PULP AND PAPER EFFLUENT ORGANIC CONSTITUENTS INTERACTIONS WITH SOIL MATRICES

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ABSTRACT

The land application of pulp and paper effluents has the potential to be a long-term sustainable solution for the requirements of industry and regulatory control of environmental impacts. A critical aspect of its success will be that the soil matrix onto which the effluents are applied is able to assimilate and remove effluent organic constituents of environmental concern. Two important processes are required for this. Firstly, the soils need to rapidly attenuate the movement of these materials through the soil column to ensure that groundwater and surface water contamination is minimised. Secondly, the accumulated constituents need to be mineralised/degraded to ensure the capacity of the soil is not exceeded with repeated effluent applications. This study aimed to use laboratory-scale systems to determine the contribution of these mechanisms to the fate and behaviour of environmentally-significant pulp and paper effluent constituents.

Resin acids (major effluent toxicants, bioaccumulative and persistent) and phytosterols (potential endocrine disruptors) were the focus of this work. Three potential land application soil types, sand, Kawerau soil, and Whakarewarewa soil were considered. Thermomechanical pulping effluent was the principal waste source for the study since it is most suitable for land application. Given the potential for effluents from other pulp and paper processes to be land applied to some degree, two other wastestreams, chemi-thermomechanical and bleached kraft effluents, were considered in a more limited fashion.

Resin acids were readily degradable in all the selected soils and with all effluent types. In most cases nearly 100% removal was obtained within 6 months incubation. The sand substrate was particularly effective in removing the compounds, possibly because of a lack of alternative carbon sources in the sand matrix. Effluent-derived acclimated microbiota may have been the principal degraders responsible for resin acid degradation. Resin acids were substantially degraded under both aerobic and anaerobic conditions. Thus, land application systems may be able to sustain resin acid removal performance even if anaerobic conditions are produced in the soils as a result of high rainfall/water table increases or over-irrigation.

Resin acids were rapidly absorbed to the soil matrices. A significant proportion of the resin acids were irreversibly adsorbed to the organic soils. The capacity and intensity of adsorption was correlated with soil carbon content. Whakarewarewa soil had the greatest sorption capacity and sand was least attentuative. High concentrations of dissolved organic carbon were leached from the Kawerau and Whakarewarewa soils. This soluble material may influence the partitioning behaviour of lipophilic compounds, such as resin acids, and thus their mobility.

Overall, this study has shown that resin acids can be very effectively removed from pulp and paper effluents when applied to a range of soils. Phytosterols were not attenuated as efficiently but are likely to be relatively immobile in the upper layers of the soil column. Other factors, such as salinity and nutrient loadings, are therefore likely to be more important limitations for the future utilisation of land application systems in the pulp and paper industry.

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LIST OF ABBREVIATIONS

TMP	Thermomechanical Pulping
CTMP	Chemithermomechanical Pulping
EST	Effective Shaking Time
COD	Chemical Oxygen Demand
TOC	Total Organic Carbon
TC	Total Carbon
MTBE	Methyl t-butyl ether
DCM	Dichloromethane
BSFTA	N-o-bis(trimethlsilyl)trifluoroacetamide
GC-MS	Gas chromatograph-mass spectrometer
Ad	Adsorption
De	Desorption
Whaka	Whakarewarewa sandy loam
T_0	theoretical zero
D_0	degradation zero
Act%	Actual degradation percentage
Ult%	Theoretical degradation percentage
½T_0	Theoretical half-life
½D_0	Degradation half-life
M	Minimum value
DHAA	Dehydroabietic Acid

INTRODUCTION

1.0 INTRODUCTION

There is continuing concern over the effect of industrial effluents on surface waters. The introduction of the Resource Management Act (1991) has led to increased restrictions on discharges into waterways. As a result there has been growing interest in land application of effluents, including those from the forestry industry.

Under the Resource Management Act 1991 (RMA) the definition of a contaminant includes substances that "when discharged onto or into land or into air, changes or is likely to change the physical, chemical, or biological condition of the land" (Resource Management Act, Part I). Pulp and paper effluents have the potential to be classified as a contaminant due to the toxicity, bioaccumulative potential and persistence of some of the constituents present. The behaviour of such compounds in the soil environment is not understood and may be the controlling factor in the sustainability of a land application scheme for pulp and paper effluents.

1.1 The Pulp and Paper Industry in New Zealand

The pulp and paper industry in New Zealand consists of eight mills, predominantly located within the North Island (Figure 1.1). The pulp and paper mills produce a total output of 1,879,000 tonnes per annum (Dell *et al.* 1997), with an effluent production of approximately 128,000,000 cubic metres per annum.

The pulp and paper industry is a substantial source of industrial effluent in New Zealand, potentially contributing to many environmental effects which are caused as a result of effluent discharge to waterways. All of the major mills are currently considering land application as a potential solution to these issues.

However little information is available to assess the long term sustainability of such schemes.

Resin acids and phytosterols are abundant in softwood trees including *Pinus radiata* (which is the dominant tree used for pulping in New Zealand) and are extracted into pulp and paper effluent during the pulping process.

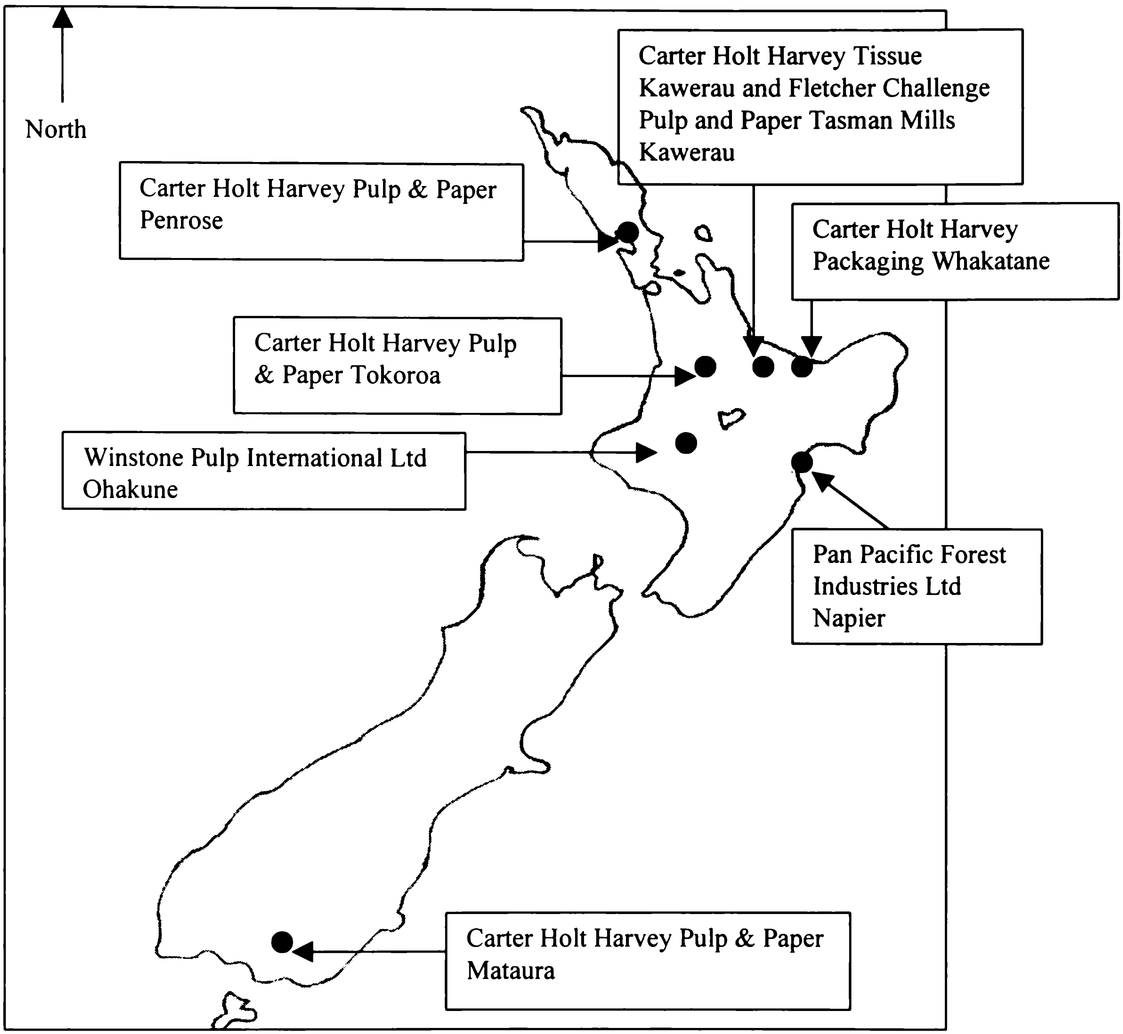

Figure 1.1: Distribution of Pulp and Paper Mills in New Zealand (Adapted from Dell *et al.* 1997).

Resin acids are of environmental concern as they are toxic, bioaccumulative and persistent in recipient aquatic systems. Phytosterols have the potential to alter the estrogenic function of organisms, in particular fish (Denton *et al.* 1985).

1.2 Land Application of Pulp and Paper Effluent

Land application of effluent is the practice of applying effluent into or onto soil utilising the soil as a treatment medium (Fuller and Warwick 1985a; NCASI 1985). Soil biological, physical and chemical processes immobilise and degrade the effluent's constituents (Hutchins *et al.* 1983; Fuller and Warwick 1985b; NCASI 1985; Loehr *et al.* 1993; Amornprasertsook and Polprasert 1996). The sustainability of an effluent irrigation scheme is dependent on the ability of the soil to assimilate the water, nutrients and possible contaminants (Bond 1998).

The main advantages of a land application scheme are a decrease in the direct surface water discharge of effluent (NCASI 1985; Balks *et al.* 1998), increased community support (Bouwer *et al.* 1981), and increased pasture or forest growth response and composition (Johnson and Ryder 1988). The effluent may also be effectively treated by interactions with the soil matrices (Johnson and Ryder 1988).

A decrease in the quality of soil (Kannan and Oblisami 1990; Mills 1997), ground waters (Hutchins *et al.* 1983; Mills 1997), and aquifer media (Mills 1997) are potential disadvantages of a land application system. Accumulation of toxic organic compounds in the soil matrix may occur (Amornprasertsook and Polprasert 1996). The extent to which organic compounds, once held by the soil, can be degraded is not fully understood. Compound breakdown is dependent upon compound toxicity and biodegradability and some organic compounds may not be degraded at all (Amornprasertsook and Polprasert, 1996). Although land application reduces direct surface water discharge, run-off from effluent application systems into surface water may occur, in which case effluent irrigation is merely delaying the contaminant's movement to the water body

(Fuller and Warwick 1985a). However, these forms of contamination should in theory only occur as a result of inappropriate land application practices, for example excessive application rates, unsuitable soil textures, or application of a potentially environmentally damaging effluent.

The fate and effects of pulp and paper effluent derived organic compounds have been studied extensively in the water column of receiving environments (Volkman *et al.* 1993; Wilkins *et al.* 1996). The fate and degradation of resin acids in sediments from receiving areas has also been assessed (Judd *et al.* 1995; Wilkins *et al.* 1996; Tavendale *et al.* 1997 a and b). It has been proposed that the extent of degradation of resin acids in anaerobic sediments is particularly slow and that sediments may act as a sink for resin acids in the aquatic environment (Tavendale 1994). Under aerobic treatment conditions it was found that 100% of sediment associated resin acids could be degraded over a 180 day period (Stuthridge *et al.* 1999).

The fate of resin acids and phytosterols in the soil environment is not fully understood. With the increasing trend towards the land application of pulp and paper effluent it is important to address the comparable issue of the behaviour of resin acids and phytosterols in soils.

In soils, the fate and mobility of organic compounds is influenced by several factors (Figure 1.2). In particular biodegradation (Kookana and Rogers, 1995; Wang *et al.* 1999) and sorption (Calvet 1989; Wang *et al.* 1999) exert the most influence on organic compounds.

A large-scale field barrel lysimeter trial conducted using pulp and paper effluent showed uptake of over 90% of resin acids and phytosterols into the soil column (Wang *et al.*1999). However, the fate of those compounds once in the soil column was unknown (Wang *et al.* 1999). The extent of the effect of degradation and adsorption of resin acids and phytosterols once within the soil column required further elucidation so that the long-term sustainability of New Zealand land application systems for pulp and paper effluents could be determined.

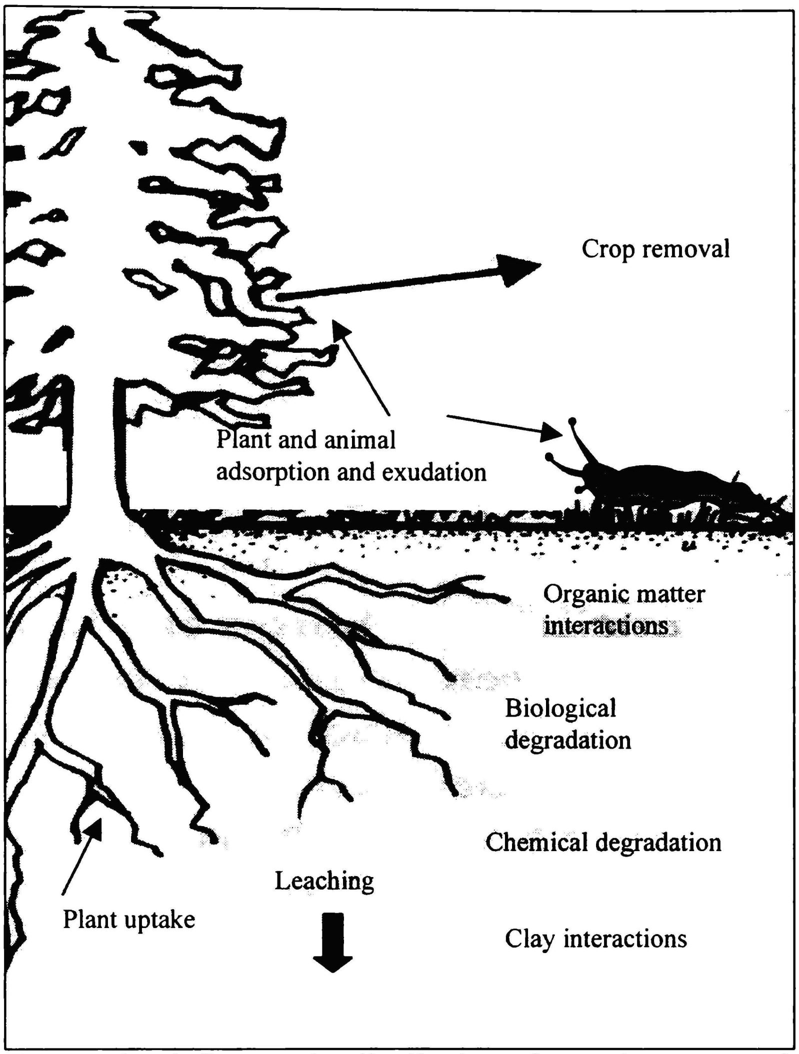

Figure 1.2: Factors that influence the distribution of organic compounds in soil (Adapted from Weber and Miller 1989).

In general soils that are well- to moderately-drained are aerobic by nature (McLaren and Cameron 1990). It might be assumed that aerobic soils are capable of degrading resin acids and phytosterols in an analogous manner to that observed in sediments. Under anaerobic conditions persistent biotransformation products can be formed in sediments (Tavendale 1994). This behaviour in soils under anaerobic conditions would be an important issue as it may lead to long-term soil contamination.

1.3 Research Context

The work reported in this thesis was undertaken within the Waste Management Systems and Technologies Project (WMST) of ***Forest Research*** in Rotorua. The overall purpose of the WMST pulp and paper land application objective is to develop a sustainable and socially acceptable management system for pulp and paper effluent land application. The WMST group is undertaking research into this area using large-scale barrel lysimeter trials, small plot forest trials, nutrient and plant growth modeling and laboratory-scale fate and mobility studies. The laboratory scale study was the first laboratory-scale assessment of the degradation and sorption behaviour of low molecular weight organics, in particular resin acids and phytosterols, in New Zealand soils. Results are to be integrated into the other parts of the land application programme and used to more effectively develop sustainable land application practices for pulp and paper effluents.

1.4 Objectives

It was hypothesised that resin acids and phytosterols from pulp and paper mill effluent would degrade under aerobic and anaerobic soil environments, and resin acids bind strongly and rapidly to the soil matrix. Since it was important to offer meaningful outcomes for a broad range of potential land application scenarios, the study chose to examine a number of pulp and paper process effluents and to utilise a range of probable land application soil types. The specific objectives of the study were to:

- Determine the degradation behaviour of resin acids and phytosterols in soil

  - Effects of aerobic and anaerobic soil conditions
  - Effects of different pulp and paper effluents
  - Effect of different soil types

- Determine the sorptive behaviour of resin acids and in soils
  - Kinetics behaviour
  - Batch equilibrium experiments to determine the extent of permanently sorbed resin acids

1.5 Summary

Due to the introduction of the Resource Management Act, restrictions in water way discharge of industrial effluents has occurred, leading to an increased interest in the land application of pulp and paper effluents. Resin acids and phytosterols from pulp and paper effluents are of environmental concern and their fate in a land application system is not fully understood. Land application utitilises the soil as a treatment system for effluent constituents. Degradation and adsorption are the soil processes that are considered to have the most effect on the fate and distribution of organic compounds in soils. The degradation and sorption interactions of resin acids and phytosterols in soils have been investigated using small-scale laboratory experiments.

LITERATURE REVIEW

2.0 LITERATURE REVIEW

There has been significant attention on the fate of organic compounds derived from pulp and paper effluents in the aquatic environment. However, their behaviour in terrestrial environments is not so fully understood. The fate and behaviour of organic compounds from pulp and paper effluents in soils is dependent upon sorption, biodegradation and transport processes within the soil environment (Figure 1.2). Sorption includes processes such as adsorption and desorption of compounds to and from soil surface. Biodegradation is the break down of compounds by microorganisms naturally present in the soil environment. In this chapter the different pulping processes and their effluent organic constituents have been outlined. A review of the environmental effects, sorption and biodegradative behaviour of resin acids and phytosterols from pulp and paper effluent is included.

2.1 The Pulping Process

There are two principal pulping processes used in the pulp and paper industry, mechanical and chemical pulping. Mechanical pulping is divided into thermomechanical pulping (TMP) and chemithermomechanical pulping (CTMP). During the thermomechanical pulping process the wood chips are disintegrated using pressure and heat, while CTMP uses additional chemicals during the presteaming stage (Figure 2.1) (Cox 1981; McFarlane *et al.* 1993; Bailey and Young 1997). Mechanical pulps are used predominantly for tissues, newsprint, drawing papers and board (Cox 1981).

Kraft pulping, the dominant chemical pulping process (Figure 2.2), utilises alkaline sulphate and high temperature and pressure to cook chip feedstock and form fibres (Rantio 1995; Bailey and Young 1997). The pulp may then be bleached to increase the brightness (Cox 1981). Bleaching removes lignaceous substances from pulp using sequential treatment with oxidative (e.g. chlorine dioxide) and alkaline stages (Cox 1981). Kraft pulps are mainly used for wrapping paper, publication grades of paper, drawing paper, fine writing paper and computer paper (Cox 1981; Dell *et al.* 1997).

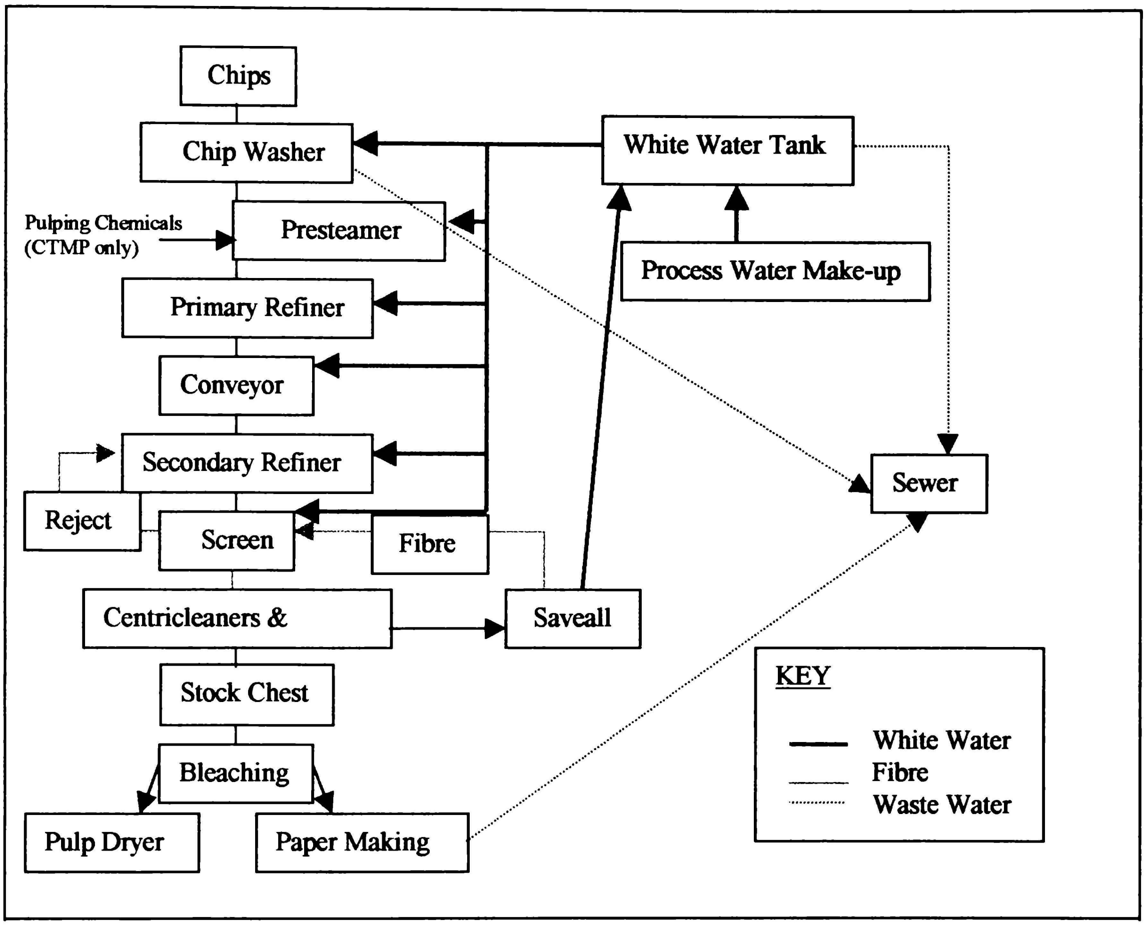

Figure 2.1: Mechanical pulping mill process flow diagram (Adapted from McFarlane *et al.* 1993).

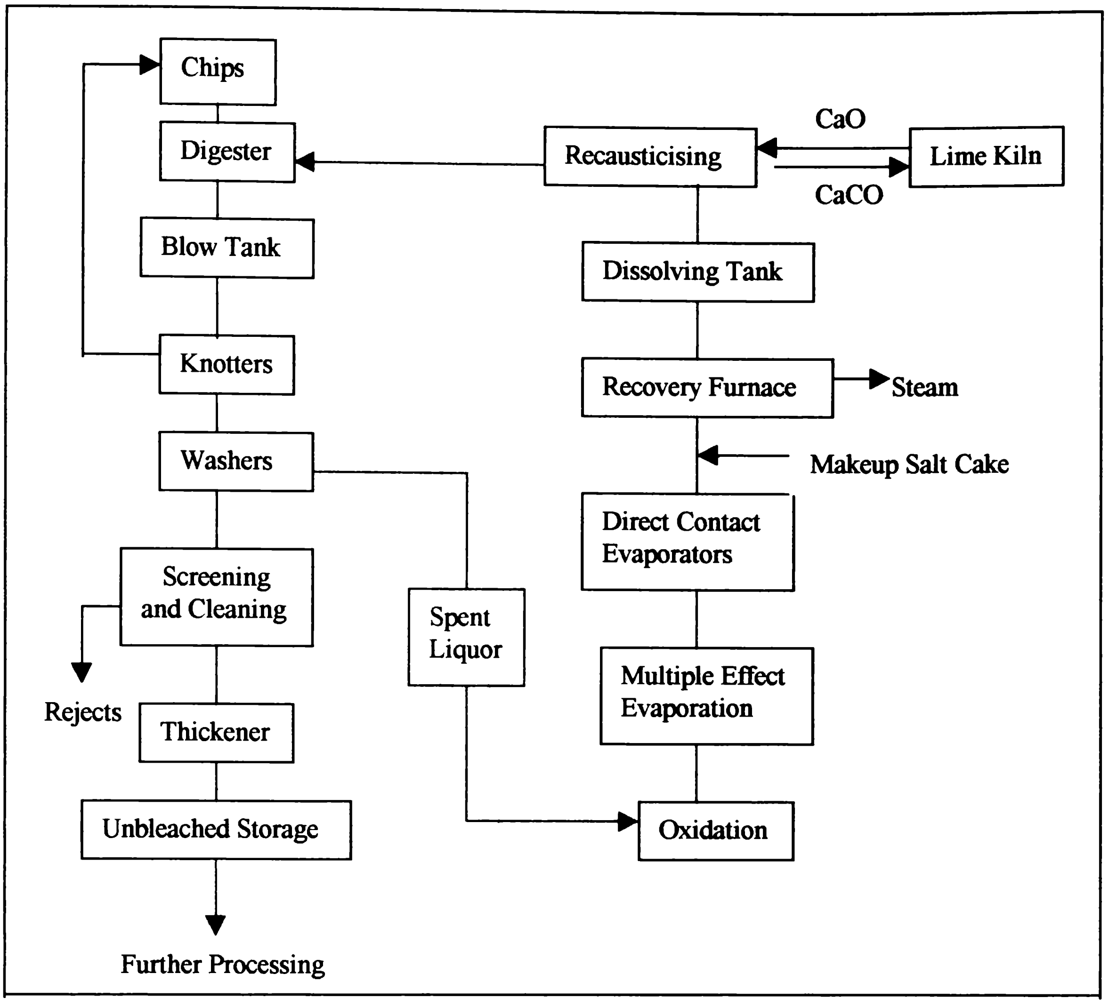

Figure 2.2: Kraft pulping process flow diagram (Adapted from Casey 1980).

2.2 Pulp and Paper Effluent

Pulp and paper effluent discharged to the environment varies from mill to mill, influenced by the pulping process, the trees used and effluent treatment processes (Cox 1981; Kovacs *et al.* 1984). Mechanical and chemical pulping produces effluents from different parts of the pulping process. Effluents from TMP and CTMP mills are predominantly produced in the refining, screening and washing stages of pulping (Figure 2.1) (McFarlane *et al.* 1993).

TMP and CTMP effluents typically consist of wood-sap compounds, wood sugars, extractives, wood particles and water (Cox 1981; McFarlane *et al.* 1993).

Chemical or kraft pulping produces a larger amount of effluent from papermaking and bleaching processes. Smaller amounts of effluent are also produced from the debarking and pulping stages (Figure 2.3) (McFarlane *et al.* 1993). New Zealand mills cover a range of pulping processes and therefore produce fundamentally different effluent types (Table 2.1).

Table 2.1: New Zealand pulp and paper mills: products, process type, effluent treatment and discharge volume (Adapted from Dell *et al.* 1997).

Mill	**Product**	**Process Type**	**Effluent Treatment Process**	**Discharge Volume ($m^3.day^{-1}$)**
CHH* Pulp & Paper Penrose	Corrugating Medium	Recycled Paper	Discharge to municipal sewer	10
CHH Pulp & Paper Kinleith	Market Pulp Liner Board	Bleached kraft NSSC	Segregated effluent 1 Main – aerated lagoon 7 days 2 – Akaline bleaching – aerated 45 days	120 000
Winstone Pulp International Ltd.	Market Pulp	Bleached and unbleached chemithermo-mechanical	Primary sedimentation	4300
Pan Pacific Forest Industries Ltd.	Market Pulp	Thermomechanical	Screening/DAF$^+$ ocean outfall	4300
Fletcher Challenge Pulp and Paper Tasman	Market Pulp Newsprint	Bleached kraft Thermomechanical	Aerated lagoon – 5-6 days retention	170 000
CHH Tissue Kawerau	Market Pulp Tissue	Bleached Sulphonated Chemi-thermomechanical	Anaerobic system (UASB)$^\#$	22 000
CHH Packaging Whakatane	Carton Board	Stone Groundwood Semi-chemical Pulp Imported kraft	Screening clarifier Screw press	22 000
CHH Pulp & Paper Mataura	Fine and Wrapping Paper	Market Pulp Recycle	Screening and clarifiers	5 400

*Carter Holt Harvey $^+$ Dispersed air flotation $^\#$ Upflow Anaerobic Sludge Blanket

The typical waste water yields are 75 m^3 of effluent per tonne of pulp for bleached kraft pulping, 110 $m^3.tonne^{-1}$ for chemimechanical pulping and 99 $m^3.tonne^{-1}$ for thermomechanical pulping (Springer 1993).

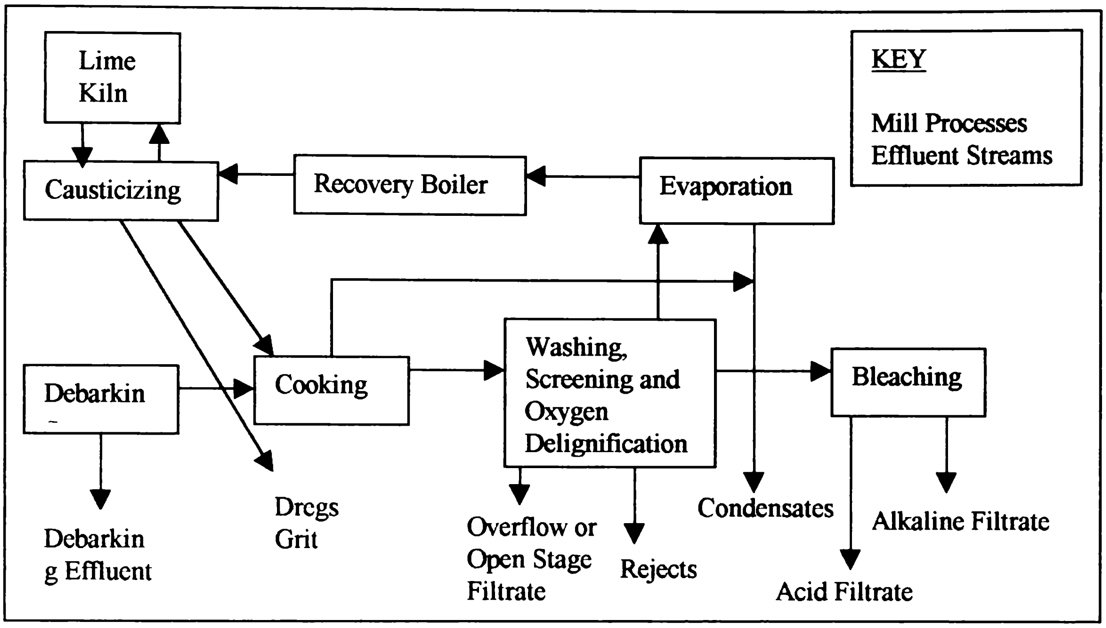

Figure 2.3: Effluent sources in a kraft pulp mill (McFarlane *et al.* 1993).

2.3 Organic Compounds In Pulp And Paper Effluent

Pulp and paper effluents contain a complex range of organic compounds, including low and high molecular weight materials. Some of the compounds in pulp mill effluents that are of environmental concern originate from the wood matrix and include resin acids and phytosterols. In this section the origin of extractives (in particular resin acids and phytosterols) and high-molecular mass organic compounds in pulp and paper effluents have been elucidated.

2.3.1 Composition of Wood

The composition of wood is important as many of the environmental but harmful compounds that are in pulp mill effluent are released indirectly from wood during pulping. Wood is composed of three major groups, polysaccharides, lignin and extractives (Table 2.2).

Table 2.2: Basic composition of wood (LaFleur 1996).

Compounds	COMPOSITION (%)	
	Hardwoods	**Softwoods**
Polysaccharides		
Cellulose	42-47	51-55
Hemicelluloses	20-30	15-20
Lignin	16-25	23-33
ρ-Hydroxyl propyl	Trace	Trace
guaiacol propyl	29-35	>95
syringyl propyl	40- 46	1
Extractives	0.2-3.5	0.5

Cellulose is a linear polymer whereas hemicellulose is branched and made up of different subunits (LaFleur 1996). Softwood (e.g *Pinus radiata*) hemicelluloses consist predominantly of galactoglucomannans, arabinoglucuronoxylans and arabinogalactans (LaFleur 1996). Lignin is an aromatic polymer that is formed in softwood trees by polymerisation of coniferyl alcohol (Kringstad and Lindström 1984).

Chemicals that can be extracted from effluents with organic solvents are termed 'extractives' (Kringstad *et al.* 1985; LaFleur 1996). Softwood extractives are the tree's natural insect and microbial defence mechanism and are biologically active (LaFleur 1996).

2.3.2 Extractives in Pulp and Paper Effluents

Extractives are found in small amounts within the tree's matrix, but can reach toxic concentrations within pulp and paper effluents. There is a range of extractives present in pulp and paper effluents (Table 2.3).

Table 2.3: Extractives in pulp and paper effluent (Adapted from Kringstad and Lindström (1984) and Tavendale (1994)).

ACIDIC COMPOUNDS	PHENOLIC COMPOUNDS$^+$	NEUTRAL COMPOUNDS
Fatty acids	Phenols	Saturated and unsaturated hydrocarbons
Hydroxy acids	Guaiacols	Aldehydes
Dibasic acids	Vanillins	Ketones
Aromatic acids	Catechols	Esters
Resin acids	Syringols*	Benzene derivatives
Aliphatic acids	Syringaldehydes*	Sulphur containing compounds
Heterocyclic acids	Phenolic ketones	Alcohols
	Phenolic aldehydes	Alkanes
		Heterocyclics
		Diterpene hydrocarbons
		Sterols

$^+$ includes both chlorinated and non-chlorinated compounds
*found in effluent that is derived from hardwood species only (Voss *et al.* 1980).

Resin acids and phytosterols are found in pulp and paper effluents at high concentrations and are the most persistent and toxic compounds of the range of extractives that are present in pulp and paper effluents. Due to these factors resin acids and phytosterols are of high environmental concern. Of the lipophilic compounds that are extracted from pulp and paper effluents, 25% are resin acids and 15% are sterols (Ekman *et al.* 1990).

2.3.2.1 Resin Acids

Native resin acids are tricyclic diterpenoid acids that are present in the resin of pine and other conifers (Ekman *et al.* 1990; Morales *et al.* 1992; Tavendale *et al.* 1997b; Martin *et al.* 1999; Mohn *et al.* 1999). Resin acids are released from wood chips during pulping and can be altered to "transformed" resin acids such as oxidised and chlorinated species in the pulping process or into biotransformation products as a result of biological treatment (Martin *et al.* 1995; Liu *et al.* 1996; Tavendale *et al.* 1997b). Resin acids are generally acidic, however, some neutral resin acids do exist (Morales *et al.* 1992). For the purpose of this study, resin acids can be divided into 2 main groups, pimaranes and abietanes, and five main classes (Table 2.4).

Table 2.4: Resin acid groups.

SATURATED	MONOENIC	DIENIC	AROMATIC	NEUTRAL
Pimaranic Isopimaranic Abietanic	Pimarenic Isopimarenic 13-Abietic Dehydroisopimaric	Pimaric Sandaracopimaric Isopimaric Palustric Abietic Neoabietic	Dehydroabietic (DHAA) Seco-1-DHAA Seco-2-DHAA 12-ChloroDHAA 14-ChloroDHAA 12,14-ChloroDHAA 7-OxoDHAA	Fichtelite Dehydroabietin Tetrahydroretene Retene

2.3.2.2 Phytosterols

Phytosterols are triterpenoids consisting of six isoprene units and are abundant in algae and higher plants (Salisbury and Ross 1992). Phytosterols are located within the lipid material (Raven *et al.* 1992; Ai, 1997) and parenchyma cells of plants and are released during refining of pulp (Ekman *et al.* 1990). β-sitosterol is the dominant sterolic compound found in pulp and paper effluents. Stigmasterol and campesterol are also found in lesser amounts (Cook *et al.* 1997).

2.3.3 High-Molecular-Mass Organic Compounds In Pulp and Paper Effluents

Lignin and its derivatives are the predominant high-molecular-mass organic compounds found in pulp mill effluents. Lignin derivatives which have a molar mass in excess of 10,000 Daltons are biologically inactive (Kringstad and Lindström 1984; Lindström and Österberg 1984). However, lignin derivatives with molar masses less than 1000 Daltons may be potentially biologically active (Crooks and Sikes 1990).

Approximately 70-90% of the organically bound chlorine in bleached kraft pulp mill effluent is associated with high molecular weight compounds (Kringstad and Lindström 1984; Lehtinen 1992; Smith *et al.* 1994). Chorolignin is generally recalcitrant and contributes a significant proportion of the colour and soluble chemical oxygen demand present in pulp and paper effluents (Kukkonen 1992; Pellinen 1994).

2.4 Environmental Effects Of Pulp And Paper Effluents

The main receiving environments for pulp and paper effluents are water bodies. The potential effects on waterways are different from those on soil environments. The environmental issues associated with the aquatic ecosystems are an important driver for land application systems of pulp and paper effluents.

2.4.1 Environmental Effects of Pulp and Paper Effluents in the Aquatic Environment

Pulp and paper effluents are of environmental concern due to the ability of their constituents to alter the receiving environment. Factors that are of the most concern are colour, suspended solids, eutrophication, oxygen demand and toxic organic compound contents.

Colour in pulp and paper effluent originates from pulping processes, pulp washing, bleaching, spills and leaks (Ramanathan 1989). Colour persists in receiving waters reducing the aesthetic quality, and may cause a range of environmental effects, such as decreased sunlight penetration and photosynthesis, and alteration of organisms' feeding behaviour (Bennett *et al.* 1971; Cox 1981; Ramanathan 1989; Crooks and Sikes 1990; McFarlane *et al.* 1993; Mills 1997). For example, the river bed community of the Tarawera River, in which pulp and paper effluent is discharged, has decreased diversity and size due to colour load (Dell *et al.* 1996).

Pulp and paper effluent may contain high suspended solid loads which can blanket benthic organisms, cover breeding grounds and cause a high oxygen demand and odours due to anaerobic degradation (Cox 1981; Crooks and Sikes 1990; Peck and Daley 1994).

Eutrophication is defined as a nutrient enrichment of a water body leading to plant growth, which upon decomposition leads to a decrease in water oxygen content (Salisbury and Ross 1992). Although pulp and paper effluents are low in nutrients, these are often added to ensure effective biological treatment (not usually in New Zealand) and can lead to eutrophication (Springer 1993). Pulp and paper effluents may contain sugar and cellulose compounds that without adequate effluent treatment can induce slime growth in the aquatic environment thus also reducing the oxygen content of the water (Cox 1981). Oxygen demand may also originate from the breakdown of organic compounds from pulp and paper effluents in waterways or long term oxygen demand can be established from the slow degradation of chromopores (Cox 1981; McFarlane *et al.* 1993).

Toxic organic compounds from pulp and paper effluents can accumulate within sediments, once sediments are contaminated with organic compounds they can become a pollutant source for the water column. Sediment concentrations may be over 10,000 times higher than the water column concentration (Wilkins *et al.* 1996). Direct transference from sediments to organisms is considered a source of exposure to pollution for some aquatic organisms that may lead to magnification through the food chain (Adams *et al.* 1992; Gifford 1996). Judd *et al.* (1995) found that sediments downstream of a kraft mill contained organic compounds directly attributable to the mill, with resin acid concentrations reaching 37.2-76.6 μg/g. The toxicity of a particular compound is a function of its physical, chemical and structural characteristics, such as water solubility, disassociation potential, lipophilicity and chlorine binding capacity all effect the toxic behaviour of an organic compound (McFarlane *et al.* 1993).

Overall the effective primary and secondary treatment of pulp and paper effluents will eliminate many of these impacts. Such systems are not always effective for toxic compounds, such as resin acids and sterols and they may cause sub-lethal effects where discharged.

2.4.1.1 Environmental Effects of Resin Acids from Pulp and Paper Effluents

Resin acids cause a range of environmental impacts including bioaccumulation, toxicity, and may be estrogenic in some species (Table 2.5).

Ten to twenty percent of pulp and paper effluent toxicity is due to the presence of resin acids (Holmbom and Lehtinen 1980). A lethal toxicity test assesses the concentration of a substance that causes mortality in a test organism (Walden and Howard 1981; Crooks and Sikes 1990; McFarlane *et al.* 1993).

Table 2.5: Environmental effects of resin acids.

COMPOUND	ENVIRONMENTAL EFFECT	REFERENCE
Resin acids	Toxic, both chlorinated and non chlorinated counterparts	Leach *et al.* 1977 Leach and Thakore, 1977 Holmbom and Lehtinen 1980 McFarlane and Clark 1988 McFarlane *et al.* 1993 Liss *et al.* 1997 Mohn *et al.* 1999
	Genotoxic	Liss *et al.* 1997
	Bioaccumulative	Liss *et al.* 1997
	Accumulative in sediments	Lee and Peart 1991 Judd *et al.* 1995
	Biologically recalcitrant	Liss *et al.* 1997
	Mutagenic (Neoabietic Acid)	Lee *et al.* 1981
	Estrogenic in breast cells and juvenile fish causing cancer (abietic and dehydroabietic acid mixture)	Mellanen *et al.* 1996
Resin acid degradation products	Bioaccumulative in fish	Crooks and Sikes 1990 Liss *et al.* 1997
	Toxic, EROD inducers (Retene)	Billiard *et al.* 1999 Brumley *et al.* 1999

The median lethal concentration or LC_{50} is the compound concentration at which the mortality rate is at 50% (Crooks and Sikes 1990). The 96-hour LC_{50} for resin acids from pulp and paper effluent is 0.2-1.7 mg/L. Depending upon the treatment system efficiency, the resin acid concentration in pulp mill effluents can be 2-4 times the LC_{50} of aquatic organisms (Liss *et al.* 1997).

2.4.1.2 Environmental Effects of Phytosterols from Pulp and Paper Effluents

Phytosterols may alter the estrogenic function of organisms, which can occur on several different biochemical levels (Table 2.6). The structure of pulp and paper effluent derived phytosterols is similar to the steroid hormones of vertebrates (Lehtinen *et al.* 1999). For example β-sitosterol closely resembles cholesterol which is the basis for steroid synthesis and cell wall fluidity in organisms (Knutson *et al.* 1995; Lehtinen *et al.* 1999).

Sterol degradation products may originate in a biological treatment system and are capable of causing sexual modifications in organisms (Denton *et al.* 1985). Once sexual modification of an organism has occurred, the characteristics do not regress once the affected organism has been removed from the area of contamination (Denton *et al.* 1985).

Table 2.6: Environmental effects of phytosterols.

ENVIRONMENTAL EFFECT	REFERENCES
Accumulation in sediments.	Koistinen *et al.* 1998
Strong masculinisation in female fish. Effect on sex characteristics in male fish. Affects reproductive behaviour in male fish.	Denton *et al.* 1985
Toxic degradation products.	Denton *et al.* 1985
Effects sex steroid levels in fish. Decreased fish hatching.	Knutson *et al.* 1995 MacLuthy and Van der Kraak, 1995 Lehtinen *et al.* 1999
Alteration of cholesterol turn over in fish.	Knutson *et al.* 1995 Lehtinen *et al.* 1999 Tremblay and Van der Kraak, 1999
Hereditary contamination of eggs passed down by female fish. Higher congenital deformities in hatched fish larvae. Decreased fish egg size.	Lehtinen *et al.* 1999
Reduced pregnenolone in fish.	Tremblay and Van der Kraak, 1999
Estrogenic.	Mellanen *et al.* 1996 Tremblay and Van der Kraak, 1999
Induced expression of vitellogenin gene in fish livers.	Knutson *et al.* 1995 Mellanen *et al.* 1996
Increased liver glycogen and number of vacuoles in fish.	Knutson *et al.* 1995
Hormonally active but not estrogenic (sitostanol).	Knutson *et al.* 1995

2.4.2 Environmental Effects of Pulp and Paper Effluents in Soils

Pulp and paper effluent effects in soils are principally associated with sodium, organic loadings and toxic organic compound contents. In this section the effects of pulp and paper effluent on the aquatic and soil environment have been outlined.

Pulp and paper effluents (especially chemithermomechanical and bleached kraft effluents) contain substantial amounts of sodium that, upon land application, can cause heightened soil sodium levels (NCASI 1985; Johnson and Ryder 1988; Howe and Wagner 1996; Howe and Wagner 1999). High soil sodium levels lead to decreased soil permeability, bulk density and microbial populations (Johnson and Ryder 1988). Deflocculation may also result from high sodium effluent application when irrigation has ceased and a rain-fed system is initiated (Balks *et al.* 1998; Bond 1998).

Organic compounds from pulp and paper effluents can lead to decreased soil infiltration after land application (Kannan and Oblisami 1990). The blocking of soil pores may originate from bacterial activity under anaerobic soil conditions caused by a high oxygen demand (Singaram 1995).

Land application of pulp and paper effluents generally utitilises at least primary treated effluents, however even secondary treated effluents may still contain significant amounts of toxic organic compounds which may impact soils (Kookana and Rogers 1995).

2.5 Adsorption of Organic Compounds onto Soils

Sorption and desorption interactions in soils control the transport and fate of organic compounds in the environment. In this section adsorption, desorption, the dominant soil fractions that impact of sorption and possible influences of sorption processes have been outlined. Sorption processes are important to study as they may have a large effect of the fate of resin acids and phytosterols in a land application system. It has been proposed that resin acids and sterols are capable of sorbing strongly to soil surfaces (Liu *et al.* 1996; Liver and Hall 1996). The movement of such organic compounds in soils will therefore be retarded by sorption processes (Bouwer *et al.* 1981; McCarty *et al.* 1981).

Organic compounds that are associated with soil colloids are either freely available or bound. Freely available compounds may exist in the interstitial pore water or be reversibly adsorbed to colloid surfaces (McBride and Wesselink 1988; Kung and McBride 1991; Rav-Acha and Rebhun 1992; Tavendale 1994). Bound compounds may be associated with either organic matter or inorganic materials (Remberger *et al.* 1990; Tavendale 1994).

Adsorption is defined as the partitioning of a compound between two phases and is due to the attraction or repulsion between a surface and a solute (Bailey and White 1964; Adams 1973; Hassett and Banwart 1989; Weber *et al.* 1991; Tan 1993; Scow *et al.* 1995).

Physical adsorption or van der Waals adsorption is due to several factors: dipole-dipole interactions (Khan 1978; Gauthier *et al.* 1987); dispersion interactions, ion-dipole interactions; polarisation/induced dipole interactions and Born repulsion interactions (Bailey and White 1964). Hydrophobic bonding is the dominant physical adsorption, and is the cause of partitioning of nonpolar organic compounds, such as phytosterols, onto soil (Dzombak and Luthy 1984; Hassett and Banwart 1989). Hydrophobic organic compounds are driven out of solution by weak interactions with water (Gauthier et al 1987; Schlautman and Morgan 1993b). Chemical adsorption is due to coulombic forces and results in bond formation between the adsorbent and adsorbate (Bailey and White 1964).

Sequestration is a form of adsorption where there are no physical or chemical reactions (Loehr *et al.* 1993; Dec and Bollage 1997).

2.5.1. Organic Matter Adsorption of Organic Compounds

Organic matter is the predominant soil component that influences the distribution of organic compounds in soil. Soil organic matter can be divided into two main groups, non-humic and humic substances (Figure 2.4).

Non-humic substances are plant and animal residues that are unaltered and may include carbohydrates, proteins, fats, waxes and resins (Stevenson 1972). Humic substances are residues that no longer resemble plant or animal material and are the most active fraction of soil organic matter (Stevenson 1972). Humic substances can be further divided into humic and fulvic acids and humins (Figure 2.4).

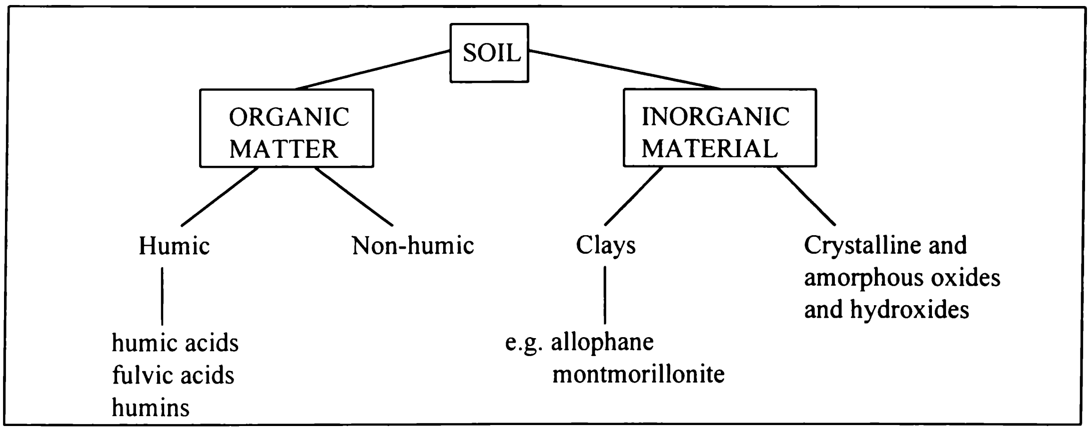

Figure 2.4: Basic soil components.

2.5.1.1 Partitioning of Organic Compounds onto Organic Matter

Partitioning is the dissolution of organic compounds into soil organic matter and is proposed as the main mechanism for hydrophobic retention of organic compounds in soils and sediments (Chiou *et al.* 1979; Briggs 1981; Dzombak and Luthy 1984; Calvet 1989; Rebhun *et al.* 1992; Murphy *et al.* 1994; Carmichael *et al.* 1997).

The extent of partitioning onto organic matter varies between soils and may be due to compositional differences between and within soils (Raber *et al.* 1998). The concentration and characteristics of dissolved organic matter can vary between soils, and controls the extent of partitioning (Voice and Weber 1985).

Generally the uptake and release of organics by soils is bimodal consisting of a fast and slow phase (Pignatello and Xing 1996). Fast adsorption of organic compounds is due to rapid uptake of labile compounds onto hydrophobic soil sites (Weissenfels *et al.* 1992) and is thought to be reversible (Karickhoff and Morris 1985). The subsequent slow adsorption phase is caused by migration of non-labile compounds into less accessible sites (Khan 1973; Weissenfels *et al.* 1992). Retardation of sorption by interactions with pore walls and organic matter is common (Pignatello *et al.* 1993).

2.5.2 Inorganic Matter Adsorption of Organic Compounds

Organic compounds are capable of binding to inorganic components in soil as well as to organic matter. The inorganic fraction of soil is composed of crystalline clay minerals and crystalline and amorphous oxides and hydroxides (Bailey and White 1964; Calderbank 1989). Clay content in soil is usually an order of magnitude higher than the organic matter content in soils (Kookana and Rogers 1995). Clays have binding sites both externally and internally (Luthy *et al.* 1997) thus creating a high potential for sorption (Bailey and White 1964). The surface area of clay is proportional to the amount of potential adsorption (Zierath *et al.* 1980). Clays affect organic compounds in several ways, swelling to close pores, changing pore water properties, sorption and catalysing chemical reactions (Chen *et al.* 1987).

Many soils of the central North Island of New Zealand are allophanic, derived from their volcanic ash parent material. Allophane is an amorphous hydrous aluminosilicate clay that is characterised by short-range order and silica-oxygen-aluminium bonds (Mora and Canales 1995; Diez *et al.* 1999). Allophane has a very large surface area and is strongly pH dependent, often being positive in charge (Mora and Canales 1995; Diez *et al.* 1999). Diez *et al.* (1999) showed that both low and high molecular weight organic compounds could be removed from solution by allophane.

The inorganic and organic fractions of soil are closely associated and determine the extent of clay surfaces available for sorption processes (Saltzman *et al.* 1972; Cox *et al.* 1998). Organic matter may occupy or fill micropores on clays reducing access of organic compounds to inner clay layers (Means and Wijayaratne 1981; Fitch and Du 1996).

2.5.3 Soil Factors that Influence Adsorption of Organic Compounds

Due to the complex nature of soil there are many factors that influence the adsorption of organic compounds, these factors interact with each other as well as acting independently.

Increasing adsorption with increasing pH (Table 2.7) is linked to the increasing amounts of hydrogen ions that compete with the solute for soil sites (Nearpass 1972; Narine and Guy, 1982). Water molecules affect the adsorption of organic

Table 2.7: Factors that influence adsorption of organic compounds in soils

SOIL FACTOR	REFERENCES
pH	
Increased adsorption with decreased pH	Bailey and White 1964 Harris and Warren 1964 Hance 1969 Nearpass 1972 Weber *et al.* 1986 Raber *et al.* 1998
Adsorption decreased with increasing pH	Zierath *et al.* 1980 Means and Wijayaratne 1981 Weber *et al.* 1986 Jota and Hassett 1991 Schlautman and Morgan 1993b
Compound speciation affected	Bailey and White 1964
Compound ionisation affected	Adams 1973 Zierath *et al.* 1980 Briggs 1981 Jota and Hassett 1991
Moisture Content (θ)	
Adsorption decreased with increasing θ	Swanson *et al.* 1954 Adams and Li 1971 Chiou *et al.* 1988
Adsorption increased with increasing θ	White *et al.* 1986
θ affected compound bioactivity	Bailey and White1964
Temperature	
Adsorption increased with increased temperature	Bailey and White 1964 Harris and Warren 1964 Karickhoff 1984
Temperature affects compound solubility	Bailey and White 1964 Harris and Warren 1964
Ionic Strength	
Adsorption increased with increased ionic strength	Calvet 1989 Schlautman and Morgan 1993a
Adsorption decreased with increased ionic strength	Schlautman and Morgan 1993b
High ionic strength causes salting out of organic compounds	Carter and Suffet 1982 Jota and Hassett 1991 Schlautman and Morgan 1993a Kan *et al.* 1994
Increased compound solubility at low ionic strengths	Kan *et al.* 1994
Organic matter structure changes at low ionic strength	Kan *et al.* 1994
Dominant Cation	
High adsorption on aluminium saturated clays	Rogers *et al.* 1980
High adsorption on hydrogen saturated clays	Leenheer and Alrichs 1971
Cation Exchange Capacity (CEC)	
Increased adsorption with increased CEC	Bailey and White 1964

compounds due to strong interactions with clay minerals (Chiou *et al.* 1981; Chiou *et al.* 1983). Increasing the soil temperature weakens the dipole-interactions between the soil and water molecules decreasing the competition from water for sites (Chiou *et al.* 1981).

Soil heterogeneity affects sorption of organic compounds (Table 2.7). Pore walls vary in composition consisting of organic and inorganic materials including aluminium and iron compounds and quartz (Cameron and Klute 1977). Organic compounds in a solute interact with different soil components at different rates and extents affecting sorption characteristics of the compounds (Cameron and Klute 1977).

2.5.4 Compound Characteristics that Influence Adsorption of Organic Compounds to Soil

Chemical characteristics of organic compounds affect the rate and extent of adsorption to soil solids. Polarity, solubility, ionic nature and functional groups determine the nature of bonding mechanisms as well as sorption (Calvet 1989; Kookana and Rogers 1995).

The water solubility of an organic compound exhibits an inverse relationship with adsorption, the lower the solubility the higher the adsorption (Calvet 1989). Low solubility and high lipophilicity are often associated. Compounds with these characteristics (such as resin acids) bind to soil surfaces strongly (Feidieker *et al.* 1995).

The molecular size of a compound is an important factor in adsorption. Adsorption of organic compounds increases with increasing molecule chain length (Means *et al.* 1980; Means *et al.* 1982). Greenland (1965) found that compounds with a molecular weight over 150 Daltons were preferentially sorbed with respect to smaller compounds, due to the ability of larger compounds to compete with water for sites. The ease and strength of organic compound bonding to clays is dependent upon molecular size (Wszolek and Alexander 1979; Tan 1993). Resin acids and phytosterols have relatively small molecular weights (~ 300 Daltons) and it is possible that due to their size would be able to bind effectively with clays.

2.6 Desorption of Organic Compounds From Soil

Desorption is an important mechanism in determining the mobility of a compound in the soil environment. Desorption is a reversal of the sorption process, and occurs when solute molecules that are held on solids are released back into solution as a result of changes in the soil system (Miller and Weber 1984). The extent of desorption determines whether the solid phase is a permanent sink for organic compounds or a temporary storage which controls the release of the chemical back into solution (Kookana and Rogers 1995).

Sorbed chemicals can be characterised by their potential for desorption as either labile (reversible) or non-labile (resistant) (MacKay and Powers 1987). Surface adsorbed compounds are often reversibly sorbed whereas compounds that are attached to pores or internal surfaces may be resistant (MacKay and Powers 1987). There are other soil factors that affect desorption of organic compounds from soil (Table 2.8).

Desorption of organic compounds from soils occurs through fast and slow stages, as in adsorption. A fast desorbing fraction is the release of solute containing organic compounds from soil mesopores (Werth and Reinhard 1997). A substantial number of organic compounds resist desorption and the resistant fraction is significantly slower in desorbing (Karickhoff and Morris 1985; Pavlostathis and Jaglal 1991; Kan *et al.* 1994).

Table 2.8: Factors that influence desorption of organic compounds in soils.

SOIL FACTOR	REFERENCE
pH Decreased desorption with decreased pH	Weber *et al.* 1986
Temperature Increased desorption with increased temperature Decreased desorption with increased temperature	Leenheer and Alrich 1971 Peck *et al.* 1980
Ionic Strength Increased desorption with increased ionic strength	Pavlosthatis and Jaglal 1991

Irreversible adsorption is a permanent interaction between compounds and soil (Kan *et al.* 1994). Organic carbon may be responsible for some irreversible compounds in the soil environment due to stronger adsorption content (Hsu and Bartha 1976; Wahid and Sethunathan 1978; ten Hulscher *et al.* 1999).

2.6.1 The Hysteresis Effect

The adsorption and desorption isotherms can be different as a result of hysteresis (Brusseau *et al.* 1989; Kan *et al.* 1994). Hysteresis was expected to occur in the batch equilibrium experiments undertaken for this thesis, and therefore the possible reasons for such behaviour were elucidated.

Hysteresis is a kinetic effect (Kan *et al.* 1994). There are several factors that are thought to be responsible for hysteresis effects in the adsorption and desorption of organic compounds in soils (Table 2.9).

Table 2.9: Factors that Influence Hysteresis of Organic Compounds in Soil.

FACTOR	**REFERENCES**
Removal by microorganisms	Koistinen *et al.* 1970 Brusseau and Rao 1989 Carmichael *et al.* 1997
Failure to reach equilibrium	Koistinen *et al.* 1970 Brusseau and Rao 1989 Carmichael *et al.* 1997
Adsorption to dissolved organic matter	Carmichael *et al.* 1997
Adsorption to clays	McCloskey and Bayer 1987
Irreversible adsorption	Curl and Keolelan 1984 Brusseau and Rao, 1989 McGroddy *et al.* 1996 Carmichael *et al.* 1997
Precipitation or volatilisation	Koistinen *et al.* 1970
Binding mechanism changes	Koistinen *et al.* 1970
Method errors	Brusseau and Rao 1989 Carmichael *et al.* 1997

2.7 Degradation of Organic Compounds From Pulp and Paper Effluents in Soils

Degradation of organic compounds from pulp and paper effluents in soils is an important factor in a land application scheme (Fuller and Warwick, 1985b). Degradation of organic compounds may be the limiting factor in a land application system for pulp and paper effluents, in that if adsorption is the only factor influencing the fate of organic compounds in soils, then when the soil reaches sorption capacity, bypass may occur. In this section biodegradation, bioavailability and the degradation of resin acids have been outlined.

Biodegradation is accomplished by a series of biochemical reactions in which a parent compound is converted to organic and/or inorganic products (Fuller and Warwick 1985; Loehr and Matthews 1992). Microorganisms will consume some of the carbon content of a compound but may not completely break down the compound (Reineke 1984). Degradation of organic compounds from pulp and paper effluents in soil is an important factor in the determination of the extent to which the compounds will act as pollutants. The degradation of a compound in soil is equivalent to its treatability (Loehr and Matthews 1992).

Many low molecular compounds contained in pulp and paper mill effluent can be co-oxidised by aerobic microorganisms (Klier *et al.* 1999). Co-oxidation is the simultaneous oxidation of non-growth substrates when other compounds are being used as substrate for growth (Reineke 1984; Atlas 1997; Klier *et al.* 1999). A lag period may exist following the application of effluent to soils, in which time the microbiota acclimatise to the changes in their environment.

Mineralisation is defined as the conversion of organic substrates to inorganic products (Subba-Rao *et al.* 1982). The rate of degradation is proportional to the concentration of the compound (Boethling and Alexander 1979; Amador and Alexander 1988; Ainsworth *et al.* 1993; Alexander 1995). Little or no biodegradation may occur at low concentrations, and a threshold would exist below which no significant mineralisation occurs (Boethling and Alexander 1979).

Organic compounds from pulp and paper effluents degrade under many environments. Abiotic factors in the soil environment, such as photochemical reactions and chemical degradation, may also lead to the breakdown of organic compounds (Weber and Miller 1989). Abiotic factors are, however, insignificant when compared to biodegradation by microorganisms present in the natural environment (Reineke 1984; Loehr and Matthews 1992; Rao *et al.* 1993; Kookana and Rogers 1995).

Soil supports a large and diverse microbial community that may be attached to colloids or freely dispersed in interstitial pore water (Calderbank 1989; Doong *et al.* 1998). It is possible that these microorganisms are capable of degrading organic compounds. The biodegradation of toxic organic compounds can result in degradation products that are equally or more toxic then the parent compounds (Kleinow *et al.* 1987). The metabolites may also have different behaviour in the environment then the parent compounds (Kleinow *et al.* 1987; Tavendale 1994). To avoid environmental contamination of effluent derived toxic compounds it is required that there is complete degradation of the compounds (Reineke 1984).

2.7.1 Bioavailability of Organic Compounds in Soil

Sorption processes significantly affect most organic compounds, including resin acids. Adsorption may increase or decrease degradation (Morgan and Wyndham 1996), depending upon where the microorganisms are (i.e in solution or attached to solid surfaces) (Kozak 1996).

Sorption can enhance the rates of degradation of organic compounds due to surface associated biological processes (Means and Wijayaratne, 1981; Scow 1993). However, sorption may also protect compounds from microbial attack and degradation (Ainsworth *et al.* 1993; Alexander 1995; White *et al.* 1998).

Organic compounds may have irreversible or partially reversible interactions with soil and their bioavailability may be limited by diffusion rather than desorption (Scow *et al.* 1995). Sorption and mineralisation have been shown to be inversely proportional (Amador and Alexander 1988). Humic substances may influence mineralisation at low concentrations of organic compounds by binding the organic substrates (Amador and Alexander 1988).

Transport of organic compounds is related to the movement of dissolved organic carbon through the soil profile (Jardine *et al.* 1990; Van de Weerd *et al.* 1999). Dissolved organic matter enhances water solubility and mobility of hydrophobic compounds and can effect the extent of residence time and biodegradation of a compound (Magee *et al.* 1991; Kookana and Rogers 1995; Diamadopoulos *et al.* 1998).

2.7.2 Degradation Of Resin Acids

Resin acid degrading microorganisms are ubiquitous in the environment although they may be in small population numbers (Martin *et al.* 1999). Fungi and bacteria are both able to degrade resin acids (Martin *et al.* 1999). Bacteria that grow on resin acids are physiologically and phylogenetically diverse, and include psychrophilic, mesophilic and thermophilic bacteria (Martin *et al.* 1999). Some resin acid degrading bacteria have been isolated from soils (Morgan and Wyndham 1996).

Under anoxic conditions resin acids can be biotransformed in sediments (Stuthridge *et al.* 1999). Transformation is a significant process influencing the fate of resin acids in the environment (Tavendale *et al.* 1997a). Resin acids are transformed anaerobically to neutral compounds by decarboxylation, demethylation and aromatisation processes (Tavendale 1994). Neutral compounds such as fichtelite and hydroabietin are indicative of decarboxylation, as they are degradation products of abietanic and dehydroabietic acid (Tavendale *et al.* 1997b).

