6	35.0	
SH2 B	2.0	1.9	12.1	4.7	1.1	7.9	1.3	31.1	
average	2.0	2.0	13.1	5.0	1.1	8.5	1.5	33.0	100%
filtration 0.45 μm									
SH30 A[a]	4.0	1.7	11.1	4.3	0.5	7.3	1.2	30.1	
SH30 B	3.4	1.6	10.1	4.0	0.5	6.9	1.0	27.5	
average	3.7	1.7	10.6	4.2	0.5	7.1	1.1	28.8	41%
SH2 A[b]	0.8	1.0	7.1	2.7	0.5	4.3	0.9	17.3	
SH2 B	0.6	0.9	7.0	2.7	0.6	4.2	1.1	17.3	
average	0.7	1.0	7.1	2.7	0.5	4.3	1.0	17.3	52%

[a]extracted 17/6/98, [b]extracted 19/6/98. Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid; Cls = 12-Cl, 14-Cl and 12,14-dichlorodehydroabietic acids; total = total resin acids.

Osborne (1991) indicated that some of the resin and fatty acids were associated with particulate matter and also noted that as the distance between the mill outfalls and the sampling sites increased, the fraction of total resin acids removed by 3 μm filtration (Table 3.1) increased. This conclusion is in contradiction with the results presented in Table 3.15 for unstabilised River water and for NaN_3 stabilised Tarawera River (see Chapter 5, Tables 5.6 and 5.7). Similar levels of particle bound resin acids were identified in the SH30 and SH2 Tarawera river water samples.

The unreliability of Osborne's result may be a consequence of several days elapsing between the liquid-liquid extraction of unstabilised unfiltered and filtered river water samples. Osborne also utilised less reliable GC/FID methodology, compared to the SIM GC/MS methodology used in the present investigation.

3.4. Conclusions

The results presented in Tables 3.2-3.3 show that extraction at pH 10 offers no advantage over extraction at pH 7.6, while extraction at pH 4 results in a lesser recovery of resin acids (ca. 79% of that recovered at pH 7.6). 0.45 μm filtration at pH 4, 7.6 and 10 reduced levels to 38-42% of that for unfiltered samples.

Liquid-liquid extraction can be used to reliably recover free and adsorbed resin acids in river water samples. The recovery of liquid-liquid extractable resin acids after filtration through 0.8 μm or 0.45 μm Millipore filter papers were 43% or 34% respectively of that recoverable from unfiltered samples. Soxhlet extraction of the air-dried 0.8 and 0.45 μm filter papers afforded resin acids levels 34% and 47% respectively of that present in an unfiltered river water sample.

The combined levels of free (liquid-liquid extraction of filtrates) and bound (Soxhlet extracted of filter papers) resin acids was 78-80% of that determined for unfiltered samples. These results agree within the expected precision of the experiment (ca. 20%) for both free and bound resin acids.

Sequential filtration experiments showed that the majority of resin acids and coloured species in Tarawera River water samples were bound to particles which were retained on filter papers with pores in the range 0.025 μm to greater than about 15 μm (glass fibre). 30-35% the particle bound resin acids were associated with particles greater than about 15 μm (glass fibre).

Biodegradation of resin acids present in natural Tarawera River water samples stored at $4^{o}C$ proceeded with a half life of ca. 19 days. This limited the obtainable precision and reproducibility of experiments, which to due to equipment limitations, were performed over several days, or weeks, after sample collection.

Since much (if not all) of the data reported in previous studies are derived from non-stabilised water samples, it is likely that similar precision and reproducibility constraints apply to published data (typically 20% or greater).

In order to carry out prolonged experiments and to monitor subtle changes as a function of time, stabilised river water samples and an analytical precision of 10% or better, are required. The decreases observed upon storing at 4°C need to be overcome. Work directed towards achieving this goal is presented in Chapter 4.

Chapter 4

Speciation effects in sodium azide stabilised Tarawera River water

4.1. Introduction

The observation that post collection biodegradation of resin acids present in natural (unstabilised) Tarawera River water samples stored at 4°C proceeded with a half life of ca. 19 days (Section 3.3) prompted an evaluation of the possibility that the addition of sodium azide would inhibit the post collection biodegradation of resin acids.

Hitherto Hall and Liver (1996b) have reported the use of sodium azide to inhibit the biodegradation of pulp mill sourced resin acids in experiments which explored the partitioning of resin acids onto biomass in an aqueous environment.

This chapter reports the results of experiments that were undertaken to ascertain if:

i) sodium azide addition inhibited the biodegradation of resin acids in Tarawera River water samples stored at 4°C for periods of up to 90 days.

ii) results of sequential filtration experiments performed using sodium azide stabilised river water samples were comparable with results obtained using natural (non-stabilised) river water.

iii) the extent to which settling during extended storage prior to the withdrawal of analytical samples from winchesters or bulk 20 L containers influenced the recovery of free and particle bound resin acids.

SEM evidence for the presence of Fe, Al, C and O rich surface deposits on particulate matter recovered by filtration of river water samples is also presented.

4.2. Experimental

Sample collection

Water samples were collected in screw capped 2.5 L glass winchesters or 2 x 20 L plastic containers from the Tarawera River at the SH30 Bridge. After the addition of 0.1% of sodium azide, water samples were transported to the laboratory and stored at 4°C (or 8°C) until required for analyses.

Resin acid analyses

Free and bound (particle associated) resin acid levels, reported as µg/L of filtered river water, were determined for well mixed sub-samples of the sodium azide stabilised SH30 Tarawera River water using the liquid-liquid or Soxhlet extraction, and SIM GC/MS methodologies described in Chapter 2, Section 2.4.2.

Sequential filtration experiments

Sequentially filtered water samples were prepared from sodium azide stabilised SH30 Tarawera River water stored in a 20 L container as follows: the bulk water sample and associated particulate matter (present at the time of collection) were thoroughly mixed (shaken) and allowed to stand for 30 min before analytical samples (2 x 1 L and 1 x 6 L) were withdrawn from a tap located 50 mm from the bottom of the container. The 6 L sample was sequentially filtered as described in Chapter 2. Sequentially filtered and duplicate unfiltered water samples were prepared and liquid/liquid or Soxhlet extracted (filter papers) on same day.

Settling experiments

Settled, sodium azide stabilised river water samples were drawn off from a 20 L plastic container which was thoroughly shaken at t = 0, and then allowed to stand without being disturbed for 30 days. Sub-samples (2 or 3 L) were withdrawn from a tap located 50 mm from the bottom of the container gently drawn off, after 15 and 30 min, 1 and 8 h, and 14, 26 and 30 days. The residue remaining in the 20 L container at the end of the sampling

period (1.6 L) was thoroughly mixed and divided into 2 x 800 mL sub-samples. The residue 1 sample was filtered thorough Whatman No. 1 and 0.45 μm filter papers prior to liquid/liquid extraction and Soxhlet extraction of the filter papers. The residue 2 sample was filtered thorough a 0.45 μm filter paper, prior to liquid/liquid extraction and Soxhlet extraction of the filter paper.

SEM analyses

Surface examination of particulate matter recovered from water samples by filtration was undertaken as described in Chapter 2.

4.3. Results and discussion

4.3.1. Inhibition of the biodegradation of resin acids

The levels of resin acids identified in liquid/liquid extractions of a series of natural and sodium azide stabilised SH30 Tarawera River water samples collected 14/1/99 and stored for 1-14 days at 8°C are compared in Figure 4.1.

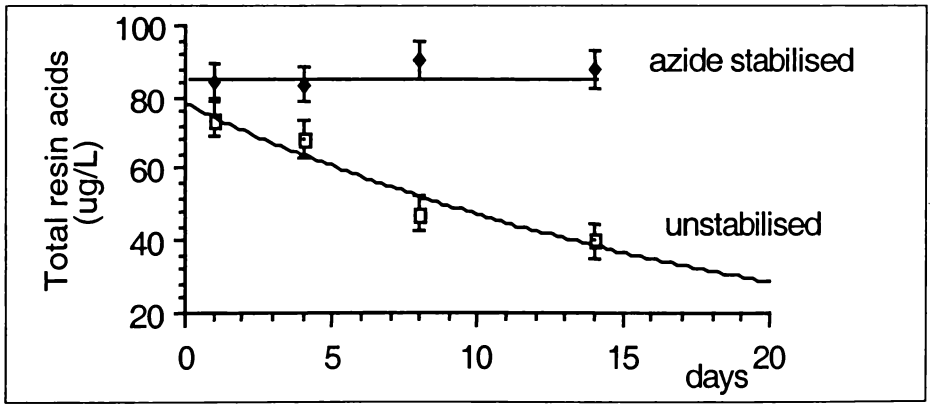


Figure 4.1 Resin acid levels determined for sodium azide stabilised and unstabilised SH30 Tarawera River water collected 14/1/99.

Figure 4.1 shows that within the expected uncertainty of the analyses, there was no degradation of resin acid acids in the sodium azide stabilised system but over the same period and under the same conditions ca. 50% of the resin acids were degraded in the unstabilised system.

Table 4.1. Resin acid levels (μg/L) determined for sodium azide stabilised and unstabilised SH30 Tarawera River water samples collected 14/1/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	recv.
unstabilised								
t = 1 day	7.3	7.2	23.5	12.9	22.4	2.4	80.2	93%
t = 4 days	5.5	6.5	22.6	11.4	21.7	1.8	69.5	93%
t = 8 days	4.5	6.3	16.9	8.0	11.6	1.3	48.6	106%
t = 14 days	3.8	5.7	14.7	5.7	9.9	0.9	40.7	112%
plus sodium azide								
t = 1 day	11.8	7.3	24.1	13.8	23.6	1.9	82.5	96%
t = 4 days	12.5	6.5	24.6	13.4	22.7	1.8	81.5	95%
t = 8 days	16.5	10.3	27.6	14.3	21.0	1.9	91.8	103%
t = 14 days	17.1	10.3	27.3	12.7	19.6	1.8	88.1	103%
average	14.5	8.6	25.9	13.5	21.7	1.8	86.0	99%
stdev	2.7	2.0	1.8	0.68	1.8	0.06	4.9	
CV	19%	23%	7.0%	5.0%	8.2%	3.2%	5.6%	4.4%

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic; Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids; total = total resin acids; recv. = % recovery of *O*-methylpodocarpic acid.

The levels of resin acids recovered from duplicate unfiltered sodium azide stabilised SH30 river samples, collected on 25/2/99 and stored for 5, 60 and 90 days at 4°C, are presented in Table 4.2.

Table 4.2. Resin acid levels (μg/L) determined for sodium azide stabilised SH30 Tarawera River water samples collected 25/2/99.

storage time	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total
5 days, + azide (n = 2)[a]	21.9	9.4	25.0	17.5	24.9	3.6	102
60 days, + azide (n = 2)[a]	16.4	7.0	24.7	18.7	26.4	2.9	96
90 days, + azide (n = 2)[a]	17.0	6.1	25.6	20.3	28.1	4.3	101

[a]Average of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic; Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids.

The 60 and 90 day results correspond to storage periods which are ca. 3 and 5 times respectively the estimated 19 day half life for resin acid degradation in unstabilised SH30 Tarawera River water samples stored at 4°C (see Chapter 3).

More detailed analyses of river water samples collected on 4/3/2000 (Table 4.3 and 4.4) showed that, within the expected reproducibility limits, sodium azide addition arrested the biodegradation of resin acids, and the recovery of resin acids was not altered by the addition of sodium azide.

Table 4.3. Resin acid levels (µg/L) identified in replicate analyses of unfiltered SH30 Tarawera River water samples collected 4/3/2000.

storage time	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	recv
SH30 A, t = 0, no azide	7.6	5.7	14.6	9.2	25.7	1.5	64.4	93%
SH30 B, t = 0, no azide	8.3	6.3	15.9	10.4	28.3	1.4	70.7	98%
SH30 C, t = 0, no azide	7.6	5.5	14.2	9.2	24.7	1.6	62.7	89%
SH30 D, t = 0, no azide	8.6	6.0	14.9	9.3	27.3	1.5	67.7	96%
SH30 E, t = 0, no azide	8.0	6.0	15.4	9.4	26.6	1.7	67.0	96%
SH30 F, t = 0, no azide	8.1	5.8	15.7	9.7	27.0	1.7	68.1	98%
average	8.0	5.9	15.1	9.5	26.6	1.6	66.8	95%
stdev	0.39	0.28	0.66	0.46	1.3	0.12	2.8	(4%)
CV	4.9%	4.7%	4.4%	4.9%	4.7%	7.7%	4.3%	
SH30 A, 30 days, + azide	7.6	5.8	14.9	9.2	25.1	1.5	64.1	92%
SH30 B, 30 days, + azide	8.3	5.8	14.9	9.2	24.3	1.6	64.1	100%
SH30 C, 30 days, + azide	7.4	5.4	12.7	8.7	22.0	2.0	57.7	93%
SH30 D, 30 days, + azide	7.7	5.6	14.7	9.6	24.5	1.6	63.6	90%
SH30 E, 30 days, + azide	8.2	6.2	14.8	9.3	24.9	1.7	65.0	92%
SH30 F, 30 days, + azide	9.1	6.5	16.8	10.5	28.4	1.7	72.9	108%
average	8.1	5.9	14.8	9.4	24.9	1.7	64.6	96%
stdev	0.62	0.40	1.3	0.60	2.1	0.17	4.9	(7%)
CV	7.7%	6.8%	8.8%	6.4%	8.3%	10%	7.5%	

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-en-oic; Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids; total = total resin acids; recv = % recovery of *O*-methylpodocarpic acid.

Generally similar results were also obtained using unfiltered Tarawera River water and river water which was filtered through sintered glass to remove visible particles such as grass, bark and leaf fragments, etc.

Table 4.4. Resin acid levels (µg/L) identified in replicate analyses of sintered glass filtered SH30 Tarawera River water samples collected 3/4/2000.

storage time	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	recv
SH30 A, t = 0, no azide	14.0	15.3	15.6	18.7	98	2.3	164	93%
SH30 B, t = 0, no azide	14.4	16.5	17.6	19.5	104	2.3	174	93%
SH30 C, t = 0, no azide	13.3	15.1	15.2	17.9	97	2.3	161	87%
SH30 D, t = 0, no azide	15.2	16.2	17.8	23.0	105	2.4	180	97%
SH30 E, t = 0, no azide	14.1	16.1	17.4	19.5	103	2.4	173	93%
average	14.2	15.8	16.7	19.7	101	2.3	170	93%
stdev	0.69	0.61	1.2	2.0	3.6	0.08	7.7	(4%)
CV	4.9%	3.8%	7.3%	9.9%	3.6%	3.6%	4.5%	
SH30 A, 1 day, + azide	14.2	16.1	17.5	18.6	104	2.4	173	91%
SH30 B, 1 day, + azide	13.4	16.3	17.4	19.0	105	2.4	174	89%
SH30 C, 1 day, + azide	13.9	15.9	16.1	18.9	102	2.2	169	89%
SH30 D, 1 day, + azide	14.6	16.3	17.9	19.9	107	2.4	178	96%
SH30 E, 1 day, + azide	14.1	16.2	17.7	20.3	106	2.6	177	95%
average	14.0	16.2	17.3	19.3	105	2.4	174	92%
stdev	0.44	0.17	0.71	0.72	1.92	0.14	3.6	(4%)
CV	3.1%	1.0%	4.1%	3.7%	1.8%	5.9%	2.1%	
SH30 A, 30 days, + azide	13.5	15.3	15.5	18.8	101	2.4	167	90%
SH30 B, 30 days, + azide	13.9	16.6	17.0	19.7	106	2.7	176	96%
SH30 C, 30 days, + azide	14.4	16.9	17.4	19.4	104	2.7	175	93%
SH30 D, 30 days, + azide	13.6	15.4	15.6	18.4	98	2.4	163	86%
SH30 E, 30 days, + azide	14.1	16.3	17.5	19.8	108	2.7	178	97%
average	13.9	16.1	16.6	19.2	103	2.6	172	93%
stdev	0.37	0.72	0.98	0.60	3.9	0.16	6.5	(5%)
CV	2.6%	4.5%	5.9%	3.1%	3.8%	6.4%	3.8%	

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic; Cls = 12-chloro, 14-chloro and 12,14-dichloro-dehydroabietic acids; total = total resin acids; recv = % recovery of *O*-methylpodocarpic acid.

4.3.2. Sequentially filtered sodium azide stabilised river water

The results of sequential filtration experiments performed using sodium azide stabilised river water which had been stored for 5, 60 and 90 days prior to analyses are presented in Tables 4.5, 4.6 and 4.7 respectively. These results show that for sodium azide stabilised river water samples that had been stored for up to 90 days, particle associated resin acid

levels and speciation effects were comparable with those determined for freshly collected, unstabilised, river water samples (see Chapter 3).

Table 4.5. Resin acid levels (μg/L) identified in sequentially filtered SH30 Tarawera River water collected 25/2/99 and stored 5 days.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30 (n = 2)	21.9	9.4	25.0	17.5	24.9	3.6	102.2	100%
glass fibre (liq/liq)	17.1	7.1	15.5	12.2	15.9	2.7	70.5	69%
3 μm (liq/liq)	15.6	5.3	11.7	10.9	12.5	2.3	58.3	57%
0.8 μm (liq/liq)	13.6	4.6	10.0	8.7	10.8	2.1	49.8	49%
0.45 μm (liq/liq)	14.8	3.5	8.9	9.8	5.7	1.9	44.7	44%
0.2 μm (liq/liq)	12.6	2.4	4.8	8.9	4.5	1.2	34.3	34%
0.05 μm (liq/liq)	7.0	1.0	1.5	12.2	1.5	0.6	24.4	22%
glass fibre (Soxhlet)	3.7	6.2	6.8	6.1	9.4	1.7	34.0	33%
3 μm (Soxhlet)	0.5	0.9	2.2	1.7	2.4	0.3	7.9	8%
0.8 μm (Soxhlet)	0.7	1.1	2.7	2.0	2.7	0.3	9.4	9%
0.45 μm (Soxhlet)	0.4	0.7	1.8	1.4	1.5	0.2	6.0	6%
0.2 μm (Soxhlet)	0.9	1.2	3.2	2.6	3.0	0.6	11.4	11%
0.05 μm (Soxhlet)	0.8	1.3	2.7	2.3	2.0	1.3	10.2	9%

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic; Cls = 12-chloro, 14-chloro and 12,14-dichloro-dehydroabietic acids; total = total resin acids, % = % recovery relative to unfiltered SH30 river water.

Table 4.6. Resin acid levels (μg/L) identified in sequentially filtered sodium azide stabilised SH30 Tarawera River water, collected 25/2/99 and stored for 60 days.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30 (n=2)	20.7	8.8	26.8	19.2	28.2	2.8	106.5	100%
glass fibre (liq/liq)	(36.9)[b]	6.0	22.5	(22.3)[a]	(-)[a]	3.3	91.0	85%
3 μm (liq/liq)	22.9	8.1	20.6	15.1	24.6	2.2	93.6	88%
0.8 μm (liq/liq)	(30.5)	3.9	6.2	(21.9)	7.8	1.5	71.8	67%
0.45 μm (liq/liq)	14.8	3.6	9.2	13.2	8.0	1.2	49.9	47%
0.2 μm (liq/liq)	18.1	3.7	7.7	8.8	8.9	0.8	48.0	45%
0.05 μm (liq/liq)	18.5	2.2	3.6	19.6	3.3	0.8	48.0	45%
glass fibre (Soxhlet)	3.2	3.7	13.6	6.2	(14.4)[a]	1.2	42.2	40%
3 μm (Soxhlet)	0.3	0.3	-	0.6	0.7	0.3	3.1	3%
0.8 μm (Soxhlet)	-	2.4	1.7	-	-	4.1	-	4%
0.45 μm (Soxhlet)	1.3	1.7	6.3	3.5	-	0.4	13.2	12%
0.2 μm (Soxhlet)	0.1	0.3	0.6	0.4	0.5	-	1.8	2%
0.05 μm (Soxhlet)	-	-	-	-	-	-	-	0%

[a] Unexpected results are bracketed. (see text). Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic; Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids; total = total resin acids, % = % recovery relative to unfiltered SH30 river water.

Table 4.7. Resin acid levels (µg/L) identified in sequentially filtered sodium azide stabilised SH30 Tarawera River water samples, collected 25/2/99 and stored for 90 days.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30 (n = 2)	17.0	6.1	25.6	20.3	28.1	4.3	101.4	100%
glass fibre (liq/liq)	13.4	4.6	16.8	14.7	21.2	2.0	72.8	72%
3 µm (liq/liq)	14.0	3.8	10.7	10.4	12.9	1.2	53.1	52%
0.8 µm (liq/liq)	13.9	3.1	10.2	11.2	9.7	1.0	49.1	48%
0.45 µm (liq/liq)	13.0	2.3	7.2	9.5	8.3	1.2	41.6	41%
0.2 µm (liq/liq)	13.7	2.7	4.9	8.8	5.6	0.7	36.4	36%
0.05 µm (liq/liq)	10.0	-	1.7	13.8	2.3	0.5	28.3	28%
glass fibre (Soxhlet)	2.1	2.4	13.2	6.0	13.3	1.1	38.0	37%
3 µm (Soxhlet)	0.7	0.8	3.7	1.9	3.8	0.4	11.3	11%
0.8 µm (Soxhlet)	0.1	0.2	0.8	0.5	0.7	0.1	2.4	2%
0.45 µm (Soxhlet)	0.3	0.4	1.2	0.7	1.2	0.1	3.9	4%
0.2 µm (Soxhlet)	-	-	2.6	1.6	2.8	0.4	7.4	7%
0.05 µm Soxhlet	0.2	0.6	1.2	1.0	0.9	0.1	4.0	4%

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic; Cls = 12-chloro, 14-chloro and 12,14-dichloro-dehydroabietic acids; total = total resin acids; % = % recovery relative to unfiltered SH30 river water.

The 5 and 90 day results were generally comparable (see Tables 4.5 and 4.7) and in accord with results presented in Chapter 3 for unstabilised filtered water samples. On the other hand, deviations from the expected pattern of results were observed for the 60 day glass fibre and to a lesser extent the 3 µm liquid-liquid extractions (but not the corresponding Soxhlet extractions).

The elevated level of secodehydroabietic acids, and the absence of abiet-13-enoic acid in these samples, suggests that unexpected contamination and/or post-extraction conversion of abiet-13-enoic acid to DHAA and/or seco-DHAA isomers (and maybe also other resin acids) may have occurred. Analytical data from these samples must, in the absence of confirmatory replicate data, therefore be interpreted with considerable caution.

The results presented in Table 4.8 show that the sum of extractable resin acids associated with 15-0.45 µm particles is very consistent, whereas there is considerable variability in the sum of extractable resin acids associated with 0.2-0.05 µm particles. This difference may be a consequence of some the variability in retention of small particles on the filter papers, possibility arising from subtle variations in filtration conditions (vacuum applied, seating of the filter paper, etc).

Table 4.8. Resin acid levels (μg/L) identified in sequentially filtered sodium azide stabilised SH30 Tarawera River water samples, collected 25/2/99 and stored for 5, 60 and 90 days.

	5 days	60 days	90 days
Liquid/liquid	102	106	101
Σ Soxhlet (glass fibre-0.45 μm)	57	58	56
Σ Soxhlet (0.2-0.05 μm)	22	1.8	11

Resin neutrals

Notwithstanding the presence of only very low levels of resin neutrals (mainly fichtelite, tetrahydroretene and retene) in Tarawera River water samples (see Chapter 3) and the comparatively large uncertainty (ca. ± 0.1 μg/L) in the levels of individual resin neutral species (typically in the range 0.3-2 μg/L for fichtelite, tetrahydroretene and retene), the results presented in Table 4.9 show that resin neutrals are also predominantly particle associated. This is consistent with the hydrophobic nature of resin hydrocarbons.

Table 4.9. Resin neutrals (μg/L) identified in a sequentially filtered sodium azide stabilised SH30 Tarawera River water samples, collected 25/2/99 and stored for 90 days.

	neutrals	%		neutrals	%
SH30 (n = 2)[a]	1.5	100%			
glass fibre (liq/liq)	0.9	60%	glass fibre (Soxhlet)	1.0	67%
3 μm (liq/liq)	0.6	40%	3 μm (Soxhlet)	0.4	27%
0.8 μm (liq/liq)	0.2	13%	0.8 μm (Soxhlet)	0.1	7%
0.45 μm (liq/liq)	0.2	13%	0.45 μm (Soxhlet)	0.1	7%

[a]Average of duplicate analyses, % recovery relative to the unfiltered SH30 sample.

4.3.3. Settling experiments

Since the results of the sequential filtration experiments showed that, in both stabilised and unstabilised SH30 Tarawera River water samples, part of the recoverable resin acids were associated with particulate material it was reasoned that if a bulk water sample was allowed to stand for an extended period, settling of particulate matter may occur and

higher levels of resin acids would accumulate in water withdrawn from the bottom of a sample container.

This proposal was explored using 2.5 L winchesters and a bulk 20 L container. Water sub-samples (2 or 3 L) were taken from the tap 15 mm from the bottom of the 20 L container after t = 0 and 15 min, 1 and 8 h, and 14, 26 and 30 days. A portion of each of the water sub-samples was liquid/liquid extracted and the total resin acid (TRA) content was determined (Table 4.10). Marginally higher levels of resin acids were detected in the 0-8 h sub-samples than was the case for the 14-30 day sub-samples.

After 30 days the residual water (1.6 L) was shaken and divided into 2 x 800 mL sub-samples (residues 1 and 2). Substantially greater levels of resin acids were identified in the two residual samples (ca. 3 times the level of resin acids identified in the 15 min-30 day sub-samples). The elevated levels of resin acids detected in the unfiltered residue 1 and 2 samples (363 and 335 μg/L respectively) can be attributed to the gradual of settling of resin acid carrying particulate matter.

The mass balance determined for the bulk container experiment is summarised in Table 4.10. A more detailed analysis of the levels of free and particle bond resin acids identified in the two residual water samples is given in Table 4.11.

Portions of each of sub-sample withdrawn from the bulk container were also filtered (0.45 μm) and liquid/liquid extracted to determine the level of free (non-particulate associated) resin acids. Additionally the t = 0, 1 h, 14 day and 30 day filter papers were Soxhlet extracted (Table 4.10).

Resin acid levels identified in the 0.45 μm filtered liquid/liquid and Soxhlet extracts (e.g. a total resin acid level of 107 μg/L for the 14 day sub-sample) were in good agreement with those determined for the corresponding unfiltered sub-samples (110 μg/L). The total mass of recovered resin acids (109% of that calculated to be present at the commencement of the experiment) was well within the uncertainty associated with a multi-step protocol utilising 9 liquid/liquid and 3 Soxhlet extractions.

The downward trend in resin acids levels of the 10 min to 30 day sub-samples withdrawn from the 20 L container was just discernible at the precision of the experiments. On the other hand, the accumulation of particulate associated resin acids in the 2 x 800 mL residual water samples was readily apparent.

The average level of particulate associated resin acids identified in the residual water samples (350 µg/L) corresponds to the settling of an average level of ca. 13 µg/L of particulate associated resin acids from the 18 L of water removed during the experiment from the 19.6 L water sample.

Similar downward trends in turbidity and suspended solid levels (Table 4.12) are consistent with the gradual settling of fine particulate matter. A moderate decrease in colour levels may be attributed to either the adsorption of some coloured species (chromophoric lignin molecules) onto particulate matter, and/or the slow aggregation (flocculation) of chromophoric molecules.

Table 4.10. Total resin acid (TRA) levels and mass balance determined for filtered and unfiltered water sub-samples from a settling experiment performed using 19.6 L of sodium azide stabilised Tarawera River water.

time (sample)	unfiltered (liquid/liquid)			0.45 µm filtered		
	TRA µg/L	volume mL	TRA mass µg	liq/liq µg/L	Soxhlet µg/L	TRA µg/L
0 min	123	3000	369	52	72	124
15 min	127	3000	381	58		
1 hour	117	3000	351	46	75	121
8 hour	118	2000	236	50		
14 days	110	3000	330	54	53	107
26 days	94	2000	188	60		
30 days	105	2000	210	50	70	120
30 days, residue 1		800	363[a]	79	284	363[a]
30 days, residue 2		800	335[a]	67	268	335[a]
total (recovered)		19600	2623 (109%)			
total (t = 0 min)	123[b]	19600	2411[b]			

[a]See Table 4.11 [b]Mass of resin acids present at the commencement of the experiment, TRA = total resin acids.

Table 4.11. Resin acid levels (μg/L) identified in liquid/liquid and Soxhlet extracts of two filtered residual water samples from the 30 day settling experiment.

sample	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total
Residue 1 sub-sample							
Soxhlet (Whatman No. 1)	16.7	22.9	113	31.1	71.6	7.0	262
Soxhlet (0.45 μm)	1.6	1.8	8.8	3.2	6.1	0.4	22
Liq/liq (What + 0.45 μm)	29.2	5.9	12.3	15.4	14.2	1.6	79
Total	47.5	30.6	134	49.7	91.9	9.0	363
Residue 2 sub-sample							
Soxhlet (0.45 μm)	18.2	26.6	113	27.9	75.5	6.4	268
Liq/liq (0.45 μm)	27.0	5.2	8.3	13.2	12.0	1.5	67
Total	45.2	31.8	121	41.1	87.5	7.9	335

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic; Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids; total = total resin acids.

Table 4.12. Colour, turbidity, and suspended solid levels determined for a bulk (19.6 L) sodium azide stabilised Tarawera River water sample, collected 25/2/99.

settling	absorbance			turbidity	TSS	ISS	OSS
time	270 nm	340 nm	440 nm	NTU	mg/L	mg/L	mg/L
0 min	0.281	0.095	0.032	7.30	8.5	4.2	4.3
15 min	0.281	0.092	0.029	7.14	6.8	2.1	4.7
1 hour	0.277	0.089	0.028	6.59	5.4	2.2	3.2
8 hour	0.275	0.089	0.028	4.91	5.6	1.8	3.8
14 day	0.278	0.087	0.024	3.67	5.2	1.5	3.7
26 day	0.261	0.079	0.020	3.34	4.0	0.5	3.5

Abbreviations: TSS = total suspended solids; ISS = inorganic suspended solids; OSS = organic suspended solids.

30 day winchester settling experiments

The possibility that a settling effect analogous to that described in Section 4.3.3 might also occur during the storage river water samples in 2.5 L winchesters was investigated in experiments in which results for sodium azide stabilised river water samples stored in undisturbed and well shaken winchesters were compared at t = 0 (control experiments) and after 30 days.

The results of these experiments are presented in Table 4.13. Duplicate SIM GC/MS analyses of the extracts of well shaken, t = 0 and 30 day 1 L sub-samples taken from two

2.5 L winchesters afforded essentially identical levels of individual and total resin acids (120 μg/L for the duplicate winchester A samples and 130 μg/L for the duplicate winchester B samples respectively).

A significantly lower level of resin acids was however identified in a 1 L sub-sample taken from the top of a third winchester that had been allowed to stand undisturbed for 30 days (84 μg/L), compared to the level of resin acids identified in a subsequent 1 L sub-sample from the same winchester (119 μg/L).

The results presented in Table 4.13 show that over a 30 day period, the level of extractable resin acids falls by ca. 30%. This difference can be attributed to the settling of resin acid containing particulate matter.

It is clear that winchester stored river water samples should be well shaken and mixed immediately before sampling and extraction. Failure to do so will lead to a lower than expected resin acid level in water from the upper portion of a winchester.

Table 4.13. Resin acid levels (μg/L) determined in settling experiments performed using sodium azide stabilised SH30 Tarawera River water samples stored in 2.5 L winchesters.

sample (storage time)	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total
winchester A (t = 0 day)							
well shaken, sub-sample 1	19.0	12.0	30.7	19.9	34.1	3.7	119
well shaken, sub-sample 2	19.6	12.0	29.8	20.2	34.7	3.6	120
winchester B (t = 30 days)							
well shaken, sub-sample 1	20.1	10.2	32.1	24.7	39.1	4.4	131
well shaken, sub-sample 2	20.1	12.3	33.0	23.1	36.4	4.1	129
winchester C (t = 30 days)							
not shaken, upper layer	17.1	8.0	19.5	14.7	22.4	2.3	84
not shaken, lower layer	20.1	11.7	28.7	20.3	33.8	3.7	118

Abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic; Cls = 12-chloro, 14-chloro and 12,14-dichloro-dehydroabietic acids; total = total resin acids.

Assessment of aggregation effects during storage at 5-8°C

The possibility that post collection aggregation of resin acid particulate matter might occur during extended storage of sodium azide stabilised Tarawera River water samples at ca. 5-8°C, prior to extraction was evaluated in experiments in which the contents of four winchesters were pre-filtered at same time (t = 0) (corresponding to ca. 12 h after collection in the field and transportation to the laboratory) through Whatman No. 1 filter papers to remove initially present gross particulate matter.

Soxhlet extraction of the filter papers used to filter the four 2.5 L river samples at time t = 0 afforded comparable levels of particle associated resin acids (19, 21, 11 and 15 μg/L (average level 16.6 μg/L, stdev 6.3 μg/L).

The filtrate from the control winchester was found to contain 107 μg/L resin. The remaining three winchesters were stored for 15, 30, or 45 days at 5-8°C without being disturbed, after which they were well shaken prior to re filtration (Whatman No. 1).

Liquid/liquid extraction of 1 L portions of the re-filtered 2.5 L river water identified levels of 76, 84, 80 μg/L total resin acids in the samples which had been allowed to stand 15, 30, or 45 days, respectively, compared to 107 μg/L total resin acids for the control sample (t = 0 days).

The levels of total resin acids recovered by Soxhlet extraction of the filter papers used for second filtrations (after 15, 30 or 45 days) were to 27, 17 and 38 μg/L respectively (average level 27.9 μg/L, stdev 10.6 μg/L and CV 38%) (Table 4.15). Not unexpectedly (see Section 3.3.2.) there was a greater variability in the Soxhlet results than was the case for the liquid/liquid (filtrate) results.

The results presented in Table 4.14 can be interpreted as showing that, at least after 15 days, there is some evidence for the aggregation of resin acid particulate matter during extended storage at 5-8°C.

The data presented in Table 4.14 can be interpreted as showing that during the initial fifteen period day some aggregation of resin acid associated micro-particulate material which initially passed through a Whatman No. 1 filter paper at t = 0 has subsequently occurred, in so much as that the second filtration of winchesters 2, 3 and 4 afforded an additional 17-38 μg/L (average level 27.8 μg/L, stdev 10.6 μg/L) of particle associated resin acids.

The sum of the resin acid levels determined for the first and second Whatman No. 1 filtrates (44.5 μg/L, stdev 16.8 μg/L) is comparable to that, which in both unstabilised and sodium azide stabilised multi-filtration experiments, is typically recovered using glass fibre filtration (see Section 4.3.2). The levels of particulate species with sizes less than 15 μm (glass fibre pore size) do not appear to have significantly decreased.

The aggregation effect noted above for the t = 15, 30 and 45 day samples, may have been influenced by the presence of a higher level of dissolved oxygen in these samples after pre-filtration (i.e. a saturated DO level of 8-10 mg/L after filtration, compared with an initial DO level in the river sample of 4-5 mg/L). Since the control sample was extracted immediately after prefiltration, enhancement of the initial DO level could not be significant factor in this experiment. However it may have been a significant factor in the 15-30 day experiments, possibly resulting in additional oxidation and aggregation of polyphenolic (lignin) materials which may contribute to resin acid absorption.

The apparent post storage aggregation effects noted here are not however likely to have significance in multi-filtration experiments (see Section 4.3.2), since like the t = 0 control river water sample, they were extracted immediately after filtration, hence effects associated with an increased DO level during additional storage for 15-30 days have no relevance in these experiments.

Table 4.14. Resin acid levels (μg/L) determined for four sodium azide stabilised SH30 Tarawera River water samples, stored in 2.5 L winchesters for 0, 15, 30 or 45 days at 5-8°C.

storage time	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total
0 days							
Soxhlet (prefiltered) [a]	1.4	1.9	6.0	3.3	5.5	0.6	19
Liquid-liquid	18.5	10.7	27.6	24.3	22.9	3.4	107
total	19.9	12.6	33.6	27.6	28.5	4.0	126
15 days							
Soxhlet (prefiltered)[a]	2.3	3.4	9.1	5.2	(-)	0.8	21
Soxhlet (15 days)	1.7	3.4	12.1	6.0	3.6	0.9	28
Liquid-liquid	17.5	7.8	16.4	13.1	18.5	2.5	76
total	21.5	14.6	37.5	24.3	22.1	4.2	124
30 days							
Soxhlet (prefiltered)[a]	0.9	1.3	4.0	2.0	3.0	0.3	11
Soxhlet (30 days)	1.8	0.1	10.7	3.5	(-)	1.2	17
Liquid-liquid	18.5	8.1	19	14.3	21.3	2.8	84
total	21.3	9.4	33.7	19.9	24.2	4.3	112
45 days							
Soxhlet (prefiltered)[a]	1.5	1.9	5.5	2.9	3.1	0.5	15
Soxhlet (45 days)	2.0	4.2	13.7	5.4	12.3	0.9	39
Liquid-liquid	17.3	7.9	16.6	16.4	19.7	2.2	80
total	20.8	14.3	35.8	24.8	35.1	3.5	134

[a] prefiltered at t = 0 days , abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic; Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids; total = total resin acids.

Table 4.15. Summary of average, stdev and CV of resin acids derived from data presented in Table 4.14 showing the aggregation of particles after passage through Whatman No. 1 filter paper at time t = 0.

storage time	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total
Average results							
Soxhlet (prefiltered at t = 0) (n = 4)	1.5	2.1	6.2	3.4	3.9	0.5	17.6
stdev	0.71	1.0	2.6	1.5	1.6	0.23	6.3
CV	47%	48%	43%	45%	43%	43%	38%
Soxhlet (filtered at t = 15, 30, 45 days)	1.8	2.6	12.2	5.0	8.0	1.0	30.6
stdev	0.16	2.2	1.5	1.3	6.2	0.19	10.6
CV	9%	84%	12%	26%	77%	19%	38%
Liq/liq (filtered at t = 15, 30, 45 days)	17.8	7.9	17.3	14.6	19.8	2.5	79.9
stdev	0.65	0.13	1.5	1.7	1.4	0.29	4.1
CV	4%	2%	8%	12%	7%	12%	5%
Sum of average Soxhlet (prefiltered and filtered) + liq/liq results (t = 0, 15, 30 and 45 days)	21.1	12.6	35.7	23.0	31.7	4.0	128
Resin acids present at t = 0	19.9	12.6	33.6	27.6	28.5	4.0	126

[a] prefiltered at t = 0 days , abbreviations: Seco = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-enoic; Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids; total = total resin acids.

The summary of data presented in Table 4.15 shows that mass balance was maintained during the series of experiments, since the level of resin acids identified in unfiltered water at t = 0 (an average level of 126 µg/L of resin acids) corresponded closely to the sum of the average prefiltered at t = 0 (Soxhlet) and filtered at t = 15, 30 and 45 day (Soxhlet and liquid/lquid) resin acid results (128 µg/L).

4.3.4. SEM examination of filtrate

Freeze dried samples (see Section 2.9) were prepared in order to overcome morphology changes likely during the evaporation of the solution phase from the wet residues. SEM analyses of particulate matter recovered after 0.45 μm filtration and freeze drying of the filtrate and filter paper revealed high surface concentrations of silica rich deposits, together with a lower level of deposits which exhibited a combination of Fe, Al, O and C responses, possibility attributable to Fe and/or Al induced flocculation and surface adsorption of organic species such as resin acids and/or phenolic lignin molecules.

The detection of silica rich surface deposits is in keeping with the well documented geothermal input of silica to the Tarawera River (McIntosh, 1995).

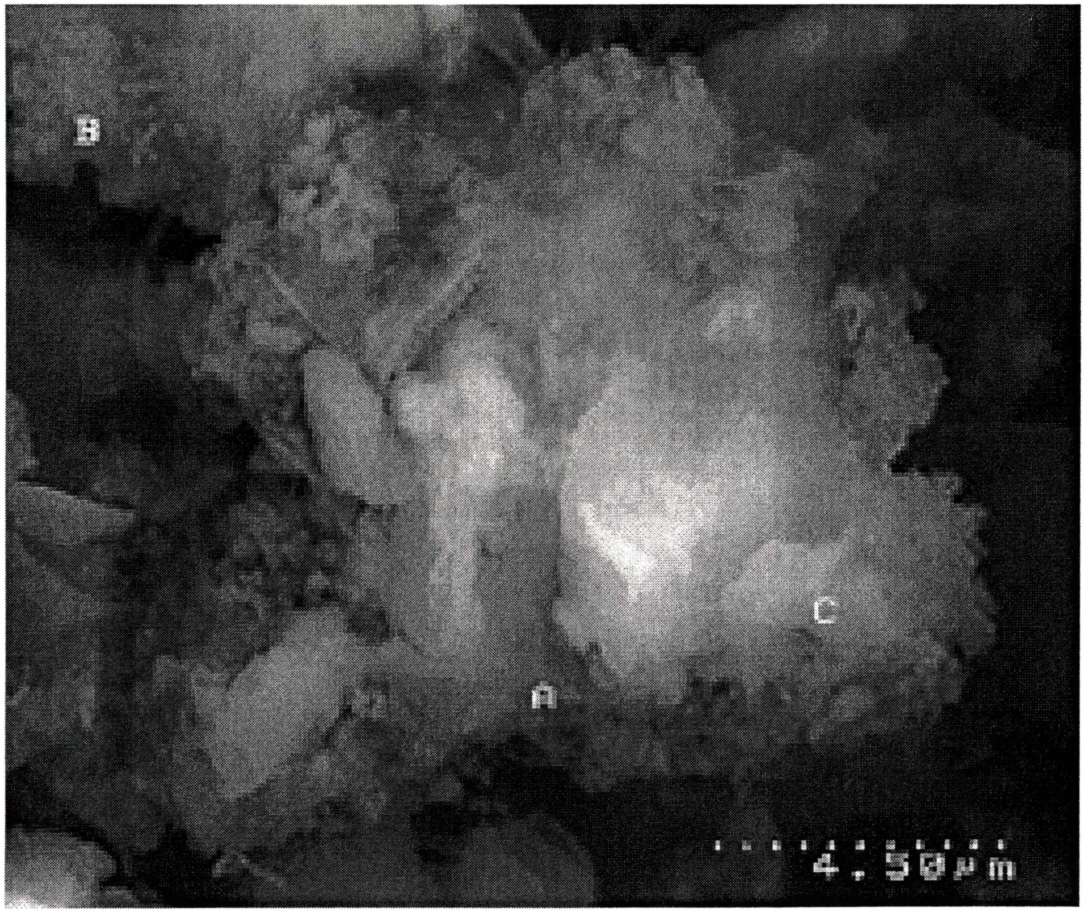
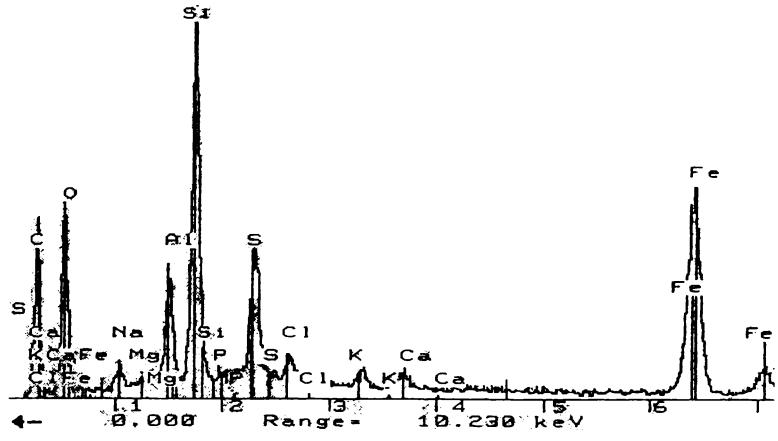
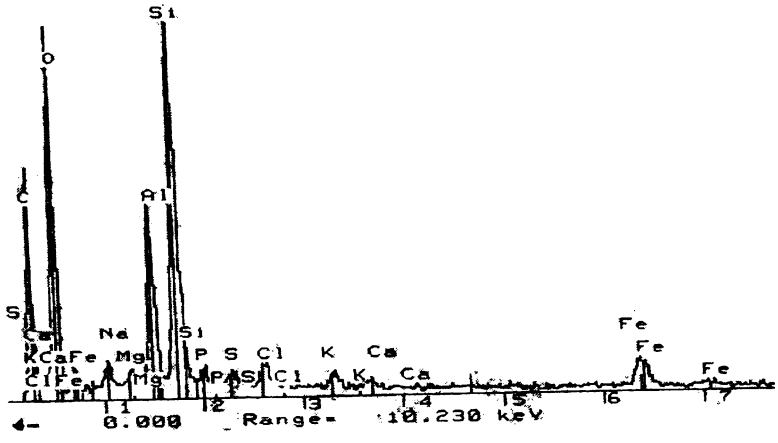


Figure 4.3. SEM micrograph of particulate matter recovered from 0.45 μm filtration of a SH30 Tarawera River water sample, collected 25/2/99.

A



B



C

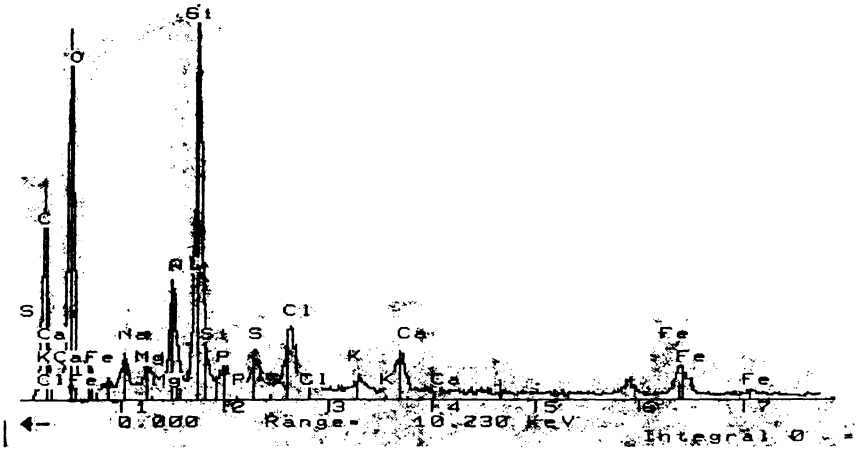


Figure 4.4. EDX spectra from points A, B and C of the SEM micrographs displayed in Figure 4.3.

4.4. Conclusions

Addition of 0.1% NaN_3 inhibited the biodegradation of resin acids in water samples for up to 3 months.

Results presented in this chapter confirmed the particle association of resin acids in Tarawera River water samples. This finding can be compared with the conclusion of Hall and Liver (1996a,b) that in the biomass system which they investigated, resin acids were principally associated with colloidal material, and with the finding of Hoel and Aarsand (1995) that in a TMP effluent resin acids were exclusively associated with particulate and colloidal fractions.

Providing samples were extracted and analysed together, total resin acid levels of azide stabilised river water samples exhibited a CV of less than 7%. Prior filtration through sintered glass to remove gross particulate matter further reduced the CV to 4%.

Over the first 15 days of the 45 day trial period, some of the resin acid containing particulates that passed through a Whatman No. 1 filter paper at t = 0 aggregated and were removed by a second filtration step through Whatman No. 1. filter paper. The total amount of particle bound resin acid remained constant.

Settling of particulate matter during the storage of SH30 Tarawera River water samples can result in the accumulation of resin acid carrying particulate matter in the lower zone of the sample container.

Chapter 5
Particle association of resin acids and chromophoric species in clarifier and treatment pond water samples

5.1. Introduction

Since previous studies have shown > 50% of recoverable resin acids present in the Tarawera River samples, collected downstream of the discharge of the Tasman and Carter-Holt-Harvey Tissue pulp mills, are bound to particles in the range 0.02-15 μm (see Chapters 3 and 4), an assessment of resin acid speciation effects during primary and secondary treatment of mill effluents was therefore of interest.

Little is presently known about the speciation of resin acids during primary and secondary treatment and the extent to which speciation effects influence the bio-degradation of resin acids during biological treatment. Hall and Liver (1996a,b) have shown that in the presence of biomass there was an initial very rapid sorption of most of the resin acids (which occurred in less than 10 minutes), followed by a slower, second sorption process which, over a 12 h to 9 day period (depending on biomass level), afforded a final equilibrium in which > 90% of the resin acids were associated with biomass. The rates of both the first and second sorption steps were faster for aerobic systems, than was the case for anaerobic systems.

It also appeared that the rate of resin acid partitioning on aerobic biomass was governed by the availability of particulate surface (Hall and Liver 1996a,b). The constant fractions (ca. 85-90%) of each of the resin acids found in anaerobic biomass experiments using different biomass to resin acid ratios showed that adsorption was not a reversible process.

Hoel and Aarsand (1995) have investigated the acute toxicity of colloidal and dissolved material in biologically treated secondary effluents from a Norwegian thermomechanical pulp mill. Resin acids were found to be the major class of compounds showing toxicity towards *Daphnia magna*. Resin acids were found to be predominantly particle associated

and it was shown that removal of particle associated material by filtration rendered the filtrates non-toxic.

