BIODEGRADATION AND COMPOSTING PROFILES OF WOOLSCOUR WASTES

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LIST OF ABBREVIATIONS

CF	Chemical Flocculation
CF-B	Chemical Flocculation – Biological
CFU	Colony-Forming Units
CSIRO	Commonwealth Scientific and Industrial Research Organisation
HUN	Hydrolysable Unidentified Nitrogen
i-TN	initial Total Nitrogen
MW	Molecular Weight
NPE	Nonylphenol Ethoxylate
OP	Organophosphate (insecticide)
PAM	Polyacrylamide
PCL	Protein Contaminant Layer
ppm	parts per million
SP	Synthetic Pyrethroid (insecticide)
TN	Total Nitrogen
USEPA	United States Environmental Protection Agency
WRONZ	Wool Research Organisation of New Zealand

ABSTRACT

This thesis investigated the final products from the current effluent treatment system for woolscouring (wool washing) plants, namely, (i) sludge produced from the chemical flocculation of solids in the wastewater from the wash bowls, and (ii) concentrated suint (sheep sweat) produced from evaporation of the liquid phase separated from the sludge. In addition, fibrous wastes from the woolscouring process were studied. The aims of the study were to (i) investigate whether suint could be applied in a sustainable way to arable land as a potassium fertiliser, and (ii) assess the conditions under which the sludge could be composted for use as a soil conditioner to return organic matter to soil.

Experiments involving suint were performed at both laboratory and glasshouse scales, while experiments involving the solid woolscour wastes were based both in the laboratory and using a small-scale (4.5 m^3 total capacity) in-vessel composting unit established at a New Zealand woolscour. Decomposition was measured using net-nitrogen mineralisation and weight loss methods.

Suint, the water-soluble contaminants on the fleece, contained high levels of potassium (20% on a dry weight basis) and also appreciable quantities of sulphur, sodium, and chlorine. Biological treatment before evaporation stabilised the resulting suint and improved the consistency of its composition. Suint did not affect the soil processes examined, in that it partly decomposed in soil, did not inhibit the turnover of model organic compounds, did not affect soil properties such as pH and electrical conductivity, and did not lead to increased leaching of mineral nitrogen. Suint was either neutral or positive towards plant performance when applied to soil at a rate of 100 kg potassium per hectare. Suint was therefore judged to be suitable for application to land and could be targeted to soils known to be deficient in potassium or to areas where crops with a high potassium demand are grown.

Sludge, composed of dirt (soil particles, faecal matter, and skin and fibre debris) and wool grease, was highly variable in terms of its rate of decomposition, ranging from 0.8 to 27.8% of the initial total nitrogen mineralised over 30 days at 37ºC. Fibrous wastes, such as opener (fibre and contaminants removed from the wool by agitation prior to scouring) and scoured wool cleaner (wool fibre and dust removed from scoured and dried wool) wastes, also showed variability in decomposition rates. Sludge decomposition was improved by as much as threefold when co-incubated with fibrous wastes. Although it was shown that the polyacrylamide and pesticide content of sludge did not inhibit its decomposition, the effect of the grease content was not fully understood. Chemical properties of woolscour sludge, such as the carbon to nitrogen ratio, suggested that sludge was a substrate of good resource quality. From a biological perspective, however, the data suggested that woolscour sludge was limited in available nutrients; sludge nitrogen was derived principally from keratin, which decomposed at a low rate resulting

in the slow release of mineral nitrogen and low levels of microbial activity. Thus, sludge appeared a poor substrate for composting.

However, the results from composting trials indicated that the sludge could be successfully processed after blending with a bulking agent such as sawdust. The blended material showed a 90% reduction in wool grease over 21 days of composting when the moisture content of the composting mass was kept optimal. Compost temperature exceeded 55ºC when wool fibre was added to the blend. Initial results from a case study involving the commercial composting of the entire sludge production (16 tonnes per day) from a New Zealand woolscour indicated that a saleable compost could be produced from a material that would otherwise go to landfill, and served to illustrate the commercial significance of these research results.

1. INTRODUCTION

1.1. INTRODUCTION

This thesis is divided into six sections. In Section 1, the Introduction, the woolscouring process and industry are described. The waste materials generated by current effluent treatment systems and waste disposal issues are evaluated. A description of the composting process, the favoured treatment for the solid wastes, and existing knowledge for the decomposition of woolscour wastes, is given. The application of potassium (K) fertilisers is discussed with respect to the K-rich concentrated suint produced. The section ends with the experimental aims of this research.

Section 2 outlines the research conducted to meet the experimental aims of this thesis and includes explanations of analytical methods employed in subsequent chapters. Section 3, the utilisation of suint, and Section 4, the characterisation of the woolscour wastes, include the experimental methods and results for the analysis of these by-products, along with a discussion of the results collected. Section 5 presents the methods, results, and discussion of research into the composting of woolscour wastes. The Conclusion in Section 6 draws together the discussions from previous sections and evaluates the beneficial re-use of woolscour wastes.

1.2. THE WOOLSCOURING INDUSTRY

1.2.1. THE WOOLSCOURING INDUSTRY AND ITS IMPORTANCE IN NEW ZEALAND

The mechanical cleaning (scouring) of wool dates back to the beginning of the industrial revolution, England 1800-1850 (Russell, 1996a). To meet the rapidly growing international demand for fibre and textile fabrics, Britain relied on its colonies, including South Africa, Australia and New Zealand, to establish such industries (WRONZ, 2001). The first permanent flock of merinos was imported into New Zealand from Australia in 1834, although Captain Cook had tried unsuccessfully to do this about 60 years earlier (Wools of New Zealand, 1997; WRONZ, 2001). Of a total land area of 27 million hectares (ha) in New Zealand, approximately half is farmed, with 11 million hectares used primarily for grazing sheep. Different sheep breeds, producing a range of wools each with their own end uses, are farmed to match the varying environments found in the country (Table 1-1). Most of the present day national flock are dual-purpose animals raised for both meat and wool production, the exceptions being Merino (fine wool) and Down (meat). Total sheep numbers peaked at 70.3 million in 1983 and have decreased to 46 million at present, being spread over about 20,000 farms and consisting of 70% breeding ewes (Wools of New Zealand, 1997; WRONZ, 2001). Sheep were traditionally shorn once a year between November and

January, producing full-length fleece wool, but shearing is now conducted more frequently to prevent the yellowing of wool and susceptibility to blowfly attack caused by high rainfall and high temperatures late in the season.

Table 1-1. The major sheep breeds farmed in New Zealand.

Breed	Numbers	Yield (%)	Fibre diameter (micron)	Location	Classification
Romney	27 million	75-80	33-40	Throughout country	Crossbred
Coopworth	5 million	75-80	35-40	Throughout country	
Perendale	3 million	75-80	31-37	Throughout country	
Borderdale	500,000	74-78	30-36	Mainly Canterbury	
Drysdale	200,000	77-83	40+	Throughout country	
Corriedale	2.6 million	65-72	26-33	East Coast South Island Dry parts North Island	Halfbred
Halfbred	3.8 million	65-72	24-31	South Island	
Merino	3.3 million	69-72	14-24	Mainly South Island	Merino
Down	500,000	50-70	23-35		

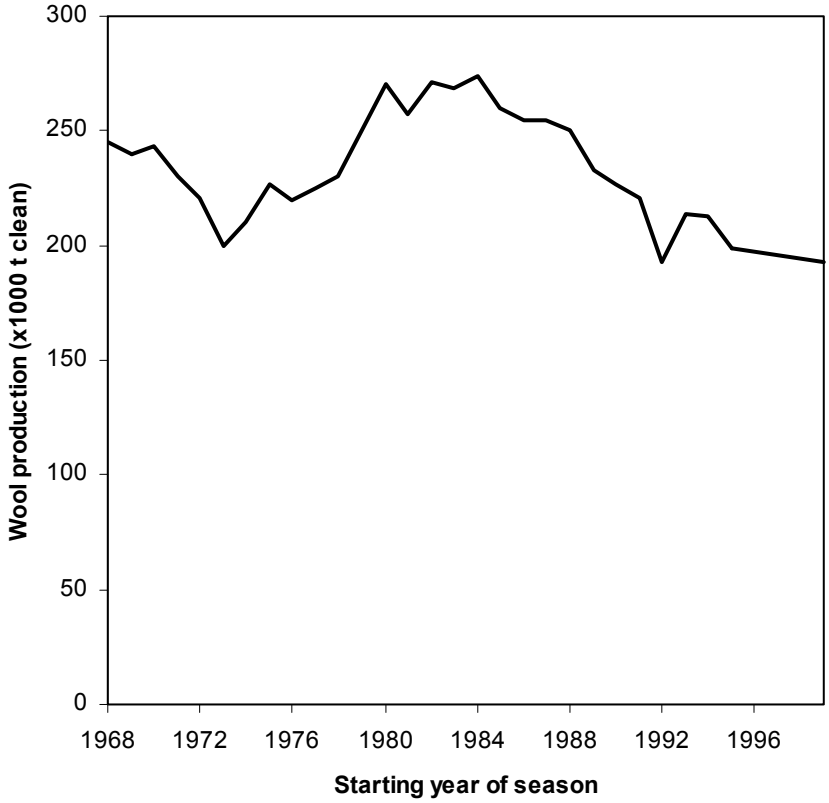
Note: yield is the percent clean, dry wool in a sample after the removal of all contaminants.
From Wools of New Zealand (1997) and WRONZ (2001).

Woolscouring operations have been established at more than 40 locations throughout New Zealand since 1860 (Bremner, 1985). In 1994, 35 plants were operating (Wool Record, 1994). Following the closure of Seaview Wools Ltd (Wellington) in August 2001 and RF Woolscour (Dunedin) in March 2002, there are currently nine plants operating, five in the South Island (in Invercargill, Timaru, Winchester, Ashburton and Christchurch) and four in the North Island (two in Hawke's Bay and two in the Manawatu). Wool was the largest export earner for New Zealand for many years, but the slump in wool prices in recent years, as well as droughts and extreme winter weather, has seen the conversion of sheep land into forestry, horticulture, and dairy and deer farming (Wools of New Zealand, 1997). The value of New Zealand wool exports in 1997 totalled NZ$946.6 million (Statistics New Zealand, 1998). During 1999/2000, Australia was the largest wool producer in the world with 438,000 tonnes clean (washed and free of contaminants); New Zealand was the largest producer of crossbred (strong) wools (Figure 1–1) with more than 30% of total world supplies (Wools of New Zealand, 1997; WRONZ, 2001). Strong wools are used for interior textiles such as carpet manufacture, upholstery, furnishings, bedding and rugs. At present, the world wool production of about 1.4 million tonnes represents only 3.3% of world textile fibre production (WRONZ, 2001).

Slipe wool originating from the pelts of lambs or sheep slaughtered for their meat accounts for approximately 12-15% of wool production in New Zealand (Wools of New Zealand, 1997; WRONZ, 2001). Wool is removed from the skins by either sweating or painting (Stewart, 1988). Sweating, often applied to merino pelts as their wool is valuable but their skins are not, involves hanging wet skins under

conditions of constant temperature and humidity to allow bacteria to loosen the wool. After two to three days, the wool can be removed from the skins by gentle pulling. Painting is used for crossbred pelts, where both the wool and the pelt are valuable, and involves the application of depilatory paste (sodium sulphide thickened with lime) to the pelt to loosen the fibres. Over 12-24 h, the fibre root is destroyed, enabling the wool to be brushed off. Due to the higher yield and lack of suint, about 50% more detergent is needed for the scouring of slipe wool and the wool requires a good dusting (vigorous shaking) before and after scouring due to contamination with depilatory and the presence of damaged fibres.

Figure 1–1. Wool production in New Zealand from the 1968/69 to 1999/2000 season.



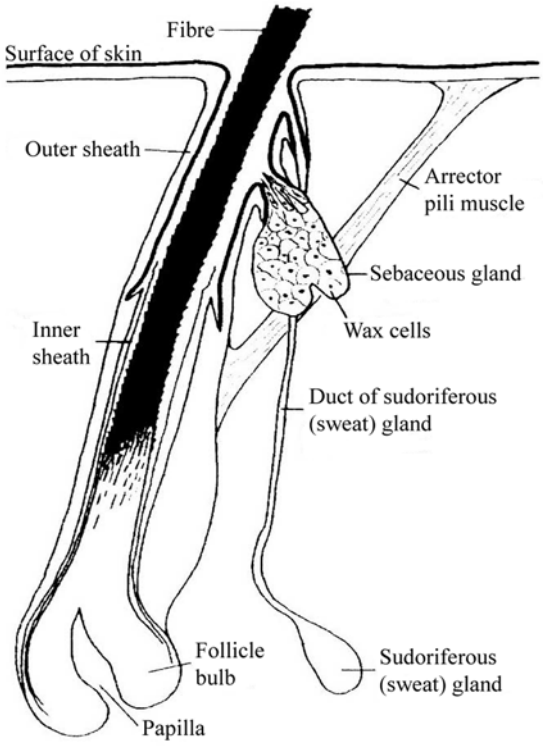
From Wools of New Zealand (1997) and WRONZ (2001).

1.2.2. STRUCTURE OF THE WOOL FIBRE

Wool, as with other α-keratin fibres, provides protection to sheep from environmental conditions on account of its durability, insolubility in water, and chemical unreactivity (Feughelman, 1997). Wool is composed of more than 90% protein (keratin) and grows from follicles in the skin (Figure 1–2), consisting of a two-part outer layer (the cuticle) and an absorbent core (the cortex) (Wools of New Zealand, 1997; WRONZ, 2001). Fibrous keratin (α-keratin) first appears in cells that form the cortex,

with the cuticle formed from the outermost layer (Mathison, 1964). As the keratin aggregates to form fibrils, matrix protein (γ-keratin) is deposited. The high molecular weight (MW) α-keratin contains low sulphur (S) proteins and low MW γ-keratin high S proteins. Like other fibrous proteins, keratin consists of folded polypeptide chains lying parallel along the axis of the fibre, cross-linked by hydrogen (H) bonds, salt cross bridges between free basic amino and acidic carboxyl groups, and disulphide bridges. Asymmetrical keratinisation of the fibre accounts for the crimp of wool (Peters, 1963). The cortex accounts for approximately 90% of the fibre and is composed of very small, elongated cells that are enclosed in a tough membrane and make the wool fibre very strong, flexible, and elastic (Wools of New Zealand, 1997; WRONZ, 2001). The cuticle is a thin porous membrane that covers overlapping scales with a wax coating and allows the wool to repel liquid but absorb moisture vapour. The wool fibre grows (in terms of length and diameter) at different rates throughout the year, depending on animal stress and the length of daylight and/or nutrition. The elemental composition of wool is approximately 52% carbon (C), 20% oxygen (O), 18% nitrogen (N), 7% H, and 4% S (the S content being higher than most proteins due to the cysteine content) distributed between 19 to 21 amino acids (Truter, 1956). It is the high cystine content that distinguishes keratins from other fibrous proteins (Feughelman, 1997). Shorn wool does not have the root system that is found in the follicle, but slipe wool will, although it will be degraded (Peters, 1963). A comprehensive review of models that propose structures for wool fibres is provided by Hearle (2000), and a review of the role of different nutrients in the production of wool provided by Hynd (2000).

Figure 1–2. The structure of a wool follicle.



From WRONZ (2001).

Contaminants on the fleece include wax (the organic solvent-extractable fraction), suint (the water-soluble fraction), dirt (including dust, faecal matter, sand, mud, and material sloughed from the skin and fibres), vegetable matter, and moisture in varying amounts depending on the breed of sheep and within the fleece itself (Truter, 1956; Stewart, 1988). The term yolk refers to all the physiological products of the fleece except the fibre (Truter, 1956).

Wool lipid (wool wax) is the heterogeneous excretion produced in the sebaceous glands (Figure 1–2) and works its way to the outside of the fleece, where it accumulates on the fibre tip (Truter, 1956; Wools of New Zealand, 1997). The wax near the fibre tip is largely oxidised while the more recently secreted wax at the fibre base is largely unoxidised. Its function is to lubricate the fibre, preventing damage during growth and providing protection from weathering, but the wax also collects dirt and dust. The amount of wool wax in the fleece generally increases as fibre diameter decreases, from 5% of crossbred fleece weight to 15% of merino fleece. Geography, nutrition, seasons and the age of the sheep may influence the wax content of the fleece. Wool wax has a molecular mass distribution from 100 to 2,000 Daltons (Jones, 1996).

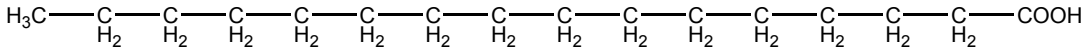
Wool grease (Table 1-2), the wool wax recovered from the greasy fleece, contains high MW esters formed from a mixture of sterols, aliphatic alcohols, and diols combined with straight chain, branched chain, and hydroxy fatty acids (Truter, 1956; Stewart, 1988). Minor constituents are free alcohols and acids. Free fatty acids may result from the hydrolysis of wool wax esters prior to scouring and a small contribution from internal wool lipids (Rankin, 1985). The acids and the alcohols occur in approximately equal amounts, but the acidic fraction is usually slightly larger (Truter, 1956). The four groups of acids (Figure 1–3) are normal, *iso*- (having a terminal *iso*-propyl residue), *anteiso*- (having a terminal *iso*-butyl residue), and the hydroxy-acids. In 1956, only three groups of alcohols were recognised as occurring in wool wax, namely, sterols (cholesterol, Figure 1–4), isocholesterol and aliphatic alcohols. Wool wax may also contain small quantities of other materials from the fleece or the washing process such as detergent, sheep dip or spray residues, dirt, some suint components, and moisture. The scouring of slipe wool may introduce large amounts of calcium ions from the depilatory process into the scour liquor, which readily precipitate fatty acids also present in the liquor and form insoluble calcium soaps that partition into the grease phase in the grease recovery process, often resulting in high soap levels in slipe wool greases (Rankin, 1985). Crude wool grease can be refined to lanolin by a process of deodorisation, bleaching, and neutralisation, producing a lighter coloured material with little odour and low free fatty acid and moisture contents (Truter, 1956). Lanolin is widely used in the pharmaceutical and cosmetic industries.

Table 1-2. The constituents of wool wax.

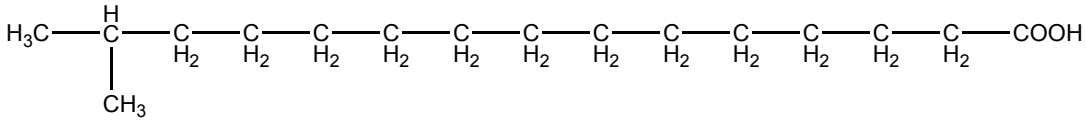
Acidic Fraction	Content (approx. %)
n-Acids (9): decanoic to hexacosanoic	7
iso-Acids (10): 8-methylnonanoic to 26-methylheptacosanoic	22
anteiso-Acids (12): (+)6-methyloctanoic acid to (+)28-methyltriacontanoic	29
α-Hydroxy-*n*-acids (4): 2-hydroxydodecanoic to 2-hydroxyoctadecanoic	25
α-Hydroxy-*iso*-acids (1): 2-hydroxy-16-methylheptadecanoic.	3
Total	86
Unidentified residue (unsaturated acids?)	14
Alcoholic Fraction	
Aliphatics	
n-Alcohols (7): octadecanol to triacontanol	4
iso-Alcohols (5): 16-methylheptadecanol to 24-methylpentacosanol	6
anteiso-Alcohols (6): (+)14-methylhexadecanol to (+)24-methylhexacosanol	7
n-Alkan-1,2-diols (1): hexadecanediol	0.5
iso-Alkan-1,2-diols (4): *iso*-octadecanediol to *iso*-tetracosanediol	3
Sterols	
cholesterol	20
7-oxocholesterol	5
cholestane-3,5,6-triol	2
cholest-7-en-3-ol and cholesta-3,5-dien-7-one	2
Isocholesterol	
lanosterol	10
dihydrolanosterol	10
agnosterol	1
dihydroagnosterol	4
7,11-dioxolanost-8-en-3-ol and 7-oxolanost-8-en-3-ol	2
Hydrocarbons	
Number and structure unknown	1
Total	78
Unidentified residue	22

Note: numbers in brackets refer to the number of compounds in each group. From Truter (1956).