Bacteria have a high degree of substrate specificity for resin acids and an apparent preference for abietane resin acids since pimaranes are degraded to a much lesser extent (Liss *et al.* 1997). Dehydroabietic acid can be degraded to dehyroabietin, tetrahydroretene, retene and methyl tetrahydrophenanthrene by anaerobic microbial processes (Hynning *et al.* 1993; Tavendale *et al.* 1997a). Depending on conditions, neutrals may degrade to a greater extent than acids. The rate of resin acid degradation in the environment may be limited by the rate of resin acid transformation to neutral constituents (Tavendale 1994).

2.8 Summary

The pulp and paper industry practices two types of pulping, mechanical and chemical pulping. These two fundamentally different processes result in different qualities of effluent, which are influenced by variations within the broad processes (i.e. chemithermomechanical pulping and thermomechanical pulping), feedstock and treatment efficiency.

Pulp and paper effluents can contain constituents known to cause a range of environmental effects, in particular colour, suspended solids, sodium, nutrient and organic compounds. Pulp and paper effluents contain a range of organic compounds of which resin acids and phytosterols are of the most environmental concern.

Resin acids are diterpenoid acids that originate from the resin of wood during pulping (Martin *et al.* 1995; Liu *et al.* 1996; Tavendale *et al.* 1997b). Phytosterols are triterpenoids, which also originate from wood during pulping (Ekman *et al.* 1990; Cook *et al.* 1997). Resin acids are toxic, bioaccumulative and persistent in the environment. Phytosterols are estrogenic and capable of impacting organisms at a range of biochemical levels (Lehtinen *et al.* 1999).

The fate and behaviour of resin acids in soils is greatly influenced by sorption of organic compounds to soils. Partitioning of compounds onto organic matter is the major mechanism for the sorption of organic compounds in soils (Calvet 1989). Partitioning processes may enhance the solubility and mobility of organic compounds in soils, including resin acids and sterols (Kookana and Rogers 1995). Organic compounds bind to clays as well but this process is not as significant as interactions with organic matter.

Adsorption of organic compounds in soils is influenced by soil factors, including soil pH, moisture content, temperature, ionic strength, and the dominant cation present (Table 2.7). A compound's characteristics also influence its ability to bind to surfaces. Desorption of organic compounds from soils is important to consider with respect to compound mobility and possible groundwater contamination.

Permanent sorption of organic chemicals is common in soils, the extent of irreversible sorption for pulp and paper effluent constituents is not fully understood. The rate of adsorption and desorption of organic compounds in soils is a two phase process consisting of a fast and a slow phase. Hysteresis of sorption isotherms is possible for organic compounds in soils.

Organic compounds can be degraded under both aerobic and anaerobic environments. The main mechanism is biodegradation. The availability of organic compounds in soil is influenced by sorption processes, which can either enhance or inhibit degradation. Resin acid degrading microorganisms are evident in soils (Morgan and Wyndham 1996). Biologically induced transformation is a major biodegradation process that influences the long term fate of resin acids (Tavendale *et al.* 19967a).

Wang *et al.* (1999) found that over 90% of the resin acids and phytosterols from a large scale barrel lysimeter trial were taken up by the soil, the fate of these compounds once in the soil is unknown. The extent of degradation and the effect of sorption upon degradation can only be assumed. The objective of this thesis was to elucidate sorptive and degradation factors that influence the fate of resin acids and phytosterols in soils.

METHODS AND MATERIALS

3.0 METHODS AND MATERIALS

3.1 Sample Collection and Preservation

3.1.1 Soils

Three soils were collected from within the Bay of Plenty area (Figure 3.1). These consisted of Kawerau sandy loam, Whakarewarewa sandy loam and beach sand (Sandy Raw Soil). The Kawerau and Whakarewarewa soils were chosen due to their potential as sites for land application of pulp and paper effluents.

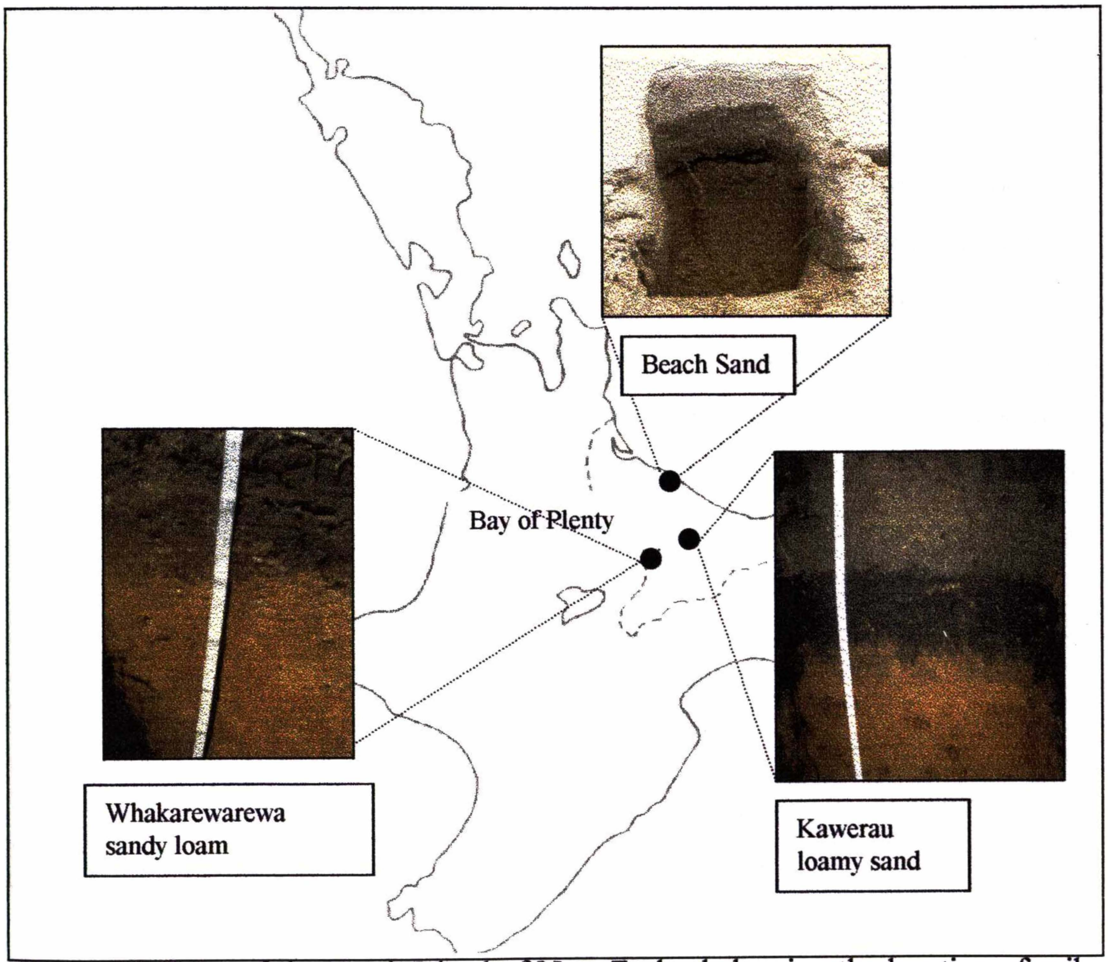

Figure 3.1: Map of the North Island of New Zealand showing the location of soils collected

The beach sand was chosen to represent a rapid infiltration irrigation system, which utilises a porous media. The A horizons of the Kawerau and Whakarewarewa soils were used for the experiments because topsoil contains the majority of organic matter (Appendix A : Soil Profiles). Soil organic matter is thought to be the controlling factor in the fate and mobility of organic compounds in soils (Kozak 1996). The beach sand was collected from Papamoa Beach (NZMS 260 U14/034 826). It was an extremely fine white sand with the majority of the grains being between 1 and 2 mm. The soils and sand were air dried and sieved to 2 mm to decrease heterogeneity, covered to avoid contamination and stored at room temperature.

3.1.2 Effluents

A representative effluent was chosen from each of the three pulping processes used in New Zealand (Figure 3.2, Table 3.1). All effluents collected were produced from the pulping of *Pinus radiata*, which is the dominant tree used for pulp and paper production in New Zealand. For this study the effluent was not filtered for any of the experiments due to associations of resin acids with colloidal material in the effluent (Hall and Liver 1996). The effluents were stored in 20 litre plastic containers at 5°C. Milli-q water was used as a control liquid.

3.2 Soil Extraction

3.2.1 Extractable Trace Organics

Soil samples from the degradation study were analysed for resin acid and phytosterol content using the ***Forest Research*** extractable trace organics method.

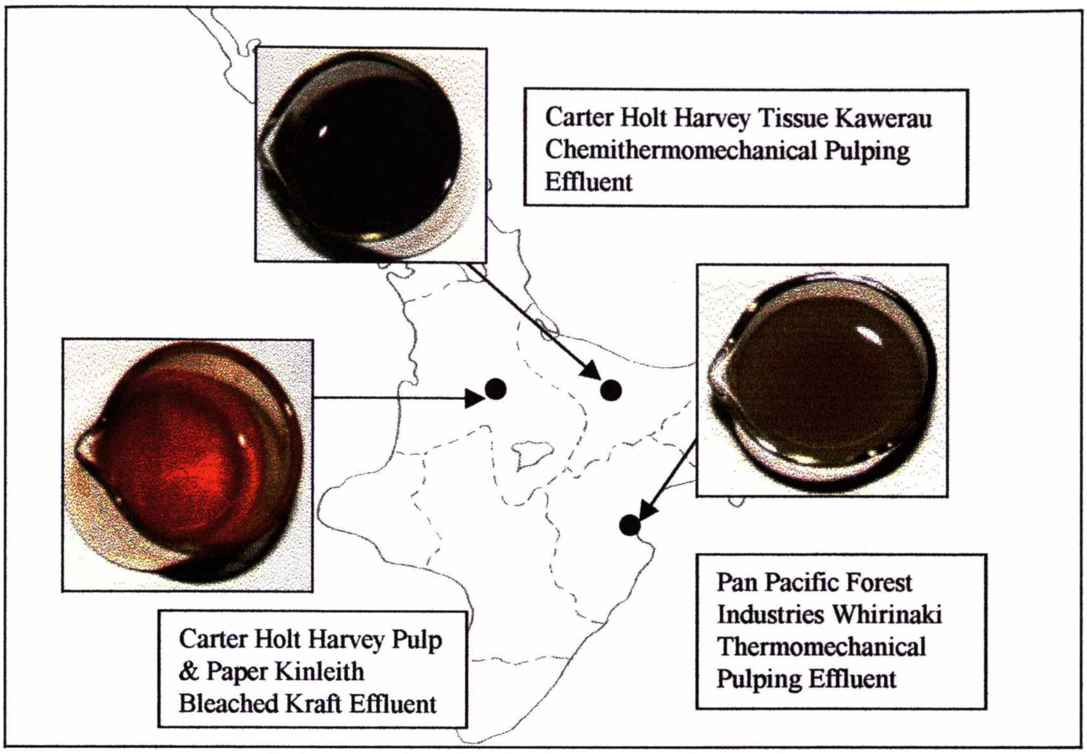

Figure 3.2: Map of the North Island of New Zealand Showing Effluent Source Locations

Glassware and sodium sulphate were muffled at 450°C for 4 hours before extraction. Each soil sample was ground in a blender with sodium sulphate at a 1:4 ratio (10 grams of soil to 40 grams of sodium sulphate). The mixture was then placed in a soxhlet (Figure 3.3), and 50 μL of surrogate standard was added. The surrogate standard consisted of 2,4,6-tribromophenol, 8(14)-abietenic acid, d_{31}-palmitic acid, D_{10}-anthracene, dihydrocholesterol, and 2,4,6-tribromoanisole in acetone (1.0 $mg.mL^{-1}$ for each compound).

A 1:1 solution of MTBE and DCM (250 m: per sample) was used to extract the soil mixture in the soxhlet (Figure 3.3). The extraction period was 4 hours. The extraction solution in the round bottomed flask was poured into a Zymark tube via a drying tube filled with sodium sulphate.

Table 3.1: Effluent Sampling Details

Mill	**Effluent Type**	**Effluent Discharge ($m^3.s^{-1}$)[1]**	**Effluent Discharge (x 10^6 $m^3.year^{-1}$)[1]**	**Sample Date**	**Sample Type**	**Effluent Issues[1,2]**
Pan Pacific Forest Industries	TMP#	0.05	1.6	26/5/99	Grab sample taken pre-screening	Colour Suspended solids Fibre Content
Cater Holt Harvey Tissue Kawerau	CTMP+	0.25	7.9	1/5/99	Grab sample taken pre-screening	Colour Clarity Dissolved oxygen Toxicity
Carter Holt Harvey Pulp & Paper Kinleith	Bleached Kraft	1.4	44.2	Stream 1 = 3/6/99 Stream 2 & 3 = 2/6/99	Grab sample taken before primary settling Synthetic effluent mixture S1* = 90% S2 = 3% S3 = 7%	Nutrients Colour Clarity Fisheries

* Stream One; Stream Two, and Stream Three of the Kinleith Effluent Treatment System.

1 Adapted from Dell *et al.* 1997

2 Principal issues for consideration of land application

#Thermomechanical Pulping Effluent

\+ Chemithermomechanical Pulping Effluent

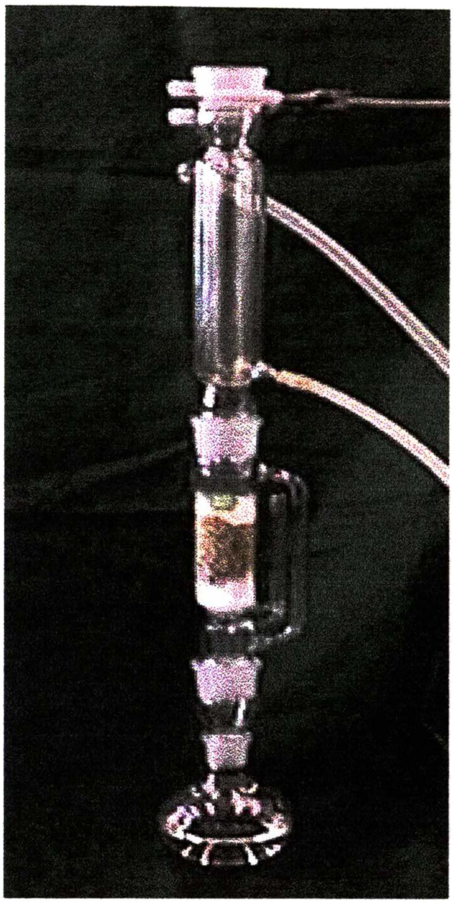

Figure 3.3: Extractable Trace Organics Soxhlet Apparatus

The anhydrous solution was concentrated to 0.5 mL using a Zymark Turbovap with a water bath temperature of 40°C and using nitrogen as a carrier gas. The solution was then transferred to a GC vial through a micro-drying tube consisting of a Volac 230-mm glass pipette filled with sodium sulphate. 50 μL of an injection standard was added consisting of dibromoanthracene in pyridine at a concentration of 1.0 $mg.mL^{-1}$. The sample was then silylated using the silylation agent N-o-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 1% TCMS and heated to 70°C in an oven for half an hour. The derivatised extract was analysed for organic compound concentrations using a HP 5971A gas-chromatograph–mass spectrometer. Resin acid and phytosterol concentrations were quantified using an on-line data system (Appendix B).

The results of the resin acid and phytosterol analyses were corrected for recovery using the appropriate surrogate standard. For the resin acids 8(14)abietenic acid was used and dihydrocholesterol was used for the phytosterols. The corrected values were then divided by the dry weight of the amount of soil that was used in the extraction, which resulted in a concentration of resin acids and phytosterols (μg) per gram of soil.

3.3 Liquid Analyses

Liquid samples from the batch equilibrium experiment were analysed for several parameters, including total carbon, total organic carbon, soluble chemical oxygen demand, colour, and resin acid content.

3.3.1 Shaker Extraction of Resin Acids

One mL of unfiltered sample was placed in a borosilicate digestion vial, 4 mL of pH 9 buffer consisting of sodium bicarbonate and sodium hydroxide was then added, followed by the surrogate standard (Section 3.3.1). The solution was then extracted three times by shaking with 5 mL of methyl *t*-butyl ether for 30 seconds. The extracts were dried, worked up and analysed as for the soil extractable trace organics method (Section 3.3.1).

3.3.2 Total Carbon and Total Organic Carbon

Total carbon (TC) and total organic carbon (TOC) were measured using a Shimadzu TOC-500 Total Organic Carbon Analyser. The sample was filtered through GF/C glass filter paper. The furnace was set to approximately 690°C and air used as a carrier gas at 150 mm.hour^{-1}. Calibration curves were established using a range of standards with a known total carbon and inorganic carbon contents, at carbon concentrations of 0, 50, 100 and 500 mg.L^{-1}. The TC of a sample was measured followed by the inorganic carbon content. TOC was determined by subtracting inorganic carbon from TC.

3.3.3 Chemical Oxygen Demand

Chemical oxygen demand (COD) is a measure of the oxidisable material (as oxygen equivalent) of the organic matter in a sample (Association *et al.* 1985). Two mL of GF/C filtered sample was placed in a borosilicate digestion vial. The following reagents were then added: 0.75 mL dichromate solution followed by 2.25 mL of a sulphuric acid solution. The dichromate solution consisted of potassium dichromate (24.518 g), sulphuric acid (100 mL) and mercury sulphate (26.6 g) dissolved in 1 litre of deionised water. The sulphuric acid solution was made up of silver sulphate (22 g) in 2.5 litres of sulphuric acid. The vial was sealed and shaken vigorously by hand after addition of the solutions. COD standards were made up using 4.25 g of potassium hydrogen phthalate in a litre of deionised water with 2 mL of concentrated sulphuric acid as a preservative, this solution has a COD of 5000 mg.L^{-1} and was diluted down to a range of standards (100, 250, 500, and 1000 mg.L^{-1}) (Anderson *et al.* 1990).

The samples and standards were digested in a heating block at 150°C for 2 hours, left to cool, then the absorbance was read on a GBC UV/VIS 918 spectrophotometer at a wavelength of 600 nm. The sample absorbance was read versus a blank containing distilled water in a 10-mm glass cell. A calibration curve of the absorbance versus the chemical oxygen demand concentration of the standards was used to determine the chemical oxygen demand concentration of the samples. All analyses were undertaken in duplicate.

3.3.4 Colour

Colour was determined using a GBC UV/VIS 918 spectrophotometer set at 465 nm wavelength. Samples were filtered through Whatman GF/C glass filter paper to remove suspended and colloidal material. The pH of the samples was then adjusted to 7.6 using dilute sodium hydroxide and sulphuric solutions (Anderson *et al.* 1990). The absorbance of a chloroplatinate standard (CPU) was then measured and all samples were standardised by the absorbance of the standard (Equation One) (Anderson *et al.* 1990).

$$\boxed{\text{Colour (CPU)} = \frac{A \times C \times n}{B}} \qquad \textit{Equation One}$$

Where A = absorbance of sample

B = absorbance of standard

C = colour of standard (500 CPU)

n = dilution factor of sample

3.4 Degradation Experimental Method

The purpose of the degradation study was to determine the ability of soils to degrade resin acids and phytosterols under aerobic and anaerobic conditions over a six-month period. Three soils (Sand, Kawerau loamy sand and Whakarewarewa sandy loam) and four effluents were used for the incubation experiment. The main focus of the work was the interactions of thermomechanical pulping effluents which contain a high concentration of resin acids and phytosterols and are the most likely of the effluents chosen to be used in a land application system.

3.4.1 Preliminary Assessments

3.4.1.1 Soil Characterisation

a) Resin Acids and Phytosterols

The soils were analysed for extractable trace organics (Table 3.2) to determine the amounts of resin acids and phytosterols present before the addition of the pulp and paper effluents (Appendix B:I:Soil Analysis Data).

Table 3.2: Soil Resin Acid and Phytosterol Content

COMPOUNDS	**SAND** ($\mu g.g^{-1}$)	**KAWERAU** ($\mu g.g^{-1}$)	**WHAKAREWAREWA** ($\mu g.g^{-1}$)
Resin Acids	n/d	0.61	0.19
Phytosterols	n/d	5.21	4.52

As expected, the sand contained no resin acids or phytosterols. Kawerau loamy sand and Whakarewarewa sandy loam did contain small amounts of resin acids and phytosterols presumably due to the presence of forested areas in the immediate vicinity of the sample sites (Table 4.1). The major resin acids were dehydroabietic and abietic acids and β-sitosterol was the predominant soil phytosterol. Cholesterol was also present in the soil in relatively large amounts and was included in the sterol quantification. These background soil constituents were taken into account when analysing the results of the experiments.

b) Beach Sand Sodium Content

Sodium can adversely affect the structural and functional behaviour of soils. High sodium content can be a characteristic of pulp and paper effluents (Johnson and Ryder 1988), in particular CTMP and bleached kraft effluents. Therefore it was important to ensure the sand did not interfere with the effluent inputs. To assess the sodium content of the sand its electrical conductivity was measured. Five grams of the beach sand was mixed with 25 ml of water then shaken by hand and left over night to settle. The process was replicated three times and the conductivity was measured. The electrical conductivity of the sand was 363 $\mu S.cm^{-1}$ ± 33 (standard deviation). The results indicated that the salt content of the sand was low enough not to inhibit the experiments, as a soil is considered saline when its electrical conductivity is greater than 4000 $\mu S.cm^{-1}$ (McLaren and Cameron 1990).

3.4.1.2 Effluent Characterisation

The pulp and paper effluents and water control were analysed for total carbon and total organic carbon, chemical oxygen demand, colour and resin acid content (Table 3.3).

Table 3.3: Effluent Characterisation

Parameters	**Water**	**CTMP**	**TMP**	**Bleached Kraft**
Total Organic Carbon ($mg.L^{-1}$)	7	5950	870	210
Chemical Oxygen Demand ($mg.L^{-1}$)	12	185100	2600	850
Colour ($CPU.L^{-1}$)	56	8820	1580	570
Extractable Trace Organics				
Resin Acids ($mg.L^{-1}$)	0	9.95	690	4
Phytosterols ($mg.L^{-1}$)	0	3.13	7	0.2

The control water contained very low carbon content relative to the effluents. Chemithermomechanical pulping effluent had high concentrations of organic carbon, chemical oxygen demand and colour (Table 3.3). All of the effluents collected contained both resin acids and phytosterols (Table 3.3). However, the amounts differed considerably, with TMP containing a substantially high level of resin acids. Due to the high concentration of resin acids and the presence of phytosterols in TMP effluent this became the main focus of the experiments.

3.4.2 Degradation Experiment

Each of the three soils was mixed with each of the four effluents and independently replicated (Table 3.4).

Table 3.4: Soil and Effluent Preparations for Degradation Study

Beach Sand	**Kawerau**	**Whakarewarewa**
Water CTMP TMP Bleached Kraft	Water CTMP TMP Bleached Kraft	Water CTMP TMP Bleached Kraft

Half of each soil preparation was made anaerobic while the other half was left aerobic. The effluent was mixed with the soil at a rate of 0.5 mL of effluent per gram of soil. Due to the low moisture holding capacity of the sand, the effluent was added to the sand at 0.25 $mL.g^{-1}$. The effluent addition rates allowed for anaerobic conditions to be induced in the anaerobic samples. Aerobic conditions were easily maintained in the aerobic samples.

For the aerobic degradation experiment the soil effluent mixtures were placed in 340 x 240 mm aluminium foil trays, which were covered with aluminium foil to reduce evaporation and maintain constant moisture content. The other half of each preparation was further divided into twelve 100 gram samples and placed in glass jars, one sample for each sampling day. The glass jars were previously sterilised in an oven at 450°C for 4 hours, the plastic lids were sterilised by wiping with 70% ethanol. The samples were then sealed and flushed with nitrogen gas for 3 minutes using in and out needles through septa in the lids.

All of the samples were then placed in a constant temperature room for the duration of the experiment until their sampling day (Figure 3.4). There were a total of 24 aerobic trays and 288 anaerobic jars.

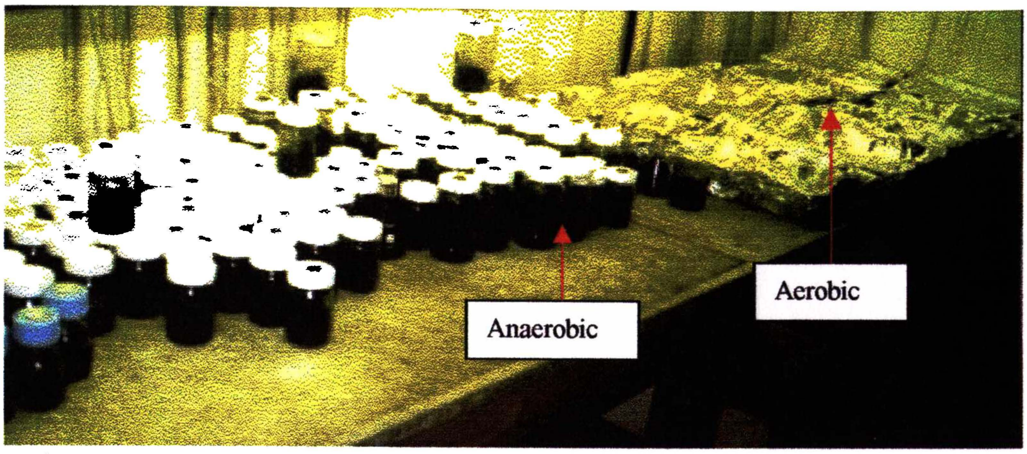

Figure 3.4: Constant Temperature Room for Degradation Study

The moisture content of the aerobic samples was monitored on an approximately weekly basis and was maintained to target by adding non-filtered Milli-q water and mixing with a glass stirring rod to re-aerate the sample. The aerobic sample moisture contents were well maintained over the duration of the degradation experiment (Figure 3.5).

A sampling regime was established using a logarithmic scale (Table 3.5). One hundred gram samples were taken from each aerobic sample tray and one anaerobic glass jar from each preparation was sacrificed on each sampling day. The samples were transferred to plastic containers (200mL) and frozen at -20°C until analysis.

Table 3.5: Sampling days for degradation study

Sampling Days	Calendar days
0	0
1	1
2	2
3	5
4	7
5	14
6	21
7	28
8	42
9	56
10	84
11	112
12	168

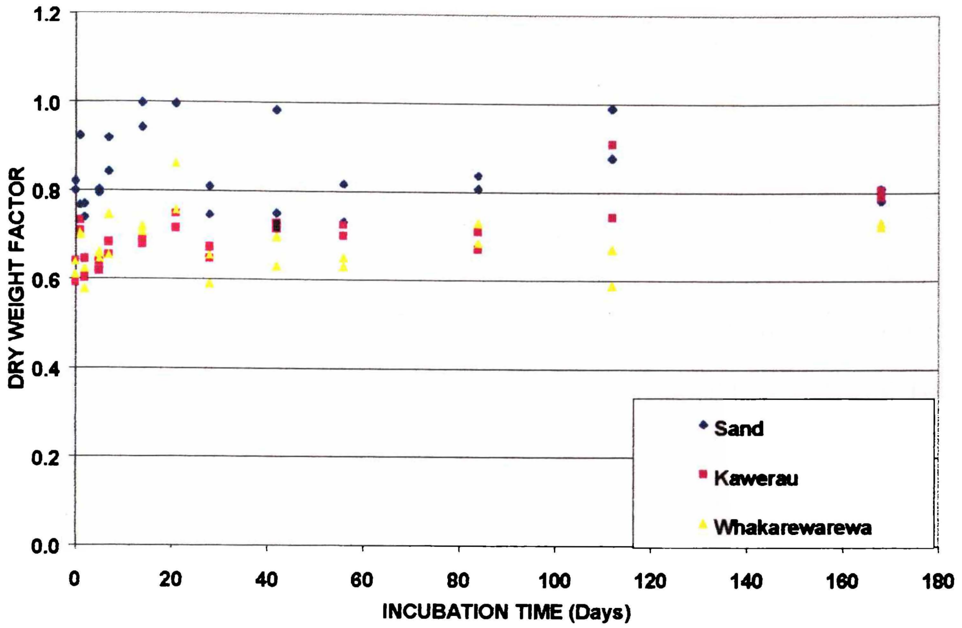

Figure 3.5: Dry weight factors for aerobic samples for soils and thermomechanical pulping effluent incubations.

The average dry weight factor for the sand was 0.85 ± 0.09, the Kawerau loamy sand was 0.70 ± 0.07 and the Whakarewarewa sandy loam was 0.68 ± 0.06.

The temperature of the constant temperature room was set at 25°C, with an average temperature during the 168 day incubation period of 24.4°C±3°. The headspace composition and general state of the samples were monitored on a random basis of approximately weekly intervals to ensure anaerobic conditions had been maintained. The headspace of the anaerobic samples were sampled through the setpa in the lid using a syringe and gas was analysed on a gas chromatograph for nitrogen content.

Although every soil sample was taken on each sampling day, time constraints and study focus meant that not all of the samples were analysed. For the CTMP, control and bleached kraft effluent sets only the day zero and day twelve samples were analysed. TMP was analysed in total throughout the trials. The remaining samples have been retained at -20°C for further studies (e.g for microbial ecology assessment or stable isotope analysis).

To aid in analysis of the data, results from the studies were summarised according to the following family groups: pimaranes, dienic and aromatic abietanes. The pimaranes consisted of pimaric, sandaracopimaric and isopimaric acids. The dienic abietanes comprised palustric, abietic and neoabietic acids, and the aromatic abietanes of dehydroabietic, seco-1-dehydroabietic and seco-2-dehydroabietic acids. The phytosterol group was made up of cholesterol, campesterol, stigmasterol and sitosterol. Although cholesterol is not a plant sterol it was present in the effluents and soils in sufficient concentrations to warrant consideration (Appendix B:I Soil and Effluent Analysis Data).

3.5 Batch Equilibrium Experimental Method

To assess the adsorption kinetics of resin acids in soils, a preliminary study was undertaken to establish the rate at which resin acids were taken up by soil. Sand, Kawerau loamy sand and Whakarewarewa sandy loam were shaken with thermomechanical pulping (TMP) effluent. The least amount of shaking time that was required for the soil and effluent to reach an equilibrium concentration was the effective shaking time (EST) which was used for the batch equilibrium experiments.

3.5.1 Preliminary Assessments

3.5.1.1 Adsorption Kinetics Pilot Study

Adsorption is the process by which solute interacts with soil surfaces until a concentration equilibrium has been established between the two phases (Tan

Adsorption is the process by which solute interacts with soil surfaces until a concentration equilibrium has been established between the two phases (Tan 1993). The rate at which the equilibrium occurs is an important factor in determining the extent of adsorption and desorption in soils. The kinetics behaviour of organic compounds from pulp and paper effluents was unknown and would affect the batch equilibrium experiments.

TMP was used for the kinetics experiment as it was the principle focus of the study, contains the largest amounts of resin acids and would probably take the longest period of time to equilibrate with each soil. Ten grams of each soil (beach sand, Kawerau and Whakarewarewa soils) and 25 mL of TMP effluent were mixed in 50-mL glass centrifuge tubes.

The soil and effluent ratio was established by small shaking tests to establish the best ratio with respect to interaction capacity of the soil and effluent. One sample was used for each sampling time. Sampling occurred at 0, 1, 10, 30, 60, 120, 180, and 240 minutes of shaking time which was achieved on an end-over-end rotating shaker.

Following shaking the samples were centrifuged for 15 minutes before the supernatant was decanted, and then analysed for resin acid content. The resin acid concentrations were used for the determination of the amount of time that was required for each soil to reach equilibrium.

The kinetics experiment indicated that the effluent rapidly reached equilibrium with the soils (Figure 3.6). Equilibrium was defined as the resin acid concentration at which no change in concentration was noted.

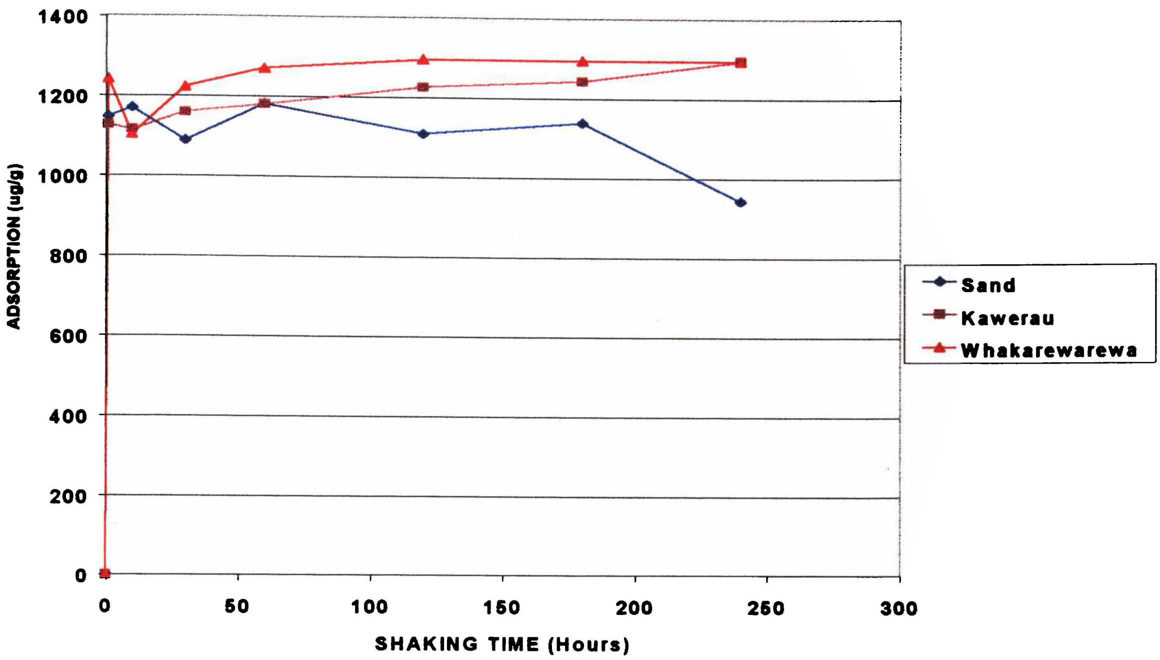

Figure 3.6: Adsorption of resin acids from thermomechanical pulping effluent by soils over a 240 minute shaking period.

The adsorption was measured in units of $\mu g.g^{-1}$, which is the amount of resin acids that was sorbed by each gram of soil and was calculated using the Sorption Equation (Equation Two). Equilibrium occurred in the Kawerau loamy sand and Whakarewarewa sandy loam before or at 240 minutes of shaking time. Therefore the standard equilibrium time for the study was chosen to be 240 minutes and was used for the shaking time of the adsorption and desorption phase of the batch equilibrium study.

3.5.2 Batch Equilibrium Experiments

The objective of the batch equilibrium study was to establish the amount of irreversible adsorption to soils of pulp and paper effluent derived resin acids. The batch equilibrium experiment consisted of two phases, adsorption and desorption. For the adsorption phase the effluent was shaken with the soil then removed. The desorption phase followed, in which water was added in several aliquots to the aliquots to the soil sample from the adsorption phase. Desorption experiments are usually performed in conjunction with adsorption experiments to determine the reversibility of freshly sorbed compounds from the soil matrix (Pavlostathis and Jaglal 1991).

Three soils (Beach sand, Kawerau loamy sand, and Whakarewarewa sandy loam) and four effluents (water, chemithermomechanical, thermomechanical and bleached kraft effluents) were used. The air dried soil was added to a constant 25 mls of effluent at concentrations of 0, 1, 2, 5, and 10 grams in 50-ml glass centrifuge tubes. The soil concentrations were chosen on a logarithmic scale with the maximum amount of soil used to correspond with the pilot kinetics study. There were a total of 60 adsorption samples and 60 corresponding desorption samples. One replication of the batch equilibrium experiment was done.

For the adsorption phase of the experiment, the soils and effluents were shaken for the effective shaking time (240 minutes as established from the adsorption kinetics pilot study) on an end-over-end shaker and then centrifuged for 15 minutes.

The desorption phase consisted of 4 separate sets of shaking with water sample. Ten mL of milli-q water was added to the centrifuge tube and shaken for 1 hour. The soil and water mixture was then centrifuged for 15 minutes and the supernatant was decanted. Five mL of water was then added and the sample shaken for 1 hour, centrifuged for 15 minutes and decanted into the same vial as the first desorption sample. The addition of 5 mL of water, shaking for 1 hour, centrifuging for 15 minutes and then decanting of the supernatant was carried out twice more resulting in a total of 4 desorptions, and a total of 240 minutes of shaking time.

The adsorption and desorption samples from the batch equilibrium experiments were analysed for total carbon, total organic carbon, chemical oxygen demand, colour, and resin acid content. The cumulative effect of shaking time on the samples was accounted for by subtracting the control data from the effluent data.

Pulp and paper effluents are characterised by high dissolved organic matter content (Kookana and Rogers 1995). The presence of dissolved organic carbon can affect the transport (Jardine *et al.* 1990; van der Weerd *et al.* 1999) and the availability of resin acids in a soil system (Diamodopoulos *et al.* 1998). Therefore, total carbon and total organic carbon and chemical oxygen demand may strongly influence resin acid behaviour in a batch equilibrium system.

An adsorption equation was applied to the results for each of the parameters measured and the adsorption and desorption phase of the batch equilibrium experiments were compared. The amount of adsorption-desorption was the difference between the initial concentration of the solute and the concentration following interaction with the soil (Equation Two.). All of the experiments were carried out at room temperature and the adsorption-desorption results were displayed in adsorption-desorption concentration isotherms.

$$\boxed{q = \frac{V(C_o - C_e)}{m}}$$

Equation Two

Where q = the amount sorbed ($\mu g.g^{-1}$)

V = the volume of the solution (mL)

C_o = the initial concentration of the solution ($\mu g.mL^{-1}$)

C_e = the measured concentration of the solution ($\mu g.mL^{-1}$)

m = the amount of soil (g)

Resin acid adsorption was also described using the Freundlich equation (Equation Three). The residual resin acid concentration in the aqueous phase and the mass of soil were used to calculate the coefficients for the Freundlich equation.

$$\boxed{q_e = K_f C^{1/n}}$$ *Equation Three*

Where q_e = amount of resin acids adsorbed ($\mu g.g^{-1}$)

C = is the equilibrium liquid-phase concentration ($\mu g.mL^{-1}$)

K_f = empirical coefficient

1/n = empirical coefficient

K_f is a constant related to the adsorptive capacity while 1/n is related to adsorption intensity. The constants were determined by regression of the linearised Freundlich equation (log q_e vs log C) where 1/n was the slope and K_f was the y-axis intercept of the regression line.

3.6 Summary

Three soils and four pulp and paper effluents were collected to investigate the degradation and sorptive behaviour of resin acids and phytosterols from pulp and paper effluents. The soils were air-dried and sieved before storage. The effluents remained unfiltered and were stored at 5°C.

From preliminary assessments, thermomechanical pulping effluent (TMP) appeared to be the best representative of the pulp and paper effluents chosen as it was the most likely to be land applied and contained a high concentration of resin acids. The degradation experiment was focused primarily on TMP effluent.

The degradation experiment was composed of 3 soils and 4 effluents combined and replicated, then incubated over for a 168 day period under aerobic and anaerobic conditions at ~25°C. The incubations were samples on a logarithmic scale and analysed for resin acid and phytosterol concentrations using the ***Forest Research*** extractable trace organics method. The TMP samples were all analysed and the other effluents incubations were partially analysed, due to time constraints and study focus.

The batch equilibrium experiment was composed of an adsorption and desorption phase, 3 soils and 4 effluents were used. A preliminary study into the effect of kinetics on adsorption revealed that the effective shaking time for adsorption was 240 minutes, this was then used in the batch equilibrium experiment as the shaking time. The samples were shaken for a total of 480 minutes, 240 minutes of adsorption shaking then 240 minutes desorption shaking time. The supernatants were decanted and analysed for total carbon, total organic carbon, chemical oxygen demand, colour and resin acid content.

BEHAVIOUR OF THERMOMECHANICAL PULPING EFFLUENT IN SOIL ENVIRONMENTS

4.0 BEHAVIOUR OF THERMOMECHANICAL PULPING EFFLUENT IN SOIL ENVIRONMENTS

Soils that are typically chosen for land application schemes are free draining or very free draining and therefore aerobic by nature (McLaren and Cameron 1990). It is important to understand the extent of resin acid and phytosterol degradation under aerobic conditions as this will be the dominant environment that occurs in a land application situation. However, during periods of high rainfall/groundwater or poor management of land application systems (e.g. by exceeding soil assimilation capacity) then it is possible that anaerobic conditions will prevail. In this section the effect of soil type and oxic state on the degradation behaviour of resin acids and phytosterols in thermomechanical pulping (TMP) effluent is assessed.

4.1 Background

The resin acid and phytosterol data from soils which were incubated with thermomechanical pulping effluent were graphed using a first order exponential decay function (Equation Four).

$$\boxed{y = y_o + A_e^{-(x-xo)/t}} \qquad \textit{Equation Four}$$

Where y_o = y offset

x_o = x offset

A = amplitude

t = time constant

Unfortunately, in some cases, non-classical decay data were found and the curve fitting algorithm was unable to be fitted to all the data.

The exponential decay curves were used to assess the degradation of compounds (both individually (Appendix B:IV Degradation Curve Data) and for family groups) for all three soils under aerobic and anaerobic conditions. In most cases the exponential decay curves for the resin acids showed a distinctive pattern consisting of a lag period in which an apparent adsorption and desorption of resin acids was noted and then a degradation phase (Figure 4.1). It was assumed that no significant degradation occurred during the desorption phase. Given the high level of colloidal material in the effluent, it is possible that the first dip was a result of filtration caused by the soil matrix and a subsequent inability for the soxhlet extraction method to adequately extract all the sorbed material. This may indicate that future studies may require a more rigorous extraction technique, for example alkaline hydrolysis, to measure total mass balances.

The decay curves were used to calculate several degradation parameters:

Theoretical zero (T_0): calculated concentration of resin acids and phytosterols in the soil following the addition of effluent or water.

Degradation zero (D_0) and Lag: compound concentration ($\mu g.g^{-1}$) at which the modeled degradation curve begins (Figure 4.1). The length of time between incubation start and the initiation was defined as the lag time.

Theoretical half-life ($T_0½$): amount of time that was required for half of the compound's theoretical zero (T_0) concentration to be removed and was back calculated from each compound's decay curve.

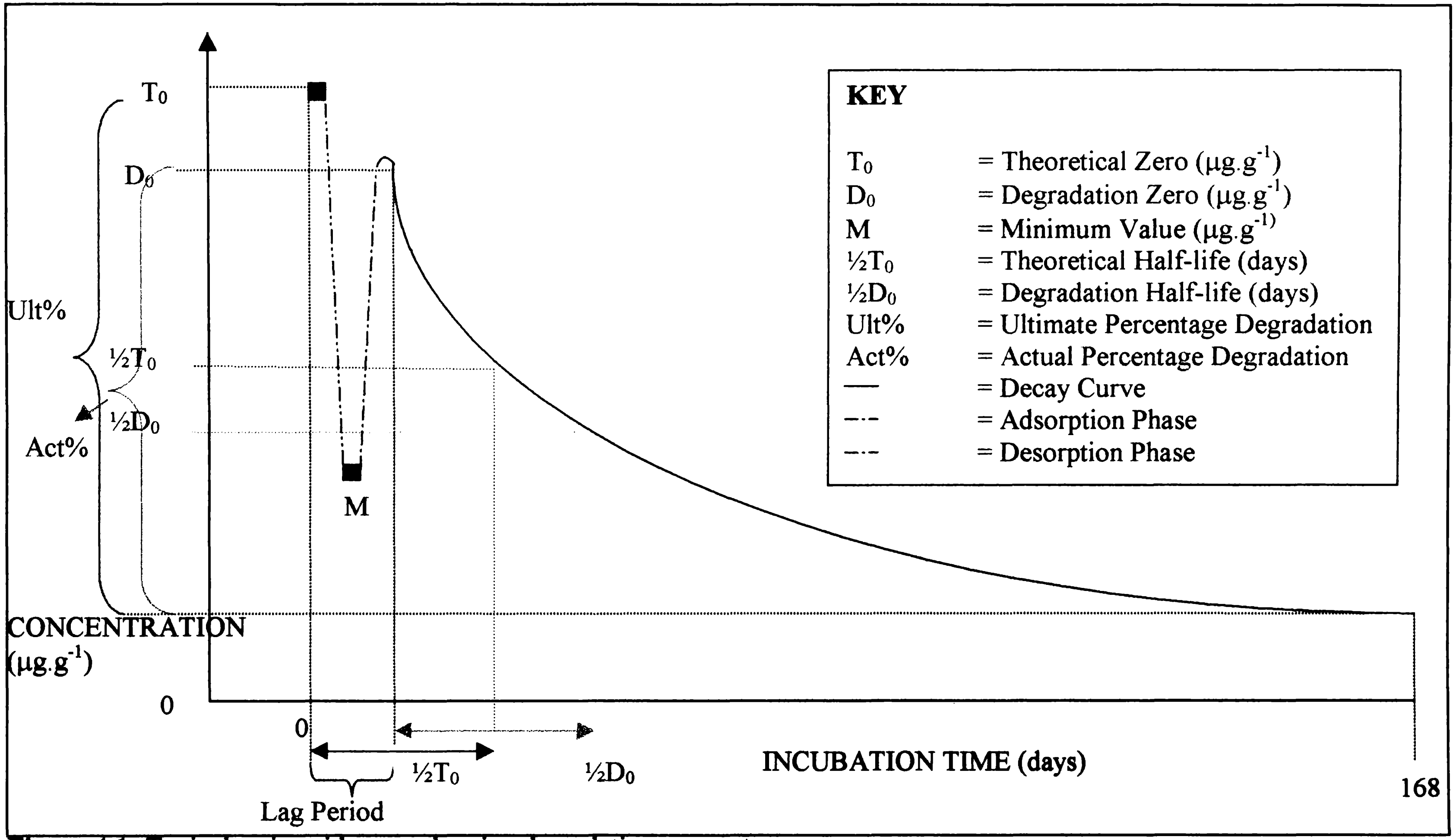

Figure 4.1: Typical resin acid curve showing degradation parameters

Degradation half-life ($D_0½$): calculated in the same manner as the theoretical half-life, but using half D_0 concentration instead of T_0 (Figure 4.1).

Minimum concentration (M): lowest point in the lag phase curve. M represents the extent to which "adsorption" occurred.

Desorption ratio (D_0/T_0): ratio between the theoretical zero and degradation zero. D_0/T_0 was determined as an estimate of the extent of unrecoverable compound during the lag phase and represents "desorption" (Figure 4.1). If D_0/T_0 is >1 incomplete desorption has occurred and the soil has held onto some unextractable fraction of resin acids or phytosterols.

Ultimate degradation: percentage degradation taken from the end of the degradation curve to T_0 (Figure 4.1).

Actual degradation: was calculated as for the ultimate degradation, except that D_0 was used instead of T_0 (Figure 4.1).

4.1.1 Degradation Kinetics

The rate of change in resin acid and phytosterol concentrations was determined as the overall rate at any time (Equation Five). A transitory rate between sample points was also determined (Equation Six).

$$\boxed{\frac{dy}{dx} = \frac{C_n - C_o}{n}}$$

Equation Five

Where dy/dx = rate of change ($ug.g.^{-1}day^{-1}$)
C_n = compound concentration after n days of incubation ($ug.g^{-1}$)
C_o = compound concentration on day zero ($ug.g^{-1}$)
n = incubation time (days)

$$\boxed{\frac{dy}{dx} = \frac{\dfrac{C_{n+1} - C_n}{(n+1) - n}}{C_n}}$$

Equation Six

Where dy/dx = rate of change (day^{-1})
C_n = incubation day concentration ($ug.g^{-1}$)
C_{n+1} = concentration of the next sample day ($ug.g^{-1}$)
n = time of incubation for first incubation day (days)
$n+1$ = time of incubation of the next sampling day (days)

The standardised rate of change took into account the compound's concentration. In non-standardised samples, while a rate change appears large due to a large initial compound concentration, the relative change may itself be small. The maximum degradation rates using both the non-standardised and standardised equations were also compared

4.2 Results

4.2.1 Aerobic Soil Environment

Resin acids derived from three pulp and paper effluents were degraded under aerobic conditions in a rapid infiltration beach sand, Kawerau loamy sand and

Whakarewarewa sandy loam (Figure 4.2; 4.3; 4.4). The removal efficiencies of the soils ranged from 25-100% for resin acids and the extent of degradation was dependent upon effluents used and soil type (Table 41, 4.2, 4.3). Overall the soils were able to effectively remove these constituents from the soils.

Removal rates of resin acids greater then 90% occurred during a comparable barrel lysimeter trial using TMP (Wang *et al.* 1999). The degradation experiment revealed lower removals of resin acids then those found in the barrel lysimeters. The barrel lysimeter trial used primary treated TMP effluent, which upon analysis contained ~35,000 ug.L^{-1} of resin acids (Wang *et al.* 1999). The untreated effluent used for the degradation experiment in this study contained ~690,000 ug.L^{-1} of resin acids. The difference in scale of the resin acid content may account for the lower resin acid removal in the degradation experiment. The difference in contact time of interaction, six months for the degradation study and 16 months for the barrel lysimeter trail, may also have been a factor.

The control sand had the highest removals of resin acids which may be explained by the lack of an alternative carbon source. In all cases resin acid degradation occurred almost immediately. Lag times were typically 2-10 days (Figure 5.5). The Whakarewarewa sandy loam had higher removals of resin acids than Kawerau loamy sand. The Whakarewarewa sandy loam exhibited large irreversible sorption during batch equilibrium experiments whereas the Kawerau loamy sand had lower sorption. The high removals of resin acids in the Whakarewarewa sandy loam may be a result of a combination of irreversible adsorption and degradation by bacteria.

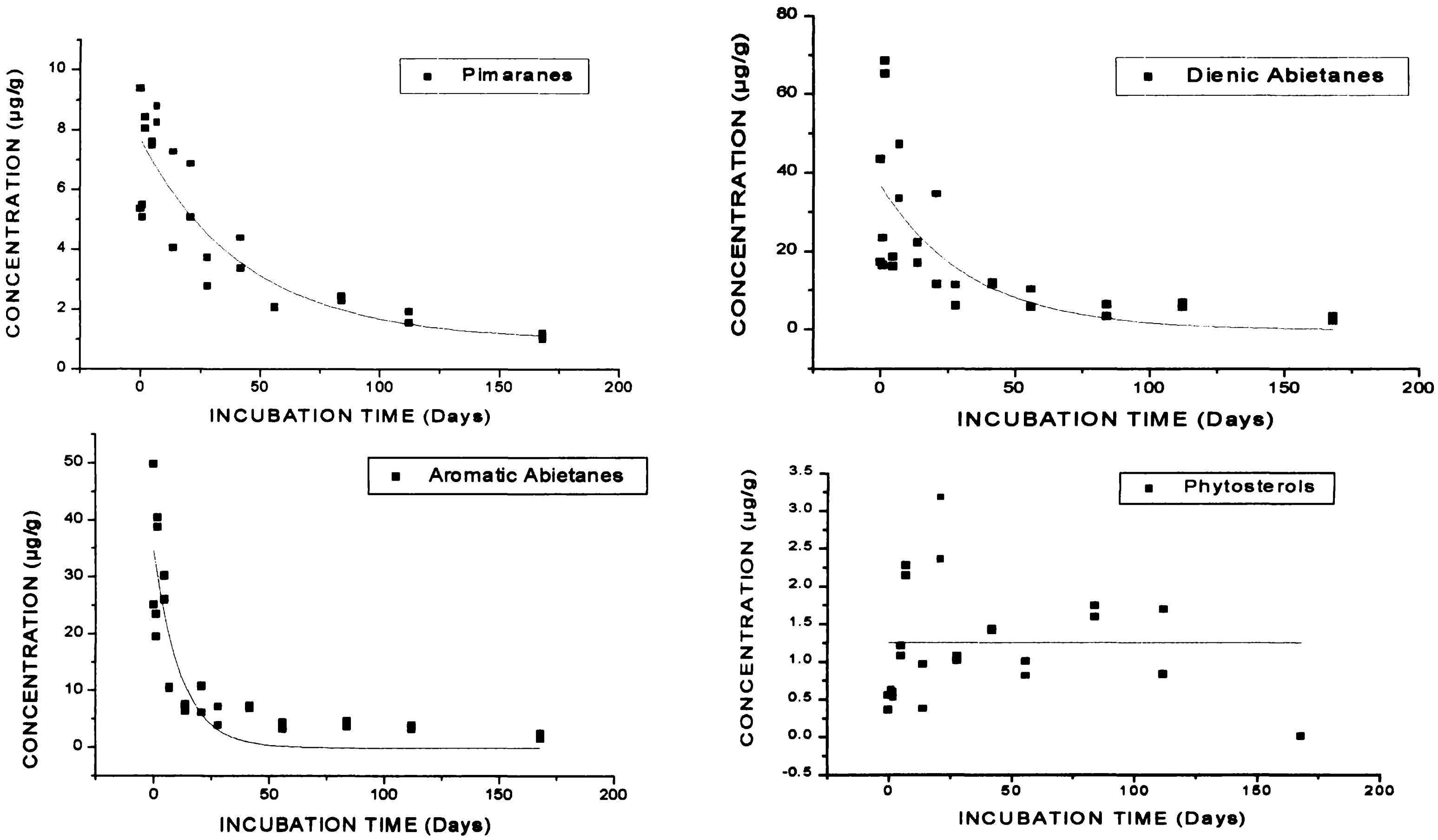

Figure 4.2: Degradation Curves for Resin Acids and Phytosterols from Thermomechanical Pulping Effluent in Aerobic Sand

Table 4.1: Degradation Parameters for Resin Acids and Phytosterols in AerobicSand and Thermomechanical Pulping Effluent Incubations.

Compound	**T_0 (μg.g^{-1})**	**Lag (Days)**	**½D_0 (Days)**	**Ult deg %**	**Act deg %**
PIMARANES	8.5	2	45.5	84	79
Pimaric Acid	4.5	10	22	85	83
Sandaracopimaric Acid	1.4	7.5	9.5	84	84
Isopimaric Acid	2.7	5	25	73	73
DIENIC ABIETANES	205	4	10	100	100
Palustric Acid	3.8	3	6	100	100
Abietic Acid	95	6.5	38.5	96	80
Neoabietic Acid	105	3	10	100	100
AROMATIC ABIETANES	11	1	10	100	100
Dehydroabietic Acid	10	5	2	75	93
Seco-1-dehydroabietic Acid	0.95	2	62.5	89	89
Seco-2-dehydroabietic Acid	0.5	3	54	88	89
PHYTOSTEROLS	1.86	n/c	n/c	n/c	n/c
Cholesterol	1.6	n/c	n/c	n/c	n/c
Campesterol	0	n/c	n/c	n/c	n/c
Stigmasterol	0	n/c	n/c	n/c	n/c
Sitosterol	0.26	n/c	n/c	n/c	n/c

*n/c = parameter can not be calculated using the decay function or graph.

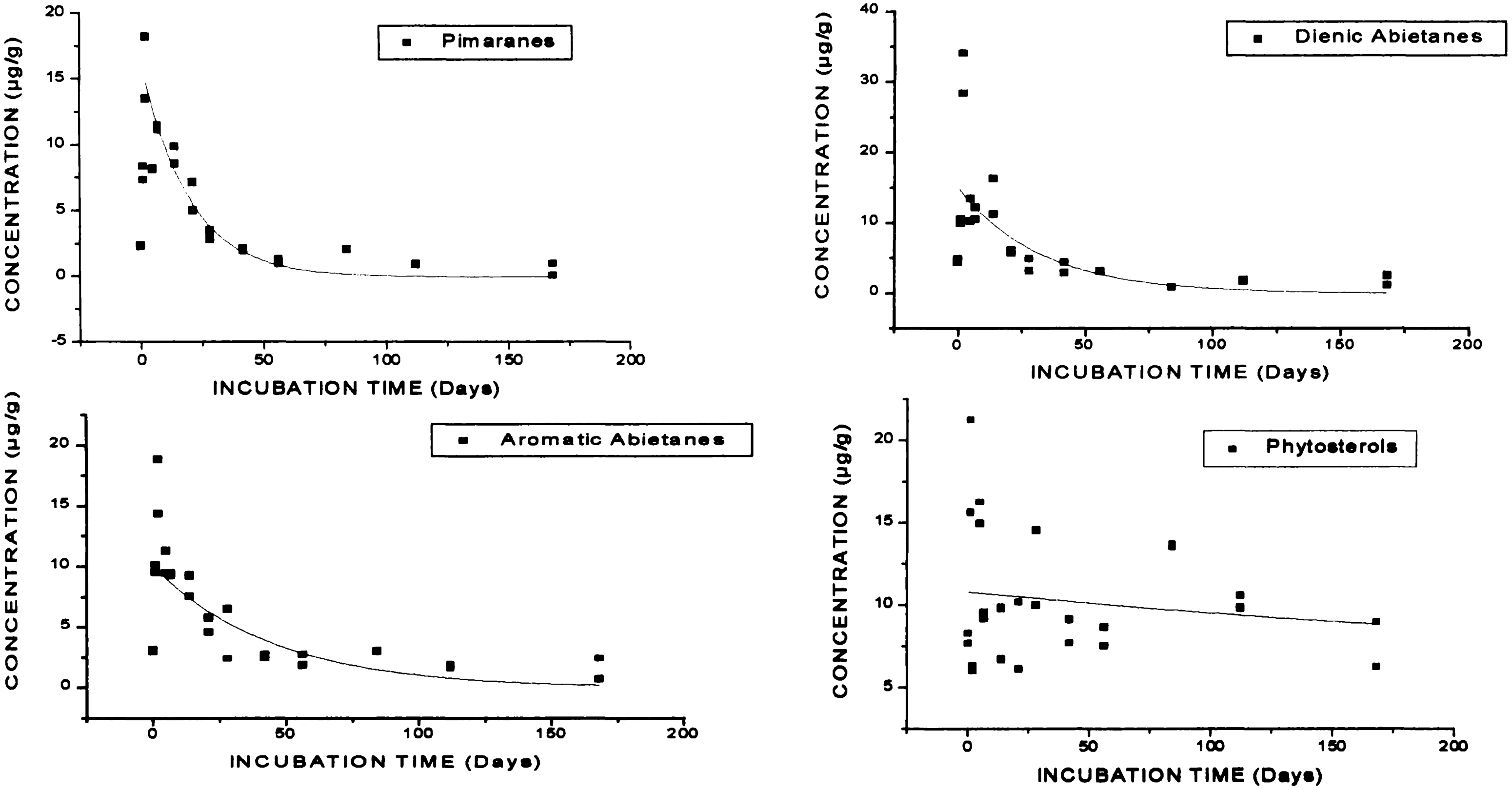

Figure 4.3: Degradation Curves for Resin Acids and Phytosterols in Aerobic Kawerau Loamy Sand and Thermomechanical Pulping Effluent Incubations.

Table 4.3: Degradation Parameters for Resin Acids and Phytosterols in Aerobic Kawerau Loamy Sand and Thermomechanical Pulping Effluent Incubations.

Compound	**T_0 (μg.g^{-1})**	**Lag (Days)**	**½D_0 (Days)**	**Ult deg %**	**Act deg %**
PIMARANES	18	3	12.5	100	100
Pimaric Acid	8.9	3	4.5	100	100
Sandaracopimaric Acid	2.7	4	10.5	100	100
Isopimaric Acid	5.7	3	9	99	93
DIENIC ABIETANES	310	0.5	18	100	93
Palustric Acid	7.7	n/c	n/c	n/c	n/c
Abietic Acid	30	5	20	99	100
Neoabietic Acid	210	n/c	n/c	n/c	n/c
AROMATIC ABIETANES	25	2.5	26.5	98	95
Dehydroabietic Acid	22	4	16	97	94
Seco-1-dehydroabietic Acid	2.0	8	15.2	90	89
Seco-2-dehydroabietic Acid	1.0	3	15.0	92	93
PHYTOSTEROLS	52	1.0	n/c	82	16
Cholesterol	11	n/c	n/c	n/c	n/c
Campesterol	2.6	n/c	n/c	n/c	n/c
Stigmasterol	7.9	0	n/c	70	-97
Sitosterol	31	n/c	n/c	n/c	n/c

* parameter could not be calculated using the decay function or graph.

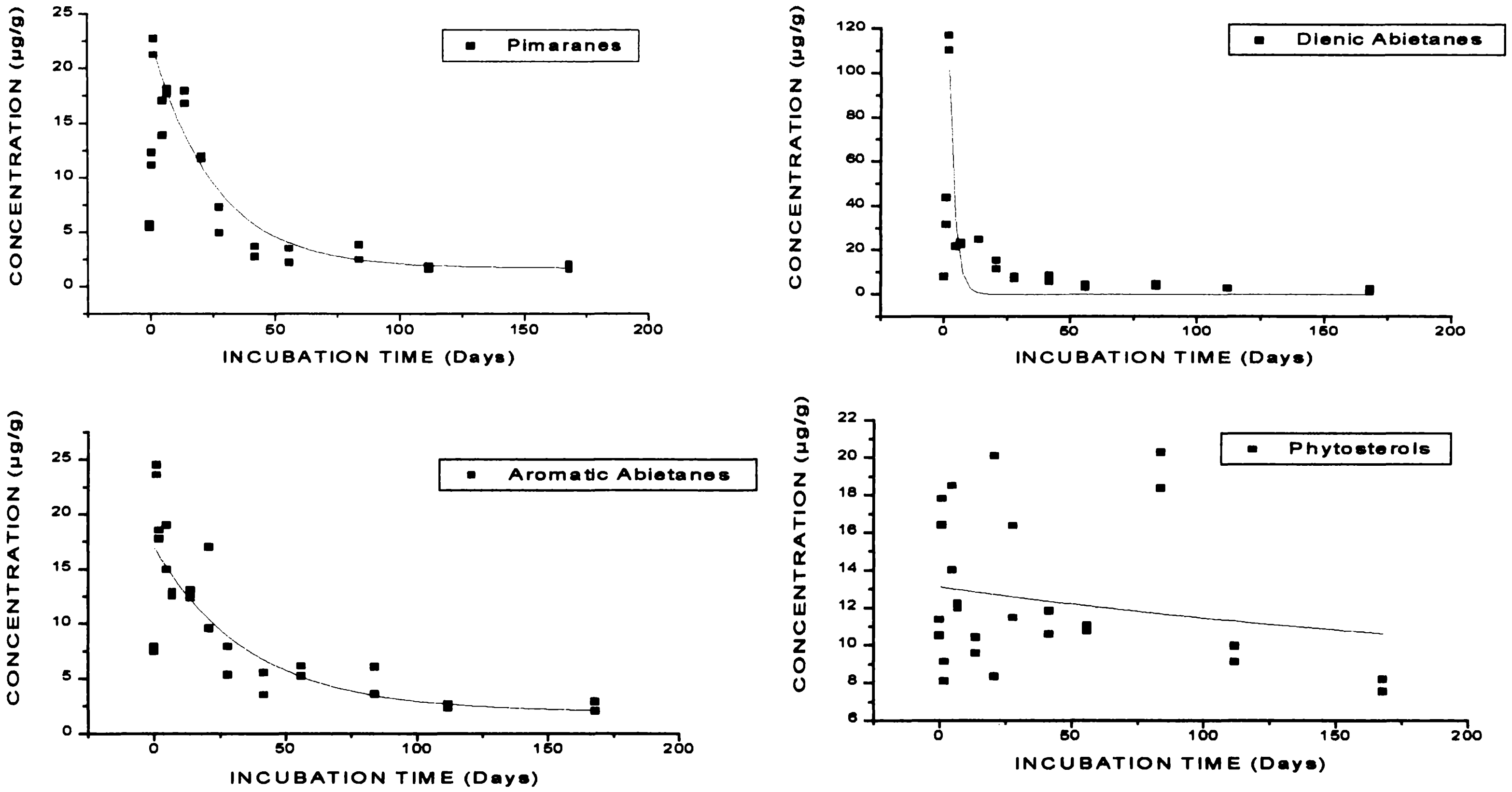

Figure 4.7: Degradation Curves for Resin Acids and Phytosterols in Aerobic Whakarewarewa Sandy Loam and Thermomechanical Pulping Effluent Incubations.

Table 4.3: Degradation Parameters for Resin Acids and Phytosterols in Aerobic Whakarewarewa Sandy Loam and Thermomechanical Pulping Effluent Incubation.