Hoel and Aarsand's (1995) conclusion that resin acids were primarily responsible for the toxicity of the CTMP effluent they investigated is consistent with the finding of Dethlefs *et al* (1995) that reverse phase C18 filtration of the toxic substances present in an alkali-oxygen-peroxide bleach effluent, 66% of which were identified as resin acids, afforded filtrates which had little or no effect on *Daphia magna*, in growth inhibition and luminescence tests.

This chapter reports:

i) the levels of free and particle associated resin acids, present in sequentially filtered, sodium azide stabilised water samples collected from Tasman's clarifier and four biological treatment ponds

ii) the particle association of chromophoric (coloured) species in sodium azide stabilised water sample from the clarifier and four treatment ponds

iii) size analyses of particles in water samples from the clarifier, Tasman's four treatment ponds, and SH30 and SH2 Tarawera River water samples

Analyses were performed using (i) freshly collected, sodium azide stabilised water samples, and (ii) stabilised samples which had been stored for up to 3 to 4 months.

5.2. Methods and materials

Water samples in screw capped 2.5 L glass winchesters or 20 L plastic containers were collected from the outflow of the clarifier and treatment ponds 1-4 (sites A-E respectively, Figure 5.1) and the Tarawera River at the SH30 and SH2 bridges. Sodium azide (0.1%) was added at the time of collection. Water samples were stored at 4-8°C until required for analyses.

Free and bound resin acid levels were determined for well mixed, sodium azide stabilised, clarifier, treatment pond and Tarawera River water samples using the liquid-liquid or Soxhlet extraction and selected ion mode SIM GC/MS methodologies reported in Chapter 2. The clarifier and treatment pond samples were derived from the filtration of 600 mL (glass fibre), 500 mL (3 μm), 400 mL (0.8 μm), 300 mL (0.45 μm) and 200 mL (0.2 μm) and liquid/liquid extraction of 100 mL sub-samples of the filtered water samples. Quantification was performed using *O*-methylpodocarpic acid as internal standard. The recovery of *O*-methylpodocarpic ethyl ester was typically 75-105%.

Absorbances of azide stabilised water samples were determined before and after sequential-filtration at 270, 340 and 440 nm were determined using a 1 cm quartz cell and a Hitachi 15-20 spectrometer. Turbidity was determined using a Hatch 2100 turbidimeter (Chapter 2). ICP-MS analyses were performed using a GBC Integra instrument. The total freeze dried solids (TFDS) contents of treatment system or river water samples (200-1000 mL depending on the site of sampling), were determined gravimetrically by pre-freezing the water sample in a beaker using a liquid nitrogen bath and freeze-drying the frozen sample for 2-4 days (Chapter 2).

Inorganic freeze-dried solids (IFDS) were determined after heating the freeze-dried material at 550°C in a furnace overnight. Organic freeze-dried solids, and % weight loss on ignition of freeze dried solids (% loi FDS) were calculated as OFDS = TFDS-IFDS, and % loi FDS = 100 x (TFDS-IFDS)/TFDS, respectively.

Laser diffraction particle size analyses were performed using a Malvern Instruments (UK) Mastersizer-S particle analyser. Tap water was added to the dispersion unit and circulated through the flow cell. The obscuration (related to turbidity) was recorded (close to zero), the tap water was drained and replaced by sample water which was diluted with tap water until the obscuration was between 18 and 28 units. System software was used to subtract the tap water background and calculate particle size distributions from the scattered intensities.

5.3. Results and discussion

5.3.1. Treatment system

Effluent waters from the Tasman and Carter-Holt-Harvey Tissue mills are combined and treated in a stabilized aeration basin comprised of a mixing pond (ca. 3 h retention time), and three oxidation ponds (retention times of 1, 2.5 and 2 days, respectively). Characteristics of the treatment system are summarised in Figure 5.1.

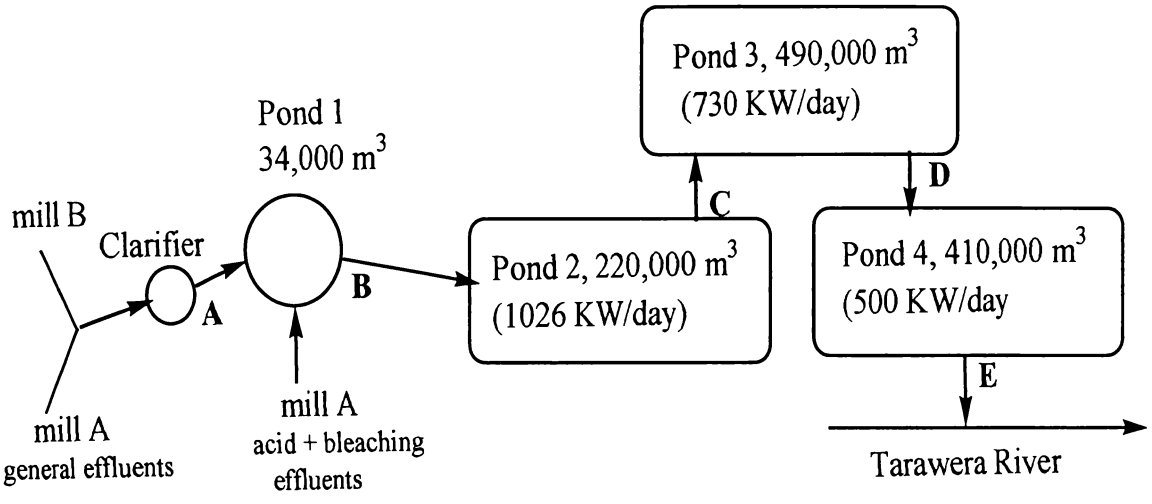


Figure 5.1. Characteristics of Tasman's effluent treatment system. Aeration capacity is given in brackets. Sampling points are designated by the letters A-E. (Mill A = Tasman; Mill B = Carter-Holt-Harvey Tissue).

5.3.2. Resin acid speciation

Freshly collected samples

Data for sequential filtration of freshly collected treatment system samples and river samples are summarised in Tables 5.1 to 5.7.

Table 5.1. Resin acid levels (µg/L) determined for sodium azide stabilised clarifier water samples, collected 1/11/99 and extracted 4/11/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Abiet	Cls	total	%
Clarifier (n = 2)[a]	305	1293	-	3485	487	1901	-	7472	
glass fibre (liq/liq)	301	1266	-	3318	462	1468	-	6815	91%
3 µm (liq/liq)	292	1234	-	3437	451	1648	-	7062	95%
0.8 µm (liq/liq)	285	1246	-	(3716)	437	(706)	-	6390	86%
0.45 µm (liq/liq)	257	1083	-	3149	394	1270	-	6153	82%
0.2 µm (liq/liq)	270	1142	-	3159	419	1445	-	6435	86%
0.05 µm (liq/liq)	370	1147	-	(4606)[b]	(-)	(-)	-	6124	82%
glass fibre (Soxhlet)	5	2	-	40	14	-	-	61	1%
3 µm (Soxhlet)	1	4	-	7	0	-	-	12	0%
0.8 µm (Soxhlet)	1	4	-	5	1	-	-	11	0%
0.45 µm (Soxhlet)	0	0		1	-	-	-	1	0%
0.2 µm (Soxhlet)	1	3	-	5	1	-	-	9	0%
0.05 µm (Soxhlet)	71	57	-	(221)[b]	(-)	(-)	-	349	5%

[a] mean of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water. [b]biodegradation of abietic acid and abiet-13-enoic acid to dehydroabietic acid indicated.

Table 5.2. Resin acid levels (µg/L) determined for sodium azide stabilised pond 1 water samples, collected 1/11/99 and extracted 19/11/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Abiet	Cls	total	%
Pond 1 (n = 2)[a]	472	1475	-	3273	2889	750	22	8881	
glass fibre (liq/liq)	456	1391	-	3318	2667	749	14	8596	97%
3 µm (liq/liq)	454	1407	-	3423	2839	801	16	8939	101%
0.8 µm (liq/liq))	435	1317	-	3121	2500	659	13	8046	91%
0.45 µm (liq/liq)	378	1225	-	3311	2533	627	19	8093	91%
0.2 µm (liq/liq)	408	1230	-	3155	2451	342	12	7599	86%
0.05 µm (liq/liq)	438	1262	-	3367	2443	578	15	8102	91%
glass fibre (Soxhlet)	13	101	-	77	321	-	tr	512	6%
3 µm (Soxhlet)	1	8	-	6	23	-	3	41	0%
0.8 µm (Soxhlet)	1	4	-	5	12	-	tr	22	0%
0.45 µm (Soxhlet)	1	4	-	4	9	-	tr	18	0%
0.2 µm (Soxhlet)	17	81	-	90	3	-	tr	191	2%
0.05 µm (Soxhlet)	12	39	-	31	83	-	2	168	2%

[a] average of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 5.3. Resin acid levels (µg/L) determined for sodium azide stabilised pond 2 water samples, collected 1/11/99 and extracted 1/12/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Abiet	Cls	total	%
Pond 2 (n=2)	267	462	702	2962	721	103	44	5261	
glass fibre (liq/liq)	249	364	321	2915	433	32	26	4339	82%
3 µm (liq/liq)	220	333	303	2768	437	16	24	4101	78%
0.8 µm (liq/liq)	235	314	186	2776	378	8	21	3918	74%
0.45 µm (liq/liq)	196	289	197	2695	336	tr	23	3737	71%
0.2 µm (liq/liq)	205	300	138	2770	329	tr	17	3759	71%
0.05 µm (liq/liq)	184	229	55	2360	254	tr	12	3095	59%
glass fibre (Soxhlet)	33	130	304	47	290	-	tr	805	15%
3 µm (Soxhlet)	3	14	36	23	21	-	1	97	2%
0.8 µm (Soxhlet)	5	19	49	36	12	-	1	122	2%
0.45 µm (Soxhlet)	3	10	17	27	18	-	2	76	1%
0.2 µm (Soxhlet)	3	14	22	24	24	-	1	87	2%
0.05 µm (Soxhlet)	11	35	47	53	50	-	1	195	4%

[a] average of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 5.4. Resin acid levels (µg/L) determined for sodium azide stabilised pond 3 water samples, collected 1/11/99 and extracted 25/12/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Abiet	Cls	total	%
Pond 3 (n = 2)	270	366	732	2771	451	69	34	4693	
glass fibre (Liq-liq)	220	261	313	2434	245	38	30	3541	75%
3 µm (Liq-liq)	229	249	219	2540	212	23	20	3493	74%
0.8 µm (Liq-liq)	254	254	173	2578	188	19	17	3483	74%
0.45 µm (Liq-liq)	235	251	171	2630	208	24	18	3538	75%
0.2 µm (Liq-liq)	226	220	124	2473	176	14	16	3250	69%
0.05 µm (Liq-liq)	202	213	126	2495	165	16	17	3235	69%
glass fibre (Soxhlet)	22	65	284	98	193	-	8	670	14%
3 µm (Soxhlet)	8	28	97	42	72	-	3	250	5%
0.8 µm (Soxhlet)	2	5	19	11	13	-	1	52	1%
0.45 µm (Soxhlet)	1	2	6	5	4	-	tr	18	0%
0.2 µm (Soxhlet)	2	5	10	10	8	-	tr	35	1%
0.05 µm (Soxhlet)	2	5	12	5	10	-	1	35	1%

[a] average of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim= pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 5.5. Resin acid levels (µg/L) determined for a sodium azide stabilised pond 4 water samples, collected 1/11/99 and extracted 9/11/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
Pond 4 (n = 4)	61	93	591	150	14	13	923	
glass fibre (Liq-liq)	54	24	236	119	2	14	449	49%
3 µm (Liq-liq)	36	34	145	69	4	7	293	32%
0.8 µm (Liq-liq)	35	32	109	62	3	5	247	27%
0.45 µm (Liq-liq)	34	25	98	66	2	4	230	25%
0.2 µm (Liq-liq)	41	28	65	80	3	4	220	24%
0.05 µm (Liq-liq)	37	14	28	97	1	3	179	19%
glass fibre (Soxhlet)	17	43	366	64	8	2	500	54%
3 µm (Soxhlet)	2	3	20	4	tr	7	36	4%
0.8 µm (Soxhlet)	1	4	24	5	tr	tr	34	4%
0.45 µm (Soxhlet)	2	4	22	4	tr	1	33	4%
0.2 µm (Soxhlet)	1	3	13	3	tr	1	20	2%
0.05 µm (Soxhlet)	3	7	33	8	1	tr	52	6%

[a] average of duplicate analyses. Abbreviations: Seco = Secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 5.6. Resin acid levels (µg/L) determined for sodium azide stabilised SH30 Tarawera River water sample, collected 1/11/99 and extracted 11/11/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30 (n = 2)[a]	4.8	5.8	22.6	9.1	20.0	0.2	62.5	
glass fibre(liq/liq)	4.7	4.7	17.0	7.4	13.3	0.2	42.5	68%
3 µm (liq/liq)	3.9	3.1	9.3	5.4	7.9	tr	29.7	48%
0.8 µm (liq/liq)	3.3	2.7	7.8	4.3	6.3	0.2	24.6	39%
0.45 µm (liq/liq)	3.3	2.3	6.8	5.1	5.4	0.1	23.0	37%
0.2 µm (liq/liq)	3.6	1.8	3.7	4.6	3.3	0.1	17.0	27%
0.05 µm (liq/liq)	3.8	1.9	2.4	5.3	-	0.1	13.4	21%
glass fibre (Soxhlet)	0.9	1.6	8.6	3.0	6.6	0.1	20.7	33%
3 µm (Soxhlet)	0.4	0.8	3.5	1.3	2.9	tr	8.8	14%
0.8 µm (Soxhlet)	tr	0.3	1.3	0.5	-	tr	2.2	3%
0.45 µm (Soxhlet)	tr	-	1.1	0.5	-	tr	1.7	3%
0.2 µm (Soxhlet)	0.1	-	0.7	0.2	-	tr	1.1	2%
0.05 µm (Soxhlet)	-	-	2.6	1.4	-	-	4.1	7%

[a] average of duplicate analyses. Abbreviations: seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 5.7. Resin acid levels (μg/L) determined for sodium azide stabilised SH2 Tarawera River water, collected 1/11/99 and extracted 13/11/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH2 (n = 2)[a]	2.5	3.4	16.4	6.8	12.3	0.1	41.7	
glass fibre (liq/liq)	1.8	1.9	8.1	3.3	6.2	0.1	21.5	52%
3 μm (liq/liq)	2.1	2.1	7.4	3.7	5.9	0.1	21.3	51%
0.8 μm (liq/liq)	1.9	2.8	4.2	6.5	3.6	tr	19.1	46%
0.45 μm (liq/liq)	1.6	1.4	6.0	3.3	-	tr	11.8	28%
0.2 μm (liq/liq)	1.6	0.8	2.4	2.6	-	tr	7.5	18%
0.05 μm (liq/liq)	1.5	-	-	3.7	-	-	5.2	13%
glass fibre(Soxhlet)	0.5	1.0	5.5	2.1	5.1	tr	14.3	34%
3 μm (Soxhlet)	0.2	0.4	1.9	0.7	1.2	tr	4.4	11%
0.8 μm (Soxhlet)	0.1	0.2	1.2	0.5	0.8	tr	2.9	7%
0.45 μm (Soxhlet)	tr	-	0.7	0.6	-	-	1.3	3%
0.2 μm (Soxhlet)	0.4	0.6	2.6	1.4	-	-	4.9	12%
0.05 μm (Soxhlet)	0	-	2.2	-	-	-	2.2	5%

[a] average of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

It is clear from the data that mainly free resin acids (not associated with particles) are present in the clarifier outlet and pond 1 outlet samples. On the other hand > 65% of the resin acids discharged from pond 4 to the Tarawera River are bound to particles with sizes in the range 15-0.05 μm (Table 5.5). This is essentially unchanged at SH30 and SH2 except that the percentage filtered by glass fibre appears to be less than in the pond 4 discharge.

The results presented in Tables 5.2-5.5 show that resin acids become increasingly associated with particulate matter during passage through the biological treatment system. Initially ca. 1% (85 μg/L) of the resin acids, exiting from the clarifier are bound to 0.45 μm or greater particles (see Table 5.1), whereas 65% (603 μg/L) of the resin acids are associated with 0.45 μm or greater particles in pond 4 (see Table 5.5).

The variation of particle bound resin acids down the treatment system is shown diagrammatically in Figure 5.2.

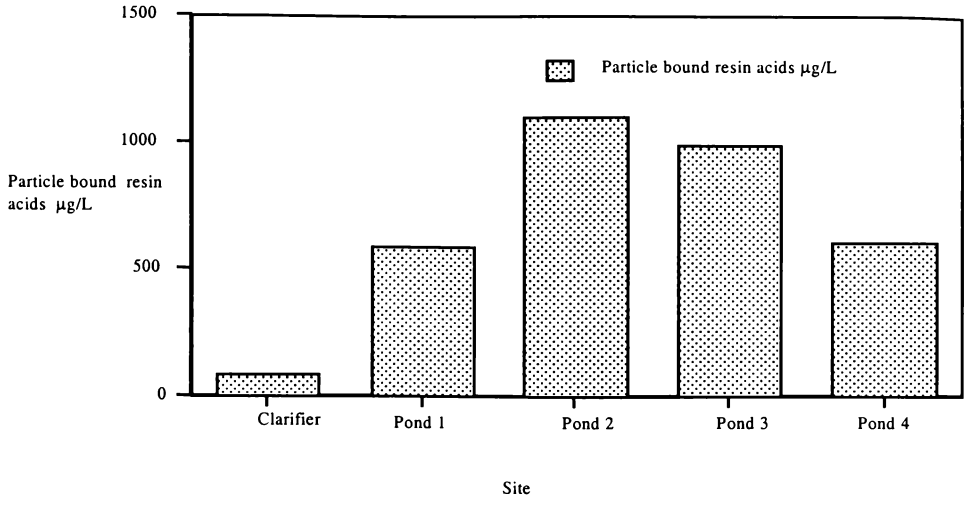


Figure 5.2. Levels of particle bound (> 0.45 µm) resin acids identified in clarifier and biological treatment pond water samples.

The amounts of free and particle bound resin acids are shown diagrammatically in Figure 5.3. The increase in total resin from the clarifier to the outlet of pond 1 is presumed to be due to bleach plant effluent, which by passes the clarifier (see Figure 1). Free resin acids decrease down the treatment system whereas particle bound resin acids increase in ponds 1 and 2 and then remain fairly constant in pond 3 and show some decrease in pond 4.

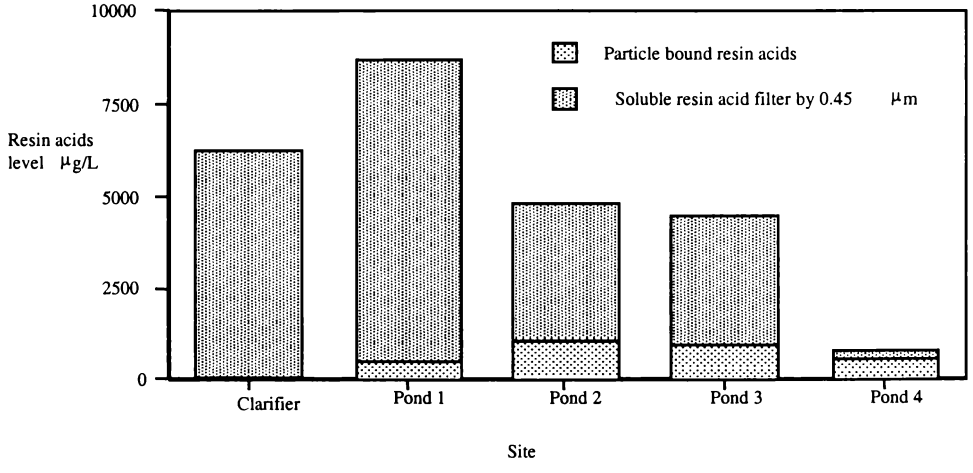


Figure 5.3. Levels of particle bound (> 0.45 µm) and free resin acids identified in clarifier and biological treatment pond water samples.

The levels of total resin acids identified in the pond 2 and 3 water samples were fairly similar (5261 and 4693 μg/L respectively (see Tables 5.3, 5.4 and Fig 5.3) indicating that at the time of sampling pond 3 was contributing little to treatment.

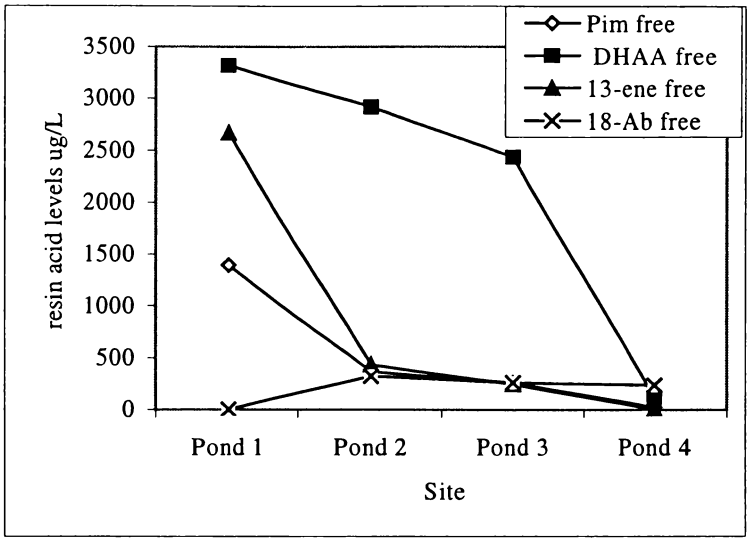


Figure 5.4. Levels of free (> 0.45 μm) pimaric acid, dehydroabietic acid, abiet-13-enoic acid and abietan-18-oic acid identified in biological treatment pond water samples.

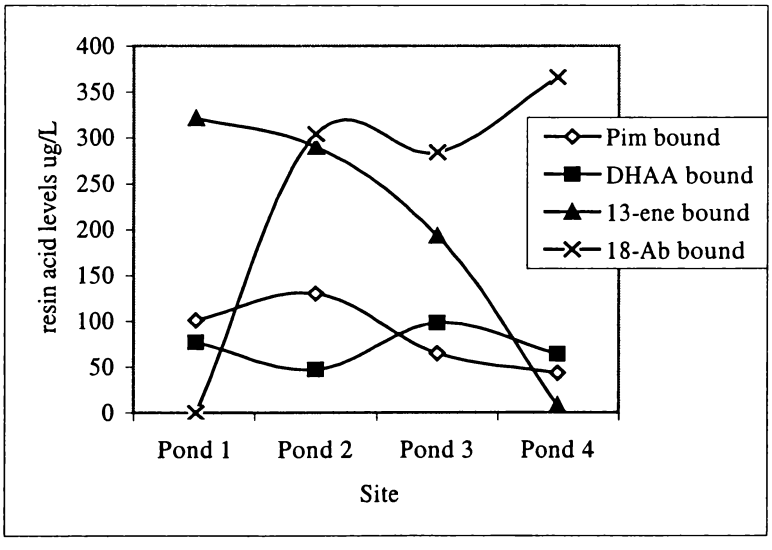


Figure 5.5. Levels of particle bound (> 0.45 μm) pimaric acid, dehydroabietic acid, abiet-13-enoic acid and abietan-18-oic acid identified in biological treatment pond water samples.

The variation of individual resin acids down the treatment system is shown diagrammatically in Figures 5.4 and 5.5.

Figure 5.4 shows that the free pimaric acid and dehydroabietic acid levels fall substantially, while the bound levels (Figure 5.5) stay approximately constant. The level of free abietan-18-oic acid remains approximately constant in ponds 2, 3 and 4. (Figure 5.4). On other hand, bound abietan-18-oic acid bound levels increase as bound abiet-13-enoic acid levels decrease. This is consistent with the postulated conversion of abiet-13-enoic acid to abietan-18-oic acid (see Figure 5.6) (Tavendale 1994). It is of interest that whereas particle binding appears to inhibit the degradation of pimaric acid and dehydroabietic acid, particle bound abiet-13-enoic acid is virtually completely transformed down the treatment system.

Comparison of the resin acid levels determined for the unfiltered pond 1 and 4 outflow samples showed that most resin acid concentrations were attenuated by ca. 85% during passage through the three oxidation ponds. Abietic acid is completely degraded in the treatment system. It is known that abietic acid can either aromatised to afford dehydroabietic acid, or saturated to afford abiet-13-enoic acid. It has been postulated that abiet-13-enoic acid is further saturated to form abietan-18-oic acid (Tavendale (1994) (Figure 5.6). Both pathways appear to be occurring in the treatment system.

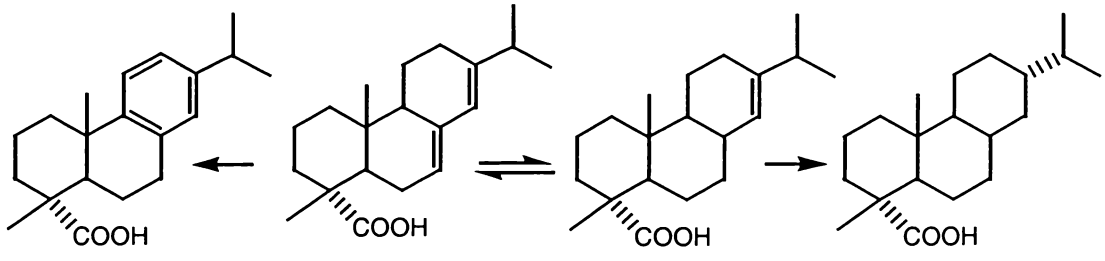


Figure 5.6. Chemical structures of some resin acids derived from abietic acid during biological treatment.

It is clear from the data that mainly free resin acids (not associated with particles) are present in the clarifier outflow and pond 1 outlet samples. On the other hand > 72% of the resin acids discharged from pond 4 to the Tarawera River are bound to particles with sizes in the range 15-0.05 μm (Table 5.5).

Resin acids in treatment system samples stored for 90-150 days.

The results determined for water samples stored for 90-150 days (Tables 5.8-5.12) were in good agreement with those determined for the corresponding freshly collected and extracted samples (Tables 5.1-5.5). For example, in each case reference unfiltered resin levels agreed within experimental error CV ca. 8%, based on the use of 600-800 mL samples and the use of different sets of winchesters). This observation is consistent with the earlier finding (see Chapter 4) that 0.1% sodium azide addition inhibits biodegradation of resin acids.

Similar levels of free resin acids were present in freshly collected and aged (ca. 3-5 months at 5°C) clarifier samples (Table 5.1 and 5.8). There was no change in the amount of particle bound resin acids over the storage period. It is possible that some aggregation of the smaller particles to form larger particles occurred. Aged samples from ponds 1 and 2 showed similar effects.

Table 5.8. SIM-GC/MS determined resin acid levels (µg/L) identified in a sodium azide stabilised, sequentially filtered clarifier outflow water sample collected 1/11/99 and extracted 28/3/00.

	Seco	Pim	18-Ab	DHAA	13-ene	Abiet	total	%
Clarifier (n = 2)	332	1576	5	4128	693	1271	8005	
glass fibre(liq/liq)	354	1645	10	3901	658	1152	7720	96%
3 µm (liq/liq)	283	1167	5	3894	491	753	6393	82%
0.8 µm (liq/liq)	297	1230	5	4154	495	1248	7427	93%
0.45 µm (liq/liq)	307	1169	6	3942	466	1049	6939	87%
0.2 µm (liq/liq)	326	1302	6	4193	534	1419	7781	97%
0.05 µm (liq/liq)	327	1222	6	4272	522	1222	7571	95%
glass fibre (Soxhlet)	8	69	-	65	45	35	222	3%
3 µm (Soxhlet)	2	13	-	19	11	-	44	0.5%
0.8 µm (Soxhlet)	0	3	-	5	-	-	8	0.1%
0.45 µm (Soxhlet)	0	3	-	12	-	-	16	0.2%
0.2 µm (Soxhlet)	0	4	-	15	-	-	19	0.2%
0.05 µm (Soxhlet)	0	28	-	36	-	-	65	0.8%

[a] average of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Abiet = abietic acid, total = total resin acids, % = recovery relative to unfiltered water.

Table 5.9. SIM GC/MS determined resin acid levels (µg/L) identified in a sodium azide stabilised, sequentially filtered pond 1 water sample collected 1/11/99 and extracted 1/4/00.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
Pond 1 (n = 2)	531	1236	26	3592	3074	17	8476	
glass fibre(liq/liq)	424	1016	15	3371	2317	10	7152	84%
3 µm (liq/liq)	428	975	10	3638	2145	9	7205	85%
0.8 µm (liq/liq)	473	1038	11	3591	2333	11	7458	88%
0.45 µm (liq/liq)	468	896	16	4239	1934	10	7663	89%
0.2 µm (liq/liq)	460	892	26	4130	1826	9	7442	87%
0.05 µm (liq/liq)	416	719	6	4956	1342	9	7448	88%
glass fibre (Soxhlet)	38	193	14	167	810	6	1272	14%
3 µm (Soxhlet)	3	15	1	19	54	0	93	1%
0.8 µm (Soxhlet)	2	6	0	8	19	0	35	0.4%
0.45 µm (Soxhlet)	2	2	1	5	6	0	16	0.2%
0.2 µm (Soxhlet)	5	9	-	21	20	0	54	0.6%
0.05 µm (Soxhlet)	11	18	-	34	32	0	96	1%

[a] average of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 5.10. SIM GC/MS determined resin acid levels (µg/L) identified in sodium azide stabilised, sequentially filtered pond 2 water sample collected 1/11/99 and extracted 29/2/00.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
Pond 2 (n = 2)	222	478	549	2627	1467	29	5373	
Glass fibre (liq/liq)	204	397	220	2599	667	18	4104	76%
3 µm (liq/liq)	229	367	170	2486	944	15	4211	78%
0.8 µm (liq/liq)	221	345	127	2543	704	12	3952	74%
0.45 µ(liq/liq)	180	309	124	2301	749	13	3676	68%
0.45 µm (liq/liq)	177	278	88	2250	345	13	3151	59%
0.05 µm (liq/liq)	177	270	45	2518	64	14	3088	57%
glass fibre (Soxhlet)	30	117	341	223	571	11	1293	24%
3 µm (Soxhlet)	5	22	49	44	51	1	173	3%
0.8 µm (Soxhlet)	2	6	19	18	-	0	45	1%
0.45 µm (Soxhlet)	0	-	16	46	-	0	62	1%
0.2 µm (Soxhlet)	2	5	12	26	-	0	45	1%
0.05 µm (Soxhlet)	10	23	27	59	61	0	180	3%

[a] average of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids-1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

The level of total resin acids in the aged samples of pond 3 and 4 are presented in Tables 5.11 and 5.12. There was no change in resin acid levels or speciation upon storage and no indication of any particle aggregation (see Tables 5.4, 5.5, 5.11 and 5.13).

Table 5.11. SIM-GC/MS determined resin acid levels (µg/L) identified in sodium azide stabilised, sequentially filtered pond 3 water sample collected 1/11/99 and extracted 4/3/00.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
Pond 3 (n = 2)	237	366	603	2384	1010	30	4597	
glass fibre (liq/liq)	212	315	373	2296	722	22	3941	85%
3 µm (liq/liq)	198	263	225	2261	534	16	3497	76%
0.8 µm (liq/liq)	203	256	157	2250	461	16	3344	72%
0.45 µm (liq/liq)	202	250	141	2300	423	15	3331	72%
0.2 µm (liq/liq)	183	226	98	2087	383	13	2991	65%
0.05 µm (liq/liq)	150	175	45	1875	274	12	2532	55%
glass fibre (Soxhlet)	10	29	155	63	146	4	408	9%
3 µm (Soxhlet)	7	20	95	48	41	3	214	5%
0.8 µm (Soxhlet)	2	6	23	13	23	0	67	1%
0.45 µm (Soxhlet)	3	4	18	8	18	0	51	1%
0.2 µm (Soxhlet)	3	7	17	24	21	0	73	2%
0.05µm (Soxhlet)	21	26	61	37	77	0	222	5%

[a] average of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids 1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 5.12. SIM-GC/MS determined resin acid levels (µg/L) identified in sodium azide stabilised, sequentially filtered pond 4 water sample collected 1/11/99 and extracted 26/3/00.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
Pond 4 (n = 2)	201	120	311	122	231	22	1006	
glass fibre (liq/liq)	182	89	137	82	123	16	630	63%
3 µm (liq/liq)	193	90	122	75	112	14	606	60%
0.8 µm (liq/liq)	124	56	90	61	76	9	416	41%
0.45 µm (liq/liq)	84	35	73	53	48	6	299	30%
0.2 µ(liq/liq)	52	21	24	37	26	3	163	16%
0.05 µm (liq/liq)	41	14	5	51	-	2	113	11%
glass fibre (Soxhlet)	31	36	170	40	104	8	389	39%
3 µm (Soxhlet)	3	5	23	6	13	1	51	5%
0.8 µm (Soxhlet)	4	4	20	5	10	1	45	4%
0.45 µm (Soxhlet)	2	3	11	4	7	1	28	3%
0.2 µm (Soxhlet)	3	2	4	2	-	0	11	1%
0.05µm (Soxhlet)	5	3	10	5	5	1	29	3%

[a] average of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

5.3.3. Resin neutrals

Freshly collected samples

Data for resin neutrals from freshly collected treatment samples are summarised in Tables 5.13-5.14.

Table 5.13. SIM GC/MS determined resin neutral levels (µg/L) identified in a sodium azide stabilised, sequentially filtered, pond 3 water sample collected 1/11/99 and extracted 25/12/99.

	fichtelite	Tetrahydro_ retene	retene	total resin neutrals	
Pond 3 (n = 2) [a]	66	115	72	252	100%
glass fibre (liq/liq)	-	31	20	51	20%
3 µm (liq/liq)	-	18	8.4	26	10%
0.8 µm (liq/liq)	-	14	-	14	5%
0.45 µm (liq/liq)	-	11	-	11	4%
0.2 µm (liq/liq)	-	-	-	-	
0.05 µm (liq/liq)	-	-	-	-	
glass fibre (Soxhlet)	57	104.	66	227	90%
3 µm (Soxhlet)	-	24	17	41	16%
0.8 µm (Soxhlet)	-	6.6	4.4	11	4%
0.45 µm (Soxhlet)	-	4.0	1.6	5.6	2%
0.2 µm (Soxhlet)	-	0.3	0.2	0.6	0.2%
0.05 µm (Soxhlet)	-	-	-	-	

[a] average of duplicate analyses.

Table 5.14. SIM GC/MS determined resin neutral levels (µg/L) identified in a sodium azide stabilised, sequentially filtered, pond 4 water sample collected 1/11/99 and extracted 9/11/99.

	fichtelite	Tetrahydro_ retene	retene	total resin neutrals	
Pond 4 (n = 2) [a]	72	15	10	97	100%
glass fibre (liq/liq)	-	-	-	-	0%
3 µm (liq/liq) [b]	-	-	-	-	0%
glass fibre (Soxhlet)	61	14	7.5	82.7	86%
3 µm (Soxhlet) [b]	-	-	-	-	0%

[a] average of duplicate analyses, [b] only traces of resin neutrals were detected in subsequent 0.8-0.05 µm Liquid/liquid and Soxhlet extractions.

Resin neutrals (decarboxylated resin acids) are formed during passage through the treatment ponds (Wilkins & Panadam, 1987). Generally only moderate levels of resin neutrals were present in treatment pond samples and were generally undetectable in downstream Tarawera River samples. Treatment system samples collected on 1/11/99 contained low levels of resin neutrals.

Resin neutrals appear to be more extensively bound to suspended solid particles than are resin acids (see Table 5.8 and 5.9). This may be a consequence of resin neutrals (= resin hydrocarbons) being less hydrophilic than resin acids.

Resin neutrals in aged samples

The results determined for water samples stored for 90-150 days (Tables 5.15-5.17) were in good agreement with those determined for the corresponding freshly collected and extracted samples (Tables 5.13 and 5.14). For example, in each case reference unfiltered resin neutral levels agreed within experimental error (CV of ca. 8%), based on the use of 600-800 mL samples and the use of water from different sets of winchesters). In the case of the pond 2 sample, the signal to noise ratio of some of the freshly collected treatment pond water samples was such that resin neutral compounds could not be reliably detected.

Table 5.15. SIM GC/MS determined resin neutral levels (µg/L) identifed in sodium azide stabilised, sequentially filtered pond 2 water sample collected 1/11/99 and extracted 25/2/00.

	fichtelite	tetrahydroretene	retene	resin neutrals	
Pond 2 (n = 2) [a]	-	104	5.2	109	100%
glass fibre (liq/liq)	-	31.4	-	31.4	29%
3 µm (liq/liq)	-	21.2	-	21.2	19%
0.8 µm (liq/liq)	-	12.4	-	12.4	11%
0.45 µm (liq/liq)	-	5.4	-	5.4	5%
0.2 µm (liq/liq)	-	-	-	0.0	
0.05 µm (liq/liq)	-	-	-	0.0	
glass fibre (Soxhlet)	-	103	1.8	105	96%
3 µm (Soxhlet)	-	19.4	0.4	19.8	18%
0.8 µm (Soxhlet)	-	7.2	-	7.2	7%
0.45 µm (Soxhlet)	-	-	-	0.0	
0.2 µm (Soxhlet)	-	-	-	0.0	
0.05 µm (Soxhlet)	-	-	-	0.0	

[a] average of duplicate analyses·

Table 5.18. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for unfiltered and filtered treatment pond and river water samples collected 1/11/99[a].

	absorbance			normalised absorbance[a]			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	norm[a]
Pond 1 (as recv)	1.794	0.744	0.283	1.00	1.00	1.00	53.0	1.00
glass fibre	1.268	0.432	0.097	0.71	0.58	0.34	19.8	0.37
3 μm	1.134	0.369	0.068	0.63	0.50	0.24	3.89	0.07
0.8 μm	1.145	0.380	0.069	0.64	0.51	0.24	1.97	0.04
0.45 μm	1.103	0.365	0.069	0.61	0.49	0.24	1.67	0.03
0.2 μm	1.015	0.335	0.065	0.57	0.45	0.23	0.65	0.01
0.05 μm	0.690	0.240	0.053	0.38	0.32	0.19	0.52	0.01
Pond 2 (as recv)	2.036	0.755	0.289	1.00	1.00	1.00	43.5	1.00
glass fibre	1.507	0.471	0.112	0.74	0.62	0.39	16.5	0.38
3 μm	1.397	0.427	0.097	0.69	0.69	0.34	7.60	0.17
0.8 μm	1.269	0.371	0.065	0.62	0.49	0.22	3.55	0.08
0.45 μm	1.279	0.379	0.074	0.63	0.50	0.26	1.93	0.04
0.2 μm	1.208	0.356	0.063	0.59	0.47	0.22	0.76	0.02
0.05 μm	0.654	0.186	0.032	0.32	0.25	0.11	0.46	0.01
Pond 3 (as recv)	1.895	0.717	0.262	1.00	1.00	1.00	44.3	1.00
glass fibre	1.468	0.495	0.124	0.77	0.69	0.47	17.2	0.39
3 μm	1.251	0.402	0.093	0.66	0.56	0.35	3.11	0.07
0.8 μm	1.219	0.309	0.095	0.64	0.43	0.36	1.40	0.03
0.45 μm	1.316	0.442	0.110	0.69	0.62	0.42	0.99	0.02
0.2 μm	1.256	0.417	0.097	0.66	0.58	0.37	0.48	0.01
0.05 μm	0.533	0.163	0.032	0.28	0.23	0.12	0.39	0.01
Pond 4 (as recv)	1.587	0.618	0.224	1.00	1.00	1.00	43.5	1.00
glass fibre	1.247	0.426	0.110	0.79	0.69	0.49	17.6	0.40
3 μm	1.224	0.429	0.121	0.77	0.69	0.54	4.12	0.09
0.8 μm	1.215	0.413	0.112	0.77	0.67	0.50	3.04	0.07
0.45 μm	1.160	0.397	0.101	0.73	0.64	0.45	0.93	0.02
0.2 μm	1.060	0.356	0.084	0.67	0.58	0.38	0.62	0.01
0.05 μm	0.661	0.212	0.047	0.42	0.34	0.21	0.46	0.01
SH30 (as recv)	0.349	0.074	0.018	1.00	1.00	1.00	7.78	1.00
glass fibre	0.339	0.068	0.016	0.97	0.92	0.89	3.83	0.49
3 μm	0.329	0.064	0.013	0.94	0.86	0.72	2.35	0.30
0.8 μm	0.323	0.060	0.011	0.93	0.81	0.61	1.46	0.19
0.45 μm	0.324	0.058	0.011	0.93	0.78	0.61	1.15	0.15
0.2 μm	0.315	0.052	0.009	0.90	0.70	0.50	0.69	0.09
0.05 μm	0.314	0.052	0.007	0.90	0.70	0.39	0.32	0.04

[a] extractions dates are given Tables 5.1 to 5.6,. Abbreviations: as recv = as received (not filtered); norm = normalised turbidity or absorbance, relative to unfiltered treatment pond or river water.

Filtration generally reduced colour and turbidity. For example, 3 μm filtration reduced the absorbance at 270, 340 and 440 nm of the pond 4 water sample to 79, 69 and 49% respectively of the absorbances determined for unfiltered water. Subsequent 0.2 μm filtration of the pond 4 sample reduced absorbances at 270, 340 and 440 nm to 67, 58 and 38%, respectively, of absorbances determined for unfiltered water.

Sub 1 μm filtration of the SH30 Tarawera River water sample reduced colour levels to a lesser extent than was the case for treatment pond samples. This was evidenced by the finding than 0.2 μm filtration of the SH30 Tarawera river water sample reduced absorbances at 270, 340 and 440 nm to 90, 70, and 50%, respectively, of the absorbances determined for unfiltered SH30 Tarawera River water. 0.2 μm filtration reduced the corresponding absorbances of the pond 1-4 samples by 57-68, 45-58 and 23-38% respectively.

Filtration (3 μm or smaller) removed virtually all turbidity.

Colour and turbidity of samples stored for 90 days

Data are summarised in Table 5.19. Colour levels in water samples stored for 90 days were slightly higher than the colour levels of freshly collected samples. This observation can be attributed to the oxidation of lignins and other chromophoric polyphenols during storage for ca. 90 days at 5^{o}C, or to some interaction between NaN_3 and lignans during the storage period.

Sequential-filtration progressively reduced the absorbances of clarifier, treatment pond and river water samples (Table 5.19). For example, 3 μm filtration reduced the absorbance at 270, 340 and 440 nm of the pond 4 water sample to 79, 70 and 49% respectively of the absorbances determined for unfiltered water. Subsequent 0.2 μm filtration of the pond 4 sample reduced absorbances at 270, 340 and 440 nm to 65, 60 and 40%, respectively, of absorbances determined for unfiltered water.

Table 5.19. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for unfiltered and filtered clarifier and treatment pond water samples collected on 1/11/99 and stored for ca. 3-5 months.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	norm[a]
Clarifer (as recv)	1.495	0.501	0.125	1.00	1.00	1.00	53.5	1.00
glass fibre	1.268	0.389	0.057	0.85	0.78	0.46	5.75	0.11
3 μm	1.193	0.366	0.049	0.80	0.73	0.39	2.3	0.04
0.8 μm	1.161	0.374	0.048	0.78	0.75	0.38	1.52	0.03
0.45 μm	1.260	0.358	0.047	0.84	0.71	0.38	1.08	0.02
0.2 μm	1.066	0.342	0.048	0.71	0.68	0.38	0.84	0.02
0.05 μm	0.792	0.250	0.025	0.53	0.50	0.20	0.76	0.01
Pond 1 (as recv)	1.689	0.675	0.242	1.00	1.00	1.00	115	1.00
glass fibre	1.203	0.407	0.084	0.71	0.60	0.35	6.5	0.06
3 μm	1.175	0.395	0.075	0.70	0.59	0.31	3.11	0.03
0.8 μm	1.129	0.376	0.070	0.67	0.56	0.29	2.44	0.02
0.45 μm	1.127	0.393	0.080	0.67	0.58	0.33	1.57	0.01
0.2 μm	0.990	0.345	0.065	0.59	0.51	0.27	1.25	0.01
0.05 μm	0.837	0.291	0.051	0.50	0.43	0.21	0.74	0.01
Pond 2 (as recv)	2.110	0.795	0.290	1.00	1.00	1.00	65.7	1.00
glass fibre	1.534	0.481	0.111	0.73	0.61	0.38	10.6	0.16
3 μm	1.374	0.407	0.075	0.65	0.51	0.26	4.46	0.07
0.8 μm	1.363	0.405	0.069	0.65	0.51	0.24	2.03	0.03
0.45 μm	1.372	0.417	0.078	0.65	0.52	0.27	1.46	0.02
0.2 μm	1.269	0.373	0.061	0.60	0.47	0.21	0.65	0.01
0.05 μm	1.290	0.389	0.065	0.61	0.49	0.22	0.35	0.01
Pond 3 (as recv)	2.044	0.801	0.288	1.00	1.00	1.00	58.2	1.00
glass fibre	1.732	0.629	0.113	0.85	0.79	0.39	21.4	0.37
3 μm	1.349	0.442	0.100	0.66	0.55	0.35	2.55	0.04
0.8 μm	1.333	0.432	0.095	0.65	0.54	0.33	2.25	0.04
0.45 μm	1.322	0.431	0.095	0.65	0.54	0.33	1.09	0.02
0.2 μm	1.229	0.401	0.089	0.60	0.50	0.31	0.68	0.01
0.05 μm	0.977	0.306	0.061	0.48	0.38	0.21	0.56	0.01
Pond 4 (as recv)	1.669	0.649	0.233	1.00	1.00	1.00	50.8	1.00
glass fibre	1.339	0.469	0.123	0.80	0.72	0.53	8.73	0.17
3 μm	1.301	0.453	0.114	0.78	0.70	0.49	5.68	0.11
0.8 μm	1.294	0.467	0.122	0.78	0.72	0.52	5.32	0.10
0.45 μm	1.215	0.446	0.123	0.73	0.69	0.53	2.75	0.05
0.2 μm	1.08	0.388	0.099	0.65	0.60	0.42	0.80	0.02
0.05 μm	0.661	0.212	0.047	0.40	0.33	0.20	0.61	0.01

as recv = as received (not filtered); [a]norm = normalised turbidity or absorbance, relative to unfiltered clarifier and treatment pond water.

The colour in pond 1 was greater than the colour of the clarifier outlet. It is likely that the additional colour originates from the acid bleaching pipe (see Figure 5.1).

5.3.5. Particle size

Only freshly collected samples were investigated. Particle size data was obtained using the Mastersizer instrument (see Section 2.6.1). Data are summarised in Figure 5.7.

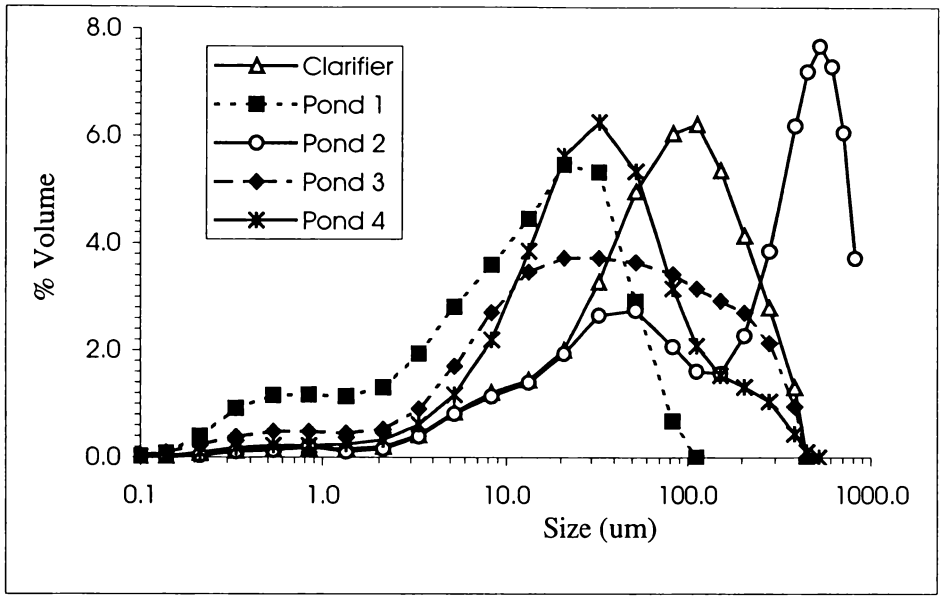


Figure 5.7. Particle size distributions (% volume) determined for clarifier and pond 1-4 water samples.

Particle size analyses showed that the bulk of the particles in the treatment system water samples were greater than 10 μm (Figure 5.7). Mechanical aeration (agitation) of pond 2, appears to contribute to the comparatively large abundance of > 200 μm particles in pond 2 water sample in this pond. Kasko (1996) has reported the presence of elevated levels of > 200 μm particles in a pulp mill effluent after biological and mechanical treatment. The % contributions of > 10 μm particles in the clarifier and the pond 1-4 water samples were 90, 57, 92, 76 and 84% respectively.

Particle size is known to be significant factor in the design pulp mill effluent treatment systems (Kasko, 1996). Currently, technical difficulties such as membrane clogging and the operating costs of large scale plants are such that removal of colour and particle associated organic species by micro-filtration has not been adopted as a viable treatment option for pulp and paper mill effluents.