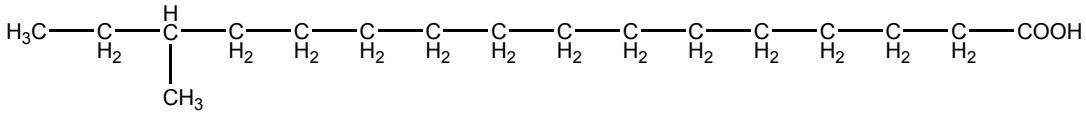
Figure 1–3. Typical acids in each series found in wool wax.



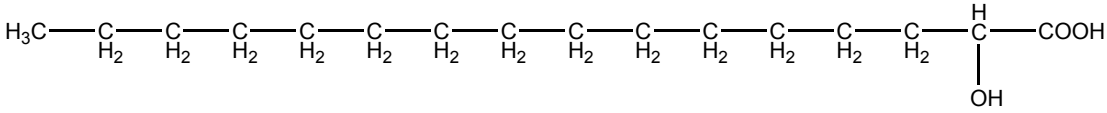
n-hexadecanoic acid (palmitic acid)



iso-hexadecanoic acid (*iso*-palmitic acid, 14-methylpentadecanoic acid)

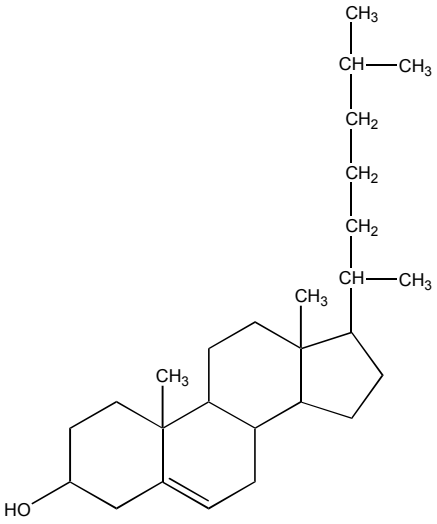


14-methylhexadecanoic acid (*anteiso*-palmitic acid, 14-ethylpentadecanoic acid)



α-hydroxypalmitic acid (2-hydroxyhexadecanoic acid)
From Truter (1956).

Figure 1–4. The structure of cholesterol.



From Garrett and Grisham (1995).

By definition, suint is the water-soluble fraction of the fleece and primarily the secretion from the sudoriferous (sweat) glands (Figure 1–2) (Hoare and Stewart, 1971; Stewart, 1988), and was first studied as early as 1802 (Truter, 1956). Suint is formed when perspiration dries on the fibre and, in contrast to the high sodium content of human sweat, is comprised mainly of K salts of fatty acids and peptides (Truter, 1956; Hoare and Stewart, 1971). It also contains other metals, inorganic material occurring as salts primarily of water-soluble organic acids, peptides secreted or derived from the wool, water-soluble or easily emulsified components of secretions from the sebaceous glands, and soluble substances from contaminants such as dirt and vegetable matter, urea and colouring matters. The K content of suint is about 25-30% and does not vary significantly between breeds, accounting for 90% of the cations present (Stewart, 1988; Bateup *et al.*, 1996). Suint will include a number of substances that cannot be regarded as true physiological products, such as compounds produced by the photochemical degradation of the fibre and glandular secretions changed by photochemical reactions. As suint solutions are excellent media for the culture of bacteria and fungi, microbial metabolic end products will also be present in stale solutions. Suint accounts for about 7-8% of the fleece weight in crossbred wools (greasy weight basis) and strong crossbred wools contain more suint than finer wools. The pH of suint ranges from 5.5-8.4 for merino wools and from 6.9-10.0 for crossbred wools (Stewart, 1988).

Suint may simply be an excretion product or, through its strongly hygroscopic properties, may protect the fleece from complete desiccation (Truter, 1956). The sudoriferous glands apparently do not play any part in temperature regulation (Truter, 1956). Suint, or the relative amounts of suint and wax, is thought to play a role in the susceptibility of wool to discolouration (Aitken *et al.*, 1994; Winder *et al.*, 1998).

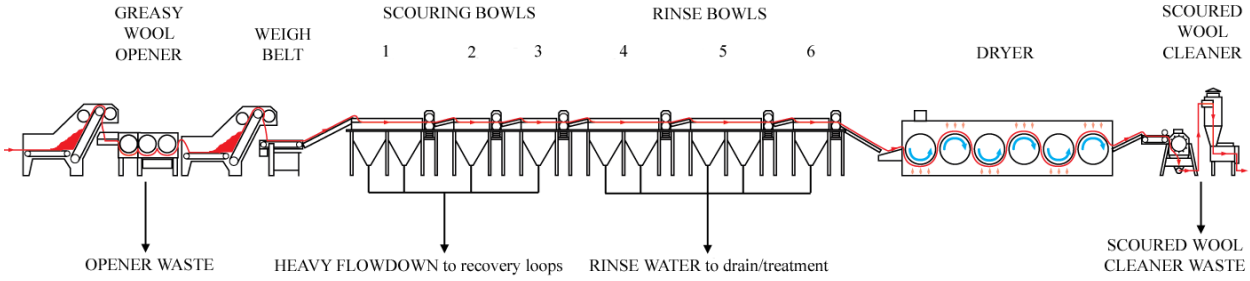
Wools from New Zealand are virtually free of vegetable matter, averaging 0.3% of the fleece weight (Wools of New Zealand, 1997). Mineral material, such as dust, dirt, and sand, picked up by the sheep adheres to the greasy fibre in varying amounts depending on grazing conditions, climate, and wool type. Most New Zealand fleeces average less than 2%, which is usually removed during scouring. Dirt is derived from soil adhering to the fleece when the sheep lies down, seeds and vegetable matter that become entangled in the fleece as the sheep grazes, and ordinary epidermal scurf and fragments of the fibre root sheath that break away when the fibre reaches the surface of the skin (Truter, 1956).

1.2.3. THE WOOLSCOURING PROCESS

The objective of woolscouring (Figure 1–5) is to remove these contaminants and leave the wool in good condition for further processing (Stewart, 1988). Woolscouring consists of four processes: (i) the removal of contaminants from the wool; (ii) the use of process loops to remove wool wax and dirt from the

scouring liquors; (iii) treatment of the discharged effluent; and (iv) disposal of sludges produced in the above processes (Bateup *et al.*, 1996).

Figure 1–5. Diagram of the ANDAR Cardmaster woolscouring system.



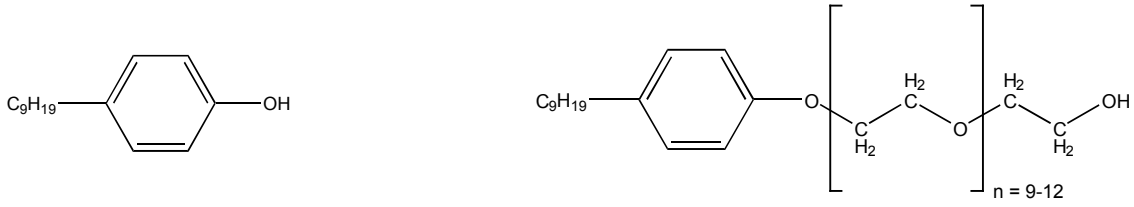
Note: while wool (shown in red) moves left to right, water flow in the bowls is in the opposite direction.

Greasy wool can be "opened" and dusted by mechanical agitation prior to scouring to remove some of the contaminants and present the wool in a form suitable for scouring, and to blend wool lots if required (Ferrier, 1960; Stewart, 1988). Wool is then scoured in hot water (60-65°C) containing synthetic detergent. An aqueous scour uses between 5 and 10 kg detergent per ton of raw wool, most of which partitions into the wool wax where it is distributed between the "cream phase" wool wax that is recovered by centrifugation and the more polar wool wax that remains suspended and/or emulsified in the scour liquor (Jones and Westmoreland, 1998). More detergent is required for the scouring of fine wools due to the high grease content (Bateup, 1986). Nonylphenol ethoxylate (NPE) detergents (Figure 1–6) are toxic to aquatic organisms and, while still used by woolscours in New Zealand, are being replaced with the faster-degrading alcohol ethoxylate type overseas. Nonylphenol, by disrupting the endocrine system, is toxic to fish, marine invertebrates and mammals, and can also inhibit plant growth (Pryor *et al.*, 2002). Concerns over the toxicological effects of nonylphenol on the soil system are related to the use of municipal biosolids as a soil amendment for agricultural land. Builders are chemicals, typically inorganic salts, that can be added to increase the effectiveness of detergents, although suint contains inorganic salts that can build the surfactant naturally (Bateup, 1986).

Grease, which softens and melts at approximately 40°C, dirt and suint appear as an irregularly deposited heterogeneous "soil" in the scouring liquor (Stewart, 1988). The stages leading to a clean fibre are an initial swelling of the non-grease contaminants (the protein contaminant layer, PCL), formation of grease globules within, or on, the swollen contaminants, removal of the swollen contaminant with attached grease globules, and breaking up of the swollen contaminant/grease complex into spherical or irregularly shaped particles in the surfactant solution (Anderson, 1983). This mechanism occurs even in the absence of suint. In scouring, oxidised grease is more difficult to remove from raw wool than the unoxidised grease found mainly close to the skin. The oxidation products of wool grease, because of their steric

configuration, have the potential to form H bonded complexes with proteins, and it is possible that the failure to remove the oxidised grease in scouring could result from characteristics of the grease/PCL complex or the nature of the PCL to which it is attached on the fibre. It may also be due to the density of oxidised grease being virtually that of water; the density of unoxidised grease, oxidised grease and water (at 80ºC) is approximately 930, 960 and 970 kg m^{-3}, respectively (personal communication, Graeme Wood, ANDAR Holdings Ltd.).

Figure 1–6. The structure of nonylphenol and nonylphenol ethoxylate.



Nonylphenol Nonylphenol ethoxylate

From Jones and Westmoreland (1998).

The PCL can constitute up to 5% of the greasy weight and consists of skin flakes and cellular debris (Bateup, 1986). It does not form a continuous layer over the fibre surface but it is highly likely that overlapping flakes at various places along the fibre, especially at the tip, could form an effective barrier to grease and dirt removal. The easily removed contaminants, consisting of the unoxidised grease, most of the oxidised grease, readily soluble suint and loosely held mineral, organic and proteinaceous dirt, comprise 80-90% of the total contaminants. Residual contaminants consist of a small fraction of the oxidised grease, slowly soluble suint, mineral material and flakes of PCL adhering to the fibre surface.

After washing in a series of three bowls, the wool is then rinsed in a series of three bowls containing hot or cold water before entering the dryer. Rinsing removes entrained liquor, water-soluble salts, and loosely held particles (Bateup, 1986). Wool drying is an energy-intensive process (Stewart, 1988). The International Wool Textile Organisation yield test calculates the percentage of clean, dry wool in a sample by the removal of all impurities (WRONZ, 2001). Wools from New Zealand tend to record high yield values in the range 75-80% for crossbred wools, whereas in other countries wool yields are around 50% and can be as low as 30%. The cleanliness of scoured wool is measured by the residual grease test. Since fibre diameter determines the end use of the fleece, this is the most important property of the wool.

1.2.4. EFFLUENT TREATMENT AND ENVIRONMENTAL REGULATIONS

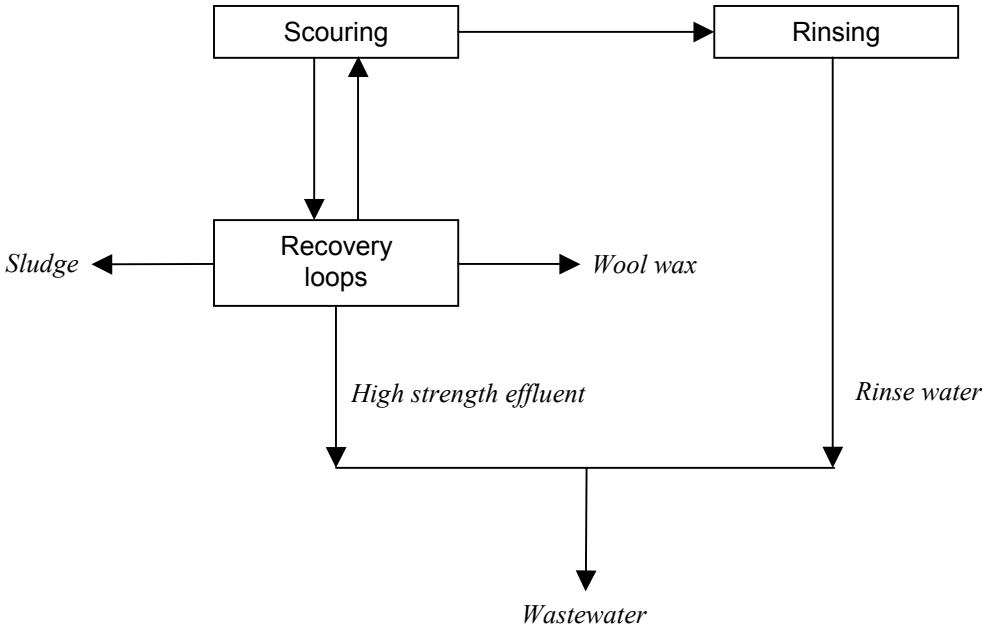
Woolscouring is easily the most polluting stage of wool processing (Russell, 1996b). The industry has traditionally been viewed as highly polluting due to the use of antiquated equipment, a lack of recycling loops, and the absence of cheap and efficient effluent treatment systems (Bateup *et al.*, 1995). Flow down from all bowls in the scouring train is toxic to algae and crustaceans, but the flow down from scouring bowls is more toxic than flow down from rinsing (Riva *et al.*, 1993). A typical woolscour plant processing about 1,500 kg raw wool per hour, discharges about 140 kg wool wax, 145 kg dirt and 70 kg suint each hour, producing an effluent with a chemical oxygen demand of approximately 25,000 mg L^{-1}, which is about 50 times higher than that of domestic sewage (Bateup *et al.*, 1996). This effluent load is equivalent to a population of 30,000 people (Christoe, 1996b; Russell, 1996a; Jones and Westmoreland, 1998), mainly due to the wool wax (Bateup *et al.*, 1996). The woolscouring industry in Uruguay generates an equivalent contamination of one million people (Gutiérrez *et al.*, 1999). The wastewater is difficult to treat due to the biologically resistant wool grease and surfactant (detergent) producing a relatively stable emulsion (Lapsirikul *et al.*, 1994a; Charles *et al.*, 1996; Poole *et al.*, 1999). Environmental responsibility is important to the wool industry and its future due to the perception of wool as a "clean green" natural fibre and the positive aspects need to be emphasised if wool is to compete with a range of synthetic fibres in the textile industry (Christoe, 1996b; Russell, 1996b).

As recently as the mid 1960s, the focus on production and economics meant that the woolscouring process was viewed as all-important (Bateup *et al.*, 1996). Contaminant recovery loops were later introduced in response to tightening discharge regulations, but also in response to the economic benefits of wool wax recovery and more efficient operation (Figure 1–7). More recently, optimisation of the recovery loops has significantly reduced the pollution load in the effluent, allowed the recovery of more of the saleable wax, and has allowed wool to be processed in cleaner liquors (Bateup *et al.*, 1995). However, even the most efficient of the current aqueous scouring systems allow a maximum of only 50% of the wax removed from the wool to be recovered in these loops. In reality only about 30% is recovered, with the remainder being discharged from the scour with the wastewater (Bateup *et al.*, 1996; Christoe, 1996a).

Increasing national and international environmental awareness has meant that legislation is in place, or under review, to prevent waste disposal into water sources or landfills (Gray *et al.*, 1996; Jones and Westmoreland, 1999). In the future, environmental regulations will place even more pressure on woolscourers to reduce their discharges to the environment (Christoe, 1996a). Europe has seen the implementation of the most stringent environmental regulations and these are likely to be adopted by other environmentally conscious countries such as Canada and New Zealand (Russell, 1996b). In general,

the location of a scour and the local environmental regulations imposed dictate what treatment systems have been installed to meet the discharge problems associated with the effluent (Hoffmann and Timmer, 1996; Russell, 1996b). In Australia, with an abundance of land and clean water, and with most cities located on the coastline, the scours do not have the same problems as those faced by scours in Europe, which tend to be clustered together on inland river systems (Russell, 1996b). The situation in New Zealand is similar to that of Australia. For scours located in rural areas with access to large areas of land, effluent has been treated using anaerobic ponds and storage dams (Bateup *et al.*, 1995; Mercz and Cord-Ruwisch, 1997). For scours located in urban areas, effluent is discharged to sewers. Woolscours produce such a large amount of effluent that local municipal plants often do not have the necessary capacity to accept this and many scours must treat their waste in-house (Stewart, 1988). For the scouring industry to remain operational, cost-effective effluent treatment processes must be available wherever its location.

Figure 1–7. The traditional use of recovery loops in woolscour effluent treatment.



Adapted from Bateup *et al.* (1996).

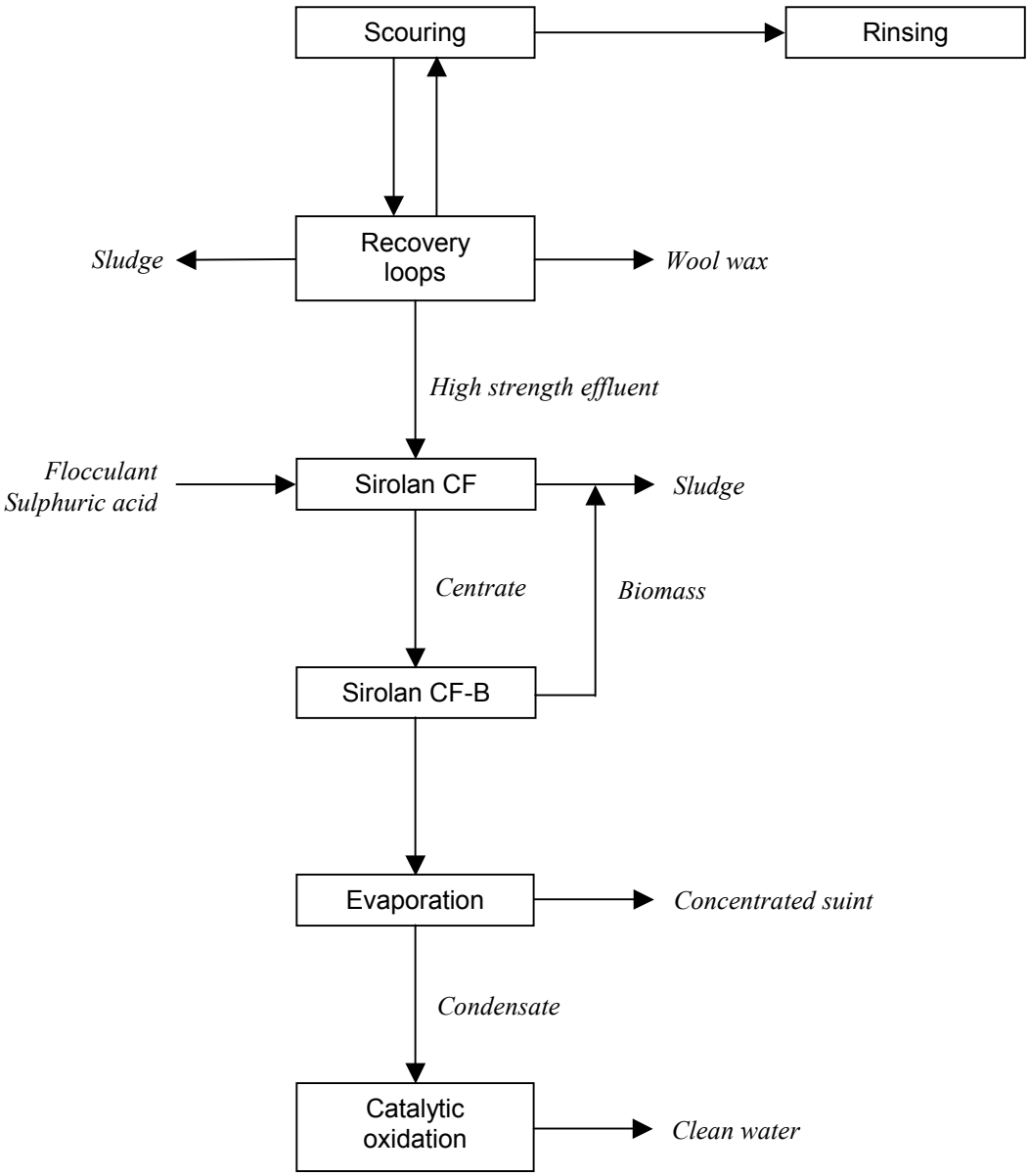
Since woolscouring is a process by which the contaminants are removed from the wool and transferred to the washing liquor, ideas of waste minimisation are not possible (Bateup *et al.*, 1995; Russell, 1996b). Reuse is an option if the wastes are viewed as a resource, an idea suggested by Easterfield and Wilson in 1890 (Russell, 1996b). Almost all methods of treating wastewaters have been applied to scouring wastes at one time or another (Stewart, 1988; Jones and Westmoreland, 1998), but no single treatment process has been successful and a combination of treatment processes appears to be necessary (Lapsirikul *et al.*, 1994b). The Enviroloop effluent treatment system developed from research by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia and ANDAR Holdings Ltd (

Figure 1–8) integrates effluent treatment with the operation of the scouring line; separately treats each waste stream using the most suitable technology; is modular, meaning that effluent treatment can be matched to local regulations; and views scouring wastes as a resource (Bateup *et al.*, 1995; Christoe, 1996a).