Compound	**T_0 (μg.g^{-1})**	**Lag (Days)**	**½D_0 (Days)**	**Ult deg %**	**Act deg %**
PIMARANES	17	5	18	87	90
Pimaric Acid	8.9	8	13	92	93
Sandaracopimaric Acid	2.7	4	8	100	100
Isopimaric Acid	5.4	4.5	14	89	91
DIENIC ABIETANES	410	4.5	0.5	100	100
Palustric Acid	7.6	n/c	n/c	n/c	n/c
Abietic Acid	190	4	9	100	100
Neoabietic Acid	210	n/c	n/c	n/c	n/c
AROMATIC ABIETANES	22	2	29	89	85
Dehydroabietic Acid	20	1	26.5	89	85
Seco-1-dehydroabietic Acid	1.9	4	21	97	98
Seco-2-dehydroabetic Acid	1.0	3	18	96	97
PHYTOSTEROLS	47	2	n/c	72	18
Cholesterol	10	n/c	n/c	n/c	n/c
Campesterol	4.6	n/c	n/c	n/c	n/c
Stigmasterol	8.9	n/c	n/c	n/c	n/c
Sitosterol	24	5	n/c	68	26

* parameter could not be calculated from decay function or graph.

The degradation curves for each soil type were comparable suggesting that soil composition, including carbon content, had no significant effect on degradability. Pimarane resin acids typically had the highest removals relative to the abietanes, suggesting that abietane resin acids might be more persistent in the soil environment. This is not consistent with previous reports on sediment degradation, which found that pimaranes are more persistent than abietanes (Liss *et al.* 1997; Stuthridge *et al.* 1999). In most cases the degradation of dienic abietanes was influenced by the unstable nature of palustric and neoabietic acids.

The low lag periods for each soil type across the compound classes (typically 2-10 days (Figure 4.5)) suggests that acclimated bacterial populations already existed or that inhibition of bacterial growth was not caused by effluent addition.

Resin acids occur naturally in the Kawerau loamy sand and the Whakarewarewa sandy loam (Appendix B:I). Resin acids have also been located in pristine sediments (Judd *et al.* 1998), indicating that soils may be able to adapt to and degrade resin acids in the natural environment. It may also contribute to the persistent nature of some of the compounds in the soils, as abietanes were located naturally in the soils and pimaranes were not. The control sand did not contain resin acids and had high removals of resin acids. Therefore it appears that the effluents contained microorganisms capable of degrading resin acids

The Kawerau loamy sand and Whakarewarewa sandy loam may have lower removals when compared to the sand due to competition between the natural soil microbial population and those in the effluent. Upon effluent application to the soils, microorganisms in both the soil and the effluents may have degraded carbon sources in the soil rather than resin acids in the effluent. This may be due to the lower levels of other degradable carbon in the sand matrix.

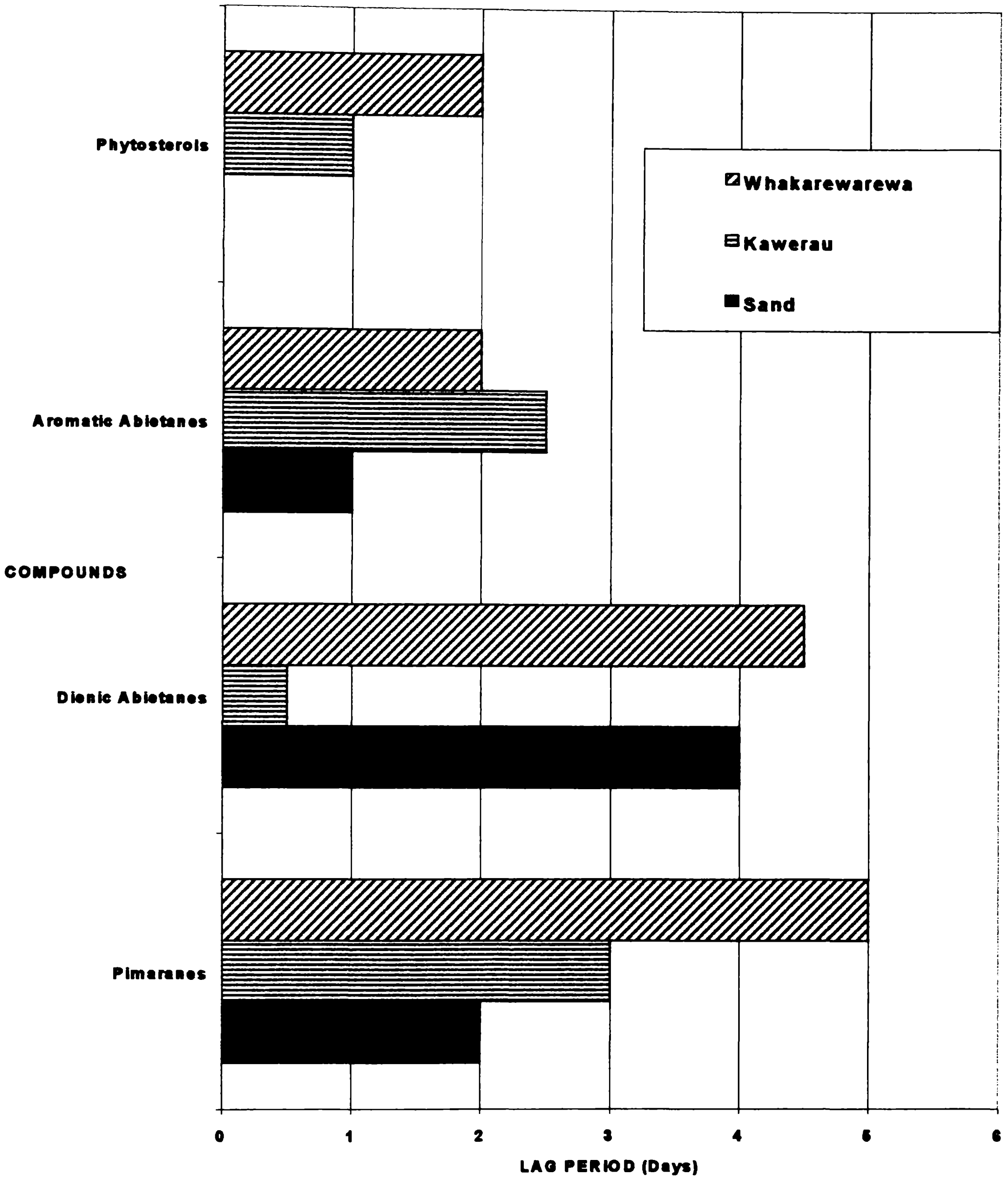

Figure 4.5: Lag periods for aerobic soil and thermomechanical pulping effluent incubations.

An assessment of the relative degradation rates of the soils indicated that little effect was seen as a result of soil type (Table 4.4). Despite differences in absolute rates, as a result of the relative effluent concentrations, the relative rates were quite comparable between compound classes and soil types.

Table 4.4: Maximum Rate of Degradation for Resin Acids and Phytosterols in Aerobic and Anaerobic Soil and Thermomechanical Pulping Effluent Incubations

Soil	**Compound**	**Maximum Degradation ($\mu g.g^{-1}.day^{-1}$)**	**Maximum Degradation (per day)**
Sand Aerobic	Pimaranes	-3.90	-0.42
	Dienic Abietanes	-21.95	-0.46
	Aromatic Abietanes	-26.32	-0.53
	Phytosterols	-0.01	-0.15
Kawerau Aerobic	Pimaranes	-0.02	-0.19
	Dienic Abietanes	-0.06	-0.21
	Aromatic Abietanes	-0.02	-0.17
	Phytosterols	-0.98	-0.71
Whakarewarewa Aerobic	Pimaranes	-0.06	-0.13
	Dienic Abietanes	-0.08	-0.27
	Aromatic Abietanes	-0.10	-0.25
	Phytosterols	-1.64	-0.55
Sand Anaerobic	Pimaranes	-3.13	-0.33
	Dienic Abietanes	-15.47	-0.31
	Aromatic Abietanes	-24.82	-0.50
	Phytosterols	-0.27	-1.00
Kawerau Anaerobic	Pimaranes	-0.05	-0.22
	Dienic Abietanes	-0.09	-0.28
	Aromatic Abietanes	-0.04	-0.19
	Phytosterols	-1.19	-0.54
Whakarewarewa Anaerobic	Pimaranes	-0.11	-0.08
	Dienic Abietanes	0	-0.20
	Aromatic Abietanes	-0.24	-0.43
	Phytosterols	-1.11	-0.48

Phytosterol behaviour was variable through the incubation samples and was probably associated with high amounts of cholesterol and β-sitosterol present naturally in the Kawerau loamy sand and the Whakarewarewa sandy loam (Appendix B:I).

It appears that soil contain naturally occurring microorganisms that are capable of degrading and producing phytosterols under both aerobic and anaerobic conditions. Phytosterols are fairly ubiquitous in the environment. They occur in most plants an are probably incorporated into soils upon the degradation of plant matter.

4.2.2 Anaerobic Soil Environment

The behaviour of resin acids in the anaerobic incubations was very similar to the degradation characteristics that occurred in the aerobic incubations. All soils were able to effectively degrade TMP resin acids under anaerobic conditions (Figure 4.6. 4.7, 4.8). Resin acid removals were generally higher in the aerobic incubations than the anaerobic incubations. This has been observed in previous studies of aerobic/anaerobic degradation of secondary treatment system sediments (Stuthridge *et al.* 1999).

High concentrations of resin acids can be toxic to anaerobic microorganisms (Liver and Hall 1996). This was not, however, seen in the soils as the lag periods for the anaerobic incubations were usually smaller than for the aerobic incubations. Therefore toxicity to anaerobic microorganisms was not a factor (Figure 4.9). Since methanogenic bacteria are predominantly affected by toxicity from resin acids, it would seem that these bacteria were not the main degraders of resin acids in these soils (McCarthy *et al.* 1990; Springer 1993).

The sands were consistently able to degrade phytosterols to a larger extent then the Kawerau loamy sand and the Whakarewarewa sandy loam. However, this may also be linked to the production of phytosterols and their natural occurrence in the soils. While some of the phytosterols were being degraded it was likely that some were also being produced in the high organic matter soils.

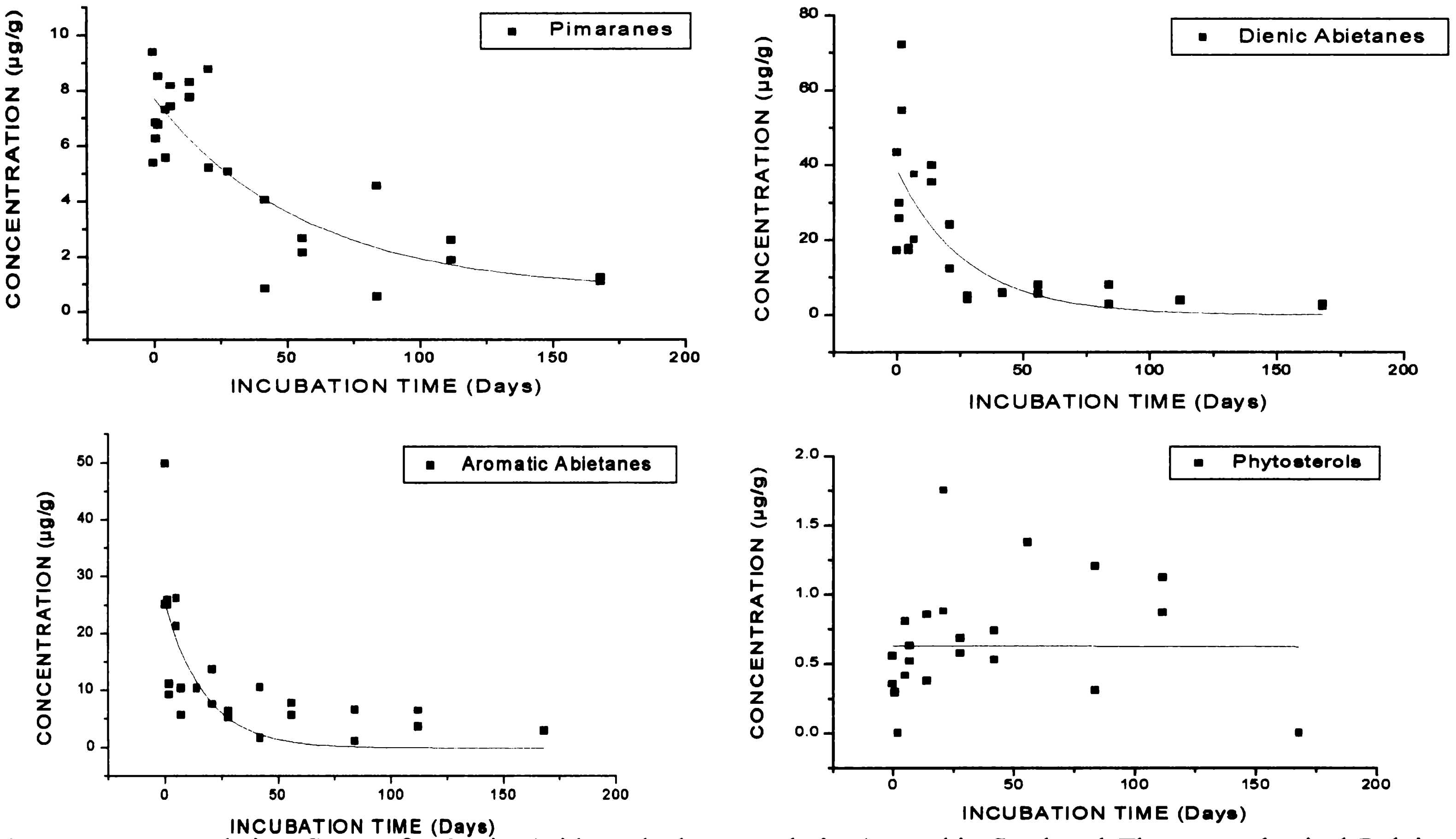

Figure 4.6: Degradation Curves for Resin Acids and Phytosterols in Anaerobic Sand and Thermomechanical Pulping Effluent Incubations.

Table 4.5 Degradation Parameters for Resin Acids and Phytosterols in Anaerobic Sand and Thermomechanical Pulping Effluent Incubations

Compound	**T_0**	**Lag**	**½D_0**	**Ult%**	**Act%**
PIMARANES	8.5	2	44	85	84
Pimaric Acid	4.5	7.5	20	85	86
Sandaracopimaric Acid	1.4	3	21	99	98
Isopimaric Acid	2.7	1	50.5	85	83
DIENIC ABIETANES	205	2	19	99	96
Palustric Acid	3.8	2.5	2.5	100	100
Abietic Acid	95	3	25.5	98	89
Neoabietic Acid	105	2	13	100	100
AROMATIC ABIETANES	11	2	5	100	100
Dehydroabietic Acid	10	1	75	100	100
Seco-1-dehydroabietic Acid	0.95	5	62	78	80
Seco-2-dehydroabietic Acid	0.5	5	61	74	74
PHYTOSTEROLS	1.86	n/c	n/c	n/c	n/c
Cholesterol	1.6	n/c	n/c	n/c	n/c
Campesterol	0	n/c	n/c	n/c	n/c
Stigmasterol	0	n/c	n/c	n/c	n/c
Sitosterol	0.26	n/c	n/c	n/c	n/c

* parameter could not be calculated from decay function or graph.

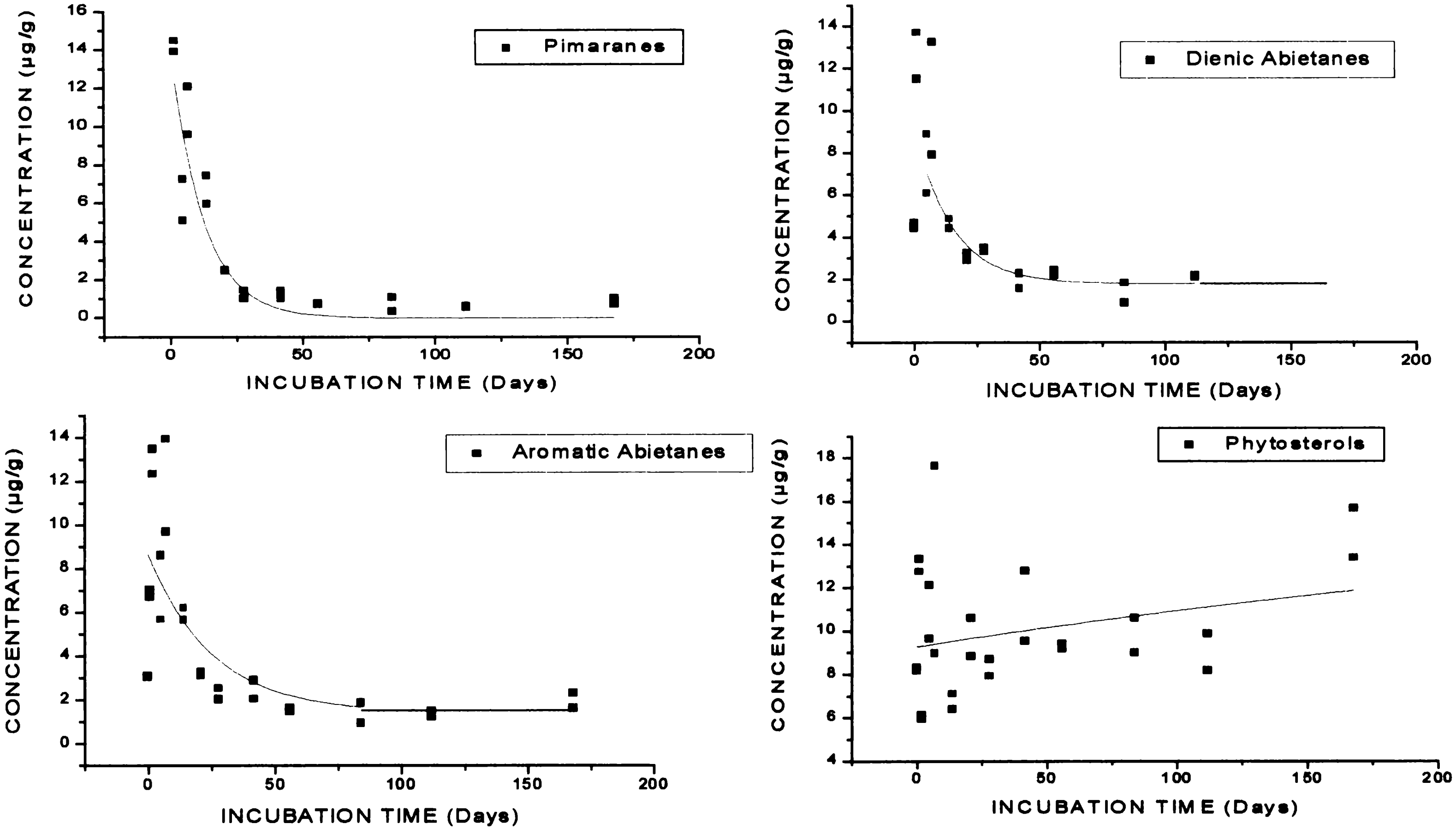

Figure 4.7: Degradation Curves for Resin Acids and Phytosterols in Anaerobic Kawerau Loamy Sand and Thermomechanical Pulping Effluent Incubations.

Table 4.6: Degradation Parameters for Resin Acids and Phytosterols in Anaerobic Kawerau Loamy Sand and Thermomechanical Pulping Effluent Incubations.

Compounds	**T_0 (μg.g^{-1})**	**Lag (Days)**	**½D_0 (Days)**	**Ult deg %**	**Act deg %**
PIMARANES	17	3	8.5	100	100
Pimaric Acid	8.9	2.5	7.5	100	100
Sandaracopimaric Acid	2.7	2.5	10	100	100
Isopimaric Acid	5.7	4	8.5	95	93
DIENIC ABIETANES	310	5	16	99	71
Palustric Acid	7.7	n/c	n/c	n/c	n/c
Abietic Acid	99	4	2	100	100
Neoabietic Acid	210	n/c	n/c	n/c	n/c
AROMATIC ABIETANES	25	1	23.5	93	79
Dehydroabietic Acid	22	4	9	97	94
Seco-1-dehydroabietic Acid	2.0	5	12	96	94
Seco-2-dehydroabietic Acid	1.0	4	11.5	100	100
PHYTOSTEROLS	52	n/c	n/c	78	22
Cholesterol	11	n/c	n/c	86	-43
Campesterol	2.6	n/c	n/c	80	-24
Stigmasterol	7.9	n/c	n/c	73	-59
Sitosterol	31	n/c	n/c	77	-9

* parameter could not be calculated for decay function or graph.

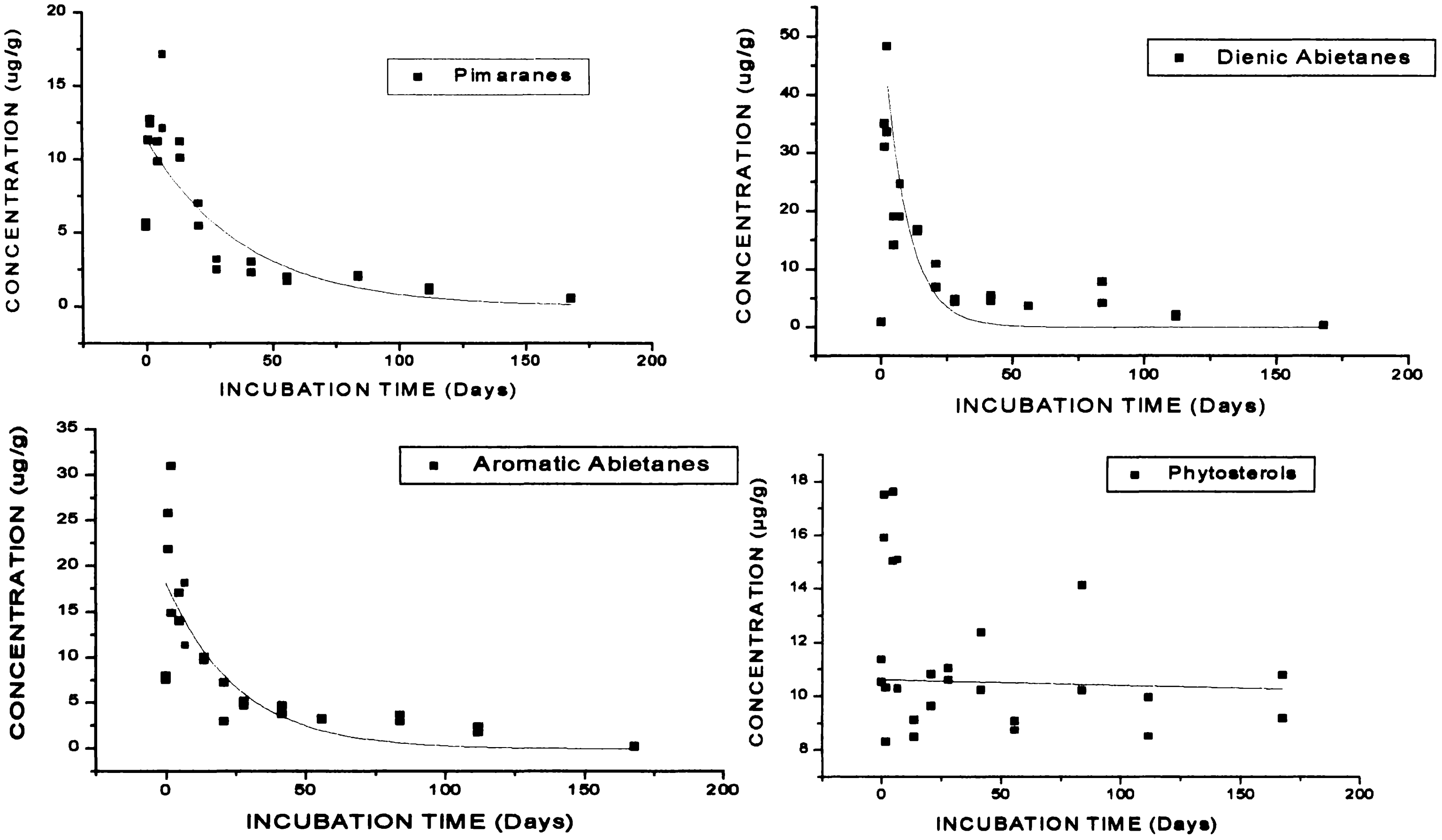

Figure 4.8: Degradation Curves for Resin Acids and Phytosterols in Anaerobic Whakarewarewa Sandy Loam and Thermomechanical Pulping Effluent Incubations

Table 4.7: Degradation Parameters for Resin Acids and Phytosterols in Anaerobic Whakarewarewa Sandy Loam and Thermomechanical Pulping Effluent Incubations.

Compounds	**T_0**	**Lag**	**½D_0**	**Ult%**	**Act%**
PIMARANES	17	4	25.5	97	95
Pimaric Acid	8.9	10	7	100	100
Sandaracopimaric Acid	2.7	2.5	17.5	98	98
Isopimaric Acid	5.4	8.5	7	100	100
DIENIC ABIETANES	410	3	7	100	100
Palustric Acid	7.6	n/c	n/c	n/c	n/c
Abietic Acid	110	4	13	100	100
Neoabietic Acid	210	n/c	n/c	n/c	n/c
AROMATIC ABIETANES	22	2	16	98	97
Dehydroabietic Acid	20	1	14	100	100
Seco-1-dehydroabietic Acid	1.9	3	22	97	97
Seco-2-dehydroabetic Acid	1.0	3	30	95	95
PHYTOSTEROLS	47	0.5	n/c	76	7
Cholesterol	10	n/c	n/c	n/c	n/c
Campesterol	4.6	2	n/c	82	28
Stigmasterol	8.9	0.5	n/c	80	2
Sitosterol	24	2	n/c	79	38

* parameter can not be calculated from decay function or graph

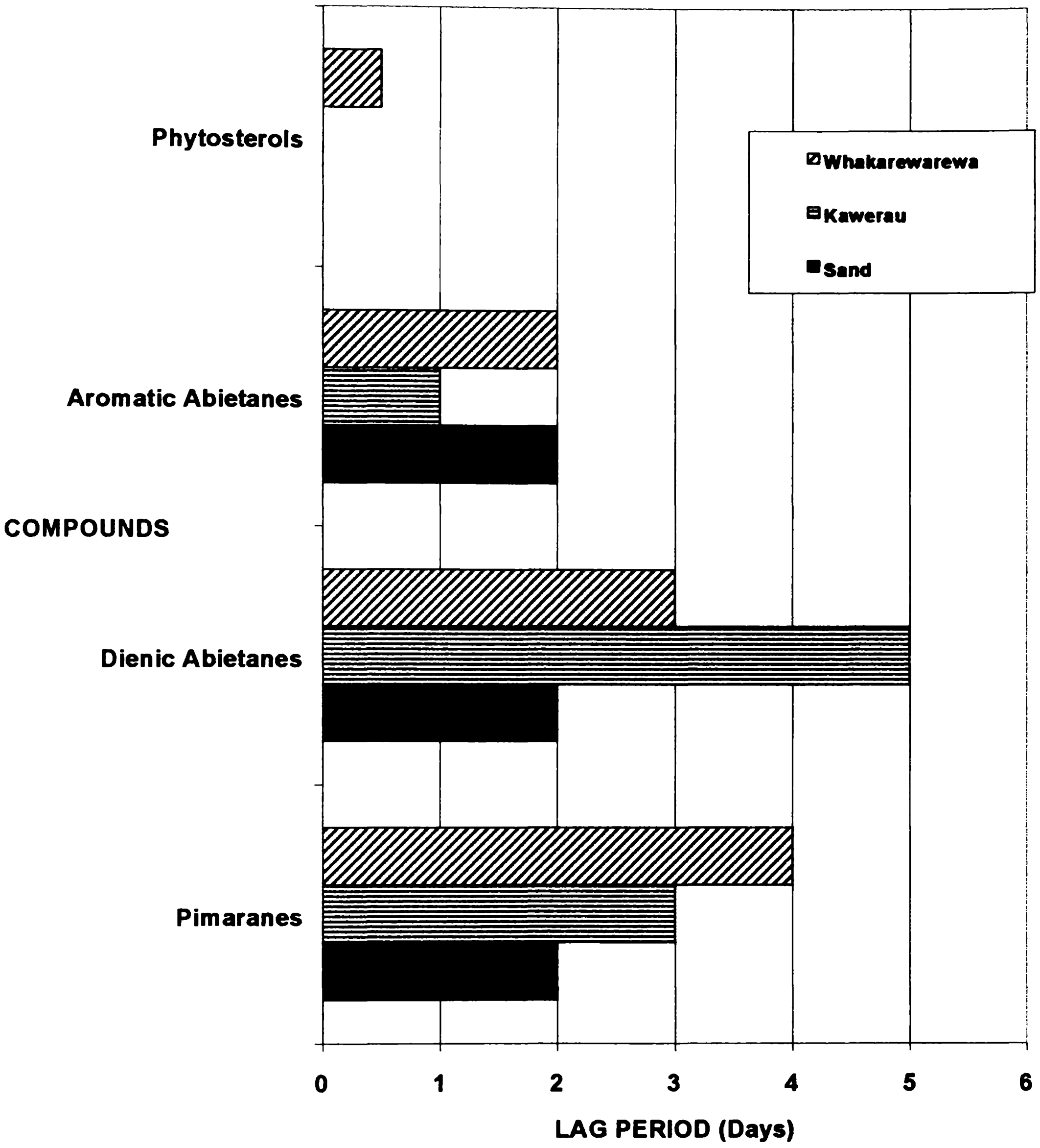

Figure 4.9: Lag periods for the Anaerobic soil and thermomechanical pulping effluent incubations.

The ratio between the extent of production and degradation by the microorganisms controlled the net changes in phytosterol concentration

During a barrel lysimeter trial using the irrigation of thermomechanical pulping effluent, over 90% of the phytosterol component of the effluent was removed by the soils (Wang *et al.* 1999), this was not seen in the incubation experiment except in the sand incubations. The barrel lysimeter trial used a primary treated TMP effluent, which contained 636 ug.L^{-1} of phytosterols, which was irrigated over the summer months on a weekly basis over a period of 16 months (Wang *et al.* 1999).

Phytosterols may have been produced in during the aerobic and anaerobic incubations due to the growth of plants in the samples. This was particularly evident in the anaerobic samples (Figure 4.10). The sand was incapable of growing plants until ~5 months into the incubation period, whereas the Kawerau loamy sand and the Whakarewarewa sandy loam had prolific plant growth initiated soon after the incubation period began. Therefore, it is possible that the production of sterols was linked to the degradation of plant matter within the incubation samples.

Figure 4.10: Plants present in Anaerobic Kawerau loamy sand and Whakarewarewa sandy loam incubations.

2.4.3. Degradation Products

Previous studies have shown that biotransformation products may be formed as intermediary compounds in the degradation of resin acids (Tavendale *et al.* 1997a). The production of resin acid degradation products in this study indicated that biological degradation of resin acids had indeed occurred in all of the soils in both aerobic and anaerobic conditions (Figure 4.11. Figure 4.12). Resin acid degrading bacteria are ubiquitous in the environment including sediments and soils but may be in small numbers, which may influence the extent of degradation in soils (Tavendale *et al.* 1997a; Martin *et al.* 1999; Mohn *et al.*1999).

7-Oxodhydroabietic acid was the predominant resin acid degradation product to be produced. 7-Oxodehydroabietic acid (7-OxoDHAA) is believed to be the product of oxidation of dehydroabietic acid (DHAA) (Beillman *et al.* 1973). Recently, however, *Pseudomonas abitaniphilia* BKME-9 has been found to degrade DHAA as well as abietane resin acids producing 7-OxoDHAA as an aromatic intermediate (Martin *et al.* 1999).

The formation of 7-OxoDHAA followed by aromatic ring attack has been proposed as the most common aerobic degradation pathway (Martin *et al.* 1999), and may have been occurring in the soil incubations. *P. abietaniphilia* BKME-9 has not been isolated in soils. However, several other resin acid degrading bacteria have been isolated and identified (Table 4.8).

To date, only aerobic bacteria have been isolated from treatment environments, especially soils. They are physiological and phylogenically diverse., but resin acid specific in their degradation behaviour (Martin *et al.* 1999; Mohn *et al.* 1999).

Table 4.8: Bacteria Isolated from Soil Samples Capable of Degrading Resin Acids (Adapted from Martin *et al.* 1999).

Organism	Source	Substrate	Reference
Burkholderia sp. strain IpA-51	Forest Soil	Isopim	Mohn *et al.* 1999
Burkholderia sp. strain DhA	Forest Soil	DHAA	Mohn *et al.* 1999
Pseudomonas vancouverensis DhA-51	Forest Soil	DHAA	Mohn *et al.* 1999
Flavobacterium resinovorum	Pine Forest Soil	DHAA	Biellman *et al.* 1973 in Martin *et al.* 1999
Mycobacterium sp. strain DhA-55	Forest Soil	DHAA	Mohn *et al.* 1999

Isopim = Isopimaric Acid
DHAA = Dehydroabietic Acid

Aromatic diterpenes were also produced in this experiment as a result of degradation of resin acids. The production of aromatic diterpenes would be of concern due to their toxic nature. For example, retene, which in water borne state is toxic and may be responsible for the induction of detoxification enzymes in fish (Billiard *et al.* 1999; Brumley *et al.* 1999). The aromatic diterpene composition in the biotransformation processes included dehydroabietin, retene, tetrahydroretene and methyldehydroabietin. Aromatic diterpenes are known to be resin acid degradation products in anaerobic sediments (Tavendale *et al.* 1997a; Martin *et al.* 1999) and are probably degradation products of resin acids in soils due to their occurrence during the most rapid phase of resin acid degradation. However, in these soil systems they were not persistent.

Aromatic diterpenes bind strongly to sediments but are biologically active (Brumley *et al.* 1999). Aromatic diterpenes were produced in the early stages of degradation and degraded within the first 28 days. In anaerobic sediments aromatic diterpene production was also rapid. However, some still persisted after 264 days of anaerobic incubation (Tavendale *et al.* 1997a).

The presence of β-abietanic and abietanic acids indicate progressive saturation as a degradation pathway (Tavendale *et al.* 1997b). These compounds were not produced at any stage during the incubation period. Therefore progressive saturation does not appear to be a significant pathway used in soils for the degradation of resin acids. The production of fichtelite and dehydroabietin indicate decarboxylation, whereas tetrahydroretene and retene indicate aromatisation (Liss *et al.* 1997; Tavendale *et al.* 1997b). As these diterpenes were produced in both the aerobic and anaerobic incubations, decarboxylation and aromatisation may have occurred as soil transformation pathways for the degradation of resin acids.

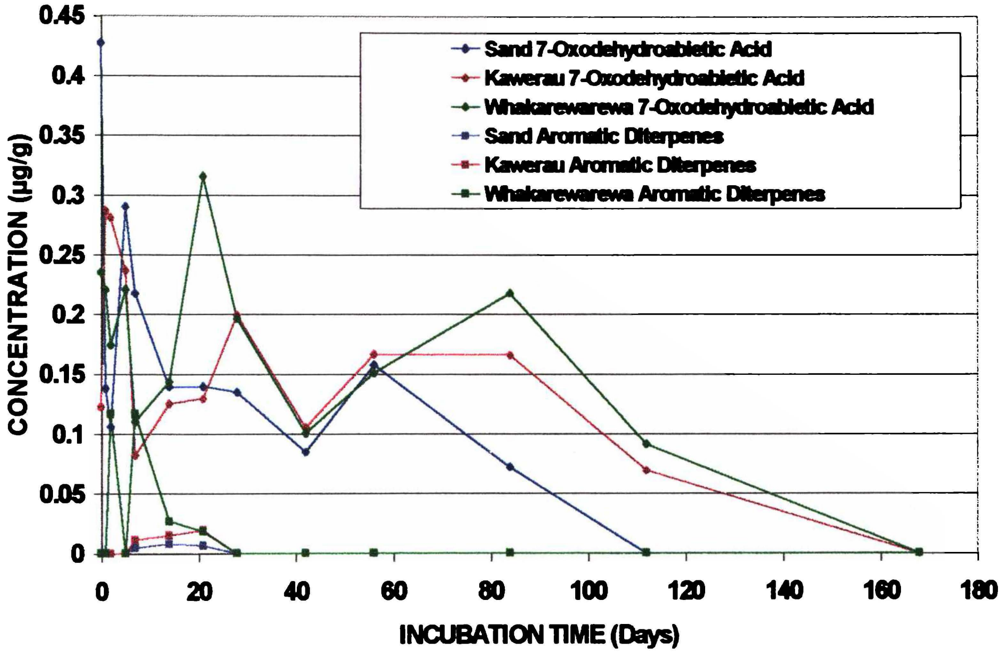

Figure 4.11: Degradation products of resin acids in aerobic soils and thermomechanical pulping effluent incubations.

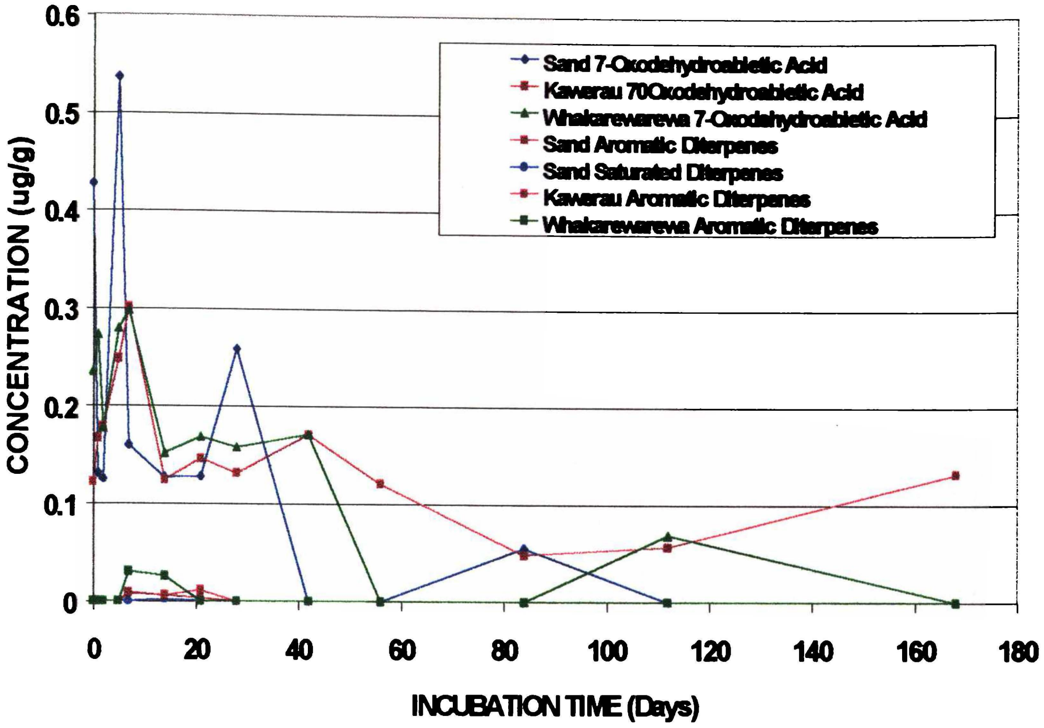

Figure 4.12: Degradation Products of resin acids in anaerobic soils and thermomechanical pulping effluent incubations.

Sitostanol was found throughout the sampling period in the Kawerau loamy sand and the Whakarewarewa sandy loam. Sitostanol production coincided with production of resin acid degradation products, between zero and 28 days. The other peak occurred between the 56 and 112 days (Figures 4.13 and 4.14).

The bacteria that are responsible for degradation of phytosterols have not been isolated from any environments as of yet. Sitostanol is a degradation product of phytosterols, although it was naturally present in the Kawerau loamy sand and the Whakarewarewa sandy loam (Appendix B:I). It was produced in the aerobic and anaerobic sands and thermomechanical pulping effluent incubations. The production of sitostanol occurred during the rapid degradation stage witnessed in the resin acids (0-28 days, including the resin acid lag period) and 56 and 112 days. The production of sitostanol was higher in the aerobic sand incubations than the anaerobic incubations.

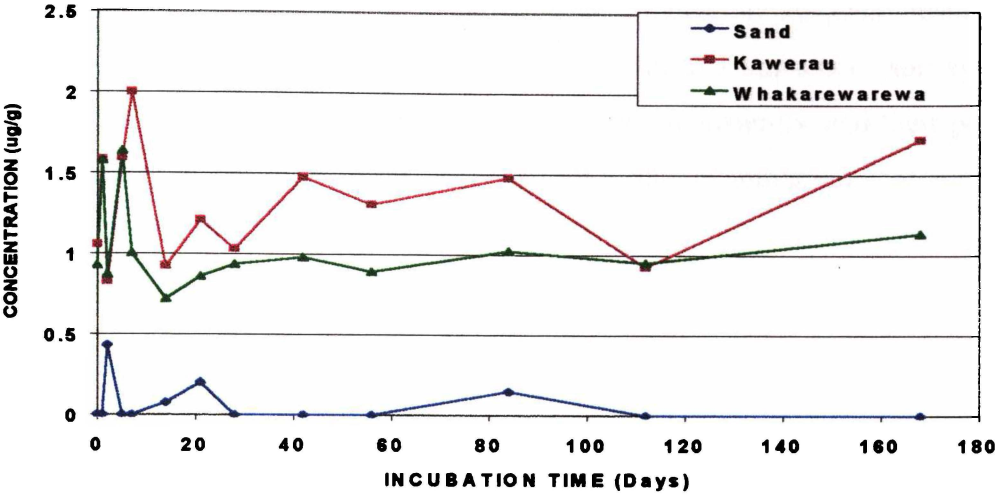

Figure 4.13: Degradation products of phytosterols in aerobic soil and thermomechanical pulping effluent incubations.

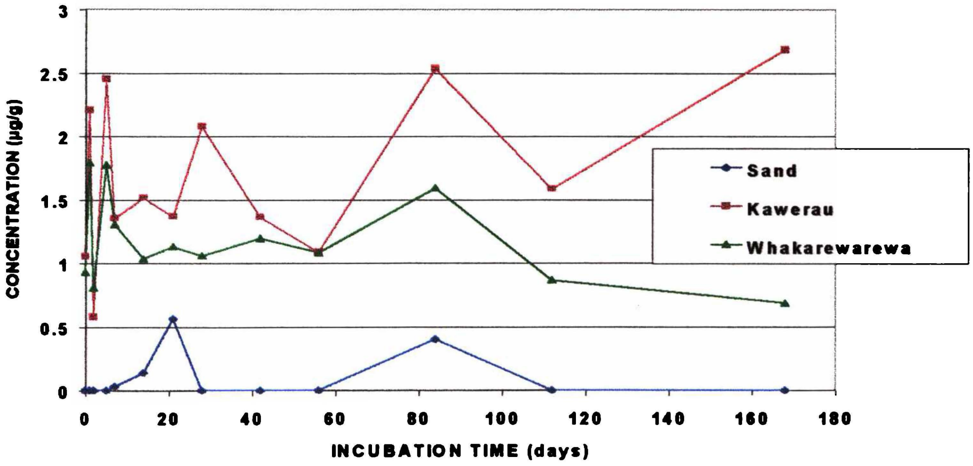

Figure 4.14: Degradation products of phytosterols in anaerobic soil and thermomechanical pulping effluent incubations

4.6 Summary

Overall, it is clear that resin acids can be readily degraded in the soil environment under both aerobic and anaerobic conditions. In general, these studies have shown that, with properly maintained land application systems, resin acids should not be a limiting factor in the management and impacts of soil systems. The apparent inability of soil systems to remove phytosterols, and their possible endocrine/reproduction impacts, may warrant further examination.

SORPTION BEHAVIOUR OF THERMOMECHANICAL EXTRACTIVES IN SOIL ENVIRONMENTS

5.0 SORPTION BEHAVIOUR OF THERMOMECHANICAL EXTRACTIVES IN SOIL ENVIRONMENTS

The batch equilibrium experiments consisted of five concentrations of three soils (sand, Kawerau loamy sand, and Whakarewarewa sandy loam) equilibrated with thermomechanical effluents. The supernatants were analysed for resin acids, total carbon, total organic carbon, chemical oxygen demand, and colour concentration to calculate adsorption and desorption isotherms.

The concentration isotherms were calculated using the protocols outlined in Chapter 3.6.2. Adsorption was depicted by lines above zero, and desorption was depicted by lines below zero.

5.1 Resin Acids

Organic compounds are thought to bind strongly to solid surfaces, in particular soils (Calvet 1989; Weber and Miller 1989). This would therefore effect the bioavailability of compounds such as resin acids.

Mixing of the TMP effluent with the soils, caused a significant decrease in resin acid concentrations for all soil types (Figure 5.1).

The interaction with the soil matrix was permanent as changes in soil concentrations did not occur during the desorption phase (Figure 5.2).

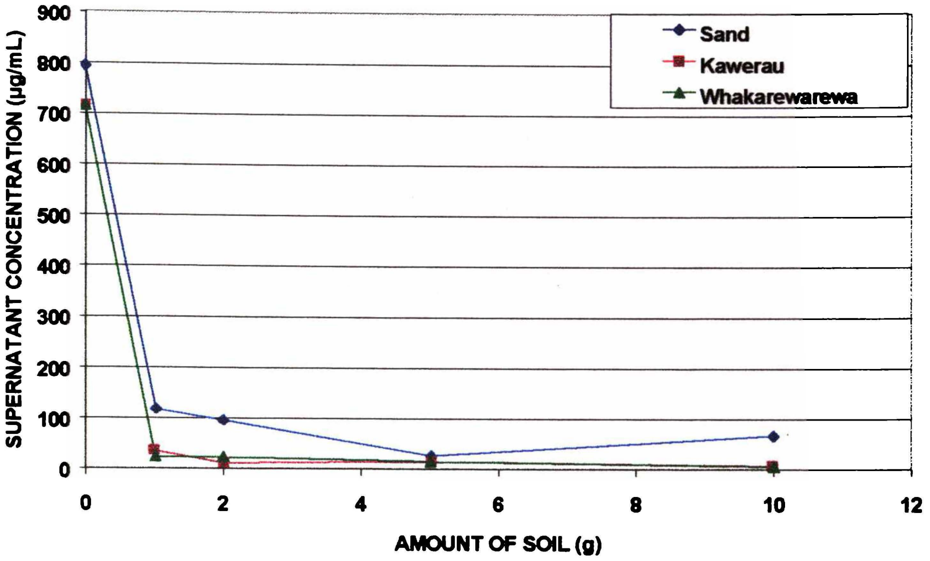

Figure 5.1: Supernatant concentration of resin acids in the adsorption phase of soil and thermomechanical effluent interaction.

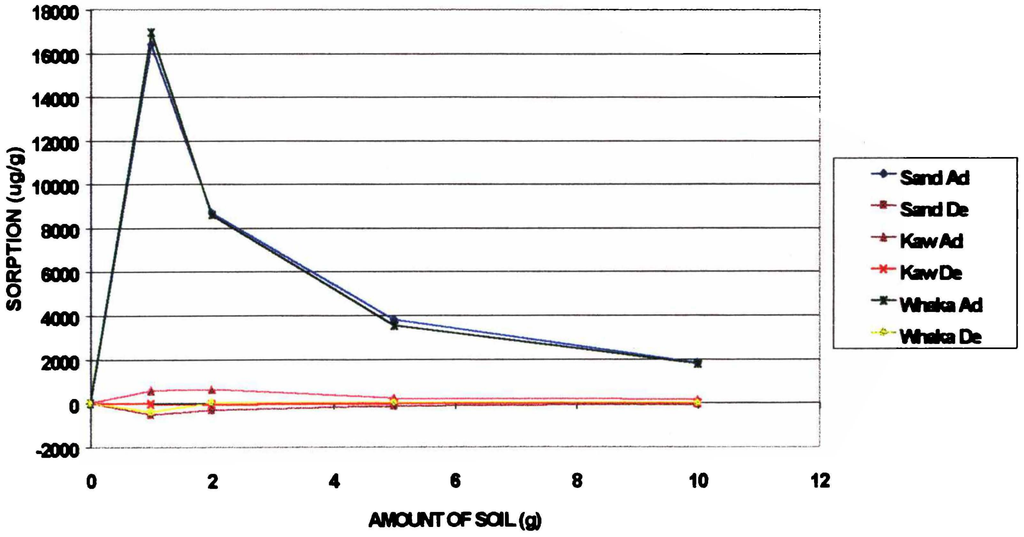

Figure 5.2: Adsorption and desorption resin acid concentration isotherms for soils and thermomechanical pulping effluent.

The resin acid adsorption and desorption isotherms exhibited classical Freundlich behaviour (Figure 5.2, Fig, 5.3, Table 5.1).

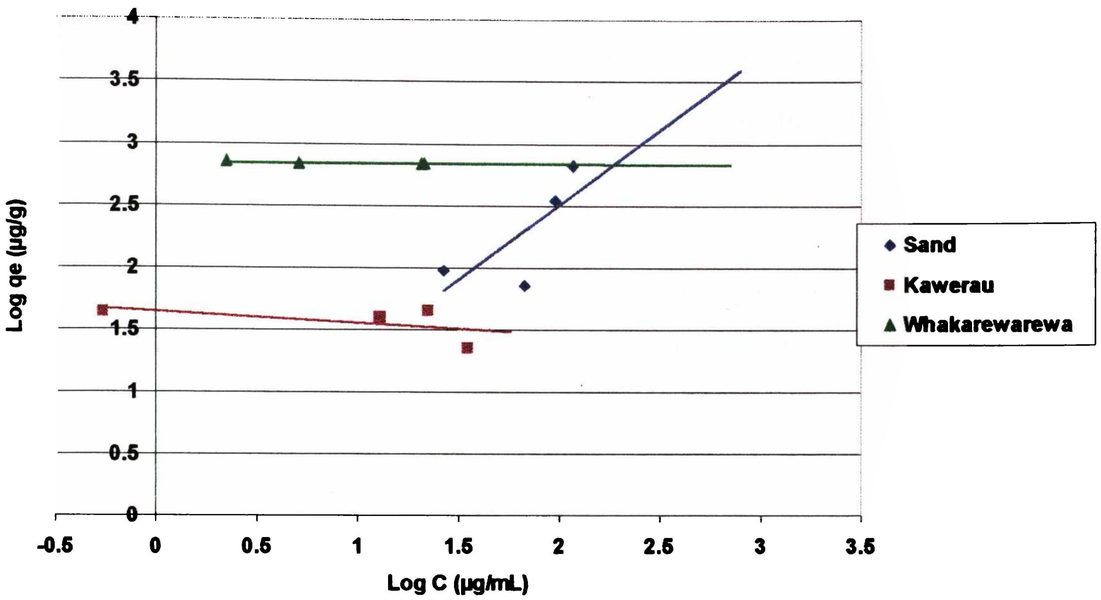

Figure 5.3: Freundlich isotherms for resin acids in soil and thermomechanical pulping effluent.

Table 5.1: Freundlich isotherm factors for resin acids from thermomechanical pulping effluent adsorption in soils

Soil	K_f	1/n
Sand	0.15	-0.32
Kawerau	1.65	0.1
Whakarewarewa	2.85	0

K_f was an indicator of adsorption capacity. The higher K_f, the higher the capacity. The Whakarewarewa soil had the highest capacity and the beach sand had the lowest capacity for resin acid adsorption. This was consistent with the relative organic carbon loadings of the soil matrices and would indicate that organic carbon concentrations have a significant influence on the partitioning behaviour of behaviour of the lipophilic resin acids in soil matrices. 1/n indicted the adsorption intensity, which appeared to correlate with the adsorption capacity of the soils. In this fashion, the higher carbon concentration of the Whakarewarewa soils also lead to the greatest amount of binding. The batch equilibrium experiment confirmed that the lag period was probably the result of sorption interactions. The apparent drop in "extractable" trace organics during the first adsorption/desorption phase of the extractable organics degradation experiment appears to be a result of this mechanism.

Sorption has the potential to affect the bioavailability of organic compounds in soils (Scow *et al.* 1995). Sorption of organic compounds onto soils can either increase or decrease biodegradation rates (Calvet 1989). Scow *et al.* (1995) found that sorption decreased bioavailability of organic compounds. This is quite possible in the soils used for the degradation experiment due to large irreversible sorption that was noted within the batch equilibrium experiments.

Desorption isotherms usually show a high retention of lipophilic organic compounds in soils (Koiskinen *et al.* 1970). Desorption controls the amount of compound that is in solution for microbial uptake (Wszolek and Alexander 1979; Subba-Rao and Alexander 1982; Pavlostathis and Jaglal 1991; Harkness *et al.* 1993; Hatzinger and Alexander 1996). Often the rates of desorption from a solid influences the rate of microbial degradation (Connaughton *et al.* 1995; Schlebaum *et al.* 1999). Degradation of compounds in solution by organisms can generate a concentration gradient, which leads to desorption of organic compounds in response to the gradient (van Leeuwen *et al.* 1996). Competitive sorption between organic pollutants and soil humic acids may lead to increased bioavailability of toxic organic compounds (Xing and Pignatello 1998).

A small but measurable incomplete degradation of resin acids often occurred in soils under both aerobic and anaerobic conditions and may have been a function the extent of irreversible sorption. As time of contact between organic compounds and soils increases the difficulty of extraction of these compounds (Scow *et al.* 1995). This may indicate that, with increasing incubation time, the compounds became less bioavailable for degradation by microorganisms, which may be influenced by the large degree of irreversible sorption that occurred in the soils used for the incubation experiment.

5.2 Total Carbon and Total Organic Carbon, Chemical Oxygen Demand and Colour

The levels of organic carbon desorption caused by simple washing mechanisms in the presence of a water media may have an influence upon the adsorption and desorption behaviour of the resin acids present in the TMP effluents.

Adsorption isotherms were prepared for the water/soil system to determine how much mobile carbon (hence aqueous phase adsorption media) was associated with each soil type (Figure 5.4).

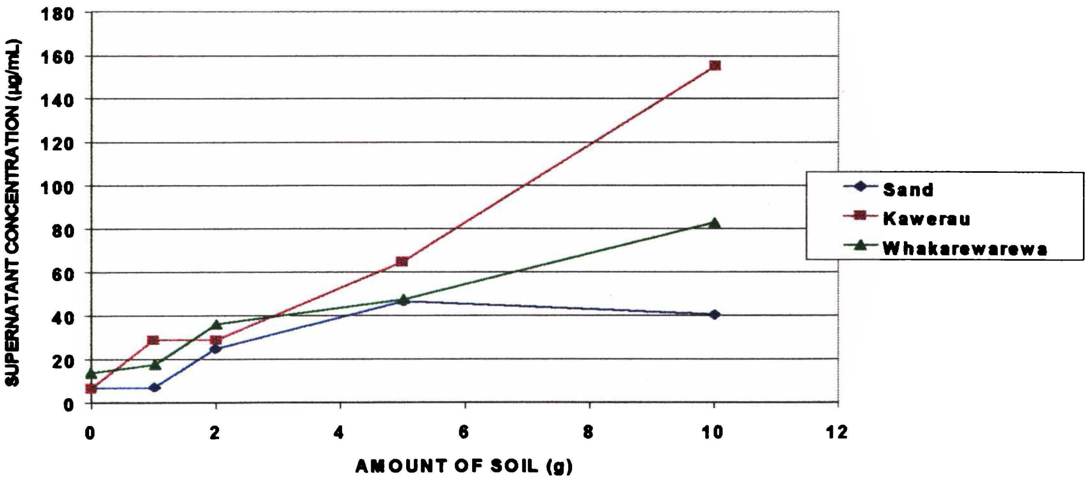

Figure 5.4: Adsorption phase total carbon concentration for water and soils.

The water shaker results indicated that with increasing soil concentration there was a corresponding increase in supernatant concentration which exhibits an approximately linear relationship.

The total carbon adsorption isotherm was represented by TC Ad and the total carbon desorption isotherm was represented by TC De. The total organic carbon isotherm was represented by TOC Ad, and the total organic carbon desorption isotherm was represented by TOC De on the graphs for the total carbon and total organic carbon concentration isotherms.

The sand, although low in organic carbon, showed adsorption interactions during the adsorption phase and desorption interactions during the desorption phase when mixed with the thermomechanical pulping effluent (Figure 5.5). Both the adsorption and desorption ratios decreased with increasing soil amount. The carbon adsorption behaviour was reversible as evidenced by the desorption isotherms (Figure 5.5).

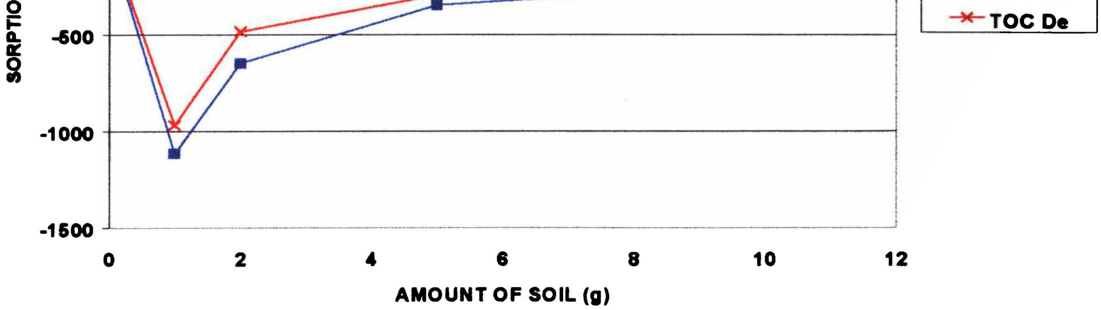

Figure 5.5: Adsorption and desorption total carbon and total organic carbon concentration isotherms for sand and thermomechanical pulping effluent.

The total carbon isotherm appears to have lower adsorption than the total organic carbon isotherm. This was due to the release of inorganic carbon from the sand, possibly as a result of mineralisation or carbonate release, which decreased the concentration of organic carbon in the supernatant (Figure 5.5).

Carbon was released during the adsorption and desorption phases of the batch equilibrium experiment for the Kawerau loamy sand and TMP (Figure 5.6). In general, the concentration of carbon in the supernatants decreased with increasing soil content indicating classical adsorption behaviour (Figure 5.6).

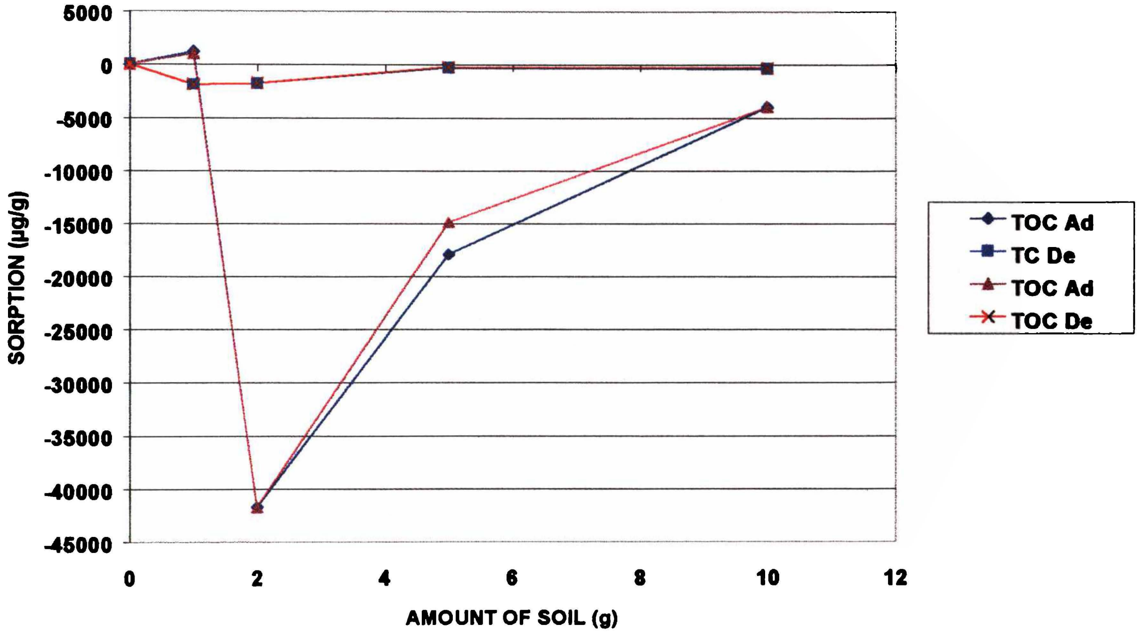

Figure 5.6: Adsorption and desorption total carbon and total organic carbon concentration isotherms for Kawerau loamy sand and thermomechanical pulping effluent

Similarly, adsorption occurred during the adsorption phase and desorption of the Whakarewarewa sandy loam and TMP batch equilibrium experiment (Figure 5.7). The carbon that was sorbed was released during the desorption phase, indicating that it was highly mobile.

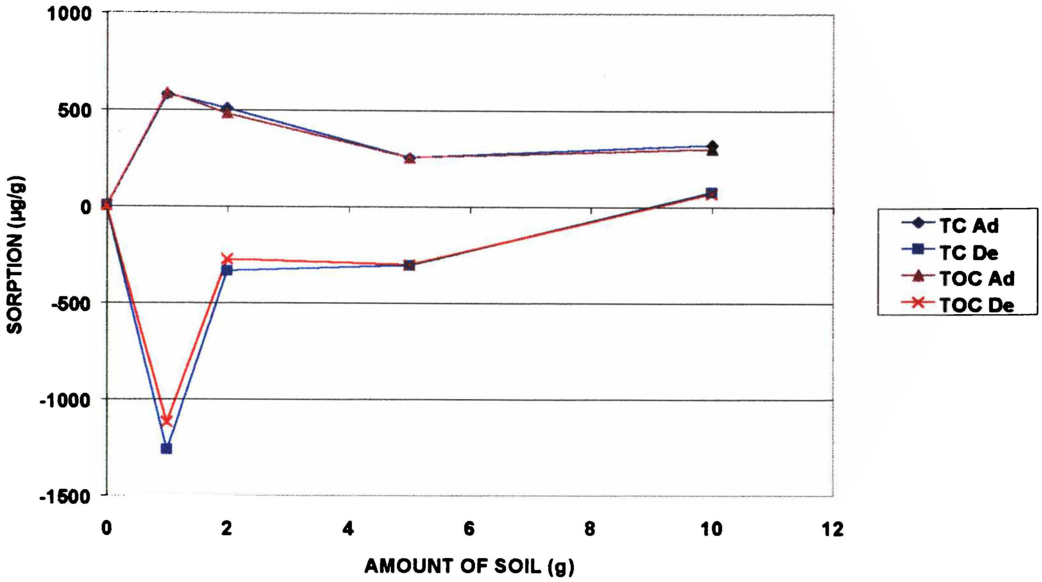

Figure 5.7: Adsorption and desorption total carbon and total organic carbon concentration isotherms for Whakarewarewa sandy loam and thermomechanical pulping effluent.

Many soil studies have correlated carbon content with the behaviour of lipophilic compounds such as resin acids (Calvet 1989). Carbon content did not appear to affect the sorption of resin acids, which was reflected particularly in the thermomechanical pulping effluent and soil batch equilibrium studies where the Whakarewarewa sandy loam and the beach sand had similar extents of irreversible sorption. The sand contained a small amount of carbon in comparison with the Whakarewarewa sandy loam. This may indicate that the principal means of resin acid removal was filtration of colloidal material associated with resin acids rather than a true adsorption process.

Chemical oxygen demand (COD) was released during the adsorption and desorption phases from all soils upon interaction with TMP (Figure 5.8). The sand released large amounts of organic matter as did the Kawerau loamy sand (Figure 5.8).

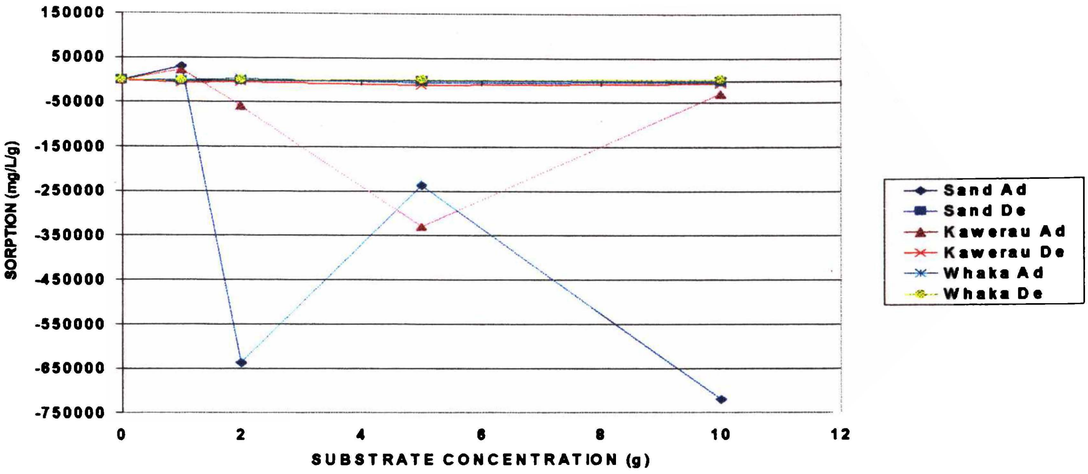

Figure 5.8: Adsorption and desorption chemical oxygen demand isotherms for soils and thermomechanical pulping effluent.