Effect of agitation

The Mastersizer-S instrument can be operated in two modes: pumping without stirring and pumping with variable stirring. The latter mode can be expected to cause greater agitation of the sample. Data for a pond 4 water sample pumped without stirring and pumped with stirring are presented in Figure 5.8.

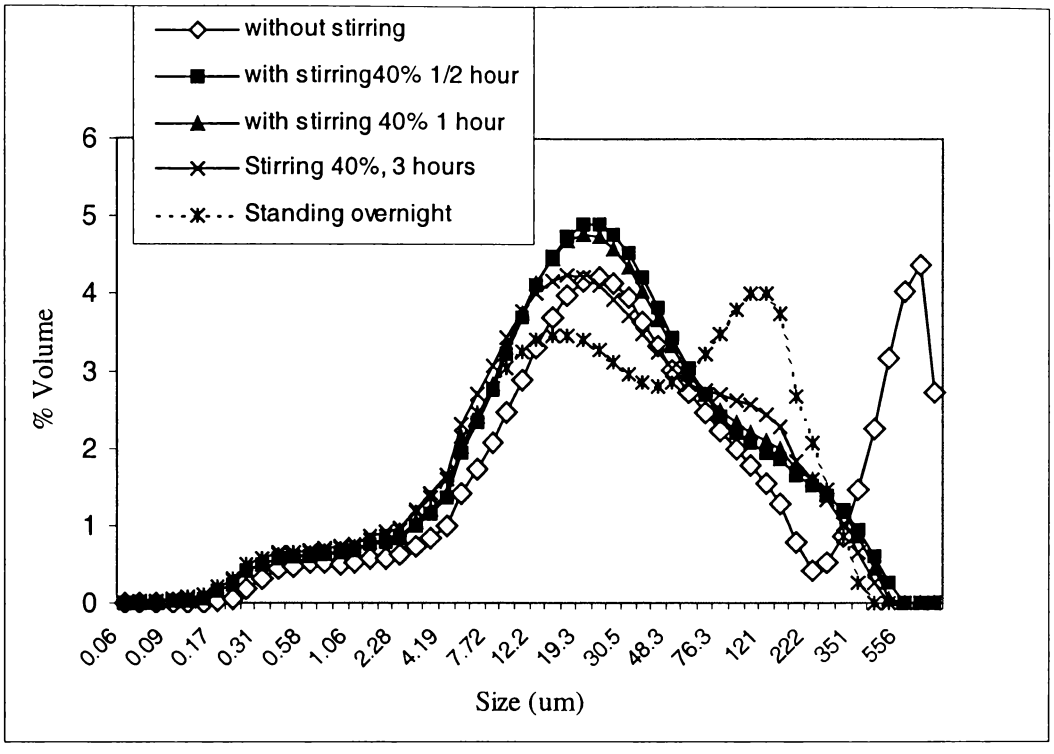


Figure 5.8. Particle size distributions (% volume) determined for a pond 4 water sample with and without stirring and standing overnight.

The data show that even short duration stirring significantly reduces the signal due to particles of size greater than 250 μm. The effect is increased by prolonged stirring and can be accelerated by more vigorous stirring. This is interpreted to mean that the stirring caused the disaggregation of the large particles. When the sample was left unstirred overnight, the larger particles are only partially reformed.

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Some evidence of the disaggregation effect can be seen in the resin acid data reported earlier. Comparison of % bound resin acids in the freshly extracted pond 4 sample (Table 5.5), with those determined for the SH30 and SH2 samples (Table 5.6 and 5.7) shows ca. 50% of resins acids in the pond 4 samples is bound to > 15 μm particles, whereas this level is reduced to 36% in the SH30 and SH2 samples. It is possible that high shear

during discharge through the outlet diffuser and the turbulent nature of the river flow provide the conditions necessary to disaggregate some of the larger particles.

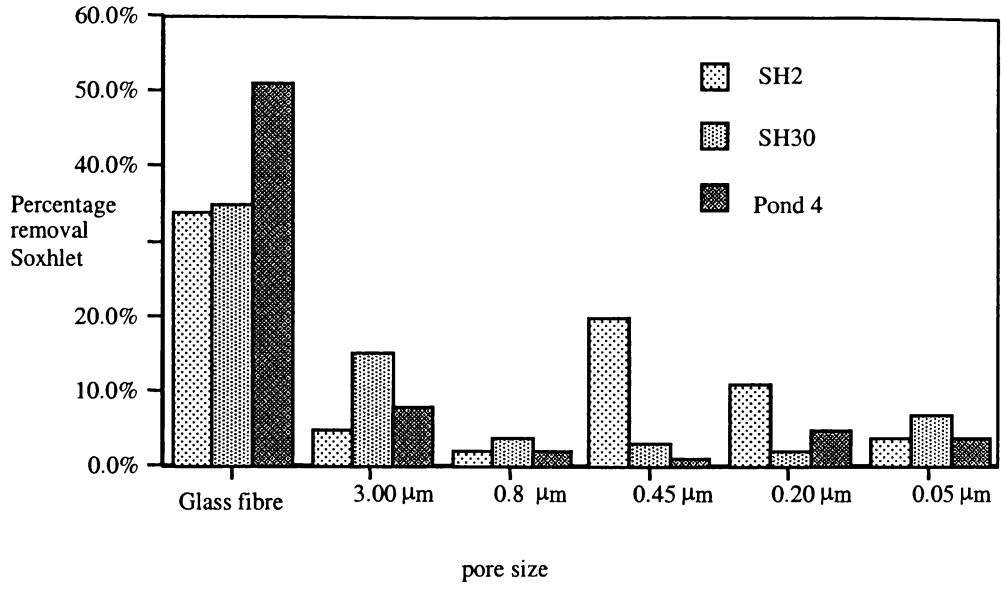

Fig 5.9. Variation of particle bound resin acids with pore size in pond 4, SH30 and SH2 Tarawera River water samples, collected 1/11/99.

5.3.6. Inorganic analyses

The levels (mg/L) of selected elements (Na K, Ca, Si, Al, Fe, As, Hg, S and B) and amounts (mg/L) of freeze-dried solids were determined for treatment system and river water (see Table 5.20). In general, cation levels in ponds 2, 3 and 4 were conservative. Levels in the SH30 and SH2 Tarawera River water samples were comparable with those reported in other investigations (Wilkins *et al* 1996a, b; McIntosh 1995), Comparison with overseas studies indicates that with the exception of sodium levels, the cation levels reported in Table 5.20 are appreciably lower than those reported by Neamade and Shrivastava (1997) but comparable with those reported by Holmbom *et al* (1993).

The levels of inorganic freeze-dried solids (IFDS) recovered from the pond 2, 3 and 4 water samples after freeze-drying and overnight furnacing at 550°C (842, 813 and 894 mg/L respectively) were greater than those determined for the clarifier and pond 1 water samples (634 and 770 mg/L respectively). On the other hand the level of organic freeze-dried solids (OFDS), calculated as total freeze-dried solids minus inorganic freeze dry

solid (TFDS-IFDS), decreased from 656 mg/L (pond 1) to 283 mg/L (pond 4) during passage through the treatment system.

Table 5.20. Elements (mg/L) and freeze-dried solid levels (mg/L) determined for treatment system and Tarawera River water samples collected 1/11/99.

	Clarifier	Pond 1	Pond 2	Pond 3	Pond 4	SH30	SH2
Na	209	243	223	223	221	70	62
Ca	25	42	63	52	45	11	11
K	3.0	3.1	2.7	2.6	2.5	2.1	1.8
Si	24	23	25	25	24	27	27
S	8.7	9.8	8.4	11	6.0	0.8	0.7
Al	0.77	0.91	0.75	0.82	0.66	0.72	0.69
Fe	0.02	0.14	0.21	0.24	0.12	0.03	0.03
B	0.26	0.27	0.27	0.25	0.26	0.54	0.47
As	0.006	0.033	0.031	0.028	0.015	0.024	0.028
Hg	< 0.007	< 0.007	< 0.007	< 0.007	< 0.007	< 0.007	< 0.007
TFDS	1074	1426	1256	1162	1087	394	354
% loi FDS	41%	46%	33%	30%	0.26	0.22	23%
OFDS	440	656	414	349	283	87	81
IFDS	634	770	842	813	804	307	273

TFDS = total freeze-dried solids, % loi FDS = loss on ignition of freeze-dried solids, OFDS = organic freeze dried solids, IFDS = inorganic freeze dried solids.

5.3.7. BOD_5 and resin acids in pond 4

Resin acid levels and BOD_5 for sequential filtration of freshly collected and unstabilised pond 4 water sample are summarised in Tables 5.21and 5.22 respectively.

Table 5.21. Resin acid levels (µg/L) identified in unstabilised freshly collected, sequentially filtered pond 4 water sample, collected and extracted 1/11/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
Pond 4	64	74	337	152	203	20	850	
Pond 4	68	77	364	158	211	20	898	
average	66	75	350	155	207	20	874	100%
glass fibre (liq/liq)	40	33	102	72	69	5	322	37%
3 µm (liq/liq)	28	25	65	61	55	0	234	27%
0.8 µm (liq/liq)	29	26	63	65	59	0	242	28%
0.45 µm (liq/liq)	28	22	55	58	42	0	205	23%

Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 5.22. BOD_5 identified in a freshly collected, unstabilised, sequentially filtered pond 4 water sample collected 1/11/99.

	BOD_5	%
unfiltered pond 4	28.6	100%
glass fibre	15.5	54%
3 μm	15.5	54%
0.8 μm	14.3	50%
0.45 μm	11.0	38%

The BOD_5 removal was monitored during the sequential filtration of an unstabilsed pond 4 samples using glass fibre, 3, 0.8 and 0.45 μm filter papers. There was a large removal (ca. 50%) of BOD_5 by glass fibre filtration and only a slight change in BOD_5 for 3-0.45 μm filtration (see Table 5.19). It appears that filtration has similar effects on both the BOD_5 and resin acids. This is illustrated in Figure 5.10.

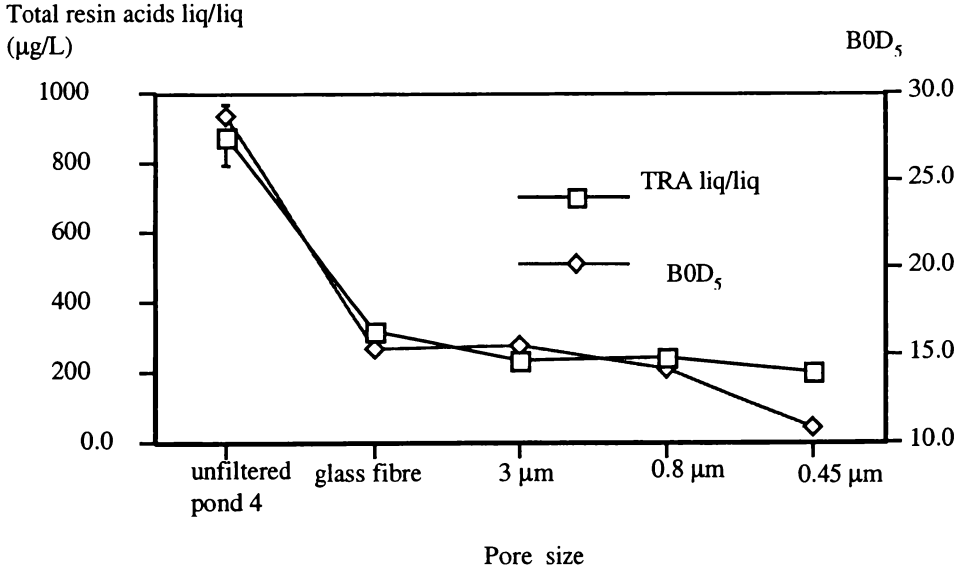

Figure 5.10. BOD_5 and total resin acids (liquid-liquid) (μg/L) determined for a sequentially filtered (glass fibre to 0.45 μm) pond 4 water sample.

5.4. Conclusions

Approximately 70% of the extractable resin acids present in effluent water discharged from Tasman's biological treatment were bound to 0.05-15 μm particles. This % corresponds with that reported in Chapters 3 and 4 for Tarawera River water samples.

The % contribution of particle bound resin acids to total resin acid levels increased from ca. 5% (clarifier) to 70% (pond 4 discharge) during the passage of effluent water through the treatment system.

Resin neutral compounds, generated from resin acids during passage through the treatment system, were predominantly (> 90%) particle bound.

Micro-filtration of the final effluent (pond 4 discharge) reduced colour levels by 33-62% for coloured species, depending on the pore size of the filtration media.

During treatment, free pimaric acid and dehydroabietic acid levels fall substantially, while the bound levels stay approximately constant. The level of free abietan-18-oic acid remains approximately constant in ponds 2, 3 and 4. On other hand, bound abietan-18-oic acid bound levels increase as bound abiet-13-enoic acid levels decrease. This is consistent with the conversion of abiet-13-enoic acid to abietan-18-oic acid. Particle binding appears to inhibit the degradation of pimaric acid and dehydroabietic acid, but particle bound abiet-13-enoic acid is virtually completely transformed down the treatment system.

The majority of volume of particulate matter in the treatment system and the river is associated with particles greater than 15 μm.

Both resin acids and BOD_5 are associated with similarly sized particles.

Because much of the BOD_5 and resin acids are associated with particulate matter, flocculation and/or filtration could provide the basis of effective removal technologies.

Chapter 6

Studies of biodegradation of treatment system samples

6.1. Introduction

Having demonstrated that degradation of resin acids and BOD_5 proceeds even when stored in sealed winchesters at 8°C, it was of interest to determine the extent of degradation that occurred in the 8 to 12 hours between sampling and analysis. In order to answer this question it was considered that it would be necessary to perform laboratory kinetic studies under aerobic conditions at 25°C. Kinetic data for BOD_5 and individual resin acids would be of value.

It was anticipated that a comparison of BOD_5 and resin acids data would show whether all resin acids decompose with similar rates and whether or not BOD_5 decomposition is similar to the decomposition of all or some of the resin acids. Details of the kinetic behaviour of individual resin acids will also provide information concerning resin acid transformations.

In Chapter 5 it was shown that the majority of BOD_5 and resin acids in the discharge from pond 4 are associated with particles. Further questions that could be usefully explored include:

(i) do particle bound resin acids and BOD_5 decompose with the same kinetics as non particle bound material?

(ii) does the formation of particle bound material continue throughout biological degradation or is it limited to a particular stage?

(iii) what is the nature and origin of particulate species?

6.2. Materials and methods

A series of bench reactor studies was envisaged. Details of the reactor system are shown in Figure 6.1. BOD_5, resin acids, absorbance and turbidity were monitored over the 6 to 31 day duration of the experiments. The principal series experiment involved sampling the clarifier, pond 1 and pond 4 (on different dates) and initiating reactor runs with the unfiltered samples (UFT0). Incubator runs were typically initiated within 8 h of sampling.

For clarifier and pond 1 water samples, two concurrent series of incubator experiments were performed. In the first series of experiments effluent water (4 x 2.5 L winchesters) was placed in a 20 L reactor vessel which was aerated and maintained at 25°C (see Figure 6.1). A glass fibre filtered at t = 0 (GFFT0) water sample (5 L) was also incubated (GFFT0).

Prior to the withdrawal of analytical samples, the reactor vessels were removed from the water bath, thoroughly shaken and allowed to stand for 10 min at room temperature. The analytical samples (2 x 100 mL sub-samples collected after discarding the first 20 mL) were withdrawn from a tap located 35 mm from the bottom of the vessel. Samples were taken at regular intervals from the start of the reactor runs and were converted to time elapsed from sampling (excluding the 8 h transportation time).

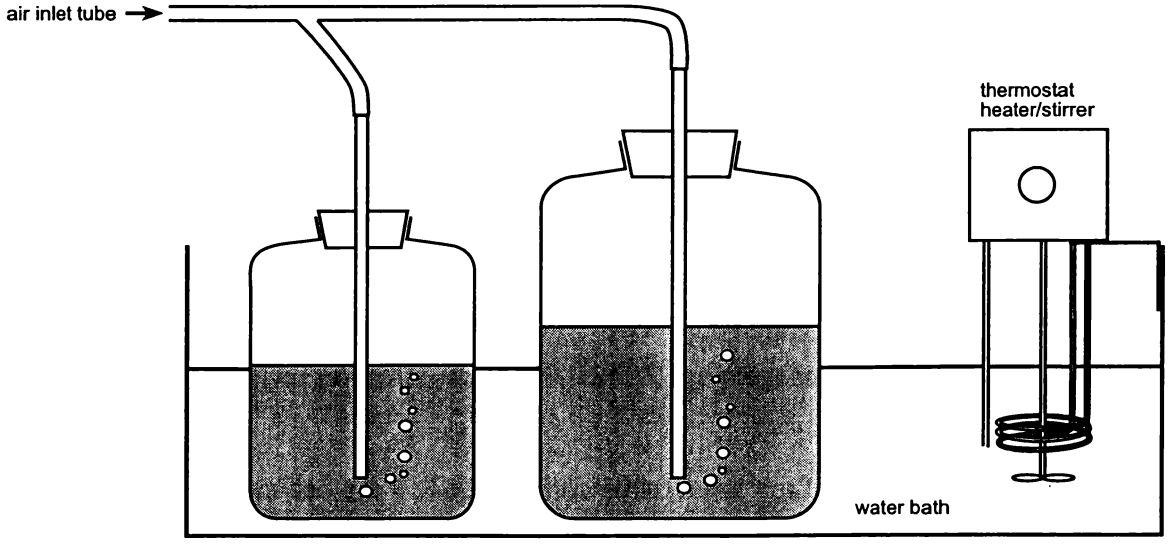

Figure 6.1. Schematic diagram of apparatus used to incubate the 5 L and 10 L wastewater samples (in 10 L and 20 L containers respectively).

For the unfiltered sample (20 L container) two sub-samples were withdrawn. One was extracted without filtration. The second sub-sample was 0.45 μm filtered and the filtrate and filter paper liquid/liquid extracted, or Soxhlet extracted, respectively. Resin acid levels were determined using the GC/MS protocols reported in Section 2.3.

Sub-samples from GFFT0 experiment (10 L container) were liquid/liquid extracted without filtration.
A summary of the samples investigated is as follows:

1. unfiltered sub-samples (liquid/liquid determination of resin acids, BOD_5, absorbance, turbidity)

2. sub-samples filtered through 0.45 μm (liquid/liquid determination of resin acids, absorbance, turbidity)

3. 0.45 μm filtration residues (Soxhlet extraction of resin acids)

Protocols for BOD_5, absorbance and turbidity measurements are given in Sections 2.7 and 2.6.2 respectively.

6.3. Results and discussion

6.3.1. Clarifier

Studies of unfiltered clarifier water

The levels of resin acids identified in sub-samples taken from the reactor vessel using clarifier water that was not filtered at t = 0 (UFT0) are presented in Table 6.1.

The results summarised in Table 6.1 show that resin acid levels remained essentially constant over the duration of the experiment, indicating the absence of microbial activity in the clarifier. Additionally, results determined for sub-samples, which were 0.45 μm filtered at the time of sampling, indicated an absence of particle formation or aggregation effects during the experiment.

Results for absorbance and turbidity changes in the reactor experiment are shown in Table 6.2. The data show no significant changes in the parameters listed.

BOD_5 analyses of clarifier water sub-samples were also undertaken, however no meaningful BOD_5 results were obtained, presumably due to the lack of biochemical activity in the clarifier effluent, which was less than 2 hours old. To determine a realistic BOD_5 for the clarifier effluent, seeding of the BOD_5 experiment may be necessary.

Table 6.1. Resin acids levels (µg/L) determined for unfiltered clarifier water (UFT0) collected 1/11/99 and subsequently aerated and incubated at 25°C for up to 6 days.

	Seco	Pim	18-Ab	DHAA	13-ene	Abiet	total
unfiltered liq/liq[b]							
day 0	415	1181	26	4571	647	248	7089
day 1	410	1088	16	4764	620	202	7101
day 2	385	1100	10	4863	626	190	7175
day 4	360	925	32	5119	589	-[a]	7025
day 6	410	1088	16	4932	625	103	7174
0.45 µm liq/liq[b]							
day 0	397	1030	13	5147	504	-[a]	7091
day 1	367	990	11	5299	463	-[a]	7131
day 2	388	1121	14	5201	591	51	7366
day 4	425	1081	14	5912	248[a]	-[a]	7679
day 6	393	1076	4	4420	584	288	6765
0.45 µm Soxhlet[b]							
day 0	27	33	4	95	43	-	202
day 1	15	39	-	100	39	-	194
day 2	26	47	-	114	29	-	217
day 4	19	33	-	99	-[a]	-	152
day 6	18	29	-	58	29	-	133

[a] partial or complete degradation of abietic acid , or abiet-13-enoic acid, to DHAA prior to GC/MS analyses indicated. Abbreviations, [b] filtered at time of sub sampling: Seco = secodehydroabietic acids 1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Abiet = abietic acid, total = total resin acids

Table 6.2. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for clarifier water, collected 1/11/1999, not filtered at t = 0, aerated and incubated at 25°C (UFT0).

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	norm
unfiltered A								
0 day	1.523	0.590	0.189	1.00	1.00	1.00	74.0	1.00
1 day	1.662	0.634	0.212	1.09	1.07	1.12	50.0	0.68
2 day	1.589	0.605	0.192	1.04	1.03	1.02	24.0	0.32
4 day	1.625	0.610	0.206	1.07	1.03	1.09	19.0	0.26
6 day	1.496	0.557	0.175	0.98	0.94	0.93	19.0	0.26
0.45μm filtered								
0 day	1.126	0.358	0.049	1.00	1.00	1.00	1.45	1.00
1 day	1.165	0.375	0.067	1.03	1.05	1.37	1.82	1.26
2 day	1.107	0.335	0.048	0.98	0.94	0.98	1.68	1.16
4 day	1.125	0.366	0.046	1.00	1.02	0.94	1.85	1.28
6 day	1.274	0.450	0.068	1.13	1.26	1.39	1.57	1.08

The low BOD5 values determined for the unseeded clarifier water samples probably indicates an absence of biological activity rather than an absence of degradable organic material in the clarifier water samples.

Studies of glass fibre filtered at t = 0 clarifier water

Only resin acid levels were determined in this experiment. Data are presented in Table 6.3.

Table 6.3. Resin acid levels (μg/L) determined for clarifier water collected 1/11/99, glass fibre filtered at t = 0, and subsequently aerated and incubated at 25°C for 6 days.

	Seco	Pim	18-Ab	DHAA	13-ene	Abiet[a]	total
liq/liq							
day 0	429	1102	-	4748	655	-	6954
day 1	409	1146	4.4	4365	645	243	6813
day 2	416	1129	3.8	4922	496	10	6977
day 4	458	1319	17	4746	444	-	6983
day 6	411	1091	14	4744	589	-	6849

[a] partial or complete degradation of abietic acid, Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Abiet = abietic acid, total = total resin acids.

Resin acid levels were similar to those determined for the unfiltered (UFT0) experiment. This result shows little resin acid is associated with gross particulate matter (fibre) or other particulate material removed by glass fibre filtration.

6.3.2. Pond 1

At each sampling time, three sub-samples were taken from the two incubation vessels (see Figure 6.1)

A sub-sample from each of the reactors was extracted without filtration A further sub-sample was withdrawn from the unfiltered experiment (20 L container) and 0.45 μm filtered at the time of sampling. These samples were analysed and extracted using the protocols reported in Sections 2.3.2 and 2.3.3.

In addition, a further sub-sample taken from the 20 L container (unfiltered experiment) was used for BOD_5, colour and turbidity measurements.

Resin acid data (pond 1)

Resin acid data for the UFT0 experiment are presented in Table 6.4. Normalised degradation curves for the total resin acid, particle bound (i.e. residue after filtration by 0.45 μm) and free (i.e. filtrate after filtration by 0.45 μm) are given in Figure 6.2

Table 6.4. Resin acid levels (µg/L) determined for unfiltered pond 1 water collected 27/1/2000, and subsequently aerated and incubated at 25°C for 31 days.

	Seco	Pim	18-Ab	DHAA	13-ene	Abiet	Cls	total	%
liq /liq (unfilt)									
day 0	606	1819	98	4591	1409	21	132	8676	100%[a]
day 1	581	1765	16	4986	602	-	159	8109	93%
day 2	470	1523	51	4436	828	-	121	7428	86%
day 3	494	1544	16	4294	864	-	112	7323	84%
day 4	390	619	7.7	2324	648	-	89	4077	47%
day 7	345	95	5.1	220	121	-	17	803	9%
day 10	227	96	-	93	14	-	6.8	436	5%
day 16	23	55	-	41	77	-	4.6	200	2%
day 21	11	24	4.6	32	38	-	1.5	112	1%
day 31	15	16	34	19	9	-	2.0	96	1%
liq /liq 0.45µm									
day 0	471	1588	55	4662	876	-	119	7770	90%
day 1	456	1479	12	4363	874	-	108	7292	84%
day 2	404	1194	11	3900	542	-	73	6125	71%
day 3	368	1105	12	3033	520	-	68	5105	59%
day 4	383	1072	36	2187	466	-	73	4216	54%
day 7	314	805	-	183	71	-	10	1383	18%
day 10	136	28	-	39	18	-	2.0	223	3%
day 16	5.9	8.9	-	18	10	-	0.8	44	1%
day 21	6.2	7.3	-	19	8.1	-	-	41	1%
day 31	15	5.5	-	16	-	-	1.0	37	0.5%
Soxhlet 0.45 µm									
day 0	77	320	2.2	450	246	-	43	1139	15%
day 1	71	298	2.4	424	244	-	42	1081	14%
day 2	54	234	2.1	345	166	-	33	835	11%
day 3	53	244	2.6	345	173	-	33	851	11%
day 4	31	139	0.9	157	86	-	18	432	6%
day 7	33	105	0.9	44	29	-	3.5	215	3%
day 10	31	78	-	56	27	-	4.0	196	3%
day 16	19	29	-	17	26	-	0.4	92	1%
day 21	11	21	-	12	18	-	1.5	64	1%
day 31	7	15	-	11	13	-	0.5	47	0.5%

[a] relative to day 0, not filtered, Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids.

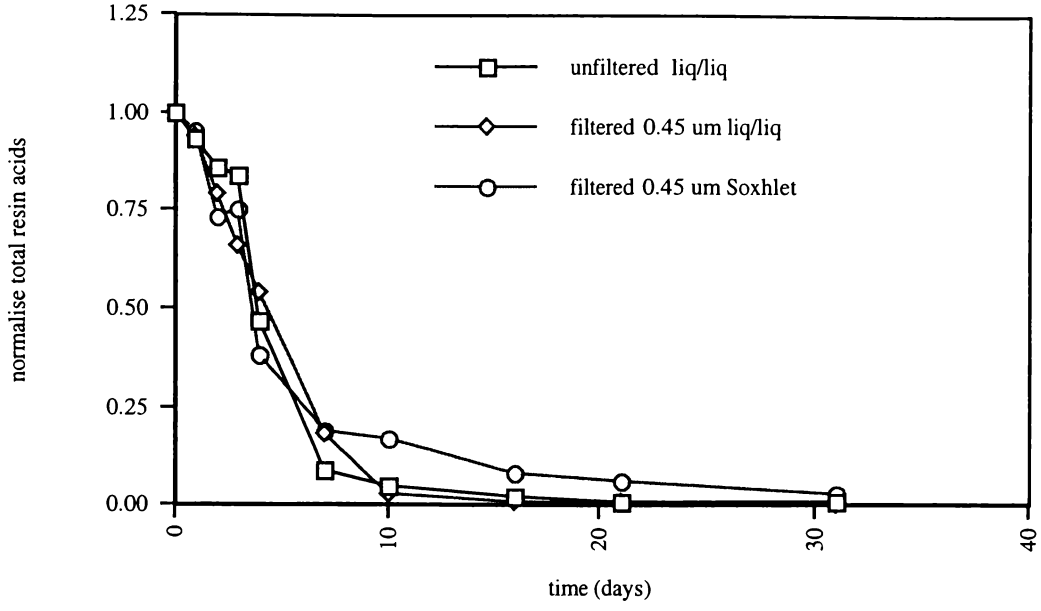

Figure 6.2. Normalised resin acid degradation curves. The data are for pond 1 samples collected 27/1/2000 and (a) unfiltered at the time of sampling, (b) filtered through 0.45 μm and (c) Soxhlet extracts of the 0.45 μm filter papers.

The similarity of the shapes of the normalised degradation curves presented in Figure 6.2 provides good evidence that total, bound and free resin acids in pond 1 water degrade at similar rates.

It was of interest to examine whether the principal resin acids groups behaved similarly. Figure 6.3 shows normalised curves for the degradation of the totals for the DHAA group (secodehydroabietic acids-1 and 2, dehydroabietic acid and abiet-13-enoic acid) and pimaric acid.

In both Figures 6.2 and 6.3, most of the degradation occurs over the first 7 to 10 days. The initial decomposition is followed at longer times by a slower process. This effect has been observed elsewhere (Hall and Liver 1996a).

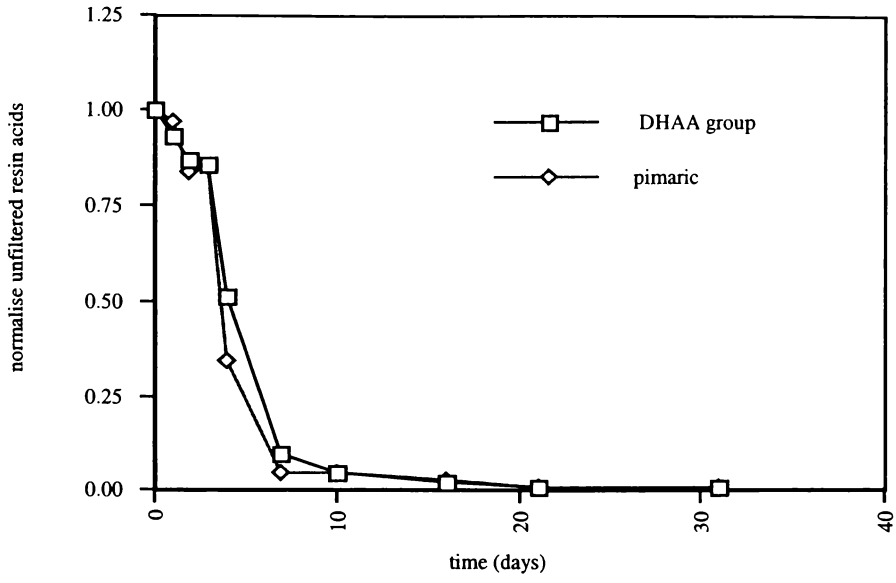

Figure 6.3. Normalised DHAA group and pimaric acid levels determined for unfiltered pond 1 water collected 27/1/2000.

Other parameters (pond 1)

Results for BOD_5, absorbance and turbidity changes in the reactor experiment are given in Table 6.5. Trends in BOD_5 data are plotted along with resin acids in Figure 6.4.

Figure 6.4. BOD_5 and total resin acid levels determined for unfiltered pond 1 water collected 27/1/2000.

Table 6.5. BOD_5, absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for unfiltered pond 1 water, collected 27/1/2000, aerated and incubated at 25°C.

	absorbance			normalised absorbance[a]			turbidity		BOD_5
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	norm	mg/L
unfiltered A									
day 0	2.236	0.880	0.283	1.00	1.00	1.00	230	1.00	96.3
day 1	2.233	0.874	0.280	1.00	0.99	0.99	128	0.56	86.3
day 2	2.129	0.824	0.252	0.95	0.89	0.89	100	0.43	78.5
day 3	1.797	0.649	0.165	0.80	0.58	0.58	90.0	0.39	71.4
day 4	1.662	0.634	0.142	0.74	0.50	0.50	88.0	0.38	60.0
day 7	1.496	0.557	0.115	0.67	0.41	0.41	48.6	0.21	30.0
day 10	1.491	0.550	0.105	0.67	0.63	0.37	36.5	0.16	22.5
day 16	1.499	0.557	0.098	0.67	0.35	0.35	21.9	0.10	19.0
day 21	1.493	0.535	0.117	0.67	0.41	0.41	4.73	0.02	16.8[b]
day 31	1.503	0.559	0.115	0.67	0.41	0.41	4.72	0.02	
0.45 µm filtered									
day 0	1.455	0.475	0.066	1.00[b]	1.00[b]	1.00[b]	3.85	1.00	
day 1	1.465	0.475	0.067	1.01	1.00	1.02	2.92	0.76	
day 2	1.477	0.475	0.068	1.02	1.00	1.03	2.68	0.70	
day 3	1.425	0.465	0.073	0.98	0.98	1.11	2.18	0.57	
day 4	1.225	0.460	0.070	0.84	0.97	1.06	1.85	0.48	
day 7	1.274	0.450	0.068	0.88	0.95	1.03	1.57	0.41	
day 10	1.265	0.448	0.065	0.87	0.94	0.98	1.26	0.33	
day 16	1.297	0.448	0.075	0.89	0.94	1.14	0.97	0.25	
day 21	1.398	0.492	0.098	0.96	1.04	1.48	0.88	0.23	
day 31	1.492	0.512	0.101	1.03	1.08	1.53	0.77	0.20	

[a]norm = normalised turbidity or absorbance, relative to unfiltered day 0,[b]relative to filtered day 0

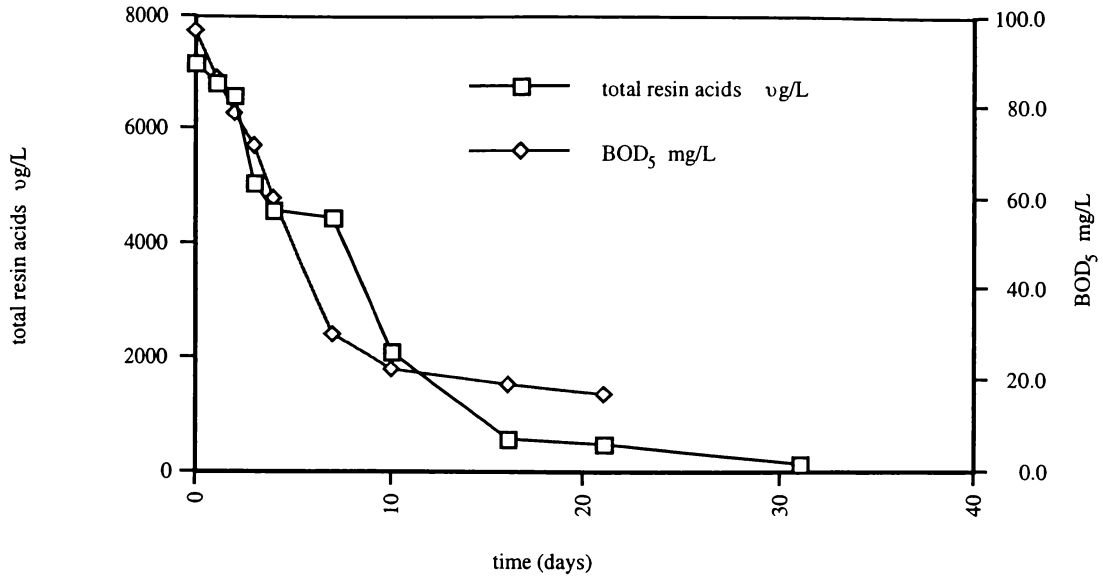

Figure 6.4. BOD_5 and total resin acid levels determined for unfiltered pond 1 water collected 27/1/2000.

There appears to be an almost linear decrease of BOD_5 over the first 7 days followed by a slower rate of decrease. The resin acid data show similar trends except that there appears to be relatively longer lived BOD_5 than resin acid. It can be estimated from the slopes of the two curves that approximately 3% of the resin acid and BOD_5 would degrade in the 12 hours that generally separates sampling and analysis. This assumes that the sample temperature remains close to 25°C.

It was noted that visible sediment formed in the system from about day 5.

Sediment studies (pond 1)

In order to investigate the sediment described above, the residual 400 mL liquid containing settled material in the reactor at the end of the degradation experiment was thoroughly mixed and divided into 4 x 100 mL sub-sample. One of the sub-samples was liquid/liquid extracted without filtration. A second sub-sample was filtered through 0.45 μm (residue A) filter paper, prior to liquid/liquid or Soxhlet extraction of the filtrates and filter paper respectively. Resin acid levels were determined using the GC/MS protocols

reported in Sections 2.3.2 and 2.3.3 respectively. A third sub-sample was 0.45 μm filtered and used for BOD_5, colour and turbidity analyses. In addition the weight loss ignition (TVSS) was determined. The fourth sub-sample was used to determine the same parameters without filtration. Data are summarised in Table 6.6.

Table 6.6. Resin acid levels (μg/L), BOD_5 and TVSS (mg/L) identified in residual water samples from unfiltered pond 1 incubation experiment.

sample	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	BOD_5	TVSS
Liq/liq (residue A)	234	833	5.9	634	1399	66	3173	38.5	
Liq/liq 0.45 μm filtered	3.4	11	-	15	20		49	6.0	
Soxhlet 0.45 μm filtered	280	819	11	560	1583	72	3325		57%

Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids.

The data indicate that abiet-13-enoic acid is the major resin acid component present in the sediment formed during the incubation experiment. Most of the resin acids and BOD_5 are particle bound and much of the particulate matter is organic.

SEM studies of pond 1 particulates

Freeze dried samples (see Section 2.9) of particulate matter (residue on the filter paper) recovered by 0.45 μm filtration of the t = 0 and t = 31 day incubation experiment water samples (see Section 6.2) were prepared in order to observe changes (if any) in the nature of particulates during the 31 days period of the incubation experiment.

SEM analyses of the t = 0 and 31 day samples revealed high concentrations of silica and calcium rich particulates together with O and C responses. It is believed that the needle-like material visible in the t = 0 micrograph (Figure 6.5), and to a much lesser extent in the t = 31 day micrograph (Figure 6.6), may be cellulose fibres. Much less of this material was present in the day 31 sample taken from the incubation experiment.

The dominant material visible in the t = 31 day micrograph appeared as amorphous carbon rich aggregate. Overnight furnacing at 550°C eliminated organic material and

afforded residual particulate matter, which was shown to be comprised mainly of Si and Ca (see Figure 6.7).

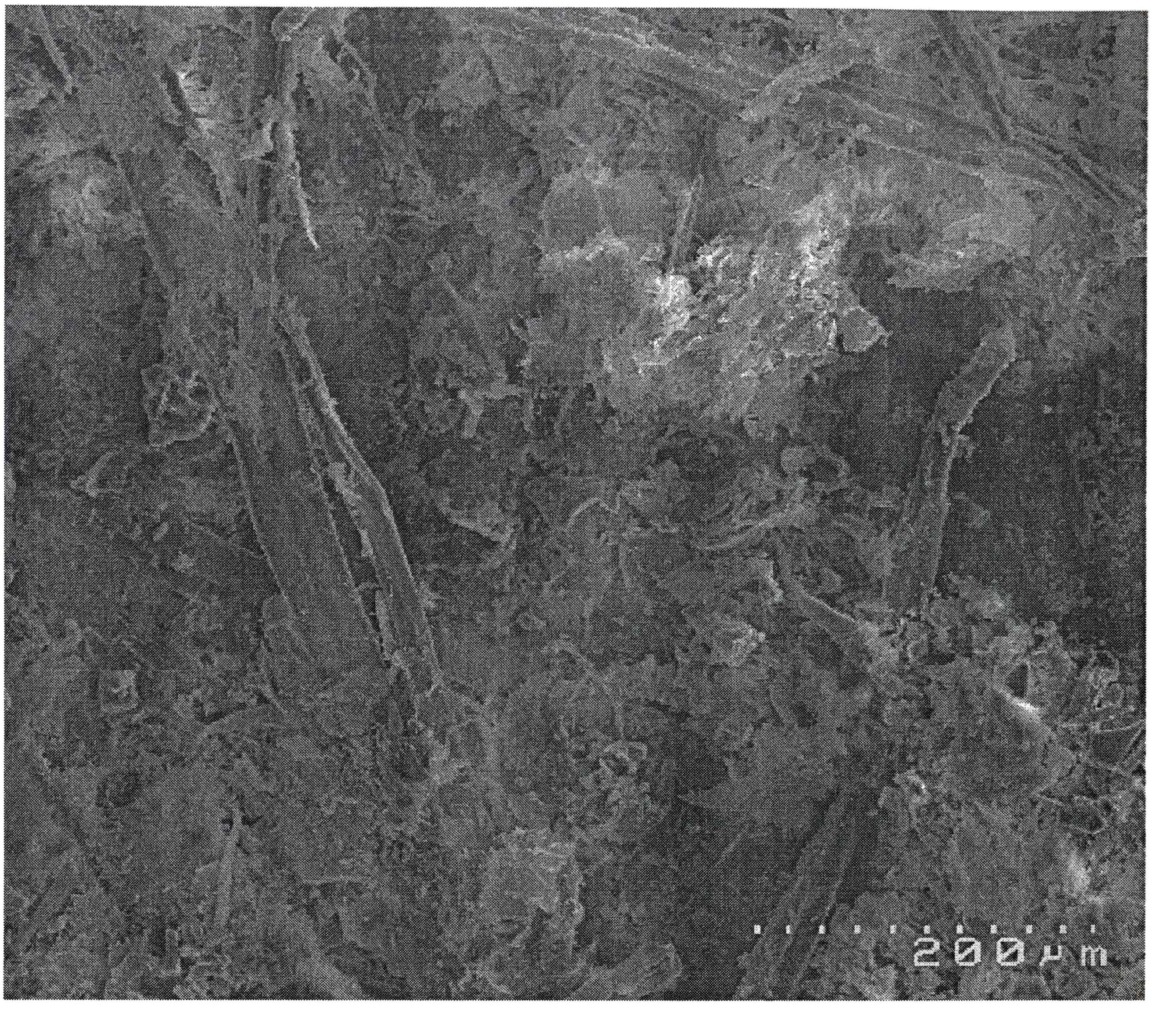

Figure 6.5. SEM micrograph of particulate matter recovered by 0.45 µm filtration at t = 0 of the unfiltered pond 1 incubation experiment (water sample collected 27/1/2000).

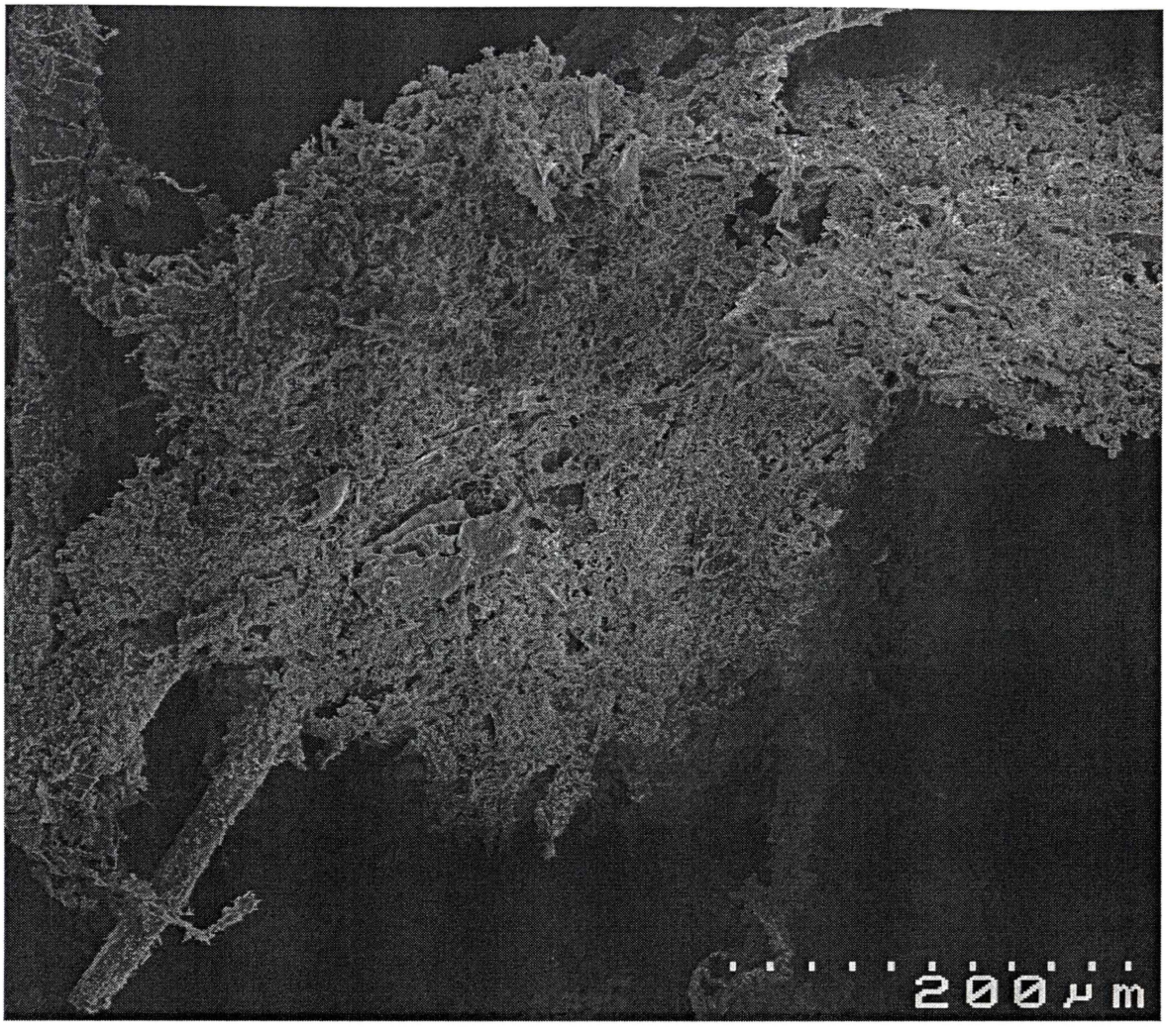

Figure 6.6. SEM micrograph of particulate matter recovered from by 0.45 µm filtration of a 31 day water sample from the unfiltered pond 1 incubation experiment. The elemental composition was principally calcium, silicon, carbon and oxygen (water sample collected 27/1/2000).

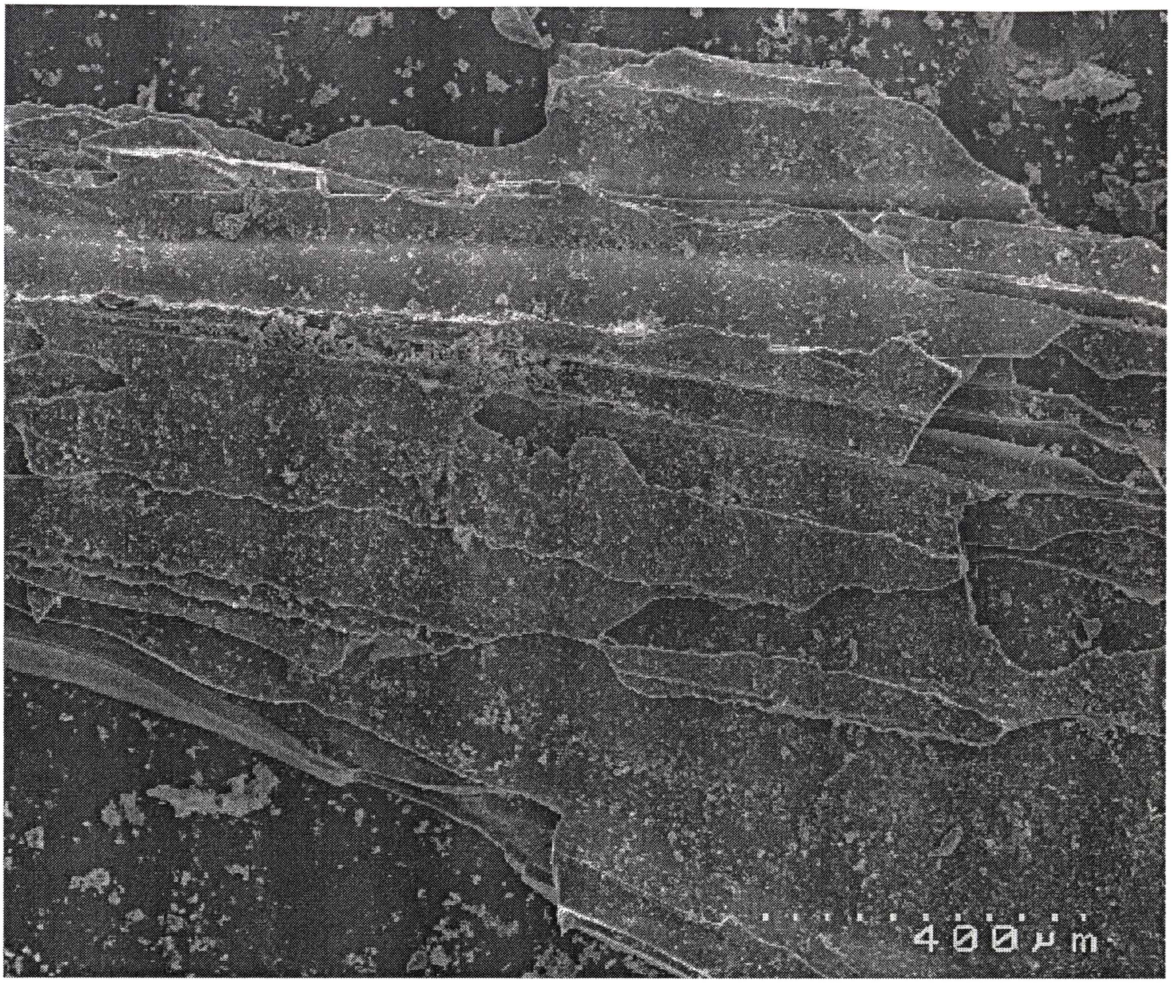

Figure 6.7. SEM micrograph of particulate matter recovered by 0.45 µm filtration of a 31 day water sample from the unfiltered pond 1 incubation experiment and then ignited at 550°C overnight. It contained principally calcium and silicon (water sample collected 27/1/2000).