The Sirolan CF (Chemical Flocculation) process transfers waste products from one stream (wastewater) to another (sludge). The process destabilises the effluent first by acidification to pH 3-4 using 98% sulphuric acid (which increases the particle size of the bulk of the emulsion) and then by the addition of a high MW cationic polyacrylamide (PAM) flocculant (Jones and Westmoreland, 1999). Every 1 m^3 of dosed effluent will contain 2.5 L sulphuric acid and 100 L flocculant (at 2 kg flocculant per m^3 water). A decanter centrifuge separates the sludge from the centrate. Practically all of the wool grease and dirt is removed from the wastewater, along with over 95% of the detergent and about 99% of the pesticide residues (Poole *et al.*, 1999). The centrate contains the water-soluble organic and inorganic compounds from the wool (suint), which still has a high chemical oxygen demand of 5,000-15,000 mg L^{-1} and requires further treatment. Turbidity of the centrate, where observed, may be due to mechanical disintegration of the flocs in the decanter centrifuge, which produces a centrate containing some wool grease, detergent and pesticide residues. Wool grease in scour wastewater causes problems by reducing the oxygen transfer rates to the biological floc by the formation of a lipid coat around the floc (Becker *et al.*, 1999).

The centrate is then further treated for 48 h in the Sirolan CF-B (Biological) process, consisting of two aerated tanks in series followed by a settling tank. A reduction in the biological oxygen demand of 90-98% and in the chemical oxygen demand of about 80% is achieved. For a detailed explanation of the CF and CF-B processes, refer to Savage (2002). The biologically treated centrate can then be evaporated to produce a high K concentrate (suint) and a condensate. Residual odour in the condensate can be removed by catalytic oxidation to produce water fit for reuse.

Figure 1–8. Current effluent treatment processes for woolscours.



Note: CF = Chemical Flocculation and CF-B = Biological treatment.
The more dilute rinse water is also being treated (by filtration) but is not discussed in this thesis.

1.2.5. CHARACTERISTICS OF THE FINAL WOOLSCOUR WASTES

In this thesis, the sludge produced from the Sirolan CF process (Figure 1–9, Figure 1–10, Figure 1–11), which is now the industry standard for woolscour wastewater treatment (currently employed by ten plants worldwide and is being increasingly adopted), and the concentrated suint produced from the evaporation of Sirolan CF centrate both before and after biological treatment (although biological treatment is considered important to the overall treatment process), were studied. In addition, two fibrous wastes, the opener and scoured wool cleaner wastes, were also examined (Figure 1–10). Opener waste is the material

removed from the wool before it enters the washbowls, consisting of wool contaminants, such as dirt and seeds, and matted wool. The scoured wool cleaner waste is short wool fibre and dust, which may still include plant seeds, produced during the scouring process and currently has no future use (Figure 1–5). This section discusses the sludge and the fibrous wastes; suint is discussed in Section 1.5.

The sludge produced from the Sirolan CF process contains more than 90% of the dirt and grease from the high strength effluent and is typically 40% dirt, 20% grease and 40% water (Bateup *et al.*, 1996). A single scour line would produce about 10 t sludge per day. The sludge is relatively dry compared to most industrial sludges, resulting in savings in terms of handling, transport, and treatment costs (Everett, 1977). Due to its chemical nature and physical characteristics, wool wax is difficult to degrade biologically (Christoe, 1996b) but, when it is emulsified in the wastes, a larger surface area is created and its biological activity is enhanced (Stewart, 1988; Riva *et al.*, 1993).

The flocculant (Figure 1–12) used in the treatment of woolscour effluent is PAM, with a high MW (1-5x10^6 g $mole^{-1}$) and medium cationic charge (10-30 mole %), which binds the grease and dirt components and will be present in the sludge at a level of approximately 0.35% on a dry weight basis. As cationic polymers have a high affinity for solids (Barvenik, 1994), the flocculant will be absent from the centrate unless the centrate is high in suspended solids. PAM will not desorb from soils and becomes irreversibly bonded if soil is dried (Seybold, 1994); for PAM to enter solution, all parts of the polymer need to simultaneously detach from the soil surface and there is only a very small probability that there is enough time for the polymer to move away from the soil surface and thus into solution (Nadler and Letey, 1989). The flocculant may contain the acrylamide monomer at trace levels (less than 0.15%) which, due to its high solubility in water and its tendency not to be absorbed by sediments and sludges (Brown *et al.*, 1980; King and Noss, 1989), will remain in the centrate after the centrifuge. While acrylamide is a potent neurotoxin that can cause behavioural disorders, damage to the central and peripheral nervous system, and can induce abnormalities in mitotic and meiotic cells in animals and plants (Abdelmagid and Tabatabai, 1982; King and Noss, 1989), it has been shown to undergo hydrolysis in both soil (Lande *et al.*, 1979; Shanker *et al.*, 1990) and water systems (Brown *et al.*, 1980; Abdelmagid and Tabatabai, 1982), producing NH_3 and acrylic acid.

Figure 1–9. High strength woolscour effluent from which sludge is produced.

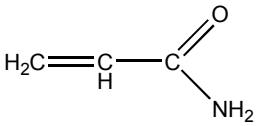
Figure 1–10. Waste materials produced by the woolscouring process.

Opener waste | Scoured wool cleaner waste | Sirolan CF sludge

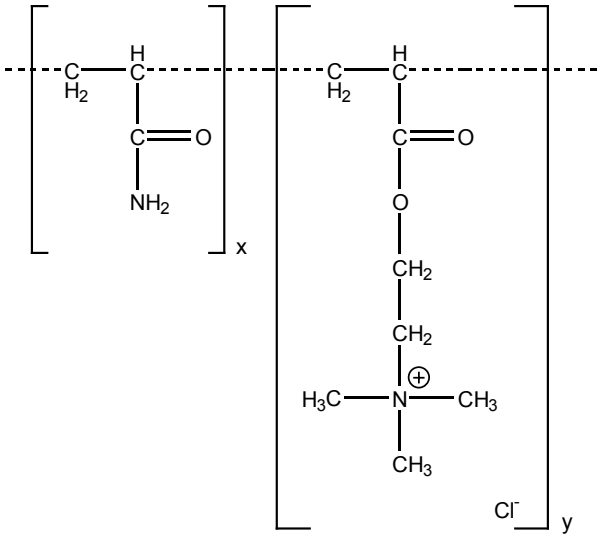
Figure 1–11. The two components of dry Sirolan CF sludge.

Dirt fraction (largely soil particles) | Grease fraction

Figure 1–12. The structure of the acrylamide monomer and a cationic polyacrylamide polymer.



Acrylamide
From Shanker *et al.* (1990)



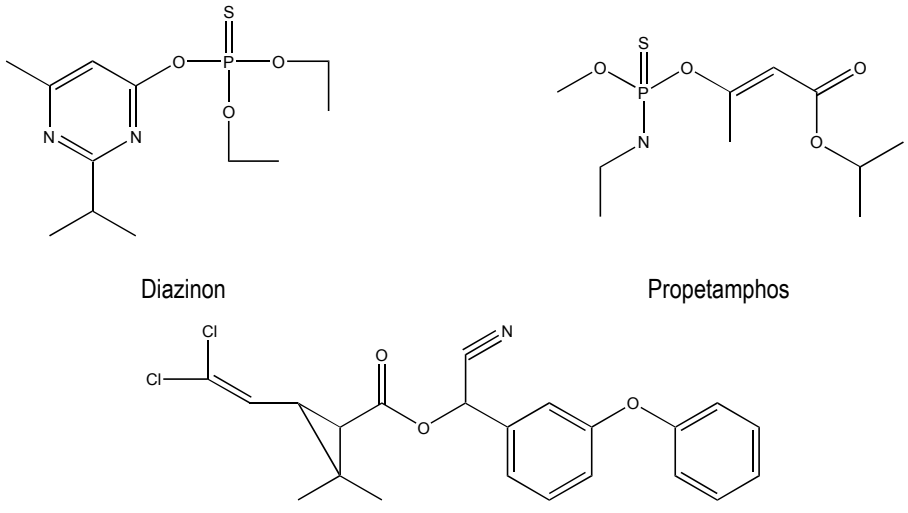
Cationic polyacrylamide
From Barvenik (1994)

High MW anionic PAM is used as a soil conditioner for erosion control and has been shown to have no adverse effects on microbial numbers in soil, but may change the distribution of mineral N species in soil on a site-specific basis and depending on its method of application (Kay-Shoemake *et al.*, 1998a; Kay-Shoemake *et al.*, 2000a). Microbes have been isolated from soils that can use PAM as a sole N source (Kay-Shoemake *et al.*, 1998b; Kay-Shoemake *et al.*, 2000b). Polymers of acrylamide are considered non-biodegradable in terms of the C chain not being attacked, although hydrolysis reactions release N from amide groups, with a rate of biotic and abiotic degradation in soil systems of about 10% per year (King and Noss, 1989; Barvenik, 1994; Grula *et al.*, 1994). The polymerisation of acrylamide with or without acrylic acid units to form PAM appears to be responsible for the inability of PAM to be a C source, since both acrylamide and acrylic acid can act as a C source (Kay-Shoemake *et al.*, 1998a). PAM is too large a molecule to be taken into microbial cells and microbes appear to lack exoenzymes to depolymerise it. The degradation of PAM does not release acrylamide as has been suggested (Smith *et al.*, 1996; Smith *et al.*, 1997), but rather it loses amide groups and forms polyacrylate and NH_3 (Ver Vers, 1999). Cationic PAM is considered much more toxic than non-ionic or anionic PAM.

The types and amounts of pesticide residues in the sludge depend on the parasites treated and the time between treatment and wool harvesting (Russell, 1996b; Jones, 1997). In New Zealand, organophosphate (OP) insecticides, such as diazinon and propetamphos (Figure 1–13), are the most widely used, killing fly, lice, ticks, and keds, with synthetic pyrethroid (SP) types, such as cypermethrin (Figure 1–13), also widely used mainly to control lice (Williamson, 1995). Insect growth regulators are also used. OP and SP pesticides are considered slightly to moderately toxic by the United States Environmental Protection

Agency (USEPA) and are highly toxic to aquatic organisms (EXTOXNET, 1996; Kamrin, 1997). Most of the pesticide residues are associated with the wool wax due to their lipophilicity (Russell, 1996b; Jones and Westmoreland, 1999). Since scouring removes 95% of the pesticide residues on greasy wool (Williamson, 1995) and the Sirolan CF process removes greater than 95% of the wool grease from the effluent, the sludge produced contains almost all of the pesticide (and detergent) residues (Jones and Westmoreland, 1999). Although this is merely a transfer of the problem, dealing with the pesticides in the sludge is considered an easier process (Russell, 1996c). A big drop in fleece dip residue levels in Australia and New Zealand was observed in the mid-1990s due to improved farming practises whereby the time between dipping and shearing was increased (Russell, 1996c; Russell, 1996b; Christian, 1998). For the 1997/98 year across all breeds in New Zealand, there was an average 3.43 ppm OP in raw wool, compared to 5.8 ppm in Australian wool, and 1.39 ppm SP, compared to 3.3 ppm in Australia. Merino fleeces averaged 15 ppm OP and 2.5 ppm SP in raw wool, and 22 ppm OP and 5 ppm SP in mid micron wools. Most of the residue loading was due to a small fraction of growers who had very high residue levels. Current levels must be further reduced to meet European environmental quality standards, which equate to 2.7 ppm OP and 0.3 ppm SP on greasy wool (Christian, 1998).

Figure 1–13. Structures of the pesticides diazinon, propetamphos, and cypermethrin.



From Kamrin (1997).

A study on the properties and decomposition of woolscour sludge (Williamson, 1998; Williamson *et al.*, 2000), produced albeit by an older technology (no flocculation or centrifugation), provides useful background information for this thesis and allows the effect of process development on sludge quality to be examined since, in theory, the sludge is derived from high strength effluent with the same properties. The sludge described was produced from the heavy solids from the first three scour bowls, settled solids and floating material retained during clarification of the flow down liquor, and fibre and dust discharged

from the wool dryers. Flow down liquor (wash and rinse water) entered settling ponds, and sludge (settled and floating material) was removed periodically and placed in drainage bins.

Results showed that woolscour sludge was a highly variable substrate in terms of the amount of net-N mineralised, and was considered of low substrate quality, possibly due to its pesticide and heavy metal content and its N (essentially all in wool fibre) being unavailable. Rates of net-N mineralisation increased as temperature was increased, possibly due to denaturation of wool fibres making the N more bioavailable, and it was suggested that composting is more appropriate than land application. There was no effect of moisture content on rates of net-N mineralisation and anaerobic conditions reduced net-N mineralisation compared to an aerobic environment. The sludge was generally neutral or weakly detrimental to the decomposition of other substrates (nutrient cycling). Wool grease in the sludge did not inhibit the decomposition of casein, implying that the grease content of the sludge did not inhibit its N mineralisation. The fibre-dirt fraction of woolscour sludge decomposed much more readily than the complete sludge (with wool grease), which was attributed to denaturation of the wool fibre during petroleum ether extraction. Sludge decomposition may have been partially limited by readily available C but not by initially available N.

1.3. THE DISPOSAL OF INDUSTRIAL WASTES

The woolscouring industry is not isolated in facing the challenge of meeting tightening environmental regulations. To put the woolscouring industry and their waste issues in context, a brief survey was conducted to determine the end use of wastes produced by other industries and what limits their application.

1.3.1. THE PRODUCTION OF INDUSTRIAL WASTES

Huge volumes of waste materials are produced in the modern world. In the United States, about 150 million tons of urban solid waste is produced each year and, in areas with a large population or large-scale agricultural production, the disposal of large amounts of such waste is both difficult and expensive (Atlas, 1998). In 1990, OECD countries (the 24 most technologically advanced countries in the world) produced $9x10^6$ t municipal waste, $1.5x10^9$ t industrial wastes (including $300x10^6$ t hazardous waste), and $7x10^9$ t other wastes, accounting for 68% of the world's industrial waste and 90% of the hazardous/special wastes (Alloway and Ayres, 1997). The total waste production of the European Community has been estimated at 2,500 million tonnes per annum, increasing annually like the United States at a rate of about 2-4%, being closely correlated to gross domestic product (Watson-Craik and Sinclair, 1995).

The USEPA defines a waste as hazardous if it exhibits ignitability, corrosivity, reactivity, or extractive procedure toxicity, if it contains any of the toxic constituents named on published lists as having toxic, carcinogenic, mutagenic, or teratogenic effects on humans or other life forms, or if it is listed on prescribed lists, naming specific chemicals and waste streams including known or suspected carcinogens, pesticides, heavy metals and acids (Watson-Craik and Sinclair, 1995). What materials the general public perceive as a threat may be different to their real threat.

Levels of heavy metals are invariably of concern when it comes to industrial wastes. Heavy metals are those with an atomic density greater than 6 g cm^{-3}, and is usually applied to elements such as cadmium, chromium, copper, mercury, nickel, lead and zinc, which are often associated with environmental pollution (Alloway and Ayres, 1997). Heavy metals are, however, ubiquitous in the parent materials of soils but the environment can receive inputs from anthropogenic sources, including agricultural and horticultural materials (such as impurities in fertilisers, sewage sludge, manures, pesticides, composts, desiccants, and wood preservatives) and waste disposal (Alloway, 1995b; Sterrett *et al.*, 1996; Alloway and Ayres, 1997). Some heavy metals are not considered essential for plant growth, such as arsenic, cadmium, lead and mercury (Alloway, 1995a; Davies, 1995; O'Neill, 1995; Epstein, 1997), while chromium, copper, zinc, and possibly nickel are essential for the growth of higher plants and animals (Baker and Senft, 1995; Kiekens, 1995; McGrath, 1995).

1.3.2. Options for the Treatment of Industrial Wastes

To illustrate the problems facing waste producers, 465 research and development projects regarding organic waste treatment were conducted in Europe in the 1990s (Papadimitriou and Diaz, 2000). Effluent treatment and disposal is now considered an important component in the operation of a company (Hart and Speir, 1992). The landfill disposal of industrial wastes is costly, a waste of potentially valuable resources, and can result in ecological problems (Maheswaran *et al.*, 1999). Agri-industrial wastes can be used as fertiliser supplements, fertiliser replacements, or soil ameliorants, either directly or after a treatment process. The use of organic residues in maintaining soil fertility decreased due the prevalence of low-cost mineral fertilisers, but recently there has been renewed interest in the use of organic residues, composts, and green manures (Badr EL-Din *et al.*, 2000).

All wastes contain valuable sources of nutrients and organic matter, but at the same time may contain heavy metals, pesticides, pathogens and weed seeds (Hart and Speir, 1992; Barry *et al.*, 1999). Since wastes have inherent value, a process needs to be applied to convert the waste to a marketable new product (Sabine, 1999) or an environmentally safe material of no commercial value. Benefit to the

environment is more achievable when a financial gain can also be made (Sabine, 1999). The pooling of appropriate waste streams can make waste management more efficient. The recycling of organic wastes onto agricultural land requires that soil and water resources are not contaminated, production from the land is not reduced, and future generations have full use of the land (Bond, 1998; Barry *et al.*, 1999). Application rates of organic wastes to land are based on the nutritional requirements of the crop, but first it must be determined what fraction of the total nutrients in the wastes can be converted to forms available for plant uptake. High application rates of these wastes are often used since they are low-grade fertilisers, which may input excessive amounts of heavy metals and toxic chemicals. As illustrated by Williamson *et al*. (2000), it is often assumed that all wastes will provide nutrients at the same rate, though this is definitely not the case.

The management of sludge requires that costs be kept to a minimum and local regulations and considerations be followed (Spinosa *et al.*, 1994). Conventional disposal systems include landfilling, agricultural use, and incineration. Agricultural use of sludge is based on its N content. Potential problems with land application include surface runoff, nitrate leaching, ammonia volatilisation, spread of pathogens, and the input of toxic organic contaminants and heavy metals. Incineration requires significant capital investment, still produces an end product for disposal (ash), and produces atmospheric pollution. The ash can be used for the production of materials such as paving materials, bricks, panels and ornaments.