The Whakarewarewa sandy loam adsorption phase isotherm generally showed that there was a decrease in carbon release with increasing soil amount (Figure 5.8). Desorption also generally decreased with increasing soil amount (Figure 5.8).

Colour was adsorbed during the sorption phase and desorbed during the desorption phase when soils interacted with TMP (Figure 5.9). Adsorption and desorption decreased with increasing soil amount (Figure 5.10). The adsorption and desorption of colour may also correlate to the filtration effect that was noted in the resin acid concentrations.

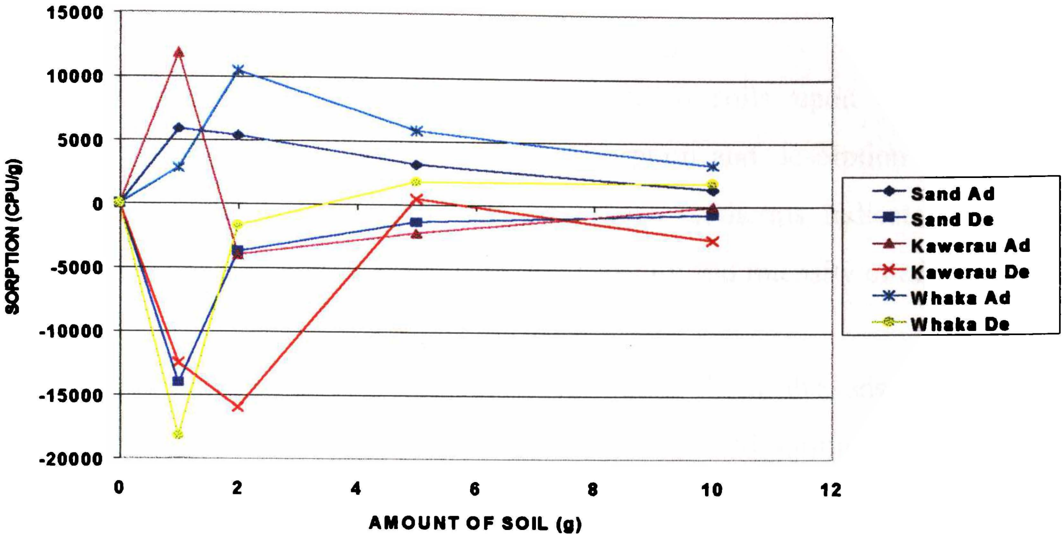

Figure 5.9: Adsorption and desorption chemical oxygen demand concentration isotherms for soils and thermomechanical pulping effluent: a closer look.

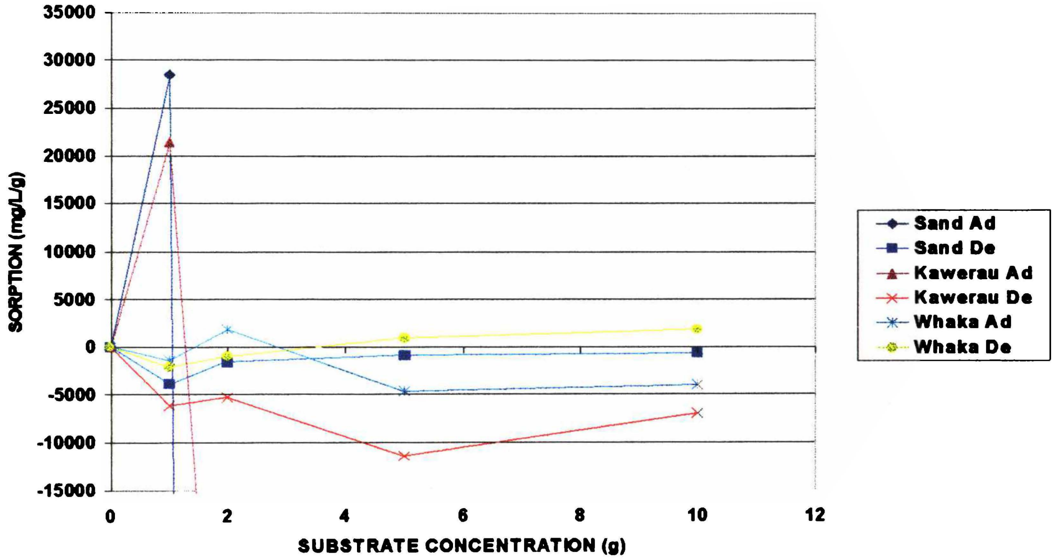

Figure 5.10: Adsorption and desorption colour concentration isotherms for soils and thermomechanical pulping effluent.

5.3 Summary

Resin acids were bound rapidly and strongly to soils upon mixing with thermomechanical pulping effluent. The adsorption and desorption isotherms exhibited irreversible adsorption. The Freundlich isotherms indicate that the Whakarewarewa sandy loam had the highest capacity and intensity of adsorption.

Carbon and organic matter were released during both the adsorption and desorption phase of the experiments. Colour was adsorbed during the adsorption phase and desorbed during the desorption phase. The Whakarewarewa sandy loam exhibited a large release of colour during the desorption phase. Adsorbed colour was not held permanently and was released during the desorption phase. Colour adsorption and desorption decreased with increasing soil amount.

Generally, it would appear that the relative degree to which adsorption of resin acids occurred in the selected soil matrices was dependent upon the soil organic matter concentration. Where highly mobile organic carbon material was present in the soil, then aqueous:solid phase competition for adsorption capacity may influence the overall mobility of these compounds.

SOIL DEGRADATION AND SORPTIVE BEHAVIOUR OF RESIN ACIDS AND PHYTOSTEROLS FROM OTHER PULP AND PAPER EFFLUENTS

6.0 SOIL DEGRADATION AND SORPTIVE BEHAVIOUR OF RESIN ACIDS AND PHYTOSTEROLS FROM OTHER PULP AND PAPER EFFLUENTS

6.1 Degradation of Resin Acids and Phytosterols

A representative effluent from each main pulping process in New Zealand was chosen for the multi-effluent degradation experiment. Chemithermomechanical and bleach kraft mill effluents were used as well as the thermomechanical effluent which was the focus of the main section of this thesis. Milli-q water was used as a control effluent. This section compares the results obtained with TMP with those found for chemithermomechanical pulping and bleached kraft effluent during incubation with soils.

Because of the significant differences in extractives content for each effluent type, the total percentage change has been calculated. The total percentage is the percentage of change that occurred at day 168 with respect to day zero and was calculated using Equation Seven.

$$\text{Change (\%)} = \left[\frac{C_e - C_0}{C_0}\right] \times 100 \qquad \textit{Equation Seven}$$

Where C_e = compound concentration at day 168 ($ug.g^{-1}$(dw))

C_0 = compound concentration at day 0 ($ug.g^{-1}$ (dw))

The degradation characteristics of chemithermomechanical pulping effluent (CTMP) and bleached kraft effluent were similar to those that occurred in the degradation of thermomechanical pulping effluent. Most of the resin acids were degraded under both aerobic and anaerobic conditions. Under both aerobic and anaerobic conditions the sand had consistently the highest removals of resin acids and phytosterols. As noted in chapter 4, this may be attributed to the lack of an alternative carbon source for the microbial population found in the effluents.

The chemithermomechanical pulping effluent (CTMP) incubations showed that nearly all of the compounds added prior to incubation were removed at day 168. However, no significant removal of these constituents was observed in aerobic Kawerau loamy sands (Figure 6.1). Indeed, when compared to the TMP results, it appears that the Kawerau soils were less able to remove these compounds.

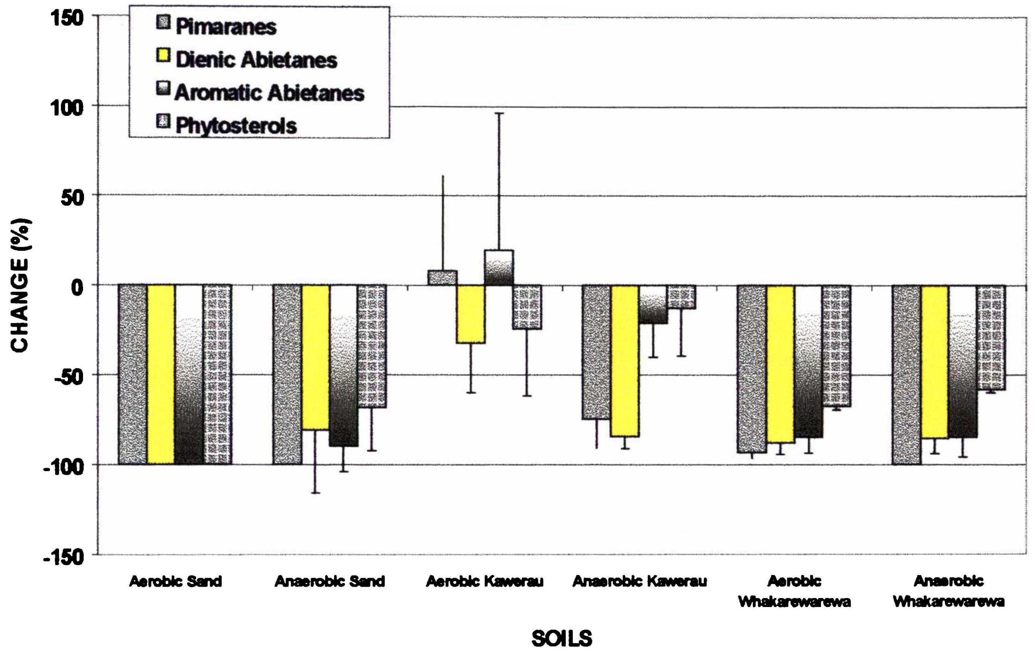

Figure 6.1: Percentage change of resin acid and phytosterol concentrations in aerobic and anaerobic soil and chemithermomechanical pulping effluent incubations.

Bleached kraft effluent incubations also saw the complete removal of most compound classes. However the anaerobic Kawerau loamy sand showed no significant degradation of all groups of resin acids and phytosterols. Phytosterols were also produced in aerobic Kawerau loamy sand and aerobic and anaerobic

Whakarewarewa sandy loam soils (Figure 6.2). The anaerobic Whakarewarewa sandy loam also had minimal removals of pimaranes and sterols (Figure 6.2).

It therefore appears that some effluent components present in CTMP and BKM effluents may impact on the relative degradability of these constituents relative to that observed in the TMP experiments. The relatively high levels of dissolved organic carbon, a result of the delignification processes in these mills, or the high salt/sodium concentrations may be factors to be considered in future studies.

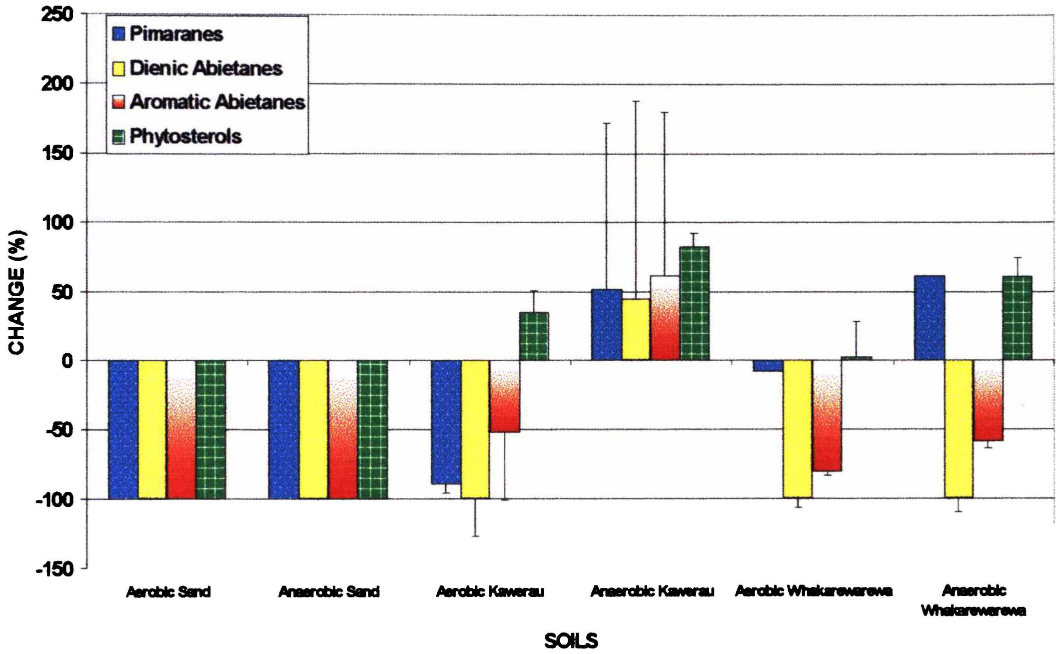

Figure 6.2: Percentage change in resin acid and phytosterol concentration in soil and bleached kraft effluent incubations.

6.2 Sorptive Behaviour of Resin Acids in Soils

6.2.1 Chemithermomechanical Pulping Effluent

Comparable sorption behaviour of resin acids occurred during the adsorption phase and desorption phases upon mixing of soils with chemithermomechanical effluent (Figure 6.3). The sand and the Whakarewarewa sandy loam showed large degrees of sorption. Compounds that were adsorbed were not completely desorbed in all soils. Irreversible adsorption had occurred in all soils, particularly in the sand and the Whakarewarewa sandy loam (Figure 6.3).

Carbon was released during the adsorption and desorption phases of the beach sand isotherms with chemithermomechanical pulping effluent (Figure 6.4). The supernatant carbon concentration decreased with increasing soil amount for both the adsorption and desorption phases (Figure 6.4). Release of carbon occurred in the adsorption and desorption phases upon interaction of Kawerau loamy sand and chemithermomechanical pulping effluent (Figure 6.5).

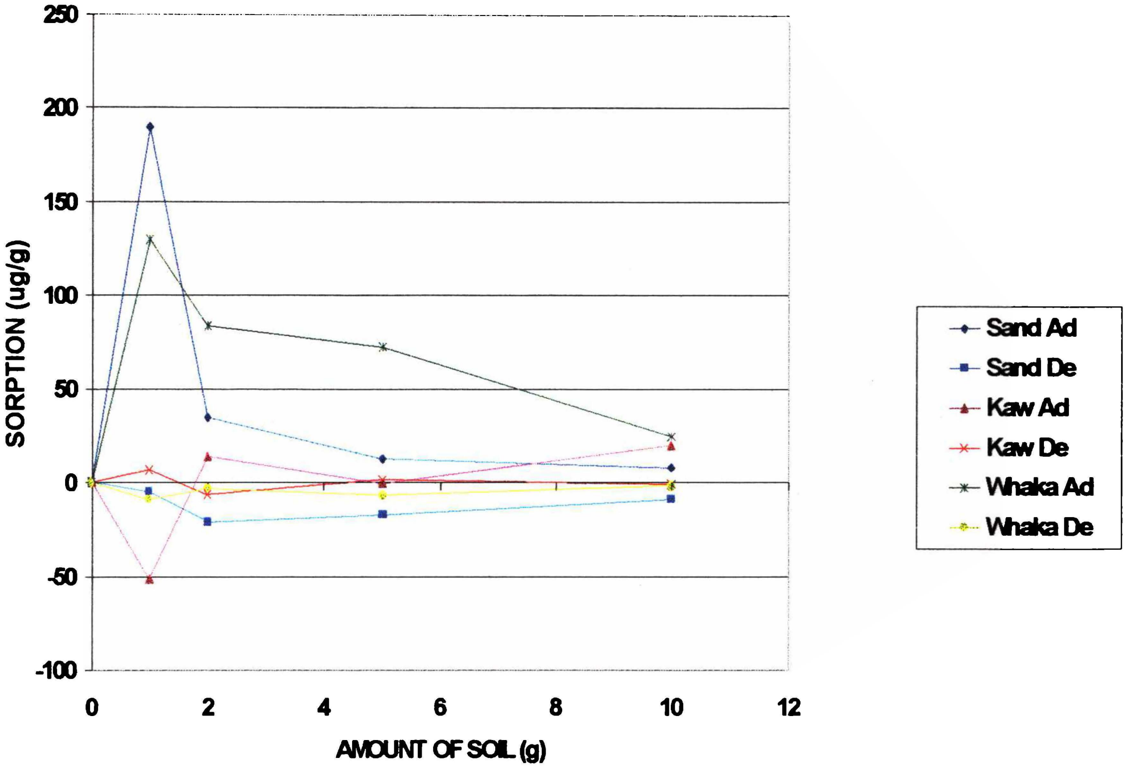

Figure 6.3: Adsorption and desorption resin acid concentration isotherms for soils and chemithermomechanical pulping effluent

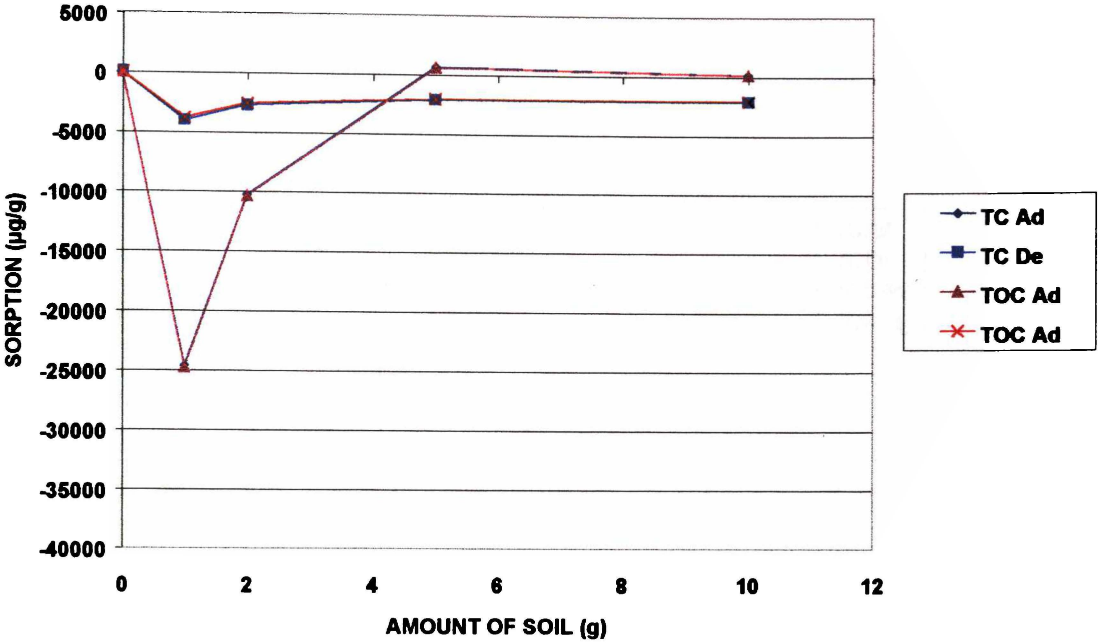

Figure 6.4: Adsorption and desorption total carbon and total organic carbon concentration isotherms for sand and chemithermomechanical pulping effluent.

Carbon was also released during the adsorption and desorption phase of the Whakarewarewa sandy loam interaction period with CTMP (Figure 6.5). The adsorption isotherm shows that the supernatant concentration of carbon increased until 5 grams of soil and then decreased at 10 grams (Figure 6.5).

Colour was also released during both the adsorption and desorption phases of all soils upon interaction with CTMP (Figure 6.7).

Overall, these results would indicate that organic matter was released during interactions with chemithermomechanical pulping effluent (CTMP) by all soils (Figure 6.8).

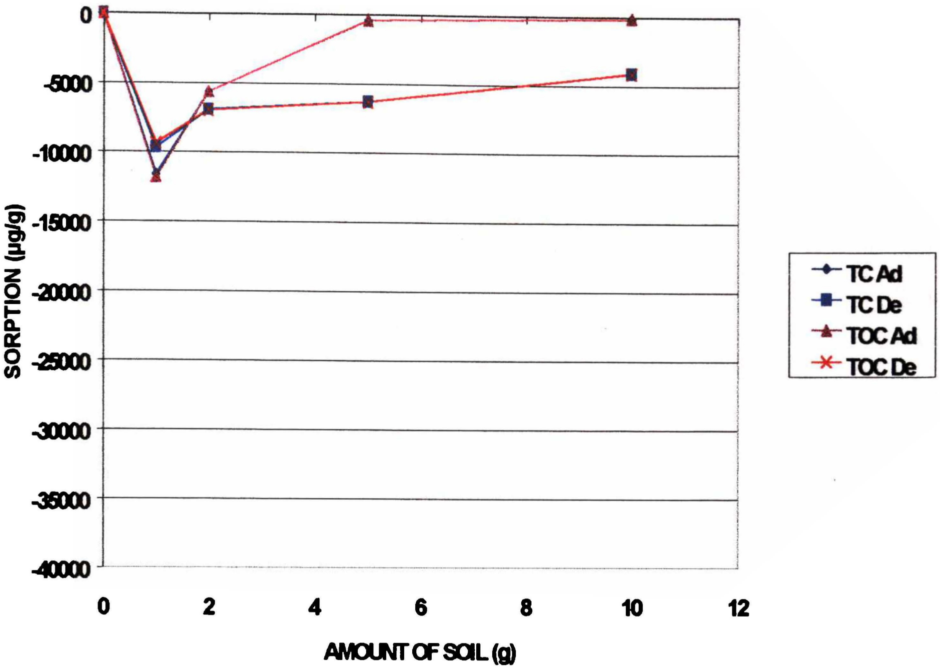

Figure 6.5: Adsorption and desorption total carbon and total organic carbon concentration isotherms for Kawerau loamy sand and chemithermomechanical pulping effluent

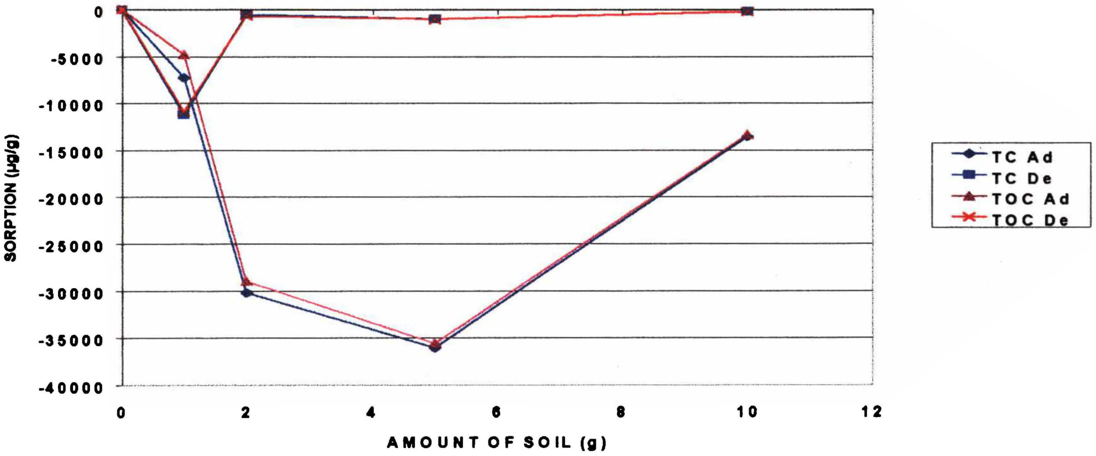

Figure 6.6: Adsorption and desorption total carbon and total organic carbon concentration isotherms for Whakarewarewa sandy loam and chemithermomechanical pulping effluent.

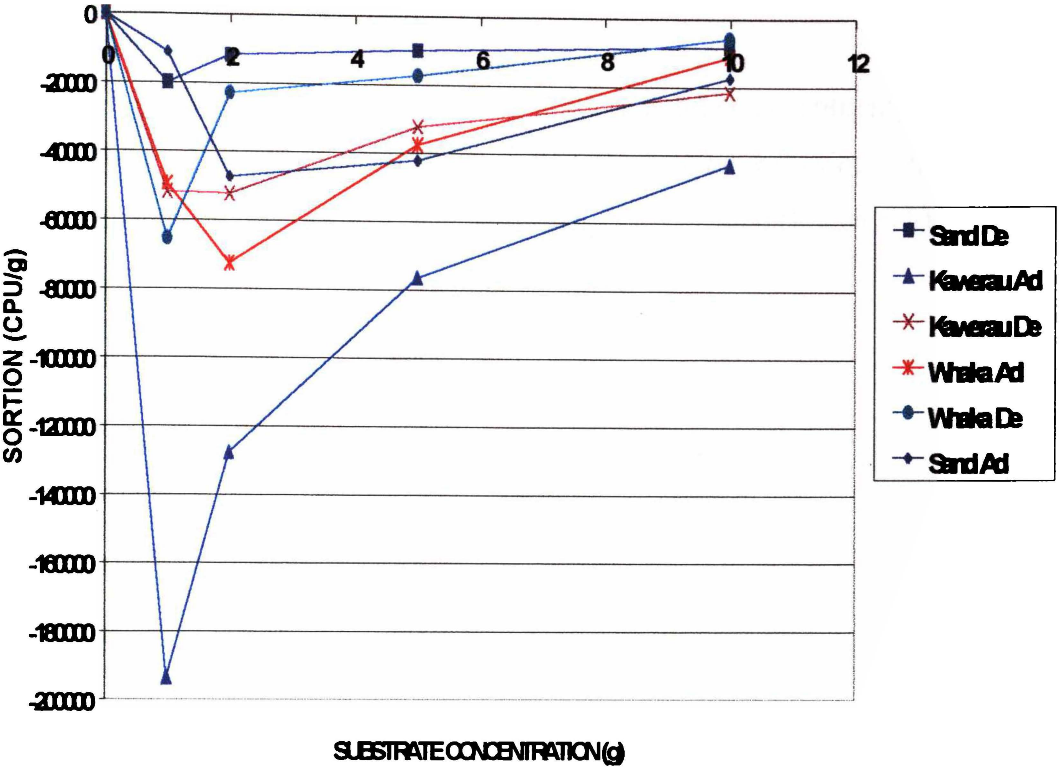

Figure 6.7: Adsorption and desorption colour concentration isotherms for soils and chemithermomechanical pulping effluent.

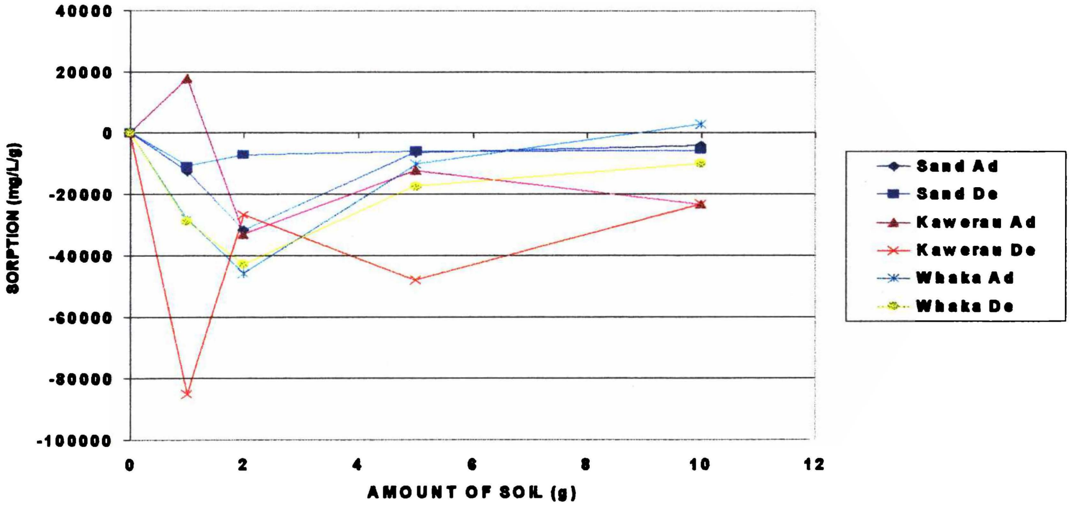

Figure 6.8: Adsorption and desorption chemical oxygen demand concentration isotherms for soils and chemithermomechanical pulping effluent.

6.2.2 Bleached Kraft Effluent

The very low concentrations of resin acids and other constituents in Bleached kraft mill effluents made an assessment of sorption behaviour difficult. The Kawerau loamy sand had the most adsorption of resin acid (Figure 6.9).

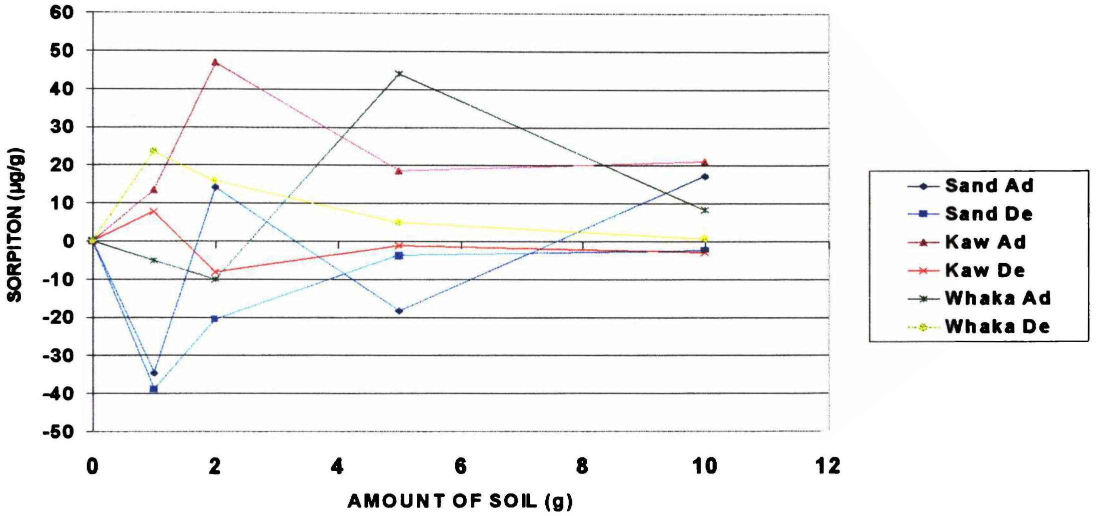

Figure 6.9: Adsorption and desorption resin acid concentration isotherms for soils and bleached kraft effluents.

The beach sand released carbon upon interaction with bleached kraft effluent, during both the adsorption and desorption phases (Figure 6.10). In general the amount of carbon released during both phases increased with increasing soil amount (Figure 6.10). this may have been a result of the high cation content of the effluent.

Incomplete desorption was found for the Kawerau soils where some of the adsorbed carbon was not released during the desorption phase (Figure 6.11).

However, general the amount of sorption decreased with increased soil amount (Figure 6.11).

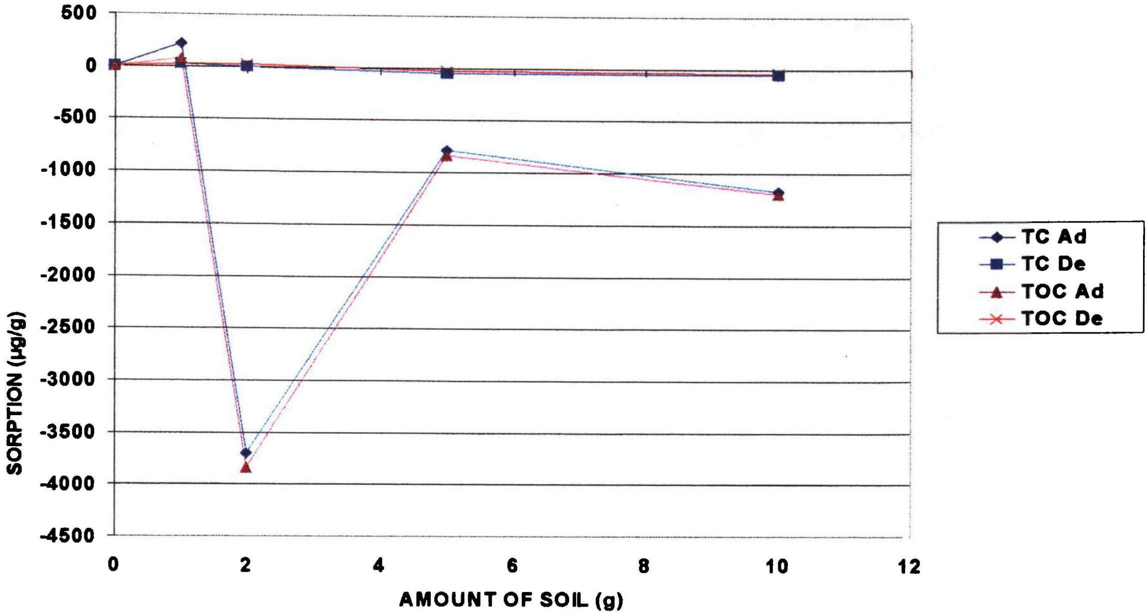

Figure 6.10: Adsorption and desorption total carbon and total organic carbon concentration isotherms for sand and bleached kraft effluent.

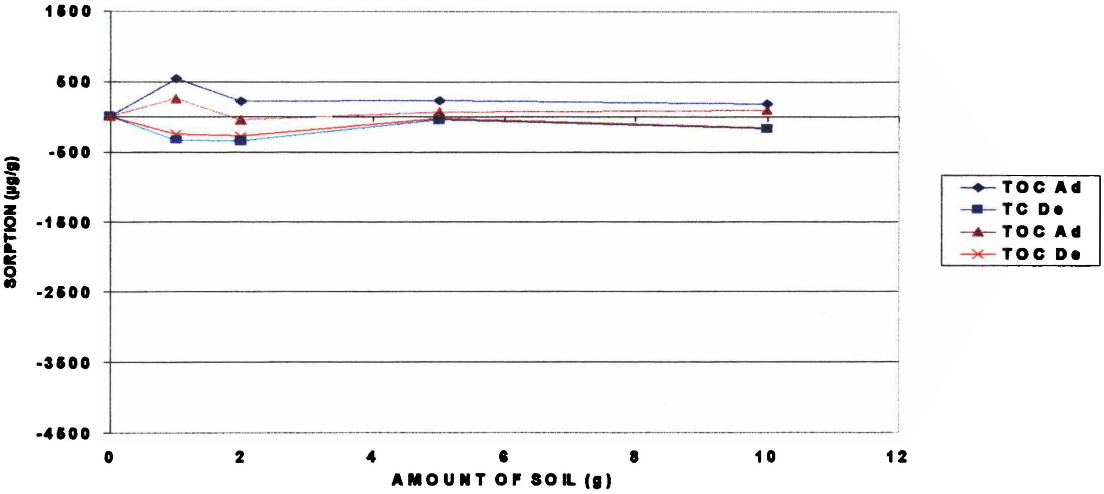

Figure 6.11: Adsorption and desorption total carbon and total organic carbon concentration isotherms in Kawerau loamy sand and bleached kraft effluent.

Release of carbon occurred in both the adsorption and desorption phase of the Whakarewarewa sandy loam and bleached kraft effluent interaction. The concentration of carbon in the supernatant of the adsorption samples decreased between 1 and 2 grams of soil then increased for 5 and 10 grams of soil, presumably as a result of the predominance of soil-sourced material at this point (Figure 6.12). Desorption decreased slightly with increasing soil concentration (Figure 6.12).

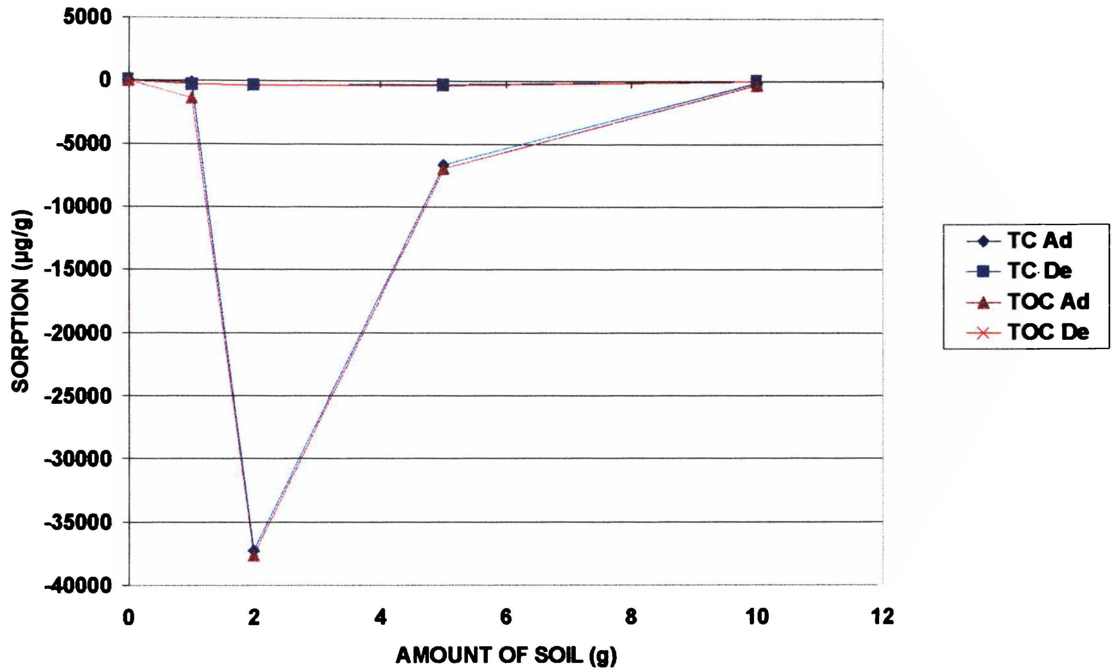

Figure 6.12: Adsorption and desorption total carbon and total organic carbon concentration isotherms for Whakarewarewa sandy loam and bleached kraft effluent.

Organic matter was released during the adsorption and desorption phase from all soils upon interaction with bleached kraft effluent (Figure 6.13). The adsorption phase isotherms generally indicate a decrease in supernatant organic matter concentration with increasing soil amount (Figure 6.13).

A release of colour occurred in both the adsorption and desorption phases of the interaction between soils and bleached kraft effluent (Figure 6.14). In general the supernatant colour concentration decreased with increasing soil concentration (Figure 6.14).

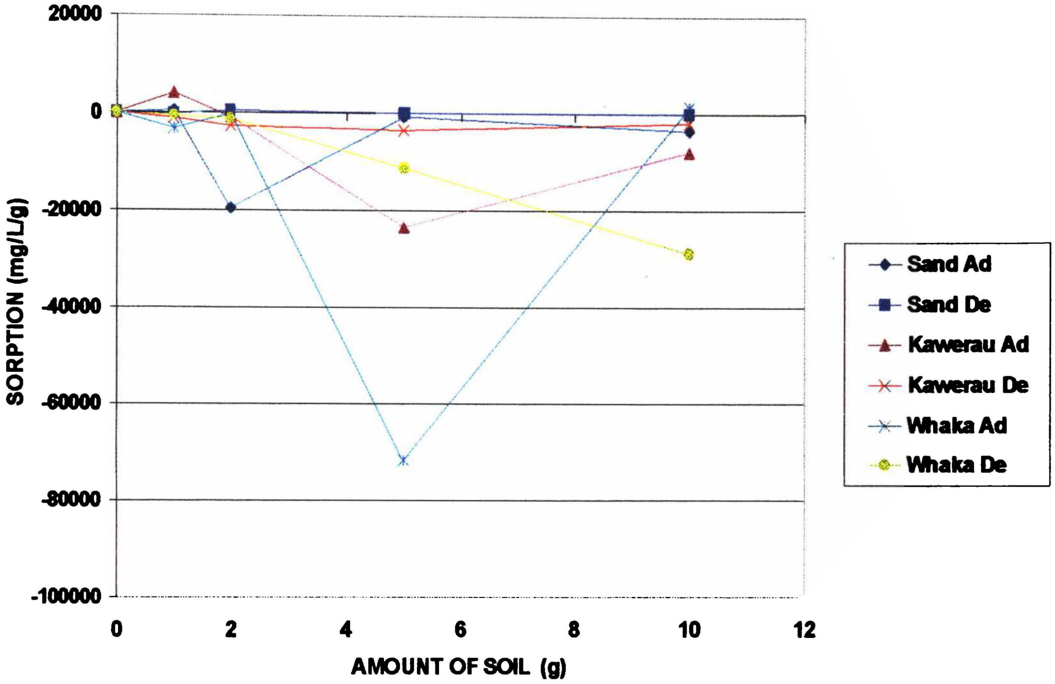

Figure 6.13: Adsorption and desorption chemical oxygen demand concentration isotherms for soils and bleached kraft effluent.

6.3 Summary

The soil and CTMP and bleached kraft effluents incubations indicated that, like the TMP incubations, most of the resin acids and phytsterols were broken down to a considerable extent at 168 of incubation. There were, however, exceptions to the trend. The anaerobic Kawerau loamy sand showed that there little removal of resin acids and phytosterols. Phytosterols were also not removed from aerobic Kawerau loamy sand and aerobic and anaerobic Whakarewarewa sandy loam soils.

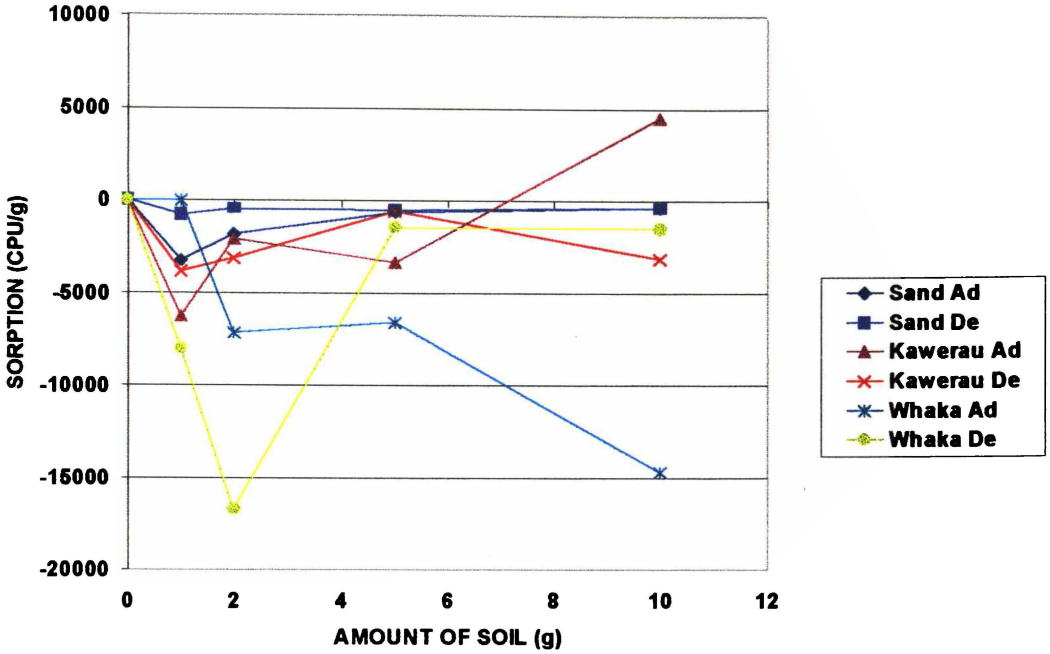

Figure 6.14: Adsorption and desorption colour concentration isotherms for soils and bleached kraft effluent.

The adsorption and desorption isotherms for CTMP and bleached kraft showed similar patterns to those that occurred in the TMP effluent. Total carbon, total organic carbon, chemical oxygen demand and colour did not adequately describe the behaviour of resin acid adsorption. It therefore appears that polarity and lipophilicity have a significant impact on the degradation and adsorption behaviour of organic effluent constituents.

CONCLUSIONS

7.0 CONCLUSIONS

7.1 Introduction

The land application of pulp and paper effluents has the potential to be a long-term sustainable solution for the requirements of industry and regulatory control of environmental impacts. A critical aspect of its success will be that the soil matrix onto which the effluents are applied is able to assimilate and remove effluent organic constituents of environmental concern. Two important processes are required for this. Firstly, the soils need to rapidly attenuate the movement of these materials through the soil column to ensure that groundwater and surface water contamination is minimised. Secondly, the accumulated constituents need to be mineralised/degraded to ensure the capacity of the soil is not exceeded with repeated effluent applications.

This study has aimed to provide fundamental information relevant to the above issues. Its focus has been on two classes of compounds, the resin acids and phytosterols, which are of particular concern with respect to their potential toxicity and persistance in the receiving environment. A range of potential land application soil types, sand (modeling rapid infiltration applications), Kawerau soil (low organic loamy sand from a site already being considered for pulp and paper effluent land application), and Whakarewarewa soil (high organic sandy loam from a site being used for municipal sewage land application) were selected for the study to ensure a broad assessment of likely land application recipients.

Thermomechanical pulping effluent was the principal focus of the project. This effluent is the most suitable type for land application due to its relatively low sodium content. It also contains very high levels of resin acids and phytosterols and therefore is perhaps the most challenging effluent type for land application performance with respect to these compounds. Given the potential for effluents from other pulp and paper processes to be land applied to some degree, two other wastestreams, chemi-thermomechanical and bleached kraft effluents, were also considered in a more limited fashion.

7.2 Degradation Processes

Soil/effluent incubation experiments were undertaken to determine the ability of the system to degrade resin acid and phytosterol consitutents under aerobic and anaerobic conditions. From these studies it can be concluded that:

- Resin acids were readily degradable in the selected soils. In most cases nearly 100% removal was obtained within 6 months incubation. Half lives for these compounds were typically 0.5-45 days and there were no significant lag periods before degradation occurred.
- The sand substrate was particularly effective in removing the compounds. It is hypothesised that this may be due to the lack of alternative carbon sources in the sand matrix. The lack of lag time and the observed removals in the sand also indicate that effluent-derived acclimated microbiota may be the principal degraders responsible for resin acid degradation. Overall, soil type did not appear to significantly influence resin acid degradation behaviour.
- Resin acids could be degraded under both aerobic and anaerobic conditions in the soils. Thus, land application systems may be able to sustain resin acid removal performance even if anaerobic conditions are produced in the soils as a result of high rainfall/water table increases or over-irrigation.
- Abietane resin acids were slightly more persistent than pimarane resin acids in soils. This may have been principally due to the significantly greater concentration of abietanes in the TMP effluents. No significant levels of resin acid biotransformation products were found in the incubated soils indicating that complete biodegradation/mineralisation occurred.
- The organic soils contained relatively high concentrations of naturally-occurring phytosterols which made an assessment of effluent degradation

more difficult. Concentrations of phytosterols did not decrease significantly during both aerobic and anaerobic incubations. This may indicate either that these compounds are relatively persistent or that there was phytosterol production in the soils.

- Degradation behaviour for the other effluents (CTMP, BKME) was comparable to that observed for TMP suggesting that the effluent matrix will not limit the ability of soils to assimilate effluent constituents of this type. Of course, other factors, such as high sodium and dissolved organic carbon, may constrain the sustainability of land application in these cases.

7.3 Sorption Processes

Soil/effluent adsorption/desorption studies were undertaken to determine the ability of the soils to accumulate and immobilise resin acid constituents. From these experiments it can be concluded that:

- Resin acids were rapidly absorbed to the soil matrices (equilibrium time < 4 hours). Subsequent desorption phases showed that a significant proportion of the resin acids were irreversibly adsorbed to the organic soils. The adsorption profiles also indicated that removal of colloidal bound resin acids via a simple filtration processes may be an important mechanism for soil/effluent interactions.
- The adsorption isotherms exhibited classical Freundlich behaviour for all soil types. The capacity and intensity of adsorption was correlated with carbon content of the soil. Whakarewarewa soil had the greatest sorption capacity and sand was least attentuative.
- High concentrations of dissolved organic carbon, chemical oxygen demand, and colour, were leached from the Kawerau and Whakarewarewa soils. This soluble material may influence the partitioning behaviour of lipophilic compounds, such as resin acids, between the soil particles and pore water and thus their mobility.

7.4 Summary

Overall, this study has shown that resin acids can be very effectively removed from each of major types of pulp and paper effluents when applied to a range of soils. Phytosterols were not attenuated as efficiently but are likely to be relatively immobile in the upper layers of the soil column. Both sorption and biodegradation processes are important contributors to the sustainability of land application systems with respect to these extractable organic compounds. Other factors, such as salinity and nutrient loadings, are therefore likely to be more important limitations for the future utilisation of land application systems in the pulp and paper industry.

7.5 Future Work

On the basis of the outcomes of this work and the literature review, it is recommended that the following studies be undertaken to further improve our fundamental understanding of land application of pulp and paper processing wastes:

- Determine the biodegradation and partitioning behaviour of resin acids and phytosterols in pulp and paper biosolids applied to comparable soil systems.
- Determine the fate of the high molecular mass lignaceous carbon in effluents when integrated into the soil matrix. For example, with respect to humic acid production, or use of stable isotope analysis to determine the long term fate of carbon loadings derived from effluents.
- Study the microbiology of soil degradation processes to determine which bacteria are responsible for the observed degradation behaviour and the impact of effluent application on soil microbial diversity.

APPENDICES

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APPENDIX A: SOIL PROFILES

Appendix A: Soil Profiles

Soil Name:	Kawerau loamy sand
Date Sampled:	9/3/99
Grid Reference:	NZMS 260 V15/323 437
Location:	Cater Holt Harvey Forest: Davies Block. Off State Highway 30, 200 metres down connecting road. 20 metres away from the fence line along forest edge
Vegetation:	Pine trees (*Pinus radiata)* Fern (*Histiopteris incisa)* Hen and Chicken Fern (*Asplenium bulbiferum var bulbiferum)* Inkweed (*Phytolacca octandra*)
NZ Soil Classification:	Typic Tephric Recent Soil
Parent Material:	Volcanic ashes over Tarawera Gravel deposits
Land form:	Footslope
Land use:	Production forestry
Drainage:	Good

Horizon	Depth (cm)	
Ah	0-9	Black (N 2/0) loamy sand, moderate polyhedral structure, nonsticky, friable with weak strength. Abrupt, wavy boundary. Few small roots.
C	9-28	Tarawera Gravel. Brownish Black (7.5 YR 2/2) gravel. Single grained apedal layer, nonplastic, non sticky. No roots, few pumice. Smooth and sharp boundary.
bAh	28-41	Paleosol. Black (5 YR 1.7/1) loamy sand, moderate polyhedral structure. Non sticky, non plastic, friable with weak strength. Distinct and irregular boundary. Few small roots
bBw	410-	Yellowish brown (10 YR 5/6) sandy clay loam, with moderate polyhedral structure. Slightly sticky, non plastic, friable with weak strength. Few Taupo pumice clasts and some small roots.

Soil Name: Whakarewarewa sandy loam
Date Sampled: 15/3/99
Grid Reference: NZMS 260 U16/969 309
Location: Whakarewarewa Forest. In unused land off Nursery Road, 5 metres from fence that divides land and 20 meters from Eucalypt trees which run perpendicular to fence.
Vegetation: Browntop grass (*Agrostis capillaris*)
Creeping bent grass (*Agrostis stolonifera*)
Rye grass
Blackberry (*Rubus fruticosis*)
Ragwort (*Senecio jacobaea*)
NZ Soil Classification: Vitric Orthic Allophanic Soil
Parent Material: Taupo, Rotorua, Rotoma, Mamaku, Waiohau and Rerewhakaaitu tephras
Land form: Hollow
Land use: Unused
Drainage: Good.

Horizon	Depth (cm)	
Ah	0-9	Very dark greyish brown (10 YR 3/2) sandy loam, weak polyhedral structure, friable with weak strength, non plastic, non sticky. Well drained. Abundant roots and few lapilli. Distinct wavy boundary.
Ah2	9-19	Dark greyish brown (10 YR 4/2) sand loam, weak platy structure, fraible with weak strength, non plastic, non sticky. Some yellow (2.5 Y 7/6) mottles. Well drained. Many roots and many pumice fragments. Diffuse occluded boundary.
Bwl	19-31	Olive brown (2.5 Y 6/6) sandy loam, moderate platy-polyhedral structure, friable with weak strength, slightly sticky, non plastic. Well drained. Many roots and few Taupo lapilli. Diffuse wavy boundary.
Bw2	31-64	Light olive brown (2.5 Y 5/6) sandy loam, moderate platy-polyhedral structure, friable with weak strength, slightly sticky, non plastic. Well drained. Few roots and few Taupo lapilli. Indistinct irregular boundary.

APPENDIX B: DEGRADATION EXPERIMENT DATA

Soil Characterisation

Compounds	Sand	Kawerau	Whakarewarewa
PIMARANES			
Pimaric Acid	0	0	0
Sandaracopimaric Acid	0	0	0
Isopimaric Acid	0	0.3	0
DIENIC ABIETANES			
Palustric Acid	0	0	0
Abietic Acid	0	1.92	0.9
Neoabietic Acid	0	0	0
AROMATIC ABIETANES			
Dehydroabietic Acid	0	4.15	1.02
Seco-1-dehydroabietic Acid	0	0	0
Seco-2-dehydroabietic Acid	0	0	0
PHYTOSTEROLS			
Cholesterol	0	7.53	7.06
Campesterol	0	2.62	4.62
Stigmasterol	0	7.87	8.94
Sitosterol	0	30.56	23.00
Sitostanol	0	5.46	3.24

Effluent Characterisation

Compounds	Water	CTMP*	TMP$^+$	Bleached Kraft
PIMARANES				
Pimaric Acid	0	1.46	17.40	0.13
Sandaracopimaric Acid	0	0	5.27	0
Isopimaric Acid	0	0.42	10.65	0
DIENIC ABIETANES				
Palustric Acid	0	0.94	14.97	0
Abietic Acid	0	4.99	189.73	2.55
Neoabietic Acid	0	0	407.16	1.33
AROMATIC ABIETANES				
Dehydroabietic Acid	0	2.14	36.35	0
Seco-1-dehydroabietic Acid	0	0	3.82	0
Seco-2-dehydroabietic Acid	0	0	1.96	0
PHYTOSTEROLS				
Cholesterol	0	0	6.34	0
Campesterol	0	0	0	0
Stigmasterol	0	0	0	0
Sitosterol	0	3.13	1.03	0.21
Sitostanol	0	0	0	0

* chemithermomechanical pulping effluent

$^+$ thermomechanical pulping effluent

Compound Concentration Data for Soil and Water Incubations

Sand aerobic						Sand anaerobic			
		Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sandaracopimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopimaric									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pimarane Resin Acids									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Palustric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.05	0.06	0.06	0.01	0.04	0.07	0.05	0.02
Abietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Neoabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic Abietanes									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-1-dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-2-Dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Abietanes									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.05	0.06	0.06	0.01	0.04	0.07	0.05	0.02
7-Oxodehydroabeitic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Dehydroabietin									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetrahydroretene									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterolstosterols									
Cholesterol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Campesterol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Stigmasterol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sitosterol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterolstosterols									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sitostanol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Kawerau aerobic						Kawerau anaerobic			
		Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sandaracopimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopimaric									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.04	0.00	0.02	0.02
Pimaranes									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.04	0.00	0.02	0.02
Palustric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Dehydroabietic Acid								
0.00	0.54	0.36	0.45	0.12	0.54	0.36	0.45	0.12
168.00	0.31	0.28	0.30	0.02	0.25	0.20	0.22	0.04
Abietic Acid								
0.00	0.13	0.16	0.14	0.02	0.13	0.16	0.14	0.02
168.00	0.17	0.18	0.17	0.01	0.13	0.13	0.13	0.00
Neoabietic Acid								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic Abietanes								
0.00	0.13	0.16	0.14	0.02	0.13	0.16	0.14	0.02
168.00	0.17	0.18	0.17	0.01	0.13	0.13	0.13	0.00
Seco-1-dehydroabietic Acid								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-2-Dehydroabietic Acid								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Abietanes								
0.00	0.54	0.36	0.45	0.12	0.54	0.36	0.45	0.12
168.00	0.31	0.28	0.30	0.02	0.25	0.20	0.22	0.04
7-Oxodehydroabeitic Acid								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietin								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetrahydroretene								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterolstosterols								
Cholesterol								
0.00	0.79	0.86	0.83	0.05	0.79	0.86	0.83	0.05
168.00	0.51	0.63	0.57	0.09	0.76	0.59	0.67	0.12
Campesterol								
0.00	0.16	0.15	0.16	0.01	0.16	0.15	0.16	0.01
168.00	0.21	0.21	0.21	0.00	0.19	0.11	0.15	0.05
Stigmasterol								
0.00	0.55	0.57	0.56	0.01	0.55	0.57	0.56	0.01
168.00	0.67	0.75	0.71	0.06	0.96	0.57	0.76	0.27
Sitosterol								

	0.00	3.70	2.97	3.33	0.52	3.70	2.97	3.33	0.52
	168.00	2.57	2.80	2.69	0.16	2.71	1.76	2.23	0.67
Phytosterolstosterols		Phytosterolstosterols							
	0.00	5.21	4.55	4.88	0.59	5.21	4.55	4.88	0.59
	168.00	3.96	4.39	4.17	0.31	4.61	3.03	3.82	1.12
Sitostanol									
	0.00	0.51	0.31	0.41	0.14	0.51	0.31	0.41	0.14
	168.00	0.64	0.63	0.63	0.01	0.16	0.37	0.27	0.15
Whakarewarewa aerobic									
		Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sandaracopimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopimaric									
	0.00	0.05	0.04	0.04	0.01	0.05	0.04	0.04	0.01
	168.00	0.04	0.03	0.04	0.01	0.07	0.05	0.06	0.01
Pimaranes									
	0.00	0.05	0.04	0.04	0.01	0.05	0.04	0.04	0.01
	168.00	0.04	0.03	0.04	0.01	0.07	0.05	0.06	0.01
Palustric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietic Acid									
	0.00	0.12	0.11	0.12	0.00	0.12	0.11	0.12	0.00
	168.00	0.12	0.12	0.12	0.00	0.12	0.12	0.12	0.00
Abietic Acid									
	0.00	0.10	0.10	0.10	0.00	0.10	0.10	0.10	0.00
	168.00	0.14	0.13	0.14	0.01	0.12	0.11	0.12	0.01
Neoabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic Abietanes									
	0.00	0.10	0.10	0.10	0.00	0.10	0.10	0.10	0.00
	168.00	0.14	0.13	0.14	0.01	0.12	0.11	0.12	0.01
Seco-1-dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-2-Dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Abietanes									
	0.00	0.12	0.11	0.12	0.00	0.12	0.11	0.12	0.00
	168.00	0.12	0.12	0.12	0.00	0.12	0.12	0.12	0.00
7-Oxodehydroabeitic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietin									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetrahydroretene									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterolstosterols									
Cholesterol									
	0.00	0.88	0.88	0.88	0.00	0.88	0.88	0.88	0.00
	168.00	0.44	0.64	0.54	0.14	1.32	1.21	1.26	0.08
Campesterol									
	0.00	0.54	0.56	0.55	0.01	0.54	0.56	0.55	0.01
	168.00	0.19	0.27	0.23	0.05	0.57	0.59	0.58	0.01
Stigmasterol									
	0.00	1.54	1.47	1.51	0.05	1.54	1.47	1.51	0.05
	168.00	0.48	1.18	0.83	0.49	1.30	1.58	1.44	0.20
Sitosterol									
	0.00	3.48	3.39	3.44	0.06	3.48	3.39	3.44	0.06
	168.00	2.54	2.44	2.49	0.08	2.71	2.93	2.82	0.16
Phytosterolstosterols									
	0.00	6.44	6.31	6.38	0.12	6.44	6.31	6.38	0.12
	168.00	3.66	4.52	4.09	0.77	5.90	6.30	6.10	0.45
Sitostanol									
	0.00	0.48	0.43	0.46	0.03	0.48	0.43	0.46	0.03
	168.00	0.36	0.61	0.49	0.18	0.22	0.55	0.39	0.23

Compound Concentration Data for Soil and Chemithermomechancial Pulping Effluent Incubations

Sand aerobic						Sand anaerobic			
		Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid									
	0.00	0.13	0.15	0.14	0.01	0.13	0.15	0.14	0.01
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sandaracopimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopimaric									
	0.00	0.12	0.08	0.10	0.03	0.12	0.08	0.10	0.03

	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pimaranes									
	0.00	0.25	0.23	0.24	0.04	0.25	0.23	0.24	0.04
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Palustric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietic Acid									
	0.00	0.50	0.49	0.49	0.01	0.50	0.49	0.49	0.01
	168.00	0.11	0.08	0.10	0.02	0.00	0.10	0.05	0.07
Abietic Acid									
	0.00	0.22	0.13	0.17	0.06	0.22	0.13	0.17	0.06
	168.00	0.00	0.00	0.00	0.00	0.00	0.07	0.03	0.05
Neoabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic Abietanes									
	0.00	0.22	0.13	0.17	0.06	0.22	0.13	0.17	0.06
	168.00	0.00	0.00	0.00	0.00	0.00	0.07	0.03	0.05
Seco-1-dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-2-Dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Abietanes									
	0.00	0.00	0.00	0.00	0.00	0.50	0.49	0.49	0.01
	168.00	0.00	0.00	0.00	0.00	0.00	0.10	0.05	0.07
7-Oxodehydroabeitic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietin									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetrahydroretene									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterolstosterols									
Cholesterol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Campesterol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Stigmasterol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sitosterol									
	0.00	1.80	1.80	1.80	0.00	1.80	1.80	1.80	0.00

	168.00	0.00	0.00	0.00	0.00	0.26	0.51	0.39	0.18
Phytosterols									
	0.00	1.80	1.80	1.80	0.00	1.80	1.80	1.80	0.00
	168.00	0.00	0.00	0.00	0.00	0.26	0.51	0.39	0.18
Sitostanol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Kawerau aerobic						Kawerau anaerobic			
		Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid									
	0.00	0.20	0.19	0.20	0.01	0.20	0.19	0.20	0.01
	168.00	0.13	0.07	0.10	0.04	0.01	0.03	0.02	0.02
Sandaracopimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopimaric									
	0.00	0.18	0.14	0.16	0.03	0.18	0.14	0.16	0.03
	168.00	0.04	0.32	0.18	0.20	0.04	0.09	0.07	0.03
Pimaranes									
	0.00	0.38	0.33	0.35	0.04	0.38	0.33	0.35	0.04
	168.00	0.17	0.39	0.28	0.24	0.05	0.12	0.09	0.05
Palustric Acid									
	0.00	0.77	0.59	0.68	0.13	0.77	0.59	0.68	0.13
	168.00	0.58	0.81	0.69	0.16	0.00	0.00	0.00	0.00
Dehydroabietic Acid									
	0.00	0.60	0.73	0.66	0.09	0.60	0.73	0.66	0.09
	168.00	0.33	1.27	0.80	0.66	0.37	0.78	0.58	0.29
Abietic Acid									
	0.00	0.79	0.91	0.85	0.08	0.79	0.91	0.85	0.08
	168.00	0.18	0.50	0.34	0.23	0.17	0.31	0.24	0.10
Neoabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic abietanes									
	0.00	1.57	1.50	1.53	0.22	1.57	1.50	1.53	0.22
	168.00	0.76	1.31	1.04	0.39	0.17	0.31	0.24	0.10
Seco-1-dehydroabietic Acid									
	0.00	0.00	0.10	0.05	0.07	0.00	0.10	0.05	0.07
	168.00	0.00	0.09	0.04	0.06	0.00	0.00	0.00	0.00
Seco-2-Dehydroabietic Acid									
	0.00	0.00	0.04	0.02	0.03	0.00	0.04	0.02	0.03
	168.00	0.00	0.07	0.03	0.05	0.00	0.00	0.00	0.00
Aromatic Abietanes									
	0.00	0.60	0.87	0.73	0.19	0.60	0.87	0.73	0.19
	168.00	0.33	1.42	0.88	0.77	0.37	0.78	0.58	0.29
7-Oxodehydroabeitic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietin									