Pond 1 water glass fibre filtered at t = 0 (GFFT0)

As was the case for the clarifier, a second reactor experiment was performed where gross visible particulate matter was removed by glass fibre filtration at t = 0 (GFFT0). Resin acids, BOD_5, absorbance and turbidity were determined over a period of 31 days. Reactor conditions were as previously described (see Section 6.2). Resin acid data are presented in Table 6.7. BOD_5, absorbance and turbidity are presented in Table 6.8.

Table 6.7. Resin acid levels (µg/L) determined for pond 1 water collected 27/1/2000, glass fibre filtered at filtered at t = 0, and subsequently aerated and incubated at 25°C for 31 days (GFFT0).

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
liq/liq								
day 0	441	1399	-	4379	854	93	7166	100%
day 1	389	1324	12	4369	613	91	6798	95%
day 2	402	1282	15	4289	516	86	6589	92%
day 3	368	1292	7.3	2791	531	77	5066	71%
day 4	326	898	10	3194	93	71	4592	64%
day 7	342	777	8.2	3178	45	91	4442	62%
day 10	449	(1314)[a]	4.3	192	67	63	2090	29%
day 16	416	58	4.7	47	20	30	575	8%
day 21	380	22	-	28	18		447	6%
day 31	51	18	-	39	18	2.8	129	2%

[a] result may be anomalous. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 6.8. Absorbance at 270, 340 and 440 nm, turbidity (NTU) and BOD_5 determined for pond 1 water, collected 27/1/2000, glass fibre filtered at t = 0, aerated and incubated at 25°C (GFFT0).

	absorbance			normalised absorbance			turbidity		BOD_5
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	norm	
day 0	1.709	0.606	0.117	1.00	1.00	1.00	3.87	1.00	75.0
day 1	1.762	0.644	0.131	1.03	1.06	1.12	3.85	0.99	70.1
day 2	1.740	0.630	0.124	1.02	1.04	1.06	3.89	1.01	63.7
day 3	1.668	0.582	0.121	0.98	0.96	1.034	3.97	1.03	55.2
day 4	1.645	0.540	0.118	0.96	0.89	1.010	3.27	0.84	48.0
day 7	1.625	0.609	0.116	0.95	1.01	0.991	3.56	0.92	22.5
day 10	1.513	0.526	0.101	0.89	0.87	0.863	3.37	0.87	14.7
day 16	1.544	0.527	0.104	0.90	0.87	0.889	3.74	0.97	10.6
day 21	1.647	0.599	0.116	0.96	0.99	0.991	3.83	0.99	7.7[a]
day 31	1.729	0.614	0.109	1.01	1.01	0.932	3.26	0.84	

[a] measured on day 22.

In general the degradation of the resin acids in the filtered systems was similar to that observed for the unfiltered system. However secodehydroabietic acids 1 and 2 showed virtually no degradation over most of the experiment. The explanation for this is not clear. On one occasion (day 10) an expectedly high pimaric acid level was also found.

The variation of total resin acids and BOD_5 is shown diagrammatically in Figure 6.8. The trends shown in Figure 6.8 are similar to those shown in Figure 6.4 for the unfiltered system except that amount of long-lived BOD_5 has been reduced by filtration. This is consistent with the removal of cellulose fibre by filtration. Glass fibre filtration has little effect on the degradation of the species remaining after filtration.

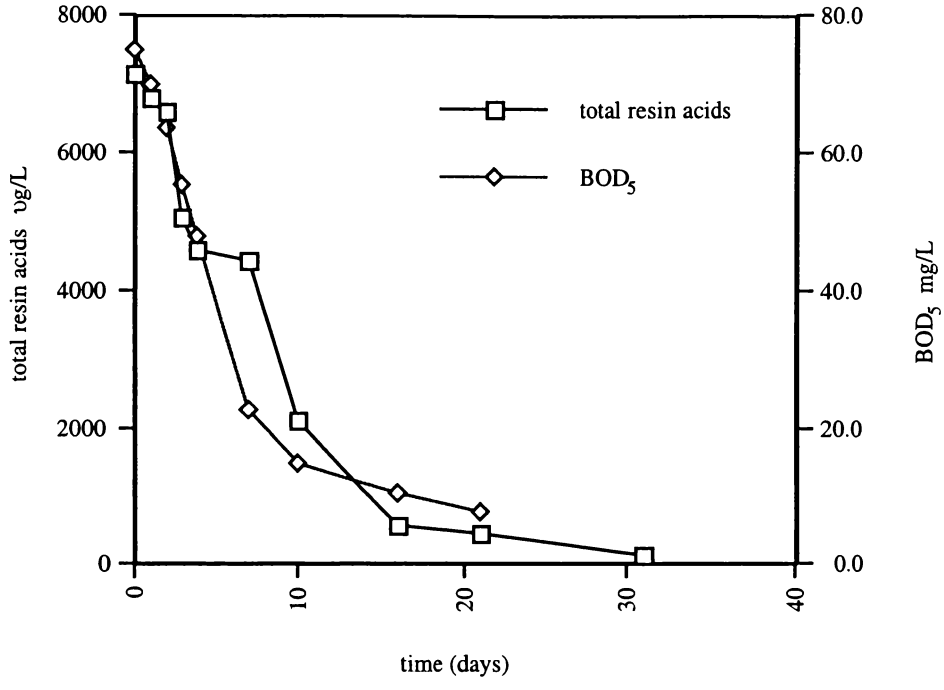

Figure 6.8. BOD_5 and total resin acid levels determined for a glass fibre filtrated pond 1 water sample at t = 0 (GFFT0), collected 27/1/2000.

It can be estimated from the slopes of the two curves that approximately 6% and 9% of the resin acid and BOD_5 respectively would degrade in the 12 hours that generally separates sampling and analysis. This assumes that the sample temperature remains close to 25°C.

The effect of initial filtration on the amounts of filtrate BOD_5 and total resin acids is illustrated in Figures 6.9 and 6.10.

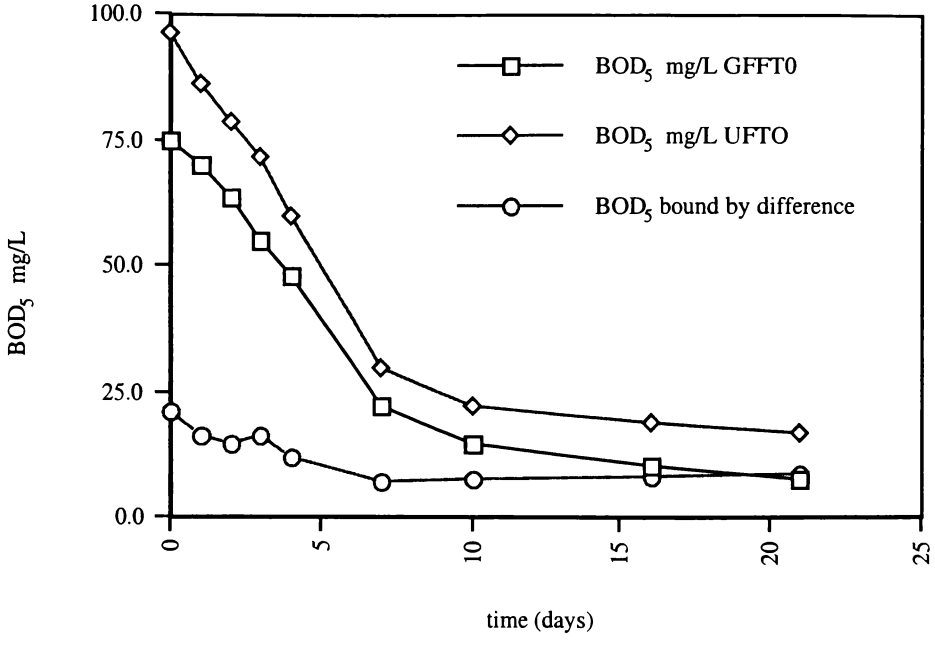

Figure 6.9. Comparison of BOD_5 curves for filtered (GFFT0) and unfiltered (UFT0) pond 1 water. The difference in BOD_5 data is also plotted.

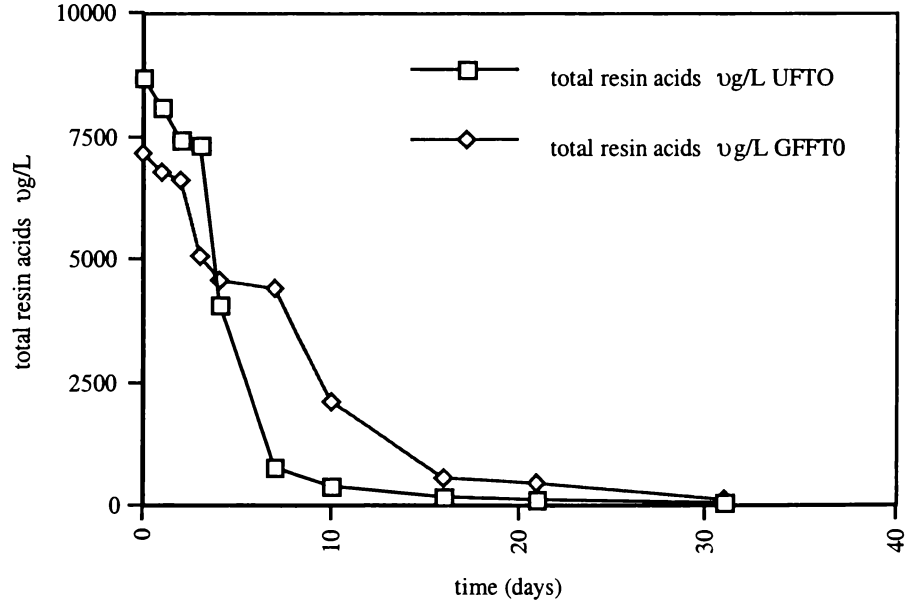

Figure 6.10. Comparison of total resin acid degradation curves for filtered (GFFT0) and unfiltered (UFT0) pond 1 water.

It is clear from the plots that glass fibre filtration at the commencement of the incubation experiments reduces the measured BOD_5 and total resin acids determined at subsequent times. The difference in values for the filtered and unfiltered experiment gives information about the rate of degradation of material removed by the initial filtration. The difference value for BOD_5 decreases at a slower rate than either the filtered or unfiltered systems indicating a slower rate of degradation of the particulate matter removed by filtration.

Prior filtration has little effect on resin acid degradation data. The normalised curves for the unfiltered and filtered water are quite similar for the first 6 days of the degradation experiment. At longer times there is some indication that in the filtered system resin acids are degraded at a slower rate than in the unfiltered system, however the apparent effect is of the order of the expected experimental uncertainty.

Other parameters (pond 1)

Data for colour, BOD_5 and turbidity are summarised in Table 6.9.

Table 6.9. Absorbance at 270, 340 and 440 nm, turbidity (NTU) and BOD_5 determined for filtered pond 1 water (GFFT0) collected 27/1/2000, aerated and incubated at 25°C.

	absorbance			normalised absorbance			turbidity		BOD_5
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	norm	
day 0	1.709	0.606	0.117	1.00	1.00	1.00	3.87	1.00	75.0
day 1	1.762	0.644	0.131	1.03	1.06	1.12	3.85	0.99	70.1
day 2	1.740	0.630	0.124	1.02	1.04	1.06	3.89	1.01	63.7
day 3	1.668	0.582	0.121	0.98	0.96	1.034	3.97	1.03	55.2
day 4	1.645	0.540	0.118	0.96	0.89	1.010	3.27	0.84	48.0
day 7	1.625	0.609	0.116	0.95	1.01	0.991	3.56	0.92	22.5
day 10	1.513	0.526	0.101	0.89	0.87	0.863	3.37	0.87	14.7
day 16	1.544	0.527	0.104	0.90	0.87	0.889	3.74	0.97	10.6
day 21	1.647	0.599	0.116	0.96	0.99	0.991	3.83	0.99	7.7[a]
day 31	1.729	0.614	0.109	1.01	1.01	0.932	3.26	0.84	

[a] determined on day 22

Colour, turbidity and general appearance of the filtered system differed markedly from the unfiltered system (see Table 6.5). The colour and turbidity of the filtered system remained essentially constant and there was much less sediment formation during the experiment.

Sediment (pond 1)

Approximately 300 mL of water remained at the end of the incubation experiment. This was divided into three samples for liquid/liquid extraction, liquid/liquid and Soxhlet extraction after 0.45 μm filtration and BOD_5 determination on an unfiltered sample. Data are summarised in Table 6.10.

Table 6.10. Resin acid levels (μg/L) identified in liquid /liquid and Soxhlet extracts of a residual water sample from the filtered incubation of pond 1 water (GFFT0).

sample	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	BOD_5
1. Unfiltered	3.3	2.4	-	5.8	-	-	12	
2. BOD_5 sample								10
3. Filtered 0.45 μm								
liquid/liquid		-	-	12	-	-	12	
Soxhlet				2.0			2.8	

Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids.

The most significant aspects of the results obtained from the experiment was the relative absence of residual precipitate (too little to weigh), the reduced BOD_5 and the low levels of particle bound resin acid formed during the experiment. However the amount of resin acid determined in the sediment studies was too low for firm conclusions to be drawn.

6.3.3. Pond 4

For pond 4 experiments were performed only with an unfiltered water sample (UFT0). At each sampling time, five 100 mL sub-samples were taken. The first sub-samples was liquid/liquid extracted. The second sub-sample was used for BOD_5, colour and turbidity measurements. The third sub-sample was filtered through 0.45 μm filter paper, prior to liquid/liquid or Soxhlet extraction of the filtrates and filter papers respectively. Resin acid levels were determined using the GC/MS protocols reported in Sections 2.3.2 and 2.3.3. The fourth and fifth samples were combined, filtered through 0.45 μm filter papers and used for BOD_5, colour and turbidity measurements.

Resin acids (pond 4)

Resin acid data for the pond 4 water samples are presented in Table 6.11.

Table 6.11 Resin acid levels (μg/L) determined for unstabilised, unfiltered, pond 4 water sample collected 22/6/2000 and extracted over 15 days from collection date (UFT0).

Time (days)	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	recv	norm
unfiltered									
day 0 (8 h)	241	297	480	354	983	5.8	2360	100%	1.00
day 2	211	251	509	363	639	6.4	1980	84%	0.84
day 3	132	155	307	314	557	5.2	1471	62%	0.62
day 4	103	131	254	279	488	7.2	1262	53%	0.53
day 7	23	64	98	127	199	0.5	511	22%	0.22
day 13	12	41	59	79	134	0.7	326	14%	0.14
day 17	14	45	58	66	87	0.3	271	11%	0.11
liq/liq (0.45 μm)									
day 1	115	70	106	146	363	5.9	806	34%	1.00
day 3	87	61	97	158	138	5.7	545	23%	0.68
day 4	69	53	99	158	123	8.4	510	21%	0.63
day 7	14	16	20	59	37	1.1	147	6%	0.18
day 13	3.3	6.5	7.5	17	16	0.8	52	2%	0.06
day 17	1.3	3.7	4.7	7.2	9.4	0.8	27	1%	0.03
Soxhlet (0.45 μm)									
day 1	69	135	436	400	394	0.2	1435	61%	1.00
day 3	60	90	191	182	343	0.9	867	37%	0.60
day 4	32	65	141	147	195	0.2	580	25%	0.40
day 7	19	57	84	99	179	0.1	438	19%	0.31
day 13	9.2	36	47	54	116	0.0	262	11%	0.18
day 17	8.4	25	23	48	54	0.0	159	7%	0.11

Abbreviations: Seco = secodehydroabietic acids 1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, recv = recovery relative to the day 0 sample, norm = normalise relative to day o sample.

Normalised degradation curves for the total resin acids, particle bound resin acids (i.e. 0.45 μm filtered) and free resin acids (i.e. not filtered) are given in Figure 6.11. Normalised resin acid levels for DHAA group resin acids, pimaric acid and 18-abietanoic acid are presented in Figure 6.12.

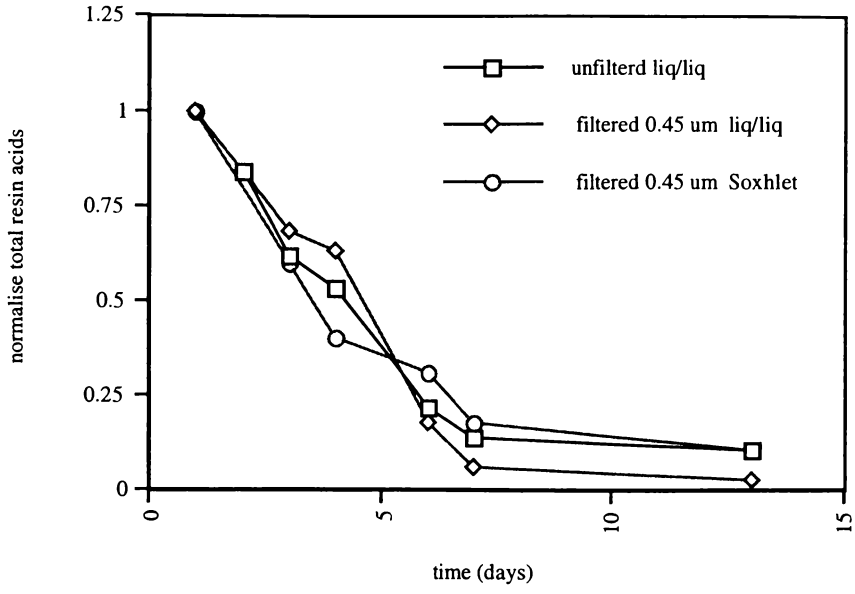

Figure 6.11. Total resin acid levels (µg/L) determined for an unstabilised, unfiltered, pond 4 water sample collected 22/6/2000 and extracted over 15 days from collection date (UFT0).

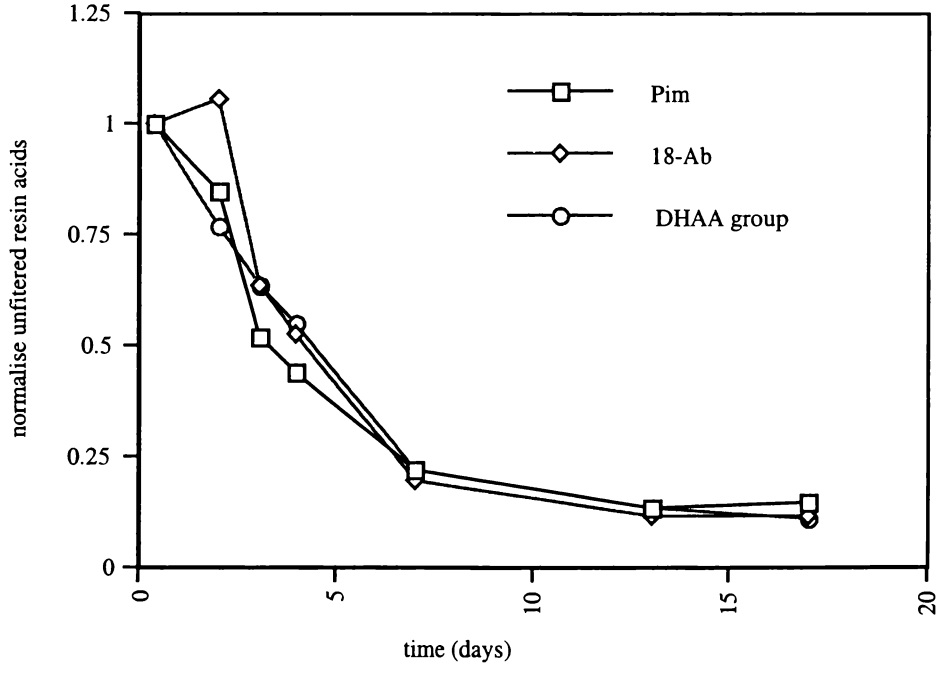

Figure 6.12. Normalised total DHAA group resin acids, pimaric acid and abietan-18-oic acid determined for pond 4 water collected 22/6/2000.

Surprisingly, the normalised degradation curves are all very similar, indicating similar rates of degradation. The plots (not given) for free and bound components of the DHAA group, pimaric acid and abietan-18-oic acid were also very similar. It had been expected that because abietan-18-oic acid is the principal survivor of the treatment process, it would degrade more slowly. This was not supported by the experimental results. Causes other than enhanced stability (under aerobic conditions) need to be found for the predominance of abietan-18-oic acid in the treatment system discharge.

Other parameters (Pond 4)

Results for BOD_5, absorbance and turbidity changes in the reactor experiment are given Table 6.12. Trends in BOD_5 data are plotted along with total resin acids in Figure 6.

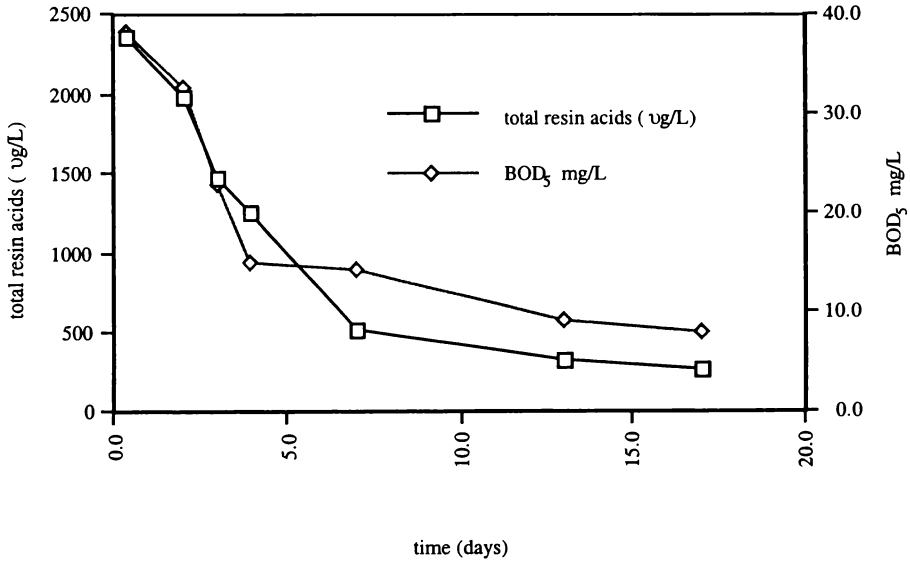

Figure 6.13. BOD_5 and total resin acids determined for an unfiltered pond 4 water collected on 22/6/2000.

Table 6.12. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for unfiltered and filtered pond 4 water sample collected 22/6/2000, and examined for 17 days following collection.

	absorbance			normalised absorbance[a]			turbidity		
time (day)	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	norm[a]	BOD_5
unfiltered									
day 0	1.912	0.818	0.377	1.00	1.00	1.00	97.7	1.00	38.3
day 1	1.865	0.781	0.326	0.98	0.95	0.86	49.8	0.51	
day 2	1.902	0.819	0.333	0.99	1.00	0.88	44.3	0.45	32.6
day 3	1.466	0.546	0.152	0.77	0.67	0.40	39.4	0.40	22.8
day 4	1.543	0.555	0.153	0.81	0.68	0.41	27.0	0.28	15.1
day 6	1.530	0.567	0.158	0.80	0.69	0.42	22.3	0.23	14.2
day 7	1.424	0.555	0.150	0.74	0.68	0.40	13.9	0.14	9.1
day 13	1.423	0.588	0.155	0.74	0.72	0.41	5.23	0.05	8.1
day 17	1.321	0.518	0.109	0.69	0.63	0.29	5.92	0.06	
filtered 0.45 μm									
day 0	1.281	0.398	0.067	1.0[b]	1.00[b]	1.00[b]	4.15	1.00[b]	
day 1	1.277	0.394	0.066	1.00	0.99	0.18	3.17	0.76	14.1
day 2	1.288	0.441	0.087	1.01	1.11	0.23	3.02	0.73	10.4
day 3	1.289	0.451	0.092	1.01	1.13	0.24	4.19	1.01	8.4
day 4	1.338	0.482	0.108	1.04	1.21	0.29	4.20	1.01	6.8
day 6	1.259	0.468	0.101	0.98	1.18	0.27	2.53	0.61	5.7
day 7	1.246	0.467	0.109	0.97	1.17	0.29	1.99	0.48	2.9
day 13	1.336	0.51	0.099	1.04	1.28	0.26	1.30	0.31	2.2
day 17	1.227	0.475	0.096	0.96	1.19	0.25	1.24	0.30	

[a] norm = normalised turbidity or absorbance, relative to unfiltered day 0, [b] relative to day 0.

BOD_5 data are shown diagrammatically in Figure 6.14. The free, bound and total BOD_5 curves are of similar shape indicating that free and particulate BOD_5 in pond 4 water degrades at similar rates. Free and bound resin acid decomposed with similar kinetics.

BOD_5 and resin acid degradation for filtered and unfiltered pond 4 samples is illustrated in Figures 6.15, 6.16 and 6.17. All the curves have similar shapes within the limits of experimental error.

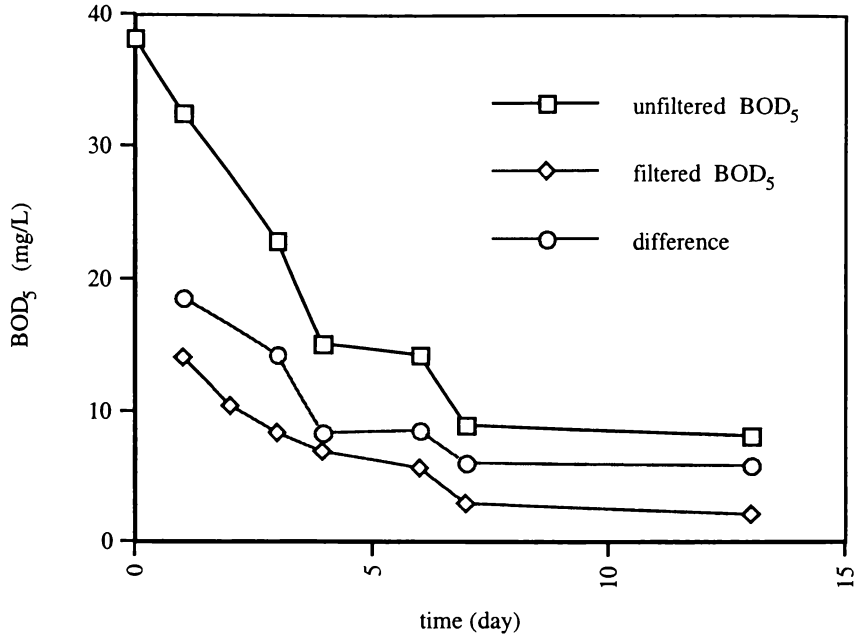

Figure 6.14. Total (= free and bound) (unfiltered), free (filtered), and bound (difference) BOD_5 determined for pond 4 water collected 22/6/2000.

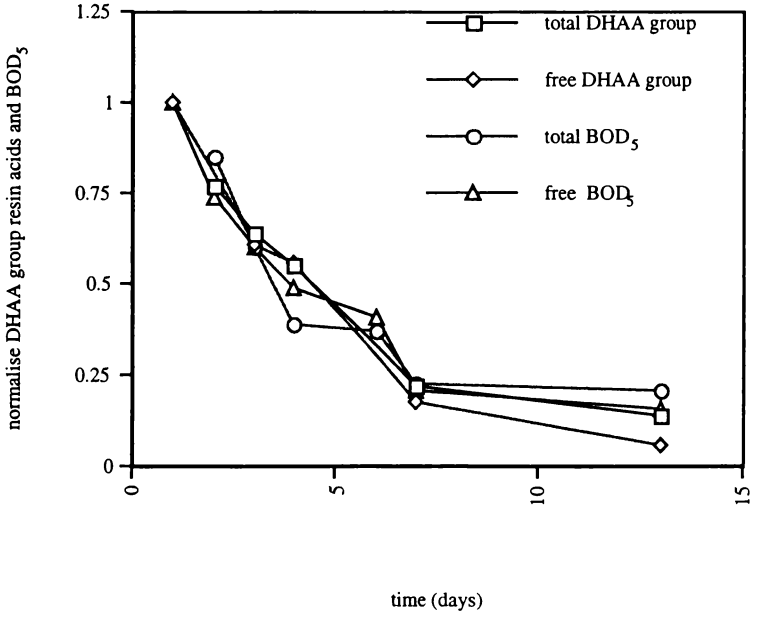

Figure 6.15. Normalised total and free DHAA group resin acids and BOD_5 determined for pond 4 water collected 22/6/2000.

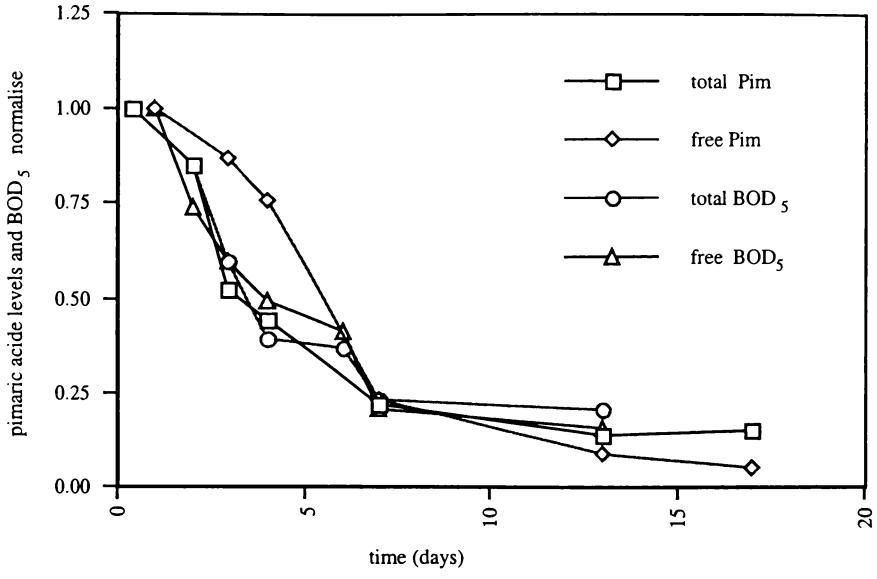

Figure 6.16. Normalised total and free pimaric acid levels and BOD_5 determined for pond 4 water collected 22/6/2000.

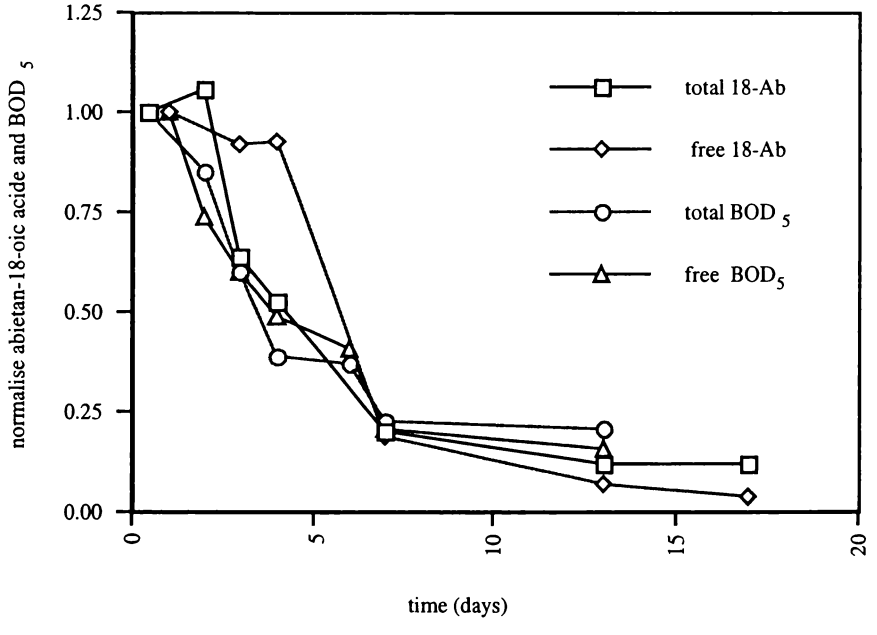

Figure 6.17. Normalised total and free abietan-18-oic acid and BOD_5 determined for pond 4 water collected 22/6/2000.

Absorbance and turbidity (pond 4)

In general significant decreases in both colour and turbidity were determined for unfiltered pond 4 during the 17 day experimental period (see Table 6.12). These results could be explained by a settling effect (similar to that identified in Chapter 4). However for 0.45 μm filtered water no significant changes occurred during the 17 day period (changes were within experimental error).

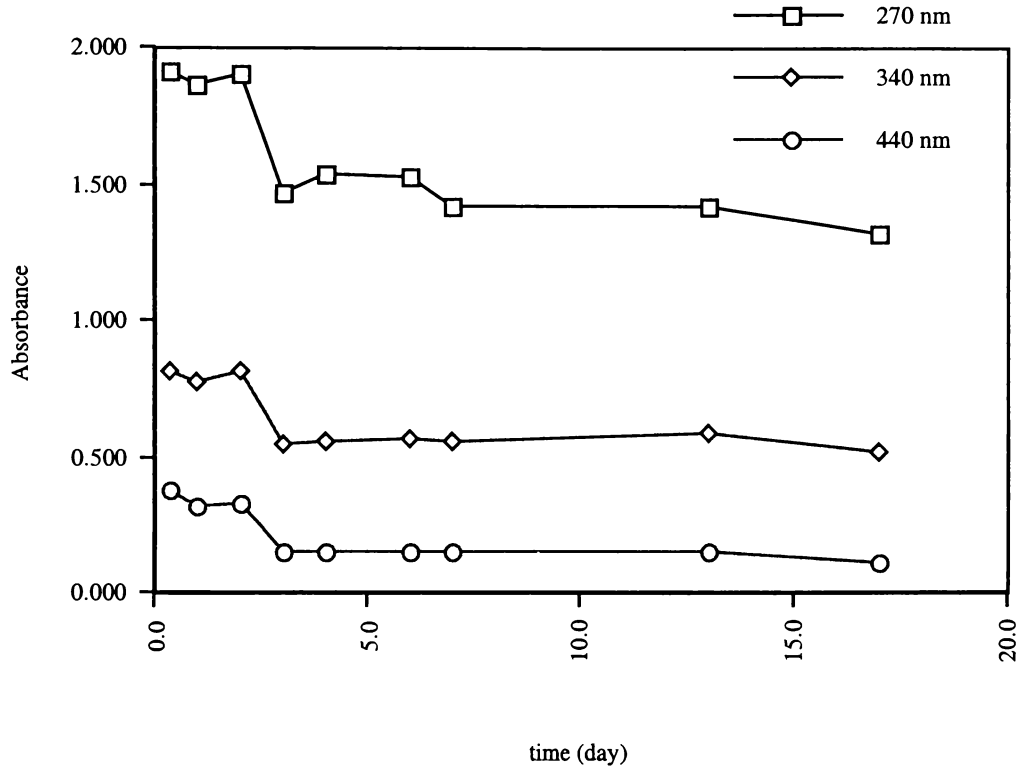

Figure 6.18. Absorbance at 270, 340 and 440 nm determined for unfiltered pond 4 water collected 22/6/2000, and examined for the following 17 days.

6.5. General discussion

An initial objective of the work described in this chapter was to follow aerobic degradation kinetics to assess whether degradation of samples in the time between sampling and receipt of samples in the laboratory was important. The kinetic studies performed at 25°C showed that in general the degradation of resin acids and BOD_5 over

the 8-12 h delay time would be between 3 to 8%. This is about the order of the error in the analysis. Samples other than those to be used in incubation studies, should be stabilised at the time of sampling.

The complete degradation curves for total resin acids, principal resin acid groups (pimaric acid and DHAA groups), abietan-18-oic acid (pond 4) and BOD_5 all indicate that the BOD_5 and resin acids behave similarly in ponds 1 and 4. This also applies to the filterable (free) and non-filterable (bound) resin acid and BOD_5 as determined by experiments where the degradation was compared for systems unfiltered and filtered at t = 0 (pond 1) and also for system not filtered initially but filtered at the time of sampling (pond 4).

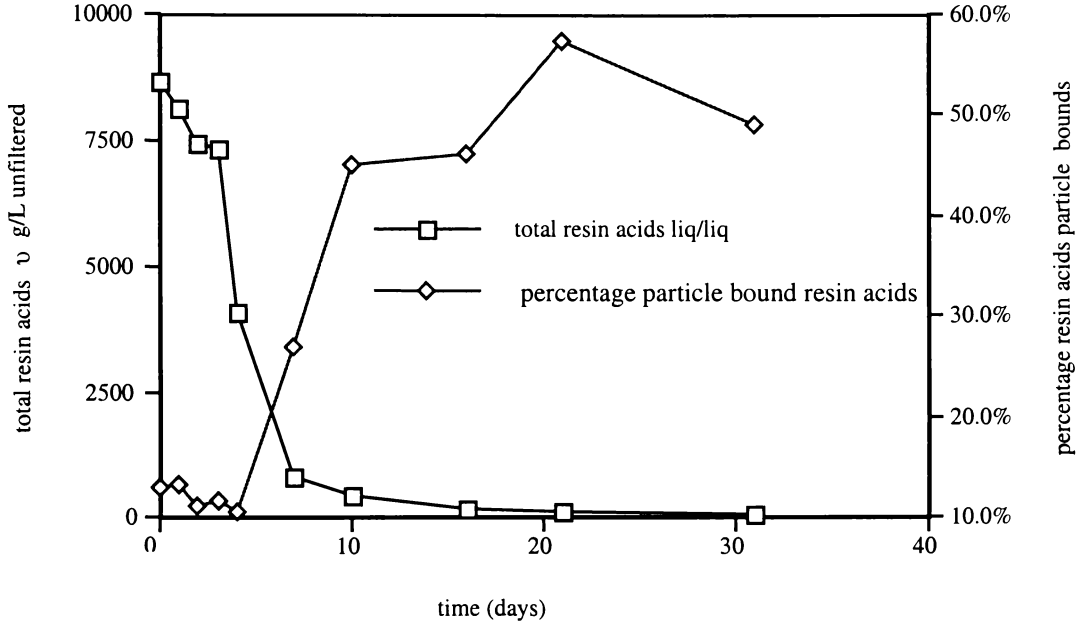

Figure 6.19. Comparison of total resin acid degradation curves for unfiltered (UFT0) pond 1 water and percentage particle bound resin acids.

The change with time of the relative amounts of free and bound resin acids is of interest. It has previously been determined that most of the resin acids in the final discharge and also in the Tarawera River are particle bound. Figure 6.19 illustrates trends in the percentage of bound resin acid with time and degradation of total resin acid. This figure shows that the percentage of particle bound resin acids increases during aerobic degradation. The effect becomes pronounced after day 4. It is not apparent in the individual curves for the degradation of total, free and bound resin acids, which, as has been noted (see Section

6.3.2), have similar shapes. This effect only appears to becomes significant when the majority of the resin acids have degraded.

The picture that emerges from the degradation studies reported in this chapter is one in which resin acids and BOD_5 undergo aerobic degradation with similar kinetics. Abietan-18-oic acid is not produced under these conditions but the percentage of particle bound resin acid increases to about 50% of the total after 4 to 10 days. This is consistent with the observation that after approximately 5 days in the treatment system, most of the resin acid is particle bound. Other processes, however, must also be occurring in the treatment system. These give rise to abietan-18-oic acid and result in the total particle bound material being close to 75%.

6.6. Conclusions

Very little degradation of species present in clarifier water occurred during incubation studies.

In pond 1 most of the resin acid and BOD_5 is free. Filtration through glass fibre removes no resin acid but about 10% of the initial BOD_5. Filtration removed the component of BOD_5 that degraded slowly. It is concluded that particulate BOD_5 degrades more slowly than free BOD_5.

The three resin acid groups (DHAA group resin acids, pimaric acid, and abietan-18-oic acid) show very similar degradation kinetics irrespective of whether they are free or bound. Soluble BOD_5 exhibits similar behaviour.

During degradation of pond 1 water, the percentage of particle bound resin acid increases dramatically after about 4 days. By the end of the experiment sediment containing high levels of resin acid was formed. The predominant resin acid in both the suspended particles and the sediment was abiet-13-enoic acid.

Colour and turbidity of pond 1 and pond 4 samples were significantly reduced by incubation. When filtered through glass fibre at $t = 0$, the changes in these parameters with degradation were much less.

Chapter 7

Flocculation and pumice filtration of Tarawera River and effluent water samples

7.1. Introduction

In Chapter 5 it was established that more than 90% of the resin acid content of primary effluent water generated by pulp and paper mill processing operations are not associated with particles. On the other hand in Chapters 3 and 4 it was shown that > 70% of the extractable resin acids discharged from Tasman's biological treatment system, to the Tarawera River, were bound to 0.05-15 micron particles.

It was therefore of interest to determine if the amount of particle associated resin acids, BOD_5 and chromophoric (coloured) species present in primary effluent water could be increased by treatment with flocculants. A combination of sedimentation and/or low cost filtration might then be used as a primary treatment, to replace or supplement biological treatment.

As effluent standards from pulp and paper mill wastewater treatment plants have become more stringent, the use of coagulants and/or flocculants as a tertiary treatment for bleached kraft effluents has already been trialed. Hodgson *et al* (1998) have reported that polyacrylamide treatment of a bleached kraft effluent reduced the colour, COD, AOX, and 2,3,7,8-tetrachlorodibenzofuran and mixed-function oxygenase induction by 61%, 24%, 23%, 80% and 18% respectively.

While it is known that flocculation of biologically treated pulp mill effluents using $FeCl_3$, $AlCl_3$, $Al_2(SO_4)_3$ or $FeSO_4$ can remove up to 90% of the colour, (Stephenson and Duff 1995), little is known about the ability of these and other flocculating agents to reduce BOD_5 and remove resin acids (which may be the major toxicants present in discharged effluents) from pulp mill effluents.

The Tarawera River is profoundly affected by pulp and paper discharges. The water quality is such that it finds little use even for irrigation. It may be possible to make the water more usable by a treatment such as flocculation.

The principle objectives of the work reported in this chapter were:

i) the determination of the ability of readily available flocculating agents to remove, resin acids, colour and turbidity from Tarawera River water

ii) an evaluation of the extent to which flocculating agents can remove resin acids, colour, BOD_5 and turbidity from mill effluent prior to, and after, biological treatment

iii) an assessment of extent to which pumice filtration, either alone or in combination with a flocculation step, can remove resin acids, colour and turbidity from untreated and treated mill effluents

iv) a preliminary evaluation of the possibility that flocculating agents can be recovered and reused.

vi) an evaluation of the possibility that, for highly diluted receiving waters, pre-concentration of resin acids by flocculation might be developed into an analytical methodology with lower detection limits than achievable using conventional liquid-liquid extraction.

7.2. Experimental

Sample collection

Water samples in screw capped 2.5 L glass winchesters or 20 L plastic containers were collected from the Tarawera River at the SH30 bridge, and from the outflow of ponds 1 and 4 of Tasman's treatment system (sites B and E respectively, see Figure 5.1). Sodium azide (0.1%) was added at the time of collection to the pond 1 and pond 4 samples, and some of the river water samples. Water samples were stored at 4-8^{o}C until required for analyses.

7.2.1. SH30 Tarawera River samples

Jar test experiment: Survey of flocculants

Preliminary coagulation and flocculation experiments were performed using SH30 Tarawera River water and the jar test procedure is described in Section 2.12. The performance of flocculants was assessed using colour and turbidity data. The following reagents were investigated as flocculating agents:

polyferric sulfate (PFS)
polyaluminium chloride (PAC)
aluminium sulfate ($Al_2(SO_4)_3.16H_2O$)
polyacrylamide
calcium oxide
calcium hydroxide
calcium chloride,
soda lime
ferric sulfate
ferrous sulfate
sodium aluminate

PAC, PFS and alum were found to be the best chemicals to remove colour.

Jar test experiment: Optimum dose and pH

Two further series of preliminary experiments were performed using SH30 Tarawera River water and the jar test procedure described in Section 2.12.

In the first series of experiments the pH during the flocculation step was maintained at 7.3 and flocculant doses in the range 5-40 mg/L (PFS) and 10-100 mg/L (PAC and alum) were used. Flocculant performance was assessed using colour and turbidity data.

In the second series of experiments 20 mg/L of PFS, or 60 mg/L of PAC or alum were added and pH of the flocculation step was varied between pH 2-12 (PFS, alum and PAC).

Flocculant performance was assessed using colour and turbidity data. The purpose of these experiments was to determine optimum dose and pH.

Stirred beaker experiments

Most of the flocculation studies were performed in a magnetically stirred 2 L beaker. In a typical experiment, SH30 Tarawera River water (1 L) was placed in a 2 L beaker and the water sample was stirred at room temperature using a magnetic stirrer. Varying amounts of PFS (5-40 mg/L), PAC (10-100 mg/L) or alum (10-100 mg/L) were added, and the pH of the solutions adjusted to pH 5.1-5.3 (PFS), or 5.9-6.1 (PAC and alum) using 2 mol/L H_2SO_4 and the resulting solutions were stirred for 1 h. Mixtures were allowed to settle for 2 h and precipitated material was separated by filtration through Whatman No. 1 filter paper. Resin acid levels (determined after adjustment of the pH of the filtrate to 7.4), colour and turbidity data were determined for the filtrates using the procedures given in Sections 2.2 and 2.6.2 respectively.

Recovery of resin acids from PFS or PAC flocculated material

Sodium azide stabilised SH30 Tarawera River water (1 L) was placed in a 2 L beaker and the pH of the water sample was adjusted to 5.9-6.1 (PAC) or 5.1-5.3 (PFS). PFS (20 mg/L) solution, or PAC (70 mg/L) was added and mixture stirred for 1 h, and then left to settle for 2 h. Precipitates were separated by filtration through Whatman No. 1 filter paper. The gel-like precipitate was transferred using a spatula to a 200 mL beaker and resolublised in ca. 100 mL by stirring at pH 8.5, 6.8, 4.5, 3.5 or 2 (PFS experiments) or 7.2, 9.0, 10.3 or 12.0 (PAC and alum experiments). pH adjustment was achieved using 2 mol/L NaOH or H_2SO_4. Resolublised solutions were liquid/liquid extracted, without further pH adjustment, as described in Section 2.2.

Comparison of centrifugation vs. filtration recovery of PAC flocculated resin acids

Unstablised SH30 Tarawera River water (1 L) was placed in a 2 L beaker and the pH of the water sample was adjusted to 5.9-6.1. The optimum dose of PAC (70 mg/L) was added and mixture stirred for 1 h, and the mixture was left to settle for 2 h. Precipitated material was separated by filtration through Whatman No. 1 filter paper, or by

centrifugation at 7500 g for 30 min using a Beckman model J2-2M. centrifuge. The gel-like precipitates recovered by filtration, or centrifugation, were transferred using a spatula to a 200 mL beaker and resolublised in ca. 100 mL of distilled water by stirring at pH 9.5-10. pH adjustment was achieved using 2 mol/L NaOH. The resolublised solutions were liquid/liquid extracted, without further pH adjustment, as described in Section 2.2.

PAC or PFS flocculation of SH30 Tarawera River water and recovery of resin acids

Unstablised SH30 Tarawera River water (3 x 2.5 L winchesters) collected on 14/1/99 was combined and sub-divided as described below. Firstly, 2 x 1 L reference river water samples were liquid/liquid extracted without pH adjustment as described in Section 2.2. Secondly, 2 x 1 L samples were flocculated with 70 mg/L PAC at pH 5.9-6.1. Flocculated material was recovered by Whatman No. 1 filtration and resolublisation at pH 10 (1st sample), or at pH 6 (2nd sample). Resin acid levels were then determined by liquid/liquid extraction of the resolublised at pH 10 and 6 respectively. Thirdly, 2 x 1 L samples were flocculated, as described above, with 20 mg/L PFS at pH 5.1-5.0. Flocculated material was recovered by Whatman No. 1 filtration and resolublised at pH 10 (1st sample), or at pH 3.5 (2nd sample). Resin acid levels were determined by liquid/liquid extraction of the resolublised solution at pH 10 and 3.5 respectively. In each the flocculation experiments, the pH of a portion of the Whatman No. 1 filtrate was adjusted to 7.0-7.4 and liquid/liquid extracted as described in Section 2.2.

Investigation of recovery and reuse of flocculating agent (PAC)

An experiment was performed using PAC (70 mg/L) where, after the initial flocculation, the floc was dissolved/dispersed using alkaline solutions and then used for a second flocculation.