Sustainable agriculture involves the principles of optimised productivity and economic returns, minimal on-site soil degradation, and minimal off-site impacts (Moody, 1999). Compared to many "natural" systems, agricultural production systems have nutrient losses, low microbial biomass, low C sequestration, and poorly structured soils. To restore degraded soils, a product ideally would be C-based, contain nutrients that are slowly released, and be neutralising to acidic soils. Use of the product may be constrained by its nutrient balance, heavy metal and/or pesticide content, pathogen content, and the rate of application needed to be of benefit.

Table 1-3 is by no means an exhaustive list but serves to show the range of wastes materials that are recycled. Reviews of literature pertaining to waste treatment are also provided by Poggi-Varaldo and Estrada-Vázquez (1997), Poggi-Varaldo *et al*. (1998), Marr and Facey (1994), and Marr and Facey (1995) for agricultural wastes and by Walsh Jr. *et al*. (1994) and Walsh Jr. *et al*. (1995) for food processing wastes. In New Zealand, a range of effluents and solid wastes has been utilised on land, including dairy shed and factory processing waste, meat processing effluent and wastes, piggery wastes, biogas-digester and stillage effluent, wood industry wastes, fly ash, and animal manures (Hart and Speir, 1992).

Table 1-3. A survey of wastes produced by industry and their applications.

Waste	Treatment	Application	Reference(s)
Spent mushroom compost	Fresh	Soil amendment Growth of container plants	Chong (1999)
Pulp and paper mill sludges	Raw or composted	Soil amendment Growth of container plants	Chong (1999), Evanylo and Daniels (1999), Jackson and Line (1997b), Sesay *et al*. (1997)
Cardboard packaging	Composted	Growth of container plants	Chong (1999)
Municipal solid waste (biosolids)	Composted	Soil amendment Growth of container plants	Chong (1999), Fürhacker and Haberl (1995), Fang and Wong (1999), Wong *et al*. (1997)
Animal hair	Milled and surface applied	Prevent moisture loss N fertiliser	Maheswaran *et al*. (1999)
Chicken manure	Fresh or composted	Fertiliser	Warman and Cooper (2000), Brown *et al*. (1994), Heathman *et al*. (1995), Brinson *et al*. (1994)
Log yard residues	Composted	Use in growth media	Campbell *et al*. (1994)
Fish waste	Composted	Soil amendment	Laos *et al*. (1998), Ndiaye *et al*. (2000), Lo and Liao (1992)
Sheep mortalities	Composted	Means of disposal	Stanford *et al*. (2000)
Piggery wastes (manure, carcases, litter, hoop structures)	Composted	Means of disposal Land application	Bhamidimarri and Pandey (1996), Imbeah (1998), Tiquia *et al*. (2000)
Paunch	Composted, composting with earthworms	Sold to nurseries Means of disposal	Herbert (1997), Dynes *et al*. (2000)
Coffee processing wastes	Composted	Alternative to landfill disposal or incineration	Nogueira *et al*. (1999), Wu (1995)
Olive processing (wastewater, press-cake, leaves)	Composted	Means of disposal	Papadimitriou *et al*. (1997)

1.4. WASTE TREATMENT BY COMPOSTING

As composting is the chosen method of treatment for the solid woolscour wastes in this study, this section reviews the composting process, the means of evaluating the quality of products, and the current knowledge pertaining to the composting of woolscour wastes.

1.4.1. A BRIEF HISTORY AND OVERVIEW OF COMPOSTING

Throughout the world, solid wastes most commonly end up either in landfills or incinerators (de Bertoldi *et al.*, 1983). Composting has been practised for the benefit of agriculture since ancient times and is considered to be very important to the reduction of municipal waste throughout the world today (Epstein, 1997; Chong, 1999). Large-scale composting began in India in the period 1924-1931, and the first full-scale composting facility in Europe was established in 1932 (Epstein, 1997). Composting generates a product that can be sold to reduce the cost of waste disposal but generally does not make the operation self-supporting (Atlas, 1998).

In the United States, where about two-thirds of municipal solid waste generated each year is biodegradable organic material, public opinion is turning away from landfills and incineration towards composting (Anon, 1994; Paul and Clark, 1996). Legislation has also promoted this change in attitude and behaviour (Anderson, 1990; Paul and Clark, 1996). It has been suggested that the potential supply of compost in the United States is only about 10% of the potential demand (Anon, 1994). In New Zealand, there has been an increase in the composting of wastes and a corresponding decrease in the use of landfills as a result of public opinion, although sewage-based products are not as well accepted (Yeates *et al.*, 2002). In Asia, composting has been the traditional method of waste treatment and, although decreasing at the individual level, like other areas of the world is increasing in use at the municipal scale (Paul and Clark, 1996).

1.4.2. THE COMPOSTING PROCESS

Composting can be used to produce a stable and beneficial product from the decomposition of putrescible organic materials, provide a more environmentally-acceptable and potentially cost-effective means of waste management, disinfect organic wastes that pose a health hazard in their current state, and bioremediate hazardous wastes (Miller, 1993; Epstein, 1997). Composting can be conducted to produce a compost product or as simply a means of waste disposal (Anderson, 1990).

The process of composting is defined as:

> *The biological decomposition and stabilisation of organic substrates, under conditions that allow development of thermophilic temperatures as a result of biologically produced heat, to produce a final product that is stable, free of pathogens and plant seeds, and can be beneficially applied to land* (Haug, 1993).

Compost is defined as:

> *An organic soil conditioner that has been stabilised to a humus-like product, that is free of viable human and plant pathogens and plant seeds, that does not attract insects or vectors, that can be handled and stored without nuisance, and that is beneficial to the growth of plants* (Haug, 1993).

Composting is a decomposition process, which changes the state of a substrate by both biological and abiotic factors and is regulated by the physico-chemical environment and substrate quality (Swift *et al.*, 1979). Substrate quality acts in a feedback manner; as organisms change the substrate by decomposition, this change affects further decomposition. The rate of decomposition varies for different compounds, decreasing from carbohydrates, through proteins, fats, hemicellulose, cellulose, lignin through to mineral matter (Epstein, 1997). Although some bacteria and fungi can degrade lignin, it is the most common component resistant to decomposition found in composting substrates. In general, about 40-60% of the dry organic matter is decomposed during composting (Anderson, 1990) and it can be assumed that (i) a certain amount of C in the waste to be composted is resistant to degradation in the composting time employed, (ii) the C decomposition rate is proportional to the amount of easily degradable C remaining in the waste, and (iii) there will be a lag before decomposition occurs due to the time required for the microorganisms to proliferate and become active (Nakasaki and Ohtaki, 2002). It can also be assumed that, in the presence of two or more substrates, the substrates will generally be decomposed in order of their ease of degradation. Physico-chemical factors include moisture, aerobic or anaerobic atmosphere, and pH (Swift *et al.*, 1979).

Although composting and soil systems have some common properties, such as occurring in a structural matrix and having similar spatial characteristics, there are some important distinctions between them (Table 1-4). There is a common ecology to all composting applications: the system is multi-phase with a high substrate density; thermophilic temperatures are generated as biological heat production exceeds losses; the process is aerobic or mainly aerobic; and decomposition is carried out by a diverse and interactive microbial community (Miller, 1993).

Table 1-4. The differences between composting and soil systems.

Composting system	Soil system
Primarily organic	Primarily inorganic
Very high substrate density	Low substrate density
High metabolic activity per volume	Low metabolic activity per volume
Biological activity alters physical environment	Physical factors imposed externally
Matrix (substrate) changes rapidly	Matrix changes very slowly (structurally stable)

From Miller (1993) and Herman and Maier (2000).

Substrates for composting may need to be reduced in size and blended for successful composting, such as with bulking agents to reduce the bulk density and increase aeration, and with readily degradable organic materials to act as an energy source (de Bertoldi *et al.*, 1983; Haug, 1993; Epstein, 1997). Bulking agents affect microbial degradative activity and the quality of the product by its effect on pH, C:N ratio, moisture content and air supply (Liao *et al.*, 1997). Hardwood sawdust is more degradable than softwood sawdust in soil, due to the presence of resins in softwoods (Allison and Murphy, 1963), which may affect the amount of available C provided in a composting environment (Liao *et al.*, 1997). Proper preparation of the materials to be composted, in terms of particle size, moisture content and C:N ratio, and process management will allow the process to proceed efficiently (Haug, 1993; Paul and Clark, 1996; Epstein, 1997). A compost with desired properties can be produced by either adjusting the process parameters, such as moisture level and temperature control, or more simply by altering the initial properties of the substrate mix, such as the C:N ratio (Eiland *et al.*, 2001).

Composting is a two-stage process, the first (high rate phase) being characterised by high rates of oxygen uptake and thermophilic temperatures, and the second (curing phase) characterised by a lower oxygen uptake rate and mesophilic temperatures where more recalcitrant compounds are degraded and the compost matures (Haug, 1993). Mesophilic organisms are those active at 18-48°C, facultative thermophiles at 40-78°C and obligate thermophiles 45-78°C (Swift *et al.*, 1979). Bacteria, fungi and actinomycetes are all involved, decomposing different fractions of the substrates (de Bertoldi *et al.*, 1983; Epstein, 1997). Protozoa, algae and viruses are not significantly involved in the decomposition process. As many bacteria prefer amino acids and other N-containing substrates, and many fungi prefer carbohydrates, the proportions of various groups of microorganisms involved in the composting process depends on the nutritional composition of the substrates (Miller, 1993). Factors that select for or against different microbial populations are themselves the product of existing populations. The mixed microbial population allows greater decomposition than pure cultures due to the increased metabolic diversity, which coordinates with products from one group of organisms becoming a substrate for other groups. Microbial populations in the wastes are generally sufficient for composting (Anderson, 1990).

Decomposition by fungi and bacteria in the early stages of composting results in the development of thermophilic temperatures that selects for thermophiles and kills most fungi since very few fungal species are thermophilic (Paul and Clark, 1996). *Bacillus* is the predominant bacterial genus. Decomposition is at a high rate during composting since biological reactions double in speed with every 10°C rise in temperature. Bacteria have a high metabolic rate due to their very high surface area to volume ratio (Haug, 1993). In the initial stages, bacterial degradation of proteins makes N available for subsequent microbial populations and, with the decomposition of simple C compounds, temperatures in the mass increase (Miller, 1993).

Fungi and actinomycetes become more prominent as the composting process develops, due to the decrease in temperature, pH and moisture, and degrade complex carbohydrates, such as cellulose, non-cellulosic polysaccharides, chitin, waxes and lignin, (de Bertoldi *et al.*, 1983; Miller, 1993). They are responsible for 30-40% of the weight loss during composting. Cellulose decomposition is intense throughout the process. Fungi can withstand broad ranges of environmental conditions, such as moisture and pH, and require less N than bacteria. Actinomycetes prefer moist, aerobic, neutral or slightly alkaline conditions and are important for the humification of organic matter and the production of aromatic compounds. The lower moisture content favours fungal growth over bacterial. The maximum temperature that fungi can grow at is 60°C (Epstein, 1997).

The generation of heat by microbial respiration is observed as an increase in temperature of the composting mass due to natural insulation (de Bertoldi *et al.*, 1983; Haug, 1993). Successful outdoor windrow composting can occur during sub-freezing conditions (Tiquia *et al.*, 2000), even when the average temperature is -7°C and falls as low as -35°C (Stanford *et al.*, 2000). The absolute maximum temperature achievable through composting is approximately 82°C (Miller, 1993) while optimum temperatures for decomposition are in the range 45-55°C (de Bertoldi *et al.*, 1983; Miller, 1993; Anon, 1994). The high temperatures achieved during composting provide for a high rate of decomposition and ensure pathogens and weed seeds are destroyed, but above approximately 70°C biological activity will be largely inhibited until the composting mass cools (Anderson, 1990; Herman and Maier, 2000). Pathogen and seed destruction is via the denaturation of enzymes due to the time-temperature relationship (Haug, 1993; Epstein, 1997). Regrowth of these pathogens can be prevented by the decomposer population within the mass outcompeting pathogens for resources. It is important to ensure that the total composting mass is exposed to these high temperatures, otherwise zones suitable for pathogen growth may exist. Bioaerosols, including living organisms and also endotoxins, mycotoxins and spores, can be generated during the process, depending on the design of the facility, to the risk of operators.

During the composting process N is lost by NH_3 volatilisation but, on a dry weight basis, the C:N ratio lowers due to the decomposition of organic matter with the subsequent release of carbon dioxide (CO_2) (de Bertoldi *et al.*, 1983). The C:N ratio of microbial cells is approximately 10:1, which is the theoretical optimum, but when the composting matrix is at low ratios such as this N loss will be a problem. If the C:N ratio is too high, decomposition will be slowed until a more favourable ratio is reached. An initial C:N ratio of 25-40:1 is recommended for successful composting (Anderson, 1990; Anon, 1994; Taylor and Taylor, 1998). During microbial growth, about 15-30 parts C is needed for every unit of N (Haug, 1993; Epstein, 1997). In the mesophilic phase of the process, some recovery occurs due to N fixation. Nitrification is not prominent during composting (de Bertoldi *et al.*, 1983). Nitrifying and denitrifying

microorganisms are generally not thermophilic; nitrous oxide (N_2O) production is limited to the very beginning and maturation phase of the composting process when the temperatures are low (Hellmann *et al.*, 1997). After N, phosphorus (P) is the element of next importance, and a C:P ratio in the materials in the range 75-150:1 is recommended (Anderson, 1990).

The optimum pH range for composting materials is 5.5 to 8, although materials with a range of pH values from 3 to 11 can be treated (de Bertoldi *et al.*, 1983; Miller, 1993). Generally, the pH will drop at the start of composting, due to the production of organic acids, and later high pH values together with thermophilic temperatures promote the volatilisation of NH_3. Composting can buffer high and low pH values due to the production of a weak acid (HCO_2) and a weak base (NH_3) during decomposition, such that materials for composting do not have to be pH-adjusted (Haug, 1993). Ammonia and pH are interdependent in the composting process (Miller, 1993). While ammonification causes a rise in pH, the pH determines the equilibrium between NH_3 and ammonium (NH_4^+). At a pH of 7 and below, the N is almost totally present in the form of NH_4^+, and at a pH greater than 9, free NH_3 dominates the balance. Ammonia produced from the microbial decomposition of organic N can be oxidised to nitrite (NO_2^-), which can lead to the emission of N_2O (He *et al.*, 2001). Production of N_2O occurs after the depletion of readily available C sources. The conversion of readily available forms of N into stable forms during composting allows it to be a source of N for higher organisms.

Water is required for microbial physiological needs, solution of substrate and salts, as a medium for bacterial colonisation, and as a determinant of gas exchange (Miller, 1993). The optimum moisture content of the composting mass is between 50 and 60% and depends on the physical properties of the substrates and the type of composting system, since there is competition between water and air for pore spaces (de Bertoldi *et al.*, 1983; Haug, 1993; Epstein, 1997). Moisture is produced during the decomposition process and is lost by evaporation. If the moisture content falls too low, biological activity will be inhibited by dehydration; at too high moisture content, aeration will be inhibited.

Aeration is required for the stoichiometric demand (for microbial decomposition), the drying demand, and the heat removal demand (Haug, 1993). The O_2 supply to the composting mass must not be limiting since composting is a biological oxidation process (de Bertoldi *et al.*, 1983; Epstein, 1997). The only way to guarantee this is through continuous turning of the mass, which would increase operating costs and disrupt the growth of certain microorganisms such as filamentous fungi. The mixture of substrates used for composting must take into account both their chemical and physical composition (Pittaway, 1999; Herman and Maier, 2000). Anaerobic conditions do not generate high temperatures and produce intermediate metabolites, such as volatile organic acids and compounds containing N and S, that can

cause odour issues (Miller, 1993). Odours are potentially the biggest problem caused by the composting process, with many composting facilities being shut down by local authorities (Haug, 1993; Epstein, 1997). The type of substrates composted greatly influences the production of odours.

The three main types of composting system are windrow, static pile, and in-vessel, each having their own advantages (Table 1-5). About 90% of composting facilities in the United States use the static pile approach, with the remainder using windrows, since in-vessel systems are more costly (Gerba, 2000). The primary use of reactors is to reduce the particle size of and homogenise the materials, with curing occurring afterwards in static piles or windrows (Haug, 1993).

Table 1-5. Advantages of the different types of composting systems.

Composting system	System advantages
Windrow	Rapid drying of material High volume of material can be utilised Good product stabilisation Relatively low capital investment
Static pile	Low capital costs High degree of pathogen destruction
In-vessel	Easier odour control (both minimisation and treatment) Good product stabilisation Space efficiency (less land required) Better process control than windrow and static pile systems Protection from climate Potential heat recovery (depending on design)

From Anderson (1990), Gomez (1998) and Gerba (2000).

The fate of pesticides during the composting process is of importance since any residues removed from the wool during scouring will be present in the grease fraction of the sludge and grease on the opener waste will also contain residues. Any pesticide residues in composting feed stocks should not persist in the compost produced, due to the risk posed to people handling the product, the chance of movement of the pesticide from the compost to the environment upon application, the potential toxicity of the pesticide to plants grown in the compost, and plant uptake of the residue (Epstein, 1997; Büyüksönmez *et al.*, 1999).

Most modern pesticides are susceptible to microbial degradation due to their organic nature and can decompose more rapidly in a composting system than in soil due to the higher level of biological activity (Büyüksönmez *et al.*, 1999). However, composting is not always beneficial to the decomposition of pesticides; recalcitrant pesticides can accumulate due to the decomposition of organic matter, metabolites can be produced that are more toxic than the original pesticide compound, and physico-chemical reactions, such as volatilisation, can occur. There are a variety of mechanisms affecting the degradation of

pesticides in a composting system, including adsorption to organic matter, leaching, volatilisation, abiotic transformations, and biological transformations (Büyüksönmez *et al.*, 1999). Composting can also be utilised for the treatment of soils contaminated with pesticides, explosives, or pharmaceutical wastes, where the soil can be processed through a composting system or, alternatively, compost can be applied to the contaminated area to enhance the rate of decomposition through its beneficial effect on microbial activity and plant growth while decreasing transport of the pesticide (Paul and Clark, 1996; Büyüksönmez *et al.*, 2000; Guerin, 2001).

1.4.3. Compost Maturity and Application to Soil

Industry is increasingly using the composting process to transform organic by-products into soil conditioners, using a variety of technologies to produce composts of varying quality (Butler *et al.*, 2001). In reality, the term compost applies to a wide range of materials, differing in their properties, uses, acceptability and value (Anderson, 1990). Composting must produce a consistent product with commercial value for it to be employed (Paul and Clark, 1996). For commercial acceptance of a compost product, targets in relation to colour and particle size, presence of contaminants, and chemical properties must be met (Haug, 1993). Heavy metals accumulate during composting due to the decomposition of organic matter (Epstein, 1997; Gomez, 1998). Compost products must be guaranteed to contain low levels of pathogens and not be amenable to their regrowth (de Bertoldi *et al.*, 1983). The allowable levels of heavy metals and temperature requirements for the reduction of pathogens in composts vary widely between countries, even within Europe (Brinton, 2001). The use of composts can be seriously limited due to contamination by plastics and other materials, which are difficult and expensive to separate out (Nakasaki and Ohtaki, 2002). Australian Standard AS4454 for composts, soil conditioners and mulches (Standards Australia, 1999) appears to have been adpoted in New Zealand. A review of the development of guidelines and comparisons between countries is provided by Brinton (2000).

Compost stability refers to the stage in the decomposition of organic matter, and is a function of biological activity, where maturity is an organo-chemical condition of the compost, indicating the presence or absence of phytotoxic metabolites (Epstein, 1997). When a compost is unstable, microbial activity is high and the substrates are undergoing rapid changes. As the easily degradable substrates are utilised, leaving behind more complex compounds, microbial activity will decrease and the compost will stabilise. Phytotoxicity is mainly attributed to the presence of fatty acids but may also be caused by salinity, trace elements, heavy metals, NH_3 and CO_2. There appear to be no universally accepted measures of compost maturity at present. In the literature, chemical, physical and biological indices are used (Epstein, 1997). The analysis of maturity is complicated by the fact that the time and means of sample

storage prior to analysis can affect the result (Butler *et al.*, 2001; Wu and Ma, 2001). The use of immature compost is detrimental to soil as anaerobic conditions develop as the soil microbial biomass uses oxygen to decompose the compost, depriving plant roots of oxygen and potentially generating toxic intermediates, NH_3, hydrogen sulphide, ethylene oxide, low MW fatty acids and nitrite (de Bertoldi *et al.*, 1983; Paul and Clark, 1996; Butler *et al.*, 2001).