	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetrahydroretene									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterolstosterols									
Cholesterol									
	0.00	0.78	0.73	0.76	0.04	0.78	0.73	0.76	0.04
	168.00	0.39	1.63	1.01	0.88	1.04	2.40	1.72	0.96
Campesterol									
	0.00	0.52	0.46	0.49	0.04	0.52	0.46	0.49	0.04
	168.00	0.30	0.90	0.60	0.42	0.41	0.68	0.55	0.19
Stigmasterol									
	0.00	1.37	1.54	1.46	0.12	1.37	1.54	1.46	0.12
	168.00	0.90	2.74	1.82	1.30	1.27	2.67	1.97	0.99
Sitosterol									
	0.00	10.94	13.60	12.27	1.88	10.94	13.60	12.27	1.88
	168.00	4.75	10.97	7.86	4.40	6.31	11.33	8.82	3.55
Phytosterolstosterols									
	0.00	13.60	16.33	14.97	2.08	13.60	16.33	14.97	2.08
	168.00	6.34	16.24	11.29	6.99	9.04	17.08	13.06	5.69
Sitostanol									
	0.00	3.20	3.69	3.45	0.34	3.20	3.69	3.45	0.34
	168.00	1.48	3.11	2.29	1.15	2.15	4.24	3.19	1.48
Whakarewarewa aerobic						Whakarewarewa anaerobic			
		Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid									
	0.00	0.22	0.47	0.34	0.18	0.22	0.47	0.34	0.18
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sandaracopimaric Acid									
	0.00	0.09	0.19	0.14	0.07	0.09	0.19	0.14	0.07
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopimaric									
	0.00	0.12	0.23	0.18	0.08	0.12	0.23	0.18	0.08
	168.00	0.04	0.04	0.04	0.00	0.00	0.00	0.00	0.00
Pimaranes			Pim				Pim		
	0.00	0.43	0.89	0.66	0.33	0.43	0.89	0.66	0.33
	168.00	0.04	0.04	0.04	0.00	0.00	0.00	0.00	0.00
Palustric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietic Acid									
	0.00	0.49	0.97	0.73	0.34	0.49	0.97	0.73	0.34
	168.00	0.11	0.09	0.10	0.02	0.16	0.11	0.13	0.03
Abietic Acid									
	0.00	0.79	1.53	1.16	0.52	0.79	1.53	1.16	0.52
	168.00	0.14	0.13	0.14	0.00	0.18	0.16	0.17	0.01
Neoabietic Acid									

0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic Abietanes								
0.00	0.79	1.53	1.16	0.52	0.79	1.53	1.16	0.52
168.00	0.14	0.13	0.14	0.00	0.18	0.16	0.17	0.01
Seco-1-dehydroabietic Acid								
0.00	0.08	0.10	0.09	0.02	0.08	0.10	0.09	0.02
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-2-Dehydroabietic Acid								
0.00	0.05	0.07	0.06	0.02	0.05	0.07	0.06	0.02
168.00	0.03	0.03	0.03	0.00	0.00	0.00	0.00	0.00
Aromatic Abietanes								
0.00	0.61	1.13	0.87	0.37	0.61	1.13	0.87	0.37
168.00	0.14	0.12	0.13	0.02	0.16	0.11	0.13	0.03
7-Oxodehydroabeitic Acid								
0.00	0.09	0.07	0.08	0.02	0.09	0.07	0.08	0.02
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietin								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Retene								
0.00	0.02	0.01	0.02	0.00	0.02	0.01	0.02	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterolstosterols								
Cholesterol								
0.00	0.98	1.00	0.99	0.02	0.98	1.00	0.99	0.02
168.00	0.87	0.63	0.75	0.17	0.87	0.75	0.81	0.08
Campesterol								
0.00	0.75	0.69	0.72	0.04	0.75	0.69	0.72	0.04
168.00	0.43	0.49	0.46	0.04	0.49	0.43	0.46	0.05
Stigmasterol								
0.00	1.63	1.50	1.56	0.09	1.63	1.50	1.56	0.09
168.00	1.09	0.98	1.04	0.08	0.97	1.25	1.11	0.20
Sitosterol								
0.00	13.92	15.37	14.65	1.03	13.92	15.37	14.65	1.03
168.00	3.47	3.61	3.54	0.10	5.14	5.09	5.11	0.03
Phytosterolstosterols								
0.00	17.27	18.56	17.92	1.18	17.27	18.56	17.92	1.18
168.00	5.86	5.71	5.78	0.39	7.47	7.52	7.50	0.37
Sitostanol								
0.00	4.51	4.92	4.72	0.28	4.51	4.92	4.72	0.28
168.00	0.76	0.84	0.80	0.05	1.73	1.71	1.72	0.02

Compound Concentration Data for Soil and Bleached Kraft Effluent Incubations

Sand aerobic					Sand anaerobic			
	Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid								
0.00	0.15	0.14	0.14	0.01	0.15	0.14	0.14	0.01
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Sandaracopimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopimaric									
	0.00	0.08	0.09	0.08	0.00	0.08	0.09	0.08	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pimaranes									
	0.00	0.23	0.22	0.23	0.01	0.23	0.22	0.23	0.01
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Palustric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietic Acid									
	0.00	0.48	0.45	0.46	0.02	0.48	0.45	0.46	0.02
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Abietic Acid									
	0.00	0.61	0.53	0.57	0.05	0.61	0.53	0.57	0.05
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Neoabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic abietanes									
	0.00	0.61	0.53	0.57	0.05	0.61	0.53	0.57	0.05
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-1-dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-2-Dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Abietanes									
	0.00	0.48	0.45	0.46	0.02	0.48	0.45	0.46	0.02
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7-Oxodehydroabeitic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietin									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetrahydroretene									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterols									
Cholesterol									
	0.00	0.37	0.90	0.64	0.38	0.37	0.90	0.64	0.38
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Campesterol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Stigmasterol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sitosterol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterols									
	0.00	0.37	0.90	0.64	0.38	0.37	0.90	0.64	0.38
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sitostanol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Kawerau aerobic						Kawerau anaerobic			
		Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid									
	0.00	0.09	0.08	0.08	0.01	0.09	0.08	0.08	0.01
	168.00	0.00	0.00	0.00	0.00	0.09	0.04	0.06	0.03
Sandaracopimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopimaric									
	0.00	0.08	0.10	0.09	0.01	0.08	0.10	0.09	0.01
	168.00	0.03	0.01	0.02	0.01	0.14	0.08	0.11	0.04
Pimaranes									
	0.00	0.17	0.18	0.18	0.02	0.17	0.18	0.18	0.02
	168.00	0.03	0.01	0.02	0.01	0.22	0.12	0.17	0.07
Palustric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietic Acid									
	0.00	0.40	0.46	0.43	0.04	0.40	0.46	0.43	0.04
	168.00	0.59	0.36	0.48	0.16	1.12	0.47	0.80	0.46
Abietic Acid									
	0.00	0.41	0.46	0.44	0.03	0.41	0.46	0.44	0.03
	168.00	0.28	0.14	0.21	0.10	0.96	0.29	0.63	0.47
Neoabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic abietanes									
	0.00	0.41	0.46	0.44	0.03	0.41	0.46	0.44	0.03
	168.00	0.28	0.14	0.21	0.10	0.96	0.29	0.63	0.47
Seco-1-dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-2-Dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Abietanes									
	0.00	0.40	0.46	0.43	0.04	0.40	0.46	0.43	0.04
	168.00	0.59	0.36	0.48	0.16	1.12	0.47	0.80	0.46

7-Oxodehydroabeitic Acid									
	0.00	0.06	0.06	0.06	0.00	0.06	0.06	0.06	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietin									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetrahydroretene									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterols									
Cholesterol									
	0.00	0.81	0.95	0.88	0.10	0.81	0.95	0.88	0.10
	168.00	0.87	0.69	0.78	0.12	1.26	2.02	1.64	0.53
Campesterol									
	0.00	0.17	0.30	0.23	0.09	0.17	0.30	0.23	0.09
	168.00	0.37	0.30	0.34	0.05	0.45	0.53	0.49	0.06
Stigmasterol									
	0.00	0.65	0.83	0.74	0.12	0.65	0.83	0.74	0.12
	168.00	0.95	1.34	1.14	0.28	1.52	2.08	1.80	0.40
Sitosterol									
	0.00	2.94	3.68	3.31	0.52	2.94	3.68	3.31	0.52
	168.00	4.55	4.83	4.69	0.20	4.75	6.22	5.48	1.04
Phytosterols									
	0.00	4.58	5.75	5.16	0.83	4.58	5.75	5.16	0.83
	168.00	6.73	7.17	6.95	0.65	7.97	10.84	9.41	2.03
Sitostanol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.71	0.70	0.70	0.01	1.10	1.37	1.23	0.19
Whakarewarewa aerobic						Whakarewarewa anaerobic			
		Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid									
	0.00	0.00	0.03	0.01	0.02	0.00	0.03	0.01	0.02
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sandaracopimaric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopimaric									
	0.00	0.00	0.05	0.03	0.04	0.00	0.05	0.03	0.04
	168.00	0.04	0.03	0.04	0.01	0.06	0.07	0.06	0.00
Pimaranes									
	0.00	0.00	0.08	0.04	0.06	0.00	0.08	0.04	0.06
	168.00	0.04	0.03	0.04	0.01	0.06	0.07	0.06	0.00
Palustric Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietic Acid									
	0.00	0.29	0.31	0.30	0.01	0.29	0.31	0.30	0.01
	168.00	0.06	0.05	0.06	0.00	0.13	0.12	0.12	0.01

Abietic Acid									
	0.00	0.31	0.30	0.30	0.01	0.31	0.30	0.30	0.01
	168.00	0.11	0.08	0.09	0.02	0.15	0.18	0.16	0.03
Neoabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic abietanes									
	0.00	0.31	0.30	0.30	0.01	0.31	0.30	0.30	0.01
	168.00	0.11	0.08	0.09	0.02	0.15	0.18	0.16	0.03
Seco-1-dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-2-Dehydroabietic Acid									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Abietanes									
	0.00	0.29	0.31	0.30	0.01	0.29	0.31	0.30	0.01
	168.00	0.06	0.05	0.06	0.00	0.13	0.12	0.12	0.01
7-Oxodehydroabeitic Acid									
	0.00	0.05	0.05	0.05	0.00	0.05	0.05	0.05	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietin									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Retene									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterols									
Cholesterol									
	0.00	0.90	0.92	0.91	0.01	0.90	0.92	0.91	0.01
	168.00	1.21	0.77	0.99	0.31	1.74	1.60	1.67	0.10
Campesterol									
	0.00	0.59	0.60	0.60	0.01	0.59	0.60	0.60	0.01
	168.00	0.52	0.41	0.47	0.08	0.86	0.79	0.83	0.05
Stigmasterol									
	0.00	1.37	1.49	1.43	0.09	1.37	1.49	1.43	0.09
	168.00	1.69	1.13	1.41	0.40	1.79	2.12	1.95	0.24
Sitosterol									
	0.00	3.44	3.53	3.48	0.06	3.44	3.53	3.48	0.06
	168.00	4.20	3.27	3.73	0.66	5.11	6.63	5.87	1.07
Phytosterols									
	0.00	6.30	6.54	6.42	0.17	6.30	6.54	6.42	0.17
	168.00	7.62	5.58	6.60	1.44	9.49	11.13	10.31	1.45
Sitostanol									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	168.00	0.68	0.48	0.58	0.14	0.95	1.41	1.18	0.33

Compound Concentration Data for Soils and
Thermomechanical Pulping Effluent Incubations

Aerobic Sand					Anaerobic Sand			
	Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid								
0.00	5.35	2.75	4.05	1.84	5.35	2.75	4.05	1.84
1.00	2.66	2.49	2.58	0.12	3.16	3.47	3.32	0.22
2.00	4.10	4.52	4.31	0.30	3.53	4.60	4.07	0.75
5.00	3.75	3.76	3.76	0.01	3.89	2.87	3.38	0.72
7.00	4.64	4.52	4.58	0.09	4.38	4.49	4.43	0.08
14.00	2.14	4.55	3.34	1.70	4.01	4.41	4.21	0.28
21.00	3.96	3.17	3.56	0.56	2.92	5.05	3.98	1.51
28.00	2.08	1.69	1.89	0.27	3.19	2.80	3.00	0.28
42.00	1.78	2.59	2.18	0.57	0.44	2.68	1.56	1.58
56.00	1.05	1.20	1.13	0.11	1.21	1.51	1.36	0.21
84.00	1.03	1.39	1.21	0.26	0.28	2.73	1.50	1.73
112.00	0.75	1.07	0.91	0.23	1.36	0.88	1.12	0.34
168.00	0.56	0.51	0.53	0.04	0.54	0.61	0.58	0.05
Sandaracopimaric Acid								
0.00	1.14	0.74	0.94	0.28	1.14	0.74	0.94	0.28
1.00	0.70	0.71	0.71	0.01	0.96	1.06	1.01	0.07
2.00	1.30	1.17	1.23	0.09	1.19	1.45	1.32	0.18
5.00	1.07	1.00	1.03	0.05	0.95	0.72	0.84	0.16
7.00	1.42	1.21	1.31	0.15	0.99	1.26	1.13	0.19
14.00	0.65	0.74	0.69	0.06	1.27	1.51	1.39	0.17
21.00	0.81	0.57	0.69	0.16	0.83	1.08	0.95	0.18
28.00	0.27	0.19	0.23	0.06	0.35	0.56	0.46	0.15
42.00	0.34	0.36	0.35	0.02	0.00	0.00	0.00	0.00
56.00	0.19	0.16	0.17	0.02	0.18	0.15	0.17	0.03
84.00	0.28	0.24	0.26	0.03	0.08	0.23	0.15	0.10
112.00	0.18	0.10	0.14	0.06	0.20	0.17	0.19	0.02
168.00	0.15	0.12	0.14	0.02	0.06	0.06	0.06	0.00
Isopimaric								
0.00	2.89	1.86	2.38	0.73	2.89	1.86	2.38	0.73
1.00	2.11	1.87	1.99	0.17	2.12	2.28	2.20	0.11
2.00	2.66	2.72	2.69	0.04	2.03	2.44	2.24	0.29
5.00	2.80	2.72	2.76	0.06	2.44	1.97	2.20	0.33
7.00	2.71	2.52	2.61	0.14	2.03	2.40	2.22	0.26
14.00	1.24	1.97	1.60	0.52	2.45	2.36	2.40	0.06
21.00	2.09	1.34	1.71	0.53	1.46	2.61	2.03	0.82
28.00	1.40	0.90	1.15	0.35	1.50	1.70	1.60	0.14
42.00	1.24	1.44	1.34	0.14	0.38	1.34	0.86	0.68
56.00	0.85	0.68	0.77	0.12	0.75	1.00	0.88	0.17
84.00	0.96	0.80	0.88	0.11	0.17	1.58	0.88	1.00
112.00	0.61	0.74	0.67	0.09	1.00	0.80	0.90	0.14
168.00	0.52	0.37	0.44	0.10	0.46	0.56	0.51	0.07
Pimarane								
0.00	9.37	5.36	7.37	2.84	9.37	5.36	7.37	2.84
1.00	5.47	5.07	5.27	0.29	6.24	6.81	6.53	0.40
2.00	8.05	8.40	8.22	0.44	6.75	8.49	7.62	1.23
5.00	7.62	7.48	7.55	0.12	7.28	5.56	6.42	1.21
7.00	8.77	8.24	8.51	0.37	7.40	8.15	7.78	0.53
14.00	4.03	7.26	5.64	2.28	7.72	8.28	8.00	0.51
21.00	6.85	5.08	5.97	1.26	5.20	8.75	6.97	2.51
28.00	3.74	2.78	3.26	0.68	5.05	5.06	5.05	0.57
42.00	3.36	4.39	3.88	0.72	0.82	4.02	2.42	2.26
56.00	2.08	2.05	2.07	0.24	2.15	2.65	2.40	0.41
84.00	2.27	2.43	2.35	0.40	0.53	4.54	2.53	2.84
112.00	1.55	1.91	1.73	0.37	2.56	1.86	2.21	0.50
168.00	1.22	1.00	1.11	0.16	1.06	1.23	1.14	0.12
Palustric Acid								
0.00	26.02	8.35	17.18	12.50	26.02	8.35	17.18	12.50
1.00	6.73	2.31	4.52	3.13	8.75	3.60	6.18	3.64
2.00	38.61	37.14	37.87	1.04	30.67	42.10	36.39	8.08
5.00	0.00	0.00	0.00	0.00	0.75	2.25	1.50	1.06

7.00	22.62	12.95	17.78	6.84	7.55	14.74	11.15	5.08
14.00	8.81	2.43	5.62	4.50	15.21	10.31	12.76	3.47
21.00	13.81	1.28	7.54	8.85	1.44	7.83	4.64	4.52
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	1.09	0.74	0.91	0.25	2.65	0.39	1.52	1.60
56.00	3.54	1.28	2.41	1.60	1.80	0.83	1.32	0.68
84.00	0.00	0.00	0.00	0.00	1.06	2.81	1.93	1.24
112.00	1.84	1.92	1.88	0.06	1.18	1.67	1.42	0.34
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietic Acid								
0.00	48.70	24.23	36.46	17.30	48.70	24.23	36.46	17.30
1.00	22.59	18.79	20.69	2.68	24.18	24.99	24.59	0.57
2.00	38.61	37.14	37.87	1.04	7.97	9.66	8.82	1.20
5.00	24.93	29.14	27.04	2.98	25.28	20.49	22.89	3.39
7.00	8.86	8.77	8.82	0.06	4.14	8.93	6.53	3.39
14.00	5.44	5.78	5.61	0.24	8.80	8.76	8.78	0.02
21.00	8.93	4.72	6.83	2.97	5.72	11.76	8.74	4.28
28.00	6.20	2.86	4.53	2.36	4.43	5.68	5.05	0.89
42.00	5.49	5.29	5.39	0.14	1.32	9.72	5.52	5.94
56.00	3.72	2.52	3.12	0.85	4.47	7.04	5.75	1.82
84.00	4.04	2.94	3.49	0.78	0.75	5.35	3.05	3.25
112.00	3.46	2.62	3.04	0.59	6.05	2.92	4.48	2.21
168.00	2.21	1.48	1.85	0.52	2.26	2.73	2.49	0.33
Abietic Acid								
0.00	17.18	8.75	12.96	5.96	17.18	8.75	12.96	5.96
1.00	16.52	13.95	15.23	1.81	16.74	19.22	17.98	1.76
2.00	20.06	19.60	19.83	0.32	15.62	19.86	17.74	3.00
5.00	18.49	15.95	17.22	1.80	17.01	14.69	15.85	1.64
7.00	17.79	15.41	16.60	1.68	8.76	17.07	12.91	5.88
14.00	10.13	12.16	11.15	1.43	18.81	19.68	19.24	0.61
21.00	16.31	8.69	12.50	5.39	9.83	12.33	11.08	1.77
28.00	11.23	6.00	8.62	3.70	3.99	4.93	4.46	0.67
42.00	10.10	9.85	9.98	0.18	1.74	4.61	3.18	2.03
56.00	6.58	4.41	5.50	1.54	3.66	7.04	5.35	2.39
84.00	6.08	3.21	4.64	2.03	1.19	4.01	2.60	2.00
112.00	3.66	4.71	4.18	0.74	2.19	2.16	2.18	0.02
168.00	3.23	2.12	2.67	0.79	2.52	2.01	2.27	0.36
Neoabietic Acid								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	4.24	2.78	3.51	1.03
2.00	9.71	8.24	8.98	1.04	7.99	9.93	8.96	1.37
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	6.65	4.95	5.80	1.20	3.64	5.59	4.62	1.38
14.00	3.07	2.17	2.62	0.63	5.65	5.22	5.43	0.31
21.00	4.27	1.37	2.82	2.05	0.99	3.72	2.36	1.92
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.73	0.66	0.70	0.05	1.30	0.80	1.05	0.35
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.32	0.94	0.63	0.43
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic Abietanes								
0.00	43.20	17.10	30.15	18.46	43.20	17.10	30.15	18.46
1.00	23.25	16.26	19.75	4.94	29.73	25.60	27.66	6.43
2.00	68.37	64.98	66.68	2.40	54.28	71.89	63.09	12.45
5.00	18.49	15.95	17.22	1.80	17.76	16.94	17.35	2.70
7.00	47.05	33.32	40.18	9.71	19.95	37.40	28.67	12.34
14.00	22.01	16.77	19.39	6.57	39.67	35.20	37.44	4.39
21.00	34.38	11.34	22.86	16.29	12.27	23.88	18.08	8.21
28.00	11.23	6.00	8.62	3.70	3.99	4.93	4.46	0.67
42.00	11.92	11.25	11.59	0.48	5.70	5.80	5.75	3.98
56.00	10.13	5.69	7.91	3.14	5.46	7.87	6.67	3.07
84.00	6.08	3.21	4.64	2.03	2.56	7.75	5.16	3.67
112.00	5.50	6.63	6.06	0.80	3.37	3.83	3.60	0.36
168.00	3.23	2.12	2.67	0.79	2.52	2.01	2.27	0.36

Seco-1-dehydroabietic Acid								
0.00	0.64	0.46	0.55	0.13	0.64	0.46	0.55	0.13
1.00	0.53	0.42	0.47	0.08	0.47	0.55	0.51	0.05
2.00	1.05	1.01	1.03	0.03	0.72	0.83	0.78	0.07
5.00	0.66	0.63	0.65	0.02	0.56	0.48	0.52	0.06
7.00	1.02	0.93	0.97	0.06	0.92	0.91	0.92	0.01
14.00	0.58	1.03	0.80	0.31	0.99	0.95	0.97	0.03
21.00	1.12	0.81	0.96	0.22	1.11	1.19	1.15	0.06
28.00	0.57	0.64	0.60	0.05	0.53	0.48	0.50	0.03
42.00	0.85	1.28	1.07	0.30	0.20	0.43	0.32	0.16
56.00	0.40	0.45	0.42	0.03	0.67	0.40	0.53	0.18
84.00	0.29	0.44	0.37	0.11	0.18	0.71	0.45	0.38
112.00	0.23	0.40	0.31	0.12	0.22	0.36	0.29	0.10
168.00	0.14	0.16	0.15	0.01	0.37	0.11	0.24	0.18
Seco-2-Dehydroabietic Acid								
0.00	0.41	0.28	0.34	0.09	0.41	0.28	0.34	0.09
1.00	0.31	0.25	0.28	0.04	0.28	0.31	0.30	0.02
2.00	0.63	0.56	0.60	0.05	0.43	0.51	0.47	0.05
5.00	0.42	0.39	0.41	0.02	0.33	0.26	0.30	0.05
7.00	0.55	0.53	0.54	0.02	0.56	0.54	0.55	0.02
14.00	0.35	0.58	0.46	0.16	0.58	0.54	0.56	0.03
21.00	0.66	0.49	0.57	0.12	0.66	0.69	0.67	0.02
28.00	0.34	0.34	0.34	0.00	0.30	0.21	0.26	0.06
42.00	0.45	0.72	0.58	0.19	0.11	0.34	0.22	0.16
56.00	0.22	0.27	0.24	0.03	0.40	0.24	0.32	0.12
84.00	0.16	0.23	0.19	0.05	0.09	0.40	0.24	0.22
112.00	0.14	0.19	0.17	0.04	0.12	0.23	0.17	0.08
168.00	0.02	0.00	0.01	0.01	0.26	0.06	0.16	0.14
Aromatic abietanes								
0.00	49.75	24.97	37.36	17.53	49.75	24.97	37.36	17.53
1.00	23.44	19.46	21.45	2.81	24.94	25.85	25.40	0.65
2.00	40.29	38.71	39.50	1.12	9.12	11.00	10.06	1.32
5.00	26.01	30.17	28.09	3.01	26.17	21.23	23.70	3.49
7.00	10.43	10.23	10.33	0.14	5.62	10.37	8.00	3.41
14.00	6.36	7.39	6.87	0.72	10.38	10.26	10.32	0.08
21.00	10.70	6.02	8.36	3.31	7.49	13.64	10.56	4.35
28.00	7.11	3.84	5.47	2.41	5.26	6.37	5.82	0.98
42.00	6.79	7.30	7.05	0.64	1.63	10.49	6.06	6.26
56.00	4.34	3.23	3.78	0.91	5.53	7.68	6.61	2.12
84.00	4.49	3.61	4.05	0.93	1.01	6.46	3.73	3.85
112.00	3.82	3.21	3.52	0.75	6.39	3.51	4.95	2.39
168.00	2.37	1.64	2.01	0.54	2.89	2.91	2.90	0.65
7-Oxodehydroabeitic Acid								
0.00	0.52	0.33	0.43	0.14	0.52	0.33	0.43	0.14
1.00	0.14	0.13	0.14	0.01	0.12	0.14	0.13	0.01
2.00	0.10	0.11	0.11	0.00	0.11	0.14	0.13	0.02
5.00	0.31	0.27	0.29	0.02	0.60	0.47	0.54	0.10
7.00	0.22	0.21	0.22	0.01	0.14	0.18	0.16	0.02
14.00	0.13	0.15	0.14	0.01	0.13	0.12	0.13	0.00
21.00	0.17	0.11	0.14	0.04	0.09	0.17	0.13	0.06
28.00	0.15	0.12	0.13	0.03	0.31	0.21	0.26	0.07
42.00	0.09	0.08	0.08	0.00	0.00	0.00	0.00	0.00
56.00	0.16	0.15	0.16	0.01	0.00	0.00	0.00	0.00
84.00	0.08	0.06	0.07	0.01	0.06	0.05	0.06	0.01
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietin								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00
14.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00
21.00	0.01	0.01	0.01	0.00	0.01	0.02	0.01	0.01
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetrahydroretene								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00
21.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic diterpenes								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00
14.00	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.00
21.00	0.01	0.01	0.01	0.00	0.01	0.02	0.01	0.01
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterols								
Cholesterol								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	1.23	1.32	1.28	0.07	0.00	0.00	0.00	0.00
14.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.15	0.08	0.11
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Campesterol			Campes	Campesterol				
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21.00	0.11	0.05	0.08	0.05	0.00	0.00	0.00	0.00
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.05	0.03	0.04
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Stigmasterol			Stigmas	Stigmasterol				
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sitosterol			Sitoster	Sitosterol				
0.00	0.55	0.35	0.45	0.14	0.55	0.35	0.45	0.14
1.00	0.60	0.62	0.61	0.01	0.29	0.28	0.29	0.00
2.00	0.59	0.53	0.56	0.05	0.00	0.00	0.00	0.00
5.00	1.21	1.07	1.14	0.10	0.80	0.41	0.61	0.28
7.00	0.91	0.94	0.92	0.02	0.63	0.51	0.57	0.08
14.00	0.37	0.96	0.67	0.42	0.85	0.37	0.61	0.34
21.00	3.06	2.30	2.68	0.53	1.75	0.87	1.31	0.62
28.00	1.00	1.07	1.03	0.05	0.57	0.68	0.62	0.08
42.00	1.40	1.44	1.42	0.03	0.52	0.74	0.63	0.15
56.00	0.99	0.81	0.90	0.13	1.38	1.37	1.37	0.01
84.00	1.73	1.59	1.66	0.10	0.30	0.99	0.65	0.49
112.00	1.69	0.82	1.25	0.61	1.12	0.87	0.99	0.18
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterols								
0.00	0.55	0.35	0.45	0.14	0.55	0.35	0.45	0.14
1.00	0.60	0.62	0.61	0.01	0.29	0.28	0.29	0.00
2.00	0.59	0.53	0.56	0.05	0.00	0.00	0.00	0.00
5.00	1.21	1.07	1.14	0.10	0.80	0.41	0.61	0.28
7.00	2.14	2.26	2.20	0.09	0.63	0.51	0.57	0.08
14.00	0.37	0.96	0.67	0.42	0.85	0.37	0.61	0.34
21.00	3.17	2.35	2.76	0.58	1.75	0.87	1.31	0.62
28.00	1.00	1.07	1.03	0.05	0.57	0.68	0.62	0.08
42.00	1.40	1.44	1.42	0.03	0.52	0.74	0.63	0.15
56.00	0.99	0.81	0.90	0.13	1.38	1.37	1.37	0.01
84.00	1.73	1.59	1.66	0.10	0.30	1.20	0.75	0.63
112.00	1.69	0.82	1.25	0.61	1.12	0.87	0.99	0.18
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sitostanol			Sitostan	Sitostanol				
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.00	0.00	0.00	0.00	0.43	0.43	0.43	0.01
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.03	0.03	0.03	0.00	0.00	0.00	0.00	0.00
14.00	0.07	0.21	0.14	0.09	0.08	0.07	0.07	0.01
21.00	0.56	0.56	0.56	0.00	0.24	0.16	0.20	0.05
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.39	0.41	0.40	0.02	0.11	0.18	0.15	0.06
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Kawerau aerobic					Kawerau anaerobic			
	Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid								
0.00	0.99	0.93	0.96	0.04	0.99	0.93	0.96	0.04
1.00	3.81	3.25	3.53	0.39	2.71	2.77	2.74	0.04
2.00	8.96	7.00	7.98	1.38	7.63	7.27	7.45	0.26
5.00	3.09	3.35	3.22	0.18	2.41	3.65	3.03	0.88
7.00	6.40	6.08	6.24	0.23	4.61	6.54	5.57	1.36
14.00	4.46	5.16	4.81	0.50	3.14	3.90	3.52	0.54
21.00	2.66	1.86	2.26	0.57	1.20	1.24	1.22	0.03
28.00	0.91	1.20	1.05	0.21	0.44	0.59	0.52	0.10
42.00	0.70	0.66	0.68	0.03	0.53	0.41	0.47	0.09
56.00	0.49	0.39	0.44	0.07	0.30	0.31	0.30	0.01

84.00	0.65	0.66	0.65	0.01	0.49	0.13	0.31	0.25
112.00	0.40	0.35	0.37	0.04	0.22	0.26	0.24	0.02
168.00	0.42	0.00	0.21	0.29	0.35	0.27	0.31	0.06
Sandaracopimaric Acid								
0.00	0.24	0.32	0.28	0.05	0.24	0.32	0.28	0.05
1.00	1.05	0.96	1.01	0.07	0.79	0.88	0.83	0.06
2.00	3.34	2.42	2.88	0.65	2.67	2.58	2.63	0.06
5.00	1.07	1.18	1.13	0.08	0.73	0.90	0.81	0.12
7.00	1.69	2.03	1.86	0.24	1.47	2.07	1.77	0.42
14.00	1.39	1.48	1.43	0.06	1.11	1.33	1.22	0.15
21.00	2.66	1.86	2.26	0.57	0.35	0.37	0.36	0.01
28.00	0.91	1.20	1.05	0.21	0.00	0.16	0.08	0.11
42.00	0.70	0.66	0.68	0.03	0.12	0.10	0.11	0.02
56.00	0.12	0.12	0.12	0.00	0.00	0.00	0.00	0.00
84.00	0.65	0.66	0.65	0.01	0.10	0.06	0.08	0.03
112.00	0.07	0.12	0.10	0.04	0.05	0.03	0.04	0.01
168.00	0.06	0.00	0.03	0.04	0.13	0.08	0.11	0.04
Isopimaric								
0.00	1.01	1.05	1.03	0.02	1.01	1.05	1.03	0.02
1.00	3.47	3.07	3.27	0.28	2.70	4.93	3.82	1.58
2.00	5.84	4.03	4.93	1.29	4.15	4.02	4.09	0.09
5.00	3.87	3.63	3.75	0.17	1.91	2.67	2.29	0.53
7.00	3.32	2.97	3.15	0.25	3.46	3.45	3.46	0.01
14.00	2.66	3.19	2.92	0.37	1.68	2.17	1.92	0.35
21.00	1.77	1.22	1.50	0.38	0.88	0.86	0.87	0.02
28.00	0.92	1.03	0.97	0.08	0.53	0.66	0.59	0.10
42.00	0.69	0.59	0.64	0.07	0.72	0.46	0.59	0.18
56.00	0.65	0.40	0.52	0.18	0.35	0.39	0.37	0.03
84.00	0.67	0.68	0.68	0.01	0.44	0.13	0.28	0.22
112.00	0.39	0.36	0.38	0.02	0.25	0.29	0.27	0.02
168.00	0.43	0.00	0.22	0.31	0.48	0.34	0.41	0.10
Pimaranes								
0.00	2.24	2.29	2.27	0.12	2.24	2.29	2.26	0.12
1.00	8.33	7.28	7.81	0.75	6.20	8.58	7.39	1.68
2.00	18.14	13.45	15.80	3.31	14.45	13.88	14.16	0.41
5.00	8.03	8.16	8.10	0.43	5.05	7.22	6.14	1.54
7.00	11.42	11.08	11.25	0.71	9.54	12.06	10.80	1.79
14.00	8.51	9.82	9.16	0.93	5.93	7.40	6.67	1.04
21.00	7.10	4.94	6.02	1.52	2.43	2.47	2.45	0.06
28.00	2.74	3.43	3.08	0.49	0.97	1.41	1.19	0.31
42.00	2.09	1.90	2.00	0.13	1.38	0.96	1.17	0.29
56.00	1.27	0.91	1.09	0.25	0.64	0.71	0.67	0.04
84.00	1.97	1.99	1.98	0.02	1.03	0.31	0.67	0.51
112.00	0.86	0.83	0.84	0.10	0.53	0.58	0.55	0.06
168.00	0.91	0.00	0.45	0.64	0.96	0.68	0.82	0.20
Palustric Acid								
0.00	0.86	0.99	0.92	0.09	0.86	0.99	0.92	0.09
1.00	2.25	2.10	2.18	0.10	0.87	0.79	0.83	0.06
2.00	11.69	10.25	10.97	1.02	9.37	16.65	13.01	5.15
5.00	0.00	0.00	0.00	0.00	1.35	1.65	1.50	0.21
7.00	0.00	0.00	0.00	0.00	1.87	0.71	1.29	0.82
14.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21.00	0.81	0.36	0.58	0.32	0.41	0.47	0.44	0.04
28.00	0.00	0.00	0.00	0.00	1.50	1.16	1.33	0.24
42.00	0.32	1.16	0.74	0.59	2.22	1.49	1.86	0.51
56.00	1.14	1.45	1.29	0.22	0.86	0.88	0.87	0.02
84.00	0.00	0.00	0.00	0.00	0.24	0.35	0.29	0.08
112.00	0.00	0.00	0.00	0.00	0.80	1.13	0.96	0.24
168.00	1.82	0.85	1.34	0.68	2.48	1.90	2.19	0.41
Dehydroabietic Acid								
0.00	2.21	2.27	2.24	0.04	2.21	2.27	2.24	0.04
1.00	8.17	7.79	7.98	0.27	5.24	5.58	5.41	0.24
2.00	15.53	11.88	13.70	2.58	11.22	10.07	10.64	0.81
5.00	7.35	9.59	8.47	1.58	4.69	7.21	5.95	1.78

7.00	6.72	7.08	6.90	0.26	11.91	7.49	9.70	3.12
14.00	5.08	7.01	6.05	1.37	4.29	4.61	4.45	0.23
21.00	3.84	3.36	3.60	0.34	2.34	2.57	2.45	0.16
28.00	1.65	5.61	3.63	2.80	1.68	2.11	1.90	0.30
42.00	1.90	2.21	2.06	0.22	2.52	1.74	2.13	0.55
56.00	2.34	1.54	1.94	0.57	1.31	1.45	1.38	0.09
84.00	2.52	2.56	2.54	0.02	1.62	0.74	1.18	0.63
112.00	1.49	1.46	1.48	0.02	1.07	1.40	1.23	0.23
168.00	2.05	0.64	1.35	1.00	2.07	1.47	1.77	0.42
Abietic Acid								
0.00	3.82	3.36	3.59	0.32	3.82	3.36	3.59	0.33
1.00	8.17	7.79	7.98	0.27	10.59	12.88	11.73	1.62
2.00	15.53	11.88	13.70	2.58	26.62	29.50	28.06	2.04
5.00	13.31	10.23	11.77	2.18	4.69	7.21	5.95	1.78
7.00	10.30	11.98	11.14	1.18	6.00	12.50	9.25	4.60
14.00	10.95	15.64	13.29	3.31	4.29	4.61	4.45	0.23
21.00	4.82	5.57	5.19	0.53	2.44	2.73	2.59	0.21
28.00	3.03	4.79	3.91	1.24	1.96	2.12	2.04	0.12
42.00	2.45	3.19	2.82	0.52	0.00	0.00	0.00	0.00
56.00	1.77	1.64	1.70	0.09	1.25	1.48	1.36	0.16
84.00	0.78	0.79	0.78	0.01	1.55	0.49	1.02	0.75
112.00	1.61	1.69	1.65	0.06	1.26	1.00	1.13	0.18
168.00	0.58	0.22	0.40	0.26	0.59	1.19	0.89	0.42
Neoabietic Acid								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	6.77	6.11	6.44	0.46	4.69	8.60	6.65	2.76
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.10	0.12	0.11	0.02	0.00	0.00	0.00	0.00
14.00	0.15	0.52	0.34	0.26	0.09	0.22	0.16	0.09
21.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic Abietanes								
0.00	4.68	4.35	4.52	0.42	4.68	4.35	4.52	0.42
1.00	10.41	9.89	10.15	0.37	11.46	13.67	12.56	1.68
2.00	33.98	28.24	31.11	4.06	40.68	54.75	47.72	9.95
5.00	13.31	10.23	11.77	2.18	6.04	8.86	7.45	1.99
7.00	10.40	12.10	11.25	1.20	7.87	13.21	10.54	5.42
14.00	11.11	16.16	13.63	3.57	4.38	4.83	4.61	0.32
21.00	5.63	5.93	5.78	0.85	2.85	3.20	3.03	0.24
28.00	3.03	4.79	3.91	1.24	3.46	3.28	3.37	0.36
42.00	2.77	4.35	3.56	1.12	2.22	1.49	1.86	0.51
56.00	2.90	3.09	2.99	0.31	2.11	2.36	2.23	0.18
84.00	0.78	0.79	0.78	0.01	1.79	0.84	1.31	0.83
112.00	1.61	1.69	1.65	0.06	2.05	2.13	2.09	0.42
168.00	2.40	1.07	1.74	0.94	3.07	3.09	3.08	0.83
Seco-1-dehydroabietic Acid								
0.00	0.48	0.48	0.48	0.00	0.48	0.48	0.48	0.00
1.00	1.15	1.02	1.08	0.09	0.92	0.86	0.89	0.04
2.00	2.01	1.55	1.78	0.32	1.37	1.39	1.38	0.02
5.00	1.25	0.99	1.12	0.19	0.56	0.80	0.68	0.17
7.00	1.66	1.33	1.50	0.24	1.21	1.34	1.27	0.09
14.00	1.55	1.36	1.45	0.14	0.88	1.02	0.95	0.10
21.00	1.21	0.75	0.98	0.32	0.50	0.44	0.47	0.04
28.00	0.44	0.51	0.48	0.05	0.19	0.23	0.21	0.04
42.00	0.34	0.26	0.30	0.06	0.22	0.17	0.20	0.03
56.00	0.24	0.17	0.20	0.05	0.13	0.14	0.14	0.01
84.00	0.33	0.33	0.33	0.00	0.15	0.14	0.14	0.01
112.00	0.20	0.13	0.17	0.05	0.08	0.09	0.08	0.01
168.00	0.20	0.00	0.10	0.14	0.12	0.08	0.10	0.03

Seco-2-Dehydroabietic Acid								
0.00	0.30	0.32	0.31	0.01	0.30	0.32	0.31	0.01
1.00	0.75	0.66	0.70	0.07	0.56	0.54	0.55	0.01
2.00	1.25	0.91	1.08	0.24	0.85	0.85	0.85	0.00
5.00	0.82	0.66	0.74	0.11	0.40	0.58	0.49	0.12
7.00	1.00	0.83	0.91	0.12	0.79	0.83	0.81	0.03
14.00	0.92	0.81	0.86	0.07	0.46	0.56	0.51	0.07
21.00	0.64	0.41	0.53	0.16	0.28	0.25	0.26	0.02
28.00	0.24	0.31	0.27	0.05	0.12	0.15	0.14	0.03
42.00	0.16	0.18	0.17	0.01	0.12	0.10	0.11	0.01
56.00	0.13	0.10	0.11	0.02	0.00	0.00	0.00	0.00
84.00	0.12	0.12	0.12	0.00	0.08	0.04	0.06	0.03
112.00	0.12	0.00	0.06	0.08	0.05	0.00	0.03	0.04
168.00	0.08	0.00	0.04	0.06	0.09	0.07	0.08	0.01
Aromatic Abietanes								
0.00	2.99	3.07	3.03	0.06	2.99	3.07	3.03	0.05
1.00	10.06	9.47	9.76	0.42	6.71	6.97	6.84	0.30
2.00	18.78	14.35	16.56	3.14	13.44	12.31	12.87	0.83
5.00	9.42	11.23	10.33	1.88	5.66	8.58	7.12	2.07
7.00	9.38	9.24	9.31	0.61	13.91	9.66	11.78	3.24
14.00	7.55	9.18	8.37	1.58	5.63	6.19	5.91	0.40
21.00	5.68	4.52	5.10	0.82	3.12	3.26	3.19	0.22
28.00	2.33	6.43	4.38	2.90	1.98	2.50	2.24	0.36
42.00	2.41	2.65	2.53	0.28	2.86	2.02	2.44	0.59
56.00	2.70	1.81	2.25	0.63	1.44	1.59	1.52	0.11
84.00	2.97	3.01	2.99	0.03	1.85	0.91	1.38	0.66
112.00	1.82	1.59	1.70	0.16	1.20	1.49	1.34	0.27
168.00	2.33	0.64	1.49	1.20	2.27	1.62	1.95	0.46
7-Oxodehydroabietic Acid								
0.00	0.11	0.14	0.12	0.02	0.11	0.14	0.12	0.02
1.00	0.30	0.27	0.29	0.02	0.17	0.17	0.17	0.00
2.00	0.36	0.20	0.28	0.11	0.17	0.18	0.18	0.01
5.00	0.23	0.25	0.24	0.01	0.23	0.27	0.25	0.03
7.00	0.07	0.10	0.08	0.02	0.37	0.23	0.30	0.10
14.00	0.12	0.13	0.13	0.01	0.11	0.14	0.12	0.02
21.00	0.17	0.09	0.13	0.06	0.13	0.16	0.15	0.02
28.00	0.15	0.24	0.20	0.06	0.16	0.11	0.13	0.04
42.00	0.10	0.11	0.11	0.00	0.21	0.14	0.17	0.05
56.00	0.21	0.13	0.17	0.06	0.12	0.13	0.12	0.01
84.00	0.16	0.17	0.17	0.00	0.06	0.04	0.05	0.01
112.00	0.05	0.09	0.07	0.03	0.06	0.05	0.06	0.00
168.00	0.00	0.00	0.00	0.00	0.15	0.12	0.13	0.02
Dehydroabietin								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00
14.00	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00
21.00	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Retene								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00
14.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
21.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00

28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Diterpenes								
0.00	0.00	0.00	0.00	0.00	0.11	0.14	0.12	0.02
1.00	0.00	0.00	0.00	0.00	0.17	0.17	0.17	0.00
2.00	0.00	0.00	0.00	0.00	0.17	0.18	0.18	0.01
5.00	0.00	0.00	0.00	0.00	0.23	0.27	0.25	0.03
7.00	0.01	0.01	0.01	0.00	0.38	0.24	0.31	0.10
14.00	0.02	0.01	0.01	0.00	0.11	0.15	0.13	0.02
21.00	0.02	0.01	0.02	0.01	0.14	0.16	0.15	0.02
28.00	0.00	0.00	0.00	0.00	0.16	0.11	0.13	0.04
42.00	0.00	0.00	0.00	0.00	0.21	0.14	0.17	0.05
56.00	0.00	0.00	0.00	0.00	0.12	0.13	0.12	0.01
84.00	0.00	0.00	0.00	0.00	0.06	0.04	0.05	0.01
112.00	0.00	0.00	0.00	0.00	0.06	0.05	0.06	0.00
168.00	0.00	0.00	0.00	0.00	0.15	0.12	0.13	0.02
Phytosterols								
Cholesterol								
0.00	0.75	0.95	0.85	0.14	1.06	0.97	1.02	0.06
1.00	2.69	2.11	2.40	0.41	2.05	1.88	1.97	0.12
2.00	0.48	0.45	0.46	0.02	0.62	0.63	0.63	0.00
5.00	1.78	1.57	1.68	0.15	1.14	1.54	1.34	0.29
7.00	1.06	1.25	1.15	0.13	1.36	1.18	1.27	0.12
14.00	0.75	0.79	0.77	0.03	0.69	0.83	0.76	0.10
21.00	0.17	0.09	0.13	0.06	1.03	1.13	1.08	0.07
28.00	0.15	0.24	0.20	0.06	0.84	1.04	0.94	0.14
42.00	0.10	0.11	0.11	0.00	1.64	1.25	1.44	0.28
56.00	0.79	0.83	0.81	0.03	0.70	0.78	0.74	0.06
84.00	0.17	0.18	0.17	0.00	1.20	1.04	1.12	0.11
112.00	0.94	1.15	1.04	0.15	1.08	1.42	1.25	0.24
168.00	0.47	0.72	0.59	0.18	2.30	1.86	2.08	0.31
Campesterol								
0.00	0.16	0.29	0.23	0.09	0.37	0.34	0.35	0.02
1.00	0.72	0.63	0.68	0.06	0.42	0.42	0.42	0.00
2.00	0.26	0.29	0.28	0.02	0.25	0.24	0.24	0.00
5.00	0.56	0.66	0.61	0.07	0.42	0.57	0.50	0.11
7.00	0.34	0.44	0.39	0.07	0.83	0.53	0.68	0.21
14.00	0.28	0.29	0.28	0.01	0.28	0.32	0.30	0.02
21.00	0.58	0.36	0.47	0.15	0.41	0.38	0.39	0.02
28.00	0.44	0.73	0.59	0.21	0.40	0.44	0.42	0.03
42.00	0.33	0.59	0.46	0.18	0.54	0.46	0.50	0.06
56.00	0.40	0.39	0.40	0.01	0.40	0.45	0.42	0.03
84.00	0.74	0.75	0.75	0.01	0.44	0.49	0.47	0.03
112.00	0.41	0.60	0.50	0.13	0.39	0.54	0.46	0.10
168.00	0.20	0.30	0.25	0.07	0.52	0.54	0.53	0.01
Stigmasterol								
0.00	1.24	1.12	1.18	0.09	1.24	1.11	1.18	0.09
1.00	3.43	2.41	2.92	0.72	2.43	2.23	2.33	0.14
2.00	0.75	0.81	0.78	0.05	0.80	0.79	0.80	0.01
5.00	1.66	1.99	1.83	0.24	1.51	1.93	1.72	0.30
7.00	1.09	1.37	1.23	0.20	1.52	1.16	1.34	0.25
14.00	0.28	0.29	0.28	0.01	1.12	1.20	1.16	0.06
21.00	1.60	1.06	1.33	0.39	1.35	1.50	1.42	0.10
28.00	1.76	2.48	2.12	0.51	1.35	1.41	1.38	0.04
42.00	1.60	1.66	1.63	0.04	2.34	1.86	2.10	0.33
56.00	1.19	1.29	1.24	0.07	1.91	1.74	1.83	0.12
84.00	2.72	2.75	2.74	0.02	1.04	1.01	1.02	0.03
112.00	2.25	1.34	1.80	0.65	1.50	1.57	1.53	0.05
168.00	3.06	3.14	3.10	0.06	3.22	2.59	2.90	0.44
Sitosterol								
0.00	5.50	5.89	5.70	0.27	5.50	5.88	5.69	0.27

1.00	14.37	10.46	12.42	2.77	8.38	8.20	8.29	0.13
2.00	4.56	4.72	4.64	0.12	4.42	4.27	4.34	0.10
5.00	10.94	12.01	11.48	0.76	6.53	8.05	7.29	1.07
7.00	6.71	6.47	6.59	0.17	13.91	6.04	9.97	5.57
14.00	5.41	8.41	6.91	2.12	4.27	4.74	4.51	0.33
21.00	7.83	4.60	6.22	2.28	7.79	5.78	6.78	1.42
28.00	7.62	11.06	9.34	2.43	5.31	5.74	5.53	0.31
42.00	5.64	6.78	6.21	0.80	8.23	5.96	7.09	1.60
56.00	5.11	6.12	5.61	0.71	6.17	6.43	6.30	0.18
84.00	9.88	10.00	9.94	0.09	6.30	8.01	7.16	1.21
112.00	6.99	6.71	6.85	0.20	5.18	6.33	5.76	0.81
168.00	2.46	4.80	3.63	1.66	9.61	8.37	8.99	0.87
Phytosterol								
0.00	7.65	8.24	7.95	0.59	8.16	8.31	8.24	0.43
1.00	21.21	15.61	18.41	3.96	13.29	12.72	13.01	0.40
2.00	6.05	6.28	6.16	0.21	6.09	5.93	6.01	0.12
5.00	14.94	16.23	15.59	1.21	9.60	12.10	10.85	1.77
7.00	9.20	9.53	9.36	0.56	17.63	8.91	13.27	6.16
14.00	6.71	9.77	8.24	2.16	6.36	7.08	6.72	0.51
21.00	10.18	6.11	8.14	2.88	10.58	8.78	9.68	1.61
28.00	9.98	14.52	12.25	3.21	7.90	8.63	8.27	0.52
42.00	7.68	9.13	8.41	1.02	12.74	9.52	11.13	2.28
56.00	7.49	8.63	8.06	0.82	9.17	9.39	9.28	0.39
84.00	13.52	13.69	13.60	0.12	8.98	10.55	9.77	1.38
112.00	10.59	9.80	10.19	1.13	8.15	9.85	9.00	1.20
168.00	6.18	8.97	7.58	1.97	15.65	13.36	14.50	1.64
Sitostanol								
0.00	1.00	1.11	1.05	0.07	1.00	1.11	1.05	0.07
1.00	2.48	1.93	2.21	0.39	1.65	1.50	1.58	0.11
2.00	0.57	0.58	0.58	0.01	0.86	0.80	0.83	0.04
5.00	2.34	2.56	2.45	0.16	1.40	1.78	1.59	0.27
7.00	1.36	1.34	1.35	0.02	2.74	1.26	2.00	1.04
14.00	1.09	1.94	1.52	0.61	0.87	0.98	0.92	0.07
21.00	1.73	1.01	1.37	0.51	1.19	1.23	1.21	0.03
28.00	1.51	2.65	2.08	0.80	0.99	1.07	1.03	0.05
42.00	1.20	1.52	1.36	0.22	1.65	1.30	1.48	0.25
56.00	0.93	1.25	1.09	0.23	1.28	1.34	1.31	0.05
84.00	2.52	2.55	2.54	0.02	1.18	1.78	1.48	0.42
112.00	1.44	1.73	1.59	0.20	1.01	0.84	0.93	0.12
168.00	2.54	2.84	2.69	0.21	1.76	1.67	1.72	0.06
Whakarewarewa aerobic								
	Cor ug/g	Cor ug/g	Ave	stdev	Cor ug/g	Cor ug/g	Ave	stdev
Pimaric Acid								
0.00	2.74	2.81	2.77	0.05	2.74	2.81	2.77	0.05
1.00	5.27	6.03	5.65	0.54	5.47	5.44	5.45	0.02
2.00	11.44	11.12	11.28	0.23	6.74	6.04	6.39	0.50
5.00	6.71	8.77	7.74	1.45	4.82	5.47	5.14	0.45
7.00	9.29	9.57	9.43	0.20	8.93	6.58	7.75	1.66
14.00	8.64	9.77	9.21	0.80	5.31	5.93	5.62	0.44
21.00	6.41	5.97	6.19	0.31	3.04	3.78	3.41	0.53
28.00	1.77	2.79	2.28	0.72	1.27	1.66	1.47	0.28
42.00	1.27	2.13	1.70	0.61	1.09	1.55	1.32	0.32
56.00	0.94	1.75	1.35	0.57	0.85	0.97	0.91	0.09
84.00	1.04	1.93	1.49	0.63	1.05	0.96	1.00	0.06
112.00	0.73	0.89	0.81	0.11	0.43	0.62	0.53	0.13
168.00	0.68	0.88	0.78	0.14	0.42	0.46	0.44	0.03
Sandaracopimaric Acid								
0.00	0.80	0.91	0.86	0.08	0.80	0.91	0.86	0.08
1.00	1.70	1.79	1.75	0.07	1.67	1.67	1.67	0.00
2.00	4.36	3.75	4.05	0.43	1.88	1.74	1.81	0.10
5.00	2.01	2.44	2.23	0.30	1.47	1.64	1.56	0.12
7.00	3.06	3.20	3.13	0.10	3.19	1.65	2.42	1.09
14.00	3.08	3.04	3.06	0.03	1.82	2.04	1.93	0.16
21.00	2.04	2.01	2.03	0.02	1.06	1.15	1.10	0.06

28.00	1.77	2.79	2.28	0.72	0.40	0.43	0.41	0.02
42.00	0.39	0.40	0.40	0.01	0.38	0.38	0.38	0.00
56.00	0.29	0.51	0.40	0.16	0.25	0.31	0.28	0.04
84.00	0.46	0.55	0.51	0.07	0.48	0.35	0.41	0.09
112.00	0.19	0.15	0.17	0.03	0.14	0.10	0.12	0.03
168.00	0.20	0.26	0.23	0.04	0.00	0.00	0.00	0.00
Isopimaric								
0.00	1.85	1.91	1.88	0.05	1.85	1.91	1.88	0.05
1.00	4.06	4.36	4.21	0.21	4.13	4.09	4.11	0.03
2.00	6.86	6.31	6.59	0.39	4.02	4.62	4.32	0.43
5.00	5.06	5.74	5.40	0.48	3.47	4.03	3.75	0.40
7.00	5.26	5.32	5.29	0.04	5.00	3.79	4.40	0.86
14.00	5.00	5.04	5.02	0.03	2.93	3.17	3.05	0.17
21.00	3.41	3.66	3.54	0.18	1.32	2.04	1.68	0.51
28.00	1.38	1.61	1.50	0.17	0.76	1.05	0.91	0.21
42.00	1.07	1.11	1.09	0.03	0.73	1.02	0.88	0.20
56.00	0.86	1.16	1.01	0.21	0.60	0.69	0.65	0.07
84.00	0.92	1.31	1.12	0.28	0.58	0.67	0.62	0.06
112.00	0.64	0.72	0.68	0.05	0.39	0.50	0.45	0.08
168.00	0.63	0.84	0.74	0.15	0.06	0.06	0.06	0.00
Pimarane								
0.00	5.39	5.64	5.51	0.18	5.39	5.64	5.51	0.18
1.00	11.03	12.18	11.61	0.82	11.27	11.20	11.23	0.05
2.00	22.66	21.18	21.92	1.05	12.64	12.40	12.52	1.02
5.00	13.79	16.94	15.37	2.23	9.77	11.14	10.45	0.97
7.00	17.61	18.09	17.85	0.34	17.12	12.02	14.57	3.60
14.00	16.72	17.85	17.29	0.86	10.06	11.14	10.60	0.77
21.00	11.86	11.65	11.75	0.51	5.42	6.97	6.20	1.10
28.00	4.91	7.19	6.05	1.61	2.43	3.14	2.79	0.51
42.00	2.73	3.64	3.19	0.64	2.20	2.95	2.58	0.53
56.00	2.09	3.42	2.76	0.94	1.70	1.97	1.83	0.19
84.00	2.42	3.80	3.11	0.97	2.11	1.98	2.04	0.22
112.00	1.56	1.76	1.66	0.20	0.97	1.22	1.09	0.24
168.00	1.51	1.97	1.74	0.33	0.47	0.52	0.50	0.04
Palustric Acid								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	1.36	2.55	1.96	0.85	1.10	1.10	1.10	0.00
2.00	45.76	45.40	45.58	0.26	9.77	1.60	5.69	5.78
5.00	0.00	0.00	0.00	0.00	1.81	1.71	1.76	0.07
7.00	0.00	0.00	0.00	0.00	1.57	1.10	1.33	0.33
14.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21.00	0.81	1.66	1.24	0.59	0.72	0.58	0.65	0.10
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	2.71	3.94	3.33	0.87	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	1.09	0.00	0.55	0.77	0.00	0.00	0.00	0.00
Dehydroabietic Acid								
0.00	6.60	6.14	6.37	0.32	6.60	6.14	6.37	0.32
1.00	22.67	21.93	22.30	0.52	24.15	20.17	22.16	2.82
2.00	14.29	13.99	14.14	0.22	12.67	29.24	20.96	11.72
5.00	12.58	16.50	14.54	2.77	15.39	12.17	13.78	2.28
7.00	9.16	9.01	9.09	0.10	14.24	9.05	11.64	3.67
14.00	9.74	9.63	9.69	0.08	7.64	7.26	7.45	0.26
21.00	6.31	14.38	10.34	5.71	1.37	5.12	3.24	2.66
28.00	4.34	6.85	5.59	1.78	3.74	4.15	3.95	0.29
42.00	2.94	4.95	3.94	1.42	3.03	3.75	3.39	0.51
56.00	4.74	5.54	5.14	0.56	2.58	2.62	2.60	0.03
84.00	3.05	5.36	4.20	1.63	2.23	3.11	2.67	0.62
112.00	1.97	2.27	2.12	0.21	1.42	1.88	1.65	0.33
168.00	2.03	2.83	2.43	0.57	0.13	0.11	0.12	0.01
Abietic Acid								
0.00	7.43	7.34	7.39	0.06	0.57	0.70	0.63	0.09

1.00	29.66	40.73	35.19	7.83	29.81	33.80	31.81	2.82
2.00	52.41	47.64	50.03	3.37	32.12	31.81	31.96	0.22
5.00	21.21	21.24	21.23	0.02	16.99	12.17	14.58	3.41
7.00	22.56	21.96	22.26	0.42	22.92	17.79	20.35	3.63
14.00	23.19	23.85	23.52	0.47	15.68	16.16	15.92	0.35
21.00	13.55	9.18	11.37	3.09	5.78	10.11	7.94	3.07
28.00	6.53	7.67	7.10	0.80	4.14	4.71	4.43	0.40
42.00	5.62	8.16	6.89	1.80	4.20	5.16	4.68	0.68
56.00	0.00	0.00	0.00	0.00	3.35	3.43	3.39	0.06
84.00	3.11	4.16	3.64	0.74	3.99	7.57	5.78	2.54
112.00	2.39	2.33	2.36	0.04	1.58	1.92	1.75	0.24
168.00	0.72	0.84	0.78	0.08	0.14	0.18	0.16	0.03
Neoabietic Acid								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	18.47	16.94	17.71	1.08	6.22	0.00	3.11	4.40
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.11	0.21	0.16	0.07	0.00	0.00	0.00	0.00
14.00	1.18	0.70	0.94	0.34	0.60	0.55	0.57	0.04
21.00	0.44	0.18	0.31	0.19	0.11	0.08	0.10	0.02
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dienic Abietanes								
0.00	7.43	7.34	7.39	0.06	0.57	0.70	0.63	0.09
1.00	31.01	43.28	37.15	8.68	30.91	34.90	32.91	2.82
2.00	116.64	109.99	113.32	4.71	48.11	33.41	40.76	10.40
5.00	21.21	21.24	21.23	0.02	18.80	13.88	16.34	3.48
7.00	22.66	22.17	22.42	0.49	24.48	18.89	21.69	3.96
14.00	24.37	24.55	24.46	0.80	16.27	16.71	16.49	0.38
21.00	14.81	11.02	12.91	3.87	6.60	10.77	8.69	3.18
28.00	6.53	7.67	7.10	0.80	4.14	4.71	4.43	0.40
42.00	5.62	8.16	6.89	1.80	4.20	5.16	4.68	0.68
56.00	2.71	3.94	3.33	0.87	3.35	3.43	3.39	0.06
84.00	3.11	4.16	3.64	0.74	3.99	7.57	5.78	2.54
112.00	2.39	2.33	2.36	0.04	1.58	1.92	1.75	0.24
168.00	1.82	0.84	1.33	0.85	0.14	0.18	0.16	0.03
Seco-1-dehydroabietic Acid								
0.00	0.77	0.80	0.78	0.02	0.77	0.80	0.78	0.02
1.00	1.07	0.99	1.03	0.06	0.96	0.94	0.95	0.01
2.00	2.65	2.32	2.49	0.23	1.17	0.98	1.08	0.14
5.00	1.40	1.51	1.46	0.08	0.96	1.03	0.99	0.05
7.00	2.27	2.14	2.20	0.09	2.34	1.27	1.81	0.76
14.00	2.43	2.11	2.27	0.23	1.44	1.42	1.43	0.02
21.00	1.94	1.53	1.74	0.29	0.84	1.13	0.99	0.21
28.00	0.61	0.62	0.61	0.01	0.40	0.50	0.45	0.07
42.00	0.34	0.30	0.32	0.03	0.34	0.45	0.40	0.07
56.00	0.29	0.33	0.31	0.03	0.24	0.28	0.26	0.03
84.00	0.30	0.43	0.37	0.10	0.28	0.22	0.25	0.04
112.00	0.26	0.24	0.25	0.02	0.16	0.21	0.19	0.04
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seco-2-Dehydroabietic Acid								
0.00	0.47	0.50	0.48	0.02	0.47	0.50	0.48	0.02
1.00	0.68	0.63	0.65	0.03	0.65	0.62	0.63	0.02
2.00	1.53	1.40	1.46	0.09	0.89	0.58	0.74	0.22
5.00	0.91	0.93	0.92	0.01	0.63	0.70	0.66	0.05
7.00	1.41	1.34	1.38	0.05	1.47	0.90	1.18	0.40
14.00	0.15	1.27	0.71	0.79	0.91	0.87	0.89	0.03
21.00	1.28	1.00	1.14	0.20	0.66	0.80	0.73	0.10
28.00	0.33	0.41	0.37	0.05	0.40	0.40	0.40	0.00
42.00	0.20	0.23	0.21	0.02	0.32	0.37	0.35	0.04
56.00	0.14	0.20	0.17	0.04	0.24	0.28	0.26	0.03

84.00	0.18	0.25	0.22	0.06	0.29	0.28	0.29	0.01
112.00	0.00	0.10	0.05	0.07	0.14	0.18	0.16	0.03
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Abietanes								
0.00	7.83	7.44	7.64	0.37	7.83	7.44	7.64	0.37
1.00	24.42	23.56	23.99	0.61	25.76	21.73	23.75	2.85
2.00	18.47	17.70	18.09	0.54	14.74	30.81	22.77	12.08
5.00	14.89	18.94	16.92	2.86	16.98	13.89	15.43	2.38
7.00	12.84	12.50	12.67	0.24	18.05	11.22	14.64	4.83
14.00	12.33	13.00	12.67	1.10	9.98	9.55	9.77	0.30
21.00	9.53	16.91	13.22	6.19	2.86	7.05	4.96	2.97
28.00	5.28	7.87	6.58	1.84	4.55	5.05	4.80	0.36
42.00	3.48	5.48	4.48	1.48	3.69	4.57	4.13	0.63
56.00	5.17	6.07	5.62	0.63	3.07	3.19	3.13	0.09
84.00	3.53	6.04	4.78	1.78	2.81	3.61	3.21	0.68
112.00	2.23	2.61	2.42	0.30	1.73	2.28	2.00	0.39
168.00	2.03	2.83	2.43	0.57	0.13	0.11	0.12	0.01
7-Oxodehydroabietic Acid								
0.00	0.24	0.23	0.24	0.01	0.24	0.23	0.24	0.01
1.00	0.24	0.21	0.22	0.02	0.28	0.26	0.27	0.02
2.00	0.21	0.14	0.17	0.05	0.15	0.20	0.18	0.04
5.00	0.20	0.25	0.22	0.04	0.29	0.27	0.28	0.02
7.00	0.14	0.08	0.11	0.05	0.40	0.20	0.30	0.14
14.00	0.15	0.14	0.14	0.01	0.17	0.13	0.15	0.03
21.00	0.16	0.47	0.32	0.22	0.19	0.15	0.17	0.03
28.00	0.21	0.18	0.20	0.02	0.16	0.16	0.16	0.00
42.00	0.08	0.12	0.10	0.03	0.17	0.17	0.17	0.01
56.00	0.17	0.13	0.15	0.03	0.00	0.00	0.00	0.00
84.00	0.19	0.25	0.22	0.04	0.00	0.00	0.00	0.00
112.00	0.13	0.06	0.09	0.05	0.05	0.08	0.07	0.02
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietin								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.02	0.02	0.02	0.00	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.01	0.01	0.01	0.00	0.02	0.01	0.01	0.00
14.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.00
21.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Retene								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.02	0.03	0.02	0.01	0.02	0.01	0.02	0.01
14.00	0.02	0.02	0.02	0.00	0.02	0.02	0.02	0.00
21.00	0.02	0.01	0.02	0.01	0.00	0.00	0.00	0.00
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methyldehydroabietin								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.11	0.09	0.10	0.01	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