Sodium azide stabilised SH30 Tarawera River water (1 L) was placed in a 2 L beaker and the pH of the water sample was adjusted to 5.9-6.1. PAC (70 mg/L) was added and mixture stirred for 1 h and then left to settle for 2 h. The precipitate was separated by filtration through Whatman No. 1 filter paper. The gel-like was transferred using a spatula to a 200 mL beaker and resolublised in ca. 100 mL by stirring at pH 10. The resulting solution was added to a second 1 L sample of SH30 Tarawera River water and the pH of

the solution adjusted to 5.9-6.1. The mixture was stirred for 1 h and then left to settle for 2 h. The precipitate was separated by filtration through Whatman No. 1 filter paper. The gel-like precipitate was transferred using a spatula to a 200 mL beaker and resolublised in ca. 100 mL of distilled water by stirring at pH 10. Resin acids were recovered by liquid/liquid extraction at pH 10 as described in Section 2.2.1.

7.2.2. Pond 1 experiments

PFS or PAC flocculation with sequential filtration

Pond 1 water samples (1 L) were flocculated using PFS (10-60 mg/L), or PAC (10, 36 or 100 mg/L) at pH 5.9-6.0. (PAC), or 5.1-5.3 (PFS), as described as above for SH30 Tarawera River samples. The flocculation process was monitored by particle size analysis. A portion of each of the thoroughly mixed flocculant solutions (250 mL) was sequentially filtered through glass fibre (250 mL), 0.8 μm (160 mL) and 0.2 μm (80 mL) filter papers. The pH of 80 mL portions of the filtrates was adjusted to 7, prior to resin acid, colour and turbidity analyses, which were performed as described in Sections 2.2.1 and 2.6.2 respectively.

After removal of the 250 mL sub-sample for sequential filtration, flocculated material was allowed to settle for 2-3 h. Precipitated material, recovered by sequential filtration, was transferred using a spatula to a 200 mL beaker and resolublised in ca. 100 mL of distilled water by stirring at pH 10 and liquid/liquid extracted at pH 10 as described in Section 2.2.1.

Pumice filtration

Pumice filtration experiments were performed using natural pumice-material collected adjacent to pond 2 of Tasman's treatment system. Following collection, the pumice was air-dried for ca. 30 days and the oven dried overnight at 35°C and sieved. Surface area, pore radius, and density of sieved material were determined by BET analysis, as described in Section 2.12. Hydraulic conductivity was determined using the methodology described in Section 2.1. The pore volume of sieved pumice was measured by placing accurately

weighed pumice material (ca. 30 g) in a 200 mL beaker. Water was added until the pumice floated and the mixture was boiled for 30 min. The excess water was decanted, the water level adjusted to the surface of the pumice and the contents of beaker were weighed. The difference between the initial and final weights were calculated as the volume of the water in the voids within and between the particles. Table 7.1 presents of the physical characteristics of the dried, sieved pumice.

Table 7.1. Physical characteristics of pumice-containing material collected on 27/1/2000 from a site adjacent pond 2 of to Tasman's treatment system.

size (mm)	void volume mL/g	surface area m^2/g	pore radius A	sample density mL/g	hydraulic conductivity m/s x 10^3
0.85	1.12	2.3	10.4	2.44	2.40
1.6	1.68	2.2	10.1	2.00	3.44
2.4	1.86	1.9	9.2	1.66	3.67
3.1	2.02	1.9	9.2	0.97	3.76
4.5	2.38	1.5	9.2	0.69	5.63

Filtration experiments were performed as described in Section 2.13. The BOD_5 of pumice flocculated filtered pond 1 water samples were determined as described in Section. 2.7.

Pumice absorption experiments

Pumice absorption experiments were performed using 1-70 g of pumice material and 200 mL of sodium azide stabilised pond 1 water. Mixtures were stirred for 2 h and allowed to stand overnight, after which the supernatant was decanted and liquid/liquid extracted as designed in Section 2.2. No pH adjustment was used in these experiments. Resin acid, colour and turbidity data were as determined as described in Section 2.2.1.

7.2.3. Pond 4 experiments

Flocculation of pond 4 water samples was performed as above for SH30 Tarawera River water samples. Pumice filtration experiments were performed as described for pond 1 water samples. The BOD_5 of pumice filtered pond 4 water samples were determined as

described in Section 2.7. Resin acid, colour and turbidity data were as determined as described in Sections 2.2.1 and 2.6.2 respectively.

7.2.4. Flocculation as an analytical pre-concentration step

The possibility of using flocculation as a pre-concentration step in the analysis of resin acids in very dilute solutions was investigated.

Undiluted experiments.

Procedures used for flocculation and recovery of resin acids from undiluted river water samples are described in Section 7.2.1.

5 fold dilution experiment.

Two x 1 L sub-samples of sodium azide stabilised SH30 Tarawera River water were taken form a well mixed 2.5 L winchester. One 1 L sub-sample was liquid-liquid extracted as described in Section 2.2. 4 L of doubly distilled water and 0.97 mL of a 360 g/L PAC solution was added with stirring to the second 1 L sub-sample. The pH of the second sample was immediately adjusted to pH 5.5-5.9 and stirring was continued for 10 h, after which the solution was allowed to stand (settle) overnight. The upper zone (ca. 4 L) was removed using a water pump. A 1 L portion of the upper zone (supernatant) was liquid/liquid extracted as described in Section 2.2. Precipitated material was recovered by Whatman No. 1 filtration and transferred using a spatula and a wash bottle to a 200 mL beaker and resolublised in ca. 100 mL of distilled water by stirring at pH 9.5-10.0. pH adjustment was achieved using 2 mol/L NaOH. The resolublised solutions were liquid/liquid extracted, without further pH adjustment, as described in Section 2.2.

10 and 50 fold dilution experiments.

The procedure above was repeated using 9 or 49 L of doubly distilled water and 1.9 or 9.72 mL of 360 g/L PAC, respectively. Resin acids were recovered using the liquid/liquid extraction protocol described in Section 2.2.

7.3. Results and discussion

7.3.1. SH30 Tarawera River water

The ability of a number of flocculating agents, including alum, CaO, soda lime, polyacrylamide, ferric sulfate, ferrous sulfate, polyferric sulfate (PFS) and polyaluminium chloride (PAC), to remove resin acids, colour and turbidity from Tarawera River water samples collected downstream of Tasman's discharge point, was investigated in a series of preliminary experiments. The effectiveness or otherwise of a flocculant was initially assessed using only colour and turbidity data.

Of the foregoing flocculating agents only PFS, PAC and alum were found to satisfactorily remove (or reduce) colour and turbidity. Two further series of preliminary experiments were performed using these flocculants, to determine their optimum dose and flocculation pH.

Optimum doses (without pH adjustment of the river water sample) were found to be ca. 20 mg/L for PFS and ca. 60 mg/L for alum or PAC. Using these dose levels, the optimum pH was 5.9-6.1 for alum and 5.9-6.1 for PAC. These pHs are similar to those found by several other authors (Beulker and Jakel 1993; Edzwald *et al* 1993). Subsequently a more detailed series of experiments was performed in which the pH was maintained at the optimum value and flocculant dose levels were varied. Resin acid, colour and turbidity data were determined in these experiments (Tables 7.2-7.7).

Colour data determined in preliminary experiments, without pH adjustment, for flocculants, other than alum, PFS and PAC are given in Tables A3.1–A3.8 of the Appendix.

7.3.2. Alum

The results obtained for SH30 Tarawera River water samples, which were dosed with 20-100 mg/L alum at pH 5.9-6.1 and subsequently Whatman No. 1, filtered, are presented in Tables 7.2 and 7.3. A 20 mg/mL alum dose of removed ca. 79% of resin acids (Table 7.2), leaving 54%, 46% and 35% of colour at 270, 340 and 440 nm respectively (Table 7.3). A

greater dose of flocculating agent (ca. 60 mg/mL) was needed to remove coloured species, which absorbed at 440 nm and to reduce turbidity to below 0.6 NTU.

Table 7.2. Resin acids level (μg/L) determined for pH 5.9-6.1 alum (20-100 mg/L) flocculated and Whatman No. 1 filtered SH30 Tarawera River water samples collected on 27/7/98.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30 A	3.8	3.3	25.4	10.2	11.3	0.8	54.8	
SH30 B	4.9	4.1	30.9	12.3	14.2	0.9	67.3	
average[a]	4.4	3.7	28.2	11.2	12.7	0.9	61.1	100%
Alum dose								
20 mg/L	0.5	0.9	5.3	3.2	3.0	0.2	13.1	21%[b]
40 mg/L	0.6	0.5	1.6	0.9	-	-	3.6	6%
60 mg/L	0.1	0.2	1.0	0.6	-	-	1.9	3%
80 mg/L	-	-	0.1	0.1	-	-	0.2	0%
100 mg/L	-	-	0.1	0.1	-	-	0.2	0%

[a] mean of duplicate analyses, [b] recovery relative to unfiltered water. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 7.3. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for alum (20-100 mg/L) flocculated and Whatman No. 1 filtered SH30 Tarawera River water collected 27/7/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440nm	270 nm	340 nm	440 nm	NTU	norm[a]
SH30	0.143	0.057	0.020	100%	100%	100%	9.56	100%
Alum dose								
20 mg/L	0.077	0.026	0.007	54%	46%	35%	8.67	91%
40 mg/L	0.070	0.025	0.009	49%	44%	45%	2.96	31%
60 mg/L	0.046	0.013	0.000	32%	23%	0%	1.06	11%
80 mg/L	0.050	0.014	0.002	35%	25%	10%	1.12	12%
100 mg/L	0.039	0.009	0.000	27%	16%	0%	1.21	13%

[a] normalised turbidity.

7.3.3. PFS

The results obtained for SH30 Tarawera River water samples which were dosed with 20-35 mg/L PFS (resin acid data) or 2.5-40 mg/mL PFS (colour and turbidity data) and subsequently Whatman No. 1 filtered are presented in Tables 7.4 and 7.5.

A 20 mg/mL PFS dose removed ca. 97% of resin acids (Table 7.4), eliminated colour at 270, 340 and 440 nm and reduced turbidity to 0.93 NTU (Table 7.5) respectively.

Table 7.4. Resin acids levels (μg/L) determined for pH 5.1-5.3 PFS (20-35 mg/L) flocculated and Whatman No. 1 filtered SH30 Tarawera River water samples collected on 16/9/98.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30 A	5.4	2.6	16.6	5.6	11.0	0.6	41.8	
SH30 B	5.3	2.3	16.2	5.8	10.8	0.6	41.0	
average	5.3	2.5	16.4	5.7	10.9	0.6	41.4	100%[a]
PFS dose								
20 mg/L	0.9	-	0.1	0.4	-	-	1.4	3%
25 mg/L	-	-	0.1	0.5	-	-	0.6	1%
30 mg/L	-	-	tr	0.2	-	-	0.2	1%
35 mg/L	-	-	0.2	0.3	-	-	0.5	1%

[a] recovery relative to unfiltered water Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 7.5. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for PFS (2.5-40 mg/L) flocculated and Whatman No. 1 filtered SH30 Tarawera River water collected 16/9/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	norm[a]
SH30	0.119	0.044	0.017	100%	100%	100%	7.04	1.00
PFS dose								
2.5 mg/L	0.025	0.008	0.003	21%	18%	18%	6.92	98%
5 mg/L	0.018	0.005	0.000	15%	11%	0%	6.92	98%
10 mg/L	0.006	0.001	0.000	5%	2%	0%	6.68	95%
20 mg/L	0.000	0.000	0.000	0%	0%	0%	0.93	13%
25 mg/L	0.018	0.005	0.000	15%	11%	0%	0.99	14%
30 mg/L	0.011	0.000	0.000	9%	0%	0%	0.99	14%
35 mg/L	0.006	0.002	0.000	5%	5%	0%	0.90	13%
40 mg/L	0.000	0.000	0.000	0%	0%	0%	0.88	13%

[a] normalised turbidity

7.3.4. PAC

The results obtained for SH30 Tarawera River water samples, which were dosed with 20-80 mg/L PAC, and subsequently Whatman No. 1 filtered are presented in Tables 7.6 and 7.7.

A 40 mg/L PAC dose removed ca. 97% of resin acids (Table 7.6), however 44%, 30% and 20% of colour at 270, 340 and 440 nm respectively remained. A greater dose (ca. 70-80 mg/L) was required to reduce colour and turbidity to acceptable levels (Table 7.7).

Table 7.6. Resin acids levels (μg/L) determined for PAC (20-80 mg/L) flocculated at pH 5.1-5.3 and Whatman No. 1 filtered SH30 Tarawera River water collected on 16/9/98.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30 A	5.4	2.6	16.6	5.6	11.0	0.6	41.8	
SH30 B	5.3	2.3	16.2	5.8	10.8	0.6	41.0	
average[a]	5.3	2.5	16.4	5.7	10.9	0.6	41.4	100%
PAC dose								
20 mg/L	0.3	0.6	3.0	2.0	-	1.1	6.9	17%
40 mg/L	-	-	0.7	0.4	-	-	1.1	3%
60 mg/L	-	-	0.5	0.4	-	-	0.8	2%
80 mg/L	-	-	-	-	-	-	-	0%

[a] mean of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 7.7. Absorbance at 270-nm, 340 and 440 nm and turbidity (NTU) determined for PAC (20-80 mg/L) flocculated and Whatman No. 1 filtered SH30 Tarawera River water collected 16/9/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	normal.
SH30	0.121	0.044	0.015	100%	100%	100%	6.99	100%
PAC dose								
20 mg/L	0.083	0.028	0.007	69%	64%	47%	1.55	22%
40 mg/L	0.053	0.013	0.003	44%	30%	20%	1.45	21%
60 mg/L	0.033	0.005	0.000	27%	11%	0%	1.07	15%
70 mg/L	0.018	0.004	0.000	15%	9%	0%	1.23	18%
80 mg/L	0.007	0.002	0.000	6%	5%	0%	1.05	15%

It is clear from the data presented in Tables 7.2-7.7 that 20-70 mg/L doses of some flocculating agents can substantially the reduce resin acids, colour and turbidity levels of Tarawera River water samples. Of the reagents trailed, those based upon Fe and Al were most effective. Generally, on a weight of reagent basis, the Fe systems were more

effective than the Al systems but prior hydrolysis to the polycationic forms had no major advantage.

7.3.5. Recovery of resin acids from flocs

In order to confirm mass balance in the flocculation experiments, the recovery of the flocculated (precipitated) resin acids by extraction of flocculated material was explored in a series of experiments, which investigated the influence of pH and compared the efficiency of recovery by filtration to recovery by centrifugation. Initial experiments in which the filtered flocs were Soxhlet extracted gave poor results.

In each of the experiments, flocculated resin acids were recovered by dissolution/dispersion of the floc at pHs ranging from 2 to 8.5, followed by liquid/liquid extraction at the pH of the resulting solution.

Influence of pH on resin acid recovery from PFS floc

The recovery of resin acids flocculated by treatment with 20 mg/mL PFS (the optimum dose identified in Table 7.5) was investigated in a series of experiments in which precipitated material, recovered by filtration, was dissolved/dispersed at pHs in the range 2 to 8.5.

The greatest recovery of resin acids (87% of that recovered by conventional extraction) was achieved by resolublisation and liquid/liquid extraction at pH 8.5 (Table 7.8). The lower recovery of resin acids at acid pHs, may in part be attributable to the lower efficiency of resin acid recovery by liquid/liquid extraction at acid pHs, as demonstrated in Chapter 3.

Table 7.8. Resin acid levels (μg/L) recovered by resolublisation and liquid/liquid extraction of PFS flocculated (20 mg/L), sodium azide stabilised SH30 Tarawera River water, collected 14/1/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30[a](no PFS)	7.4	9.4	21.0	11.4	19.5	0.6	69.3	100%
PFS flocs								
pH 8.5	2.8	7.2	21.7	11.8	14.5	0.7	58.7	85%[b]
pH 6.8	1.5	3.5	10.8	6.9	9.3	0.5	32.4	47%
pH 4.5	0.6	1.5	4.8	2.7	4.0	0.4	14.1	20%
pH 3.5	0.3	0.9	1.2	1.2	1.5	-	5.1	7%
pH 2	0.2	0.5	0.7	1.1	0.9	-	3.4	5%

[a] mean of duplicate analyses, [b] recovery relative to unfiltered water. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Similar resin acid recoveries were also obtained in experiments performed using PAC as flocculant. In these experiments resin acids were dissolved/desorbed from the floc at pHs in the range 7.2 to 12.0. The greatest recovery of resin acids (92% of that recovered by conventional extraction) was achieved by dissolution/desorption and liquid extraction at pH 9 (Table 7.9).

Satisfactory recovery was also achieved at pH 10.3 and 12 (84-86% of that recovered by conventional extraction).

Table 7.9. Resin acid levels (μg/L) recovered by resolublisation and liquid/liquid extraction of PAC flocculated (70 mg/L), sodium azide stabilised SH30 Tarawera River water samples, collected 25/2/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30 A	15.1	5.9	24.3	17.6	27.1	2.7	92.7	
SH30 B	18.9	6.3	27.0	18.6	29.0	5.9	106	
average[a]	17.0	6.1	25.6	18.1	28.1	4.3	99.2	100%
PAC flocs								
pH 7.2	7.9	4.0	10.5	10.5	11.7	0.2	44.8	45%
pH 9.0	16.5	6.8	25.3	15.6	24.7	2.5	91.5	92%
pH 10.3	8.9	5.9	28.2	12.1	25.2	2.9	83.1	84%
pH 12.0	10.7	6.4	27.6	15.5	23.7	0.9	84.9	86%

[a] mean of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Comparison of pH 6 and 10 recovery of PFS and PAC flocculated resin acids

In order to check the finding obtained above the experiment was repeated using PAC and PFS and a common sample of unstablised SH30 Tarawera River. A comparison of the efficiency of resin acid recovery by resolublisation and liquid/liquid extraction of flocculated (precipitated) at pH 6 and 10, and the level of resin acids remaining in filtrates, was also performed. The SH30 Tarawera River water samples were collected on 14/1/99. Results are presented in Table 7.10. Because water samples were not sodium azide stabilised, results are substantially lower than those reported in Table 7.8. Data for portions of the filtrates, which were liquid/liquid extracted at pH 7.4, are also presented in Table 7.10.

The results presented in Table 7.10 are consistent with those presented in Tables 7.8 and 7.9. Sodium azide has no effect on the flocculation or recovery.

Table 7.10. Resin acid levels (μg/L) recovered by resolublisation and liquid/liquid extraction of PFS and PAC flocculated and Whatman No. 1 filtered unstabilised SH30 Tarawera River water collected 14/1/99 and extracted 7/2/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30 A	1.7	2.9	9.3	5.1	6.8	0.8	26.6	
SH30 B	1.7	3.1	8.9	5.4	8.0	0.7	27.8	
average [a]	1.7	3.0	9.1	5.3	7.4	0.8	27.2	100%
PFS treatment								
filtrate, pH 7.4 [b]	0.4	0.3	0.4	0.9	-	0.0	2.1	8%
floc, pH 10	2.8	0.5	14.2	8.9	-	1.4	27.9	102%
floc, pH 6	0.0	-	3.8	1.8	-	0.0	5.6	20%
PAC treatment								
filtrate, pH 7.4[b]	0.3	0.3	0.5	0.9	0.5	0.0	2.4	9%
floc, pH 10	1.8	4.0	11.4	7.1	6.6	0.9	31.8	117%
floc, pH 6	0.0	-	1.1	1.0	-	0.0	2.1	8%

[a] mean of duplicate analyses. [b] resin acid levels identified in a portion the pH 7.4 filtrate. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Floc recovery by centrifugation

Up until this time, floc recovery was achieved by filtration through Whatman No. 1 filter paper. It was of interest to determine whether centrifugation could be used for floc recovery. Table 7.11 compares resin acid levels which were recovered by filtration with those obtained by centrifugation, followed by resolublisation of flocculated material and subsequent liquid/liquid extraction at pH 9.5-10.0.

Because unstabilised SH30 Tarawera River water used in these experiments, resin acid levels were substantially lower than those reported in Tables 7.9 and 7.10. It is however apparent that, within the sensitivity and precision limits of the experiments, filtration and centrifugation results are comparable.

Table 7.11. Resin acid levels (μg/L) recovered by resolublisation and liquid/liquid extraction of Whatman No. 1 filtered, or centrifuged, PAC flocculated unstabilised SH30 Tarawera River water, collected 14/1/99.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30[a]	0.7	1.6	4.1	2.5	3.3	0.3	12.5	100%
centrifuge								
liq/liq	0.2	0.2	0.2	0.6	-	-	1.2	10%
floc	0.8	0.7	5.3	3.1	-	-	9.9	79%
filtration								
liq/liq	0.4	0.1	0.2	1.3	-	-	2.1	16%
floc	0.7	1.6	4.3	2.6	2.6	0.3	12.0	96%

[a] mean of duplicate analyses. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichloro-dehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

7.3.6. Recovery of flocculating agents

The observation that resin acids could, under some circumstances, be separated from floc suggested the possibility that a flocculating agent could be recovered and reused. This was investigated in a series of experiments performed at differing pHs. Resin acid analysis was used to monitor the outcomes of the experiments.

Regeneration of flocculant

Alkaline recycling was investigated. As the pH is raised above the isoelectric point (IEP) of aluminium hydroxide (ca. pH 8.5), the colloidal particles of the floc will become negatively charged and will tend to disperse. It was expected that resin acids and other contaminants would be released during this step. It may be possible to regenerate the colloidal constituents of PAC without chemical dissolution.

Summary of the alkaline recovery procedure

(i) flocculate with PAC at pH 5.9

(ii) regenerate reagent at alkaline pH

(iii) determine resin acids (liquid/liquid extraction) in a sub-sample of the resulting system

(iv) add the dispersed floc to a second water sample, adjust the pH to 5.9 and repeat steps (i) to (iii)

Table 7.12 presents the results in obtained in the series of experiments performed using the protocol.

In a single cycle of the experiment (Experiment 1) following steps (i)-(iii) above, 13.0 μg/L total resin acids (ca. 65%) were recovered after flocculation at pH 5.9, followed by filtration, resolublisation of the floc at pH 10.0 and extraction of a sub-sample of the dissolved/dispersed floc at this pH 10.0 (see Table 7.12).

A two cycle experiment was performed using a second SH30 Tarawera River water sample, which contained a slightly higher level of resin acids (26.9 μg/L compared to 20.2 μg/L in the first experiment). The pH 10 solution from the first cycle was added to the second river water sample, the pH was adjusted to 5.9 (step iv of the protocol) and steps (i)-(iii) of the protocol were repeated. Resin acid data determined for the two step procedure (Experiment 2) are also presented in Table 7.12 (Experiment 2 data).

The results presented in Table 7.12 demonstrate, that within reasonable precision limits (65 and 90% respectively in steps 1 and 2), the flocculating agent can be recovered and recycled, with essentially additive accumulation of resin acids in the resulting floc.

Table 7.12. Resin acid levels (μg/L) determined in single and two step flocculation experiments (with recycling of flocculating agent at pH 10.0) using PAC (70 mg/L) and a SH30 Tarawera River water sample collected on 14/1/00.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	% recv
Experiment 1 (1 step)								
SH30, sample 1	1.2	2.5	6.7	3.8	5.6	0.4	20.2	
flocculated[a]	0.7	1.6	4.7	2.3	3.5	0.3	13.0	65%
filtrate[b]	0.2	0.5	0.7	0.9	0.6	-	3.0	
Experiment 2 (2 steps)								
SH30, sample 2	1.7	3.2	9.4	5.3	6.8	0.5	26.9	
1st flocculation[c]	0.7	1.6	4.7	2.3	3.5	0.3	13.0	
2nd flocculation[d]	2.2	4.8	13.2	5.7	9.9	-	35.8	90%
filtrate[e]	0.3	0.4	0.1	0.9	-	-	1.7	
total available[f]	2.4	4.8	14.1	5.6	10.3	0.8	39.9	

[a]Resin acids flocculated in the 1st step, [b]Liquid/liquid extraction of the 1st filtrate, [c]Resin acids recycled with the flocculant recovered from step 1 (Experiment 1), [d]Resin acids flocculated in the 2nd step, [e]Liquid/liquid extraction of the 2nd filtrate, [f]total recoverable resin acids, calculated as the sum of resin acids in the 1st flocculant and the SH30 sample2 water. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to expected resin acid levels.

Possible cyclic flocculation technology

The ability of the dissolved/dispersed floc to flocculate a second sample of SH30 water suggests the possibility of regenerating and reusing the flocculating agent. For this to be viable it would be necessary to regenerate the flocculating agent, with release of resin acids and coloured species into a concentrated waste stream which could be separately processed and disposed off.

Factors, which would need to be taken into account when investigating the feasibility of such a technology, include the significance of pH changes and the need to minimise the consumption of reagent. For example the experimentally measured amounts of base required to disperse a PAC floc at different pHs are summarised in Table 7.13 and

presented graphically in Figure 7.1. To minimise OH^- consumption, it would be desirable to disperse the floc at the lowest possible pH. This was found to be approximately pH 8.

Table 7.13. Al (III)/OH^- mole ratios required for floc dispersion

pH	volume (μL) NaOH added	moles OH added x 10^6	conc OH moles/L x 10^6	moles OH in solution x 10^6	moles OH in disperse x 10^6	moles Al in disperse x 10^6	Ratio Al/OH
8.00	15	21	1.0	0.013	21.0	182	8.7
9.02	20	28	10.5	0.14	27.9	182	6.5
9.78	25	35	60	0.78	34.2	182	5.3
10.05	30	42	112	1.46	40.5	182	4.5
10.42	45	63	263	3.42	59.6	182	3.1
10.59	50	70	389	5.06	64.9	182	2.8
11.05	70	98	1122	14.6	83.4	182	2.2

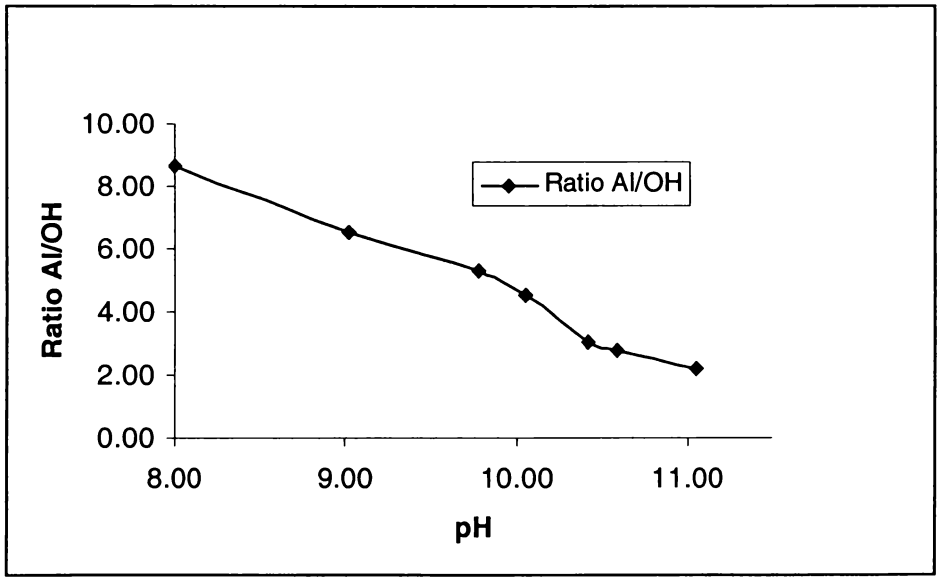

Figure 7.1. Relationship between pH and Al/OH^- mole ratio for dispersed floc.

From a consideration of the chemical principles involved, it is possible to write chemical equations for the steps involved in the envisaged recovery sequence.

1. First flocculation step:

pH 5.6-6.1 PAC + organic(effluent) → $Al(OH)_3$/organic(floc)

2. Regeneration of flocculant:

pH > 8 $Al(OH)_3$/organic(floc) → organic + $Al(OH)_{3\ (colloid)}$ -

3. Second flocculation step:

pH 5.6-6.1 $Al(OH)_{3(colloid)-}$ + organic(effluent) → $Al(OH)_3$/organic(floc)

The domain of stability of $Al(OH)_3$ covers the pH range 4.6 to 7.8 (see Figure 7.2). The optimum flocculation pH of 5.6 to 6.1 (established in Section 7.3.1) is understandable in terms of this behaviour. Dispersion of the floc occurs at pHs above that at which the $Al(OH)_3$ begins to dissolve.

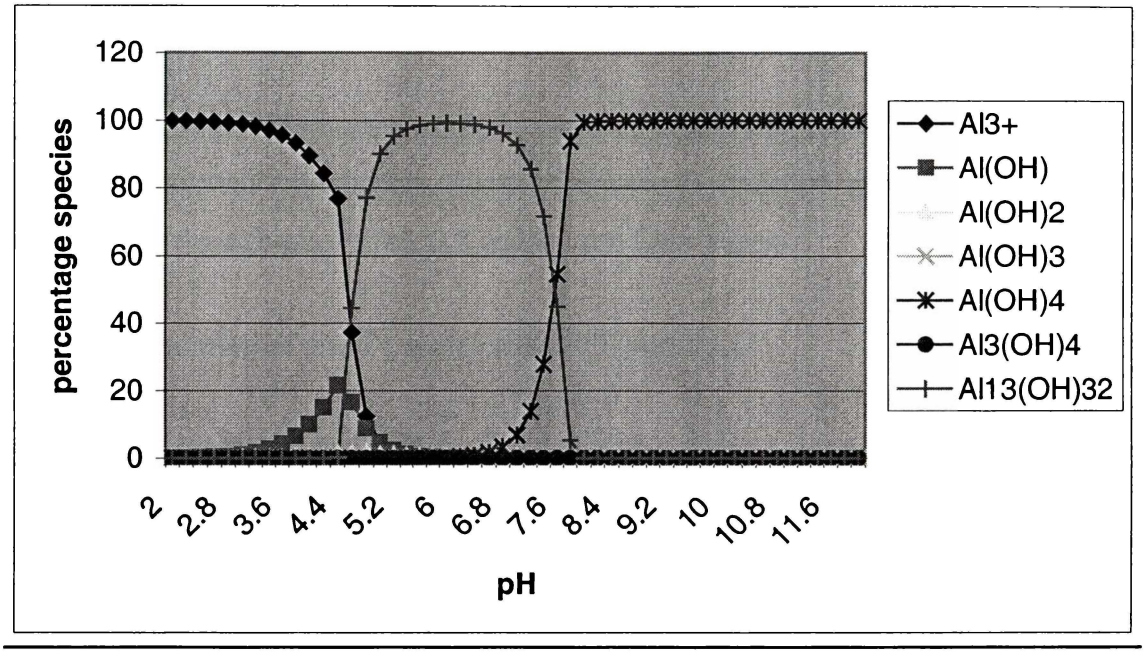

Figure 7.2. Percentage species distribution diagram for Al hydrolysis, calculated using software and pK_a values cited by Powell (1999).

By careful manipulation of pH, it may be possible to define conditions where the organic material is desorbed but the aluminum remains principally in an insoluble form allowing separation. This may be easier to achieve with the iron system. A detailed evaluation of this possibility is beyond the scope of the work reported in thesis. Further work in this area is in progress in the Department.

7.4. Pond 1 experiments: Flocculation/filtration of primary effluent

The ability of flocculating agents or pumice filtration, alone or in combination, to reduce resin acid and colour levels in untreated effluent water was investigated, since (based on the SH30 Tarawera River results presented above) it was envisaged that the application of these techniques might substantially reduce resin acid, colour, BOD_5 and turbidity of the untreated effluent water. Effectively flocculation/filtration would be used as a primary treatment step. This possibility does not appear to have been extensively investigated.

Pond 1 outlet water was used in these experiments since it was the first point in the treatment system from which a total effluent sample (comprised of clarifier and bleaching effluents) could be collected (see Figure 5.1).

In order that some information might be obtained concerning changes in speciation effects during flocculation experiments, filtrates from the flocculation experiments were filtered sequentially through glass fibre, 0.8 and 0.2 μm filter papers.

7.4.1. Flocculation of pond 1 water with PFS and PAC

Flocculation with PFS

Resin acid results obtained using PFS, coagulation followed by glass fibre, 0.8 or 0.2 μm filtration are presented in Table 7.14. These results can be compared to those obtained in the absence of flocculant. Colour and turbidity levels were also determined for each of the filtered wastewater samples (Table 7.15).

PFS treatment (20 mg/L at pH 5.1-5.3) followed by glass fibre filtration removed 86% of the total resin acids, and 47%, 65% and 88% of colour at 270, 340 and 440 nm (Table 7.15) respectively.

Table 7.14. Resin acid levels (μg/L) determined for sequentially filtered natural and PFS (10-60 mg/L) flocculated pond 1 treatment system water samples collected 27/1/00.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
No flocculant								
pond 1 (A)	559	1647	19	4770	1700	160	8855	
pond 1 (B)	573	1803	14	4439	1984	164	8977	
mean (n = 2)[a]	566	1725	53	4605	1842	162	8917	100%
glass fibre liq/liq	482	1264	12	4293	1125	99	7275	82%[b]
0.8 μm liq/liq	488	1200	10	4634	938	86	7355	82%
0.2 μm liq/liq	512	1172	10	4948	719	76	7438	83%
glass fibre Soxhlet	70	364	4.9	445	637	49	1569	18%
0.8 μm Soxhlet	17	76	-	105	-	12	210	2.3%
0.2 μm Soxhlet	18	69	12	83	91	7.5	280	3.1%
10 mg/L PFS								
glass fibre liq/liq	251	472	6.0	3190	698	32	4649	52%
0.8μm liq/liq	172	322	6.4	2306	155	23	2985	33%
0.2 μm liq/liq	154	282	4.6	2102	172	18	2734	31%
glass fibre Soxhlet	194	710	6.3	1049	1058	84	3101	35%
0.8 μm Soxhlet	7.2	21	0.7	40	2.5	2.9	74	0.8%
0.2 μm Soxhlet	9.8	29	2.1	60	-	3.7	105	1.2%
15 mg/L PFS								
glass fibre liq/liq	243	544	12	2850	397	41	4087	46%
0.8 μm liq/liq	194	391	4.8	2514	238	25	3367	38%
0.2 μm liq/liq	167	306	3.5	2273	167	18	2935	33%
glass fibre Soxhlet.	208	852	9.8	992	1405	91	3558	40%
0.8 μm Soxhlet	28	106	1.3	133	137	14	419	4.7%
0.2 μm Soxhlet	5.7	26	-	47	-	2.7	81	0.9%
20 mg/L PFS								
glass fibre liq/liq	50.	76	4	1102	44	10	1285	14%
0.8 μm liq/liq	45	68	6	961	34	9	1122	13%
0.2 μm liq/liq	43.4	59	-	1007	-	8	1117	13%
glass fibre Soxhlet	445	1260	8	3087	1268	127	6196	69%
0.8 μm Soxhlet	-	-	-	9	-	-	9.3	0.1%
0.2 μm Soxhlet	-	-	-	19	-	-	19	0.2%
30 mg/L PFS								
glass fibre liq/liq	25.4	33	-	561	-	6.3	626	7.0%
0.8 μm liq/liq	15.3	24	-	495	14	6.5	555	6.2%
0.2 μm liq/liq	-	17	-	426	-	-	444	5.0%
glass fibre Soxhlet	470	1442	9	3152	1732	123	6928	77%
0.8 μm Soxhlet	-	-	-	6	-	-	6.2	0.1%
0.2 μm Soxhlet	-	24	-	43	-	-	67	0.7%

Table 7.14. continued.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	
40 mg/L PFS								
glass fibre liq/liq	24	33	1.4	666	18	3.0	745	8.3%
0.8 µm liq/liq	-	2.8	-	13	-	-	16	0.2%
0.2 µm liq/liq	18	26	1.9	553	16	3.6	618	6.9%
glass fibre Soxhlet	575	1869	18	4217	239	129	7048	79%
0.8 µm Soxhlet	13	17	0.7	432	9.2	4.0	476	5.3%
0.2 µm Soxhlet	3.3	4.5	-	97	3.6	4.5	113	1.3%
60 mg/L PFS								
glass fibre liq/liq	-	-	-	85	-	-	85	0.9%
0.8 µm liq/liq	-	-	-	54	-	-	54	0.6%
0.2 µm liq/liq	-	-	5.5	50	-	-	56	0.6%
glass fibre Soxhlet	448	1370	9.5	3556	1517	118	7018	78%
0.8 µm Soxhlet	-	-	-	13	-	-	13	0.1%
0.2 µm Soxhlet	-	-	-	2.5	-	-	2.5	0.0%

[a] mean of duplicate analyses, [b] recovery relative to unfiltered water Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

It is apparent from the results presented in Tables 7.14 and 7.15 that soluble resin acids and colour present in pond 1 water is flocculated and becomes filterable by all of the doses used in these experiments.

However at the lower doses, the particles formed were smaller and smaller pore size filters were required for their removal. Above doses of 20 mg/L, glass fibre filtration is adequate for efficient removal.

Table 7.15. Absorbance at 270 nm, 340 and 440 nm and turbidity (NTU) determined for PFS (10-60 mg/L) flocculated pond 1 treatment system water samples collected 27/1/00.

	absorbance			% remaining[a]			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	norm[b]
no flocculant								
not filtered	2.242	0.884	0.319	100%	100%	100%	123	100%
glass fibre	1.711	0.551	0.103	76%	62%	32%	13.3	11%[a]
0.8 µm	1.490	0.461	0.068	76%	52%	21%	5.24	4.3%
0.2 µm	1.365	0.425	0.061	61%	48%	19%	2.37	1.9%
10 mg/L PFS								
glass fibre	1.490	0.470	0.066	66%	53%	21%	10.2	8.3%
0.8 µm	1.398	0.432	0.057	62%	49%	18%	2.17	1.8%
0.2 µm	1.256	0.384	0.050	56%	43%	16%	1.57	1.3%
15 mg/L PFS								
glass fibre	1.403	0.417	0.067	63%	47%	21%	7.73	6.3%
0.8 µm	1.224	0.368	0.058	55%	42%	18%	0.90	0.7%
0.2 µm	1.121	0.332	0.052	50%	38%	16%	0.46	0.4%
20 mg/L PFS								
glass fibre	1.181	0.309	0.037	53%	35%	12%	1.32	1.1%
0.8 µm	0.938	0.193	0.021	42%	22%	7%	0.75	0.6%
0.2 µm	0.810	0.170	0.011	36%	19%	3%	0.61	0.5%
25 mg/L PFS								
glass fibre	0.853	0.229	0.021	38%	26%	7%	1.34	1.1%
0.8 µm	0.800	0.165	0.012	36%	19%	4%	0.58	0.6%
0.2 µm	0.735	0.140	0.009	33%	16%	3%	0.45	0.5%
30 mg/L PFS								
glass fibre	0.659	0.123	0.007	29%	14%	2%	0.64	1.1%
0.8 µm	0.634	0.118	0.006	28%	13%	2%	0.36	0.5%
0.2 µm	0.578	0.110	0.004	26%	12%	1%	0.21	0.4%
40 mg/L PFS								
glass fibre	0.518	0.114	0.007	23%	13%	2%	0.54	0.5%
0.8 µm	0.510	0.109	0.006	22%	12%	2%	0.33	0.3%
0.2 µm	0.507	0.100	0.003	12%	11%	1%	0.43	0.2%
60 mg/L PFS								
glass fibre	0.434	0.056	0.001	19%	6%	> 1%	0.54	0.4%
0.8 µm	0.420	0.057	0.000	19%	6%	0%	0.32	0.3%
0.2 µm	0.358	0.039	0.000	16%	4%	0%	0.47	0.4%

[a] remaining relative to unfiltered water, normalise relative to unfiltered water.

Flocculation with PAC

The results obtained using PAC, flocculation followed by glass fibre, 0.8 or 0.2 μm filtration are presented in Table 7.16. The results can be compared with those obtained in the absence of flocculant. PAC treatment (100 mg/L, pH 5.9-6.1) followed by glass fibre filtration removed 56% of the total resin acids and 35%, 51% and 84% of colour at 270, 340 and 440 nm (Table 7.17) respectively.

Table 7.16. Resin acid levels (μg/L) determined for sequentially filtered natural and PAC (10-100 mg/L) flocculated pond 1 treatment system water samples collected 27/1/00.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
No flocculant								
pond 1 mean (n = 2)	566	1725	53	4605	1842	162	8952	100%
10 mg/L PAC								
glass fibre liq/liq	403	939	7.8	3689	605	66	5709	64%[a]
0.8 μm liq/liq	343	748	8.9	3343	478	47	4968	55%
0.2 μm liq/liq	322	604	7.2	3221	318	35	4506	50%
glass fibre Soxhlet	119	544	3.3	534	853	66	2119	24%
0.8 μm Soxhlet	20	83	-	79	65	10	258	2.9%
0.2 μm Soxhlet	-	29	-	37	-	3.6	69	0.8%
36 mg/L PAC								
glass fibre liq/liq	353	778	5.9	3381	490	51	5059	57%
0.8 μm liq/liq	352	211	7.8	3472	454	45	4541	51%
0.2 μm liq/liq	272	173	5.4	2792	315	33	3590	40%
glass fibre Soxhlet	145	677	3.9	600	1019	79	2524	28%
0.8 μm Soxhlet	-	17	-	21	17	1.5	57	0.6%
0.2 μm Soxhlet	-	9.3	-	22	-	1.2	33	0.4%
100 mg/L PAC								
glass fibre liq/liq	260	513	4.5	2795	296	29	3899	44%
0.8 μm liq/liq	234	428	6.5	2743	272	24	3708	41%
0.2 μm liq/liq	206	358	5.7	2679	175	22	3446	38%
glass fibre Soxhlet	234	1029	6.0	1093	1436	104	3902	44%
0.8 μm Soxhlet	2.8	8.5	2.3	15	7.5	0.8	37	0.4%
0.2 μm Soxhlet	7.3	12	-	23	-	1.3	43	0.5%

[a] recovery relative to unfiltered water Abbreviations: Seco = secodehydroabietic acids 1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids total = total resin acids, % = recovery relative to unfiltered water.

Colour and turbidity levels were also determined for each of the filtered wastewater samples (Table 7.17).

Table 7.17. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for sequential filtration PAC (10-100 mg/L) flocculated pond 1 treatment system water samples collected 27/1/00.

	absorbance			% remaining [a]			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	%
no flocculant								
not filtered	2.242	0.884	0.319	100%	100%	100%	123	100%
10 mg/L								
glass fibre	1.870	0.600	0.095	83% [a]	68%	30%	9.38	8% [a]
0.8 μm	1.848	0.588	0.094	82%	67%	29%	2.36	2%
0.2 μm	1.554	0.49	0.075	69%	55%	24%	0.56	2%
36 mg/L								
glass fibre	1.784	0.548	0.073	80%	62%	23%	3.06	2%
0.8 μm	1.544	0.479	0.069	69%	54%	22%	1.48	1%
0.2 μm	1.106	0.324	0.05	49%	27%	16%	0.96	1%
100 mg/L								
glass fibre	1.457	0.429	0.051	65%	49%	16%	3.41	3%
0.8 μm	1.354	0.399	0.050	60%	45%	16%	1.79	1%
0.2 μm	1.267	0.375	0.049	57%	42%	15%	0.67	1%

[a] remaining relative to unfiltered water.

The Soxhlet data obtained from the 0.8 and 0.2 μm filter papers are anomalously low. Low data were also obtained if the filtrates were resolublised at pH 10 and then liquid/liquid extracted. There is no apparent explanation for this anomaly.

7.4.2. Floc particle size

Most of the particles present in the pond 1 water sample consisted of small particles with diameters ranging between 0.05 and 1 μm (see Figure 7.3). Most of the material present

consisted of larger particles (ca. 10 to 200 μm in diameter). These particles while present in low numbers were the predominant contributors on a volume basis. Volume and frequency data for natural and PAC flocculated (10, 36 and 100 mg/L doses) pond 1 samples are depicted graphically in Figure 7.4.

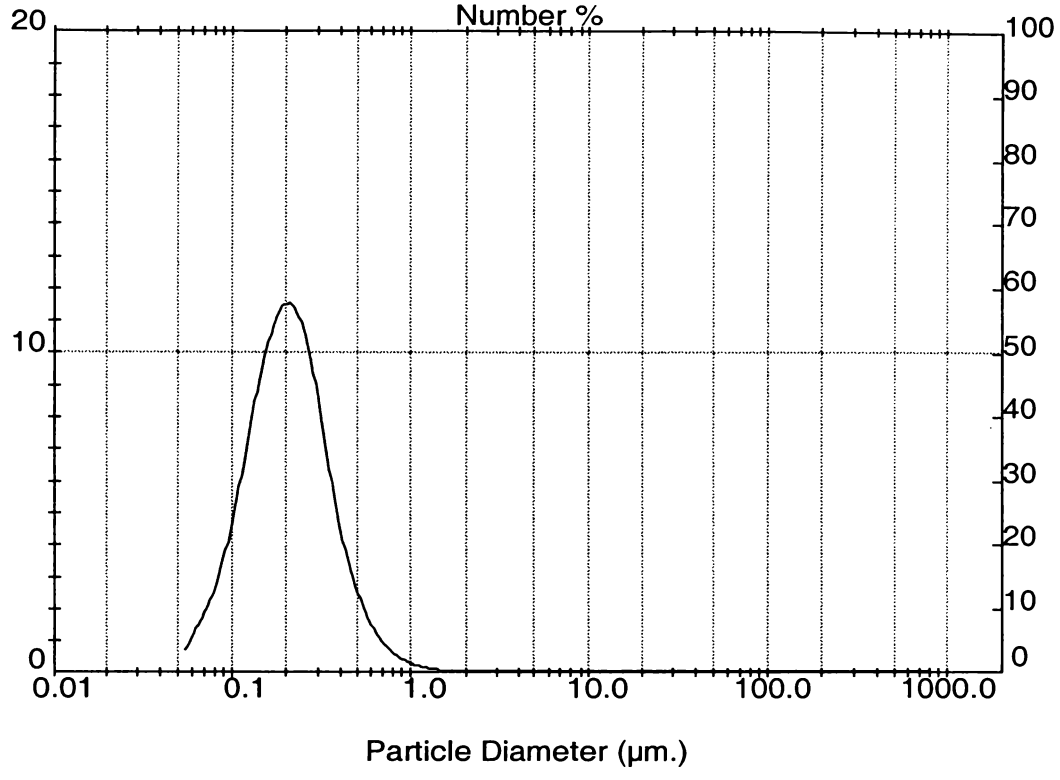

Figure 7.3. Particle size distributions (% number) determined for natural pond 1 water, collected 27/1/2000.

The % volume contributions of large and small particles present natural and flocculated pond 1 water samples were monitored for 24 h, following the in addition of flocculant. No significant changes in % volume contributions were observed for the natural pond 1 water sample during the 24 h period. Following the addition of flocculant, turbidity increased by up to 100% and small particles (< 10 μm) appeared to aggregate to form larger particles (between 10 and 250 μm). The volume contributions of larger particles appeared to increase with the dose of PAC.

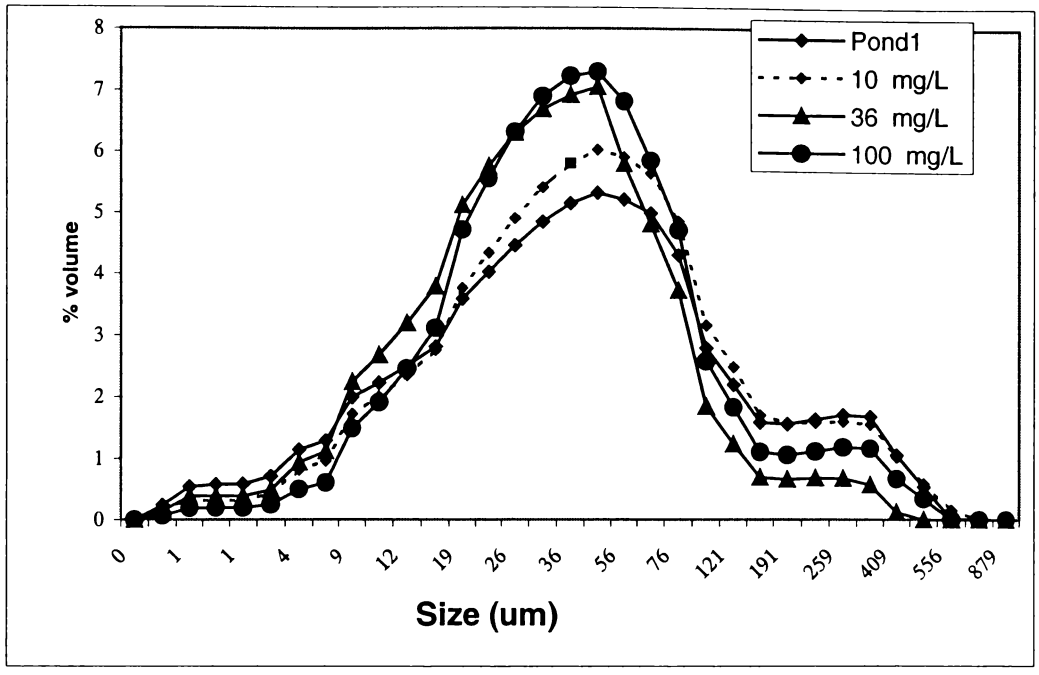

Figure 7.4. Particle size distributions (% volume) determined for natural and PAC (100, 36 and 10 mg/L) flocculated pond 1 water, collected 27/1/2000.