While chemical fertilisers are used in agriculture to provide nutrients for plant growth, organic products such as compost are slow release fertilisers used to supply organic matter and improve soil structure, such as bulk density, air and water permeability, water retention, and reduce the potential for run-off and erosion (Epstein, 1997; Atlas, 1998; Yeates *et al.*, 2002). While allowing better root penetration and structure, the neutral pH of most composts also suits the growth of most plants. The largest effect organic matter has on soil chemical properties involves its cation exchange capacity, which dictates the fertility of the soil (Epstein, 1997). The cation exchange capacity is a measure of the amount of readily exchangeable cations neutralising negative charge in the soil (Rhoades, 1982a), and an increase allows more nutrients to be retained and made available to plants, and reduces the loss of cations by leaching (Epstein, 1997). More recently, composts have been used for reclamation of disturbed soils, biofiltration and air pollution control, stimulation of microbial activity in forest soils, and as a suppressor of plant diseases (Craft and Nelson, 1996; Epstein, 1997; Borken *et al.*, 2002). Composts can offer disease suppression due to the presence of antibiotic compounds, by reducing the competitiveness of disease-causing organisms, and by its application resulting in healthier plants (Paul and Clark, 1996). The application of compost to soil increases the soils adsorptive capacity for heavy metals, reducing their mobility and potential for leaching to groundwater (Epstein, 1997).

Most of the N in compost is in the organic form, largely insoluble and unavailable to plants (Epstein, 1997). It must be mineralised (converted to the inorganic species NH_4^+ and NO_3^-) before being available to support plant growth. It is for this reason that the available and not the total N content is important for estimating the supply of N to plants from compost. If the N supply does not meet the plants requirmements, supplemental N will have to be applied; if the supply exceeds the plants uptake, contamination of groundwater can occur. The situation is different for K; as it is taken up in the K^+ form, it is equally available in organic wastes as it is in fertiliser (Wen *et al.*, 1997). If a compost is applied to soil sufficient in organic C but lacking in other nutrients, microbial activity will be stimulated and nutrients will be drawn from the soil, preventing their use by plants (Epstein, 1997; Pittaway, 1999).

1.4.4. THE COMPOSTING OF WOOLSCOUR WASTES

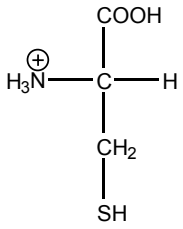
Components of interest in the composting of woolscour wastes are the wool grease, detergent, and pesticide components of Sirolan CF sludge and the keratin-based fibrous wastes. Existing knowledge regarding the composting of woolscour wastes is limited.

About 90% of the keratin (both α and γ types, although γ-keratin is more resistant) in wool is resistant to attack by normal proteolytic enzymes and chemical and physical means, due to its supercoiled helical structure, high degree of cross-linking by disulfide bonds (Figure 1–14), H bonds, hydrophobic interactions, and its total insolubility in water (Noval and Nickerson, 1959; Mathison, 1964). Although most microorganisms decompose keratin slowly and incompletely, the fact that it does not accumulate in nature and wool is treated to prevent mildew damage suggests that certain microorganisms can decompose it (Noval and Nickerson, 1959; Lewis, 1975). Fungi and bacteria can damage wool fibres, especially under conditions of high humidity, warm temperature, and neutral pH (Lewis, 1975). Wool is more susceptible to microbial attack if it contains impurities that can act as a source of readily available nutrients or if it has been chemically or physically damaged during processing. About 10% of the weight of wool fibre, accounted for by membrane material, nuclear remnants, cytoplasmic debris, and endocuticle, can be solubilised by proteinase and peptidase ezymes. The remaining 90% of the wool, the cortex, cannot be degraded by these enzymes unless the disulphide bonds have been broken. Keratinophilic microorganisms, such as dermatophytes (pathogenic fungi), will increase the pH during keratin hydrolysis due to the production of NH_3 from deamination reactions (Sangali and Brandelli, 2000).

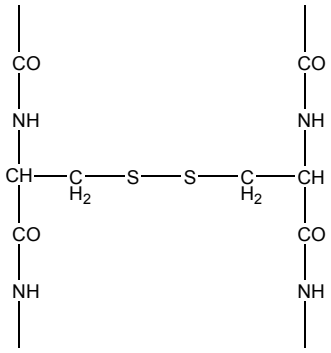
Although bacteria, fungi and actinomycetes produce active proteolytic enzymes, actinomycetes and especially *Streptomyces fradiae* have strong keratinolytic properties that have been suggested as being potentially very useful in the decomposition of keratinous substrates (Noval and Nickerson, 1959; Katuzewska *et al.*, 1991). *Streptomyces fradiae* was isolated from soil by Noval and Nickerson (1959) and found to digest wool in shaken cultures in two phases, the first phase being limited growth within the clumps of wool that did not change the appearance of the wool, and the second phase being the disintegration of the physical structure resulting in solubilisation of the wool. *S. fradiae* was suggested to be able to reduce the disulphide bonds in wool, as evidenced by the accumulation of soluble sulfhydryl compounds. Ammonia was the main nitrogenous decomposition product, with amino acids and peptides also present. In a microscopic study using proteolytic enzymes isolated from culture and degreased sheep wool, Katuzewska *et al*. (1991) illustrated detachment and disintegration of the keratin plates of the hair sheath after 24 h. After 48 h, elongated cells comprising the hair cortex were loosened and after 72 h the cortex cells were fully detached. Most of the wool fibres showed complete disintegration after 4 days.

Thermoactinomyces candidus has been shown to completely digest wool in culture after 9 days at 65°C, as measured by a decrease in the weight of wool able to be filtered from solution, with wool being the sole source of C and N (Ignatova *et al.*, 1999). Soil appears to be a good reservoir of keratinophilic fungal species (De and Chandra, 1982; Rai and Qureshi, 1994). It has been suggested, without supporting data, that wool fibres can be successfully degraded by composting with sawdust and waste treatment plant sludge (Chiampo *et al.*, 1995).

Figure 1–14. The structure of cysteine and the formation of disulphide bonds between cysteine residues.



Cysteine
From Garrett and Grisham (1995)



Disulphide bridge between polypeptides
From Peters (1963)

A case study in Williamson (1998) provided information on the composting of woolscour wastes using a forced-air static composting system of 40 L capacity for 6 weeks followed by a further six in windrows for curing. As previously stated, the woolscour sludge used by Williamson was not the same as that used in this study. It was found that most post-composted mixes were not "compost" in the true meaning of the word, based on visual assessment and the small reduction in organic matter due to the lack of a thermophilic phase. There was no change in total N between raw and composted mixes and, individually, half of the mixes showed a decrease in total N, suggesting N loss by volatilisation. Only one mixture showed a significant decrease in C:N ratio. Most of the composted mixes were unsuitable for seedling establishment, and seedlings established better when grown in mixes diluted with seed raising mix. Most composted mixes produced less biomass than either commercial compost or seed raising mix. It was concluded that, while the lack of decomposition could have been due to the heavy metal and/or pesticide content of the sludges, the poor level of compost production was most likely due to technical problems with the system.

The CSIRO have conducted research into the composting of Sirolan CF sludge. When mixed with other materials (not specified), temperatures up to 70°C were attained (Bateup *et al.*, 1996). The blending of sludge with greenwaste (proportions not given) produced an immediate temperature rise up to 80°C in the mass. The effluent produced from woolscours was considered to contain a microbial community that

survived woolscouring temperatures, as temperatures rapidly increased without a significant acclimation period during the composting of sludge and greenwaste (Jones and Westmoreland, 1999).

Wool grease was shown to break down under composting conditions in two different heaps, the rates being a 90% reduction in 8 weeks and a 70% reduction in 14 weeks (Bateup *et al.*, 1996). The degradation of cypermethrin, propetamphos and diazinon present in the grease, was shown to follow a similar trend to the breakdown of wool grease. Using a radish bioassay, the mature product was shown to be as good as a commercial potting mix, as judged by seed germination and root growth. The static pile composting of Sirolan CF sludge blended with green waste over 14 weeks showed 80% and 96% degradation of the wool grease and NPE detergent, respectively (Jones and Westmoreland, 1998). The degradation pathway appeared to be the stepwise oxidation and cleavage of the polyoxyethylene chain either by hydrolysis or an oxidative hydrolytic mechanism. No fission of the aromatic ether bond was observed. As well as chain shortening, there was a rapid loss of the nonylphenol moiety from the compost, although this was not as fast as the loss of ethylene oxide units. Residual nonylphenol and ethoxylates were expected to further degrade during the use of the compost. Shortening of the polyethoxylate chain has also been observed during aerobic and anaerobic waterwater treatment (Pryor *et al.*, 2002). The rate and extent of degradation of nonylphenol in soil under field conditions is uncertain. The higher the degree of branching of nonylphenol, the slower the rate of microbial degradation. The rate of wool grease decomposition increased with the maximum initial temperature rise during the composting of 2 m^3 sludge with 4 m^3 greenwaste (Jones and Westmoreland, 1999). After 100 days, 95% of the grease and 100% of the NPE had decomposed. Diazinon had a half life of 6-11 days and cypermethrin 31-36 days, which were correlated to the half life of the wool grease. While OP residues degraded at two to three times faster than the wool grease, SP residues degraded at half the rate of the wool grease. The fate of diazinon during composting depends on the composting system and substrates used (Büyüksönmez *et al.*, 2000). IMHP (2-isopropyl-6-methyl-4-hydroxy pyrimidine) is formed from the degradation of diazinon and is water soluble and much less toxic (10% of that of diazinon), and undergoes further degradation (Michel *et al.*, 1997).Two bacterial cultures have been isolated from woolscour effluent that could grow on agar with pesticides as the sole C source (Mickelson *et al.*, 1990). The biological treatment of fats and oils at thermophilic temperatures is expected to be advantageous due to favourable changes in most physical properties of these compounds (Becker *et al.*, 1999). In the liquid form, these compounds become more accessible to microorganisms and their lipolytic enzymes.

Geelong Wool Combing in Australia have a zero waste policy and have investigated the treatment of the solid wastes by composting (Maheswaran *et al.*, 1999). Sludge was composted with wood chips as the bulking agent and source of C, waste hair from the hide and skin processing industry as a N source, and high-K suint for a source of water and K. The compost produced was used in the market gardening area

of Werribee, which has poor soils due to 30 years of continuous cropping, and was found to improve water conservation, bulk density and porosity, provide nutrients, and reduce the harvesting time for broccoli.

1.5. SUINT AND POTASSIUM FERTILISATION

Essential elements are those that are required for the health and normal growth and development of an organism (During, 1984). For plants there are between 16 (White, 1997) and 20 (Bennett, 1993) elements considered essential, K being a member of the group of macronutrients (major elements). The essentiality of K was recognised by von Liebig in 1840 (Kirkman *et al.*, 1994). While C, O and H are supplied by the atmosphere, water, and soil organic matter, the other elements are supplied by the soil in generally insufficient amounts for maximum plant growth, such that fertilisers are required (During, 1984).

1.5.1. THE USE OF POTASSIUM IN SUINT

The first attempt to extract K from suint was made in 1831 (Truter, 1956). At this time the water was first evaporated and the dried suint was heated in retorts to provide gases suitable for illumination, with raw potash remaining in the retorts. In 1956, raw potash recovery (up to 3% of the raw wool scoured) was standard practice in the larger mills in Germany. It was suggested in 1960 that, even though degreased wastes could be evaporated for the recovery of K, this would not be cost effective due to the cheaply produced potash on the market and the cost of large-scale evaporation (Ferrier, 1960). No efforts had been made by New Zealand woolscourers by 1969 to recover K from scouring liquors, in part due to a lack of information regarding the amounts present in New Zealand wools (Hoare *et al.*, 1969). Their study showed that there was an average of 2.5% K on a greasy weight basis on Romney crossbred wool and 27.4% K on a suint weight basis. It was estimated that the quantity of potentially recoverable K (as potassium chloride (KCl)) from the 1966/67 clip would be approximately 11,800 tons, which was less than 10% of that imported into New Zealand in that year. Using ion exchange resin, it was concluded that K recovery was not economical compared to the cost of imported fertiliser.

More recently, the flow down from a desuint bowl, high in K and suspended solids (dirt), was concentrated by flash evaporation in preliminary work by CSIRO, generating clean water (which required further treatment to remove odours) and a K-rich liquid concentrate (Table 1-6) (Bateup *et al.*, 1996). Figure 1–15 shows the appearance of concentrated suint produced from the evaporation of biologically treated effluent in this thesis.

Table 1-6. Analysis of suint liquor before and after flash evaporation.

%	Effluent to evaporator	After evaporation	
		Concentrate	Distillate
Total solids	2.61	46.6	0.014
Suint	2.00	35.7	0.010
Wool grease	0.15	2.7	0.004
Dirt	0.46	8.2	0
Potassium	0.56	10.0	0

From Bateup *et al.* (1996).

Figure 1–15. Concentrated suint produced from the evaporation of biologically treated woolscour effluent.

Concentrated suint Biologically-treated effluent

A scouring line can produce 100-150 tonnes of K per year (Bateup *et al.*, 1995). Suint contained a range of minerals and organic compounds in addition to K (Table 1-7), although only the K was at a concentration high enough to have fertiliser value (Bateup *et al.*, 1996). There were no compounds present at concentrations high enough to limit its use on food crops. Therefore, suint may have use in the organic farming market as the K is organically derived. Studies have suggested that K applied with organic wastes to land is equally available as fertiliser K, which could potentially reduce the fertiliser costs for crop production (Shehu *et al.*, 1997; Wen *et al.*, 1997). With organic materials low in K, however, the application rates needed to supply enough K and replace fertilisers would be unacceptably high.

Suint-derived K can be applied to land as a fertiliser, provided amounts and concentrations applied avoid soil salinification problems (Bateup *et al.*, 1995). It has been calculated that about 1,000 ha are needed to dispose of the effluent from a single 2 m scouring line in an environmentally sustainable way (Christoe,

1996b). Australia already has major problems with soil salinity, and with commonly-used K fertiliser (KCl) having a K:Cl ratio of 1.1:1, suint appears advantageous with a K:Cl ratio of about 4 (Bateup *et al.*, 1996). A CSIRO study reported in Bateup *et al*. (1996) using a K-deficient soil (details of which were not provided) showed that suint was just as good as KCl in enhancing grazing pasture crop yields. Other CSIRO research reported in Maheswaran *et al*. (1999) suggested that suint could be used as an alternative source of K to potash for pasture, with no detrimental effects. However, it was not stated at what dilution(s) of suint these effects were observed.

Table 1-7. Analysis of a typical suint concentrate.

Major compounds	% w/v	Trace metals	ppm
Potassium	10.0	Iron	800
Sodium	1.7	Aluminium	340
Calcium	0.2	Zinc	41
Magnesium	0.2	Manganese	45
Carbonate	6.7	Boron	42
Chloride	3.0	Lead	9
Sulphate	0.5	Copper	3
Phosphate	0.04	Nickel	2.5
Soluble organics	11.6	Chromium	1
Nitrogen compounds	0.5	Cobalt	0.9
Dirt	2.5	Molybdenum	0.5
Wool grease	3.0	Arsenic	0.4
Water	60.1	Cadmium	0.1
		Mercury	>0.1

Note: ppm = parts per million. From Bateup *et al.* (1996).

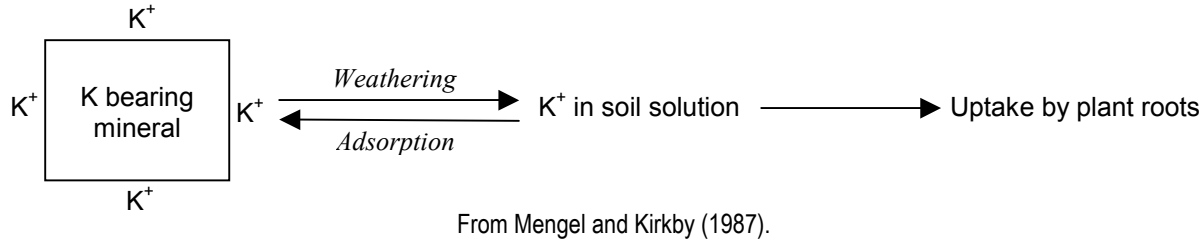
1.5.2. THE FORMS OF POTASSIUM IN SOIL

Potassium makes up about 2.3-2.6% of the earth's crust, making it the seventh most abundant element (McLaren and Cameron, 1990; Kirkman *et al.*, 1994). In modern agricultural practise, soil gains nutrients from weathering and mineralisation, the use of fertilisers (both organic and inorganic), atmospheric fixation and precipitation, and loses nutrients by crop removal, leaching, volatilisation and erosion (Mengel and Kirkby, 1987).

Potassium exists in soil in structural, fixed, exchangeable, and solution forms (Mengel and Kirkby, 1987; McLaren and Cameron, 1990). Structural K is the largest pool of K in most soils (90-98%) and consists of K bonded covalently within the crystal structure of the minerals, the amount depending on the nature of the parent rock material and the degree of weathering. Fixed K (1-10%) is not readily exchanged with other solution cations as it is held between the layers of micaceous clay minerals. Fixed K and structural K together are referred to as non-exchangeable K, with the release of fixed K being reversible and

structural K irreversible. Exchangeable K is that which occupies sites in soil clay particles and is normally less than 2% of the total soil K, depending on the type of clay and its negative charge. Soil solution K (0.1-0.2%) is available for plant uptake, the amount depending on depletion and replenishment from exchangeable and non-exchangeable forms (Figure 1–16).

Figure 1–16. The forms of potassium in soil.



From Mengel and Kirkby (1987).

Inert K held in clay, silt and sand particles may be released at annual rates of 30-60 kg ha^{-1} due to weathering processes (During, 1984). There may be 70-120 kg K^+ ha^{-1} in soil fauna and micro-flora (excluding plant roots), which can be considered part of the K cycle since it will be released after death.

Fixation of K onto clay minerals occurs when the amount of K^+ in the soil solution increases due to fertilisation and other inputs and the release of K^+ by weathering (McLaren and Cameron, 1990; Kirkman *et al.*, 1994). The degree of K fixation depends on the type of clay mineral. In New Zealand, most soils have medium or high K retention capacities such that losses by leaching are generally low (During, 1984). This, coupled with the low rates of K fertilisation used, means that slow release fertilisers are not important. In soils considered high in total K, the top 30 cm contains 40-55 t ha^{-1} and those considered low in total K 2.5-20 t ha^{-1} (During, 1984).

Potassium deficiency can occur in soils that have been leached, in organic soils and peats, and soils that have been heavily cropped (Gauch, 1972; Mengel and Kirkby, 1987). Organic and sandy soils are frequently poor in K bearing minerals, which do not provide an endless source of K^+. There are few cases of K^+ toxicity since an abundance of K^+ generally occurs only as a result of excesive fertiliser application and the fact that K^+ is fixed in exchangeable and non-exchangeable forms in soil (Gauch, 1972; Bennett, 1993).

1.5.3. POTASSIUM AS A MACRONUTRIENT

Potassium is taken up at high rates by plant tissues and is highly mobile throughout the entire plant, frequently transported from older to younger plant parts (Gauch, 1972; Marschner, 1986; Mengel and Kirkby, 1987). It is important for the correct physiological and biochemical functioning of plants,

including initiation and promotion of meristematic growth, control of water balance, cell pH stabilisation, translation process of protein synthesis, enhancement of photosynthesis and translocation of photosynthates, and the activation of more than 50 various enzyme systems. It differs from C and N in that it is not a constituent of the plant fabric (Russell, 1973). It plays an important role in the disease resistance of plants, by directly affecting the pathogen, affecting the severity of the pathogen on the host, affecting the establishment and spreading of the pathogen within the host, and affecting the ability of the plant to recover from the pathogen (Perrenoud, 1977; Mengel and Kirkby, 1987). The balance between N and K appears to be very important (Perrenoud, 1977).