7.00	0.06	0.11	0.08	0.03	0.04	0.02	0.03	0.01
14.00	0.00	0.00	0.00	0.00	0.02	0.03	0.03	0.00
21.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Diterpenes								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.12	0.11	0.12	0.01	0.00	0.00	0.00	0.00
5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.00	0.08	0.15	0.12	0.05	0.08	0.04	0.06	0.03
14.00	0.03	0.03	0.03	0.01	0.04	0.06	0.05	0.01
21.00	0.02	0.01	0.02	0.01	0.00	0.00	0.00	0.00
28.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytosterols								
Cholesterol								
0.00	1.23	1.48	1.36	0.18	1.23	1.48	1.36	0.18
1.00	2.13	2.21	2.17	0.06	2.29	2.69	2.49	0.28
2.00	0.87	0.79	0.83	0.06	1.14	1.68	1.41	0.38
5.00	1.85	1.96	1.90	0.07	2.23	2.17	2.20	0.04
7.00	1.37	1.54	1.46	0.12	1.60	1.34	1.47	0.19
14.00	1.24	1.08	1.16	0.11	0.94	1.17	1.05	0.16
21.00	1.11	2.54	1.82	1.01	1.78	1.32	1.55	0.33
28.00	1.42	1.20	1.31	0.15	1.34	1.31	1.33	0.03
42.00	1.86	1.31	1.59	0.39	1.65	1.70	1.68	0.03
56.00	1.96	1.25	1.61	0.50	0.94	1.16	1.05	0.16
84.00	3.24	3.45	3.34	0.15	1.90	1.82	1.86	0.06
112.00	1.64	1.41	1.52	0.16	1.45	1.41	1.43	0.03
168.00	1.20	1.13	1.16	0.05	1.67	1.55	1.61	0.09
Campesterol								
0.00	0.79	1.01	0.90	0.15	0.79	1.01	0.90	0.15
1.00	1.39	1.63	1.51	0.17	1.32	1.49	1.41	0.12
2.00	1.00	0.91	0.96	0.07	0.67	1.01	0.84	0.24
5.00	1.16	1.53	1.35	0.26	1.44	1.80	1.62	0.25
7.00	1.08	1.13	1.10	0.04	1.26	1.34	1.30	0.05
14.00	0.79	0.83	0.81	0.03	0.78	0.99	0.88	0.15
21.00	0.79	1.88	1.33	0.77	0.89	1.01	0.95	0.08
28.00	1.13	7.67	4.40	4.63	1.14	1.23	1.18	0.06
42.00	1.09	1.16	1.13	0.05	1.00	1.28	1.14	0.19
56.00	0.82	1.08	0.95	0.18	0.94	1.16	1.05	0.16
84.00	1.55	2.05	1.80	0.35	0.93	1.31	1.12	0.27
112.00	1.46	1.44	1.45	0.01	0.73	1.01	0.87	0.20
168.00	0.52	0.60	0.56	0.06	0.83	0.76	0.80	0.05
Stigmasterol								
0.00	1.93	2.04	1.99	0.08	1.93	2.04	1.99	0.08
1.00	2.28	2.13	2.21	0.11	2.27	2.05	2.16	0.15
2.00	1.30	1.12	1.21	0.12	1.20	1.22	1.21	0.01
5.00	2.07	2.42	2.24	0.25	2.24	2.38	2.31	0.10
7.00	1.42	1.77	1.60	0.25	2.25	1.52	1.88	0.51
14.00	1.76	1.52	1.64	0.17	1.81	1.52	1.66	0.21
21.00	1.42	3.25	2.34	1.29	1.92	1.67	1.79	0.18
28.00	1.78	1.47	1.63	0.22	1.99	1.82	1.90	0.12
42.00	1.72	1.66	1.69	0.05	1.75	1.94	1.85	0.13
56.00	1.72	1.83	1.77	0.08	1.64	1.50	1.57	0.09
84.00	3.44	3.78	3.61	0.24	1.86	2.62	2.24	0.54
112.00	1.46	1.44	1.45	0.01	1.54	1.59	1.56	0.04
168.00	1.66	1.65	1.66	0.01	1.72	2.05	1.88	0.23

Sitosterol								
0.00	6.53	6.79	6.66	0.18	6.53	6.79	6.66	0.18
1.00	10.54	11.79	11.17	0.89	9.99	11.26	10.62	0.90
2.00	5.92	5.23	5.57	0.49	5.28	6.36	5.82	0.77
5.00	8.88	12.55	10.71	2.59	9.10	11.25	10.17	1.52
7.00	8.09	7.76	7.92	0.23	9.95	6.04	7.99	2.77
14.00	6.59	6.09	6.34	0.35	4.93	5.40	5.16	0.34
21.00	4.97	12.39	8.68	5.25	6.21	5.60	5.90	0.43
28.00	7.09	5.97	6.53	0.79	6.11	6.65	6.38	0.39
42.00	7.11	6.42	6.76	0.49	5.79	7.43	6.61	1.16
56.00	6.22	6.84	6.53	0.44	5.19	5.23	5.21	0.03
84.00	10.11	10.93	10.52	0.58	5.50	8.35	6.92	2.02
112.00	5.34	4.78	5.06	0.40	4.76	5.91	5.34	0.81
168.00	4.14	4.77	4.46	0.45	4.92	6.41	5.67	1.05
Phytosterols								
0.00	10.49	11.33	10.91	0.59	10.49	11.33	10.91	0.59
1.00	16.35	17.77	17.06	1.23	15.87	17.49	16.68	1.45
2.00	9.09	8.04	8.57	0.74	8.28	10.27	9.27	1.40
5.00	13.96	18.46	16.21	3.18	15.00	17.60	16.30	1.91
7.00	11.95	12.20	12.07	0.64	15.06	10.23	12.65	3.52
14.00	10.38	9.53	9.95	0.67	8.45	9.08	8.77	0.85
21.00	8.29	20.05	14.17	8.31	10.79	9.59	10.19	1.02
28.00	11.42	16.32	13.87	5.79	10.58	11.00	10.79	0.59
42.00	11.78	10.55	11.17	0.97	10.20	12.35	11.27	1.52
56.00	10.72	11.00	10.86	1.20	8.70	9.06	8.88	0.44
84.00	18.34	20.21	19.27	1.32	10.18	14.09	12.14	2.89
112.00	9.89	9.07	9.48	0.58	8.48	9.92	9.20	1.08
168.00	7.52	8.15	7.83	0.57	9.15	10.76	9.95	1.42
Sitostanol								
0.00	0.80	1.05	0.93	0.17	0.80	1.05	0.93	0.17
1.00	1.78	1.80	1.79	0.02	1.56	1.59	1.58	0.02
2.00	0.93	0.68	0.81	0.18	0.81	0.93	0.87	0.08
5.00	1.62	1.92	1.77	0.21	1.52	1.75	1.63	0.16
7.00	1.40	1.21	1.30	0.13	1.30	0.71	1.00	0.42
14.00	1.13	0.94	1.04	0.13	0.72	0.72	0.72	0.00
21.00	0.71	1.55	1.13	0.59	1.03	0.69	0.86	0.24
28.00	1.11	1.01	1.06	0.07	0.87	1.00	0.93	0.09
42.00	1.24	1.14	1.19	0.07	0.89	1.07	0.98	0.12
56.00	1.04	1.12	1.08	0.06	0.90	0.88	0.89	0.01
84.00	1.47	1.71	1.59	0.17	0.89	1.16	1.02	0.19
112.00	1.03	0.70	0.87	0.23	0.84	1.07	0.95	0.16
168.00	0.67	0.70	0.68	0.02	0.91	1.36	1.14	0.32

Dry weights of samples

Day		Dry Weight Factors
Day Zero		
	1.00	0.75
	2.00	0.75
	3.00	0.78
	4.00	0.79
	5.00	0.82
	6.00	0.80
	7.00	0.76
	8.00	0.77
	9.00	0.61
	10.00	0.61
	11.00	0.66
	12.00	0.61
	13.00	0.59
	14.00	0.64
	15.00	0.65
	16.00	0.61
	17.00	0.64
	18.00	0.60
	19.00	0.69
	20.00	0.60
	21.00	0.61
	22.00	0.64
	23.00	0.63
	24.00	0.67
Day 1		
5a		0.77
5b		0.76
6a		0.92
6b		0.76
13a		0.71
13b		0.65
14a		0.73
14b		0.67
21a		0.70
21b		0.63
22a		0.70
22b		0.62
Day 2		
5a		0.74
5b		0.76
6a		0.77
6b		0.77
13a		0.60
13b		0.66
14a		0.64
14b		0.66
21a		0.58
21b		0.63
22a		0.62
22b		0.61
Day 3		
5a		0.79
5b		0.78
6a		0.80
6b		0.79
13a		0.62
13b		0.67
14a		0.64
14b		0.66
21a		0.66
21b		0.62
22a		0.65

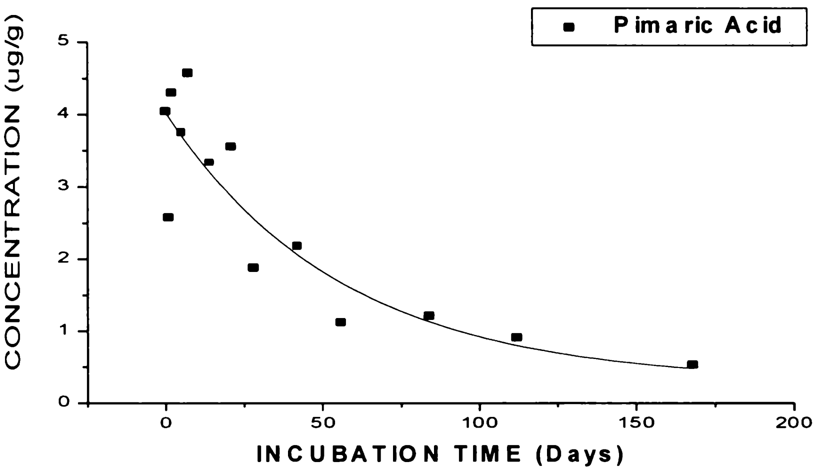
22b	0.63
Day 4	
5a	0.92
5b	0.80
6a	0.84
6b	0.74
13a	0.65
13b	0.66
14a	0.68
14b	0.67
21a	0.74
21b	0.43
22a	0.65
22b	0.62
Day 5	
5a	1.00
5b	0.79
6a	0.94
6b	0.79
13a	0.68
13b	0.69
14a	0.69
14b	0.64
21a	0.70
21b	0.63
22a	0.72
22b	0.63
Day 6	
5a	1.00
5b	0.79
6a	1.00
6b	0.78
13a	0.75
13b	0.65
14a	0.71
14b	0.65
21a	0.86
21b	0.64
22a	0.76
22b	0.64
Day 7	
5a	0.75
5b	0.81
6a	0.81
6b	0.77
13a	0.67
13b	0.66
14a	0.65
14b	0.65
21a	0.59
21b	0.62
22a	0.65
22b	0.64
Day 8	
5a	0.75
5b	0.80
6a	0.98
6b	0.77
13a	0.73
13b	0.66
14a	0.71
14b	0.66
21a	0.63
21b	0.64

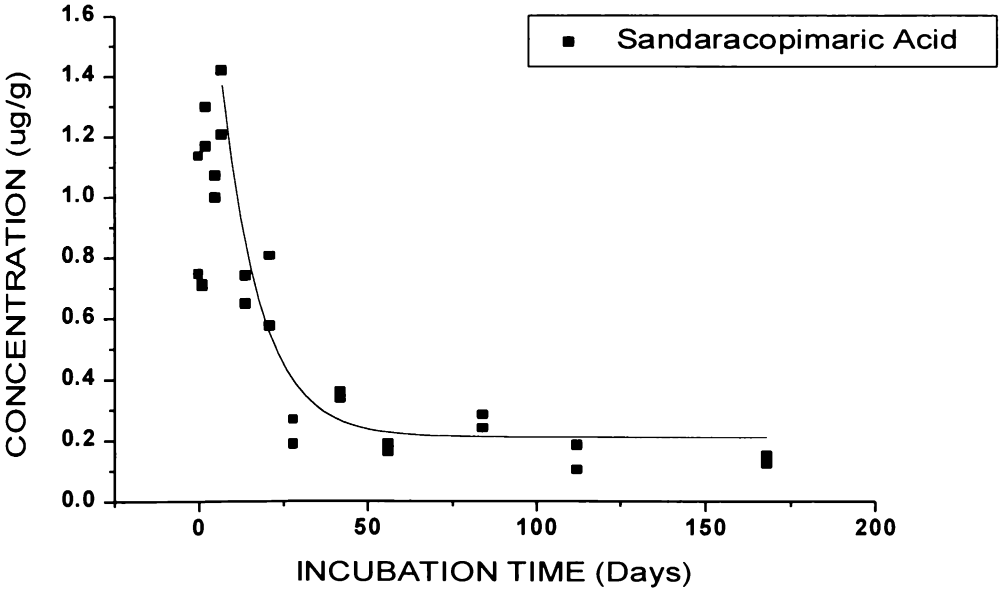
22a	0.70
22b	0.62
Day 9	
5a	0.82
5b	0.79
6a	0.73
6b	0.76
13a	0.70
13b	0.66
14a	0.72
14b	0.69
21a	0.63
21b	0.65
22a	0.65
22b	0.63
Day 10	
5a	0.84
5b	0.80
6a	0.81
6b	0.78
13a	0.71
13b	0.68
14a	0.67
14b	0.68
21a	0.68
21b	0.64
22a	0.73
22b	0.66
Day 11	
5a	0.99
5b	0.76
6a	0.88
6b	0.77
13a	0.91
13b	0.69
14a	0.74
14b	0.70
21a	0.67
21b	0.64
22a	0.59
22b	0.63
Day 12	
1a	0.86
1b	0.71
2a	0.82
2b	0.79
3a	0.86
3b	0.76
4a	0.89
4b	0.80
5a	0.81
5b	0.83
6a	0.78
6b	0.81
7a	0.92
7b	0.83
8a	0.93
8b	0.80
9a	0.79
9b	0.67
10a	0.82
10b	0.71
11a	0.82
11b	0.69
12a	0.81

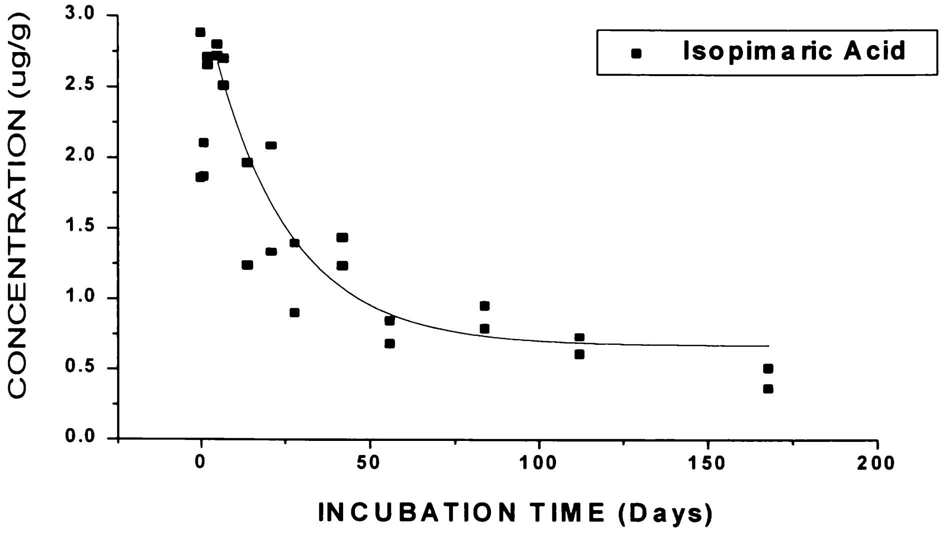
12b	0.69
13a	0.79
13b	0.71
14a	0.81
14b	0.71
15a	0.75
15b	0.66
16a	0.77
16b	0.67
17a	0.67
17b	0.62
18a	0.73
18b	0.65
19a	0.74
19b	0.62
20a	0.73
20b	0.67
21a	0.73
21b	0.66
22a	0.72
22b	0.65
23a	0.73
23b	0.61
24a	0.67
24b	0.62

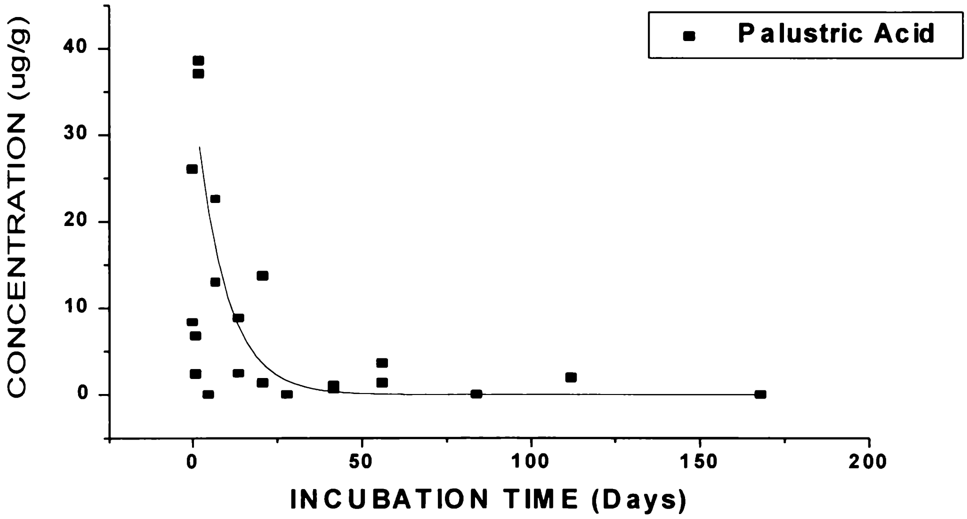
Degradation Curve Data for the Degradation Experiment.

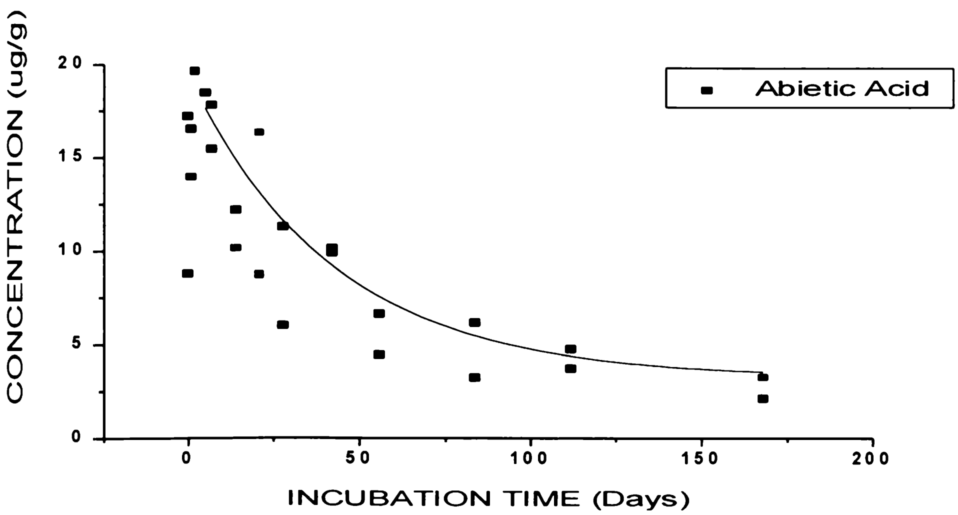
Aerobic Sand and Thermomechanical Pulping Effluent Incubations

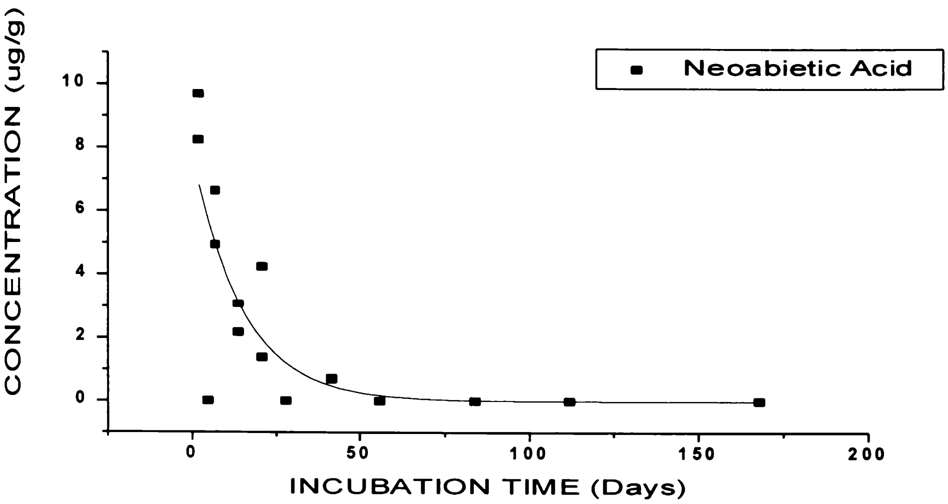


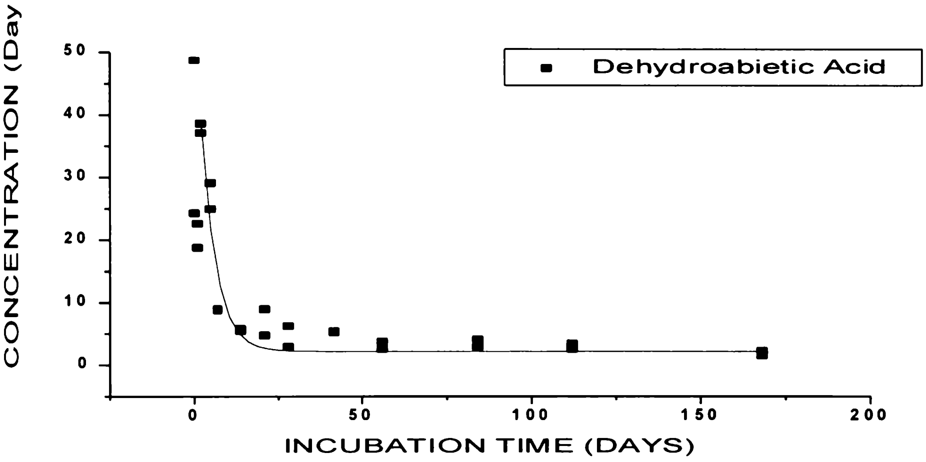


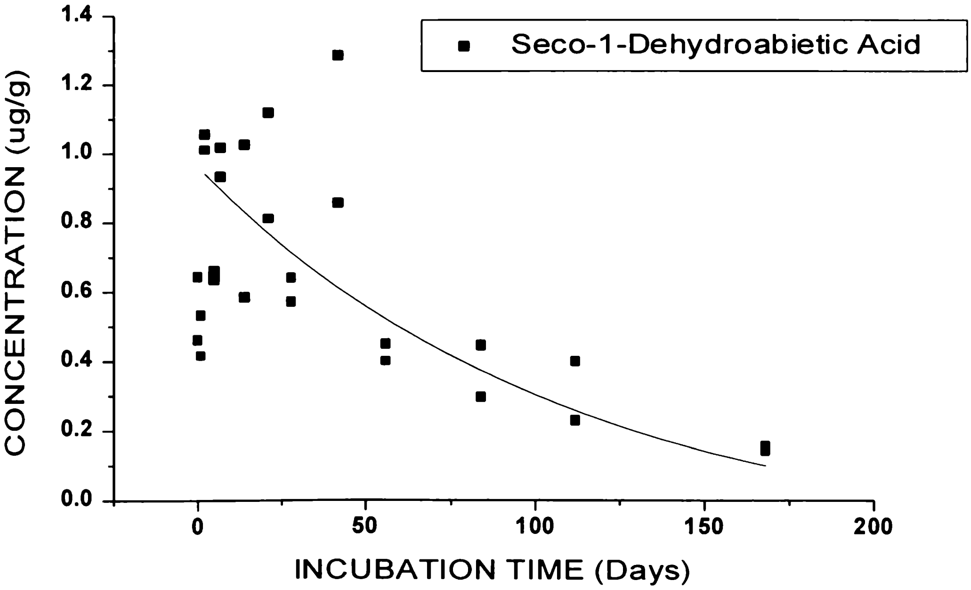

CONCENTRATION (ug/g)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
INCUBATION TIME (Days)
Isopimaric Acid

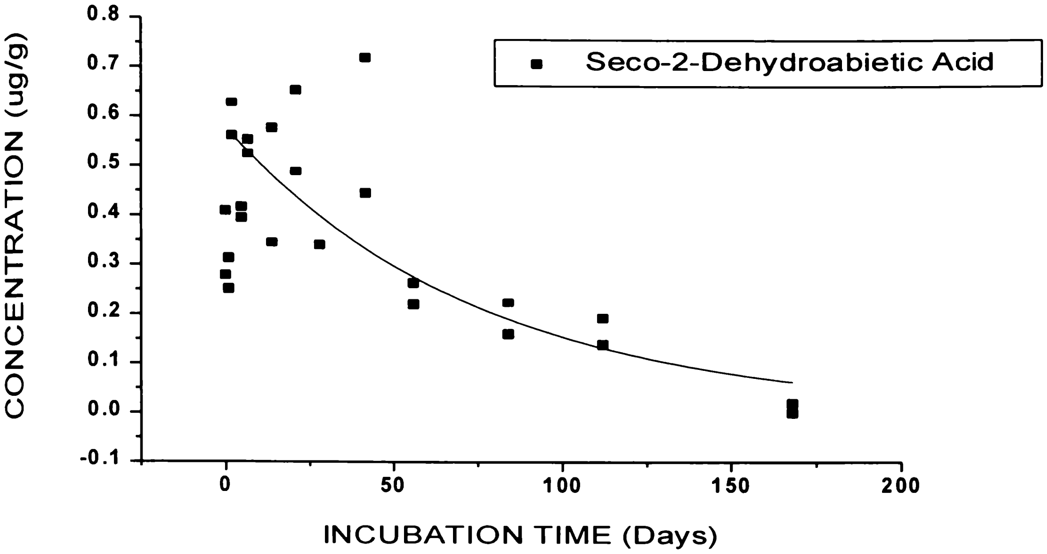

CONCENTRATION (ug/g)
40
30
20
10
0
0
50
100
150
200
INCUBATION TIME (Days)
Palustric Acid

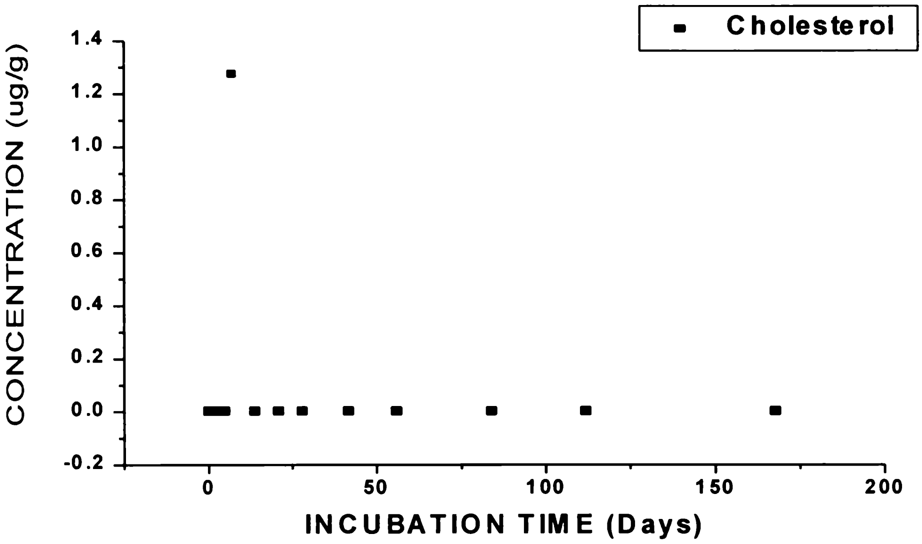

CONCENTRATION (ug/g)
20
15
10
5
0
0
50
100
150
200
INCUBATION TIME (Days)
Abietic Acid

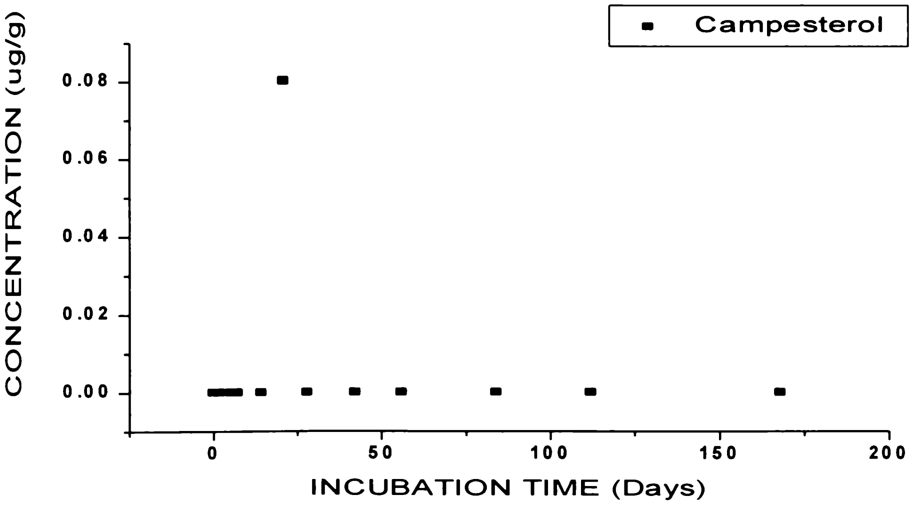

CONCENTRATION (ug/g)
10
8
6
4
2
0
0
50
100
150
200
INCUBATION TIME (Days)
■ Neoabietic Acid

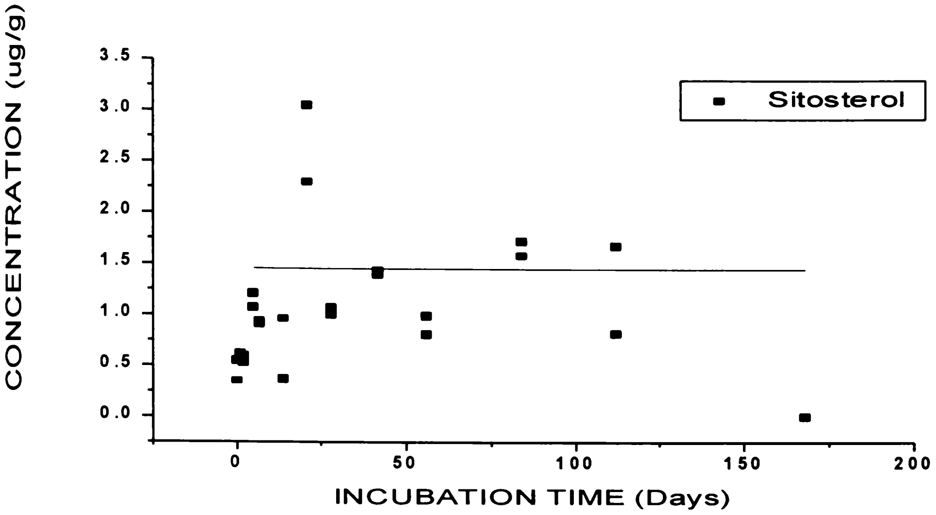

CONCENTRATION (Day
50
40
30
20
10
0
0
50
100
150
200
INCUBATION TIME (DAYS)
■ Dehydroabietic Acid


CONCENTRATION (ug/g)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
INCUBATION TIME (Days)
■ Seco-1-Dehydroabietic Acid

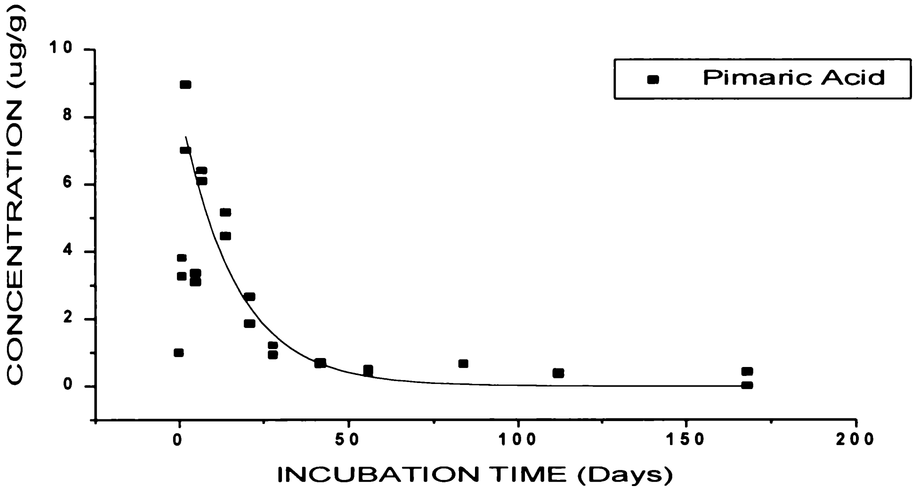

CONCENTRATION (ug/g)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0
50
100
150
200
INCUBATION TIME (Days)
Seco-2-Dehydroabietic Acid

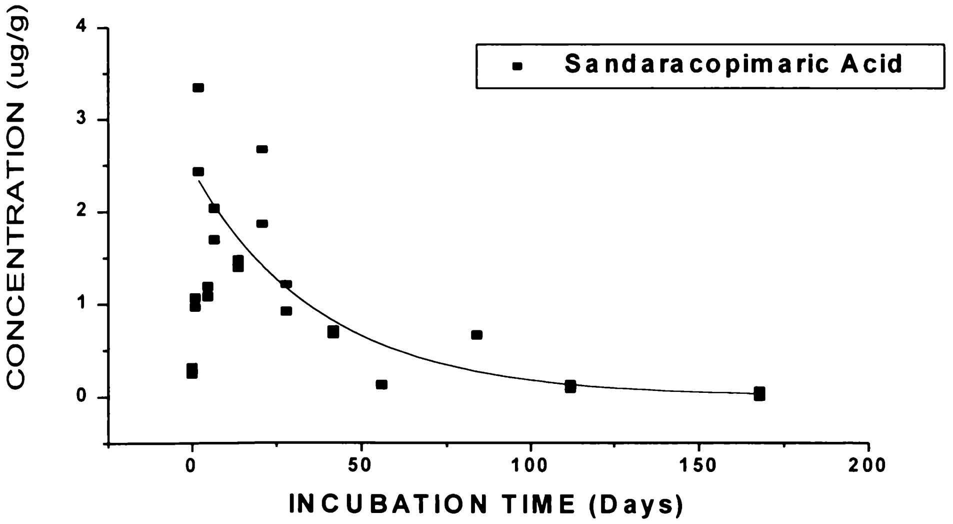

CONCENTRATION (ug/g)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
0
50
100
150
200
INCUBATION TIME (Days)
Cholesterol

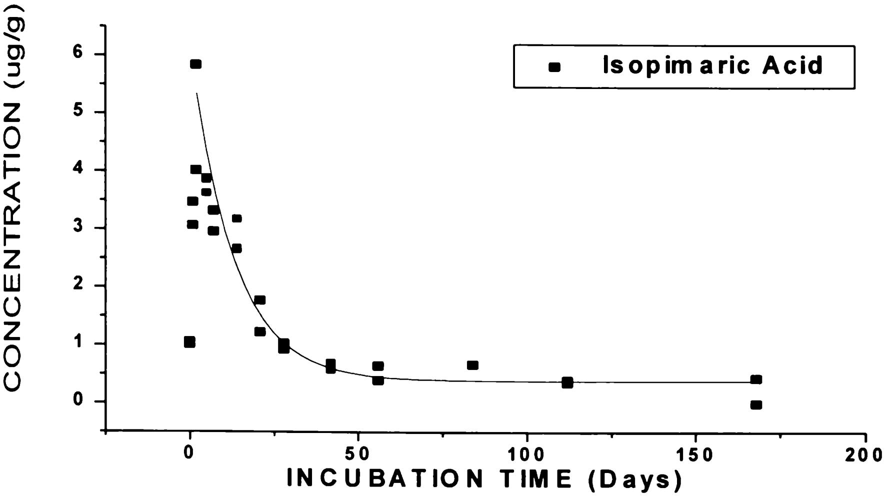

CONCENTRATION (ug/g)
0.08
0.06
0.04
0.02
0.00
0
50
100
150
200
INCUBATION TIME (Days)
Campesterol

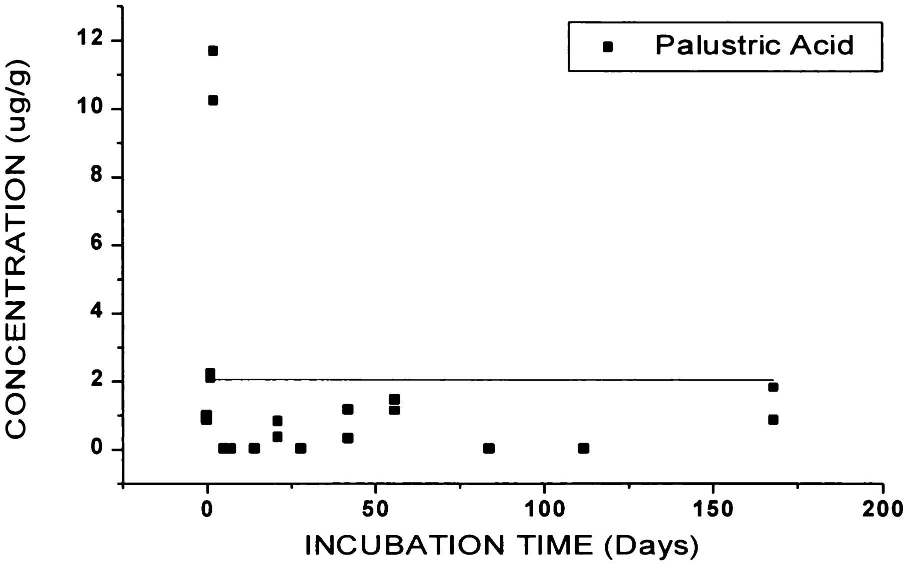


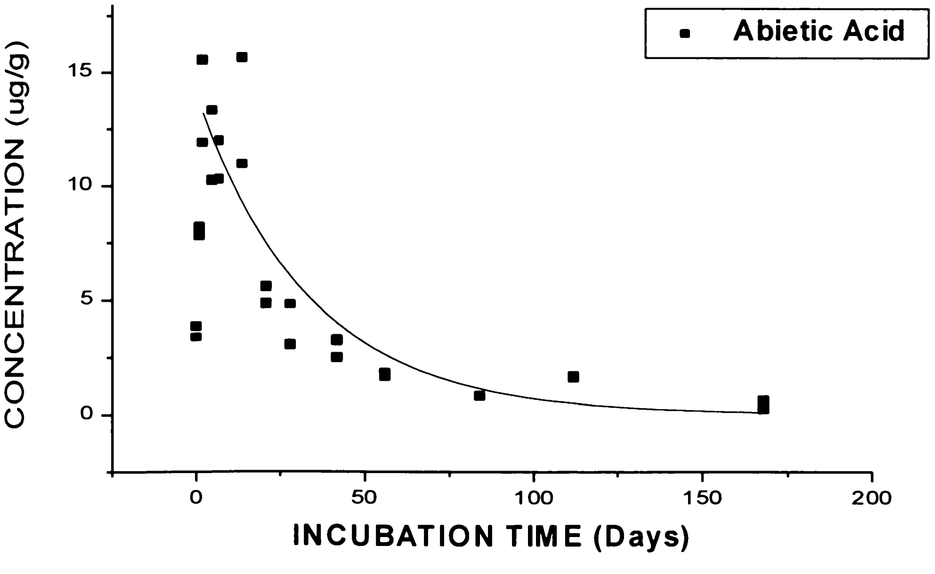
Aerobic Kawerau Loamy Sand and Thermomechanical Pulping Effluent Incubations

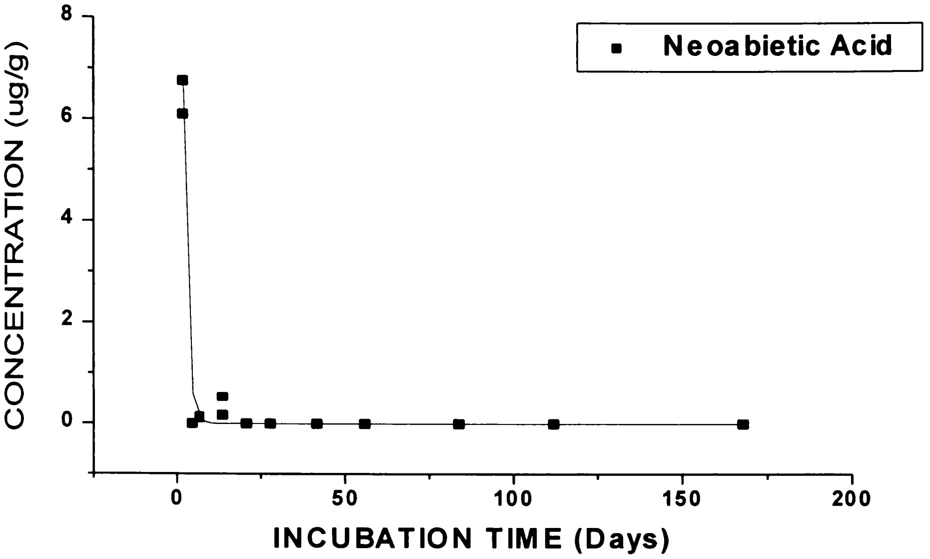


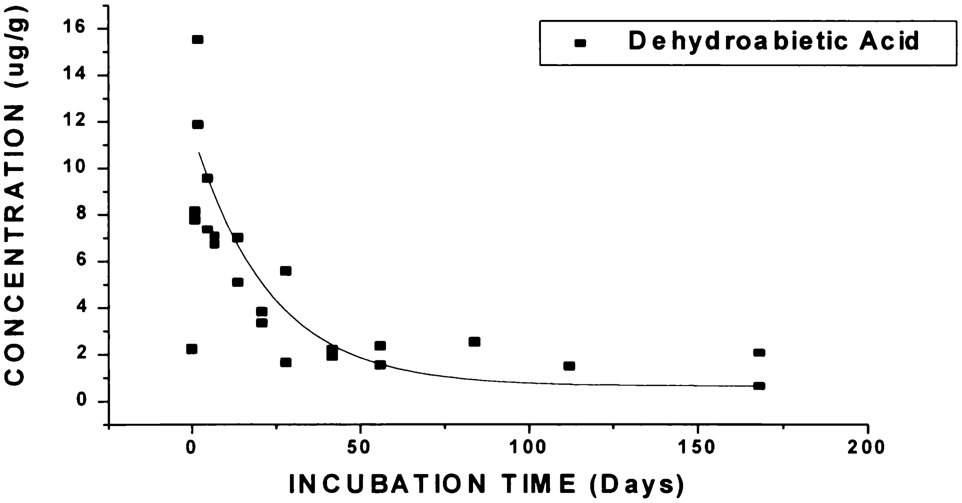


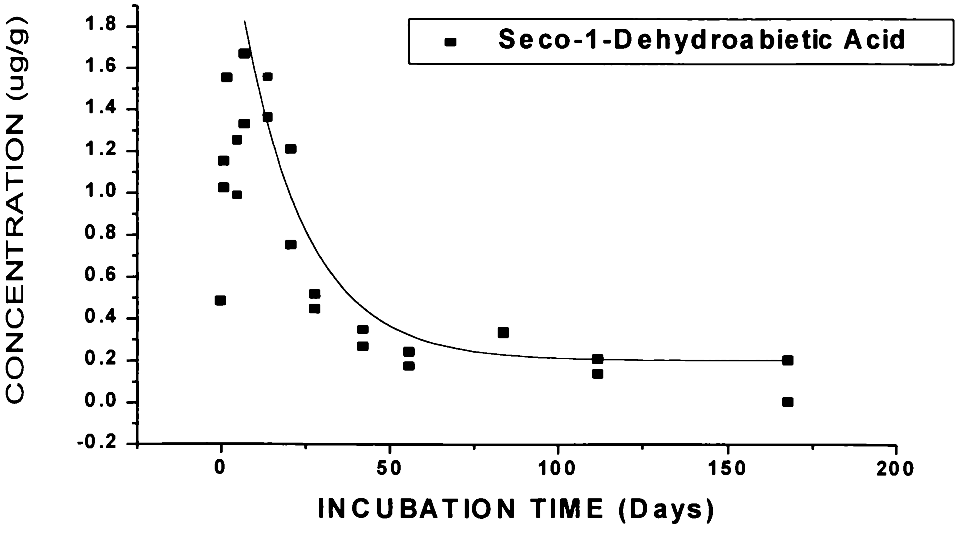

CONCENTRATION (ug/g)
INCUBATION TIME (Days)
Isopimaric Acid
0
1
2
3
4
5
6
0
50
100
150
200

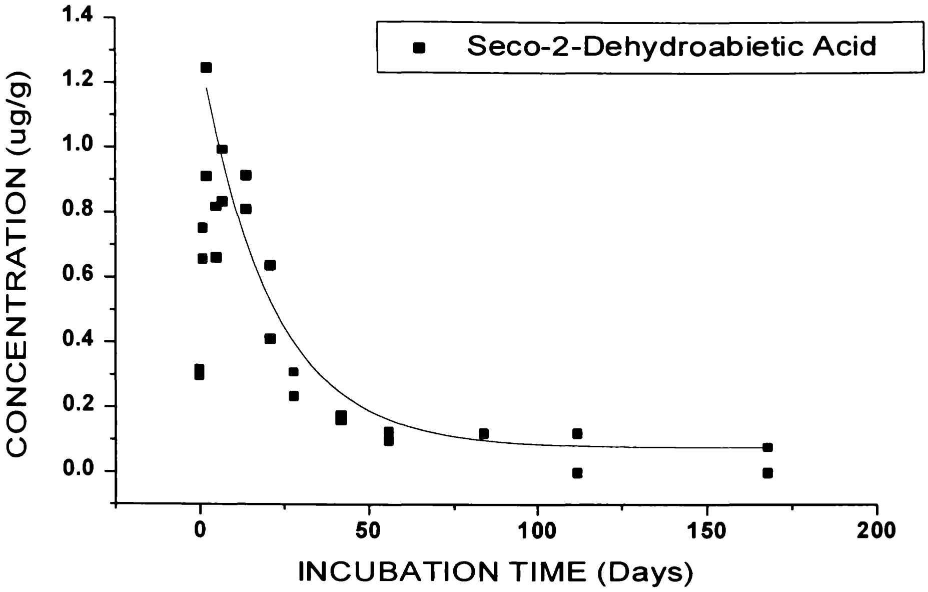

CONCENTRATION (ug/g)
INCUBATION TIME (Days)
Palustric Acid
0
2
4
6
8
10
12
0
50
100
150
200

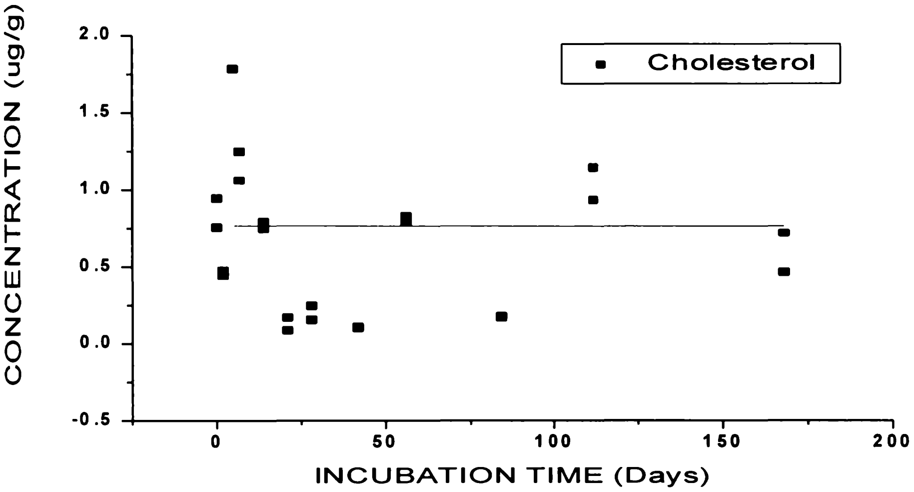

CONCENTRATION (ug/g)
INCUBATION TIME (Days)
Abietic Acid
0
5
10
15
0
50
100
150
200

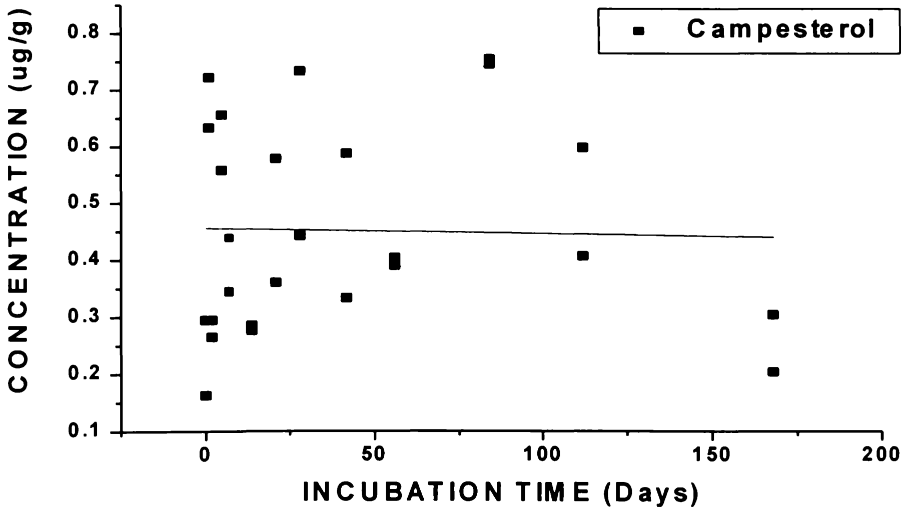

Neoabietic Acid
CONCENTRATION (ug/g)
8
6
4
2
0
0
50
100
150
200
INCUBATION TIME (Days)

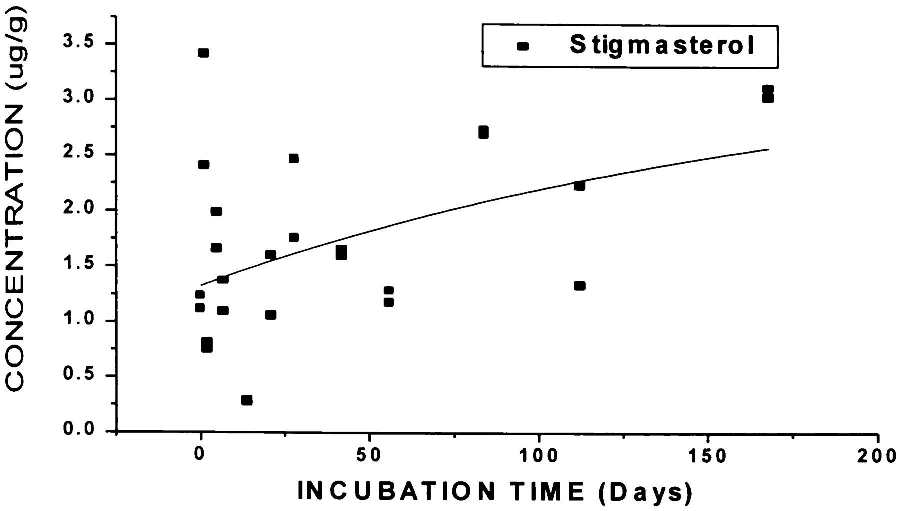

Dehydroabietic Acid
CONCENTRATION (ug/g)
16
14
12
10
8
6
4
2
0
0
50
100
150
200
INCUBATION TIME (Days)

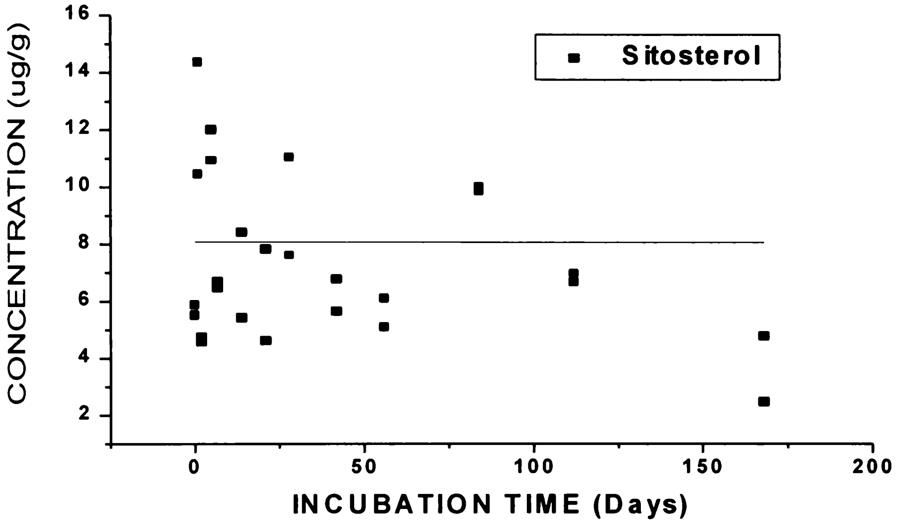

Seco-1-Dehydroabietic Acid
CONCENTRATION (ug/g)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
0
50
100
150
200
INCUBATION TIME (Days)


■ Seco-2-Dehydroabietic Acid
CONCENTRATION (ug/g)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
INCUBATION TIME (Days)

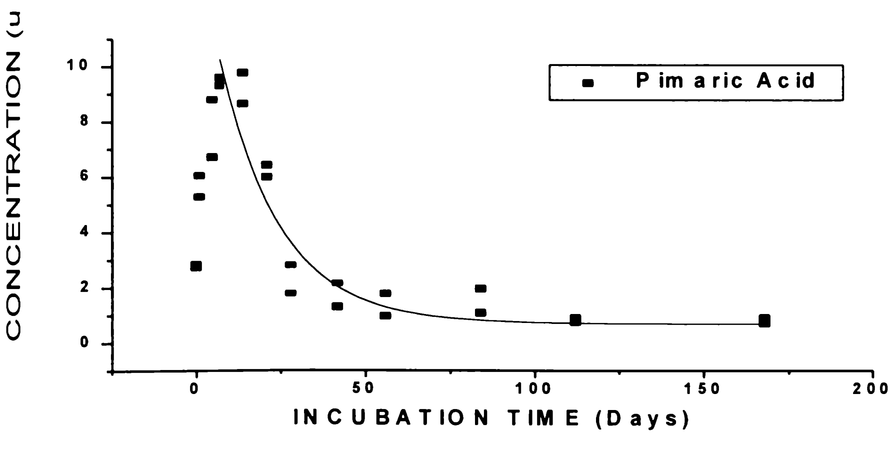

■ Cholesterol
CONCENTRATION (ug/g)
2.0
1.5
1.0
0.5
0.0
-0.5
0
50
100
150
200
INCUBATION TIME (Days)

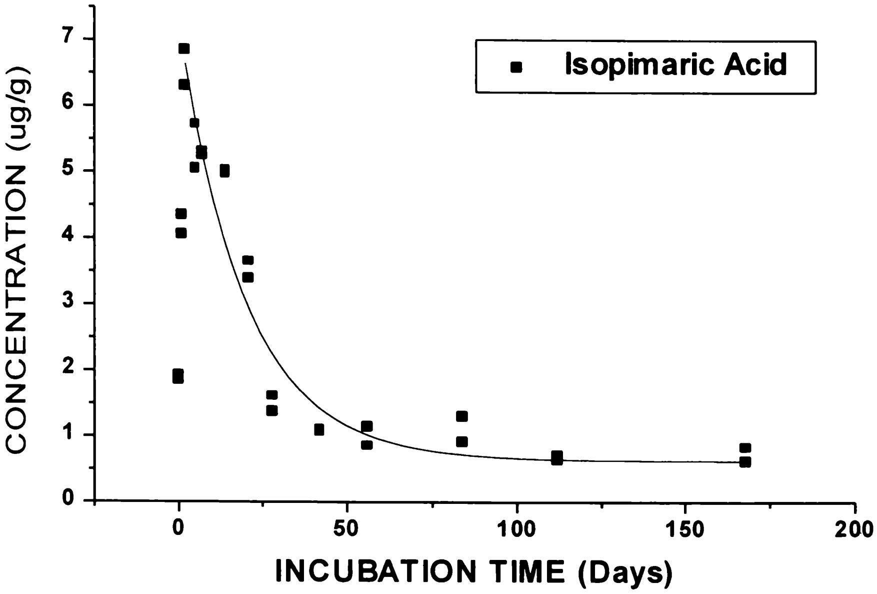

■ Campesterol
CONCENTRATION (ug/g)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
100
150
200
INCUBATION TIME (Days)

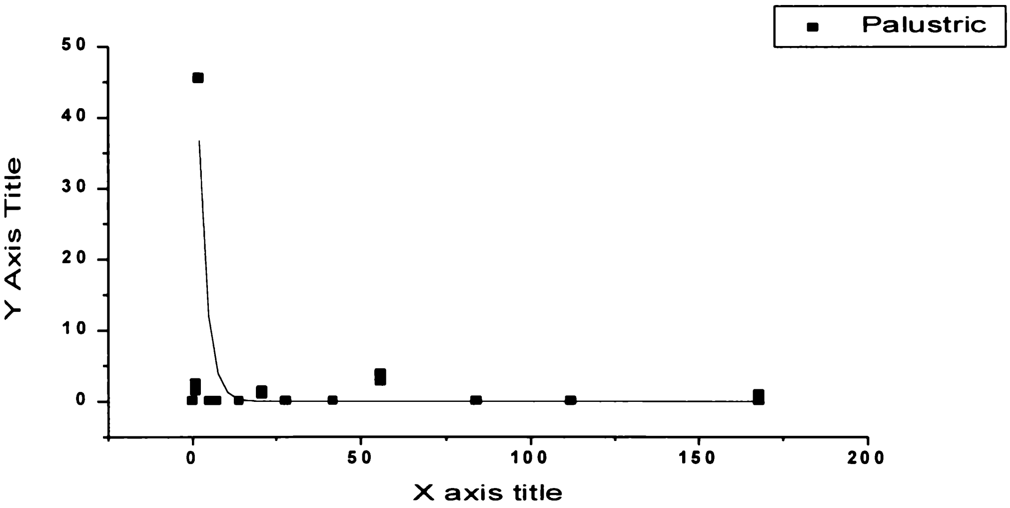


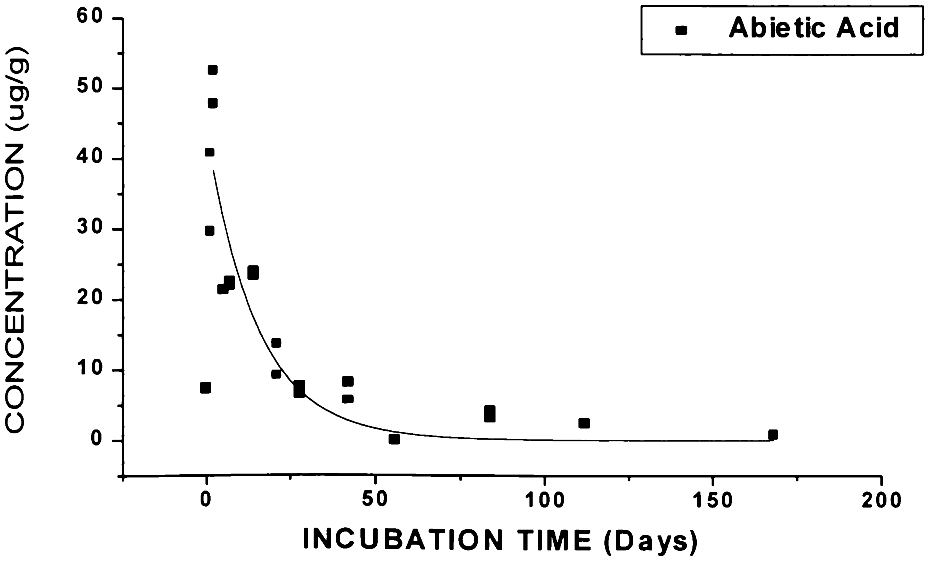


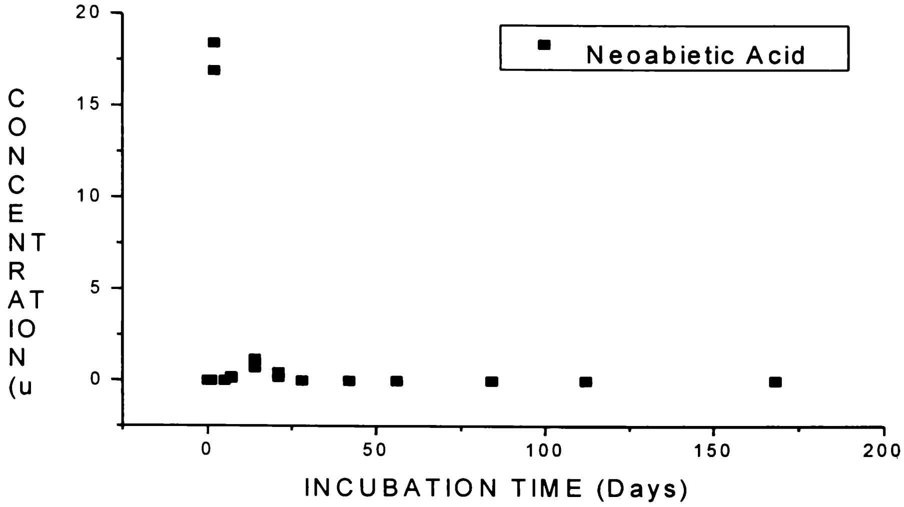
Aerobic Whakarewarewa Sandy Loam and Thermomechanical Pulping Effluent Incubations

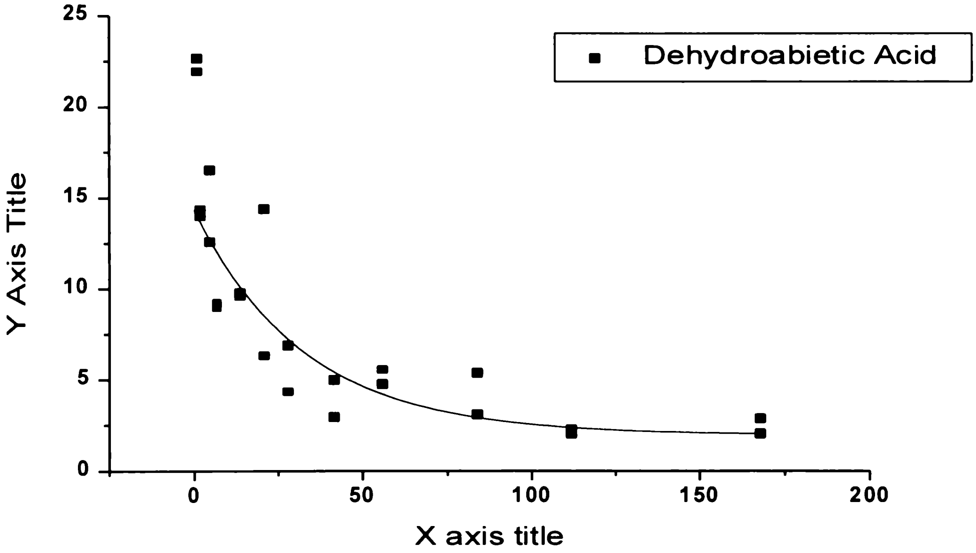


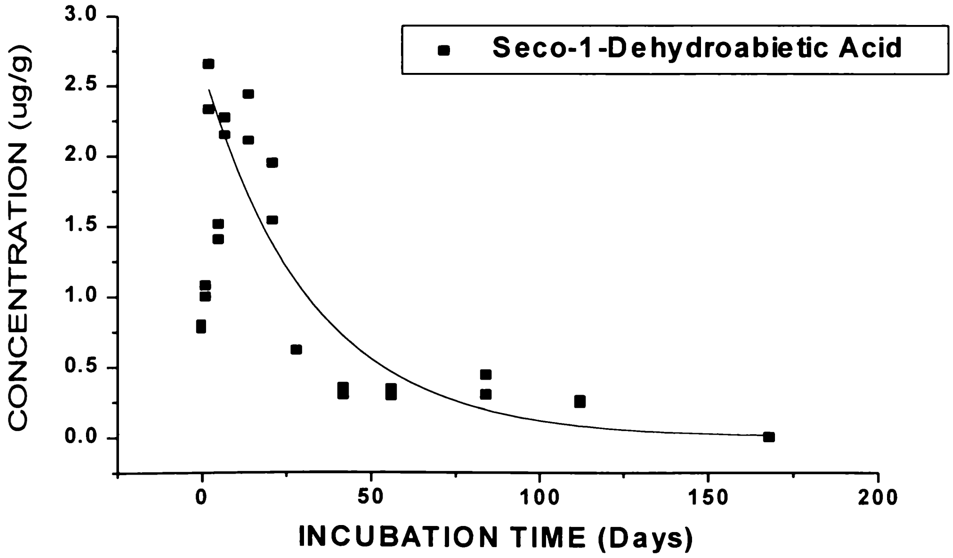

■ Isopimaric Acid
CONCENTRATION (ug/g)
0
1
2
3
4
5
6
7
0
50
100
150
200
INCUBATION TIME (Days)