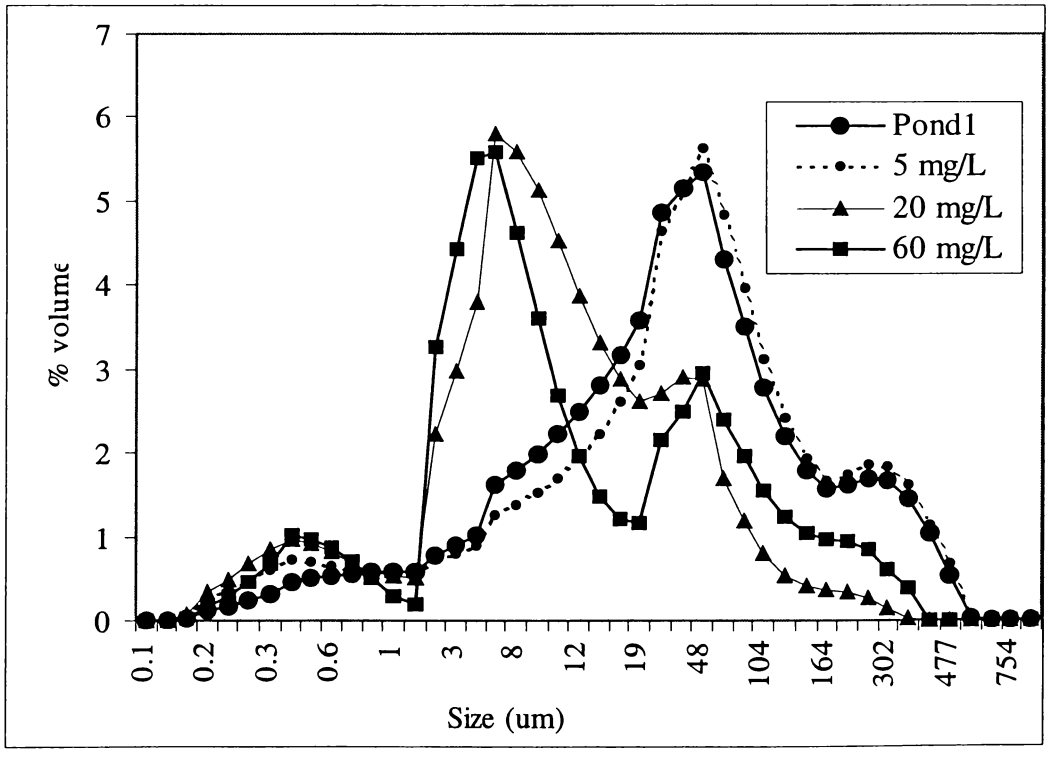

Figure 7.5. Particle size distributions (% volume) determined for natural and PFS (5, 20 and 60 mg/L) flocculated pond 1 water, collected 27/1/2000.

On the other hand, PFS doses in the range 20-60 mg/L led to the formation of medium sized particles (between 1 and 20 μm). This was associated with a decrease in the % volume contributions of large particles (> 20 μm). It is possible that this effect was due the aggregation and settling of the large particles. For additions of PFS greater than 20 mg/L, turbidity increased by up to 100%.

The appearance of particles in the size range 3 to 20 μm appears to be a indicator of the onset of coagulation and may be useful in determining the critical coagulation concentration (CCC) in the PFS system.

Pumice filtration

The abundance of pumice material in close proximity to pond 1 provides an inexpensive material that could be used for filtration. Pumice has recently been developed as a filter medium (Hill and Langdon 1991). In initial experiments, the adsorption capacity of pumice for effluent species was investigated. In later work the effectiveness of pumice as a filter medium for pulp and paper effluent was tested.

The pumice used was as described in Section 7.2.2.

Resin acid levels determined for pond 1 waters which were allowed to stand for 12 h in contact with varying quantities of pumice containing material are presented in Table 7.18. Only modest reductions in resin acid levels (1-21%) were observed. The greater the quantity of pumice used (up to 350 g/L of pond 1 water), the greater the reduction in resin acid levels. Only small colour reductions (or on some occasions a modest increase in colour) were observed (Table 7.19).

Table 7.18. Resin acid levels (μg/L) identified in pond 1 supernatant after (standing for 12 h) with 0-350 gm/L of unsieved pumice.

	Seco	Pim	18-Ab	DHAA	13-ene	abiet	Cls	total	%
pond 1 water [a]	367	1136	9	3275	1424	2147	56	8415	100%
pond 1+ pumice									
5 gm/L	352	1142	12	3136	1447	2200	51	8340	99%[b]
15 gm/L	376	1121	22	3334	1286	1944	46	8131	97%
50 gm/L	338	956	10	3115	1061	1864	37	7380	88%
150 gm/L	314	855	11	2934	906	1495	32	6548	78%
350 gm/L	291	799	9	2993	952	1535	34	6612	79%

[a]collected 25/2/2000, [b] recovery relative to unfiltered water Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 7.19. Absorbance at 270, 340 and 440 nm determined for pond 1 supernatant after standing for 12 h in contact with 0-350 gm/L of pumice-containing material.

	absorbance			% remaining		
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm
pond 1 water [a]	3.292	1.453	0.657			
pond 1 + pumice						
5 gm/L	3.189	1.430	0.625	97%	98%	95%
15 gm/L	3.223	1.410	0.623	98%	97%	95%
50 gm/L	3.353	1.470	0.595	102%	101%	91%
150 gm/L	3.141	1.330	0.560	95%	92%	85%
350 gm/L	3.161	1.350	0.585	96%	94%	96%

[a]collected 25/2/2000

These data indicate that adsorption effects are minor. For example, at the highest additions of pumice, approximately 5 μg total resin acid/g pumice is adsorbed.

Pumice filtration of flocculated pond 1 effluent

The protocol used in filtration experiments was as described in Section 2.13. Results determined for a series of experiments in which PFS treatment (0-40 mg/L) was followed by filtration through a column packed with pumice (0.85 mm diameter) are presented in

Table 7.20. Flocculation using 20-40 mg/L PFS followed by filtration removed 89-97% of resin acids.

Table 7.20. Resin acid levels (μg/L) identified in pond 1 water samples after flocculation with 0-40 mg/L polyferric sulfate and filtration through 0.85 mm pumice (95 g/L of water).

	Seco	Pim	18-Ab	DHAA	13-ene	Abiet	Cls	total	%
pond 1 A	494	1833	11	3265	2200	2699	77	10579	
pond 1 B	502	1896	16	3346	2272	2801	79	10912	
average[a]	498	1865	14	3306	2236	2750	78	10746	100%
PFS dose									
0 mg/L	292	801	5.8	2622	597	634	24	4976	46%[b]
5 mg/L	334	804	5.8	2797	425	445	21	4832	45%
10 mg/L	282	649	-	2589	350	583	17	4470	42%
15 mg/L	232	435	6.2	2374	183	189	9.7	3429	32%
20 mg/L	61	120	-	961	60	-		1202	11%
25 mg/L	54	90	-	815	33	29		1021	10%
30 mg/L	27	67	-	363	43	33		533	5%
40 mg/L	18	21	-	292	-	15		345	3%

[a]average of duplicate extraction of pond 1 water, collected 27/4/00, [b] recovery relative to unfiltered water
Abbreviations: Seco = secodehydroabietic acids 1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14 dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

The significance of pumice material size was assessed in experiments in which a fixed dose of PFS (20 mg/L) was utilised, and variable sizes of sieved pumice material were used. The greatest removal of flocculated resin acid material was achieved using 0.85 mm pumice (Table 7.21). Flocculation using 20 mg/L PFS followed by variable sizes of sieved pumice , 0.85 mm pumice removed 91% of resin acids.

Table 7.21. Resin acid levels (μg/L) identified in pond 1 water after flocculation with 20 mg/L PFS and filtration through a column containing 0.85-2.1 mm pumice material.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
pond 1 water [a,b]	919	1110	20	(8121)	-	56	10225	100%
pond 1 + pumice								
0.85 mm (190 g)[c]	46	54	5.6	813	31	0.3	950	9%[c]
1.6 mm (143 g)	127	171	4.2	2135	31	16	2485	24%
2.4 mm (120 g)	304	449	7.2	3626	-	22	4408	43%
3.1 mm (93 g)	761	802	17.3	5847	11	20	7459	73%

[a] collected 27/4/00, [b] not filtered, [c] the weight of pumice, [d] recovery relative to unfiltered water. Abbreviations: Sec = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

PFS flocculation and pumice filtration of BOD_5 and colour.

The extent to which PFS flocculation, in combination with 0.85 mm pumice filtration. reduced BOD_5 and turbidity was determined. Results are presented in Table 7.22.

A 20 mg/L dose of PFS, followed by 0.85 mm pumice filtration, reduced colour at 440 nm and turbidity by 89% and BOD_5 by 75% (Table 7.22).

The data presented represented in Table 7.22 can be compared with resin acid data presented in Table 7.20. It is clear that the decline in BOD_5 with increasing PFS dose, corresponds closely to that determined for resin acids (Figure 7.6).

Table 7.22. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for pond 1 water samples after flocculation with 0-40 mg/L PFS and filtration through a 0.85 mm pumice column (95 g/L of water).

	Absorbance			% remaining			turbidity	BOD_5
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	
pond 1	3.303	1.489	0.673	100%	100%	100%	230	187
PFS dose								
0 mg/L	2.428	0.808	0.212	73%	54%	32%	83.6	95
5 mg/L	2.318	0.782	0.164	70%	53%	24%	70.8	73
10 mg/L	2.197	0.727	0.131	67%	49%	19%	30.0	-
15 mg/L	2.015	0.601	0.090	61%	40%	13%	20.9	45
20 mg/L	1.228	0.494	0.076	27%	23%	11%	3.90	22
25 mg/L	1.213	0.490	0.074	27%	23%	11%	2.20	17
30 mg/L	1.001	0.274	0.036	23%	18%	5%	1.70	-
40 mg/L	0.714	0.269	0.036	12%	18%	5%	2.10	5

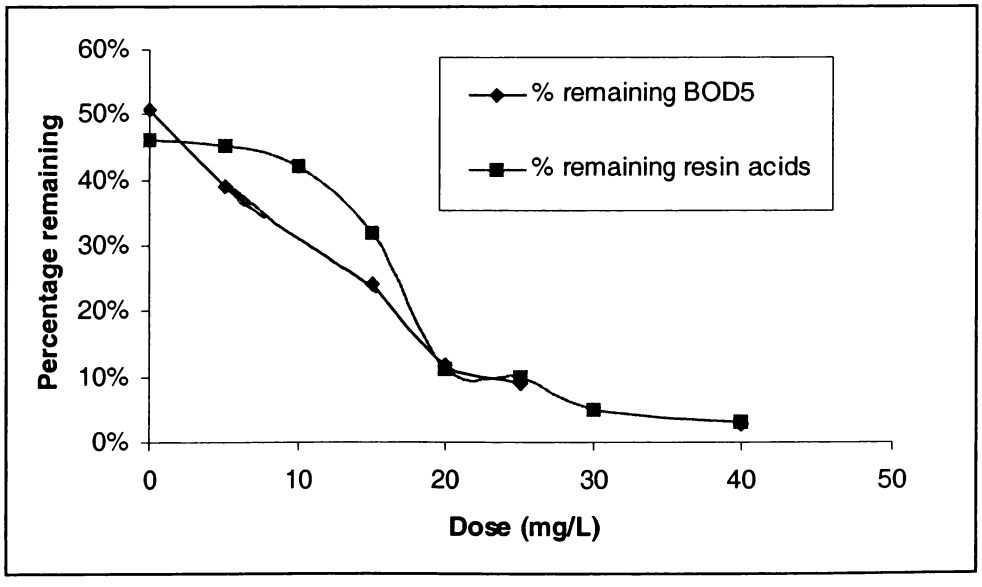

Figure 7.6. BOD_5 and resin acid levels determined for pond 1 water, collected 27/4/00, following treatment with various doses of PFS and filtration through 0.85 mm pumice.

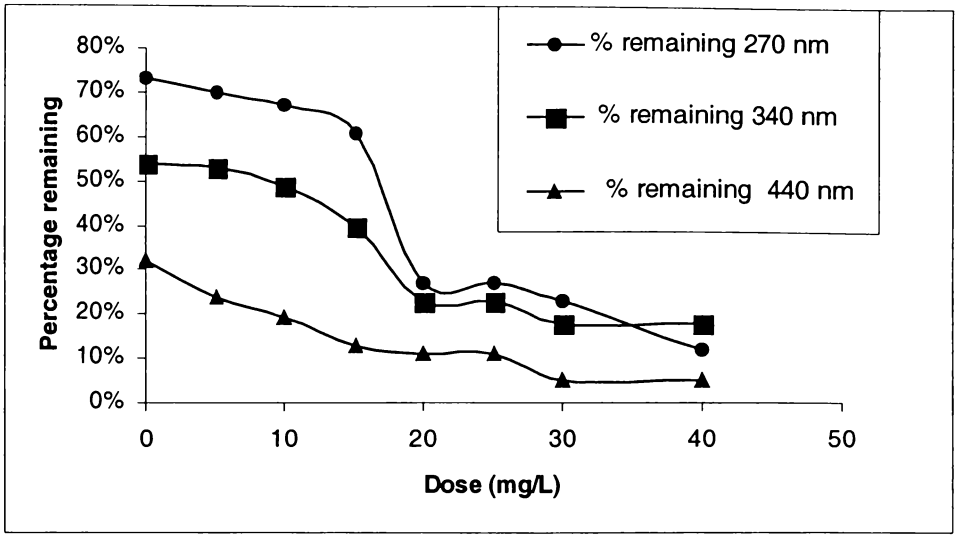

Figure 7.7. % Absorbances at 270 340, and 440 nm determined for pond 1 water, collected 27/4/00, following treatment with various doses of PFS and filtration through 0.85 mm pumice.

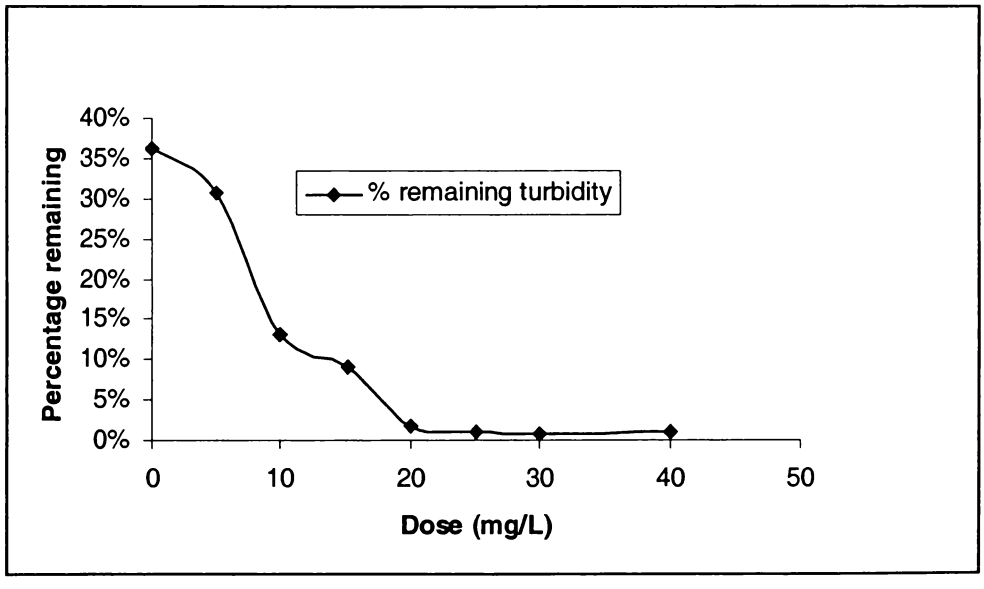

Figure 7.8. % Turbidity remaining for pond 1 water, collected 27/4/00, following treatment with various doses of PFS and filtration through 0.85 mm pumice.

The results presented in Tables 7.21 and 7.22 show that the total resin acids, BOD_5 (Figure 7.6), absorbance at 440 nm (Figure 7.7) and turbidity (Figure 7.8) of pulp and paper primary effluent can be reduced by greater than 90% by PFS flocculation followed by pumice filtration

Cost calculations

Using the data obtained from the flocculation/filtration studies reported above it is possible to estimate the cost of PFS required to treat Tasman's primary effluent. Assuming a daily discharge of 160 ML/day, a PFS requirement of 20 mg/L comes to 3.2 tonne/day. At the bulk cost of PFS (Orica Chemnet 2001) the chemical cost would be of the order of $1.5 M/year. Any recovery of flocculant would reduce this chemical consumable cost.

Other operating costs that would have to be met include the cost of pumice mining, preparation, transportation and disposal. Depending on the flocculation and filtration technologies chosen, other operating costs would be incurred. However, flocculation/ filtration treatment of primary effluent appears as an attractive option that warrants further investigation. It offers the possibility of reduced total effluent treatment costs (if it can take the place of secondary treatment) and improved effluent quality, particularly in regard to colour reduction.

7.5. Pond 4

Having determined the ability of flocculation and pumice filtration methods to reduce colour, BOD_5, turbidity and resin acid levels in untreated effluent water, it was of interest to ascertain the extent which these methods could reduce residual colour, BOD_5, turbidity and resin acid levels in biologically treated effluent water.

Pumice filtration

Filtration through pumice alone was not effective in removing resin acids and coloured species. The greatest removal of resin acids (ca. 22% reduction) was achieved using 0.85 mm pumice (Table 7.23). This size of pumice reduced colour at 440 nm by 32% (Table 7.24) and BOD_5 by 33% (Table 7.25).

It is apparent from the graphical representation of the normalized results shown in Figure 7.9 that resin acid, colour and BOD_5 levels are strongly correlated.

Table 7.23. Resin acid levels (μg/L) identified in pond 4 water, collected 22/6/2000, before and after passage through a column containing 0.85-4.5 mm pumice material.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
pond 4	232	304	737	2134	1008	6.5	4422	100%
pond 4 + pumice								
0.85 mm (190 g)[a]	200	217	412	1761	836	5.8	3431	78%[b]
1.6 mm (143 g)	216	267	544	1846	845	5.8	3724	84%
2.4 mm (131 g)	244	164	614	2233	551	5.3	3812	86%
4.5 mm (93 g)	228	279	625	2034	915	5.1	4086	92%

[a]Weight of pumice, [b] recovery relative to unfiltered water. Abbreviations: Seco = secodehydroabietic acids 1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 7.24. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for pond 4 water, collected 22/6/2000, before and after passage through columns packed with 0.85-4.5 mm pumice material.

	absorbance			% remaining[a]				
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	%.
pond 4	1.912	0.818	0.377	100%	100%	100%	97.7	100%
pumice size								
0.85 mm	1.544	0.608	0.238	81%	74%	63%	66.0	68%[a]
1.6 mm	1.640	0.677	0.293	86%	83%	78%	79.9	82%
2.4 mm	1.684	0.702	0.307	89%	86%	81%	82.0	84%
4.5 mm	1.809	0.767	0.347	95%	94%	92%	90.2	92%

[a] remaining relative to unfiltered water

Table 7.25. BOD_5 determined for pond 4 water, collected 22/6/2000, before and after filtration through 0.85-4.5 mm pumice columns.

	BOD_5	% remaining[a]
pond 4	38.9	100%
pumice size		
0.85 mm	29.8	73%[a]
1.6 mm	32.7	84%
2.4 mm	34.6	89%
4.5 mm	38.3	98%

[a] remaining relative to unfiltered water

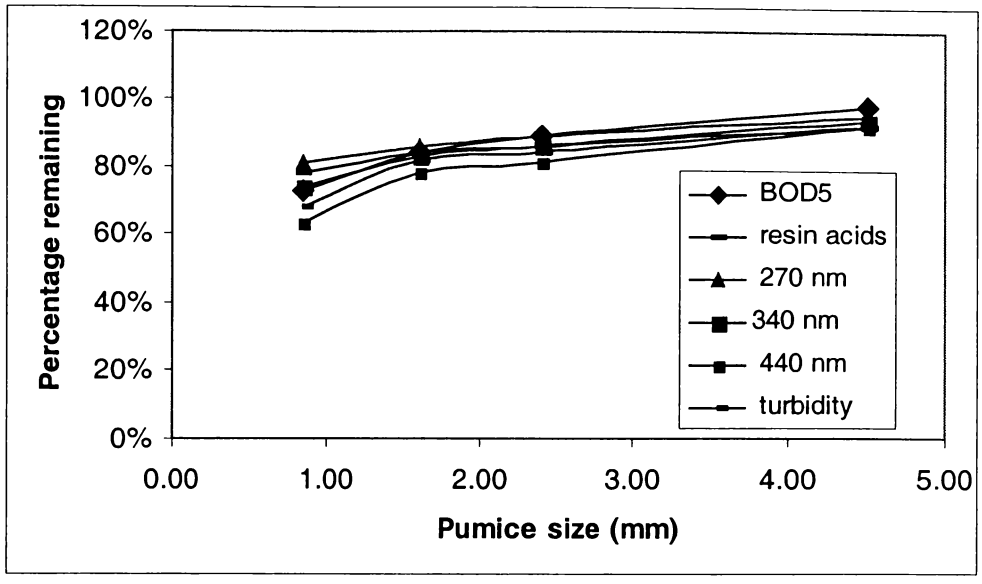

Figure 7.9. Plots of percentage remaining BOD_5, total resin acid levels, turbidity and colour at 270, 340, 440 nm determined after 0.85-4.5 mm pumice filtration of pond 4 water collected 22/6/2000.

Flocculation with PFS

A series of flocculation experiments were performed using pond 4 water. It was found that the flocs formed settled rapidly so that filtration was not necessary.

Flocculation using 20 mg/L PFS eliminated > 99% of residual resin acids (Table 7.26) and coloured species (Table 7.27). Turbidity was also reduced by ca. 99% (Table 7.27).

Table 7.26. Resin acid levels (μg/L) identified in pond 4 supernatant, after addition of PFS and settling for 10 hours.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	
pond 4[a]	232	304	737	2134	1008	6.5	4422	100%
PFS dose								
20 mg/L	1.7	2.7	1.1	7.5	-	0.1	13.1	0.3%[b]
30 mg/L	-	-	-	4.8	-	0.4	5.1	0.1%

[a] no PFS added, [b] recovery relative to unfiltered water. Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 7.27. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for pond 4 supernatant, after addition of PFS and settling for 10 h.

	absorbance			% remaining			turbidity
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU
pond 4 [a]	1.912	0.818	0.377	100%	100%	100%	96.2
PFS dose							
20 mg/L	0.217	0.030	0.000	11%	4%	0%	0.98
30 mg/L	0.207	0.016	0.000	11%	2%	0%	0.52

[a] no PFS added.

7.6. Dilution experiments

The observation that resin acids could be successfully recovered from flocs prompted the hypothesis that it might be possible to design an analytical technique based on pre-concentration (by flocculation) of the low levels of resin acids in massively diluted receiving water samples, by extraction of the resolublised floc, rather than extraction of the receiving water sample.

This proposal was evaluated using 1 L Tarawera River samples, which were diluted to 5, 10, and 50 L. PAC was added at a dose rate of 70 mg/L i.e. 350, 700 and 3500 mg of flocculant were added to the respective samples. The flocs recovered from these experiments were resolublised at pH 9.5-10 and liquid/liquid extracted.

The levels of resin acid acids recovered from the series of diluted Tarawera River water samples, expressed as µg/L of undiluted river water are given in Table 7.28. The recovery of resin acids was 92-104% of that determined for an undiluted river water sample. Some variations in % recoveries were observed for individual resin acids, including secodehydroabietic acids and chlorodehydroabietic acids.

It is apparent from these results that the flocculation/concentration technique can recover very low levels of resin acids. The approach described here has considerable potential as a methodology to trace resin acid plumes in highly diluted receiving waters.

Table 7.28. Resin acid levels (μg/L) determined for a sodium azide stabilised Tarawera River water sample, collected 14/12/00 and diluted 5-50 fold, and flocculated using 70 mg/L PAC.

	Seco	Pim	18-Ab	DHAA	13-ene	Cls	total	%
SH30	17.9	10.4	24.4	18.5	25.9	4.1	101[a]	
Dilution experiments								
undiluted, floc	16.5	6.8	25.3	15.6	24.7	2.5	91.5	91%[b]
undiluted, filtrate		0.2	0.8	0.3	-	-	1.3	1.3%
5 fold, floc	12.4	12.2	26.6	21.7	29.5	2.9	105	104%
5 fold, filtrate	-	-	0.1	0.5	-	-	1.8	1.8%
10 fold, floc	7.1	9	31.4	15.3	27.9	2.1	92.8	92%
10 fold, filtrate	-	0.1	0.8	0.2	-	-	1.1	1.1%
50 fold, floc	6.3	9.6	34.2	14.8	31.6	2.5	99	98%
50 fold, filtrate	-	0.1	0.3	0.3	-	-	0.7	0.7%

[a]mean of duplicate analyses, [b]recovery of mean relative to unfiltered water, Abbreviations: Seco = secodehydroabietic acids -1 and 2, Pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

7.7. Summary

Based on the results presented in this chapter, the following conclusions can be drawn:

1) Readily available flocculating agents, particularly those based upon iron and aluminium are able to remove turbidity, colour and resin acids from Tarawera River SH30 and treatment pond water samples. Optimum removal was achieved using 20 mg/L PFS or 60-70 mg/L PAC doses, followed by filtration, centrifugation or settling.

2) The use of PFS flocculation, followed by pumice filtration, reduced the levels of resin acids, colour and BOD_5 in pond 1 water by more than 90% and appears to at least as effective as the existing secondary treatment system.

3) Flocculation alone of pond 4 water using 20 mg/L PFS removed most of the colour, turbidity and resin acids. Natural settling or filtration could be used before discharge.

4) Observations 2) and 3) indicates that primary flocculation/filtration technology could be as least as efficient as the existing secondary system process for resin acid, BOD and turbidity removal and more effective for colour removal. Preliminary cost estimates indicate its probable cost effectiveness. It is possible this could be improved by recovery or partial recovery and reuse of the flocculating agent.

5) Particle size analysis offers insights into the understanding of the flocculation process and appears to be allow determination of critical coagulation concentrations.

6) The finding that resin acids could be recovered from flocs prompted the hypothesis that it might be possible to design an analytical technique based on pre-concentration by flocculation of the low levels of resin acids in highly diluted receiving water samples. 95-100% of expected resin acid levels were recovered in experiments performed using undiluted, 5, 10 and 50-fold diluted Tarawera River water.

Chapter 8

Summary and recommendations

8.1. Introduction

In this chapter the findings of this study are briefly summarised and recommendations for further research are presented.

8.2. Accuracy and precision of resin acid analysis

In the initial phase of the investigations reported in this thesis it was established that biodegradation of resin acids present in natural Tarawera River water samples stored at 4°C proceeded with a half life of ca. 19 days. This limited the obtainable precision and reproducibility of experiments, which due to equipment limitations, were often performed over several days, or weeks, after sample collection.

Addition of 0.1% sodium azide, at the time of collection was found to inhibit resin acid biodegradation for periods of up to 90 days. Provided samples were extracted and analysed together, the total resin acid levels of sodium azide stabilised river water samples exhibited CVs (for 5 or 6 replicates) of less than 7%. Prior filtration through sintered glass to remove gross particulate matter further reduced the CVs to 4%.

8.3. Speciation of resin acids and coloured species in Tarawera River and treatment pond water samples.

The presence of micro-particulate matter in natural and sodium azide stabilised Tarawera River water samples was established. Particle size analysis showed that the bulk of the volume of particulate matter in treatment system and river water samples were associated with particles greater than 5 μm. Sequential filtration experiments, using glass fibre, 3, 0.8, 0.45, 0.2 and 0.05 μm filtration, showed that resin acids were predominantly (typically > 70%) associated with 0.2-15 μm particles.

Mass balance was obtained from experiments which defined the levels of free, bound and total resin acids. Since similar results were obtained for both non-stabilised and sodium azide stabilised river water samples, it was concluded that sodium azide addition did not change speciation effects.

Experiments performed using water samples collected from Tasman's clarifier and biological treatment ponds showed that the % contribution of particle bound resin acids increased from ca. 5% (clarifier) to 70% (pond 4 discharge) during the passage of effluent water through the treatment system. Resin neutral compounds, generated from resin acids during passage through the treatment system, were predominantly (> 90%) particle bound.

Micro-filtration of the final effluent (pond 4 discharge) also reduced colour levels by 33-62%, depending on the pore size of the filtration media.

During biological treatment free pimaric acid and dehydroabietic acid levels fall substantially, while the bound levels were approximately constant. The level of free abietan-18-oic acid remained approximately constant in pond 2, 3 and 4 water samples. On other hand, bound abietan-18-oic acid levels increased as bound abiet-13-enoic acid levels decreased.

Particle binding appeared to inhibit the degradation of pimaric acid and dehydroabietic acid, whereas particle bound abiet-13-enoic acid was virtually completely transformed during passage through the treatment system. Both resin acids and BOD_5 are associated with similarly sized particles.

8.4. Settling effect

The possibility that settling effects occurred during the storage river water samples was investigated in experiments in which 2.5 L samples in winchesters and a 20 L sample in a plastic container were monitored over 30 days.

A significantly lower level of resin acids was identified in a 1 L sub-sample taken from the top of a winchester that had been allowed to stand undisturbed for 30 days compared to the level of resin acids determined in a second 1 L sub-sample taken from the bottom of the winchester.

It is clear that stored river water samples should be well shaken and mixed immediately before sampling and extraction. Failure to do so will lead to lower than expected resin acid levels in water from the upper portion of a sample container since settling of particulate matter will result in the accumulation of resin acids bound to particulate matter in the lower zone of the sample container.

8.5. Filtration

The finding that the majority of the resin acids in Tarawera River and pond 4 discharge water samples were particle bound indicated that filtration might substantially reduce resin acid levels, and to lesser extent also colour levels. Results indicated that 0.85 mm pumice filtration removed 37 and 22% of colour and resin acids respectively.

8.6. Flocculation/pumice filtration

It was found that addition of flocculating agents led to the particle binding of the majority of resin acids and species contributing to colour and BOD. Based on results obtained for pond 1 water samples, it was proposed that flocculation followed, by filtration, might provide a useful means of treating Tasman's primary effluent. A local supply of pumice was available to provide a low cost filtration medium. The significance of pumice grain size was assessed in experiments in which a dose of PFS (20 mg/L) was utilised. The greatest removal of flocculated resin acids, colour and BOD_5 from pond 1 water was achieved using 0.85 mm pumice.

8.7. Dilution experiments

The finding that resin acids could be successfully recovered from flocs prompted the hypothesis that it might be possible to design an analytical technique based on pre-concentration (by flocculation) of the low levels of resin acids in highly diluted receiving

water samples, by extraction of the resolublised floc, rather than extraction of the receiving water sample.

It is apparent from results obtained for dilution experiments performed using SH30 Tarawera River water, that the flocculation/concentration technique can recover very low levels of resin acids. The approach described here has considerable potential as a methodology to trace resin acid plumes in highly diluted receiving waters.

8.8. Recommendations for further work

The investigations reported in this thesis have identified areas that could be studied further. These are listed below:

1. Parallel studies of other New Zealand pulp and paper effluents and receiving waters would be valuable in establishing the generality of the effects described in the thesis.

2. Detailed studies of resin acid transformations under aerobic and anaerobic conditions are needed to elucidate the aspects of resin acid chemistry that are unique to New Zealand. In particular the transformation of abiet-13-enoic acid to abietan-18-oic acid has been hypothesised and needs to be confirmed.

3. Detailed studies of particulates are needed to determine the nature of the particles that bind resin acids and species which contribute to BOD_5.

4. An investigation of the chemistry of flocculant regeneration may allow the development of technologies for reuse of at least some of the flocculant. This would make the flocculation/filtration treatment of effluent more cost effective.

5. Pilot plant scale flocculation/filtration trials are needed to determine the optimum system and evaluate realistic costs. A detailed cost/benefit analysis could then be performed. Studies of both flocculation/filtration of primary effluent and secondary treated effluent should be included.

6. Further studies of the flocculation pre-concentration technique to establish optimum procedures and reliability may allow it to be applied to study the fate of effluent species at the much lower concentrations of the Waikato River and hydro lakes.

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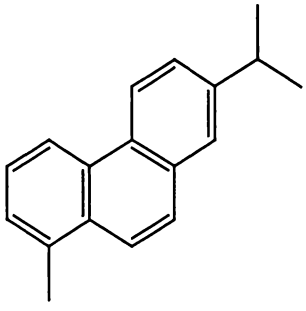
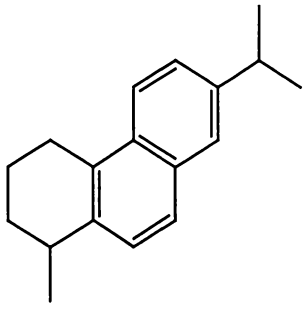
Appendix 1

Structure of some compounds discussed in this study

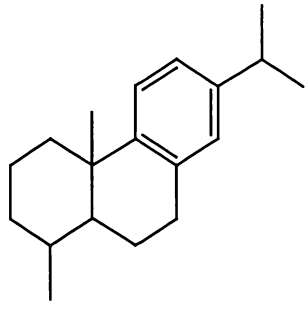
a) Resin neutral and standards



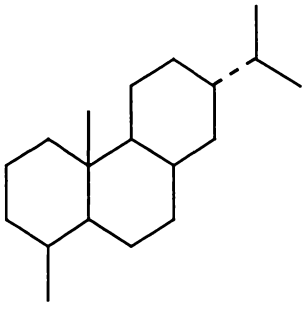
retene



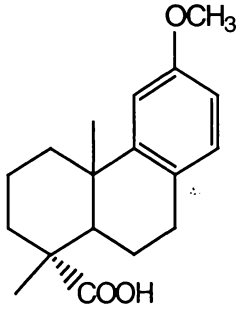
tetrahydroretene



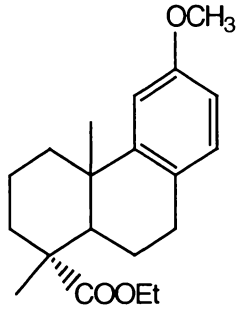
dehydroabietin



fichtelite

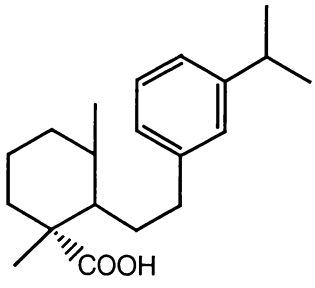


O-methylpodocarpic acid (PDA)

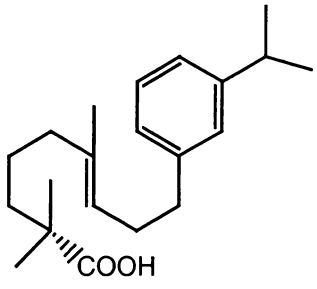


O-methylpodocarpic acid ethyl ester (PDA-Et)

b) Resin acids



secodehydroabietic acid-1 (seco-1)



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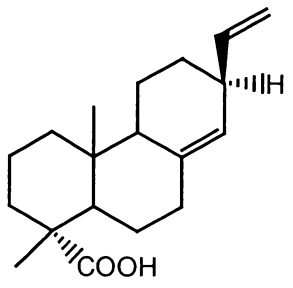
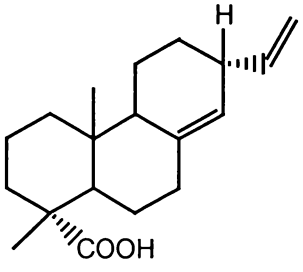
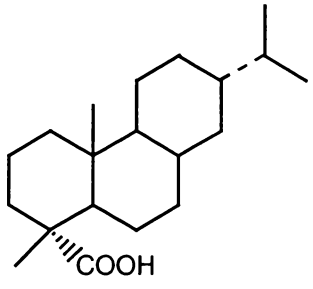


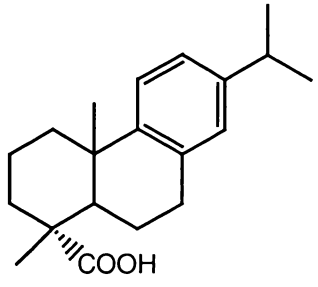
pimaric acid



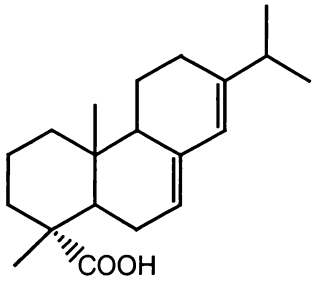
sandaracopimaric acid



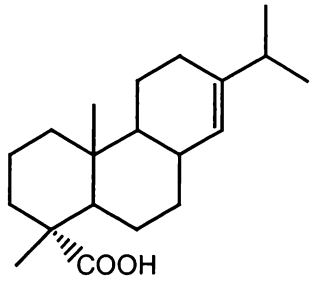
abietan-18-oic acid



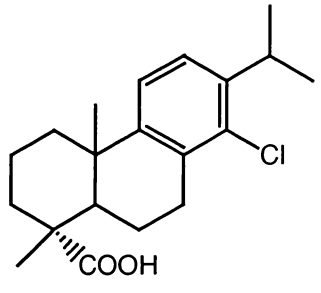
dehydroabietic acid (DHAA)



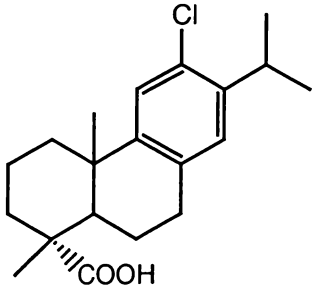
abietic acid



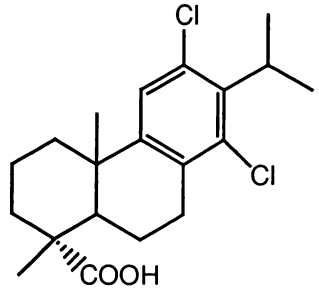
abiet-13-enoic acid



14-chlorodehydroabietic acid (14-Cl-DHAA)



12-chlorodehydroabietic acid (12-Cl-DHAA)



12,14 -dichlorodehydroabietic acid (12,14-diCl-DHAA)

Appendix 2

Calibration curves

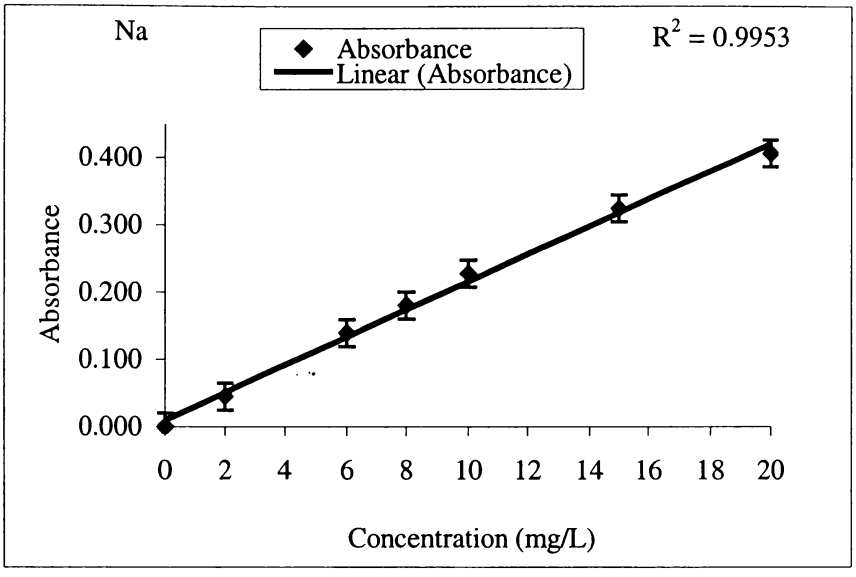


Figure A2.1. Na calibration curve using AA.

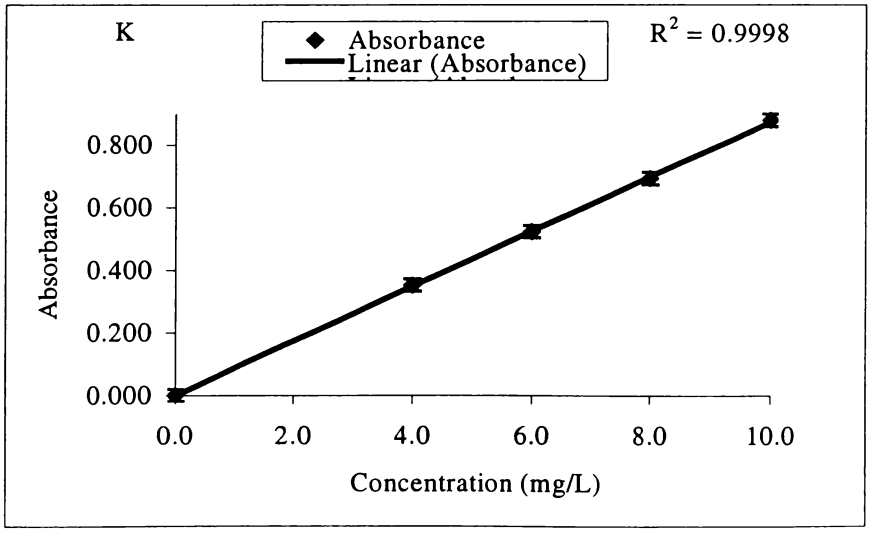


Figure A2.2. K calibration curve using AA.

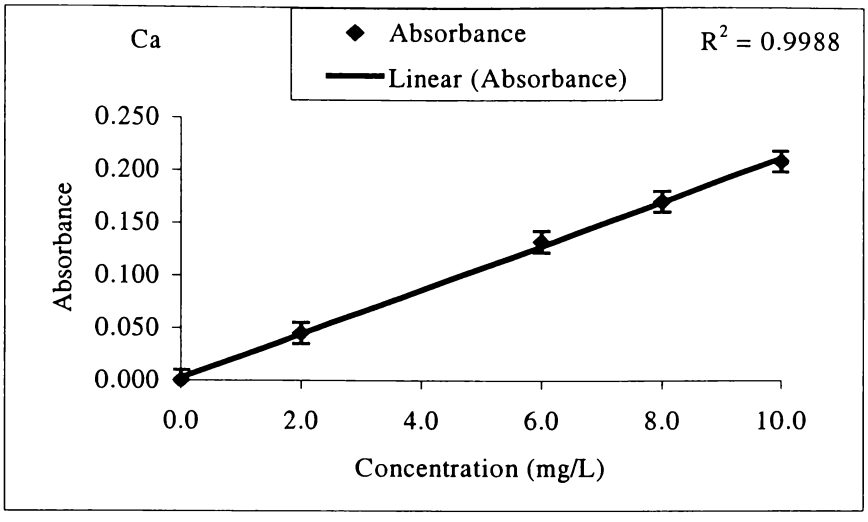


Figure A2.3. Ca calibration curve using AA.

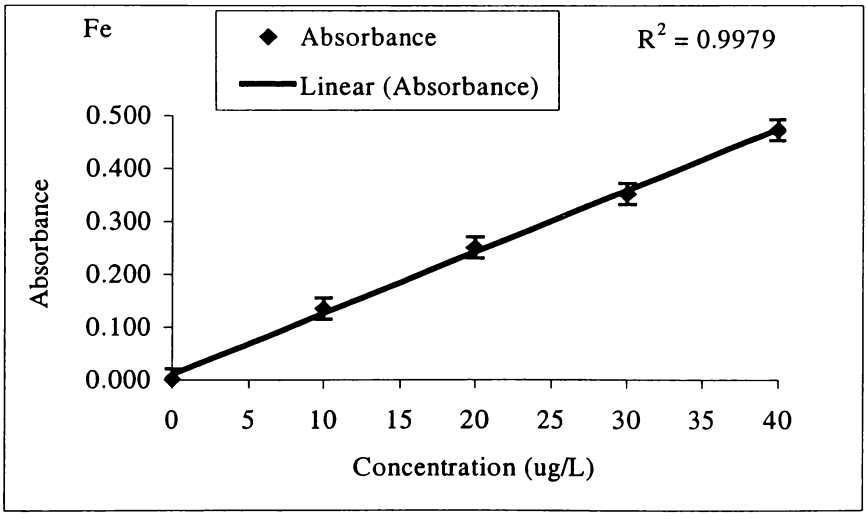


Figure A2.4. Fe calibration curve using furnace AA.

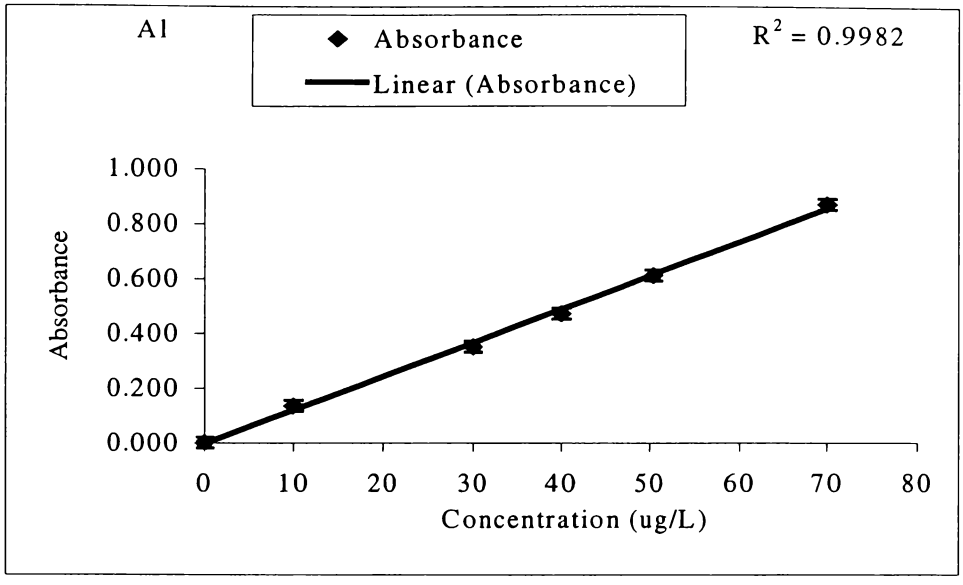


Figure A2.5. Al calibration curve using furnace AA.

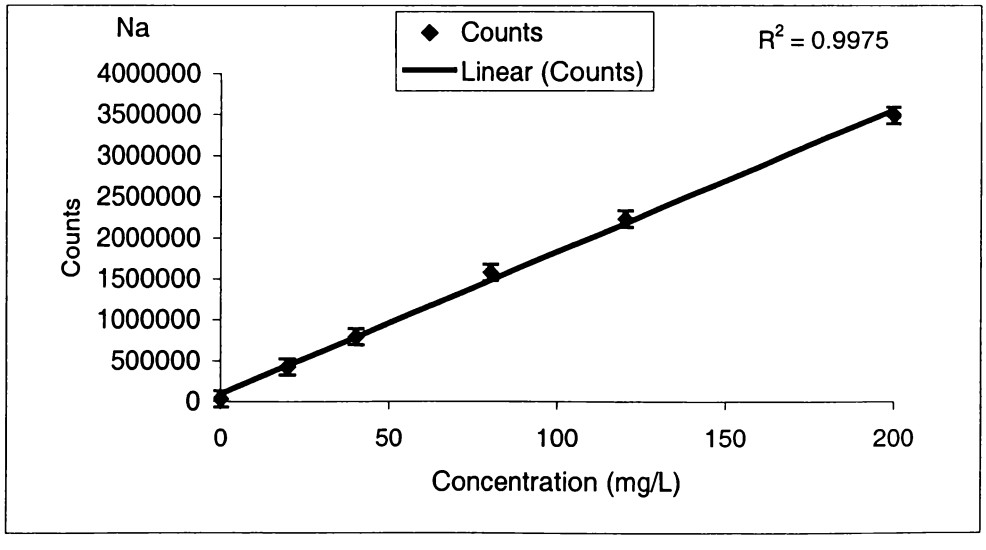


Figure A2.6. Na calibration curve using ICP

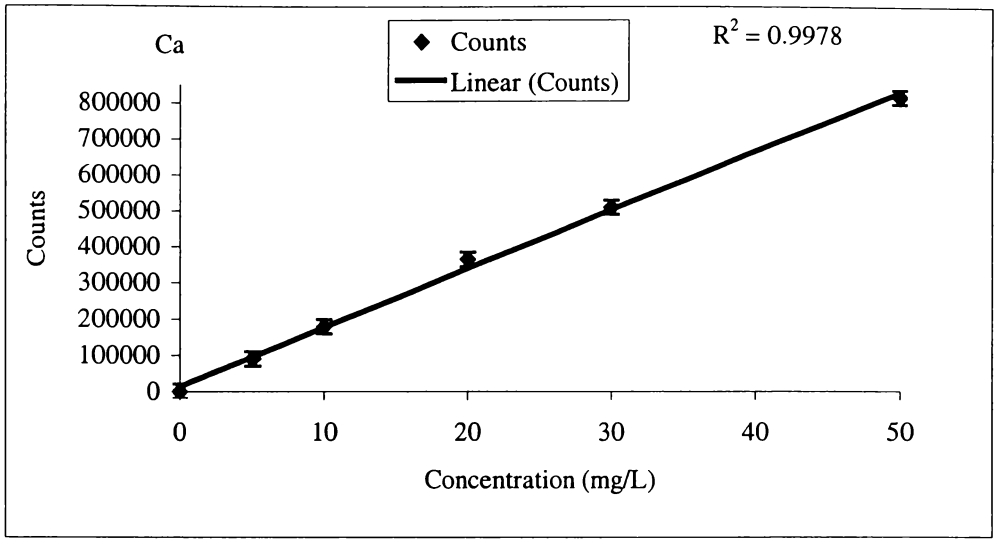


Figure A2.7. Ca calibration curve using ICP.