Plants suffering from K deficiency do not exhibit visual symptoms at first (Mengel and Kirkby, 1987; McLaren and Cameron, 1990). Rather, a reduction in growth rate is followed by chlorosis and necrosis, generally in the margins and tips of leaves, which occurs first in older leaves since K^+ is transported from these to newer ones. A decrease in turgor affects the resistance of plants to drought, frost damage, fungal attack, and saline conditions. At the tissue and organelle level, K^+ deficiency can impair lignification of vasular bundles, cause collapse of chloroplasts and mitochondria, and impair cuticle development. Soluble carbohydrates and N compounds can accumulate while starch levels decrease (Marschner, 1986). Deficiencies in K are generally most severe during periods of maximum growth (During, 1984; McLaren and Cameron, 1990).

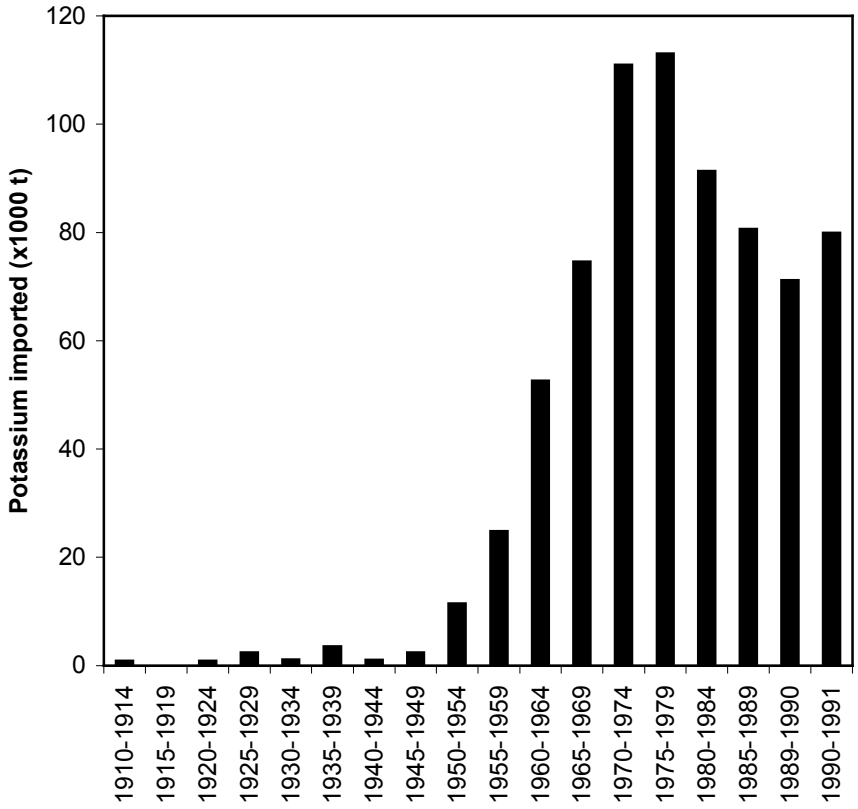
1.5.4. POTASSIUM FERTILISATION

In most agricultural systems, nutrients are applied as fertilisers or manures to address the imbalance between removal by crops and leaching and release by weathering and mineralisation (Mengel and Kirkby, 1987). The increase in world agricultural production is due to the increasing use of fertilisers, from 14 Mt NPK in 1950 to 146 Mt in 1989 (White, 1997). Precipitation only supplies a few percent of the total K demands of crops (Mengel and Kirkby, 1987); K contained in precipitation and dry deposition is estimated to be 1-20 kg ha^{-1} $year^{-1}$ (McLaren and Cameron, 1990; White, 1997). K is mainly applied in the chloride (which contains about 50% K) or sulphate (about 43% K) forms and occasionally in the nitrate and polyphosphate forms. Muriate of potash (KCl), the cheapest fertiliser, and potassium sulphate (K_2SO_4) do not affect soil pH. All potash fertilisers, except metaphosphate and silicate, are soluble in water and have the same availability so that differences are due to the anions. Crops sensitive to chloride, such as fruit trees, potatoes, and tomatoes, receive K_2SO_4 (Mengel and Kirkby, 1987; White, 1997).

New Zealand imports K fertilisers (Figure 1–17) mainly from Canada and the United States (During, 1984; McLaren and Cameron, 1990). The main import is KCl but the more expensive K_2SO_4 is also used

where chloride is harmful. In Australia, approximately 150,000 tonnes K fertiliser per year is used, almost all imported as KCl (Bateup *et al.*, 1996). Low rates of K fertiliser usage in the past in New Zealand can be attributed to the naturally high levels of available K in our soils, an abundance of easily weathered minerals in soils, the recycling of K due to pastoral farming, and a lack of suitable methods to detect K deficiencies (Kirkman *et al.*, 1994). Soil K reserves in New Zealand are estimated to be depleted at an annual rate of about 226,000 t, equivalent to 11 kg ha^{-1} $year^{-1}$ over 20.5 million ha, even at the 1990-91 level of fertiliser input.

Figure 1–17. Mean annual imports of potassium into New Zealand.



From Kirkman *et al.* (1994).

Liquid fertilisers (either completely dissolved or in suspension) have advantages over solid types in that they are easier to transport, handle and apply, and are more homogeneous (Mengel and Kirkby, 1987). It could be argued, however, that transporting large volumes of water is not sensible. Liquid fertilisers containing N and P are available but, since the addition of KCl causes precipitation, K is still applied in the solid form.

Rates of removal by crops indicate the rates of application required to balance the loss; the normal range is 40 (e.g. barley grain and straw) to 300 (e.g. grass-clover pasture) kg K ha^{-1} $year^{-1}$ (Mengel and Kirkby,

1987; McLaren and Cameron, 1990; White, 1997). This is only an indication, as K^+ removal depends on yield, rate of leaching, and the availability of K^+ in the soil, and plant requirements depends on the length of the growing period, the type of root system, and the N nutrition status of the plant. For optimal plant growth, the K^+ requirement is generally in the range of 2-5% of the dry weight of the vegetative parts, fleshy fruits, and tubers (Marschner, 1986).

1.6. EXPERIMENTAL AIMS

For the concentrated suint, the overall objective of this research was to determine its composition and assess whether it could be used, in a sustainable manner, as a K fertiliser on arable land.

For Sirolan CF sludge, opener waste and scoured wool cleaner waste, the overall objective was to chemically and biologically characterise these products and assess their composting potential, thereby preventing their disposal to landfill.

The experiments employed to meet these objectives are outlined in Section 2.1.

2. MATERIALS AND METHODS

2.1. EXPERIMENTAL DESIGN

In this thesis, experiments are grouped into three chapters (Table 2-1): the utilisation of concentrated suint (Chapter 3); the characterisation and decomposition of woolscour wastes (Chapter 4); and the development of composting technology for woolscour wastes (Chapter 5).

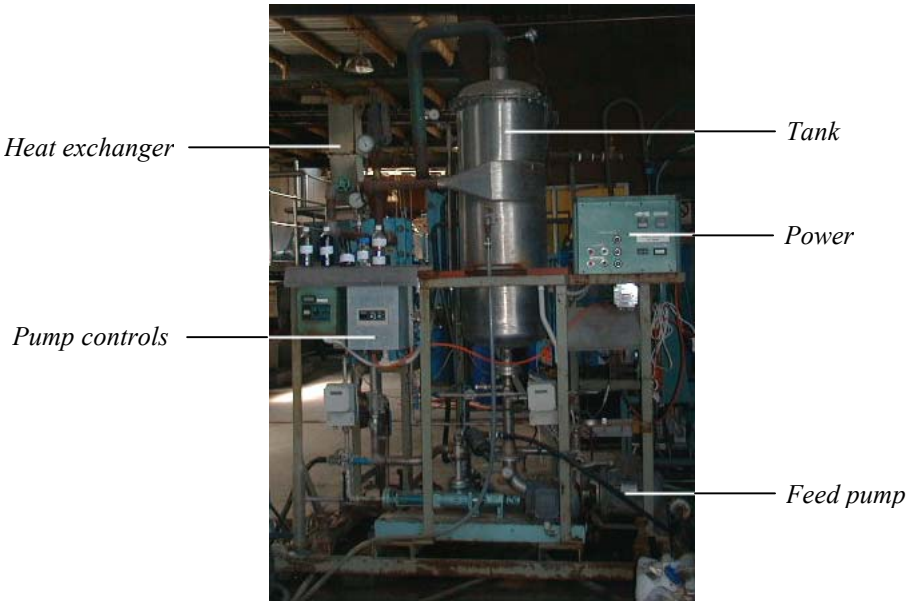
Table 2-1. Research conducted to meet the experimental aims of this thesis.

Chapter	Chapter description	Experimental details	Thesis section
Chapter 3: Utilisation of concentrated suint	• Chemical characterisation	• K, N, Cl, P, pH, heavy metals, electrical conductivity, organic matter, inorganic elements, grease, pesticides	Section 3.2.1
	• Decomposition	• Variation on a daily timescale	Section 3.2.2
		• Decomposition profile (effect of time, temperature, atmosphere)	Section 3.2.3
	• Effect of suint application to soil	• Effect on turnover of model organic compounds	Section 3.2.4
		• Effect on electrical conductivity, pH and mineral nitrogen leaching	Section 3.2.5
	• Phytotoxicity and use of suint as fertiliser	• Plant assays – land disposal and as K fertiliser	Section 3.2.6
		• Forestry applications (*Pinus radiata*)	Section 3.2.7
Chapter 4: Characterisation and decomposition of woolscour wastes	• Chemical characterisation	• Moisture, N, P, organic matter, pH, heavy metals, grease, pesticides, inorganic elements	Section 4.2.1
	• Decomposition	• Variation on daily and weekly timescales, cause of variation	Section 4.2.2
		• Composting profiles (high temperature)	Section 4.2.3
	• Constraints on sludge decomposition	• Decomposition of dirt fraction of sludge	Section 4.2.4
		• Effect of inoculation and nutrient addition	Section 4.2.5
		• Polyacrylamide decomposition and effect on organic matter turnover	Section 4.2.6
		• Effect of pesticides on casein decomposition	Section 4.2.7
	• Sludge phytotoxicity	• Plant assay – effect on plant performance	Section 4.2.8
	• Microbial activity in sludge	• Plate counts, substrate-induced respiration	Section 4.2.9
Chapter 5: Composting technology development	• Methodology	• Operation of Rotocom trial unit	Section 5.1
	• Composting trials	• Trials at the Ashburton Woolscour	Section 5.2
	• Case study	• Composting of Kaputone Woolscour sludge	Section 5.3

2.2. SAMPLING OF WOOLSCOUR WASTES

Concentrated suint samples studied in Chapter 3 were produced using a flash evaporator installed for trial purposes at the Fairlie Woolscour in Timaru, South Canterbury (Figure 2–1). Suint was produced from two points in the effluent treatment process (Figure 1–8), from the liquid (centrate) separated from the sludge by the Sirolan CF process (CF suint), and from Sirolan CF centrate that had been biologically-treated for 48 h in two sequential reactors (CFB suint).

Figure 2–1. Flash evaporator used for the concentration of suint.

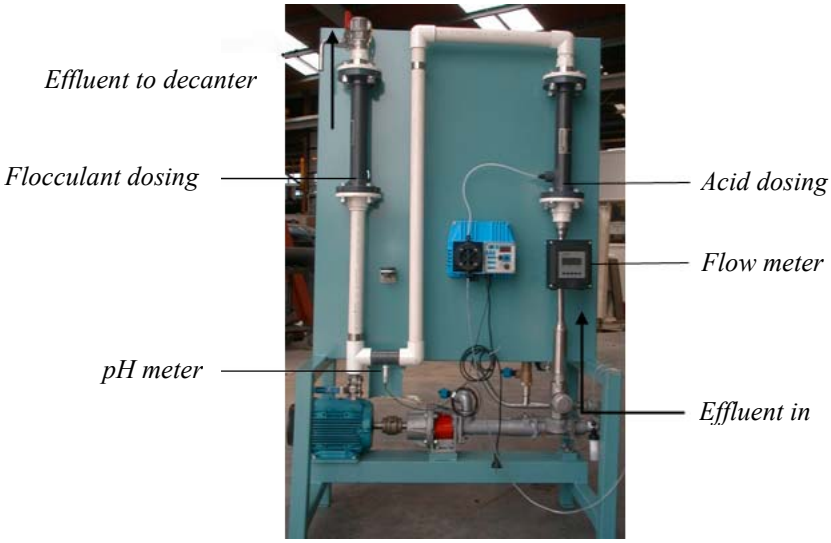


Concentrated suint samples were produced by feeding the liquid stream (250-300 L h^{-1}) to the flash evaporator over a 6-7 h period in a continuous manner. At a temperature of 115°C, the feed to the evaporator "flashed" when hitting the lower pressure in the tank, evaporating off the water. The volume of liquid fed to the evaporator was reduced by about 95%. At the end of the run, the concentrate was drained from the evaporator and stored at room temperature. No problems with sample quality (e.g. microbial growth or change in composition) were noted during storage, presumably due to their concentrated nature.

The woolscour wastes analysed in Chapter 4 were collected from either the Fairlie Woolscour, the Ashburton Woolscour in Mid Canterbury, or the Kaputone Woolscour in Christchurch. Opener waste and scoured wool cleaner waste samples (Figure 1–5 and Figure 1–10) were continually produced when the scours were operational (in some instances depending on the type of wool being scoured) and could be collected at any time. On sampling days, samples were collected at different times of the day and thoroughly mixed to achieve a composite sample representative of that day. Sirolan CF sludge collected

from the Fairlie Woolscour was produced as required by operating the Sirolan CF module for at least 4 h (Figure 2–2). Sludge samples sourced from Ashburton or Kaputone were produced under their direction, where centrate quality (turbidity) had priority. The type of wool being scoured on the days of sample collection was recorded. Samples were stored in a refrigerator until they were used, which was generally within five days. When sludge samples were used in decomposition experiments, particles of the smallest size (typically 5 mm) were used, since sieving was difficult due to the sticky nature of the material.

Figure 2–2. Sirolan CF module, decanter and sludge skip installed at the Fairlie Woolscour, Timaru.



Sirolan CF module

Decanter and sludge skip

2.3. ANALYTICAL METHODS

2.3.1. DRY WEIGHT (TOTAL SOLIDS)

The dry weight of samples was determined by oven drying at 105°C for 24 h. A known weight of sample (1-3 g) was placed in a pre-weighed crucible and oven dried. The crucible was then cooled in a desiccator and re-weighed, and the dry weight was calculated (Equation 2-1).

$$\text{Total Solids (\%)} = \left(\frac{\text{Sample dry weight (mg)}}{\text{Sample wet weight (mg)}} \right) * 100$$

Equation 2-1

2.3.2. PH

Sample pH was determined as described by McLean (1982). The ratio of sample to distilled water depended on the substrate (from 1:4 for sludge to 1:15 for sawdust). Sample pH was determined on the settled suspension using a calibrated Cole Palmer Digi-Sense pH meter, model 5985-20.

2.3.3. ORGANIC MATTER AND CARBON

Organic matter was determined by weight loss-on-ignition. Oven-dried samples of known weight were ignited in a muffle furnace at 560°C for 6 h. Samples were cooled in a desiccator and re-weighed. Organic matter was calculated as the loss of dry sample weight (Equation 2-2).

$$\text{Organic Matter (\%)} = \left(\frac{\text{Loss of weight due to ignition (mg)}}{\text{Oven dry weight before ignition (mg)}} \right) * 100$$

Equation 2-2

Carbon was estimated from the organic matter content using Equation 2-3 (Haug, 1993).

$$\text{Carbon (\%)} = \left(\frac{\text{Organic Matter (\%)}}{1.8} \right)$$

Equation 2-3

2.3.4. INORGANIC ELEMENTS

Oven-dried samples were prepared for analysis by ignition in a muffle furnace (800ºC for 6 h). Ashed samples were mixed with standard Norrish formula flux and formed into a bead by fusion at 1030ºC. Inorganic elements were determined by X-ray fluorescence spectroscopy using a PW1400 spectrophotometer by Mr Stephen Brown of the Geochemistry Laboratory, Department of Geological Sciences, University of Canterbury.

2.3.5. GREASE CONTENT

The grease content of samples was determined as described by Williamson (1998). A known weight of sample was added to a pre-weighed 20 mL cellulose thimble and placed in the sample chamber of a Soxhlet apparatus. This was connected to a pre-weighed boiling flask (including anti-bumping granules) and petroleum spirit (AnalaR grade, BDH Laboratory Supplies) was added to the sample chamber until three siphons had occurred. The sample chamber and flask were connected to a condenser and the whole apparatus was placed on a thermostatically controlled electric heating mantle in a fume cupboard. After extraction at 60°C for 3 h, the apparatus was allowed to cool and solvent in the flask was evaporated by gentle heating in the fume cupboard. The grease (in the pre-weighed flask) was then dried at 50°C for 72 h and the flask was reweighed. The remaining (solvent-insoluble) material in the thimble was dried at 105°C for 24 h and reweighed. The grease content of the sample (Equation 2-4) and the extraction efficiency were calculated (Equation 2-5).

$$\text{Grease}\,(\%) = \left(\frac{\text{Grease dry weight}\,(\text{g})}{\text{Sample dry weight}\,(\text{g})} \right) * 100$$

Equation 2-4

$$\text{Efficiency}\,(\%) = \left(\frac{\text{Grease dry weight}\,(\text{g}) + \text{Insoluble fraction dry weight}\,(\text{g})}{\text{Sample dry weight}\,(\text{g})} \right) * 100$$

Equation 2-5

2.3.6. PESTICIDE RESIDUE ANALYSIS

The detection of the organophosphate pesticides diazinon (O,O-diethyl 0-(2-isopropyl-4-methyl-pyrimidine-6-yl) phosphorothioate) and propetamphos ((E)-O-2-isopropoxycarbonyl-1-methylvinyl O-methyl ethylphosphoramidothioate) (both PestAnal grade, Riedel-deHaën Laborchemikalien GmbH & Co., Germany) was made using a Hewlett Packard HP6890 series gas chromatography system in the Environmental Engineering Laboratory of the Department of Civil Engineering, University of Canterbury. For each pesticide, a range of standards of known concentration from 0 to approximately 350 mg L^{-1} was produced and a calibration curve was plotted based on peak areas (see Appendix Section 8.1 p.195). Dichloromethane (BDH AnalaR grade) was used as the solvent in all analyses, with samples placed in 2 mL vials and 1 μL injected using an auto sampler through the front inlet in splitless mode. An HP-5 (5% phenyl methyl siloxane) column was used (30 m length, nominal diameter 320 μm, nominal film thickness 0.25 μm), with helium as the carrier gas and compounds analysed using flame ionisation detector. The initial oven temperature was 80°C, ramped at 30°C min^{-1} to 170°C, then at 2°C min^{-1} to 184°C, and finally at 50°C min^{-1} to 300°C, where it was held for 1 min.

Samples for pesticide analysis first had their grease extracted (Section 2.3.5), and known weights of oven-dried grease were made up to 25 mL with dichloromethane and shaken thoroughly. From the peak areas of the pesticide residues detected, the concentration (ppm) of each pesticide in the grease and in the sample from which the grease was extracted was calculated (Equation 2-6 and Equation 2-7).

$$\text{Pesticide (ppm in grease)} = \left(\frac{1{,}000{,}000 * \text{pesticide concentration (mg L}^{-1}\text{)}}{\text{grease concentration (mg L}^{-1}\text{)}} \right)$$

Equation 2-6

$$\text{Pesticide (ppm in dry sample)} = \text{Pesticide (ppm in grease)} * \left(\frac{\text{Grease content (\%)}}{100} \right)$$

Equation 2-7

2.3.7. HEAVY METAL AND POTASSIUM ANALYSIS

Samples collected prior to July 2002 were supplied to Mr Dennis Matthews of the Christchurch Wastewater Treatment Works, Christchurch City Council. Sample dissolution was achieved using nitric acid/hydrogen peroxide microwave digestion or refluxing with nitric acid at 90°C for 1 h. Samples collected after August 2002 were supplied to RJ Hill Laboratories in Hamilton, where nitric/hydrochloric

acid digestion was used according to United States Environmental Protection Agency 200.2. Inductively coupled plasma-optical emission spectroscopy was used for the detection of potassium, while inductively coupled plasma-mass spectroscopy was used for the detection of heavy metals.