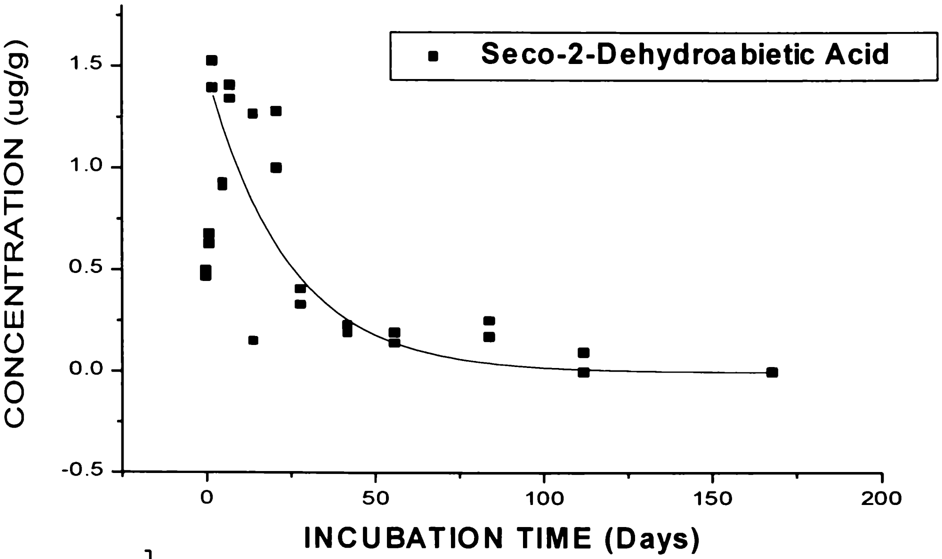

■ Palustric
Y Axis Title
50
40
30
20
10
0
0
50
100
150
200
X axis title

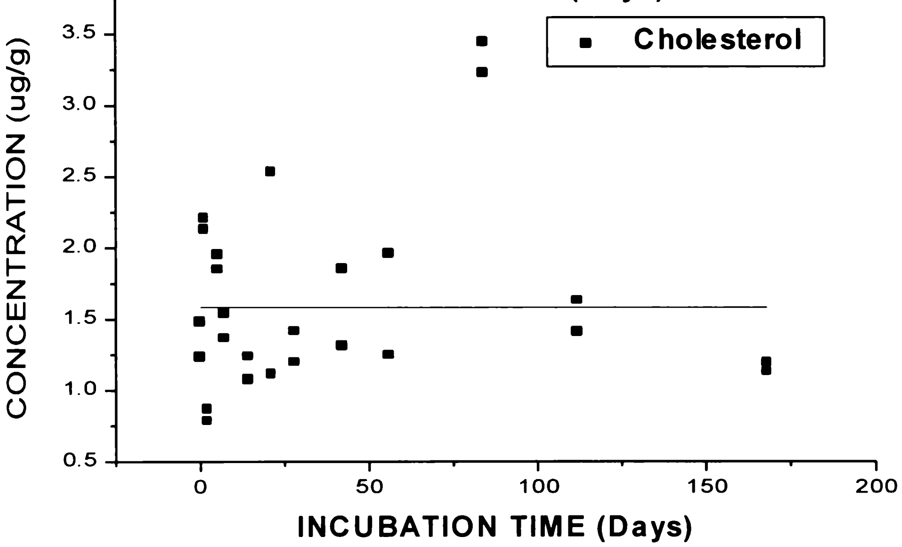

■ Abietic Acid
CONCENTRATION (ug/g)
60
50
40
30
20
10
0
0
50
100
150
200
INCUBATION TIME (Days)

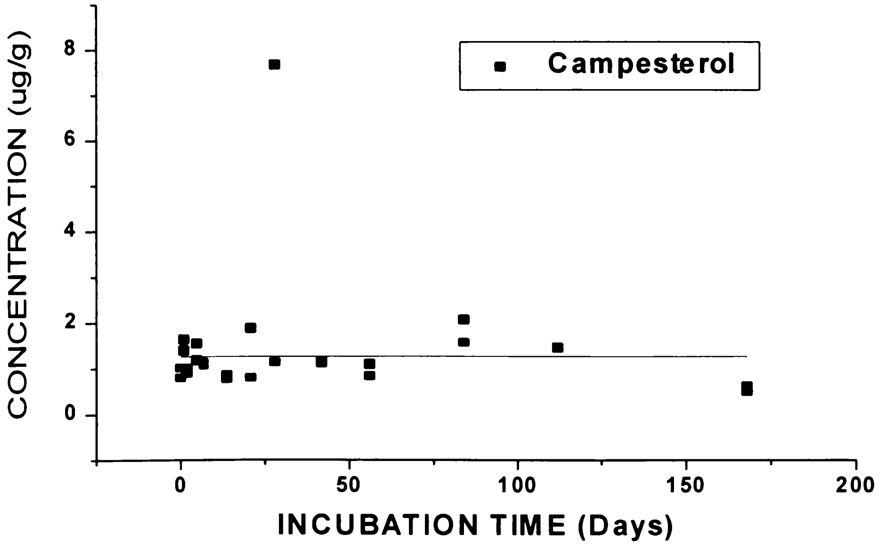

Neoabietic Acid
CONCENTRATION (u
20
15
10
5
0
0
50
100
150
200
INCUBATION TIME (Days)

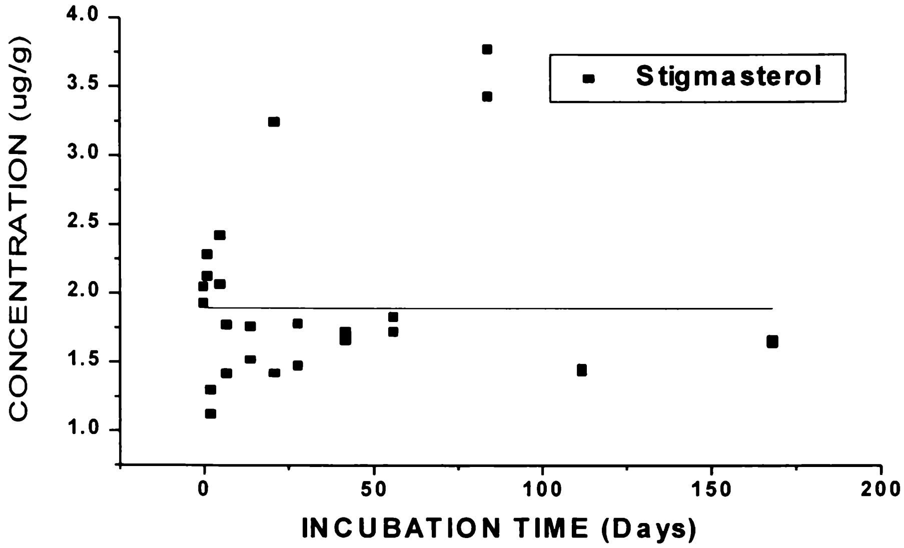

Dehydroabietic Acid
Y Axis Title
25
20
15
10
5
0
0
50
100
150
200
X axis title

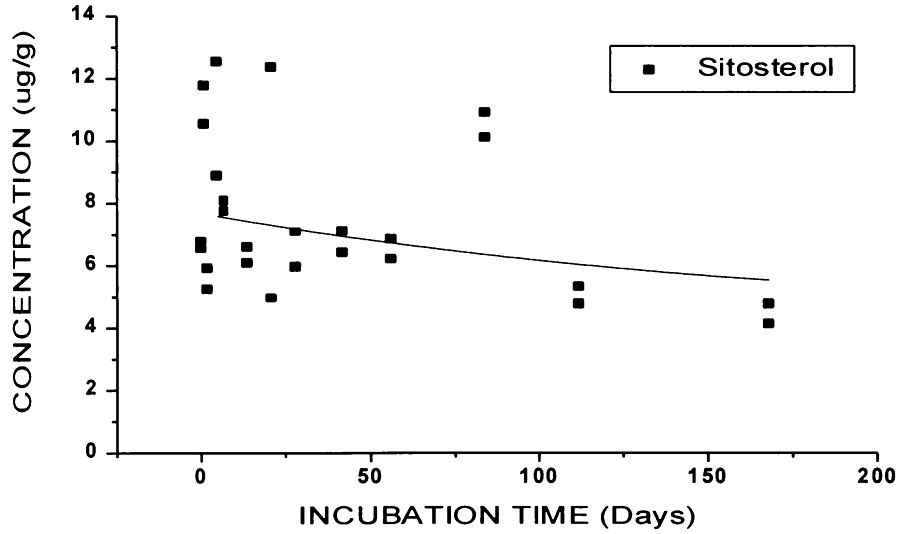

Seco-1-Dehydroabietic Acid
CONCENTRATION (ug/g)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
INCUBATION TIME (Days)


Seco-2-Dehydroabietic Acid
CONCENTRATION (ug/g)
1.5
1.0
0.5
0.0
-0.5
0
50
100
150
200
INCUBATION TIME (Days)

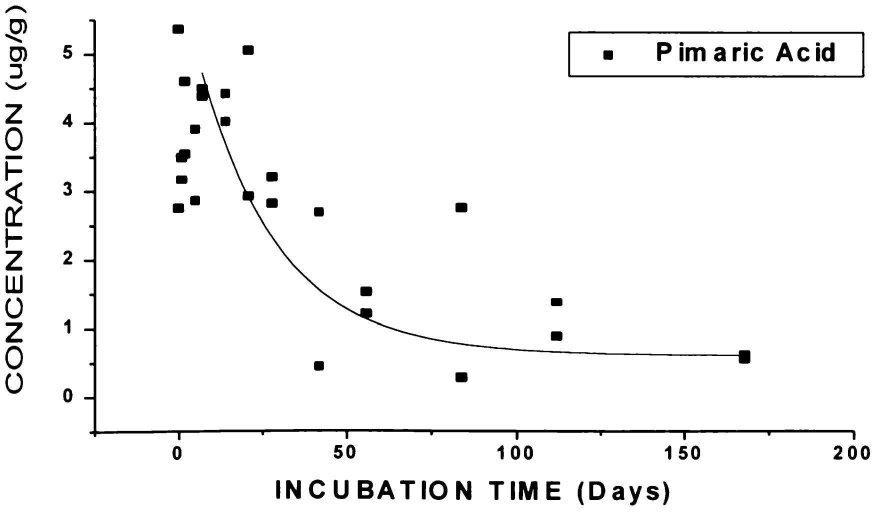

Cholesterol
CONCENTRATION (ug/g)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
50
100
150
200
INCUBATION TIME (Days)

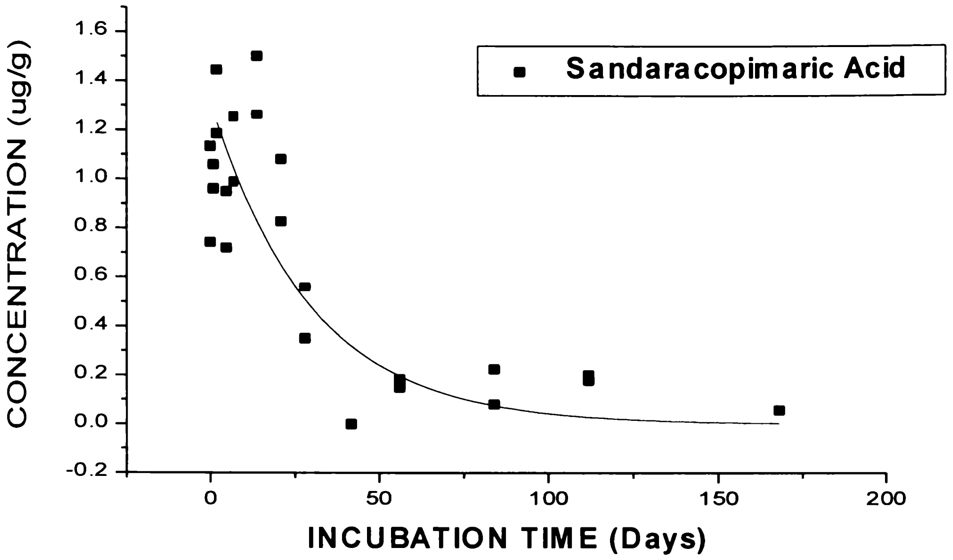

Campesterol
CONCENTRATION (ug/g)
8
6
4
2
0
0
50
100
150
200
INCUBATION TIME (Days)

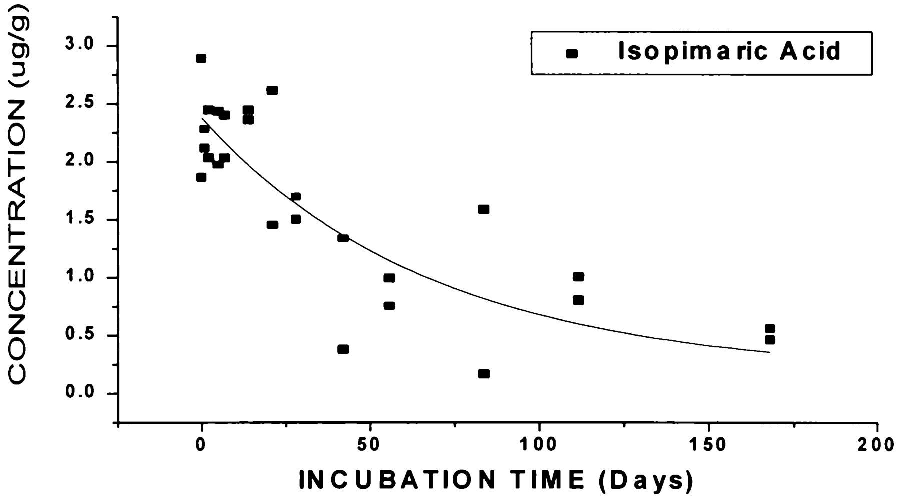


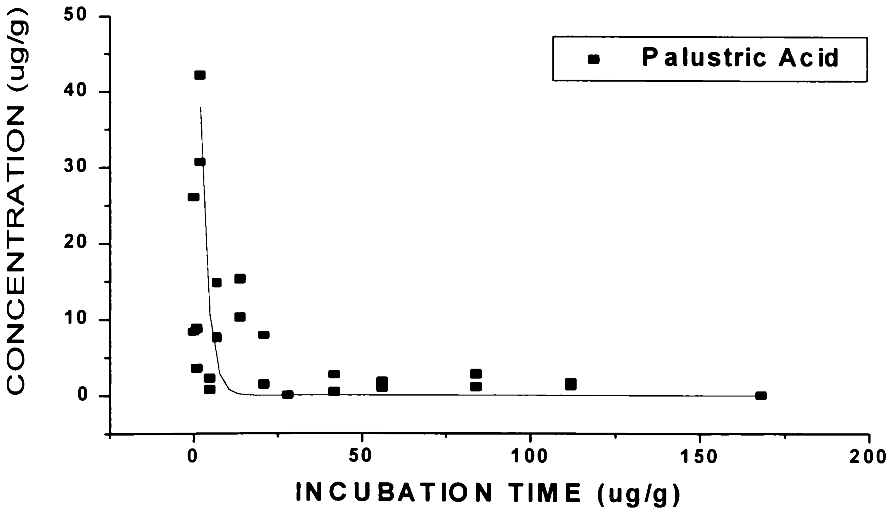


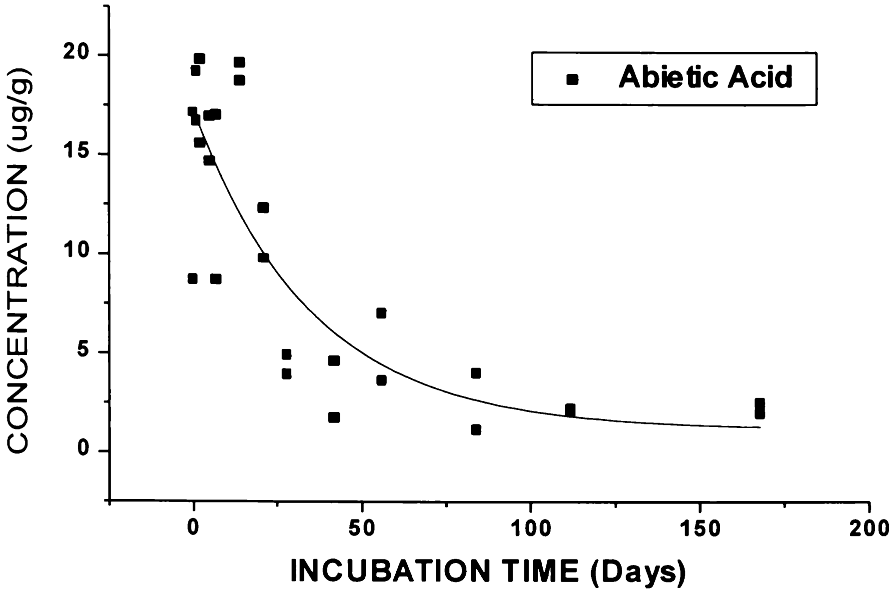
Anaerobic Sand and Thermomechanical Pulping Effluent Incubations

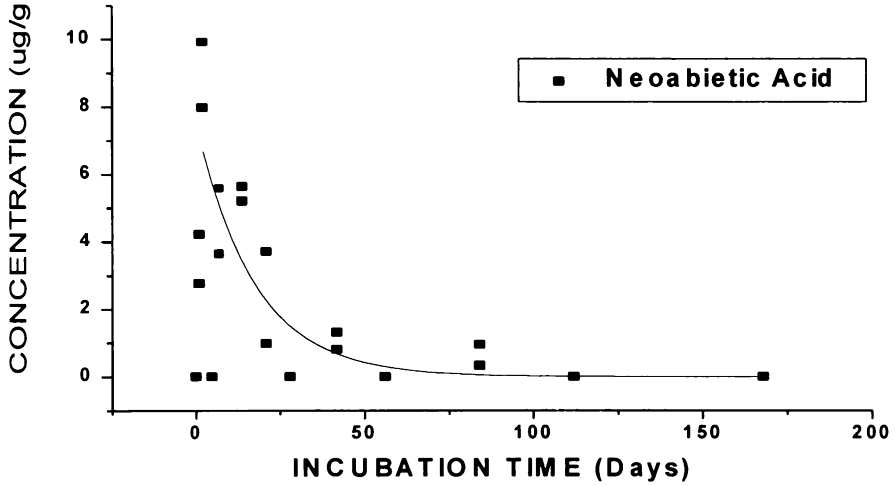


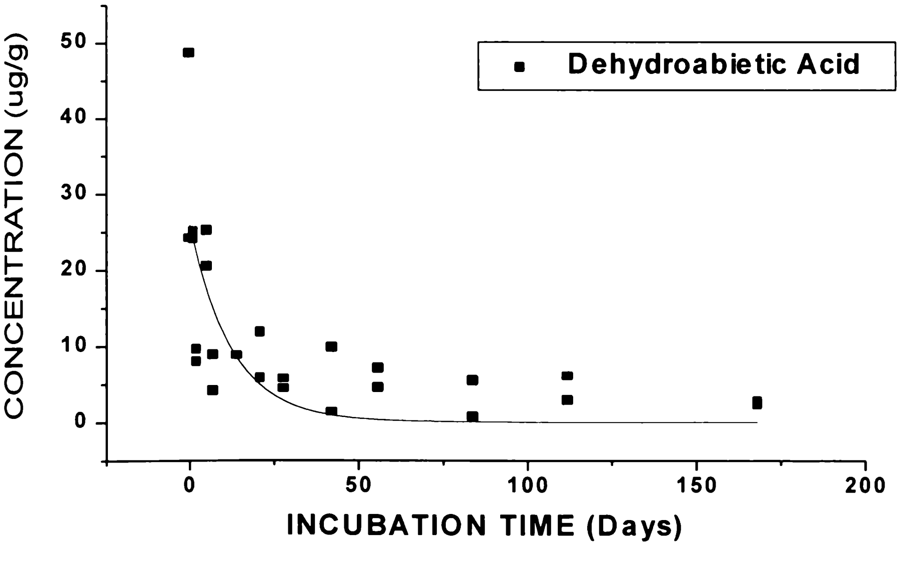

Sandaracopimaric Acid
CONCENTRATION (ug/g)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
0
50
100
150
200
INCUBATION TIME (Days)

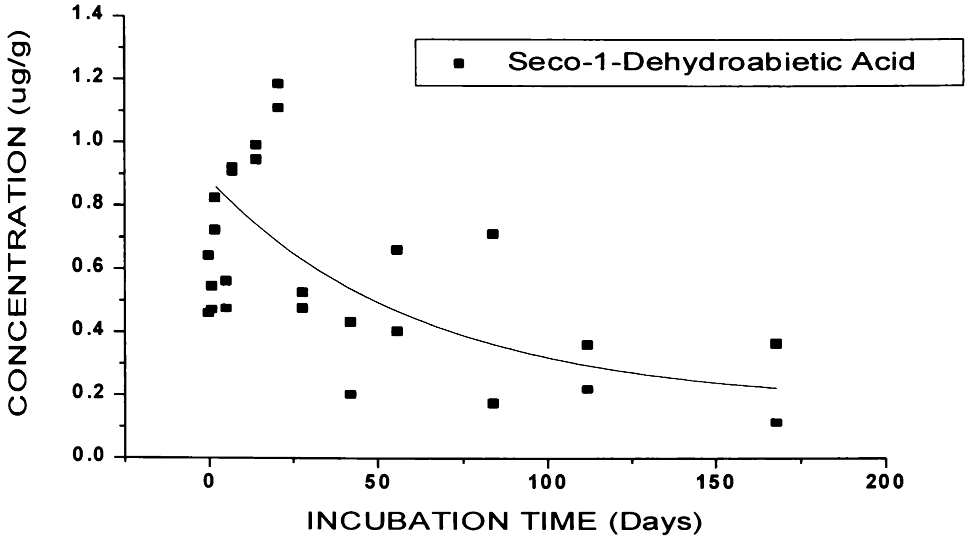

Isopimaric Acid
CONCENTRATION (ug/g)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
INCUBATION TIME (Days)

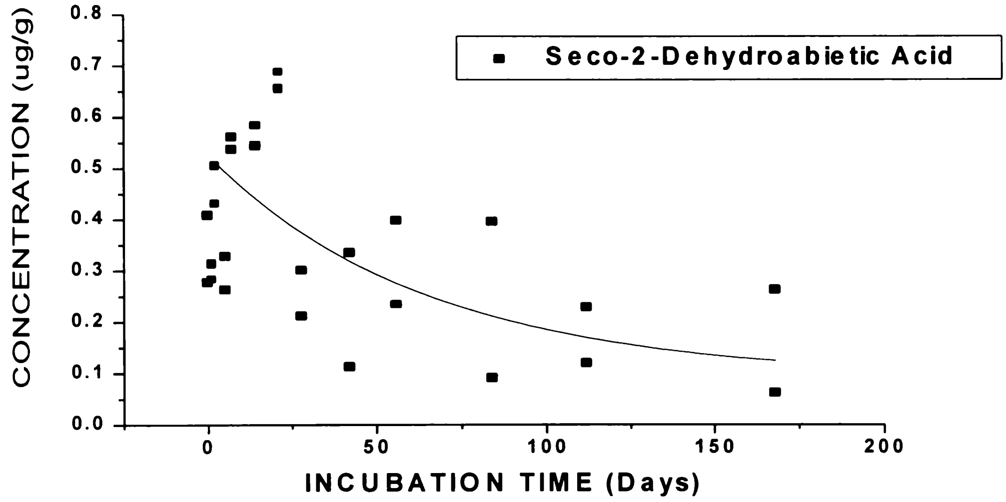

Palustric Acid
CONCENTRATION (ug/g)
50
40
30
20
10
0
0
50
100
150
200
INCUBATION TIME (ug/g)

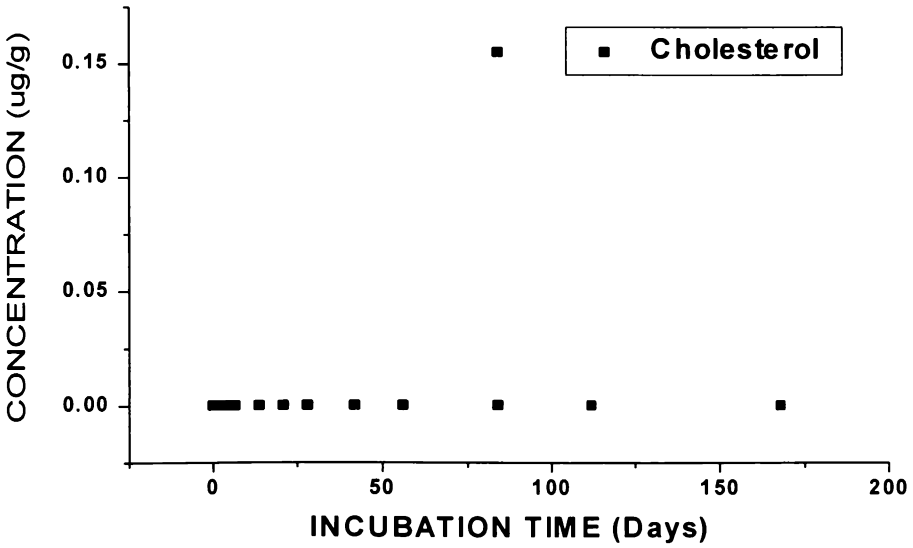

■ Abietic Acid
CONCENTRATION (ug/g)
0
5
10
15
20
0
50
100
150
200
INCUBATION TIME (Days)

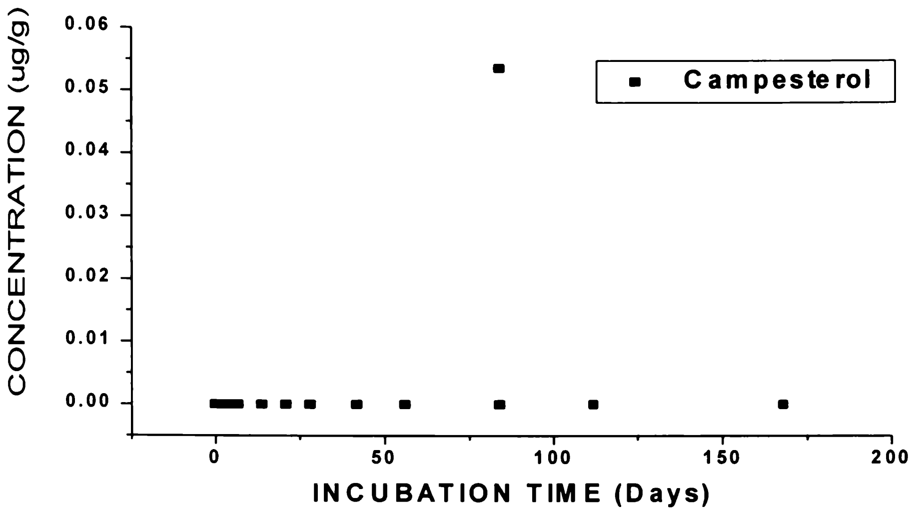

■ Neoabietic Acid
CONCENTRATION (ug/g)
0
2
4
6
8
10
0
50
100
150
200
INCUBATION TIME (Days)

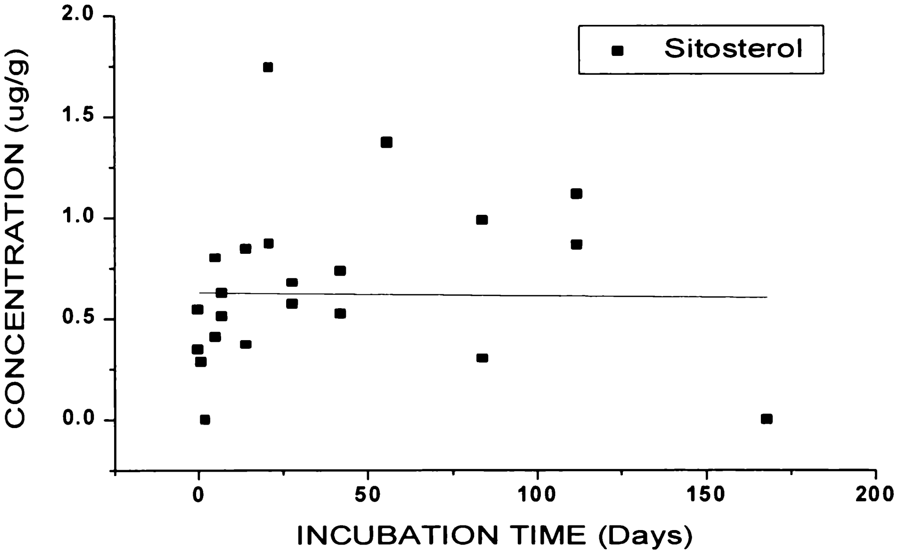

■ Dehydroabietic Acid
CONCENTRATION (ug/g)
0
10
20
30
40
50
0
50
100
150
200
INCUBATION TIME (Days)


■ Seco-1-Dehydroabietic Acid
CONCENTRATION (ug/g)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
INCUBATION TIME (Days)

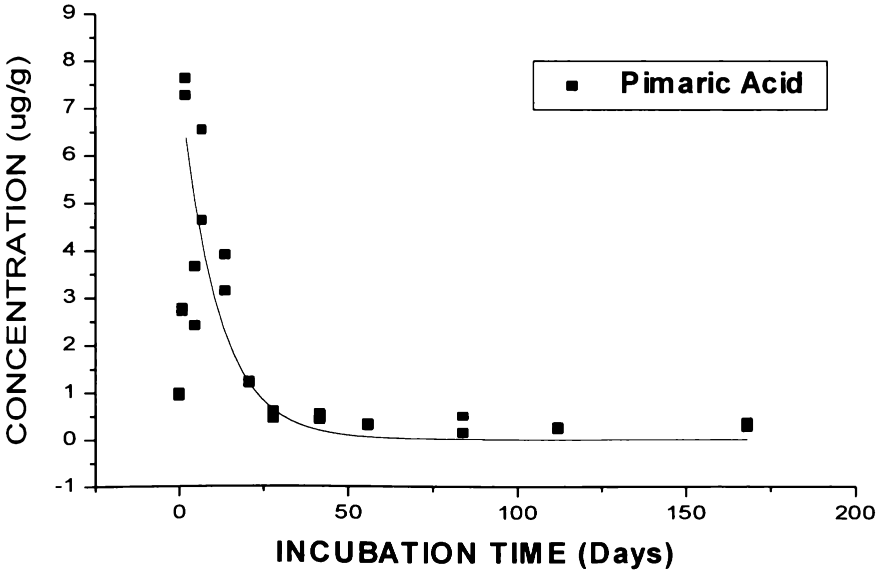

■ Seco-2-Dehydroabietic Acid
CONCENTRATION (ug/g)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
50
100
150
200
INCUBATION TIME (Days)

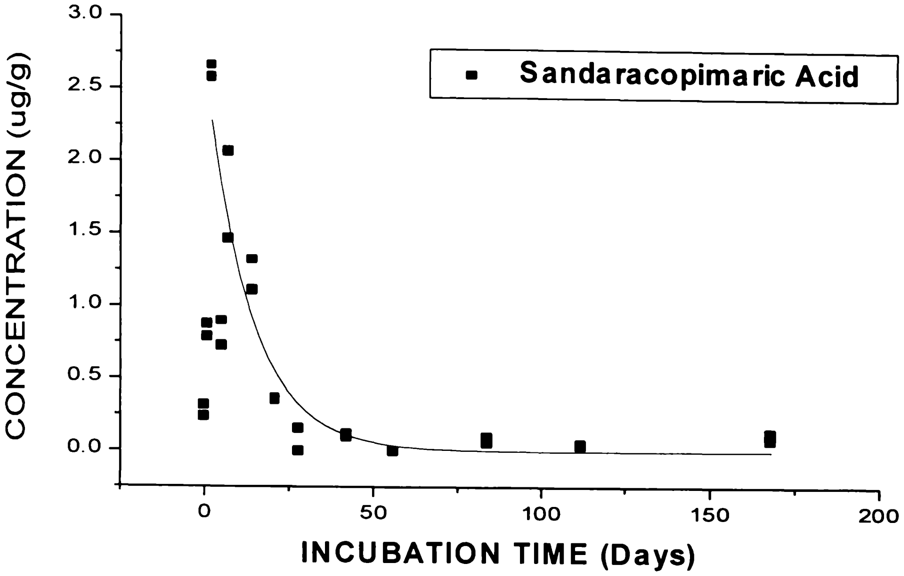

■ Cholesterol
CONCENTRATION (ug/g)
0.15
0.10
0.05
0.00
0
50
100
150
200
INCUBATION TIME (Days)

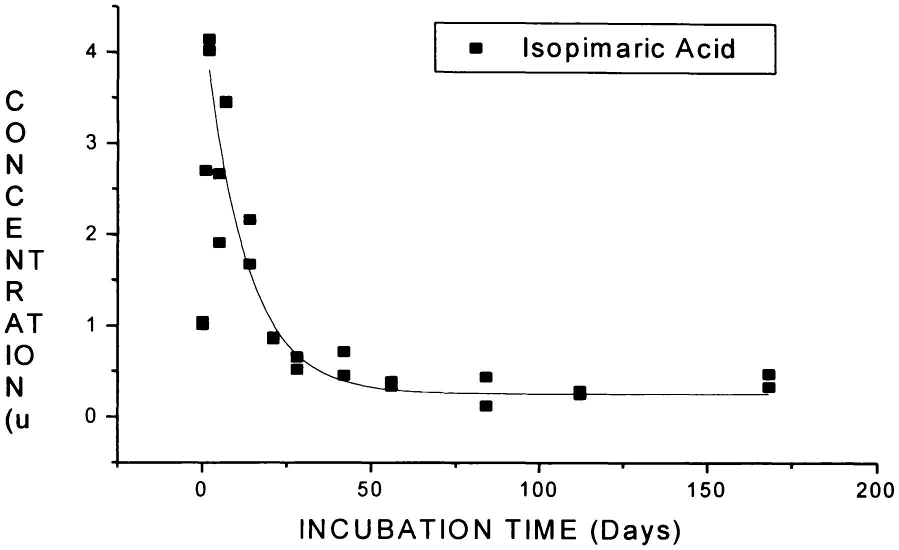


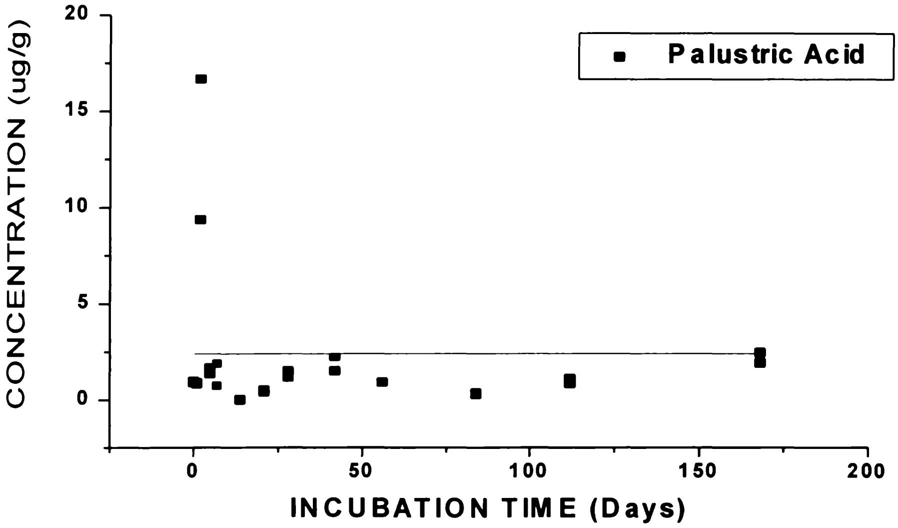


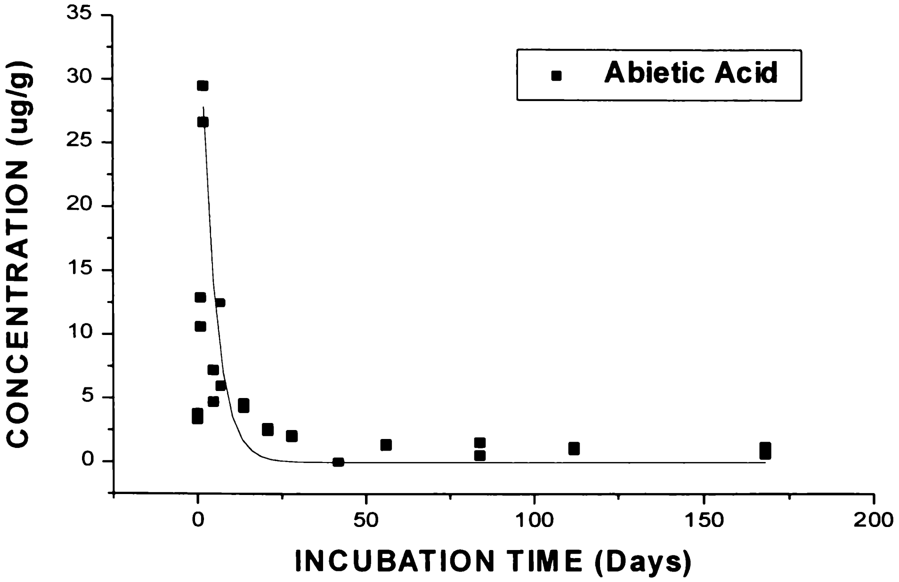
Anaerobic Kawerau Loamy Sand and Thermomechanical Pulping Effluent Incubations

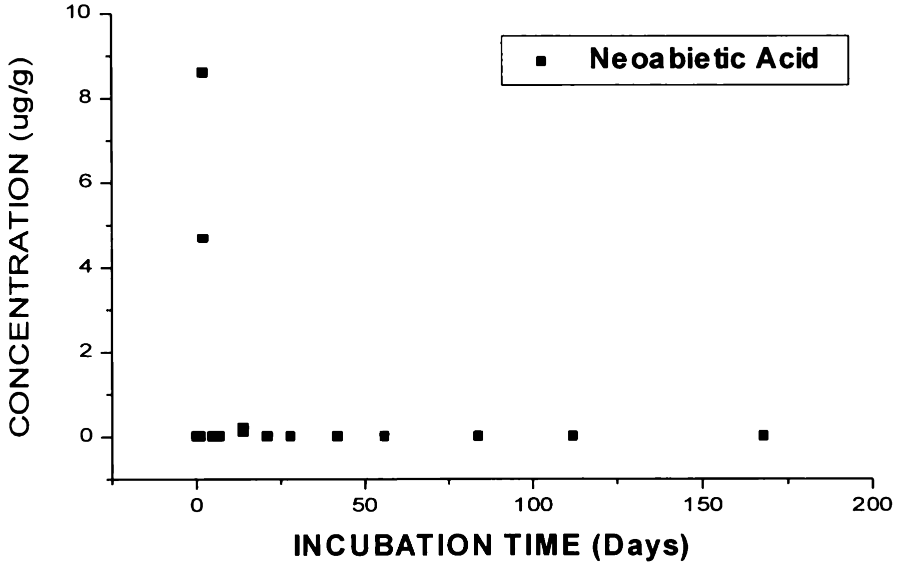


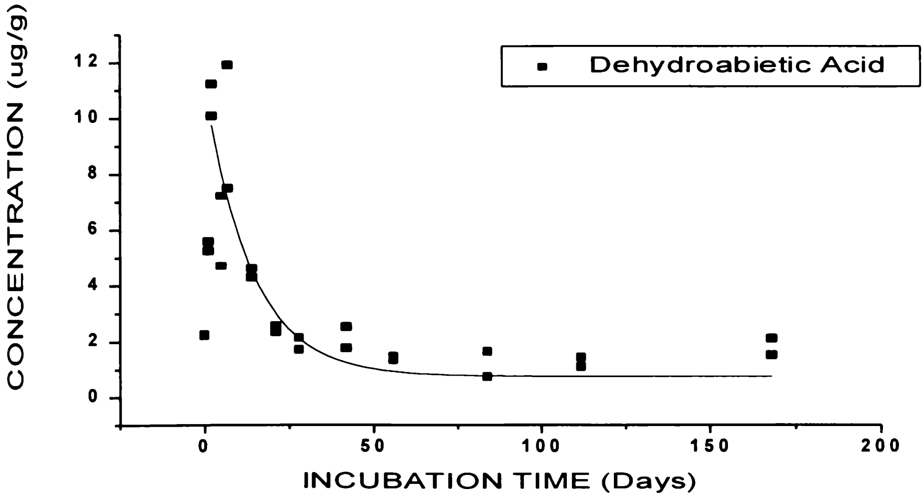

Sandaracopimaric Acid
CONCENTRATION (ug/g)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
INCUBATION TIME (Days)

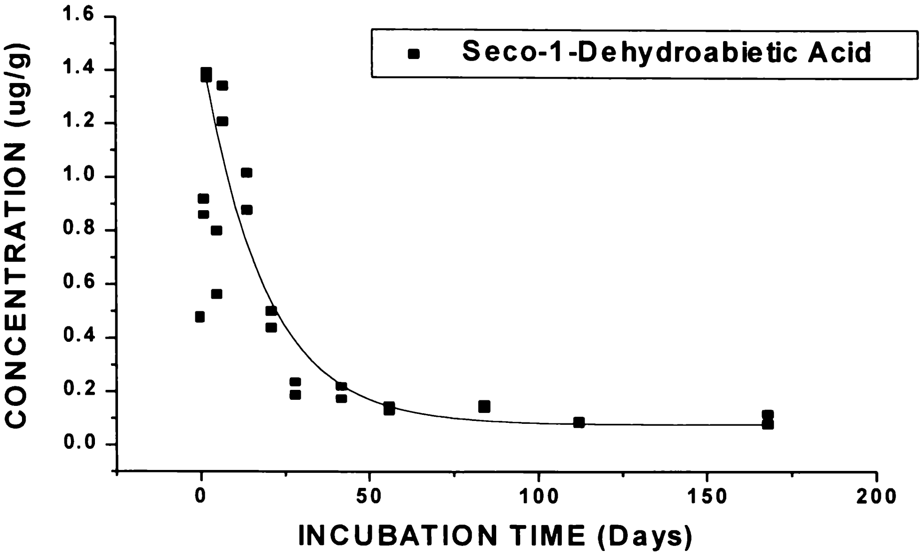

Isopimaric Acid
CONCENTRATION (u
4
3
2
1
0
0
50
100
150
200
INCUBATION TIME (Days)

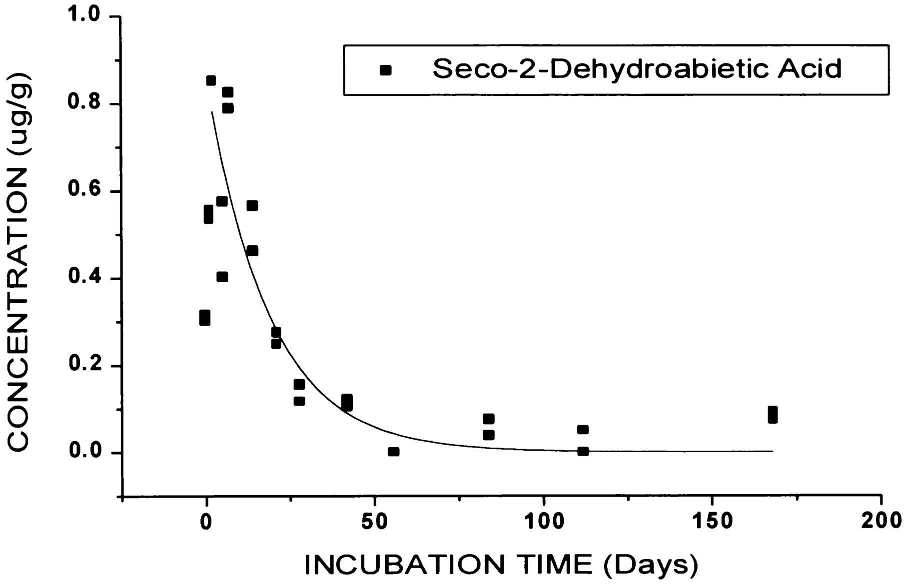

Palustric Acid
CONCENTRATION (ug/g)
20
15
10
5
0
0
50
100
150
200
INCUBATION TIME (Days)

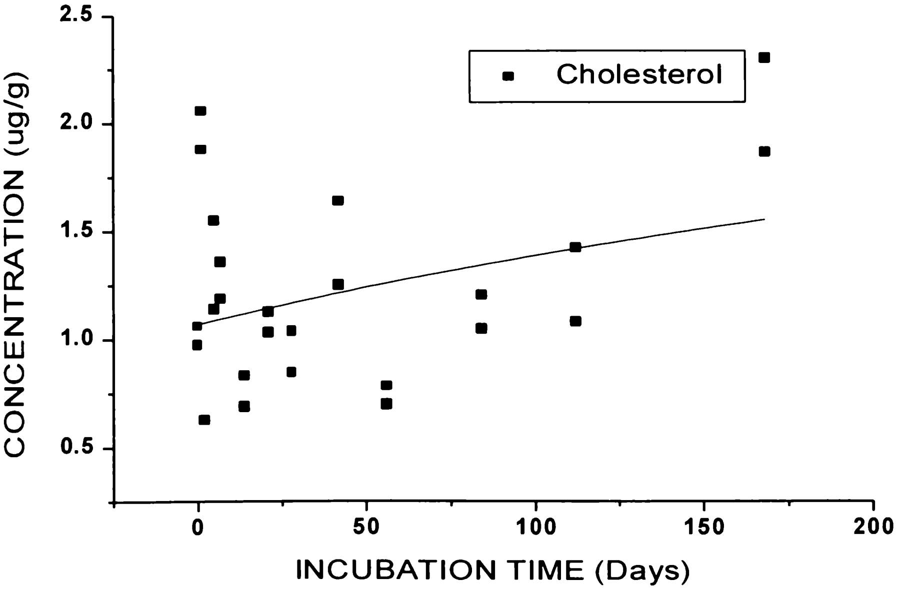

CONCENTRATION (ug/g)
35
30
25
20
15
10
5
0
0
50
100
150
200
INCUBATION TIME (Days)
■ Abietic Acid

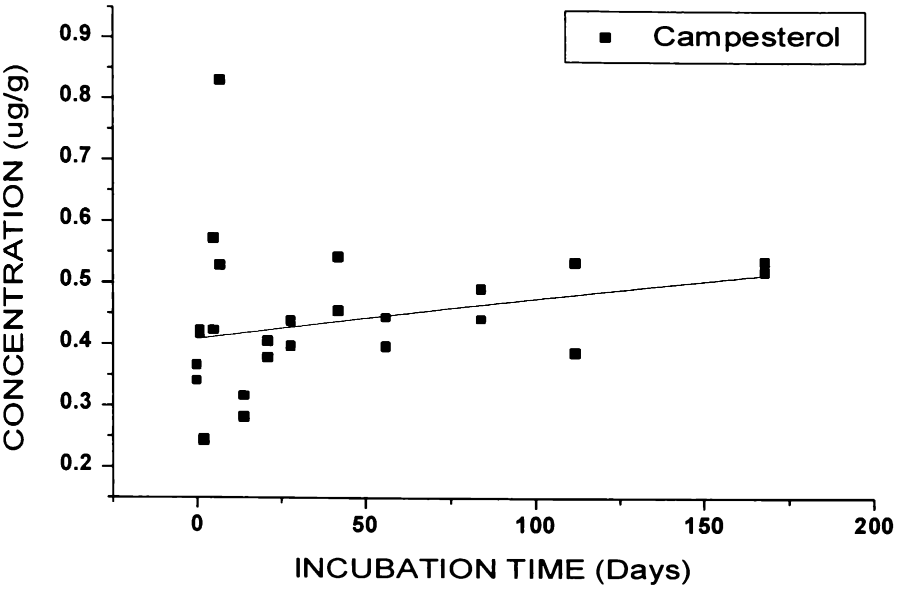

CONCENTRATION (ug/g)
10
8
6
4
2
0
0
50
100
150
200
INCUBATION TIME (Days)
■ Neoabietic Acid

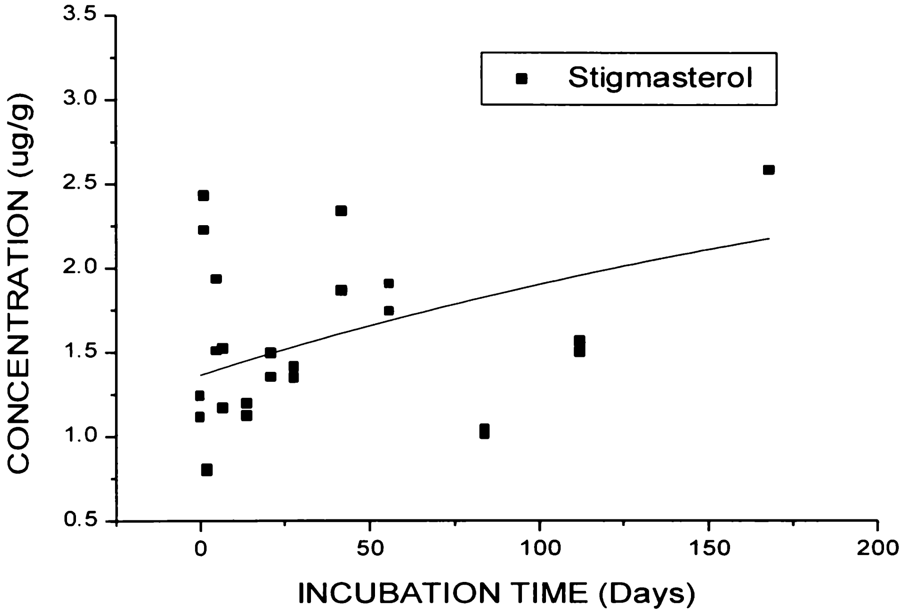

CONCENTRATION (ug/g)
12
10
8
6
4
2
0
0
50
100
150
200
INCUBATION TIME (Days)
■ Dehydroabietic Acid

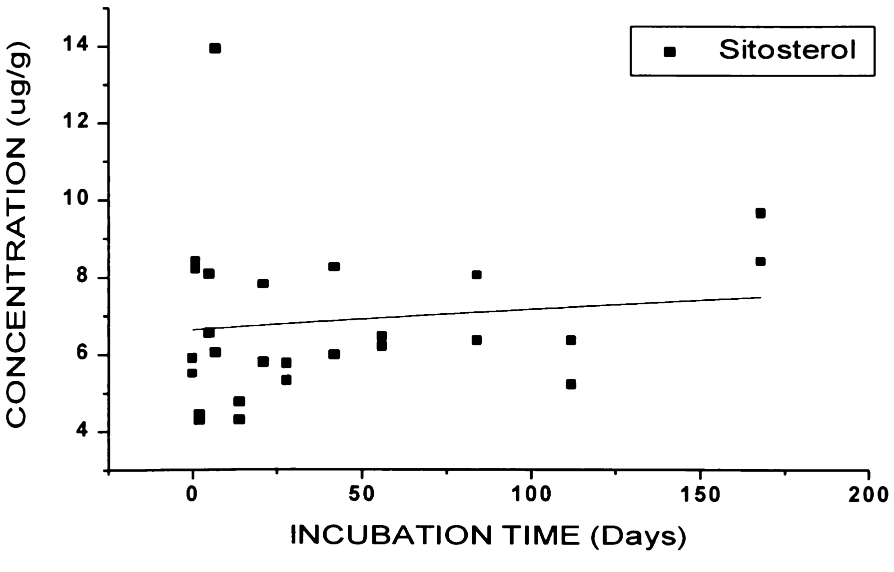

■ Seco-1-Dehydroabietic Acid
CONCENTRATION (ug/g)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
INCUBATION TIME (Days)


■ Seco-2-Dehydroabietic Acid
CONCENTRATION (ug/g)
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
INCUBATION TIME (Days)

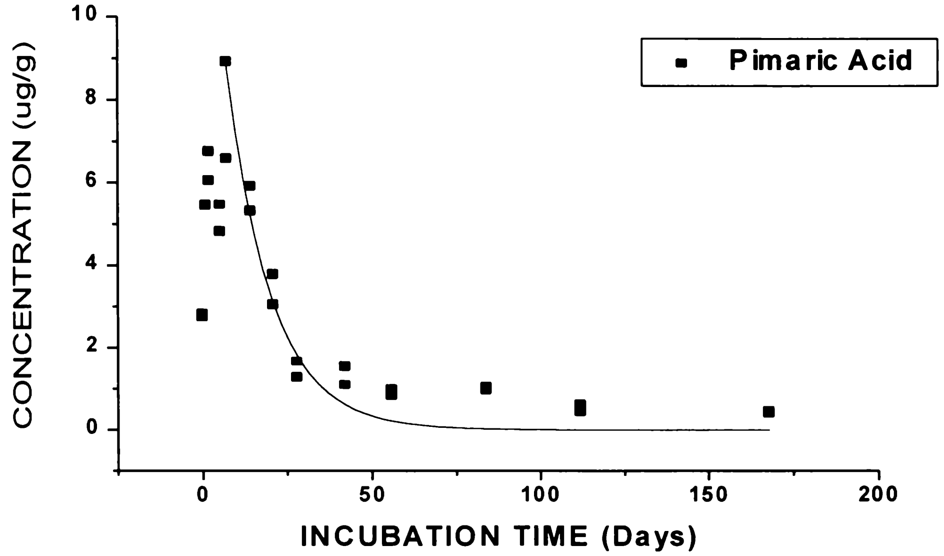

■ Cholesterol
CONCENTRATION (ug/g)
2.5
2.0
1.5
1.0
0.5
0
50
100
150
200
INCUBATION TIME (Days)

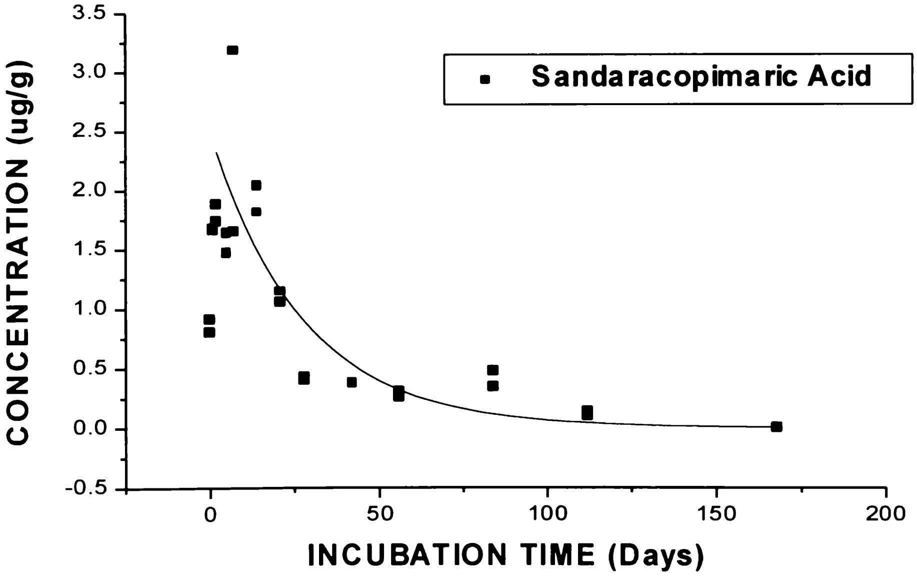

■ Campesterol
CONCENTRATION (ug/g)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
50
100
150
200
INCUBATION TIME (Days)

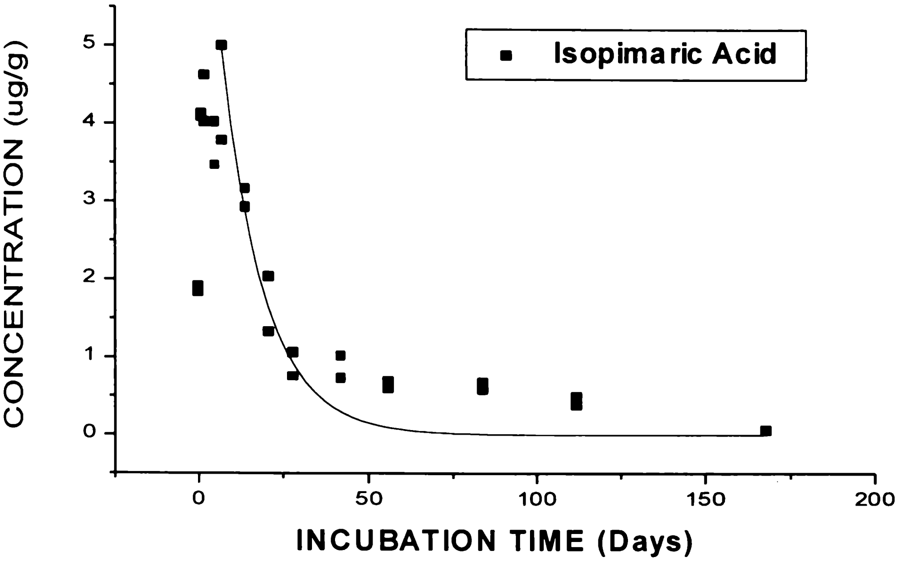

■ Stigmasterol
CONCENTRATION (ug/g)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
50
100
150
200
INCUBATION TIME (Days)

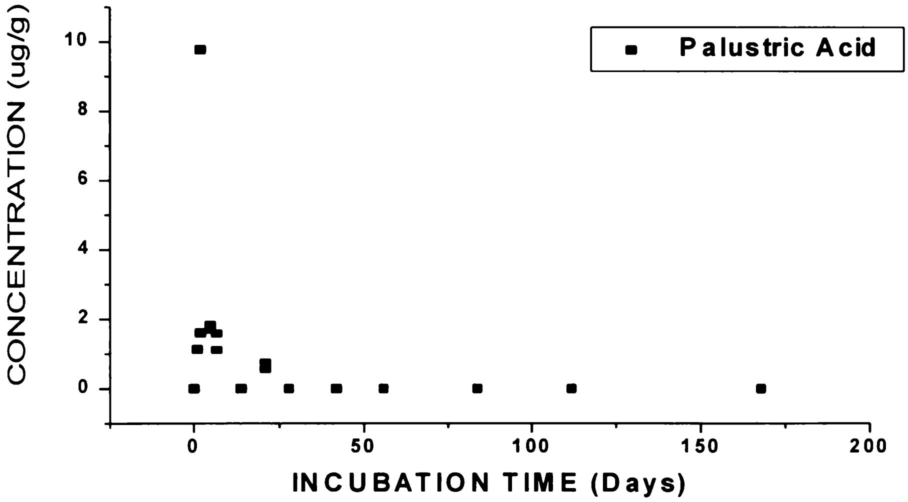

■ Sitosterol
CONCENTRATION (ug/g)
14
12
10
8
6
4
0
50
100
150
200
INCUBATION TIME (Days)

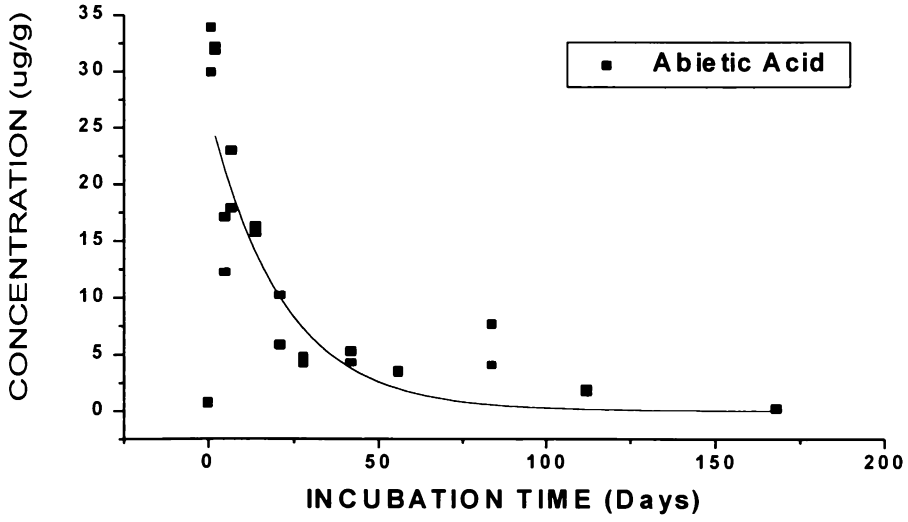
Anaerobic Whakarewarewa Sandy Loam and Thermomechanical Pulping Effluent Incubations

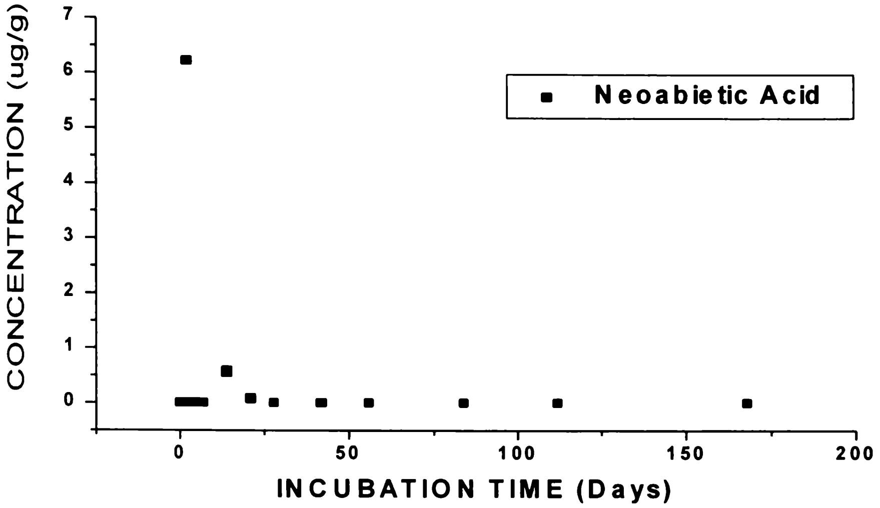


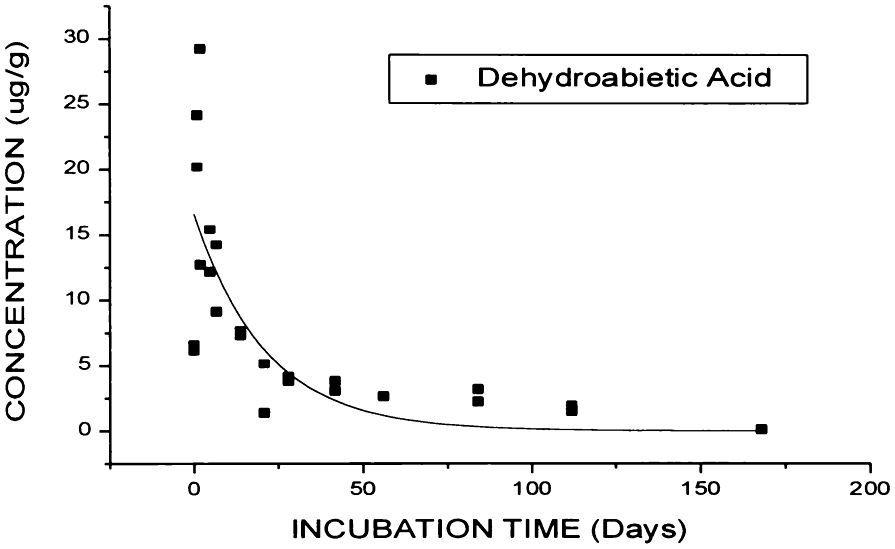


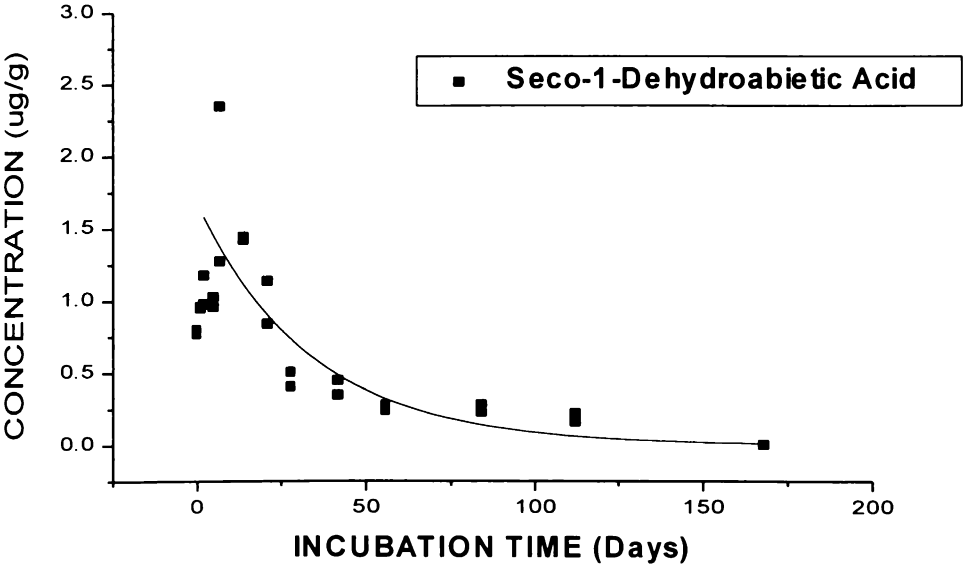

■ Isopimaric Acid
CONCENTRATION (ug/g)
5
4
3
2
1
0
0
50
100
150
200
INCUBATION TIME (Days)