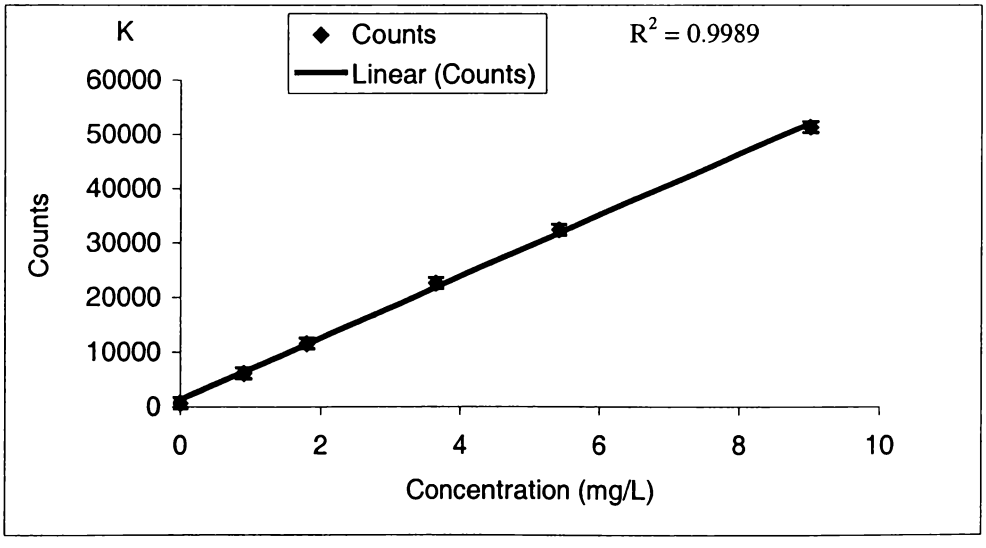


Figure A2.8. K calibration curve using ICP.

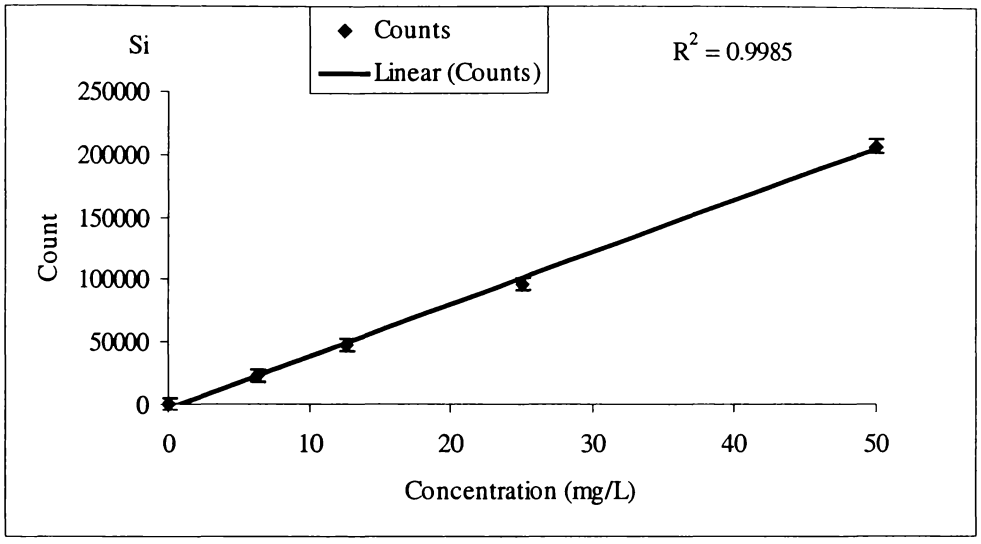


Figure A2.9. Si calibration curve using ICP.

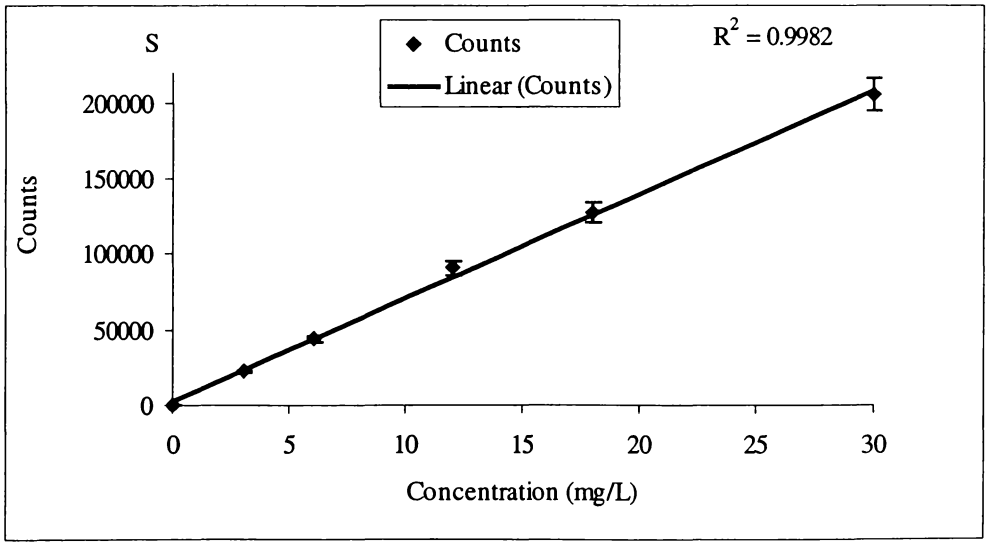


Figure A2.10. S calibration curve using ICP.

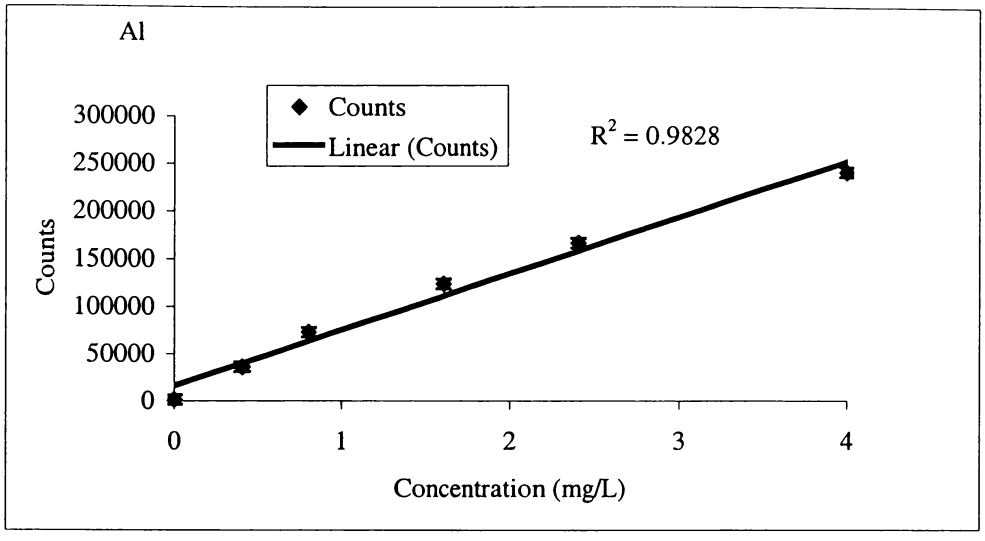


Figure A2.11. Al calibration curve using ICP.

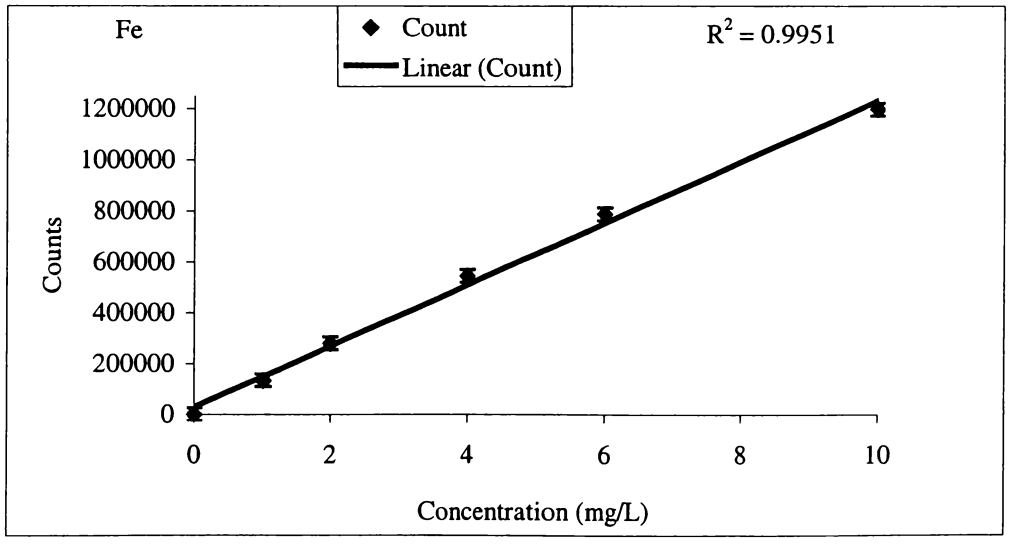


Figure A2.12. Fe calibration curve using ICP.

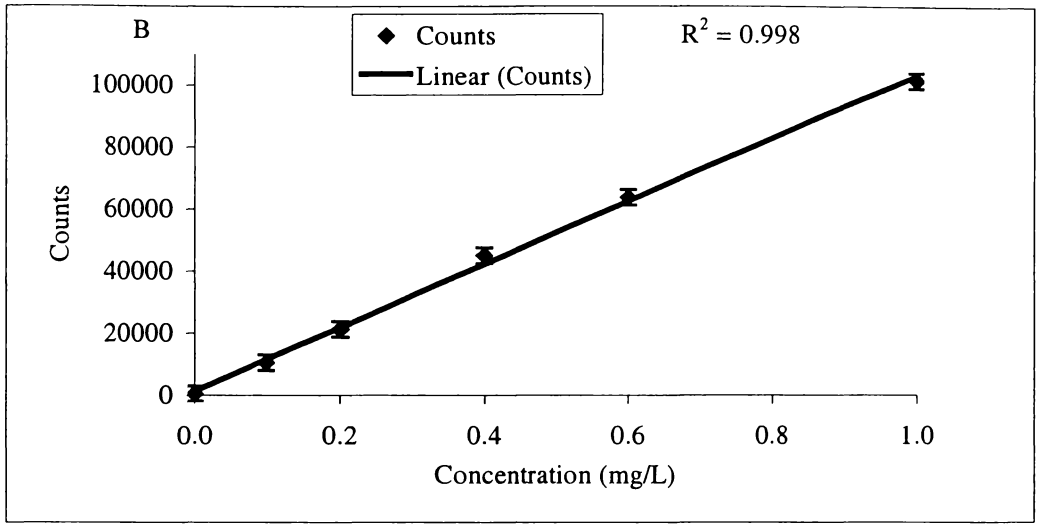


Figure A2.13. B calibration curve using ICP.

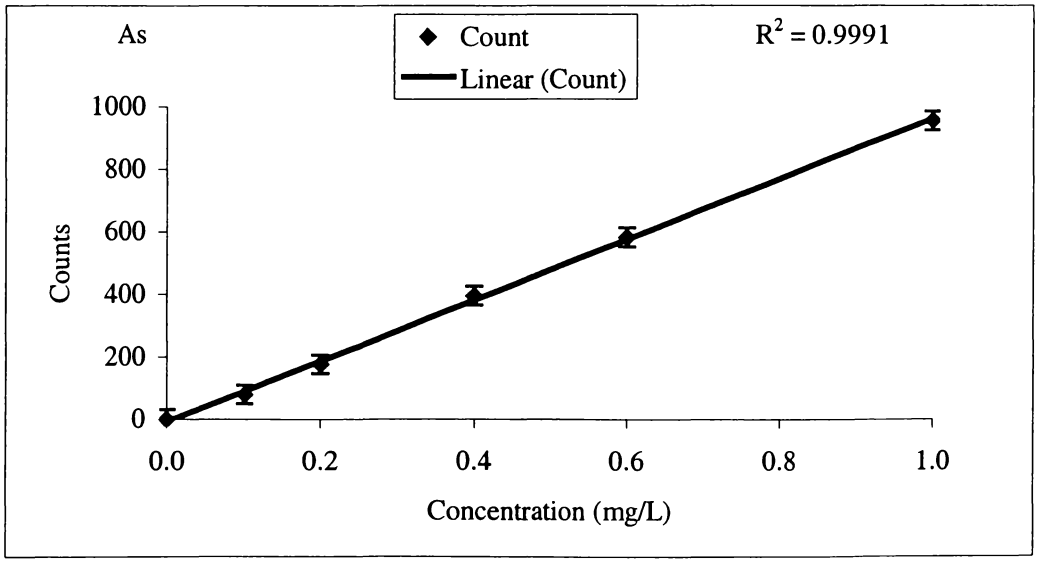


Figure A2.14. As calibration curve using ICP.

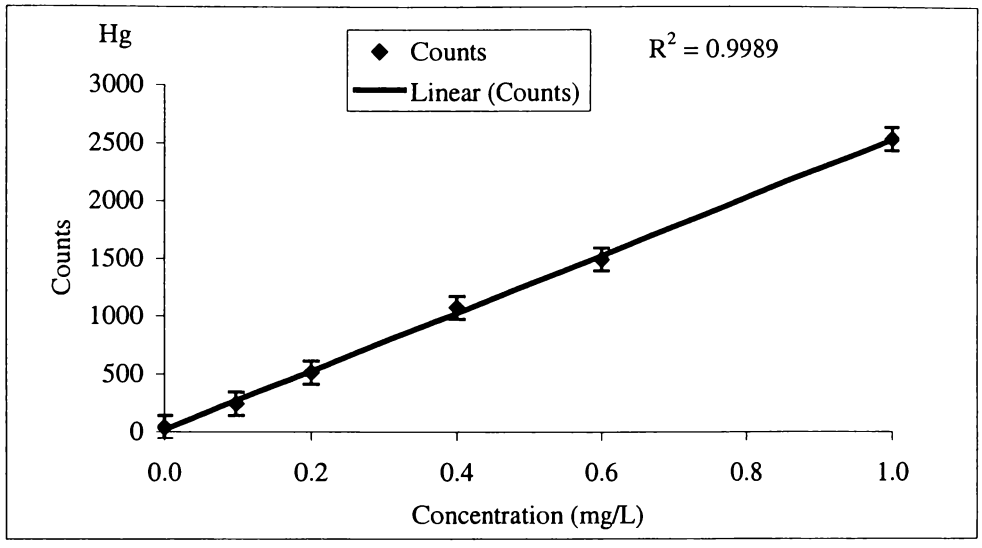


Figure A2.15. Hg calibration curve using ICP.

Appendix 3

Data Tables

Table A3.1. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for ferric sulphite (10-70 mg/L) flocculated and Whatman No. 1 filtered SH30 Tarawera River water collected 27/7/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	normalised
SH30	0.172	0.068	0.020	1.00	1.00	1.00	6.24	1.00
10 mg/L	0.365	0.162	0.026	2.12	2.38	1.30	6.56	1.05
20 mg/L	0.299	0.108	0.027	1.74	1.59	1.35	6.15	0.99
30 mg/L	0.466	0.215	0.041	2.71	3.16	2.05	6.45	1.03
40 mg/L	0.577	0.271	0.046	3.35	3.99	2.30	6.61	1.06
50 mg/L	0.622	0.302	0.051	3.62	4.44	2.55	6.88	1.10
60 mg/L	0.646	0.318	0.053	3.76	4.68	2.65	6.61	1.06
70 mg/L	0.628	0.326	0.049	3.65	4.79	2.45	6.61	1.06

Table A3.2. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for ferrous sulphite (10-130 mg/L) flocculated and Whatman No. 1 filtered SH30 Tarawera River water collected 27/7/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	normalised
SH30	0.195	0.075	0.023	1.00	1.00	1.00	4.26	1.00
10 mg/L	0.305	0.125	0.023	1.56	1.67	1.00	6.10	143
20 mg/L	0.568	0.253	0.044	2.91	3.37	1.91	6.15	1.44
30 mg/L	0.434	0.188	0.023	2.23	2.51	1.00	6.15	1.44
40 mg/L	0.705	0.324	0.054	3.62	4.32	2.35	5.45	1.28
50 mg/L	0.805	0.378	0.062	4.13	5.04	2.70	6.61	1.55
60 mg/L	0.906	0.428	0.067	4.65	5.71	2.91	4.88	1.15
70 mg/L	1.187	0.588	0.144	6.09	7.84	6.26	5.61	1.32
80 mg/L	1.313	0.66	0.113	6.73	8.80	4.91	4.62	1.08
90 mg/L	1.291	0.65	0.108	6.62	8.67	4.70	4.95	1.16
100 mg/L	1.364	0.687	0.113	6.99	9.16	4.91	6.75	1.58
110 mg/L	1.435	0.751	0.132	7.36	10.01	5.74	11.5	2.70
120 mg/L	1.405	0.76	0.137	7.21	10.13	5.96	15.7	3.69
130 mg/L	1.118	0.614	0.121	5.73	8.19	5.26	13.0	3.05

Table A3.3. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for calcium oxide (10-100 mg/L) flocculated and Whatman No. 1 filtered SH30 Tarawera River water collected 27/7/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	normalised
SH30	0.162	0.064	0.018	1.00	1.00	1.00	6.51	1.00
10 mg/L	0.168	0.067	0.018	1.04	1.05	1.00	7.81	1.20
20 mg/L	0.158	0.063	0.020	0.98	0.98	1.11	4.95	0.76
30 mg/L	0.151	0.055	0.016	0.93	0.86	0.89	5.10	0.78
40 mg/L	0.146	0.058	0.016	0.90	0.91	0.89	5.64	0.87
50 mg/L	0.146	0.056	0.014	0.90	0.88	0.78	5.03	0.77
60 mg/L	0.151	0.06	0.014	0.93	0.94	0.78	5.49	0.84
70 mg/L	0.148	0.058	0.015	0.91	0.91	0.83	6.03	0.93
80 mg/L	0.116	0.046	0.009	0.72	0.72	0.50	5.07	0.78
90 mg/L	0.115	0.045	0.010	0.71	0.70	0.56	6.04	0.93
100 mg/L	0.085	0.033	0.008	0.52	0.52	0.44	4.90	0.75

Table A3.4. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for polyacrylamide (10-100 mg/L) flocculated and Whatman No. 1 filtered SH30 Tarawera River water collected 27/7/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	normalised
SH30	0.170	0.071	0.021	1.00	1.00	1.00	5.96	1.05
10 mg/L	0.192	0.079	0.029	1.13	1.11	1.38	6.65	1.17
20 mg/L	0.191	0.073	0.028	1.12	1.03	1.33	6.65	1.17
30 mg/L	0.197	0.078	0.030	1.16	1.10	1.43	6.6	1.16
40 mg/L	0.183	0.070	0.023	1.08	0.99	1.10	5.69	1.00
50 mg/L	0.173	0.065	0.018	1.02	0.92	0.86	5.69	1.00
60 mg/L	0.165	0.062	0.017	0.97	0.87	0.81	5.71	1.00
70 mg/L	0.164	0.059	0.015	0.96	0.83	0.71	5.73	1.01
80 mg/L	0.160	0.057	0.015	0.94	0.80	0.71	4.72	0.83
90 mg/L	0.159	0.056	0.014	0.94	0.79	0.67	4.74	0.83
100 mg/L	0.158	0.058	0.014	0.93	0.82	0.67	4.83	0.85

Table A3.5. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for sodalime (30-100 mg/L) flocculated and centrifuged SH30 Tarawera River water collected 27/7/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	normalised
SH30	0.163	0.065	0.019	1.00	1.00	1.00	4.04	1.00
30 mg/L	0.151	0.063	0.016	0.93	0.97	0.84	3.56	0.88
40 mg/L	0.147	0.061	0.015	0.90	0.94	0.79	2.88	0.71
50 mg/L	0.148	0.059	0.015	0.91	0.91	0.79	2.68	0.66
60 mg/L	0.145	0.059	0.015	0.89	0.91	0.79	2.76	0.68
70 mg/L	0.144	0.058	0.014	0.88	0.89	0.74	2.76	0.68
80 mg/L	0.143	0.058	0.014	0.88	0.89	0.74	3.04	0.75
90 mg/L	0.142	0.057	0.014	0.87	0.88	0.74	3.00	0.74
100 mg/L	0.138	0.056	0.013	0.85	0.86	0.68	2.84	0.70

Table A3.6. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for sodium aluminate (10-90 mg/L) flocculated and centrifuged SH30 Tarawera River water collected 27/7/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	normalised
SH30	0.165	0.068	0.019	1.00	1.00	1.00	4.00	1.00
10 mg/L	0.178	0.072	0.021	1.08	1.06	1.11	4.42	1.11
20 mg/L	0.175	0.073	0.020	1.06	1.07	1.05	4.21	1.05
30 mg/L	0.162	0.063	0.016	0.98	0.93	0.84	3.37	0.84
40 mg/L	0.147	0.059	0.015	0.89	0.87	0.79	3.16	0.79
50 mg/L	0.145	0.055	0.013	0.88	0.81	0.68	2.74	0.68
60 mg/L	0.151	0.059	0.019	0.92	0.87	1.00	2.85	0.71
70 mg/L	0.146	0.057	0.014	0.88	0.84	0.74	2.95	0.74
80 mg/L	0.146	0.057	0.014	0.88	0.84	0.74	2.95	0.74
90 mg/L	0.141	0.056	0.013	0.85	0.82	0.68	2.74	0.68

Table A3.7. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for calcium chloride (10-80 mg/L) flocculated and Whatman No. 1 filtered SH30 Tarawera River water collected 27/7/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	normalised
SH30	0.172	0.061	0.019	1.00	1.00	1.00	4.04	1.00
10 mg/L	0.153	0.051	0.012	0.89	0.84	0.63	3.32	0.82
20 mg/L	0.156	0.056	0.010	0.91	0.92	0.53	3.36	0.83
30 mg/L	0.163	0.058	0.009	0.95	0.95	0.47	3.40	0.84
40 mg/L	0.156	0.051	0.008	0.91	0.84	0.42	3.32	0.82
50 mg/L	0.14	0.045	0.007	0.81	0.74	0.37	3.12	0.77
60 mg/L	0.137	0.044	0.006	0.80	0.72	0.32	3.60	0.89
70 mg/L	0.134	0.043	0.007	0.78	0.70	0.37	4.04	1.00
80 mg/L	0.134	0.043	0.007	0.78	0.70	0.37	3.60	0.89

Table A3.8. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for calcium hydroxide (20-10 mg/L) flocculated and centrifuged SH30 Tarawera River water collected 27/7/98.

	absorbance			normalised absorbance			turbidity	
	270 nm	340 nm	440 nm	270 nm	340 nm	440 nm	NTU	normalised
SH30	0.172	0.067	0.021	1.00	1.00	1.00	7.5	1.00
40 mg/L	0.169	0.064	0.019	0.98	0.96	0.90	5.4	0.72
60 mg/L	0.166	0.063	0.180	0.97	0.94	8.57	6.2	0.83
80 mg/L	0.164	0.060	0.017	0.95	0.90	0.81	5.2	0.69
100 mg/L	0.163	0.059	0.016	0.95	0.88	0.76	4.9	0.65

Appendix 4

Publications

1) Kanber, S. Ali, Wilkins, A. L., and Langdon, A. G., (2000). Speciation of Pulp Mill Derived Resin Acids in the Tarawera River, New Zealand, *Bull. Environ. Contam. Toxicol.,* **64**, 622-629.

2) Kanber, S. Ali, Wilkins, A. L., and Langdon, A. G., (2001). Particle Association of Pulp and Paper Mill Sourced Resin Acids in Sodium Azide Stabilised Recipient Water, *Bull. Environ. Contam. Toxicol.,* **65**, in press.

3) Kanber, S. Ali, Wilkins, A. L., and Langdon, A. G., (2001). Particle association of resin acids and chromophoric species in water samples from the biological treatment system of two New Zealand pulp mills, *Bull. Environ. Contam. Toxicol.,* **65**, in press.

Speciation of Pulp Mill Derived Resin Acids in the Tarawera River, New Zealand

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We have previously reported the levels of resin acids and degraded resin neutrals in Tarawera River water and sediment samples, collected downstream of the discharge points of two pulp and paper mills (Wilkins, et al 1996a, 1996b, Wilkins & Panadam, 1987). While much is known about the levels of resin acids, cations, anion, and absorbance of Tarawera River water samples, and adjacent ground waters (Wilkins et al 1996b, 1998), no account of resin acid speciation in this natural receiving water has appeared. Previous work in our laboratory has shown that ultra filtration significantly reduces the recovery of resin acids from Tarawera River water samples (Osborne 1991).

In this paper we report an assessment of the level of extractable resin acids recoverable from Whatman No 1, glass fiber, and 3, 0.8, 0.45, 0.2, 0.05 and 0.025 μm filtered SH30 Tarawera River water samples. The results presented here show that in natural Tarawera River water (pH 7.3-7.6) resin acids are predominantly surface adsorbed (bound) to suspended solid material with particle sizes in the range 0.02-15 microns.

MATERIALS AND METHODS

Water samples, in screw capped 2.5 L glass winchesters, were collected from the Tarawera River at the SH30 bridge on 16/6/98 and 14/12/98, and transported to our laboratory on the day of collection. Unless otherwise specified, water samples were stored at 5°C until required for extraction. Cation and color levels were determined using filtered (Whatman No 1) solutions. Na, K (diluted 5 fold), and Ca levels were determined at 422.7, 766.5 and 589.0 nm respectively, using a GBC 909 AA spectrometer and an air-acetylene flame. Fe levels were determined at 386 nm using a GBC 905 furnace AA spectrometer. Absorbances at 270, 340 and 440 nm were determined using a 1 cm quartz cell and a Hitachi 15-20 spectrometer. The pH of water samples was determined using an EPM-120 pH meter, calibrated against pH 6.86 and 4.00 buffer solutions. Conductivity was determined at 25°C using a Philip PR 9501 conductivity meter, calibrated against 0.01 mol/L KCl. Turbidity was determined using a Hach 2100 Turbidimeter. Total and free resin acid levels were determined for well mixed 1 L sub-samples of river water, typically prepared by combining 3 x 2.5 L of river water in a 10 L vessel. After vacuum assisted filtration through Whatman No 1, glass fiber (Whatman), or 3, 0.8, 0.45, 0.2, 0.05 or 0.025 μm (Millipore) filter papers, water samples were liquid/liquid extracted with CH_2Cl_2 for 16 h. *O*-Methylpodocarpic acid ethyl ester as internal standard was added to

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the extractive solution which was concentrated using a rotary evaporator, derivatised with CH_2N_2, and analysed using selected ion mode (SIM) GC/MS detection, as reported previously (Wilkins et al. 1996b). Bound resin acid levels were determined by Soxhlet extraction of Whatman No 1, glass fiber, or 3 to 0.025 μm (Millipore) filter papers with CH_2Cl_2 *O*-Methylpodocarpic acid ethyl ester, as internal standard, was added to extractive solutions which were concentrated using a rotary evaporator, derivatised with CH_2N_2, and analysed using selected ion mode (SIM) GC/MS detection, as reported previously (Wilkins et al. 1996b). Bound resin acid levels are reported as □g/L of filtered river water. Recovery of *O*-methylpodocarpic acid spiked directly into water samples or onto filter papers, prior to liquid-liquid extraction or Soxhlet extraction, respectively, was typically in the range 75-115%. Replicate data (n = 4, 5 or 6), standard deviation and % CVs are reported for SH30, Whatman No 1 and glass fiber filtered river water samples (Table 2). Summary data for other river water samples are given in Table 3. Calculation were performed using purpose written Excel spreadsheets. Resin acid concentrations (Tables 1, 2, 3, 5 and 7) are rounded to ± 0.1, or 0.01 μg/L for concentrations in the range 0.02-0.99, or 1.0-65.0 μg/L, respectively.

River water collected on 14/12/98 was sequentially filtered through glass fiber (7.5 L), and 3 μm (6.4 L), 0.8 μm (5.3 L), 0.45 μm (4.2 L), 0.2 μm (3.1 L), 0.05 μm (2 L) and 0.025 μm (0.8 L) filter papers. After each filtration step, 1 L (or 0.7 L for 0.025 μm) filtered water and the corresponding filter paper were liquid-liquid extracted, or Soxhlet extracted, respectively. Filtered water samples were prepared and liquid/liquid, or Soxhlet extracted (filter papers), on the same day. Cation, color, conductivity and turbidity levels were also determined for each of the filtered river water samples.

RESULTS AND DISCUSSION

In recent years pHs ranging from 2 to 12 have been used in liquid-liquid extraction of resin acid from pulp mill effluents. Some workers have advocated the use of an acidic extraction medium to minimise dissociation of resin acids, while other worker have recommended an alkaline extraction media in order to minimise resin acid isomerisation (Li et al, 1996; Morales et al, 1992; Voss & Rapsomatiotis, 1985, Richardson & Bloom, 1982).

Resin acid levels identified in replicate pH 4, pH 7.6 (natural river pH) and pH 10 liquid/liquid extractions of Tarawera River water samples collected at the SH30 bridge, ca 4 km downstream of the discharge points of two pulp and paper mills are presented in Table 1. These results show that for highly colored Tarawera River water samples, extraction at pH 10, offers no advantage over extraction at pH 7.6, while extraction at pH 4 results in a lesser recover of resin acids (ca 80% of that recoverable at pH 7.6).

The decreased recovery obtained after 0.45 μm filtration of pH 4, 7.6 and 10 river water samples (Table 1) suggested that some of the recoverable resin acids were bound to suspended solid materials (sediment particles, macromolecular aggregates of lignans, etc). While some information is available in respect of cation speciation in natural waterways (for example Shkinev et al (1996) have recently reported an assessment of Na, K, Mg, Ca, Mn, Ni, Al, Zn and Fe speciation in two German rivers, no information is available in respect of resin acid speciation in New Zealand recipient waters.

Table 1. SIM GC/MS determined resin acid levels (μg/L, mean of duplicate analyses) identified in pH adjusted SH30 Tarawera River water samples, collected 16/6/1998.

	Seco1/2	Pim	18-Ab	DHAA	Abiet	13-ene	Cl's	TRA	%
pH 7.6 (as collected)	11.6	3.8	23.4	8.5	2.4	16.1	3.6	69.4	
pH 4	9.6	3.1	17.8	8.4	1.7	12.0	2.2	54.8	79%
pH 10	10.8	3.6	22.0	8.5	2.2	15.6	2.7	65.4	94%
pH 7.6 0.45 μm filtered	3.7	1.7	10.6	4.2	0.5	7.1	1.1	28.9	42%
pH 4 0.45 μm filtered	4.5	1.8	8.9	5.4	0.5	6.7	1.0	28.8	41%
pH 10 0.45 μm filtered	3.4	1.5	9.3	4.0	0.5	6.4	1.0	26.1	38%

Abbreviations: Seco 1/2 = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid; Abiet = abietic acid; 13-ene = abiet-13-en-18-oic acid; Cl's = 12-Cl, 14-Cl and 12,14-dichlorodehydroabieyic acids; TRA = total resin acids; % = % resin acids relative to unfiltered SH30 water, pH 7.6.

Replicate extractions of 0.45 μm filtered river water samples, collected 16/6/98, resulted in resin acid recoveries of 38-42% of that obtained for unfiltered pH 7.6 (natural) river water, irrespective of the extraction pH. Subsequently, multiple extractions (n = 3 to 6) of Whatman No 1, glass fiber , 0.8 and 0.45 μm filtered river water (collected 12/12/98) at its natural pH, verified the presence of appreciable levels of particle bound resin acids (Tables 2 and 3). Reproducibility and standard deviation data established the reliability and significance of the results. Color, conductivity and selected cation (Na K, Ca and Fe) levels were also determined in replicate (n = 3 to 6) for the filtered river water samples (Table 4).

The analyses of organic substances in recipient water samples is compounded by the continuing bio-degradation of organic substances after sample collection. Degradation can (for example) be arrested by the addition of sodium azide or mercuric salts, however these species interfere with cation analyses and may function as resin acid focculation agents (eg by formation of mercuric resin acid salts). Application of curve fitting techniques to resin acid levels determined for river water samples stored at 5°C in screw capped glass winchesters for 1, 6 and 22 days (see Tables 2 and 3) were consistent with the conclusions that total resin acid levels decayed exponentially with a half-life of 19 days, and that over a 3 day period resin acid levels typically decayed by 5-7%. This decrease is of the order of, or in most cases less than, the standard deviation established for replicate extractions (see Table 2). Equipment limitations necessitated that groups of filtration and extraction experiments were typically carried out over 2-3 day periods. The results presented in Tables 2 and 3 should be interpreted accordingly. On two occasions unfiltered river water samples, sample F (Table 2) and samples E and F (Table 3), were allowed to stand in open beakers, at 5°C for 24 hr, before liquid/liquid extraction. These samples exhibited resin acid levels 79-83% of those determined for replicate samples (ex fully filled, capped, winchesters) extracted the preceding day.

Filtration through glass fiber and Whatman No 1 filter paper reduced total resin acid levels to 64 and 68% respectively of the average level determined for SH30 water samples extracted 24-48 hours previously. The bulk of resin acids removed by filtration were recovered by Soxhlet extraction of the filter papers. The standard deviation and % coefficient of variation (%CV) determined for the Soxhlet extractions were higher than those determined for liquid/liquid extraction of filtered river water samples (see Table 2). Filtration through 0.45 μm and 0.8 μm filter papers (performed 6 and 22 days after collection respectively), resulted in resin acid reductions of 34-35% relative to similarly aged river water samples.

Table 2. SIM GC/MS determined resin acid levels (μg/L, mean of replicate analyses) identified in Tarawera River SH30 water samples, collected 14/12/98.

	seco 1/2	pim	18-Ab	DHAA	13-ene	Cl's	TRA	%
SH30 A [a]	8.3	6.7	17.8	10.0	15.8	2.4	61.0	
SH30 B	8.2	6.5	18.0	10.1	15.2	2.7	60.7	
SH30 C	9.0	7.0	17.0	10.1	15.5	2.5	61.1	
SH30 D	9.2	7.1	17.9	10.6	16.0	2.3	63.0	
SH30 E	8.1	6.8	17.7	10.5	15.7	2.5	61.2	
average	8.6	6.8	17.7	10.3	15.6	2.5	61.4	
stdev	0.49	0.23	0.39	0.29	0.31	0.14	0.94	
% CV	5.8%	3.3%	2.2%	2.8%	2.0%	5.7%	1.5%	
SH30 F (+24 hr)[b]	5.8	5.7	14.0	8.5	12.0	2.0	48.0	78%
Whatman No 1 filt. A[c]	5.8	5.9	12.3	7.7	10.8	2.0	44.3	
Whatman No 1 filt. B	5.9	6.3	13.3	7.8	11.7	2.2	47.1	
Whatman No 1 filt. C	5.9	6.1	12.6	8.0	11.2	1.9	45.7	
Whatman No 1 filt. D	4.3	4.6	9.9	6.5	8.9	1.5	35.7	
Whatman No 1 filt. E	5.3	5.7	12.1	7.4	10.7	1.9	43.2	
Whatman No 1 filt. F	4.0	4.2	9.1	8.3	8.3	1.4	35.2	
average (n = 6)	5.2	5.5	11.6	7.6	10.3	1.8	41.9	68%
stdev	0.85	0.84	1.67	0.62	1.36	0.29	5.15	
% CV	16%	15%	14%	8.2%	13%	16%	12%	
Whatman No 1 Sox. A[c]	0.73	0.80	2.4	1.33	2.2	0.24	7.7	
Whatman No 1 Sox. B	0.49	0.53	1.4	0.85	1.3	0.27	4.8	
Whatman No 1 Sox. C	0.43	0.47	1.2	0.68	1.0	0.23	4.0	
Whatman No 1 Sox. D	0.37	0.40	1.1	0.62	0.8	0.12	3.4	
Whatman No 1 Sox. E	0.42	0.32	0.9	0.55	0.7	0.28	3.2	
Whatman No 1 Sox. F	0.54	0.60	1.4	0.83	1.2	0.04	4.3	
average (n = 6)	0.45	0.52	1.4	0.81	1.2	0.20	4.6	7.5%
stdev	0.13	0.17	0.53	0.28	0.54	0.09	1.7	
% CV	26%	32%	39%	35%	46%	48%	36%	
Glass fiber filtered A[b]	6.5	5.2	11.5	11.5	8.8	1.8	45.2	
Glass fiber filtered B	6.2	4.9	10.8	8.6	8.1	1.6	40.1	
Glass fiber filtered C	6.1	4.9	10.8	6.8	8.4	1.7	38.5	
Glass fiber filtered D	5.5	4.5	10.1	7.1	7.9	1.7	36.7	
Glass fiber filtered E	6.0	4.8	10.7	7.0	8.1	1.6	38.3	
Glass fiber filtered F	5.8	4.6	9.6	6.6	7.1	1.6	35.3	
average (n = 6)	5.9	4.7	10.46	7.2	7.9	1.6	39.0	64%
stdev	0.34	0.24	0.65	1.91	0.56	0.09	3.5	
% CV	5.8%	5.0%	6.2%	27%	7.1%	5.8%	8.9%	
Glass fiber Soxhlet A[b]	1.5	1.3	4.5	2.8	3.4	0.51	14.0	
Glass fiber Soxhlet B	1.6	1.4	4.3	3.1	3.0	0.52	13.9	
Glass fiber Soxhlet C	1.8	1.9	5.5	3.1	4.8	0.66	17.8	
Glass fiber Soxhlet D	1.5	1.4	4.1	2.6	3.5	0.52	13.6	
Glass fiber Soxhlet E	1.7	1.7	5.1	2.7	4.4	0.56	16.2	
Glass fiber Soxhlet F	1.4	1.1	3.8	1.9	2.7	0.42	11.3	
average (n = 6)	1.6	1.5	4.6	2.7	3.7	0.54	14.4	24%
stdev	0.15	0.28	0.63	0.45	0.82	0.08	2.2	
%CV	9.5%	19%	14%	17%	22%	15%	15%	

Abbreviations are as in Table 1, [a] extracted 15/12/98, [b] extracted 16/12/98, [c] extracted 17/12/98.

Table 3. SIM GC/MS determined resin acid levels (µg/L) (mean of replicate analyses) identified in SH30 Tarawera River, and 0.45 and 0.8 µm filtered, water samples, collected 14/12/1998.

	seco 1/2	pim	18-Ab	DHAA	13-ene	Cl's	TRA	%
SH30[a] (n = 4)	6.0	4.2	17.1	9.7	12.8	1.9	51.6	
stdev	0.34	0.10	0.34	0.50	0.32	0.10	1.1	
% CV	5.7%	2.4%	2.0%	5.2%	2.5%	5.0%	2.2%	
SH30 (+24 hr)[b] (n = 2)	4.5	3.6	13.9	8.0	10.9	2.2	42.9	83%
0.45 µm filtered (n = 4)	2.5	1.5	5.5	5.0	3.1	0.71	17.5	34%
stdev	0.33	0.21	1.36	0.53	0.58	0.10	3.2	
% CV	13%	14%	25%	11%	19%	14%	18%	
0.45 µm Soxhlet (n = 6)	2.5	1.7	8.2	5.3	6.0	0.81	24.6	47%
stdev	0.53	0.47	1.64	1.36	1.70	0.25	5.7	
% CV	21%	27%	20%	26%	28%	31%	23%	
SH30[c] (n = 3)	1.8	0.95	9.2	9.0	5.7	2.2	28.9	
stdev	0.12	0.09	0.35	0.35	0.75	0.0	1.6	
% CV	6.5%	9.5%	3.8%	3.8%	13%	-	5.5%	
0.8 µm filtered (n = 3)	0.93	0.29	2.5	4.1	1.6	0.67	10.0	35%
stdev	0.09	0.06	0.32	0.67	0.12	0.20	1.0	
%CV	9.9%	19%	13%	16%	7.4%	29%	10%	
0.8 µm Soxhlet (n = 3)	0.68	0.43	4.2	3.4	3.3	1.2	13.2	47%
stdev	0.09	0.04	0.44	0.42	0.46	0.19	0.9	
% CV	14%	8.4%	10%	12%	14%	8.3%	6.8%	

Abbreviations are as in Table 1; [a] extracted 20/12/98; [b] extracted 21/12/98 after overnight storage in a beaker at room temperature; [c] extracted 5/1/99.

Table 4. Color (absorbance), conductivity, and Na, K, Ca and Fe levels (mg/L) determined for SH30 Tarawera River water samples, collected 14/12/98.

	270 nm	340 nm	440 nm	cond x 10^{-3}	Na ppm	K ppm	Ca ppm	Fe ppm
SH30 (15/12/98)[a]	0.186	0.074	0.027	0.410	67.6	8.2	0.80	0.18
stdev (n = 6)	0.002	0.000	0.001	0.000	1.7	0.1	0.10	0.05
Whatman No1	0.179	0.071	0.023	0.410	66.5	8.0	0.84	0.18
stdev (n = 6)	0.002	0.001	0.002	0.000	1.8	0.1	0.07	0.01
Glass fiber	0.169	0.061	0.019	0.410	66.4	7.9	0.62	0.21
stdev (n = 6)	0.003	0.002	0.002	0.000	0.9	0.2	0.07	0.05
SH30 (20/12/98)[a]	0.163	0.060	0.019	0.410	61.8	8.5	0.82	0.12
stdev (n = 6)	0.002	0.001	0.001	0.000	2.5	0.4	0.02	0.01
0.45 µm filtered	0.137	0.047	0.013	0.406	56.9	8.5	0.86	0.11
stdev (n = 6)	0.003	0.001	0.001	0.000	0.9	0.3	0.05	0.02
SH30 (7/1/98)[a]	0.161	0.060	0.019	0.410	65.3	8.1	0.80	0.13
stdev (n = 4)	0.001	0.001	0.001	0.000	2.0	0.3	0.08	0.02
0.80 µm filtered	0.130	0.046	0.011	0.406	64.9	8.3	0.84	0.11
stdev (n = 4	0.003	0.001	0.001	0.000	2.5	0.1	0.07	0.06

[a]extraction date

Greater levels of resin acids were recovered by Soxhlet extraction of the respective filter papers (c 47% of the levels in unfiltered river water samples). Filtration through Whatman No 1, glass fiber, 0.45 and 0.8 μm filter papers did not alter cation or conductivity levels (Table 4). Color levels were however attenuated, especially so at 340 and 440 nm. The downward trend in color levels exhibited by unfiltered SH30 Tarawera River water samples (eg absorbances of 0.186, 0.074 and 0.027 at 270, 340 and 440 nm respectively when first collected compared to absorbances of 0.163, 0.060 and 0.019 respectively after 6 days) can be attributed to the gradual flocculation (precipitation) of lignans and other chromophoric polyphenols during storage at 5°C.

The results obtained for river water sequentially filtered through glass fiber, 3, 0.8, 0.45, 0.2, 0.05 and 0.025 μm filtered papers are presented in Tables 5 and 6. Resin acid removal was consistent with results reported in Tables 3 and 4. The design of the multi-filtration experiment is such that for a particular pore size, the sum of the liquid/liquid and Soxhlet extracted resin acid levels should equal the liquid/liquid determined level of resin acids in the preceding filtered water sample (Figure 1).

Table 5 SIM GC/MS determined resin acid levels (μg/L) identified in multi-filtered Tarawera River SH30 water samples

	seco	1/2 pim	18-Ab	DHAA	13-ene	Cl's	TRA	%
SH30 A (24/12/98)[a]	3.1	3.8	12.9	8.3	11.0	1.8	40.9	
SH30 B (24/12/98)	3.0	2.9	11.4	8.2	10.5	1.8	37.8	
average	3.1	3.4	12.2	8.3	10.8	1.8	39.6	100%
glass fiber (liq/liq)	1.7	1.9	6.6	5.5	5.4	1.1	22.20	56%
3 μm (liq/liq)	1.4	1.4	5.1	4.9	3.8	0.9	17.5	44%
0.8 μm (liq/liq)	1.3	0.9	2.8	4.8	2.2	0.5	12.5	32%
0.45 μm (liq/liq)	1.2	1.0	3.4	4.0	2.5	0.6	12.7	32%
0.2 μm (liq/liq)	1.0	0.7	2.5	1.8	2.1	0.6	8.7	22%
0.05 μm (liq/liq)	0.9	0.5	1.1	3.2	-	0.3	6.0	15%
0.025 μm (liq/liq)	0.5	0.4	0.2	2.4	-	-	3.5	9%
glass fiber (Soxhlet)	0.5	0.6	2.6	1.8	3.2	0.4	9.1	23%
3 μm (Soxhlet)	0.23	0.4	1.3	1.1	1.7	0.2	4.9	13%
0.8 μm (Soxhlet)	0.08	0.1	0.5	0.4	0.6	0.1	1.8	5%
0.45 μm (Soxhlet)	0.06	0.1	0.2	0.3	0.3	tr	1.0	3%
0.2 μm (Soxhlet)	0.1	0.2	0.6	0.6	0.7	0.1	2.3	6%
0.05 μm (Soxhlet)	0.3	0.6	1.5	1.7	1.3	0.2	5.6	14%
0.025 μm (Soxhlet)	-	-	0.2	0.9	-	0.1	1.2	3%

[a] Extraction date.

There appears to be a logarithmic relationship between filter pore size and resin acid level (Figure 2). A downward trend was apparent in color levels with the greatest change (% reduction) in color occurring at 440 nm. A similar downward trend was apparent in turbidity levels. Conductivity, Na, K and Ca levels were not affected by filtration. On the other hand, Fe levels were substantially attenuated by 0.05 μmfiltration, as was also the case in the conventional filtration experiment. This suggests the presence in Tarawera River water samples of fine Fe colloidal particles < 0.1 μm in size. Resin acid levels did not correlate with Fe levels.

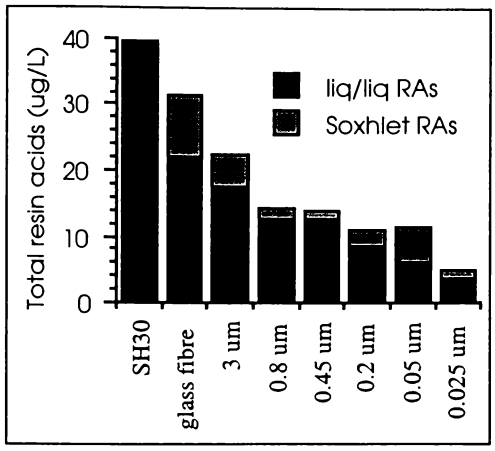

Figure 1. Plot of free and bound resin acid levels determined for multi-filtered Tarawera River water samples.

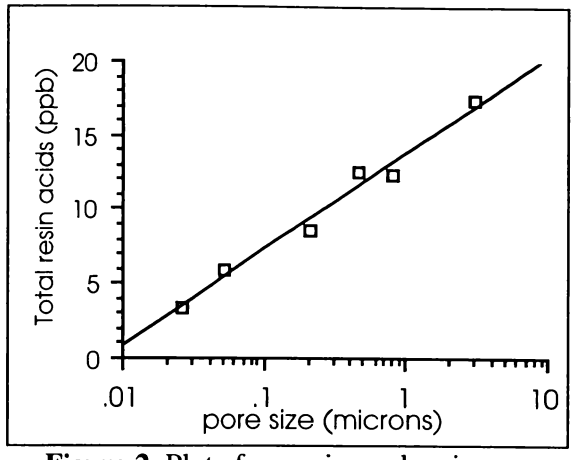

Figure 2. Plot of pore size and resin acid levels determined for filtered Tarawera River water samples.

Table 6. Color, turbidity, conductivity and cation levels (ppm) determined for SH30 Tarawera River water, collected 14/12/98.

	270 nm	340 nm	440 nm	turbidity	cond x 10^{-3}	Na ppm	K ppm	Ca ppm	Fe ppm
SH30	0.147	0.051	0.016	2.94	0.410	65.2	9.0	0.86	0.24
glass fiber filtered	0.145	0.048	0.013	1.50	0.406	66.3	7.9	0.70	0.22
3 μm filtered	0.136	0.044	0.011	1.14	0.406	69.1	8.2	0.84	0.21
0.8 μm filtered	0.132	0.042	0.007	1.20	0.406	63.9	8.0	0.72	0.26
0.45 μm filtered	0.126	0.037	0.006	1.20	0.406	68.0	8.3	0.77	0.20
0.2 μm filtered	0.117	0.034	0.006	0.97	0.404	66.3	8.3	0.68	0.22
0.05 μm filtered	0.117	0.033	0.005	0.87	0.404	66.3	8.7	0.71	0.02
0.025 μm filtered	0.111	0.030	0.004	0.80	0.404	68.9	8.0	0.74	0.02

In addition to resin acids, degraded resin neutrals may be present in Tarawera River water samples (Wilkins & Panadam, 1987). Generally only low levels of resin neutrals are present, however on some occasions elevated levels of resin neutrals may be present (released, for example, during routine dredging of effluent treatment ponds). Water samples collected on 16/6/98 contained greater than normal levels of resin neutrals (Table 1). Resin neutrals were more efficiently recovered from unfiltered water samples, without pH adjustment, than was the case at pH 4 and pH 10. 0.045 μm filtration prior to liquid extraction substantially reduced the recoverability of resin neutrals.