2.3.8. PHOSPHORUS

Samples for phosphorus analysis were prepared using the methodology of Nicholson (1984), which entailed ashing a known amount of oven-dried sample (0.5-2.5 g as appropriate) at 480°C for 4 h. After cooling, the resulting ash was moistened with distilled water and treated with 5 mL of a 1:1 solution of concentrated HCl and distilled water. The crucible was placed on a boiling water bath for 5 min to ensure ash dissolution. After cooling, the digest solution was filtered through Whatman #41 paper into a 50 mL volumetric flask, and rinsed using hot distilled water. The solution was made up to volume with distilled water when cool.

The phosphorus content of the digest solution was determined according to Kitson and Mellon (1944). A calibration curve was plotted using solutions of known phosphorus concentration (see Appendix Section 8.2 p.195). To a beaker containing 8 mL distilled water and 7 mL nitric-vanadomolybdate reagent, 10 mL of digest solution was added. After mixing, the absorbance was determined at 465 nm using a Pye Unicam SP6-350 spectrophotometer, from which the ppm phosphorus in the vanadomolybdo-phosphate solution and the phosphorus content of the sample was determined (Equation 2-8).

$$\text{P (\% in oven dry sample)} = \left(\frac{\text{P}_{(\text{ppm})}}{\text{Sample weight (g)}} \right) * 0.0125$$

Equation 2-8

2.3.9. BIOLOGICAL AND CHEMICAL OXYGEN DEMANDS

Samples were supplied to Environment Canterbury (Canterbury Regional Council) in Timaru for determination of biological and chemical oxygen demands. Biological oxygen demand was analysed according to American Public Health Association 20th Edition 1998 method 5210B and chemical oxygen demand to method 5220B (Clesceri *et al.*, 1998). In brief, biological oxygen demand was determined by measuring the dissolved oxygen uptake in the diluted sample over 5 days incubation at 20°C. Chemical oxygen demand was determined by digesting the sample with sulphuric acid and known excess potassium

dichromate under open reflux for 2 h, then titrating excess potassium dichromate with ferrous ammonium sulphate.

2.3.10. CHLORIDE

Chloride in suint was determined using the mercury (II) thiocyanate method as described by Adriano and Doner (1982). A known volume of suint was transferred to a 25 mL volumetric flask together with 2 mL ferric (III) nitrate nonahydrate solution and 2 mL saturated mercury (II) thiocyanate solution. The solution was mixed, made up to volume with distilled water, and mixed again. The absorbance at 460 nm was measured after 10 min, blanked against a solution containing the reagents but no suint. The chloride concentration was determined from a calibration curve plotted from different sodium chloride solutions (see Appendix Section 8.3 p.196). Chloride in suint was calculated using Equation 2-9 and Equation 2-10.

$$\text{Cl (ppm in suint)} = \left(\frac{\text{Cl (ppm in solution)}}{\text{Suint dilution (Suint volume (mL)/Total volume (mL))}} \right)$$

Equation 2-9

$$\text{Cl (\% of oven dry suint)} = \left(\frac{\text{Cl (ppm in suint)}/1000}{\text{Suint oven dry weight L}^{-1}\text{ (g)}} \right) * 100$$

Equation 2-10

2.3.11 ELECTRICAL CONDUCTIVITY

Electrical conductivity (the ability of a solution to conduct electricity) of samples was examined using a Hach SensIon 156 portable multiparameter (Hach Company, Colorado, USA). Conductivity was measured as micro- or milli-Siemens per centimetre ($\mu S\ cm^{-1}$ or $mS\ cm^{-1}$) depending on the sample.

2.4. NITROGEN ANALYSES

2.4.1. TOTAL NITROGEN

Total N (TN) in samples was determined by the semi-micro Kjeldahl method as described by Bremner and Mulvaney (1982). A known amount of sample (20-200 mg as appropriate) was placed in a 50 mL Kjeldahl flask, to which half a mercury catalyst tablet (containing about 0.05 g HgO and 0.45 g K_2SO_4)

and 1 mL concentrated sulphuric acid (H_2SO_4) were added. The flasks were placed on a Kjeldahl digestion stand in a fume cupboard, and the digestion proceeded for about 2 h, until the flask contents were white. For liquid samples, aliquots were added to flasks followed by the addition of 1.5 mL acid, and the flasks were placed on the digestion stand on half heat for 20 min and then full heat until fuming to evaporate down the liquid. The flasks were then allowed to cool, catalyst was added, and digestion proceeded as above. Following digestion, the flasks were allowed to cool, 10 mL distilled water was added while the flasks were cooled under tap water, and samples were distilled in the distillation apparatus (Bremner and Mulvaney, 1982) with the addition of 10 mL 10M sodium hydroxide (NaOH) with thiosulphate ($Na_2S_2O_3$). The ammonia (NH_3) released was collected in 5 mL boric acid for 2 min, and the distillate was titrated against 0.005N H_2SO_4, with 1 mL acid equivalent to 70 µg N and the titre of the control (reagents only) subtracted from that of the samples. The amount of N present in the sample was determined and converted to a percentage of the sample by weight (Equation 2-11 and Equation 2-12).

$$\text{TN (mg)} = (\text{Sample titre} - \text{control titre (mL } H_2SO_4)) * 0.07 \text{ (mg N mL}^{-1} H_2SO_4)$$

Equation 2-11

$$\text{TN (\%)} = \left(\frac{\text{TN (mg)}}{\text{Oven dry sample weight (mg)}} \right) * 100$$

Equation 2-12

2.4.2. MINERAL NITROGEN

Mineral N species, i.e. ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-), were determined as described by Keeney and Nelson (1982). To a known weight of sample, 50 mL of 2M KCl was added, and the flasks were placed on an orbital shaker for 30 min. A 10 mL aliquot was taken after the samples had settled and placed in a 150 mL flask for steam distillation, with ammonium-N reduced to NH_3 in the presence of about 0.2 g heavy magnesium oxide (MgO) then in the same flask nitrate- and nitrite-N reduced to NH_3 in the presence of about 0.2 g Devarda's alloy. Liquid samples were diluted with distilled water and distilled directly. Titration and N determination was as described in Section 2.4.1. A multiplication factor was used to convert mineral N in the aliquot distilled to mineral N in the total volume of KCl added and moisture in the sample.

Ammonia-N produced during decomposition experiments was analysed by rinsing the contents of acid traps (Section 2.5.2) into distillation flasks with 10 mL distilled water. The sample was made alkaline with 3 mL of 10M NaOH and distilled on the Bremner apparatus, as described in Section 2.4.1.

Together, NH_4^+-N, NO_3^--N and NO_2^--N represents the extractable mineral N of a sample or microcosm (Equation 2-13). Mineralised N included NH_3-N collected over the incubation period by the acid traps and the extractable NH_4^+-N, NO_3^--N and NO_2^--N (Equation 2-14). Net-N mineralisation was the mineral N present after a period of incubation less the N present in the sample at the beginning of the experiment, less that mineralised in control microcosms (no substrate), and was presented as a percentage of the initial TN (i-TN) (Equation 2-15).

$$\text{Mineral-N (mg)} = NO_3^- + NO_2^- + NH_4^+ \text{ (mg)}$$

Equation 2-13

$$\text{Mineralised N (mg)} = NO_3^- + NO_2^- + NH_4^+ + NH_3 \text{ (mg)}$$

Equation 2-14

$$\text{Net - N Mineralisation (\%)} = \left(\frac{\text{Mineral - N (Final) - Mineral - N (Initial) (mg)}}{\text{i - TN (mg)}} \right) * 100$$

Equation 2-15

2.4.3. HEXOSAMINE NITROGEN

Hexosamine N in samples following reflux hydrolysis (Section 2.4.5) was determined indirectly by the addition of 11 mL phosphate borate buffer to 10 mL sample. Samples were distilled on a Bremner apparatus for 4 min (Section 2.4.1). Hexosamine N was determined from the total (hexosamine and ammonia) N detected by the subtraction of ammonia-N, determined as described in Section 2.4.2, and was multiplied by 1.75 to correct for decomposition of hexosamine during hydrolysis. The difference between the corrected and uncorrected amounts was subtracted from the amount of ammonia-N.

2.4.4. α-AMINO ACID NITROGEN

α-Amino acid N was determined by the addition of 5 mL sample to a 150 mL distillation flask together with 1 mL of 0.5N NaOH. Samples were placed in boiling water for 30 min and then cooled. Ninhydrin (0.1 g) and citric acid (0.52 g) were added to the samples, which were then boiled for 10 min. Once cool, samples were distilled with 11 mL phosphate borate buffer and 0.6 mL of 10M NaOH for 2 min on a Bremner apparatus, as described in Section 2.4.1.

2.4.5. ACID HYDROLYSIS NITROGEN DISTRIBUTION ANALYSIS

An amount of sample equal to about 10 mg TN and 20 mL of 6N HCl were added to a hydrolysis flask, which was placed on a hydrolysis stand for 24 h at 110ºC under reflux. Once cooled, the solution was filtered and the insoluble material was oven dried at 105ºC for 1 h. The filtered solution was neutralised to pH 6.5 by the addition of ice cold 10N NaOH with stirring. This was added to a 100 mL volumetric flask and made to volume. The pH was retested before use. Total N was determined on both the insoluble material and the solution (as described in Section 2.4.1), with ammonia-N, hexosamine-N, and α-amino acid-N forms determined on the solution (described in Sections 2.4.2, 2.4.3, and 2.4.4 respectively). These N forms (insoluble, ammonia, hexosamine, and α-amino acid) were expressed as a percentage of the TN. The percent N unaccounted for was termed hydrolysable but unidentified N (HUN).

2.5. DECOMPOSITION EXPERIMENTS

Decomposition of substrates reported in this thesis was evaluated on a microcosm scale using net-N mineralisation (Sections 2.5.2 and 2.5.3) and weight loss (Section 2.5.4) methods, with five replicates unless stated otherwise.

2.5.1. SOIL INOCULUM PREPARATION

A soil inoculum was prepared by adding 20 g Ilam soil (refer to Section 8.4 p.197 in the Appendices for its chemical properties) collected from the University campus to 60 mL distilled water. The suspension was stirred and allowed to settle for 5-10 min, filtered through muslin cloth, and 300 μL of the suspension was evenly distributed over the surface of substrates in weight loss and N mineralisation microcosms.

2.5.2. Decomposition as Measured by Net-Nitrogen Mineralisation

Microcosms consisted of 125-mL conical flasks with about 5 g organic matter-free (ignited) sand as the matrix. Before samples were incubated, sub-samples were oven dried to determine the moisture content (Section 2.3.1) and TN (Section 2.4.1). Enough fresh material was added to give about 10 mg TN (mineral N at day 0 was also determined). The inoculum (Section 2.5.1) and additional distilled water was added to achieve the desired moisture content, which was determined gravimetrically. An acid trap containing 1.5 mL of 1M H_2SO_4 was suspended in each microcosm to trap evolved NH_3 and microcosms were covered with plastic film, secured with rubber bands, and incubated aerobically at the desired temperature. Microcosms were checked by weighing and watered regularly to ensure constant moisture conditions, also allowing the change of gases in the microcosms when the plastic film was removed. Control microcosms containing no substrate were always run concurrently.

After the designated incubation period, the plastic covers were removed from the microcosms and ammonia and extractable mineral N was analysed, as described in Section 2.4.2. Net-N mineralisation was reported (Equation 2-15).

2.5.3. Net-Nitrogen Mineralisation Under Anaerobic Conditions

Net-N mineralisation under anaerobic conditions was examined using Merck Anaerocult A kits, according the manufacturer's instructions. Briefly, the kits contained oxygen-binding chemicals, which also produced carbon dioxide, to produce an anaerobic environment as indicated by a test strip. Microcosms, prepared as described in Section 2.5.2 but not covered with plastic film, were placed in 3.2 L airtight plastic canisters ("Click Clack" brand). Controls were placed in separate canisters to treatments, and since the microcosms were not covered (to allow for the removal of all oxygen from the atmosphere), there was effectively no replication since the acid traps were absorbing NH_3 from the general headspace. Had control microcosms been placed in canisters with treatment microcosms, they may have absorbed NH_3 from the treatment, giving an elevated level of control mineralisation. Microcosms were analysed as for aerobic incubations (Section 2.5.2).

2.5.4. Decomposition as Measured by Weight Loss

Weight loss experiments were conducted in 50-mL glass centrifuge tubes. An amount of fresh sample, to give 1 g oven dry weight, was added to pre-weighed tubes followed by the addition of a soil inoculum (Section 2.5.1) and moisture, added drop wise to give the desired moisture content. Tubes were sealed

with plastic film and the moisture content checked periodically and adjusted when required. Controls consisted of sample without the addition of an inoculum or moisture; instead, about 1 mL of chloroform was added to prevent microbial activity and tubes were sealed with rubber bungs rather than plastic film. After the incubation period, the film was removed from the tubes and the tubes were oven dried overnight at 105°C. After cooling in a desiccator, the tubes were reweighed and the weight loss was calculated (Equation 2-16).

$$\text{Weight loss}\,(\%) = \left(\frac{\text{Initial dry weight - Final dry weight (mg)}}{\text{Initial dry weight (mg)}} \right) * 100$$

Equation 2-16

2.6. STATISTICAL ANALYSIS

Statistical analysis, including analysis of variance and *t*-tests, was performed using Statistix Version 7 (Analytical Software, Tallahassee, FL.). Where the assumptions of parametric tests (normally distributed data, tested by the Shapiro Wilk test, and homogeneous treatment variances, tested by the F-max test) were not met, data was transformed to meet these assumptions or the equivalent non-parametric tests were conducted.

Analysis of variance was used to test for differences among the means of various treatments. Where significant differences were found at α=0.05, comparisons of means were performed by least significant differences. Observed (experimentally-determined) values were compared to expected (theoretical) values using one-sample *t*-tests (two sided). Two-sample *t*-tests (or the non-parametric equivalent Wilcoxon Rank Sum test) were used to test for differences in the means of two groups.

3. THE UTILISATION OF CONCENTRATED SUINT

3.1. INTRODUCTION

In this section, the composition of suint and its effect on soil were determined to assess its potential application to land as a potassium fertiliser. Its suitability for this purpose could be judged by suint not containing any compounds at concentrations likely to negatively affect normal soil functioning, nor suint acting in a manner to the detriment of the soil system following application. Specifically, the hypotheses in Table 3-1 were tested.

Table 3-1. Hypotheses tested during suint research.

Hypothesis		Experimental
H3-1 Suint will have a consistent composition and not contain compounds at concentrations that would limit its application to soil	(a)	Laboratory analysis of CF and CFB suint types for total solids, pH, organic matter, grease, pesticides, heavy metals, chloride, nitrogen, inorganic elements, phosphorus and electrical conductivity
H3-2 Suint samples will decompose at similar rates and will mineralise different amounts of N under different environmental conditions	(a)	Decomposition of daily suint samples as assessed by net-N mineralisation (in a sand matrix with aerobic incubation at 37ºC for 30 days)
	(b)	Effect of temperature on net-N mineralisation (in a soil matrix with aerobic incubation at 10 and 22ºC for 60 days)
	(c)	Effect of anaerobic conditions on net-N mineralisation (in a soil matrix with incubation at 22ºC for 60 days)
H3-3 Suint will not inhibit the decomposition of other organic compounds	(a)	Net-N mineralisation when suint was co-incubated with chitin, casein or woolscour sludge (in a sand matrix with aerobic incubation at 37ºC for 30 days)
H3-4 CFB suint will not affect soil properties when applied to soil columns at a rate of 100 kg K ha^{-1}	Glasshouse study using soil columns comparing the effect of CFB suint on soil electrical conductivity, pH and mineral N leaching to that of KCl and water	
	(a)	Soil type: soil and soil-coarse sand mixture
	(b)	Columns: planted with perennial ryegrass or left unplanted
H3-5 Suint is not phytotoxic to plants	(a)	Effect of various dilutions of CF and CFB suint on germination and growth of white clover, ryegrass and cucumber (in glasshouse)
	(b)	Effect of CFB suint added at 100 kg K ha^{-1} on ryegrass, white clover and radish germination and growth compared to KCl and water (in glasshouse)
	(c)	Effect of CFB suint added at 100 kg K ha^{-1} on *Pinus radiata* growth compared to KCl and water (in glasshouse)

3.2. MATERIALS AND METHODS

3.2.1. CHEMICAL CHARACTERISATION OF SUINT

Samples of CF suint (the liquid separated from the sludge by the chemical flocculation process) were produced daily from 12-16 February 2001 inclusive, and CFB suint samples (biologically treated CF suint) were produced daily from 26-30 March 2001 inclusive, using the procedures described in Section 2.2. The type of wool being scoured at the time of CF suint production was recorded. This was not done for CFB suint, since the tanks from which the feed was taken contained mixed daily inputs and therefore produced composite samples.

Samples were analysed for total solids (Section 2.3.1), pH (Section 2.3.2), organic matter (Section 2.3.3), grease content (Section 2.3.5), pesticides (Section 2.3.6), heavy metals (Section 2.3.7), chloride (Section 2.3.10), and their N distribution profile (Section 2.4.5). Inorganic elements (Section 2.3.4), phosphorus (Section 2.3.8), and electrical conductivity (Section 2.3.11) were determined on composite CF and CFB suint samples composed of equal volumes of the five daily samples. Composite samples were also diluted 1:10 with distilled water for determination of the N profiles of the solid and liquid fractions (Section 2.4.5). The solutions were centrifuged at 5,000 rpm for 5 min, filtered through GF/A filter paper, and the solid fractions were rinsed and oven dried overnight at 105°C. N profiles following acid hydrolysis were conducted on the liquid and solid fractions.

3.2.2. VARIATION IN THE DECOMPOSITION OF SUINT

The decomposition of undiluted CF and CFB suint samples (1 mL) was determined using net-N mineralisation (Section 2.5.2), with microcosms incubated in an aerobic environment at 37°C for 30 days. Distilled water was added drop wise following suint addition until the matrix was moist (overall moisture content approximately 35%).

Microbial growth in suint samples that were diluted with distilled water (1:10), centrifuged at 5,000 rpm for 5 min, and filtered through Whatman GF/A filter paper, was also assessed. The initial pH of each sample was recorded and 50 mL of the filtrates were added to 125-mL flasks, together with 300 μL of a soil inoculum (Section 2.5.1). Flasks were placed on an orbital shaker at room temperature (20-25°C) for 3 weeks. Microbial growth was observed as cloudiness and floc formation in the solutions, compared to control flasks containing chloroform (to inhibit microbial growth) that remained clear, and the final pH was recorded.

3.2.3. SUINT DECOMPOSITION PROFILE

The effect of temperature and atmosphere on the decomposition of composite CF and CFB suint solutions was assessed by net-N mineralisation, as described in Sections 2.5.2 and 2.5.3, with the exception that a soil matrix was used instead of a sand matrix.

Composite suint samples were made by mixing equal volumes of the five daily samples, which were then diluted 1:10 with distilled water. To each microcosm, 20 g (fresh weight) Ilam soil (see Appendix Section 8.4 p.197 for soil properties) was added, which was oven dried at 50°C to reduce the moisture content such that on addition of 5 mL suint (or 5 mL distilled water in the case of the controls) the overall moisture content was 30%. An inoculum from the same soil (Section 2.5.1) was added since air drying disturbs the microbial population (Wu and Ma, 2001).

For each suint type, 10 microcosms were incubated aerobically at both 10 and 22°C, with five sampled after 30 days and the remainder after 60 days. Four control microcosms were incubated at each temperature, two of which were sampled at the same times as the treatments. Four microcosms each of CF and CFB suint and controls were incubated anaerobically at 22°C and sampled after 60 days. The Anaerocult A reagent was replaced twice during the incubation period when moisture was replenished. The amount of decomposition was determined as described in Section 2.5.2, taking into account the initial mineral N supplied by the soil matrix.