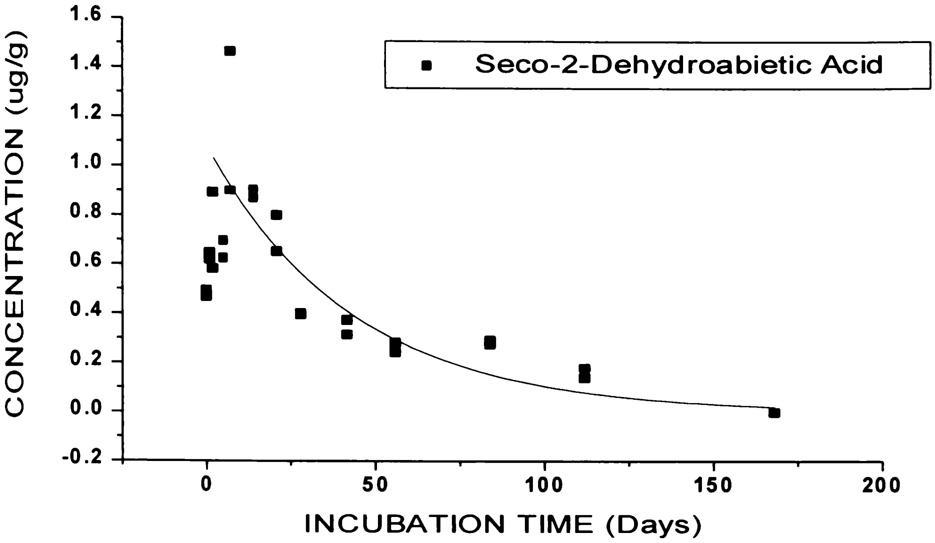

■ Palustric Acid
CONCENTRATION (ug/g)
10
8
6
4
2
0
0
50
100
150
200
INCUBATION TIME (Days)

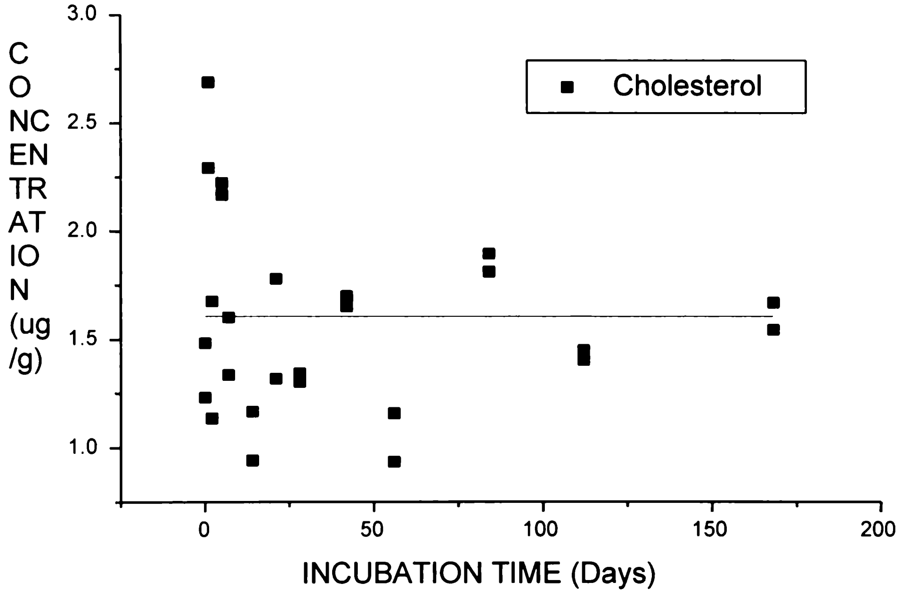

■ Abietic Acid
CONCENTRATION (ug/g)
35
30
25
20
15
10
5
0
0
50
100
150
200
INCUBATION TIME (Days)

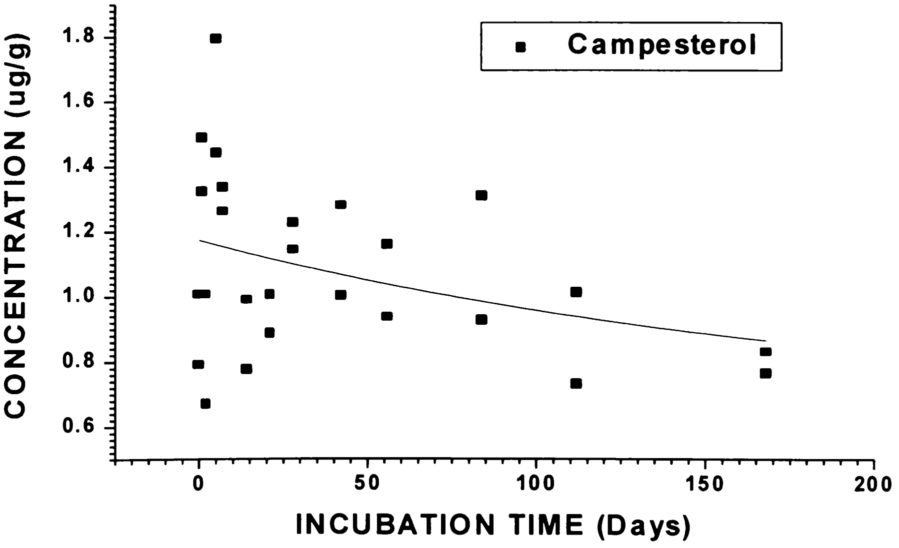

CONCENTRATION (ug/g)
7
6
5
4
3
2
1
0
0
50
100
150
200
INCUBATION TIME (Days)
■ Neoabietic Acid

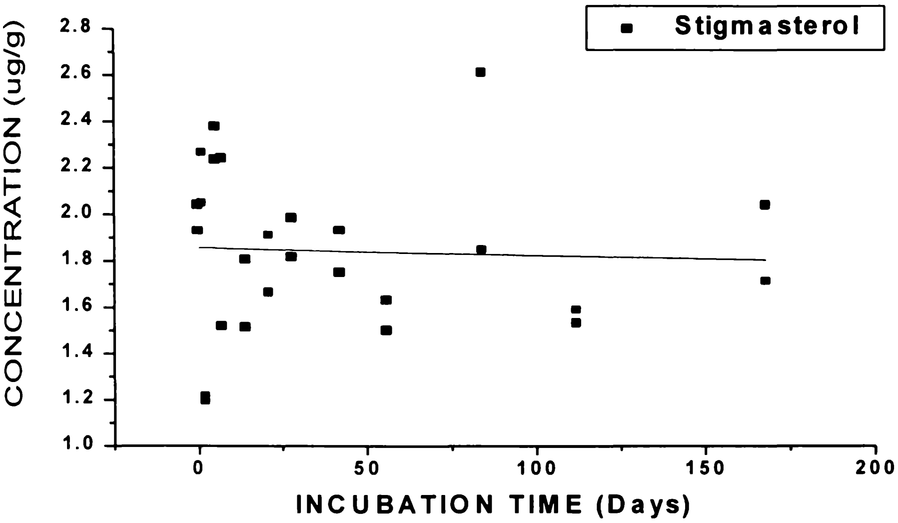

CONCENTRATION (ug/g)
30
25
20
15
10
5
0
0
50
100
150
200
INCUBATION TIME (Days)
■ Dehydroabietic Acid

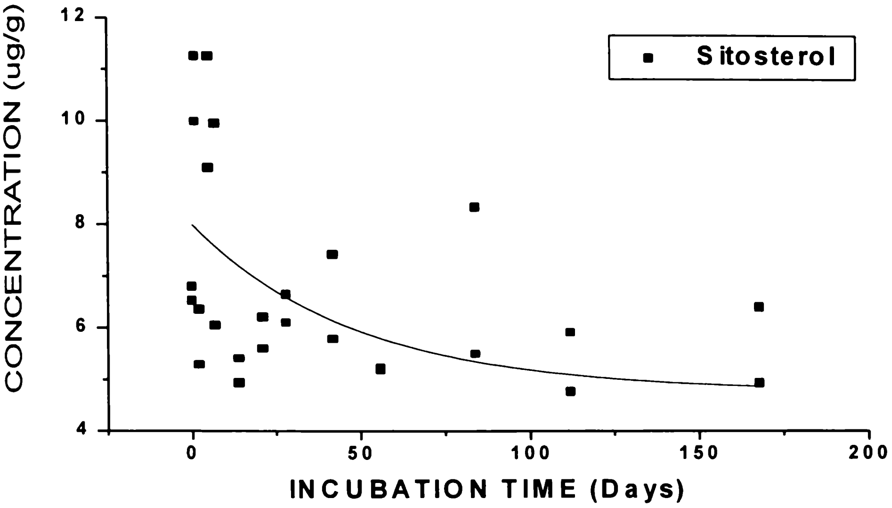

CONCENTRATION (ug/g)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
INCUBATION TIME (Days)
■ Seco-1-Dehydroabietic Acid


Seco-2-Dehydroabietic Acid
CONCENTRATION (ug/g)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
0
50
100
150
200
INCUBATION TIME (Days)


Cholesterol
CONCENTRATION (ug/g)
3.0
2.5
2.0
1.5
1.0
0
50
100
150
200
INCUBATION TIME (Days)


Campesterol
CONCENTRATION (ug/g)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0
50
100
150
200
INCUBATION TIME (Days)


■ Stigmasterol
CONCENTRATION (ug/g)
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0
50
100
150
200
INCUBATION TIME (Days)


CONCENTRATION (ug/g)
12
10
8
6
4
0
50
100
150
200
INCUBATION TIME (Days)
■ Sitosterol

Aerobic Sand and Thermomechanical Pulping Effluent Incubation Decay Curve Data

Compound	Y0	X0	A1	T1
PIMARANES	0.99826±0	0±0	6.67086±0.46301	44.34467±9.06607
Pimaric Acid	0.6361±0.53785	0±0	4.56803±1.09665	28.4158±15.00715
Sandaracopimaric Acid	0.20903±0.07381	0±0	2.1428±0.52558	11.4343±3.43956
Isopimaric Acid	0.67702±0.2342	0±0	2.48292±0.45619	23.18166±9.88148
DIENIC ABIETANES	0±0	0±0	68.83301±15.65078	8.0517±3.03616
Palustric Acid	0±0	0±0	35.94373±12.91754	9.01429±5.42779
Abietic Acid	3.22958±0	0±0	16.24008±1.87849	41.88939±10.04112
Neoabietic Acid	0±0	0±0	7.82428±2.51664	14.94137±9.12233
AROMATIC ABIETANES	0±0	0±0	34.78038±3.31178	1168.789±2.93019
Dehydroabietic Acid	2.21233±0	0±0	57.80789±9.43181	4.44022±0.92375
Seco-1-DHAA	0±0	0±0	1.09488±0.69427	108.07562±136.66805
Seco-2-DHAA	0±0	0±0	0.57905±0.06324	76.21738±22.96578
PHYTOSTEROLS	3.17172±0	0±0	-1.91518±0.20246	38.361377.18594±2.4088E12
Cholesterol	-	-	-	-
Campesterol	-	-	-	-
Stigmasterol	-	-	-	-
Sitosterol	3.0587±0	0±0	-1.60231±0.42585	2598813991.86969±2.4378E16

Aerobic Kawerau Loamy Sand and Thermomechanical Pulping Effluent Incubations Decay Curve Data

Compound	Y0	X0	A1	T1
PIMARANES	0±0	0±0	16.44667±2.02093	19.25165±4.73823
Pimaric Acid	0±0	0±0	8.39191±1.30101	16.52216±4.96772
Sandaracopimaric Acid	0±0	0±0	2.46222±0.50202	37.65314±17.79187
Isopimaric Acid	0.39165±0	0±0	5.82005±0.37614	12.7504±1.51013
DIENIC ABIETANES	39.15507	0±0	14.96161±2.32883	32.84908±14.49152
Palustric Acid	11.6856±0	0±0	-9.63549±1.55931	66870475652.05798±1.0307E19
Abietic Acid	0±0	0±0	14.02378±1.86068	33.16732±9.91375
Neoabietic Acid	0±0	0±0	37.86057±8.70298	1.15346±0.15063
AROMATIC ABIETANES	10.178	0±0	10.14533±1.1199	44.28946±14.39828
Dehydroabietic Acid	0.64±0	0±0	11.00988±1.06212	22.82887±4.57333
Seco-1-DHAA	1.9996±0	0±0	2.3644±0.38847	18.67631±3.96235
Seco-2-DHAA	0.07788±0	0±0	1.22091±0.11569	21.11206±4.08564
PHYTOSTEROLS	6.04555±0	0±0	4.79987±1.0401	317.38348±446.10633
Cholesterol	1.7829±0	0±0	-1.01381±0.2719	1.0272E12±3.8434E21
Campesterol	0.16137±0	0±0	0.29433±0.04471	2913.85199±21964.24837
Stigmasterol	3.42595±0	0±0	-2.10143±0.21492	181.05277±83.71045
Sitosterol	14.37192±0	0±0	-6.28286±0.75771	1.9602E32±7.1748E61

Aerobic Whakarewarewa Sandy Loam and Thermomechanical Pulping Effluent Incubations Decay Curve Data

Compounds	Y0	X0	A1	T1
PIMARANES	1.7592±0	0±0	21.16853±1.5259	25.14579±3.843
Pimaric Acid	0.68091±0	0±0	14.24205±2.48356	17.65764±3.88326
Sandaracopimaric Acid	0±0	0±0	3.92136±0.46853	28.92572±7.55423
Isopimaric Acid	0.63099±0	0±0	6.66543±0.53347	19.80871±3.19467
DIENIC ABIETANES	0±0	0±0	241.04912±71.06805	33012.18725±894085.189
Palustric Acid	0±0	0±0	0.52577±0.27784	2.31735±0.64347
Abietic Acid	0±0	0±0	43.67178±6.3406	15.16097±4.19142
Neoabietic Acid	-	-	-	-
AROMATIC ABIETANES	2.02675±0	0±0	14.99775±1.47507	36.20014±10.2022
Dehydroabietic Acid	1.96737±0	0±0	17.75289±1.90558	12.47994±2.99057
Seco-1-DHAA	0±0	0±0	2.63525±0.36705	32.03976±9.97652
Seco-2-DHAA	0±0	0±0	1.47812±0.30418	24.06646±10.40171
PHYTOSTEROLS	7.5195±0	0±0	5.60631±1.07295	284.86697±327.36535
Cholesterol	0.78636±0	0±0	0.79937±0.17266	7566277.63173±1912877326.47866
Campesterol	0.51717±0	0±0	0.73915±0.35052	181388.10708±241703663.67482
Stigmasterol	1.12338±0	0±0	0.77684±0.17104	779892.17858±2073812042.60265
Sitosterol	4.13937±0	0±0	3.5514±0.96857	179.68818±181.70126

Anaerobic Sand and Thermomechanical Pulping Effluent Incubations Decay Curve Data

Compound	Y0	X0	A1	T1
PIMARANES	0.76028	0±0	7.00411±1.30553	56.23317±26.65405
Pimaric Acid	0.59962±0.45952	0±0	5.54275±1.19127	23.73935±9.89165
Sandaracopimaric Acid	0±0	0±0	1.32176±0.16986	29.52995±8.33243
Isopimaric Acid	0.16587±0	0±0	2.2146±0.1397	68.57882±13.71689
DIENIC ABIETANES	1.36724	0±0	38.3091±4.73923	28.03656±9.66162
Palustric Acid	0±0	0±0	94.44974±42.39954	2.19813±0.90699
Abietic Acid	1.18589±0	0±0	16.17501±1.32113	35.195±10.73986
Neoabietic Acid	0±0	0±0	7.51199±2.35971	17.43052±10.73986
AROMATIC ABIETANES	0±0	0±0	25.48257±3.26333	17.69454±6.08536
Dehydroabietic Acid	0±0	0±0	25.921899±3.48128	12.54985±4.45173
Seco-1-DHAA	0.17541±0	0±0	0.708552±0.15308	63.70403±36.11731
Seco-2-DHAA	0.09152±0	0±0	0.43433±0.09456	65.42732±37.66086
PHYTOSTEROLS	0±0	0±0	0.63331±0.1204	12619.04332±472041.01149
Cholesterol	-	-	-	-
Campesterol	-	-	-	-
Stigmasterol	-	-	-	-
Sitosterol	0±0	0±0	6.2922±0.11851	4319.45929±55530.48508

Anaerobic Kawerau Loamy Sand and Thermomechanical Pulping Effluent Incubations Decay Curve Data

Compound	Y0	X0	A1	T1
PIMARANES	0±0	0±0	14.5152±2.31302	12.096067±3.48743
Pimaric Acid	0±0	0±0	7.63257±1.30562	11.23884±3.41899
Sandaracopimaric Acid	0±0	0±0	2.66029±0.4551	13.25069±4.1906
Isopimaric Acid	0.25478±0	0±0	4.19043±0.61099	12.29899±3.25897
DIENIC ABIETANES	1.78819±0	0±0	7.34768±1.30407	14.96337±3.95673
Palustric Acid	16.65056±0	0±0	-14.2418±0.91501	2.2867E16±5.02019E29
Abietic Acid	0±0	0±0	45.53878±8.65725	4.09567±0.95782
Neoabietic Acid	-	-	-	-
AROMATIC ABIETANES	1.44019±0	0±0	7.26794±2.04001	25.19878±19.54361
Dehydroabietic Acid	0.7365±0	0±0	10.4256±0.60948	13.76816±1.50076
Seco-1-DHAA	0.07743±0	0±0	1.42914±0.18332	18.445±4.69656
Seco-2-DHAA	0±0	0±0	0.87321±0.11853	18.46654±4.97678
PHYTOSTEROLS	17.62515±0	0±0	-8.33151±0.75078	450.84714±344.96575
Cholesterol	2.29836±0	0±0	-1.22918±0.11511	338.84299±215.91559
Campesterol	0.83196±0	0±0	-0.42268±0.01335	574.48709±442.01829
Stigmasterol	3.21715±0	0±0	-1.8527±0.14535	289.14247±137.64166
Sitosterol	13.91365±0	0±0	-7.28219±0.53843	1396.37836±2377.91292

Anaerobic Whakarewarewa

Compounds	Y0	X0	A1	T1
PIMARANES	0±0	0±0	11.45494±0.9857	38.37844±9.53989
Pimaric Acid	0±0	0±0	15.15773±1.66691	13.15991±1.60803
Sandaracopimaric Acid	0±0	0±0	2.50193±0.44253	27.13443±10.34492
Isopimaric Acid	0±0	0±0	8.76151±1.19692	12.38342±1.82972
DIENIC ABIETANES	0±0	0±0	51.60824±7.47172	9.30284±2.27747
Palustric Acid	-	-	-	-
Abietic Acid	0±0	0±0	26.61303±4.31613	21.29083±7.06487
Neoabietic Acid	-	-	-	-
AROMATIC ABIETANES	0±0	0±0	18.24359±1.95058	25.36688±7.48192
Dehydroabietic Acid	0±0	0±0	16.58492±1.98907	21.2326±6.92119
Seco-1-DHAA	0±0	0±0	1.67664±0.13906	33.71161±14.50453
Seco-2-DHAA	0±0	0±0	1.08401±0.16271	43.19582±15.50086
PHYTOSTEROLS	8.28051±0	0±0	2.35428±0.7612	1055.4283±6063.1467
Cholesterol	2.69068±0	0±0	-1.08402±0.1182	108966816.7153±1.8964E13
Campesterol	0.66907±0	0±0	0.50444±0.07294	176.06433±113.36177
Stigmasterol	1.19685±0	0±0	0.66212±0.09062	2261.03741±11264.45522
Sitosterol	4.76334±0	0±0	3.23161±0.61149	49.31864±27.92039

Maximum Production and Degradation Rate Data for Resin Acid Family Groups and Phytosterols

	Sand aerobic				Kawerau aerobic				Whakarewarewa aerobic			
	µg/g/day	µg/g/day	per day	per day	µg/g/day	µg/g/day	per day	per day	µg/g/day	µg/g/day	per day	per day
Pimaranes												
0.00	0.00	0.00	-0.42	-0.05	0.00	0.00	2.72	2.18	0.00	0.00	1.05	1.16
1.00	-3.90	-0.28	0.47	0.66	6.09	4.99	1.18	0.85	5.64	6.54	1.06	0.74
2.00	-0.66	1.52	-0.02	-0.04	7.95	5.58	-0.19	-0.13	8.64	7.77	-0.13	-0.07
5.00	-0.35	0.43	0.08	0.05	1.16	1.17	0.21	0.18	1.68	2.26	0.14	0.03
7.00	-0.09	0.41	-0.08	-0.02	1.31	1.26	-0.04	-0.02	1.75	1.78	-0.01	0.00
14.00	-0.38	0.14	0.10	-0.04	0.45	0.54	-0.02	-0.07	0.81	0.87	-0.04	-0.05
21.00	-0.12	-0.01	-0.06	-0.06	0.23	0.13	-0.09	-0.04	0.31	0.29	-0.08	-0.05
28.00	-0.20	-0.09	-0.01	0.04	0.02	0.04	-0.02	-0.03	-0.02	0.06	-0.03	-0.04
42.00	-0.14	-0.02	-0.03	-0.04	0.00	-0.01	-0.03	-0.04	-0.06	-0.05	-0.02	0.00
56.00	-0.13	-0.06	0.00	0.01	-0.02	-0.02	0.02	0.04	-0.06	-0.04	0.01	0.00
84.00	-0.08	-0.03	-0.01	-0.01	0.00	0.00	-0.02	-0.02	-0.04	-0.02	-0.01	-0.02
112.00	-0.07	-0.03	0.00	-0.01	-0.01	-0.01	0.00	-0.02	-0.03	-0.03	0.00	0.00
168.00	-0.05	-0.03	0.01	0.01	-0.01	-0.01	0.01	#DIV/0!	-0.02	-0.02	0.01	0.01
Dienic Abietanes												
0.00	0.00	0.00	-0.46	-0.05	0.00	0.00	1.23	1.27	0.00	0.00	3.17	4.89
1.00	-21.95	-0.84	1.94	3.00	5.73	5.54	2.26	1.86	23.58	35.94	2.76	1.54
2.00	11.59	23.94	-0.24	-0.25	14.65	11.94	-0.20	-0.21	54.61	51.32	-0.27	-0.27
5.00	-5.34	-0.23	0.77	0.54	1.73	1.18	-0.11	0.09	2.76	2.78	0.03	0.02
7.00	0.26	2.32	-0.08	-0.07	0.82	1.11	0.01	0.05	2.18	2.12	0.01	0.02
14.00	-1.66	-0.02	0.08	-0.05	0.46	0.84	-0.07	-0.09	1.21	1.23	-0.06	-0.08
21.00	-0.52	-0.27	-0.10	-0.07	0.05	0.07	-0.07	-0.03	0.35	0.17	-0.08	-0.04
28.00	-1.21	-0.40	0.00	0.06	-0.06	0.02	-0.01	-0.01	-0.03	0.01	-0.01	0.00
42.00	-0.79	-0.14	-0.01	-0.04	-0.05	0.00	0.00	-0.02	-0.04	0.02	-0.04	-0.04
56.00	-0.63	-0.20	-0.01	-0.02	-0.03	-0.02	-0.03	-0.03	-0.08	-0.06	0.01	0.00
84.00	-0.47	-0.17	0.00	0.04	-0.05	-0.04	0.04	0.04	-0.05	-0.04	-0.01	-0.02
112.00	-0.35	-0.09	-0.01	-0.01	-0.03	-0.02	0.01	-0.01	-0.05	-0.04	0.00	-0.01
168.00	-0.25	-0.09	0.01	0.01	-0.01	-0.02	0.01	0.01	-0.03	-0.04	0.01	0.01

Aromatic Abietanes												
0.00	0.00	0.00	-0.53	-0.22	0.00	0.00	2.37	2.08	0.00	0.00	2.12	2.17
1.00	-26.32	-5.50	0.72	0.99	7.07	6.40	0.87	0.52	16.59	16.12	-0.24	-0.25
2.00	-4.73	6.87	-0.12	-0.07	7.90	5.64	-0.17	-0.07	5.32	5.13	-0.06	0.02
5.00	-4.75	1.04	-0.30	-0.33	1.29	1.63	0.00	-0.09	1.41	2.30	-0.07	-0.17
7.00	-5.62	-2.11	-0.06	-0.04	0.91	0.88	-0.03	0.00	0.71	0.72	-0.01	0.01
14.00	-3.10	-1.26	0.10	-0.03	0.33	0.44	-0.04	-0.07	0.32	0.40	-0.03	0.04
21.00	-1.86	-0.90	-0.05	-0.05	0.13	0.07	-0.08	0.06	0.08	0.45	-0.06	-0.08
28.00	-1.52	-0.75	0.00	0.06	-0.02	0.12	0.00	-0.04	-0.09	0.02	-0.02	-0.02
42.00	-1.02	-0.42	-0.03	-0.04	-0.01	-0.01	0.01	-0.02	-0.10	-0.05	0.03	0.01
56.00	-0.81	-0.39	0.00	0.00	-0.01	-0.02	0.00	0.02	-0.05	-0.02	-0.01	0.00
84.00	-0.54	-0.25	-0.01	0.00	0.00	0.00	-0.01	-0.02	-0.05	-0.02	-0.01	-0.02
112.00	-0.41	-0.19	-0.01	-0.01	-0.01	-0.01	0.01	-0.01	-0.05	-0.04	0.00	0.00
168.00	-0.28	-0.14	0.01	0.01	0.00	-0.01	0.01	0.01	-0.03	-0.03	0.01	0.01
Phytosterols												
0.00	0.00	0.00	0.10	0.77	0.00	0.00	1.77	0.89	0.00	0.00	0.56	0.57
1.00	0.05	0.27	-0.02	-0.15	13.56	7.37	-0.71	-0.60	5.85	6.44	-0.44	-0.55
2.00	0.02	0.09	0.35	0.35	-0.80	-0.98	0.49	0.53	-0.70	-1.64	0.18	0.43
5.00	0.13	0.14	0.39	0.56	1.46	1.60	-0.19	-0.21	0.69	1.43	-0.07	-0.17
7.00	0.23	0.27	-0.12	-0.08	0.22	0.18	-0.04	0.00	0.21	0.12	-0.02	-0.03
14.00	-0.01	0.04	1.08	0.21	-0.07	0.11	0.07	-0.05	-0.01	-0.13	-0.03	0.16
21.00	0.12	0.10	-0.10	-0.08	0.12	-0.10	0.00	0.20	-0.10	0.42	0.05	-0.03
28.00	0.02	0.03	0.03	0.02	0.08	0.22	-0.02	-0.03	0.03	0.18	0.00	-0.03
42.00	0.02	0.03	-0.02	-0.03	0.00	0.02	0.00	0.00	0.03	-0.02	-0.01	0.00
56.00	0.01	0.01	0.03	0.03	0.00	0.01	0.03	0.02	0.00	-0.01	0.03	0.03
84.00	0.01	0.01	0.00	-0.02	0.07	0.06	-0.01	-0.01	0.09	0.11	-0.02	-0.02
112.00	0.01	0.00	-0.02	-0.02	0.03	0.01	-0.01	0.00	-0.01	-0.02	0.00	0.00
168.00	0.00	0.00	#DIV/0!	#DIV/0!	-0.01	0.00	0.01	0.01	-0.02	-0.02	0.01	0.01

	Sand anaerobic				Kawerau anaerobic				Whakarewarewa anaerobic			
	µg/g/day	µg/g/day	per day	per day	µg/g/day	µg/g/day	per day	per day	µg/g/day	µg/g/day	per day	per day
Pimaranes												
0.00	0.00	0.00	-0.33	0.27	0.00	0.00	1.77	2.75	0.00	0.00	1.09	0.99
1.00	-3.13	1.46	0.08	0.25	3.96	6.29	1.33	0.62	5.88	5.56	0.12	0.11
2.00	-1.31	1.57	0.03	-0.11	6.11	5.79	-0.22	-0.16	3.63	3.38	-0.08	-0.03
5.00	-0.42	0.04	0.01	0.23	0.56	0.99	0.45	0.33	0.88	1.10	0.38	0.04
7.00	-0.28	0.40	0.01	0.00	1.04	1.40	-0.05	-0.06	1.68	0.91	-0.06	-0.01
14.00	-0.12	0.21	-0.05	0.01	0.26	0.36	-0.08	-0.10	0.33	0.39	-0.07	-0.05
21.00	-0.20	0.16	0.00	-0.06	0.01	0.01	-0.09	-0.06	0.00	0.06	-0.08	-0.08
28.00	-0.15	-0.01	-0.06	-0.01	-0.05	-0.03	0.03	-0.02	-0.11	-0.09	-0.01	0.00
42.00	-0.20	-0.03	0.12	-0.02	-0.02	-0.03	-0.04	-0.02	-0.08	-0.06	-0.02	-0.02
56.00	-0.13	-0.05	-0.03	0.03	-0.03	-0.03	0.02	-0.02	-0.07	-0.07	0.01	0.00
84.00	-0.11	-0.01	0.14	-0.02	-0.01	-0.02	-0.02	0.03	-0.04	-0.04	-0.02	-0.01
112.00	-0.06	-0.03	-0.01	-0.01	-0.02	-0.02	0.01	0.00	-0.04	-0.04	-0.01	-0.01
168.00	-0.05	-0.02	0.01	0.01	-0.01	-0.01	0.01	0.01	-0.03	-0.03	0.01	0.01
Dienic Abietanes												
0.00	0.00	0.00	-0.31	0.50	0.00	0.00	1.45	2.14	0.00	0.00	53.55	48.89
1.00	-15.47	8.50	0.83	1.81	6.78	9.32	2.55	3.01	30.35	34.20	0.56	-0.04
2.00	4.54	27.40	-0.22	-0.25	18.00	25.20	-0.28	-0.28	23.77	16.35	-0.20	-0.19
5.00	-5.49	-0.03	0.06	0.60	0.27	0.90	0.15	0.25	3.65	2.64	0.15	0.18
7.00	-3.61	2.90	0.14	-0.01	0.46	1.27	-0.06	-0.09	3.42	2.60	-0.05	-0.02
14.00	-0.39	1.29	-0.10	-0.05	-0.02	0.03	-0.05	-0.05	1.12	1.14	-0.08	-0.05
21.00	-1.57	0.32	-0.10	-0.11	-0.09	-0.05	0.03	0.00	0.29	0.48	-0.05	-0.08
28.00	-1.47	-0.43	0.03	0.01	-0.04	-0.04	-0.03	-0.04	0.13	0.14	0.00	0.01
42.00	-0.94	-0.27	0.00	0.03	-0.06	-0.07	0.00	0.04	0.09	0.11	-0.01	-0.02
56.00	-0.71	-0.16	-0.02	0.00	-0.05	-0.04	-0.01	-0.02	0.05	0.05	0.01	0.04
84.00	-0.51	-0.11	0.01	-0.02	-0.03	-0.04	0.01	0.05	0.04	0.08	-0.02	-0.03
112.00	-0.37	-0.12	0.00	-0.01	-0.02	-0.02	0.01	0.01	0.01	0.01	-0.02	-0.02
168.00	-0.25	-0.09	0.01	0.01	-0.01	-0.01	0.01	0.01	0.00	0.00	0.01	0.01

Aromatic Abietanes												
0.00	0.00	0.00	-0.50	0.04	0.00	0.00	1.25	1.27	0.00	0.00	2.29	1.92
1.00	-24.82	0.89	-0.63	-0.57	3.72	3.91	1.00	0.77	17.93	14.29	-0.43	0.42
2.00	-20.31	-6.98	0.62	0.31	5.22	4.62	-0.19	-0.10	3.45	11.68	0.05	-0.18
5.00	-4.72	-0.75	-0.39	-0.26	0.53	1.10	0.73	0.06	1.83	1.29	0.03	-0.10
7.00	-6.30	-2.08	0.12	0.00	1.56	0.94	-0.09	-0.05	1.46	0.54	-0.06	-0.02
14.00	-2.81	-1.05	-0.04	0.05	0.19	0.22	-0.06	-0.07	0.15	0.15	-0.10	-0.04
21.00	-2.01	-0.54	-0.04	-0.08	0.01	0.01	-0.05	-0.03	-0.24	-0.02	0.08	-0.04
28.00	-1.59	-0.66	-0.05	0.05	-0.04	-0.02	0.03	-0.01	-0.12	-0.09	-0.01	-0.01
42.00	-1.15	-0.34	0.17	-0.02	0.00	-0.02	-0.04	-0.02	-0.10	-0.07	-0.01	-0.02
56.00	-0.79	-0.31	-0.03	-0.01	-0.03	-0.03	0.01	-0.02	-0.09	-0.08	0.00	0.00
84.00	-0.58	-0.22	0.19	-0.02	-0.01	-0.03	-0.01	0.02	-0.06	-0.05	-0.01	-0.01
112.00	-0.39	-0.19	-0.01	0.00	-0.02	-0.01	0.02	0.00	-0.05	-0.05	-0.02	-0.02
168.00	-0.28	-0.13	0.01	0.01	0.00	-0.01	0.01	0.01	-0.05	-0.04	0.01	0.01
Phytosterols												
0.00	0.00	0.00	-0.47	-0.19	0.00	0.00	0.63	0.53	0.00	0.00	0.51	0.54
1.00	-0.26	-0.06	-1.00	-1.00	5.13	4.41	-0.54	-0.53	5.38	6.16	-0.48	-0.41
2.00	-0.27	-0.17	#DIV/0!	#DIV/0!	-1.04	-1.19	0.19	0.35	-1.11	-0.53	0.27	0.24
5.00	0.05	0.01	-0.11	0.13	0.29	0.76	0.42	-0.13	0.90	1.25	0.00	-0.21
7.00	0.01	0.02	0.05	-0.04	1.35	0.09	-0.09	-0.03	0.65	-0.16	-0.06	-0.02
14.00	0.02	0.00	0.15	0.19	-0.13	-0.09	0.09	0.03	-0.15	-0.16	0.04	0.01
21.00	0.06	0.03	-0.10	-0.03	0.11	0.02	-0.04	0.00	0.01	-0.08	0.00	0.02
28.00	0.00	0.01	-0.01	0.01	-0.01	0.01	0.04	0.01	0.00	-0.01	0.00	0.01
42.00	0.00	0.01	0.12	0.06	0.11	0.03	-0.02	0.00	-0.01	0.02	-0.01	-0.02
56.00	0.01	0.02	-0.03	0.00	0.02	0.02	0.00	0.00	-0.03	-0.04	0.01	0.02
84.00	0.00	0.01	0.10	-0.01	0.01	0.03	0.00	0.00	0.00	0.03	-0.01	-0.01
112.00	0.01	0.00	-0.02	-0.02	0.00	0.01	0.02	0.01	-0.02	-0.01	0.00	0.00
168.00	0.00	0.00	#DIV/0!	#DIV/0!	0.04	0.03	0.01	0.01	-0.01	0.00	0.01	0.01

APPENDIX C: BATCH EQUILIBRIUM DATA

Adsorption Kinetics Data for Preliminary Assessments in the Batch Equilibrium Experiments								
Resin Acid Concentration in Solution								
Soils	0	1	10	30	60	120	180	240
Sand	1633.18	46.9041	37.3447	34.7143	36.532	28.649	45.251	121.67
Kawerau	1633.18	25.74	33.8701	18.3966	17.69185	12.41816	8.287425	0
Whaka	1633.18	18.621	28.1096	15.209	5.209581	0	0	0
Resin Acid Adsorption								
Soil	0	1	10	30	60	120	180	240
Sand	0	2906.26	3145.24	3211	3169.638	3366.713	2951.663	1020.88
Kawerau	0	3439.44	3232.11	3618.94	3616.29	3764.334	3867.602	4082.94
Whakare	0	3617.41	3363.93	3702.71	3944.548	4078.859	4082.938	4074.79
Soils	0	1	10	30	60	120	180	240
Sand	0	71.1805	77.0338	78.6444	77.6313	82.4581	72.29262	25.0036
Kawerau	0	84.2393	79.1613	88.6358	88.57078	92.1967	94.72597	100
Whaka	0	88.5983	82.39	90.6875	96.61055	99.9001	100	99.8004

Resin Acid Adsorption and Desorption for the Batch Equilbrium Experiments

Soil	Effluent	Soil Concen	Resin Ad	Adsorption	Resin De	Desorption
Sand	water	0	0	0	0	0
Sand	water	1.02	0	0	0	0
Sand	water	2	0	0	0	0
Sand	water	5.02	0	0	0	0
Sand	water	10.02	0	0	0	0
Sand	CTMP	0	13.84680192	0	1.93333333	0
Sand	CTMP	1.03	6.026361067	189.816479	2.14376005	-5.1074528
Sand	CTMP	2.02	11.04510333	34.6744638	3.64545006	-21.189568
Sand	CTMP	5	11.30544559	12.7067721	5.41541197	-17.410395
Sand	CTMP	10	10.67387771	7.93230572	5.61457073	-9.2030943
Sand	TMP	0	793.19	0	2.22532899	0
Sand	TMP	1.03	117.45	16401.4563	24.644809	-544.16214
Sand	TMP	2.01	95.59	8676.61692	28.7672711	-330.12366
Sand	TMP	5.03	26.72	3809.49304	31.4496137	-145.24992
Sand	TMP	10.01	67.03	1813.58641	27.8586901	-64.019383
Sand	Kraft	0	8.522497801	0	1.25704341	0
Sand	Kraft	1.05	9.980897326	-34.723793	2.89248705	-38.939144
Sand	Kraft	2.01	7.391937309	14.0617001	2.91719892	-20.648705
Sand	Kraft	5.01	12.18760582	-18.288961	2.04292995	-3.9215916
Sand	Kraft	10	1.620847526	17.2541262	2.23422563	-2.4429566
Kawerau	water	0	0	0	0.44973672	0
Kawerau	water	1	0	0	1.61458333	-29.121158
Kawerau	water	2.01	2.553159085	-31.75571	1.34916723	-11.186943
Kawerau	water	5	2.439282744	-12.196414	1.85846126	-7.0436213
Kawerau	water	10.03	6.757980828	-16.844419	1.87159188	-3.5440052
Kawerau	CTMP	0	3.679487183	0	1.32141051	0
Kawerau	CTMP	1	5.731151922	-51.291623	2.23257498	-22.779099
Kawerau	CTMP	2.04	5.153201607	-18.060228	2.78264594	-17.907291
Kawerau	CTMP	5.01	6.173123224	-12.443295	2.47763893	-5.7696004
Kawerau	CTMP	10.01	2.514150944	2.91042971	3.1239704	-4.5018966
Kawerau	TMP	0	714.331	0	1.17528193	0
Kawerau	TMP	1	35.43543704	561.810574	3.88846738	-67.829634
Kawerau	TMP	2.02	10.72587502	583.935458	7.66923987	-80.370766
Kawerau	TMP	5.04	15.26930834	211.500752	7.01224663	-28.953198
Kawerau	TMP	10	7.30853862	126.498303	5.6445949	-11.173282
Kawerau	Kraft	0	3.113816055	0	0.48025435	0
Kawerau	Kraft	1.03	2.560530346	13.4292634	1.36698091	-21.522498
Kawerau	Kraft	2.04	1.868122402	15.2658529	2.0560671	-19.311435
Kawerau	Kraft	5.01	1.847463303	6.31912524	2.16565521	-8.4101857
Kawerau	Kraft	10.02	1.388177161	4.30548612	3.09380744	-6.5208419
Whaka	water	0	1.573771937	0	0.8345984	0
Whaka	water	1.03	1.859624833	-6.9381756	0.76291593	1.73985604
Whaka	water	2.01	1.447740098	1.56756097	1.9914139	-14.388257
Whaka	water	5.02	9.00390625	-37.002661	2.0578394	-6.0918396
Whaka	water	10.02	2.943972472	-3.4186639	1.2201692	-0.962004
Whaka	CTMP	0	13.80043862	0	0.49777418	0
Whaka	CTMP	1.02	8.798283279	122.60188	0.80535712	-7.5388019
Whaka	CTMP	2.01	6.947170163	85.2396746	1.92519429	-17.753984
Whaka	CTMP	5.01	6.772241668	35.07085	3.14330183	-13.201237
Whaka	CTMP	10	5.380338033	21.0502549	1.64383562	-2.865154
Whaka	TMP	0	714.31	0	4.66273725	0
Whaka	TMP	1.02	22.65	16952.451	21.3984063	-410.18797
Whaka	TMP	2.01	22.74	8601.61692	5.1172758	-5.6534676
Whaka	TMP	5.02	14.13	3486.95219	1.77454781	14.3834123
Whaka	TMP	10.02	5.18	1769.28643	3.37462586	3.21385016
Whaka	Kraft	0	4.375258998	0	2.66046277	0
Whaka	Kraft	1.02	4.865506375	-12.015867	1.63216562	25.2033672
Whaka	Kraft	2.01	5.047438885	-8.3604463	2.54375663	1.45157176
Whaka	Kraft	5.02	2.981247658	6.94228756	2.8854114	-1.120261
Whaka	Kraft	10.04	2.40145206	4.91485792	2.80244828	-0.353549

Total Carbon and Total Organic Carbon for the Batch Equilibrium Experiment

Soil	Effluent	Concen	Ad TC	TC adsorpti	De TC	TC Desorpti	Ad TOC	TOC Adsorpti	De TOC	TOC Desorp
Sand	water	0	6.806	0	6.806	0	6.806	0	6.806	0
Sand	water	1.02	7.12	-7.6960784	15.68	-217.5	2.573	103.75	10.2	-83.18627451
Sand	water	2	24.69	-223.55	14.9	-101.175	20.4	-169.925	9.09	-28.55
Sand	water	5.02	46.4	-197.18127	14.76	-39.611554	39.56	-163.11753	7.538	-3.645418327
Sand	water	10.02	40.26	-83.468064	16.59	-24.411178	30.44	-69.5284431	6.02	1.961077844
Sand	CTMP	0	5487	0	83.61	0	5487	0	77.25	0
Sand	CTMP	1.03	6503	-24660.194	259.4	-4266.7476	6503	-24660.1942	237.9	-3899.271845
Sand	CTMP	2.02	6334	-10482.673	314.4	-2856.3119	6334	-10482.6733	287.6	-2603.341584
Sand	CTMP	5	5403	420	517.6	-2169.95	5403	420	491.9	-2073.25
Sand	CTMP	10	5457	75	943.9	-2150.725	5457	75	911.2	-2084.875
Sand	TMP	0	637.4	0	27.96	0	637.4	0	27.96	0
Sand	TMP	1.03	626.2	271.84466	82.99	-1335.6796	598.1	953.8834951	71.38	-1053.883495
Sand	TMP	2.01	643.1	-70.895522	88.5	-752.98507	605.3	399.2537313	69.3	-514.1791045
Sand	TMP	5.03	630.1	36.282306	106.4	-389.86083	587.1	250	88.34	-300.0994036
Sand	TMP	10.01	629.3	20.22977	132.9	-262.08791	574.6	156.8431568	110.8	-206.8931069
Sand	Kraft	0	225.6	0	14.88	0	168.5	0	10.65	0
Sand	Kraft	1.05	217	204.7619	22.94	-191.90476	161.2	173.8095238	13.3	-63.0952381
Sand	Kraft	2.01	541.5	-3929.1045	22.91	-99.875622	490.9	-4009.95025	11.12	-5.845771144
Sand	Kraft	5.01	424	-990.01996	32.81	-89.471058	368.9	-1000	17.09	-32.13572854
Sand	Kraft	10	729.1	-1258.75	44.55	-74.175	676.34	-1269.6	23.97	-33.3
Kawerau	water	0	6.393	0	11.88	0	6.393	0	10.96	0
Kawerau	water	1	28.68	-557.175	15.21	-83.25	21.151	-368.95	15.21	-106.25
Kawerau	water	2.01	28.63	-276.5796	33.62	-270.39801	28.63	-276.579602	33.62	-281.840796
Kawerau	water	5	64.54	-290.735	116.73	-524.25	64.54	-290.735	116.7	-528.7
Kawerau	water	10.03	155	-370.40628	149.7	-343.51944	155	-370.406281	149.7	-345.8125623
Kawerau	CTMP	0	5173	0	71.1	0	5173	0	68.71	0
Kawerau	CTMP	1	5660	-12175	463.1	-9800	5660	-12175	449	-9507.25
Kawerau	CTMP	2.04	5657	-5931.3725	662.1	-7242.6471	5657	-5931.37255	662.1	-7271.936275
Kawerau	CTMP	5.01	5316	-713.57285	1447	-6865.7685	5316	-713.572854	1447	-6877.694611
Kawerau	CTMP	10.01	5374	-501.998	1865	-4480.2697	5374	-501.998002	1865	-4486.238761

Kawerau	TMP	0	613.8	0	30.49	0	613.8	0	27.05	0
Kawerau	TMP	1	588	645	110.3	-1995.25	588	645	107.3	-2006.25
Kawerau	TMP	2.02	4008	-42007.426	200.8	-2107.797	4008	-42007.4257	194.2	-2068.688119
Kawerau	TMP	5.04	3674	-18224.206	196.9	-825.44643	3674	-15179.5635	178	-748.7599206
Kawerau	TMP	10	2350	-4340.5	317.5	-717.525	2350	-4340.5	287.11	-650.15
Kawerau	Kraft	0	214.5	0	23.98	0	162.8	0	18.73	0
Kawerau	Kraft	1.03	215.2	-16.990291	41.39	-422.57282	167.4	-111.650485	33.28	-353.1553398
Kawerau	Kraft	2.04	219.4	-60.04902	74.57	-619.97549	189	-321.078431	64.5	-560.9068627
Kawerau	Kraft	5.01	228.4	-69.361277	138.1	-569.46108	208.8	-229.540918	130.9	-559.7305389
Kawerau	Kraft	10.02	290.6	-189.87026	229	-511.52695	275.6	-281.437126	220.9	-504.4161677
Whakarewar	water	0	13.58	0	8.757	0	13.58	0	8.757	0
Whakarewar	water	1.03	17.4	-92.718447	20.07	-274.58738	17.4	-92.7184466	17.83	-220.2184466
Whakarewar	water	2.01	35.78	-276.1194	38.33	-367.82338	33.55	-248.383085	38.33	-367.8233831
Whakarewar	water	5.02	47.36	-168.22709	62.36	-266.94721	47.36	-168.227092	62.36	-266.9472112
Whakarewar	water	10.02	82.58	-172.15569	220.7	-528.7999	74.47	-151.921158	220.7	-528.7999002
Whaka	CTMP	0	5560	0	108.9	0	5660	0	100.99	0
Whaka	CTMP	1.02	5861	-7377.451	581.7	-11588.235	5861	-4926.47059	555.5	-11139.95098
Whaka	CTMP	2.01	8014	-30522.388	184.2	-936.56716	8014	-29278.607	184.2	-1034.950249
Whaka	CTMP	5.01	12823	-36242.515	368.3	-1294.4112	12823	-35743.513	368.3	-1333.882236
Whaka	CTMP	10	11050	-13725	392.2	-708.25	11050	-13475	392.2	-728.025
Whaka	TMP	0	569.7	0	50.31	0	569.7	0	48	0
Whaka	TMP	1.02	549.8	487.7451	113.1	-1538.9706	549.6	492.6470588	102.7	-1340.686275
Whaka	TMP	2.01	551.1	231.34328	106.9	-703.85572	551.1	231.3432836	99.74	-643.5323383
Whaka	TMP	5.02	552.7	84.661355	165.5	-573.65538	552.7	84.66135458	162.5	-570.2191235
Whaka	TMP	10.02	509.7	149.7006	232.2	-453.81737	509.7	149.7005988	232.2	-459.5808383
Whaka	Kraft	0	206.6	0	23.2	0	150.4	0	17.54	0
Whaka	Kraft	1.02	214.8	-200.98039	45.98	-558.33333	210.8	-1480.39216	38.46	-512.745098
Whaka	Kraft	2.01	3224	-37529.851	83.19	-746.14428	3202	-37955.2239	75.79	-724.5024876
Whaka	Kraft	5.02	1578	-6829.6813	141.1	-587.15139	1578	-7109.56175	136.3	-591.4342629
Whaka	Kraft	10.04	331.5	-311.00598	225.5	-503.73506	331.5	-450.946215	222.1	-509.3625498

Chemical Oxygen Demand Data for Batch Equilibrium Experiments

Soil	Effluent	Concen	COD(AD)	COD ADSO	COD(DE)	COD DESORP
	water	0	11.98753	0	76.86623	0
Sand	water	1.02	4.614955	180.700368	14.93657	1517.89346
Sand	water	2	78.34075	-829.41525	50.32495	331.770913
Sand	water	5.02	107.8311	-477.308616	10.51302	330.44623
Sand	water	10.02	75.39172	-158.194087	29.68173	117.726779
Sand	CTMP	0	13570.62	0	223.9542	0
Sand	CTMP	1.03	14081.06	-12389.3204	669.9708	-10825.6456
Sand	CTMP	2.02	16195.73	-32488.9851	833.182	-7539.94802
Sand	CTMP	5	14956.1	-6927.4	1409.416	-5927.309
Sand	CTMP	10	15247.77	-4192.875	2535.01	-5777.6395
Sand	TMP	0	3672.792	0	84.66188	0
Sand	TMP	1.03	2493.757	28617.3544	249.28	-3995.58544
Sand	TMP	2.01	55095.43	-639585.05	247.873	-2029.98905
Sand	TMP	5.03	51390.27	-237164.404	259.3579	-868.270477
Sand	TMP	10.01	17224.93	-33846.4985	349.1765	-660.625924
Sand	Kraft	0	542.6228	0	36.82413	0
Sand	Kraft	1.05	516.9259	611.830952	52.30105	-368.498095
Sand	Kraft	2.01	2191.44	-20507.6766	39.63811	-34.9997512
Sand	Kraft	5.01	755.4357	-1061.94062	60.743	-119.355639
Sand	Kraft	10	1964.702	-3555.198	84.66188	-119.594375
Kawerau	water	0	10.52799	0	32.85994	0
Kawerau	water	1	171.8478	-4032.99525	35.73166	-71.793
Kawerau	water	2.01	70.4858	-745.743905	90.29436	-714.358458
Kawerau	water	5	183.2687	-863.70355	343.0058	-1550.7293
Kawerau	water	10.03	369.3926	-894.478091	411.9271	-944.8334
Kawerau	CTMP	0	23341.11	0	248.5833	0
Kawerau	CTMP	1	22790.35	13769	3656.637	-85201.3425
Kawerau	CTMP	2.04	26094.92	-33747.6716	2485.833	-27417.2757
Kawerau	CTMP	5.01	25957.23	-13054.491	10188.74	-49601.5803
Kawerau	CTMP	10.01	32979.44	-24071.7532	9899.651	-24103.5657
Kawerau	TMP	0	3914.645	0	303.6332	0
Kawerau	TMP	1	3219.317	17383.2	550.0991	-6161.6475
Kawerau	TMP	2.02	8689.824	-59098.75	791.0573	-6032.47649
Kawerau	TMP	5.04	70738.54	-331467.733	2926.18	-13008.6647
Kawerau	TMP	10	16623.86	-31773.0375	3463.172	-7898.847
Kawerau	Kraft	0	505.9504	0	65.16655	0
Kawerau	Kraft	1.03	510.3739	-107.366505	110.0376	-1089.10316
Kawerau	Kraft	2.04	626.8607	-1481.74387	342.958	-3404.30699
Kawerau	Kraft	5.01	5391.553	-24379.2545	1068.653	-5007.41742
Kawerau	Kraft	10.02	3990.763	-8694.64222	1212.239	-2861.95721
Whaka	water	0	33.36974	0	-4.22465	0
Whaka	water	1.03	46.21822	-311.856311	62.86161	-1628.30728
Whaka	water	2.01	110.4606	-958.841542	80.36237	-1052.07736
Whaka	water	5.02	143.2956	-547.439542	169.3246	-864.289094
Whaka	water	10.02	218.9589	-463.046806	659.3459	-1655.61514
Whaka	CTMP	0	16330.25	0	419.1064	0
Whaka	CTMP	1.02	17486.6	-28341.9118	1663.95	-30510.8725
Whaka	CTMP	2.01	20088.39	-46743.0348	3940.374	-43796.8607
Whaka	CTMP	5.01	18498.41	-10819.1617	4083.96	-18287.6926
Whaka	CTMP	10	15318.45	2529.5	5017.269	-11495.4065
Whaka	TMP	0	10018.27	0	154.9086	0
Whaka	TMP	1.02	10087.12	-1687.5	306.8911	-3725.06127
Whaka	TMP	2.01	9949.425	856.281095	318.7515	-2037.84701
Whaka	TMP	5.02	11050.95	-5142.82869	146.3053	42.8451195
Whaka	TMP	10.02	11808.25	-4466.01796	73.93271	202.035654
Whaka	Kraft	0	515.9017	0	186.4295	0
Whaka	Kraft	1.02	664.373	-3639.00245	281.8284	-2338.20833
Whaka	Kraft	2.01	610.1239	-1171.91791	368.5546	-2265.23756
Whaka	Kraft	5.02	15043.37	-72347.9497	2615.922	-12099.0662
Whaka	Kraft	10.04	161.8546	881.591384	12429.17	-30484.9116

Colour Sorption Data for Batch Equilibrim Experiments

Colour Adsorption

Soil	Effluent	Concen	pH	Dilution	Absorbance	Colour (CPU	Adsorption
Sand	water	0	7.56	1	0.015	55.56	0
Sand	water	1.02	7.63	1	0.011	40.74	363.235294
Sand	water	2	7.58	1	0.012	44.44	139
Sand	water	5.02	7.58	1	0.017	62.96	-36.8525896
Sand	water	10.02	7.65	1	0.028	103.7	-120.10978
Sand	CTMP	0	7.57	10	0.24	8823.53	0
Sand	CTMP	1.03	7.61	10	0.252	9264.71	-10708.2524
Sand	CTMP	2.02	7.58	10	0.344	12647.06	-47320.9158
Sand	CTMP	5	7.6	50	0.094	17279.41	-42279.4
Sand	CTMP	10	7.61	50	0.086	15808.82	-17463.225
Sand	TMP	0	7.57	10	0.043	1580.88	0
Sand	TMP	1.03	7.6	10	0.036	1323.53	6246.35922
Sand	TMP	2.01	7.57	10	0.031	1139.71	5487.18905
Sand	TMP	5.03	7.64	10	0.026	955.88	3106.36183
Sand	TMP	10.01	7.58	10	0.03	1102.94	1193.65634
Sand	Kraft	0	7.58	1	0.154	566.18	0
Sand	Kraft	1.05	7.59	1	0.187	687.5	-2888.57143
Sand	Kraft	2.01	7.6	1	0.192	705.88	-1737.56219
Sand	Kraft	5.01	7.61	1	0.192	705.88	-697.105788
Sand	Kraft	10	7.64	1	0.213	783.09	-542.275
Kawerau	water	0	7.64	1	0.042	160.13	0
Kawerau	water	1	7.64	1	0.058	221.37	-1531
Kawerau	water	2.01	7.61	1	0.112	427.48	-3325.24876
Kawerau	water	5	7.62	10	0.013	481.48	-1606.75
Kawerau	water	10.03	7.62	50	0.009	1666.67	-3755.08475
Kawerau	CTMP	0	7.56	10	0.185	6851.85	0
Kawerau	CTMP	1	7.57	50	0.078	14661.65	-195245
Kawerau	CTMP	2.04	7.57	50	0.092	17557.25	-131193.627
Kawerau	CTMP	5.01	7.59	50	0.118	22519.08	-78179.7904
Kawerau	CTMP	10.01	7.62	50	0.134	25572.52	-46754.9201
Kawerau	TMP	0	7.6	1	0.389	1430.15	0
Kawerau	TMP	1	7.57	1	0.277	1018.38	10294.25
Kawerau	TMP	2.02	7.58	50	0.011	2022.06	-7325.61881
Kawerau	TMP	5.04	7.58	50	0.012	2205.88	-3847.86706
Kawerau	TMP	10	7.55	50	0.016	2941.18	-3777.575
Kawerau	Kraft	0	7.65	1	0.136	503.7	0
Kawerau	Kraft	1.03	7.6	1	0.223	825.93	-7821.1165
Kawerau	Kraft	2.04	7.6	1	0.256	948.15	-5446.69118
Kawerau	Kraft	5.01	7.61	10	0.04	1503.76	-4990.31936
Kawerau	Kraft	10.02	7.65	10	0.061	225.93	693.038922
Whaka	water	0	7.65	1	0.008	29.63	0
Whaka	water	1.03	7.6	1	0.049	181.48	-3685.67961
Whaka	water	2.01	7.65	1	0.079	292.59	-3270.64677
Whaka	water	5.02	7.55	1	0.113	418.52	-1936.70319
Whaka	water	10.02	7.63	1	0.212	785.19	-1885.12974
Whaka	CTMP	0	7.64	10	0.229	8419.12	0
Whaka	CTMP	1.02	7.64	10	0.288	10588.24	-53164.7059
Whaka	CTMP	2.01	7.59	50	0.079	14522.06	-75907.2139
Whaka	CTMP	5.01	7.56	50	0.089	16360.29	-39626.5968
Whaka	CTMP	10	7.61	50	0.074	13602.94	-12959.55
Whaka	TMP	0	7.63	10	0.043	1580.88	0
Whaka	TMP	1.02	7.62	10	0.044	1617.65	-901.22549
Whaka	TMP	2.01	7.64	1	0.273	1003.67	7179.22886
Whaka	TMP	5.02	7.64	1	0.219	805.15	3863.19721
Whaka	TMP	10.02	7.64	1	0.282	1036.76	1357.58483
Whaka	Kraft	0	7.6	20	0.01	763.36	0
Whaka	Kraft	1.02	7.57	10	0.024	916.03	-3741.91176
Whaka	Kraft	2.01	7.6	10	0.042	1603.05	-10443.9055
Whaka	Kraft	5.02	7.6	50	0.013	2480.92	-8553.58566
Whaka	Kraft	10.04	7.63	50	0.039	7442.75	-16631.9472

Colour	Desorption						
Soil	Effluent	Concen	pH	Dilution	Absorbance	Colour (CPU	Desorption
Sand	water	0	7.56	1	0.008	29.63	0
Sand	water	1	7.62	1	0.005	18.52	272.303922
Sand	water	2	7.64	1	0.007	25.93	46.25
Sand	water	5	7.59	1	0.013	48.15	-92.2310757
Sand	water	10	7.62	1	0.027	100	-175.573852
Sand	CTMP	0	7.61	1	0.117	446.56	0
Sand	CTMP	1	7.63	10	0.033	1259.54	-19732.5243
Sand	CTMP	2	7.64	10	0.037	1412.21	-11951.1139
Sand	CTMP	5	7.6	50	0.013	2480.92	-10171.8
Sand	CTMP	10	7.6	50	0.02	3816.79	-8425.575
Sand	TMP	0	7.6	1	0.048	188.21	0
Sand	TMP	1	7.62	1	0.198	755.73	-13774.7573
Sand	TMP	2	7.63	1	0.127	484.73	-3688.0597
Sand	TMP	5	7.57	1	0.127	484.73	-1473.75746
Sand	TMP	10	7.62	1	0.135	515.27	-816.833167
Sand	Kraft	0	7.59	1	0.013	49.62	0
Sand	Kraft	1	7.62	1	0.019	72.52	-545.238095
Sand	Kraft	2	7.61	1	0.023	87.79	-474.751244
Sand	Kraft	5	7.6	1	0.046	175.57	-628.493014
Sand	Kraft	10	7.58	1	0.075	286.26	-591.6
Kawerau	water	0	7.64	1	0.04	147.06	0
Kawerau	water	1	7.64	1	0.099	363.97	-5422.75
Kawerau	water	2	7.59	1	0.287	1055.15	-11294.6517
Kawerau	water	5	7.58	10	0.066	2426.47	-11397.05
Kawerau	water	10	7.62	10	0.077	2830.88	-6689.48156
Kawerau	CTMP	0	7.61	1	0.067	246.32	0
Kawerau	CTMP	1	7.63	10	0.069	2536.76	-57261
Kawerau	CTMP	2	7.59	10	0.148	5441.18	-63662.5
Kawerau	CTMP	5	7.55	50	0.049	9007.35	-43717.7146
Kawerau	CTMP	10	7.58	50	0.063	11580.88	-28308.0919
Kawerau	TMP	0	7.56	1	0.041	150.74	0
Kawerau	TMP	1	7.6	1	0.236	867.65	-17922.75
Kawerau	TMP	2	7.56	10	0.064	2352.94	-27254.9505
Kawerau	TMP	5	7.57	10	0.064	2352.94	-10923.6111
Kawerau	TMP	10	7.61	10	0.106	3897.06	-9365.8
Kawerau	Kraft	0	7.63	1	0.025	91.91	0
Kawerau	Kraft	1	7.62	1	0.129	474.26	-9280.33981
Kawerau	Kraft	2	7.64	1	0.346	1272.06	-14462.6225
Kawerau	Kraft	5	7.57	10	0.068	2500	-12016.4172
Kawerau	Kraft	10	7.57	10	0.11	4044.12	-9860.80339
Whaka	water	0	7.55	1	0.014	52.63	0
Whaka	water	1	7.57	1	0.077	289.47	-5748.54369
Whaka	water	2	7.61	1	0.208	781.95	-9071.14428
Whaka	water	5	7.63	10	0.037	1360.29	-6512.251
Whaka	water	10	7.65	10	0.05	1838.24	-4455.11477
Whaka	CTMP	0	7.59	1	0.149	547.79	0
Whaka	CTMP	1	7.62	10	0.094	3455.88	-71276.7157
Whaka	CTMP	2	7.61	10	0.85	3125	-32054.8507
Whaka	CTMP	5	7.6	10	0.145	5330.88	-23867.7146
Whaka	CTMP	10	7.65	10	0.127	4669.12	-10303.325
Whaka	TMP	0	7.65	1	0.44	1617.65	0
Whaka	TMP	1	7.58	10	0.031	1139.71	11714.2157
Whaka	TMP	2	7.61	10	0.28	1029.41	7316.41791
Whaka	TMP	5	7.58	10	0.03	1102.94	2563.29681
Whaka	TMP	10	7.54	10	0.033	1213.24	1009.00699
Whaka	Kraft	0	7.58	1	0.036	132.35	0
Whaka	Kraft	1	7.56	1	0.189	694.85	-13786.7647
Whaka	Kraft	2	7.62	10	0.06	2205.88	-25790.1741
Whaka	Kraft	5	7.62	10	0.047	1727.94	-7946.16534
Whaka	Kraft	10	7.62	10	0.069	2536.76	-5987.07669

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