Table 7. SIM GC/MS determined resin neutral levels (□g/L) identified in SH30 Tarawera River water samples collected 16/6/98. % recoveries relative to natural, unfiltered, river water are given in brackets.

	fichtelite	dehydro-abietin	tetrahydro-retene	retene	total resin neutrals
SH30	5.7	0.70	4.2	11.0	21.6
SH30 pH 4	4.8 (84%)	0.42 (61%)	2.9 (68%)	7.1 (64%)	15.2 (70%)
SH30 pH 10	4.5 (79%)	0.50 (71%)	3.0 (72%)	7.7 (70%)	15.8 (73%)
SH30 0.45 □m	2.2 (38%)	0.16 (23%)	0.44 (10%)	0.8 (7%)	3.6 (17%)
SH30 pH 4 0.45 □m	2.6 (45%)	0.17 (25%)	0.66 (15%)	1.1 (10%)	4.5 (21%)
SH30 pH10 0.45 □m	2.1 (36%)	0.10 (14%)	0.41 (10%)	0.8 (7%)	3.3 (15%)

The greater the aromaticity of the substrate (3, 2, 1 and 0 aromatic rings are present in retene, tetrahydroretene, dehydroabietin and fichtelite respectively), the greater the removal by 0.45 μm filtration. It is apparent that resin neutrals, which because of their hydrocarbon nature and absence of a carboxyl group are less hydrophilic than resin acids, are more extensively surface absorbed to suspended solid particles than are resin acids (Table 1).

This work shows that liquid/liquid extraction can be used to reliably recover free and adsorbed resin acids in Tarawera River (but not necessarily other) water samples. Our results have implications in respect of the ability of some extraction protocols to recover both free and particle bound resin acids and resin neutrals. In particular, there appears to be a need to critically assess if solid phase methods (eg those using Bond-elut type C8 or C18 cartridges) recover resin acids and resin neutrals by a combination of absorption (from the aqueous phase to the C8 or C18 phase), and by filtration (trapping of particulates, which may or may not release absorbed resin acids when flushed with methanol or other eluents). We also anticipate that a knowledge of resin acid speciation effects and associations with particulate matter and chromophoric macromolecules, will contribute to the development of improved treatment technologies for pulp mill and other effluent waters.

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Particle Association of Pulp and Paper Mill Sourced Resin Acids in Sodium Azide Stabilised Recipient Water

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We have previously reported an investigation of the levels of free and bound resin acids present in Tarawera River (North Island, New Zealand) water samples collected at the State Highway 30 (SH30) bridge down stream of the discharge points of two pulp and paper mills (Ali Kanber et al, 2000). Our analyses showed that typically >50% of recoverable resin acids were bound to particles in the range 0.025-15 μm. A difficulty encountered in these investigations was the continuing degradation of resin acids during reproducibility and sequential filtration experiments, which were typically performed several days, or weeks, after collection. This constraint prompted us to investigate the possibility that post-collection biodegradation of resin acids could be inhibited by the addition of 0.1% sodium azide to the water samples at the time of collection.

In this paper we report the outcomes of experiments which showed (a) sodium azide addition inhibited the biodegradation of resin acids in Tarawera River water samples for periods of up to 90 days, (b) azide stabilised sequential filtration experiments afforded results which were comparable to those previously reported for non-stabilised water samples, and (c) settling during storage prior to the withdrawal of analytical samples influenced the recovery of free and particle bound resin acids. We also report SEM evidence for the presence of Fe, Al, C and O rich surface deposits on particulate matter recovered by filtration of river water samples.

MATERIALS AND METHODS

Water samples in screw capped 2.5 L glass Winchesters or 20 L plastic containers were collected from the Tarawera River at the SH30 Bridge. After the addition of 0.1% of sodium azide, water samples were stored at 4°C (or 8°C; preliminary experiments) until required for analyses. Turbidity was determined using a Hach 2100 turbidimeter. Absorbances at 270, 340 and 440 nm were determined using a 1 cm quartz cell and a Hitachi 15-20 spectrometer. The pH of water samples was determined using an EPM-120 pH meter, calibrated against pH 6.86 and 4.0 buffer solutions. Total suspended solid (TSS) levels were determined gravimetrically by collecting suspended solid material on pre-weighed filter papers (Whatman 0.45 μm) followed by furnacing at 550°C overnight to afford the level of inorganic suspended solids (ISS). Organic suspended solids (OSS) were calculated as TSS-ISS. Free and bound resin acid levels (μg/L) of filtered river water, were determined for well mixed sub-samples of sodium azide stabilised Tarawera River water using previously reported liquid-liquid or Soxhlet extraction and selected ion GC-MS methodologies (Ali Kanber et al, 2000). The recovery of *O*-methylpodocarpic acid was typically 75-105%. Sodium azide stabilised river water, in a 20 L plastic container, was thoroughly shaken and allowed to stand for 30 min before analytical samples (2 x 1 L and 1 x 6 L) were withdrawn from a tap located 50 mm from the bottom of the container. The 6 L sample was sequentially filtered through glass fibre (6 L), 3 μm (4.9 L), 0.8 μm (3.8 L), 0.45 μm (2.7 L),

0.2 μm (1.6 L) and 0.05 μm (0.6 L) filter papers. After each filtration step, the filter papers and 1 L (or 0.6 L for the 0.05 μm filtered sample) portions of the filtered water were Soxhlet or liquid-liquid extracted respectively. Filtered and unfiltered water samples were prepared and liquid/liquid or Soxhlet extracted (filter papers) on same day.

Settled, sodium azide stabilised river water in a 20 L plastic container was thoroughly shaken at t = 0, and allowed to stand without being disturbed for 30 days. Sub-samples (2 or 3 L) were gently drawn off from a tap located 50 mm above the bottom of the container after 15 and 30 min, 1 and 8 h, and 14, 26 and 30 days. The residue (1.6 L) remaining in the container (below the tap) at the end of the sampling period was thoroughly mixed and divided into 2 x 800 mL sub-samples which were filtered thorough Whatman No 1 and 0.45 μm filter papers (residue 1), or a 0.45 μm filter paper (residue 2), prior to liquid/liquid extraction or Soxhlet extraction.

Surface examination of particulate matter recovered from water samples by filtration was undertaken using a Hitachi S4000 scanning electron microscope (SEM). Energy dispersive X-ray analyses was performed using a Kevex microanalyser. River water (0.5 L) was filtered using a 0.45 μm filter paper and the filtrate was freeze dried (DYNAVAC FD12). Small portions of the freeze residue, or a small piece of filter paper covered with suspended solid material were smeared on double sided conductive carbon sellotape (Shrinton, Japan), which were mounted on an SEM stub and coated with 200 to 500 Å of platinum-palladium using a diode sputtering system (Hitachi E1030). Distribution maps were used to identify the location of surface concentrations of elements.

RESULTS AND DISCUSSION

Our earlier finding that post collection biodegradation of resin acids present in natural (unstabilised) Tarawera River water samples stored at 4°C proceeded with a half life of c 19 days (Ali Kanber et al, 2000) prompted us to investigate the possibility that the addition of sodium azide would inhibit the biodegradation of resin acids. The levels of resin acids identified in preliminary experiments by liquid/liquid extraction of natural and sodium azide stabilised SH30 Tarawera River water samples stored for 1-14 days at 8°C are compared in Figure 1. Within the expected uncertainty of the analyses (Ali Kanber et al, 2000), there was no degradation of resin acids in the sodium azide stabilised system but c 50% of the resin acids were degraded in the unstabilised (natural) system.

The levels of resin acids recovered from duplicate unfiltered sodium azide stabilised SH30 river samples, collected on 25/2/99 and stored for 5, 60 and 90 days at 4°C, are presented in Table 1. The 60 and 90 day results correspond to storage periods which are c 3 and 5 times respectively the estimated 19 day half life for resin acid degradation in unstabilised SH30 Tarawera River water samples

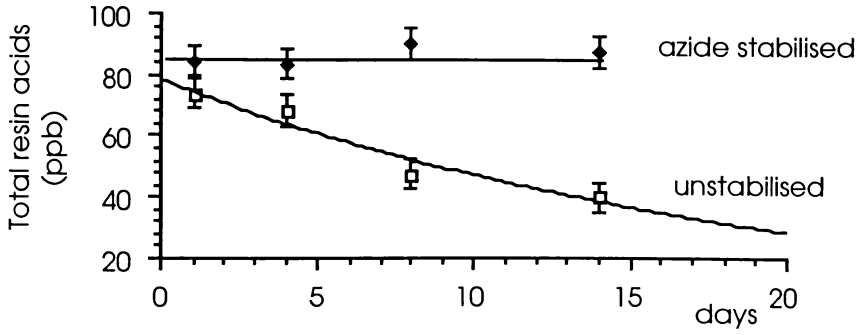

Figure 1. Resin levels determined for sodium azide stabilised and unstabilised Tarawera River water collected 14/1/99 and stored at 8°C.

stored at 4°C (Ali Kanber et al, 2000). More detailed analyses of river water samples collected on 4/3/2000 and 3/4/2000 (Table 2) validated our initial conclusion that sodium azide addition arrested the biodegradation of resin acids and the recovery of resin acids was not altered by the addition of sodium azide. Generally similar results were obtained using unfiltered Tarawera River water and river water which was filtered through sintered glass to remove visible particles such as grass, bark and leaf fragments. Differing levels of resin acids (especially abiet-13-enoic acid, believed to be an intermediate in the bioconversion of abietic acid to abietan-18-oic acid) were identified in the 3/4/2000 samples. The recovery and standard deviation data reported in Tables 2 and 3 for dehydroabietic acid (DHAA) and other resin acids can be compared to those reported elsewhere using other extraction, derivatization and analytical protocols (Morales et al, 1992; Lee et al, 1990; Richardson & Bloom, 1982; Voss & Rapsomatiotis, 1985).

The results of sequential filtration experiments performed using sodium azide stabilised river water which had been stored for 5 and 90 days prior to analyses are presented in Tables 3 and 4 respectively. These results showed that for sodium azide stabilised river water samples that had been stored for up to 90 days, particle associated resin acids levels and speciation effects were comparable to those which we have previously reported for freshly collected, unstabilised, river water samples (Ali Kanber et al, 2000). Our results are also consistent with the finding of Hall and Liver (1996) that, in the biomass system which they investigated, sodium azide addition inhibited resin acid degradation during partitioning experiments.

Table 1. Resin acid levels (μg/L) determined for sodium azide stabilised SH30 Tarawera River water samples collected 25/2/99.

storage time	seco1/2	pim	18-Ab	DHAA	13-ene	Cls	TRA
5 days, + azide (n = 2)[a]	21.9	9.4	25.0	17.5	24.9	3.6	102
60 days, + azide (n = 2)[a]	16.4	7.0	24.7	18.7	26.4	2.9	96
90 days, + azide (n = 2)[a]	17.0	6.1	25.6	20.3	28.1	4.3	101

[a] Average of duplicate analyses. Abbreviations: seco1/2 = secodehydroabietic acids-1 and 2; Pim = pimaric acid, 18-Ab = abietan-18-oic; DHAA = dehydroabietic acid; 13-ene = abiet-13-en-18-oic acid; Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, TRA = total resin acids

Table 2. Resin acid levels (μg/L) identified in replicate analyses of unfiltered SH30 Tarawera River water samples collected 4/3/2000.

storage time	secol/2	pim	18-Ab	DHAA	13-ene	Cls	TRA	recv[a]
SH30 A, t = 0, no azide	7.6	5.7	14.6	9.2	25.7	1.5	64.4	93%
SH30 B, t = 0, no azide	8.3	6.3	15.9	10.4	28.3	1.4	70.7	98%
SH30 C, t = 0, no azide	7.6	5.5	14.2	9.2	24.7	1.6	62.7	89%
SH30 D, t = 0, no azide	8.6	6.0	14.9	9.3	27.3	1.5	67.7	96%
SH30 E, t = 0, no azide	8.0	6.0	15.4	9.4	26.6	1.7	67.0	96%
SH30 F, t = 0, no azide	8.1	5.8	15.7	9.7	27.0	1.7	68.1	98%
average (n = 6)	8.0	5.9	15.1	9.5	26.6	1.6	66.8	95%
stdev (n = 6)	0.39	0.28	0.66	0.46	1.3	0.12	2.8	(4%)
% cv	4.9%	4.7%	4.4%	4.9%	4.7%	7.7%	4.3%	
SH30 A, 30 days, + azide	7.6	5.8	14.9	9.2	25.1	1.5	64.1	92%
SH30 B, 30 days, + azide	8.3	5.8	14.9	9.2	24.3	1.6	64.1	100%
SH30 C, 30 days, + azide	7.4	5.4	12.7	8.7	22.0	2.0	57.7	93%
SH30 D, 30 days, + azide	7.7	5.6	14.7	9.6	24.5	1.6	63.6	90%
SH30 E, 30 days, + azide	8.2	6.2	14.8	9.3	24.9	1.7	65.0	92%
SH30 F, 30 days, + azide	9.1	6.5	16.8	10.5	28.4	1.7	72.9	108%
average (n = 6)	8.1	5.9	14.8	9.4	24.9	1.7	64.6	96%
stdev (n = 6)	0.62	0.40	1.3	0.60	2.1	0.17	4.9	(7%)
% cv	7.7%	6.8%	8.8%	6.4%	8.3%	10.1%	7.5%	

[a]recv = % recovery of *O*-methylpodocarpic acid. Other abbreviations are as in Table 1.

Table 3. Resin acid levels (μg/L) identified in replicate analyses of sintered glass filtered SH30 Tarawera River water samples collected 3/4/2000.

storage time	secol/2	pim	18-Ab	DHAA	13-ene	Cls	TRA	recv[a]
SH30 A, t = 0, no azide	14.0	15.3	15.6	18.7	98	2.3	164	93%
SH30 B, t = 0, no azide	14.4	16.5	17.6	19.5	104	2.3	174	93%
SH30 C, t = 0, no azide	13.3	15.1	15.2	17.9	97	2.3	161	87%
SH30 D, t = 0, no azide	15.2	16.2	17.8	23.0	105	2.4	180	97%
SH30 E, t = 0, no azide	14.1	16.1	17.4	19.5	103	2.4	173	93%
average (n = 5)	14.2	15.8	16.7	19.7	101	2.3	170	93%
stdev (n = 5)	0.69	0.61	1.22	1.95	3.65	0.08	7.7	(4%)
% cv (n = 5)	4.9%	3.8%	7.3%	9.9%	3.6%	3.6%	4.5%	
SH30 A, 1 day, + azide	14.2	16.1	17.5	18.6	104	2.4	173	91%
SH30 B, 1 day, + azide	13.4	16.3	17.4	19.0	105	2.4	174	89%
SH30 C, 1 day, + azide	13.9	15.9	16.1	18.9	102	2.2	169	89%
SH30 D, 1 day, + azide	14.6	16.3	17.9	19.9	107	2.4	178	96%
SH30 E, 1 day, + azide	14.1	16.2	17.7	20.3	106	2.6	177	95%
average (n = 5)	14.0	16.2	17.3	19.3	105	2.4	174	92%
stdev (n = 5)	0.44	0.17	0.71	0.72	1.9	0.14	3.6	(4%)
% cv (n = 5)	3.1%	1.0%	4.1%	3.7%	1.8%	5.9%	2.1%	
SH30 A, 30 days, + azide	13.5	15.3	15.5	18.8	101	2.4	167	90%
SH30 B, 30 days, + azide	13.9	16.6	17.0	19.7	106	2.7	176	96%
SH30 C, 30 days, + azide	14.4	16.9	17.4	19.4	104	2.7	175	93%
SH30 D, 30 days, + azide	13.6	15.4	15.6	18.4	98	2.4	163	86%
SH30 E, 30 days, + azide	14.1	16.3	17.5	19.8	108	2.7	178	97%
average (n = 5)	13.9	16.1	16.6	19.2	103	2.6	172	93%
stdev (n = 5)	0.37	0.72	0.98	0.60	3.9	0.16	6.5	(5%)
% cv (n = 5)	2.6%	4.5%	5.9%	3.1%	3.8%	6.4%	3.8%	

[a] recv = % recovery of *O*-methylpodocarpic acid. Other abbreviations are as in Table 1.

Table 4. Resin acid levels (µg/L) identified in sequentially filtered SH30 Tarawera River water, collected 25/2/99.

	secol/2	pim	18-Ab	DHAA	13-ene	Cls	TRA	%[a]
SH30 (n = 2)[b]	21.9	9.4	25.0	17.5	24.9	3.6	102.2	100%
glass fibre (liq/liq)	17.1	7.1	15.5	12.2	15.9	2.7	70.5	69%
3 µm (liq/liq)	15.6	5.3	11.7	10.9	12.5	2.3	58.3	57%
0.8 µm (liq/liq)	13.6	4.6	10.0	8.7	10.8	2.1	49.8	49%
0.45 µm (liq/liq)	14.8	3.5	8.9	9.8	5.7	1.9	44.7	44%
0.2 µm (liq/liq)	12.6	2.4	4.8	8.9	4.5	1.2	34.3	34%
0.05 µm (liq/liq)	7.0	1.0	1.5	12.2	1.5	0.6	24.4	22%
glass fibre (Soxhlet)	3.7	6.2	6.8	6.1	9.4	1.7	34.0	33%
3 µm (Soxhlet)	0.5	0.9	2.2	1.7	2.4	0.3	7.9	8%
0.8 µm (Soxhlet)	0.7	1.1	2.7	2.0	2.7	0.3	9.4	9%
0.45 µm (Soxhlet)	0.4	0.7	1.8	1.4	1.5	0.2	6.0	6%
0.2 µm (Soxhlet)	0.9	1.2	3.2	2.6	3.0	0.6	11.4	11%
0.05 µm (Soxhlet)	0.8	1.3	2.7	2.3	2.0	1.3	10.2	9%

[a] % = % recovery relative to the unfiltered SH30 sample; other abbreviations are as in Table 1.
[b]Average of duplicate analyses.

Table 5. Resin acid levels (µg/L) identified in sequentially filtered sodium azide stabilised SH30 Tarawera River water, collected 25/2/99 and stored for 90 days.

	secol/2	pim	18-Ab	DHAA	13-ene	Cls	TRA	%
SH30 (n = 2)[a]	17.0	6.1	25.6	20.3	28.1	4.3	101.4	100%
glass fibre (liq/liq)	13.4	4.6	16.8	14.7	21.2	2.0	72.8	72%
3 µm (liq/liq)	14.0	3.8	10.7	10.4	12.9	1.2	53.1	52%
0.8 µm (liq/liq)	13.9	3.1	10.2	11.2	9.7	1.0	49.1	48%
0.45 µm (liq/liq)	13.0	2.3	7.2	9.5	8.3	1.2	41.6	41%
0.2 µm (liq/liq)	13.7	2.7	4.9	8.8	5.6	0.7	36.4	36%
0.05 µm (liq/liq)	10.0	-	1.7	13.8	2.3	0.5	28.3	28%
glass fibre (Soxhlet)	2.1	2.4	13.2	6.0	13.3	1.1	38.0	37%
3 µm (Soxhlet)	0.7	0.8	3.7	1.9	3.8	0.4	11.3	11%
0.8 µm (Soxhlet)	0.1	0.2	0.8	0.5	0.7	0.1	2.4	2%
0.45 µm (Soxhlet)	0.3	0.4	1.2	0.7	1.2	0.1	3.9	4%
0.2 µm (Soxhlet)	-	-	2.6	1.6	2.8	0.4	7.4	7%
0.05 µm (Soxhlet)	0.2	0.6	1.2	1.0	0.9	0.1	4.0	4%

[a] % = % recovery relative to the unfiltered SH30 sample; other abbreviations are as in Table 1.
[b]Average of duplicate analyses.

Since our results showed that, in both stabilised and unstabilised Tarawera River water samples, part of the recoverable resin acids are associated with particulate material we reasoned that if a bulk water sample was allowed to stand for an extended period, settling of particulate matter should occur and higher levels of resin acids would accumulate in water withdrawn from the bottom of a sample container. This proposal was explored using 2.5 L Winchesters and a bulk 20 L container. 2 or 3 L water sub-samples were withdrawn from a tap located 50 mm from the bottom of the 20 L container after t = 0 and 15 min, 1 and 8 h, and 14, 26 and 30 days. A portion of each of the water sub-samples was liquid/liquid extracted and the total resin acid (TRA) content was determined (Table 6).

Marginally higher levels of TRAs were detected in the 0-8 h sub-samples than was the case for the 14-30 day sub-samples.

After 30 days the residual water (1.6 L) remaining in the container was shaken and divided into 2 x 800 mL sub-samples (residues 1 and 2). Greater levels of resin acids (c 3 times that identified in the 15 min-30 day sub-samples) were identified in the two residual samples. The elevated levels of resin acids detected in the two residual samples (363 and 335 μg/L respectively) can be attributed to the gradual settling of resin acid carrying particulate matter. The mass balance determined for the bulk container experiment is summarised in Table 6. A more detailed analysis of the levels of free and particle bond resin acids identified in the two residual water samples is given in Table 7. Portions of each of the sub-samples withdrawn from the bulk container were also filtered (0.45 μm) and liquid/liquid extracted to determine the level of free (non-particulate associated) resin acids. The t = 0, 1 h, 14 day and 30 day filter papers were also Soxhlet extracted (Table 7). Resin acid levels identified in the filtered liquid/liquid and Soxhlet extracts (eg a total resin acid level of 107 μg/L for the 14 day sub-sample) were in good agreement with those determined for the corresponding unfiltered sub-sample (110 μg/L).

The downward trend in TRA levels of the 10 min to 30 day sub-samples was just discernible at the precision of the experiments. On the other hand the accumulation of particle associated resin acids in the two residual samples was readily apparent. The average level of particle associated resin acids found in the residual water samples (350 μg/L) corresponds to the settling of c 13 μg/L of particle associated resin acids from the 18 L of water removed during the experiment from the 19.6 L water sample. Similar downward trends in turbidity and suspended solid levels (Table 8) are consistent with the gradual settling of fine particulate matter. A moderate decrease in color levels may be attributed to either the adsorption of some colored species (chromophoric lignin molecules) onto particulate matter and/or the slow aggregation (flocculation) of chromophoric molecules.

Table 6. Total resin acid (TRA) levels and mass balance determined for filtered and unfiltered water sub-samples from a settling experiment performed using 19.6 L of sodium azide stabilised Tarawera River water.

time (sample)	unfiltered (liquid/liquid)			0.45 μm filtered		
	TRA (μg/L)	volume (mL)	mass (μg)	liq/liq (μg/L)	Soxhlet (μg/L)	TRA (μg/L)
0 min	123	3000	369	52	72	124
15 min	127	3000	381	58		
1 hour	117	3000	351	46	75	121
8 hour	118	2000	236	50		
14 days	110	3000	330	54	53	107
26 days	94	2000	188	60		
30 days	105	2000	210	50	70	120
30 days, residue 1	363[a]	800	290[a]	79	284	363[a]
30 days, residue 2	335[a]	800	268[a]	67	268	335[a]
TRA (recovered)		19600	2623 (109%)			
TRA (t = 0 min)	123	19600	2411[b]			

[a]See Table 7. [b]Mass of resin acid present at commencement of the experiment (t = 0).

The results of experiments performed using water stored in 2.5 L Winchesters were also consistent with the foregoing observations. Generally similar levels (to within 6-10%) where identified in duplicate, well shaken, t = 0 and 30 day 1 L sub-samples taken from the same Winchester. However a significantly lower level of resin acids was identified in a 1 L sub-sample taken from the top of a Winchester that had been allowed to stand undisturbed for 30 days (84 µg/L), compared to the level of resin acids identified in a subsequent (second) 1 L sub-sample withdrawn from the same Winchester (119 µg/L). It is apparent from the results presented in Tables 6, 7 and 9 that if a bulk water sample is allowed to stand, settling of fine particles occurs and elevated levels of resin acids are likely to be present in analytical samples taken from the bottom of the container.

Table 7. Resin acid levels (µg/L) identified in liquid/liquid and Soxhlet extracts of two filtered residual water samples from the 30 day settling experiment.

sample	seco1/2[a]	pim	18-Ab	DHAA	13-ene	Cls	TRA
Residue 1 sub-sample							
Soxhlet (Whatman No 1)	16.7	22.9	113	31.1	71.6	7.0	262
Soxhlet (0.45 µm)	1.6	1.8	8.8	3.2	6.1	0.4	22
Liq/liq (What + 0.45 µm)	29.2	5.9	12.3	15.4	14.2	1.6	79
Total	47.5	30.6	134	49.7	91.9	9.0	363
Residue 2 sub-sample							
Soxhlet (0.45 µm)	18.2	26.6	113	27.9	75.5	6.4	268
Liq/liq (0.45 µm)	27.0	5.2	8.3	13.2	12.0	1.5	67
Total	45.2	31.8	121	41.1	87.5	7.9	335

[a]Abbreviations are as in Table 1.

Table 8. Color, turbidity and suspended solid levels determined for a bulk (19.6 L) sodium azide stabilised Tarawera River water sample, collected 25/2/99.

settling time	absorbance 270 nm	340 nm	440 nm	turbidity (NTU)	TSS mg/L	ISS mg/L	OSS mg/L
0 min	0.281	0.095	0.032	7.30	8.5	4.2	4.3
15 min	0.281	0.092	0.029	7.14	6.8	2.1	4.7
1 hour	0.277	0.089	0.028	6.59	5.4	2.2	3.2
8 hour	0.275	0.089	0.028	4.91	5.6	1.8	3.8
14 days	0.278	0.087	0.024	3.67	5.2	1.5	3.7
26 days	0.261	0.079	0.020	3.34	4.0	0.5	3.5

Abbreviations: TSS = total suspended solids; ISS = inorganic suspended solids; OSS = organic suspended solids.

SEM analyses of particulate matter recovered after 0.45 µm filtration and freeze drying of the filtrate revealed high surface concentrations of silica rich deposits, consistent with a well document geothermal input of silica to the river (McIntosh, 1995) together with a lower level of deposits which exhibited a combination of Fe, Al,, O and C responses, possibility attributable to Fe and/or Al induced flocculation and surface adsorption of organic species such as resin acids, microbial biomass and/or phenolic lignin molecules.

Table 9. Resin acid levels (μg/L) determined in settling experiments performed using 2.5 L Winchesters and sodium azide stabilised Tarawera River SH30 water.

storage time	secol/2[a]	pim	18-Ab	DHAA	13-ene	Cls	TRA
Winchester A							
well shaken, t = 0	19.0	12.0	30.7	19.9	34.1	3.7	119
well shaken, 30 days	19.6	12.0	29.8	20.2	34.7	3.6	120
Winchester B							
well shaken, t = 0	20.1	10.2	32.1	24.7	39.1	4.4	131
well shaken, 30 days	20.1	12.3	33.0	23.1	36.4	4.1	129
Winchester C, 30 days							
not shaken, upper layer	17.1	8.0	19.5	14.7	22.4	2.3	84
not shaken, lower layer	20.1	11.7	28.7	20.3	33.8	3.7	118

[a]Abbreviations are as in Table 1.

Our results show that settling of particles during the storage of Tarawera River water samples can lead to the accumulation of resin acid carrying material in the lower zone of the sample container. This finding can be compared to the conclusion of Hall & Liver (1996) that in the biomass system which they investigated, resin acids were principally associated with colloidal material, and with the finding of Hoel and Aarsand (1995) that in a TMP effluent resin acids were exclusively associated with particulate and colloidal fractions.

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Particle association of resin acids and chromophoric species in water samples from the biological treatment system of two New Zealand pulp mills

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Previous investigations of Tarawera River samples collected downstream of the discharge point of two New Zealand pulp and paper mills have shown that > 50% of the recoverable resin acids present in river water samples are bound to particles in the range 0.02-15 μm (Ali-Kanber et al, 2000, 2001). Little is however known about the speciation of resin acids during primary and secondary treatment of the pulp and paper mill effluents, prior to their discharge to the Tarawera River.

This paper reports the levels of free and particle associated resin acids and the particle association of chromophoric (coloured) species in sodium azide stabilised water samples from the clarifier and four treatment ponds and the size analyses of particles in these water samples.

Methods and materials

Water samples in screw capped 2.5 L glass winchesters or 20 L plastic containers were collected from the outflow of the clarifier and treatment ponds 1-4 (sites A-E respectively, Figure 1) and the Tarawera River at the SH30 bridge. Water samples were stabilised at the time of collection of 0.1% of sodium azide (Ali Kanber et al, 2001). Water samples were stored at 4-8°C until required for analyses. Free and bound resin acid levels were determined for well mixed, sodium azide stabilised, clarifier, treatment pond and Tarawera River water samples using the liquid-liquid or Soxhlet extraction and selected ion mode SIM-GC-MS methodologies reported previously (Ali Kanber et al, 2001). Clarifier and pond 1-4 samples were derived from sequential filtration of 600 mL (glass fibre), 500 mL (3 μm), 400 mL (0.8 μm), 300 mL (0.45 μm) and 200 mL (0.2 μm) and liquid/liquid extraction of 100 mL subsamples of the sodium stabilised water samples. Quantification was performed using *O*-methylpodocarpic acid as internal standard. (Ali Kanber et al, 2001). The recovery of *O*-methylpodocarpic ethyl ester was typically 75-105%. Absorbances of sodium azide stabilised water samples were determined before and after sequential filtration at 270, 340 and 440 nm using a 1 cm quartz cell and a Hitachi 15-20 spectrometer. Turbidity was determined using a Hatch 2100 turbidimeter. ICP-MS analyses were performed using a GBC Integra instrument. The total freeze dried solids (total S) contents of treatment system or river water

samples (200-1000 mL depending on the site of sampling), were determined gravimetrically by pre-freezing the water sample in a beaker using a liquid nitrogen bath and freeze-drying the frozen sample for 2-4 days. Inorganic freeze-dried solids (inorg FDS) were determined after the heating freeze-dried residue at 550°C in a furnace overnight. Organic freeze-dried solids (org FDS), and % weight loss on ignition of freeze dried solids (% loi) were calculated as org FDS = total FDS - inorg FDS, and % loi = 100 x (total FDS - inorg FDS)/total FDS, respectively. Laser diffraction particle size analyses were performed using a Malvern Instruments (UK) Mastersizer-S particle analyser. Tap water was added to the dispersion unit and circulated through the flow cell. The obscuration (related to turbidity) was recorded (close to zero), the tap water was drained and replaced by sample water which was diluted with tap water until the obscuration was observed. System software was used to subtract the tap water background and calculate particle size distributions from the scattered intensities.

Results and discussion

After primary treatment (clarification) effluent waters from two New Zealand pulp and paper mills (mills 1 and 2) situated on the banks of the Tarawera River, are combined with bleaching effluent from mill 1 and subsequently treated in a stablised aeration basin with (at the time of sampling) an average retention time of 5.5 days. Treatment system characteristics are presented in Figure 1. Free and bound resin acid levels identified in water samples from the clarifier, treatment ponds 1-4 and a SH30 Tarawera River sample are presented in Tables 1-3.

Our results show that virtually none of the resin acids exciting from the clarifier are particle associated (Table 1) whereas 65% of the resin acids are associated with 0.45 μm or greater particles in pond 4 (Table 4). It is also apparent that while the total level of resin acid falls, the % contribution of particle associated resin acids increases during passage through the treatment system

The levels of total resin acids identified in the pond 2 and 3 water samples were similar (5261 and 4693 μg/L respectively; Table 2) indicating that, at the time of sampling, pond 3 was contributing little to treatment. During passage through the areation basin free pimaric acid and dehydroabietic acid levels fall substantially, while bound pimaric acid and dehydroabietic acid levels stay approximately constant. The level of free abietan-18-oic acid was approximately constant in ponds 2, 3 and 4. However bound abietan-18-oic acid bound levels increase as bound abiet-13-enoic acid levels decrease (Table 3).

Greater than 70% of the resin acids discharged from pond 4 to the Tarawera River are bound to particles with sizes in the range 15-0.05 μm (Table 3). Abietic acid was almost completely degraded in the treatment system. It is believed abietic acid can be either aromatised to afford dehydroabietic acid, or hydrogenated to afford abiet-13-enoic acid and abietan-18-oic acid (Tavendale 1994) (Figure 2). Both pathways appear to be operative in the treatment system.

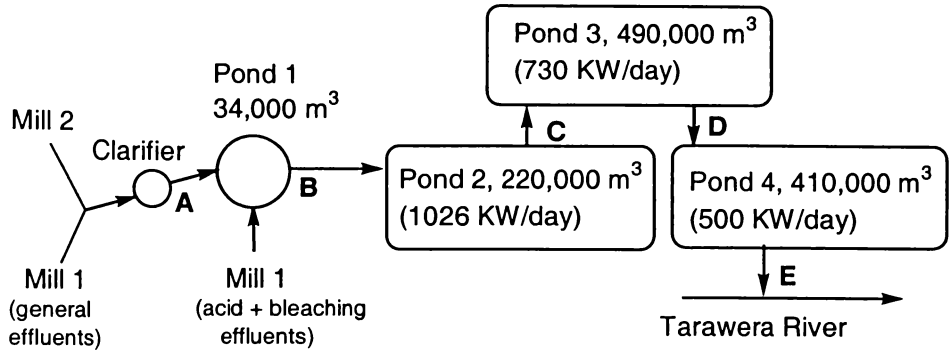

Figure 1. Treatment system characteristics. Sampling points are designated by the letters A-E.

Table 1. Resin acid levels (µg/L) determined for clarifier and pond 1 water samples, collected 1/11/99.

	seco	pim	18-Ab	DHAA	13-ene	abiet	Cls	total	%
Clarifer (n = 2)[a]	305	1293	tr	3485	487	1901	-	7472	
glass fibre (liq/liq)	301	1266	-	3318	462	1468	-	6815	91%
3 µm (liq/liq)	292	1234	-	3437	451	1648	-	7062	95%
0.8 µm (liq/liq)	285	1246	-	3716	437	706	-	6390	86%
0.45 µm (liq/liq)	257	1083	-	3149	394	1270	-	6153	82%
0.2 µm (liq/liq)	270	1142	-	3159	419	1445	-	6435	86%
glass fibre (Sox)	5	2	-	40	14	-	-	61	1%
3 µm (Sox)	1	4	-	7	tr	-	-	12	0%
0.8 µm (Sox)	1	4	-	5	1	-	-	11	0%
0.45 µm (Sox)	tr	1	-	2	tr	-	-	3	0%
0.2 µm (Sox)	1	3	-	5	1	-	-	9	0%
Pond 1 (n = 2)[a]	472	1475	25	3273	2889	750	22	8904	
glass fibre (liq/liq)	456	1391	15	3318	2667	749	14	8596	97%
3 µm (liq/liq)	454	1407	10	3423	2839	801	16	8949	101%
0.8 µm (liq/liq))	435	1317	8	3121	2500	659	13	8054	91%
0.45 µm (liq/liq)	378	1225	6	3311	2533	627	19	8099	91%
0.2 µm (liq/liq)	408	1230	5	3155	2451	342	12	7604	86%
glass fibre (Sox)	13	101	5	77	321	-	tr	517	6%
3 µm (Sox)	1	8	tr	6	23	-	3	41	0%
0.8 µm (Sox)	1	4	-	5	12	-	tr	22	0%
0.45 µm (Sox)	1	4	-	4	9	-	tr	18	0%
0.2 µm (Sox)	17	81	-	90	3	-	tr	191	2%

[a] average of duplicate analyses. Abbreviations: tr = trace, seco = secodehydroabietic acids 1 and 2, pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Table 2. Resin acid levels (µg/L) determined for pond 2, 3 and 4 water samples, collected 1/11/99.

	seco	pim	18-Ab	DHAA	13-ene	abiet	Cls	total	%
Pond 2 (n=2)	267	462	702	2962	721	103	44	5261	
glass fibre (liq/liq)	249	364	321	2915	433	32	26	4339	82%
3 µm (liq/liq)	220	333	303	2768	437	16	24	4101	78%
0.8 µm (liq/liq)	235	314	186	2776	378	8	21	3918	74%
0.45 µm (liq/liq)	196	289	197	2695	336	tr	23	3737	71%
0.2 µm (liq/liq)	205	300	138	2770	329	tr	17	3759	71%
glass fibre (Sox)	33	130	304	47	290	-	tr	805	15%
3 µm (Sox)	3	14	36	23	21	-	1	97	2%
0.8 µm (Sox)	5	19	49	36	12	-	1	122	2%
0.45 µm (Sox)	3	10	17	27	18	-	2	76	1%
0.2 µm (Sox)	3	14	22	24	24	-	1	87	2%
Pond 3 (n = 2)	270	366	732	2771	451	69	34	4693	
glass fibre (liq-liq)	220	261	313	2434	245	38	30	3541	75%
3 µm (liq-liq)	229	249	219	2540	212	23	20	3493	74%
0.8 µm (liq-liq)	254	254	173	2578	188	19	17	3483	74%
0.45 µm (liq-liq)	235	251	171	2630	208	24	18	3538	75%
0.2 µm (liq-liq)	226	220	124	2473	176	14	16	3250	69%
glass fibre (Sox)	22	65	284	98	193	-	8	670	14%
3 µm (Sox)	8	28	97	42	72	-	3	250	5%
0.8 µm (Sox)	2	5	19	11	13	-	1	52	1%
0.45 µm (Sox)	1	2	6	5	4	-	tr	18	0%
0.2 µm (Sox)	2	5	10	10	8	-	tr	35	1%
Pond 4 (n = 4)[a]	61	93	591	150	14	-	13	923	
glass fibre (liq-liq)	54	24	236	119	2	-	14	449	49%
3 µm (liq-liq)	36	34	145	69	4	-	7	293	32%
0.8 µm (liq-liq)	35	32	109	62	3	-	5	247	27%
0.45 µm (liq-liq)	34	25	98	66	2	-	4	230	25%
0.2 µm (liq-liq)	41	28	65	80	3	-	4	220	24%
glass fibre (Sox)	17	43	366	64	8	-	2	500	54%
3 µm (Sox)	2	3	20	4	tr	-	7	36	4%
0.8 µm (Sox)	1	4	24	5	tr	-	tr	34	4%
0.45 µm (Sox)	2	4	22	4	tr	-	1	33	4%
0.2 µm (Sox)	1	3	13	3	tr	-	1	20	2%

[a]Average of duplicate analyses. Abbreviations: tr = trace, seco = secodehydroabietic acids 1 and 2, pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

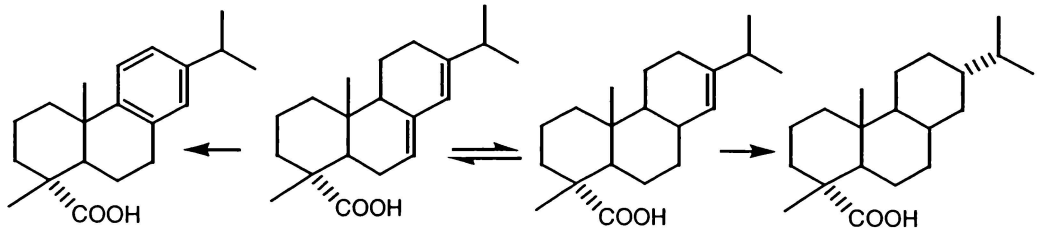

Figure 2. Chemical structures of some resin acids derived from abietic acid during biological treatment.

Table 3 Resin acid levels (µg/L) determined for a SH30 water sample, collected 1/11/99.

	seco	pim	18-Ab	DHAA	13-ene	abiet	Cls	total	%
SH30 (n = 2)[a]	4.8	5.8	22.6	9.1	20.0	tr	0.2	62.5	
glass fibre(liq/liq)	4.7	4.7	17.0	7.4	13.3	tr	0.2	42.5	68%
3 µm (liq/liq)	3.9	3.1	9.3	5.4	7.9	-	tr	29.7	48%
0.8 µm (liq/liq)	3.3	2.7	7.8	4.3	6.3	-	0.2	24.6	39%
0.45 µm (liq/liq)	3.3	2.3	6.8	5.1	5.4	-	0.1	23.0	37%
0.2 µm (liq/liq)	3.6	1.8	3.7	4.6	3.3	-	0.1	17.0	27%
glass fibre (Sox)	0.9	1.6	8.6	3.0	6.6	-	0.1	20.7	33%
3 µm (Sox)	0.4	0.8	3.5	1.3	2.9	-	tr	8.8	14%
0.8 µm (Sox)	tr	0.3	1.3	0.5	-	-	tr	2.2	3%
0.45 µm (Sox)	tr	-	1.1	0.5	-	-	tr	1.7	3%
0.2 µm (Sox)	0.1	-	0.7	0.2	-	-	tr	1.1	2%

[a] Average of duplicate analyses. Abbreviations: tr = trace, seco = secodehydroabietic acids 1 and 2, pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, abietic = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Absorbance and turbidity data for sequentially filtered clarifier, treatment pond and river water samples are presented in Table 4. Filtration generally reduced colour and turbidity levels. For example, 3 µm filtration reduced the absorbance of the pond 4 water sample at 270, 340 and 440 nm to 79, 69 and 49% respectively of the absorbances determined for unfiltered pond 4 water. Similarly, 0.2 µm filtration of the pond 4 sample reduced absorbances at 270, 340 and 440 nm to 67, 58 and 38%, respectively, of absorbances determined for unfiltered water. Similarly 3µm filtration reduced turbidity 7% (pond 1) or 9% pond 4 (relative to unfiltered water).

On the other hand filtration of SH30 Tarawera River water reduced the turbidity to 40% of unfiltered water presumably this reflects the higher concentration of small particles in the river water sample.

Table 4. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for pond1-4 and SH30 Tarawera River water samples collected 1/11/99.

	absorbance (nm)			% absorbance (nm)[a]			turbidity	
	270	340	440	270	340	440	NTU	%[a]
Pond 1 (NF)[b]	1.794	0.744	0.283				53.0	
glass fibre	1.268	0.432	0.097	71%	58%	34%	19.8	37%
3 μm	1.134	0.369	0.068	63%	50%	24%	3.89	7%
0.8 μm	1.145	0.380	0.069	64%	51%	24%	1.97	4%
0.45 μm	1.103	0.365	0.069	61%	49%	24%	1.67	3%
0.2 μm	1.015	0.335	0.065	57%	45%	23%	0.65	1%
Pond 2 (NF)	2.036	0.755	0.289				43.5	
glass fibre	1.507	0.471	0.112	74%	62%	39%	16.5	38%
3 μm	1.397	0.427	0.097	69%	69%	34%	7.60	17%
0.8 μm	1.269	0.371	0.065	62%	49%	22%	3.55	8%
0.45 μm	1.279	0.379	0.074	63%	50%	26%	1.93	4%
0.2 μm	1.208	0.356	0.063	59%	47%	22%	0.76	2%
Pond 3 (NF)	1.895	0.717	0.262				44.3	
glass fibre	1.468	0.495	0.124	77%	69%	47%	17.2	39%
3 μm	1.251	0.402	0.093	66%	56%	35%	3.11	7%
0.8 μm	1.219	0.309	0.095	64%	43%	36%	1.40	3%
0.45 μm	1.316	0.442	0.110	69%	62%	42%	0.99	2%
0.2 μm	1.256	0.417	0.097	66%	58%	37%	0.48	1%
Pond 4 (NF)	1.587	0.618	0.224				43.5	
glass fibre	1.247	0.426	0.110	79%	69%	49%	17.6	40%
3 μm	1.224	0.429	0.121	77%	69%	54%	4.12	9%
0.8 μm	1.215	0.413	0.112	77%	67%	50%	3.04	7%
0.45 μm	1.160	0.397	0.101	73%	64%	45%	0.93	2%
0.2 μm	1.060	0.356	0.084	67%	58%	38%	0.62	1%
SH30 (NF)	0.349	0.074	0.018				7.78	
glass fibre	0.339	0.068	0.016	97%	92%	89%	3.83	49%
3 μm	0.329	0.064	0.013	94%	86%	72%	2.35	30%
0.8 μm	0.323	0.060	0.011	93%	81%	61%	1.46	19%
0.45 μm	0.324	0.058	0.011	93%	78%	61%	1.15	15%
0.2 μm	0.315	0.052	0.009	90%	70%	50%	0.69	9%

[a] % absorbance, or turbidity relative to unfiltered water. [b] NF = not filtered.

The levels of selected elements (Na K, Ca, Si, Al, Fe, As, Hg, S and B). total, organic and inorganic freeze-dried solids and loss on ignition (loi) determined for treatment system and river water are presented in Table 5. In general, cation levels in ponds 2, 3 and 4 were conservative, while levels in the SH30 Tarawera River water sample were comparable with those reported in other investigations (Wilkins and Panadam 1987; Wilkins et al 1996a, 1996b; McIntosh 1995). The levels of inorganic freeze-dried solids recovered from the pond 2, 3 and 4 water samples after freeze-drying and overnight furnacing at 550°C (842, 813 and 894

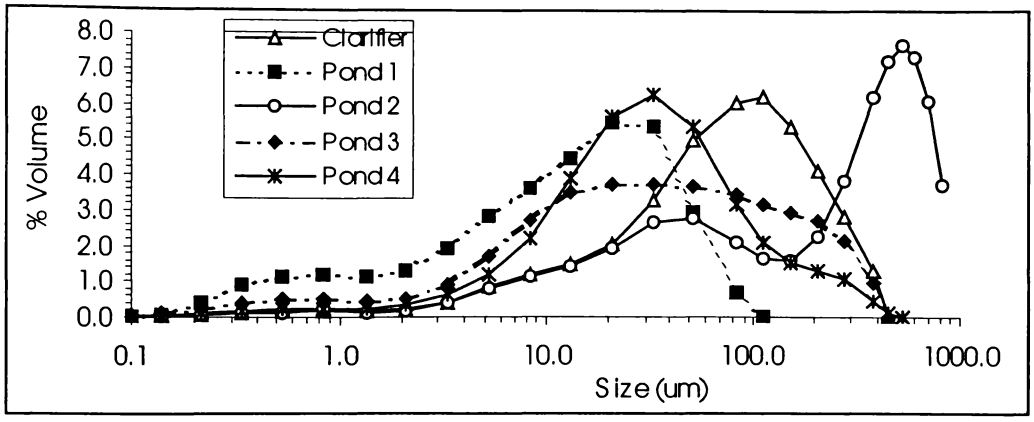

Figure 3. Particle size distributions (% volume) determined for clarifier and treatment pond samples.

Table 5. Elements (mg/L), freeze-dried solid levels (mg/L) and loss on ignition determined for treatment system and Tarawera River water samples collected 1/11/99.

	clarifier	pond 1	pond 2	pond 3	pond 4	SH30
Na	209	243	223	223	221	70
Ca	25	42	63	52	45	11
K	3.0	3.1	2.7	2.6	2.5	2.1
Si	24	23	25	25	24	27
S	8.7	9.8	8.4	11	6.0	0.8
Al	0.77	0.91	0.75	0.82	0.66	0.72
Fe	0.02	0.14	0.21	0.24	0.12	0.03
B	0.26	0.27	0.27	0.25	0.26	0.54
As	0.006	0.033	0.031	0.028	0.015	0.024
Hg	< 0.007	< 0.007	< 0.007	< 0.007	< 0.007	< 0.007
total FDS	1074	1426	1256	1162	1087	394
% loi	41%	46%	33%	30%	0.26	0.22
org FDS	440	656	414	349	283	87
inorg FDS	634	770	842	813	804	307

total FDS = total freeze-dried solids, % loi = % weight loss on ignition of freeze-dried solids, org FDS = organic freeze dried solids, inorg FDS = inorganic freeze dried solids.

mg/L respectively) were greater than those determined for the clarifier and pond 1 water samples (634 and 770 mg/L respectively). On the other hand the level of organic freeze-dried solids decreased from 656 mg/L (pond 1) to 283 mg/L (pond 4) during passage through the treatment system.

Particle size analyses showed that the bulk of the particles in the clarifer and pond 1-4 water samples were greater than 10 μm (90, 57, 92, 76 and 84% respectively, see Figure 3). Mechanical aeration (agitation) of pond 2 appears to contribute to the comparatively large abundance of > 200 μm particles in the pond 2 water sample. Kasko (1996) has reported the presence of elevated levels of > 200 μm particles in a pulp mill effluent after biological and mechanical treatment.

Conclusions

Our results can be compared with those Hall and Liver (1996) who observed that in a laboratory experiment resin acids were strongly absorbed onto biomass.

Our results have implications in respect of the development of strategies to reduce the toxicity of pulp mill effluents discharged from biological treatment systems since Hoel and Aarsand (1995) have shown that the toxicity of pulp mill effluents towards to *Daphne magna* is predominantly attributable to the presence of particle bound resin acids. While it is clear that filtration can substantially reduce resin acid levels, technical difficulties such as membrane clogging and the operating costs of large scale plants are such that removal of particle or biomass associated organic species by micro-filtration has not been adopted as a viable treatment option for pulp and paper mill effluents.

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