The production of mineral N under anaerobic (waterlogged) conditions was also determined according to Keeney (1982). Using weight loss tubes (as described in Section 2.5.4), 5 mL suint was added followed by the addition of distilled water to provide minimal headspace when the tubes were stoppered with a rubber bung. For each suint type, five treatment tubes (containing an inoculum – refer Section 2.5.1) and two control tubes (containing 5 drops chloroform instead of an inoculum to inhibit biological activity) were incubated at 37°C for 7 days. Mineral N produced (final mineral N less initial mineral N) was determined as described in Section 2.4.2 and expressed as a percentage of the i-TN.

3.2.4. THE EFFECT OF SUINT ON THE TURNOVER OF MODEL ORGANIC COMPOUNDS

The effect of CF and CFB suint on the decomposition of chitin (*N*-acetyl glucosamine) and casein (both Sigma Chemical Co., St. Louis, MO), and Sirolan CF sludge, was determined by co-incubating the substrates in microcosms (Section 2.5.2) and comparing the observed rates of net-N mineralisation to the

theoretical rates. The theoretical rates of net-N mineralisation were determined from the individual rates of net-N mineralisation for each of the substrates, determined separately under the same conditions. Net-N mineralisation was calculated as described in Section 2.5.2.

Composite suint samples were made from equal volumes of the five daily samples that were subsequently diluted 1:10 with distilled water. Equal amounts (on a TN basis) of suint and chitin or suint and casein were co-incubated aerobically at 37°C for 30 days. When co-incubating suint with Sirolan CF sludge, the ratios of the two components were 25:75, 50:50 and 75:25 on a TN basis. For example, 25:75 suint:sludge contained 2.5 mg TN from the suint and 7.5 mg TN from sludge. The sludge sample used was a composite sample consisting of equal amounts (fresh weight basis) of five daily samples. The amount of sand used as the matrix depended on the volume of suint added; enough sand was added to ensure there was no excess moisture in the microcosms.

3.2.5. The Effect of Suint on Soil Electrical Conductivity, pH and Leaching of Mineral Nitrogen

The effect of CFB suint and KCl application on the pH and electrical conductivity of soil and the leaching of mineral N was assessed using glass columns of 30 cm height and 4.5 cm internal diameter (surface area 15.9 cm^2).

Organic matter-free gravel was used to fill the tapered region of the columns and was separated from soil by a GF/A filter paper. Two soil types were assessed, the first being soil and the second being a 1:1 v/v mixture of soil and coarse sand mixed thoroughly by hand. Both soil and sand were obtained from a local commercial supplier (Laings Gardenmakers; see Appendix Section 8.4 p.197 for soil properties). A volume of soil or soil-sand mixture (320 cm^3) to provide 20 cm soil depth was added to each of 18 columns. Distilled water was added to each column to saturate the soil (200 mL to the soil columns and 150 mL to the soil-sand mixture) and the combined leachate for each soil type was analysed for the initial pH (Section 2.3.2) and electrical conductivity (Section 2.3.11). Soil, sand and suint samples were analysed for TN (Section 2.4.1) and mineral N (Section 2.4.2) to calculate the total amounts present initially in the soil columns.

For each soil type, a set of nine columns were planted with perennial ryegrass (*Lolium perenne*) seeds and nine were left unplanted, and for each set three columns served as controls, three were amended with suint and three with KCl (both providing K at a rate of 100 kg ha^{-1}). Unplanted columns were amended with the appropriate solutions 2 days after being brought to water holding capacity by the addition of 15 mL distilled water, suint (1:60 dilution) or KCl, as appropriate. Planted columns were thinned to 10 plants

per column after seeds had germinated and were amended, as described above, 4 weeks after seeds were sown.

Soils were leached every 3 weeks by the addition of a volume of distilled water to provide about 20 mL leachate (all columns of the same soil type received the same volume at each leaching event). Universal bottles were placed under each column to collect the leachate, with the volume of leachate recorded. Leachate was analysed for pH, electrical conductivity, and mineral N. Amounts of mineral N leached over the duration of the experiment were cumulated. Columns were leached eight times. Planted columns were watered between leaching events to ensure the soil was moist and plant growth was maintained.

3.2.6. PHYTOTOXICITY OF SUINT

The phytotoxicity of suint was assessed in two glasshouse experiments involving perennial ryegrass, white clover (*Trifolium repens* "Huia"), cucumber (*Cucumis sativus*, Watkins "Lebanese"), and radish (*Raphanus sativus*, Watkins "Salad Crunch").

The first experiment investigated the regular disposal of suint in dilute form onto land. Ilam soil (see Appendix Section 8.4 p.197 for its properties) collected from the University campus was sieved through a 5 mm screen to remove coarse material before being added to 1.5 L pots. Ten seeds each of ryegrass and white clover and five of cucumber were added to each of three separate pots according to instructions on the seed packets. Composite CF and CFB suint solutions composed of equal volumes of five daily samples were diluted 1:10, 1:100, and 1:1,000 with distilled water, and tap water was used as a control. Immediately after planting, 100 mL of the appropriate solution (suint or tap water) was applied to the surface of each pot, and every week a further 50 mL was added. Between weekly applications of suint, water was applied as necessary to keep the soil moist. Pots were raised to prevent the mixing of leachates and their location respective to each other was re-randomised each week. Germination of cucumber was recorded after 1 and 2 weeks and plants were then thinned to two per pot. Germination of ryegrass and white clover was recorded for 7 weeks, at which time the shoot biomass produced per pot was determined on an oven dry basis (105°C for 48 h). Shoot biomass was analysed for its N and K contents (Sections 2.4.1 and 2.3.7 respectively). At this time, cucumber plants were checked for flower set (being inside a glasshouse, natural pollination would not have occurred).

The second assay compared the effect on plant growth of CFB suint to that of KCl, with each supplying 100 kg K ha^{-1}, and to a control that received only water. Three replicates each of ryegrass (25 seeds per pot, thinned to 20 after three weeks), white clover (25 seeds per pot, thinned to 15 after four weeks),

radish (10 seeds per pot, thinned to 5 after one week), and a mix of white clover and ryegrass (thinned to 10 of each species after four weeks), were established in 1.5 L pots containing soil obtained from a commercial supplier (Laings Gardenmakers; see Appendix Section 8.4 p.197 for its properties). All pots were thoroughly watered prior to the amendments being applied, and seeds were sown a day later. Pots were regularly and evenly watered and were raised to prevent the mixing of leachates. Their locations respective to each other was re-randomised every second week. Germination was recorded once there were no changes in the germination rates over a week, and plants were thinned so that all pots had the same number. After 6 weeks, the edible portion of radishes were harvested and the total fresh weights per pot were recorded. New seeds were immediately planted, such that three harvests were made, with the second and third harvests being made after a period of 8 weeks each. Shoot biomass from other pots was frequently harvested over a total period of 27 weeks and oven dried at 105°C for 48 h.

3.2.7. FORESTRY APPLICATIONS OF SUINT

To examine the potential application of CFB suint onto forestry land, its effect on the growth of *Pinus radiata* seedlings was evaluated. Seedlings were obtained commercially from a local supplier (Rangiora Nurseries) on 1 March 2002 and transplanted into pots on 6 March. The seeds were sown on 11 October 2001 and germinated on 25 October; at the time of transplanting the seedlings measured 12-13 cm from the lowest needles to the crown.

Two soil types were evaluated, the first being a Marshlands peat loam collected from an organic farmer, and the second made from 22% by volume coarse sand obtained from a local supplier (Laings Gardenmakers) and 78% by volume peat loam obtained from an adjacent Marshlands farm (40.7% organic matter, 1.4% N). Refer to Appendix Section 8.4 p.197 for properties of the Marshlands soil and sand. Both soils were sieved through a 5-mm screen to remove plant material and stones. Pots of 30 cm diameter (providing a surface area of 707 cm^2) and 60 cm depth, with drainage holes in the bottom, were filled first with 4 L road metal and then 36 L of soil or soil/sand mix. For each soil type, 18 pots each containing two seedlings (which were thinned to one per pot three months later) were established, six as controls and six each for suint and KCl addition. Pots were placed in a glasshouse in a randomised fashion and were re-randomised every month (Figure 3–1). The pots were also raised off the glasshouse floor to allow drainage and weeds, if present, were removed to prevent competition for nutrients.

Suint or KCl was applied to pots on 25 September 2002, approximately 6 months after the seedlings were transplanted to the pots. Prior to the addition of treatments, tree height and basal diameter was recorded, and three fascicles were taken from the top half of the stems of each seedling for nutrient analysis.

Fascicles were pooled for each soil type, dried at 105°C for 72 h, ground, and sent to New Zealand Forest Research in Rotorua for analysis ("basic plant test"). For each soil type, trees were blocked by height into three groups, and within each group two trees each received suint, KCl, or water (which was assigned randomly). A dilute suint solution was made (approximately 1:45 v/v) so that each pot received 500 mL solution adding K at a rate of 100 kg ha^{-1}. A KCl solution was made containing the same concentration of K; control pots received 500 mL tap water. After the solutions were applied evenly to the soil surfaces, each pot received a further 2 L of tap water. Pots were automatically watered using two spikes placed in each pot for 3 minutes three times a week for 8 months. Two, 4, 6 and 8 months post application, the seedlings were measured for height and basal diameter. After 8 months, 10 fascicles were taken from random branches from each seedling for nutrient analysis, as described above. Fascicles were bulked by treatment for each soil type.

Figure 3–1. *Pinus radiata* experiment in the university glasshouses.

3.3. RESULTS

3.3.1. CHEMICAL CHARACTERISATION OF SUINT

The five CFB suint samples collected were more homogeneous than the five CF suint samples, as illustrated by the smaller standard errors of the means (Table 3-2). CFB suint contained significantly more potassium than CF suint, while CF suint contained significantly more zinc than CFB suint. On an ash (inorganic) basis, both suint types had similar amounts of potassium, being 30 and 33% of the ash weight for CF and CFB suint, respectively. The pH values and densities were statistically different; no other significant differences were detected. Two CF suint samples and four CFB suint samples were

analysed for their grease and pesticide residue contents. The efficiency of the grease extraction for all suint samples was 96-100%. CFB suint contained less grease than CF suint. Both grease samples extracted from CF suint contained no diazinon or propetamphos residues; insufficient grease was extracted from CFB suint samples for pesticide levels to be determined. Average K:Cl ratios for CF and CFB suint were 0.9:1 and 1.6:1, respectively, compared to a ratio of 1.1:1 for KCl.

Table 3-2. Chemical properties of CF and CFB suint samples collected from the Fairlie Woolscour.

Property	CF Suint	CFB Suint	Significance
Moisture (%)	59.9 (5.20)	62.7 (1.16)	NS
Density (g mL^{-1})	1.15 (0.02)	1.23 (0.02)	*
pH	4.5 (0.02)	6.2 (0.07)	**
Organic matter (%)	51.3 (6.16)	40.5 (1.09)	NS
Potassium (%)	14.5 (1.04)	19.6 (0.48)	**
Phosphorus (%)	0.19	0.16	ND
Chloride (%)	16.3 (5.21)	12.1 (1.61)	NS
Grease (%)	3.4 (0.36)	0.2 (0.09)	ND
Arsenic (mg kg^{-1})	1.3 (0.33)	ND	ND
Cadmium (mg kg^{-1})	0.8 (0.43)	0.5 (0.08)	NS
Chromium (mg kg^{-1})	5.5 (1.04)	7.9 (0.66)	NS
Copper (mg kg^{-1})	52.3 (18.77)	14.6 (5.29)	NS
Lead (mg kg^{-1})	2.3 (0.42)	2.8 (0.88)	NS
Nickel (mg kg^{-1})	10.2 (2.73)	11.5 (0.71)	NS
Zinc (mg kg^{-1})	137.7 (13.80)	35.9 (7.47)	***
Total N (mg mL^{-1})	15.1 (2.18)	12.9 (0.58)	NS
Acid-insoluble N (% of TN)	1.8 (0.29)	3.7 (0.51)	*
NH_4-N (% of TN)	46.0 (1.39)	27.8 (1.31)	***
Hexosamine-N (% of TN)	1.2 (0.49)	2.5 (0.52)	NS
α-Amino acid-N (% of TN)	25.2 (1.31)	38.3 (0.55)	***
HUN (% of TN)	25.9 (1.02)	27.7 (1.03)	NS

Note: all results (except moisture, density and pH) are on an oven dry basis. Numbers in brackets are the standard errors of the means, n=5. *,** and *** refer to significant differences between suint types at the 0.05, 0.01 and 0.001 levels, respectively. NS = not significant, ND = not determined. TN = total N, HUN = hydrolysable but unidentified N. Hexosamine-N values were corrected for decomposition.

CF suint samples on average contained more TN than CFB suint samples, although the difference was not significant (Table 3-2). Amounts of TN were highly variable in the case of CF suint. CF suint contained statistically higher levels of mineral N (73% and 51% of which was pre-existing in CF and CFB suint, respectively), while CFB suint samples contained statistically more α-amino acid N. Hexosamine N in both suint types was low. The increase in α-amino acid N between direct determinations on the samples and after acid hydrolysis (from 2.9 to 25.2% of TN and from 7.1 to 38.3% of TN for CF and CFB, respectively) indicates the presence of proteins in the samples. As the N distribution analyses of daily suint samples showed little variation (Table 3-2), the profiles of the solid and liquid fractions (separated by centrifugation and filtration) were conducted on composite CF and CFB suint samples (Table 3-3).

The liquid fraction contained more ammonium N than the solid fraction, which contained predominantly α-amino acid N. The solid fraction of CFB suint contained three times the TN than that of CF suint.

Table 3-3. Nitrogen distribution analysis of the solid and liquid fractions of suint following acid hydrolysis.

	CF Suint		CFB Suint	
	Liquid fraction	Solid fraction	Liquid fraction	Solid fraction
Total N (mg mL^{-1} or mg g^{-1})	17.2	25.0	10.7	76.8
Insoluble N (% of TN)	1.8	8.0	3.6	4.1
NH_4-N (% of TN)	47.8	16.8	32.8	8.6
Hexosamine-N (% of TN)	2.6	1.8	1.8	2.0
α-Amino acid-N (% of TN)	25.8	48.3	27.0	53.5
HUN (% of TN)	22.1	25.1	34.8	31.8

Note: TN = total N, HUN = hydrolysable but unidentified N. Hexosamine-N values were corrected for decomposition.

Compared to soil, inorganic element analysis indicated high levels of sodium, potassium and sulphur in the ash of CF and CFB suint (Table 3-4). Consequently, suint was in low in silicon and aluminium. Both suint types were very similar in terms of the proportions of inorganic elements. On a K basis, CF suint contained four times as much chloride than sodium, and CFB suint contained twice as much chloride than sodium.

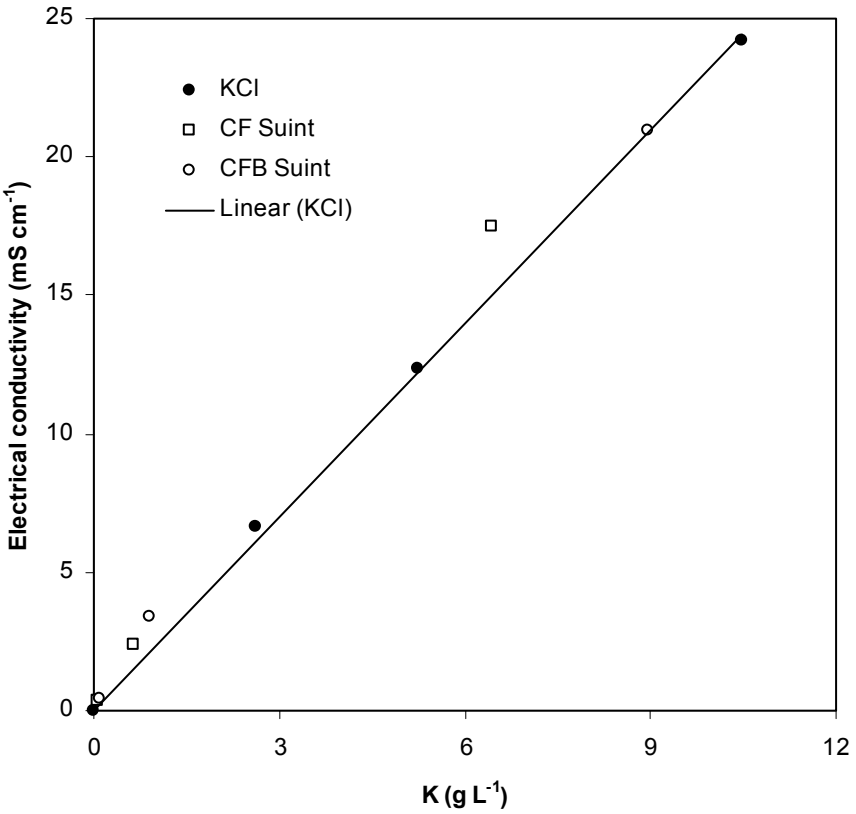
Table 3-4. Inorganic element analysis of CF and CFB suint compared to that of soil.

	% of Ashed Sample		
Element	CF Suint	CFB Suint	Soil[#]
Silicon	5.79	4.80	74.84
Titanium	0.04	0.01	0.92
Aluminium	1.92	1.28	10.94
Iron	1.43	0.44	5.14
Manganese	0.07	0.09	0.18
Magnesium	1.53	1.45	1.09
Calcium	1.85	1.62	2.03
Sodium	13.17	14.34	1.52
Potassium	48.37	47.23	3.15
Phosphorus	0.84	0.43	0.10
Sulphur	24.99	28.31	0.09

Note: [#]Inorganic elements typically found in soil (Williamson, 1998).

Compared to the K content of KCl, the most commonly used K fertiliser, suint diluted 1:10, 1:100 and 1:1,000 with distilled water had a higher or similar conductivity (Figure 3–2). For reference, the conductivity of tap and seawater (from Caroline Bay, Timaru, 23/4/03) was 0.126 and 38.6 mS cm^{-1}, respectively.

Figure 3–2. Electrical conductivity of suint dilutions compared to KCl based on K content.



3.3.2. VARIATION IN THE DECOMPOSITION OF SUINT

Large variation, as indicated by standard error values, was found between replicates in the decomposition of concentrated suint using sand-based microcosms, with some microcosms showing net-N mineralisation and some N immobilisation within a treatment (Table 3-5). CF suint solutions had a low initial pH due to the acidified flocculation process, and most microcosms did not exhibit a neutral pH, indicative of microbial growth with ammonification, after 30 days. Three of the five samples exhibited net-N mineralisation over the incubation period, while the remaining two showed N immobilisation. Of the microcosms containing CF suint collected on Tuesday, three showed no visible microbial growth and had a final pH of 5.2 and immobilised 0.2% of the i-TN, while the remaining two microcosms exhibited microbial growth and had a final pH of 7.0 and mineralised 16% of the i-TN. All CFB suint microcosms showed an increase in pH of more than one pH unit over the 30 day incubation, visible microbial growth, and net-N mineralisation.

Table 3-5. Daily variation in the decomposition of suint samples as measured by net-N mineralisation.

	Monday	Tuesday	Wednesday	Thursday	Friday
			CF Suint		
Wool type	Cross-bred	Slipe	Cross-bred	Cross-bred	Cross-bred
Initial pH	4.6	4.6	4.5	4.5	4.5
Final pH	5.1	5.2/7.0	4.9	4.9	5.0
Net-N Mineralised (% of i-TN)	-5.2 (0.54)	5.2 (4.42)	8.4 (0.16)	0.8 (0.13)	-1.9 (0.32)
			CFB Suint		
Initial pH	6.2	6.2	6.3	6.4	6.0
Final pH	7.8	7.8	7.4	8.1	8.2
Net-N Mineralised (% of i-TN)	5.2 (1.59)	2.0 (1.97)	2.4 (0.75)	9.2 (2.26)	9.2 (2.10)

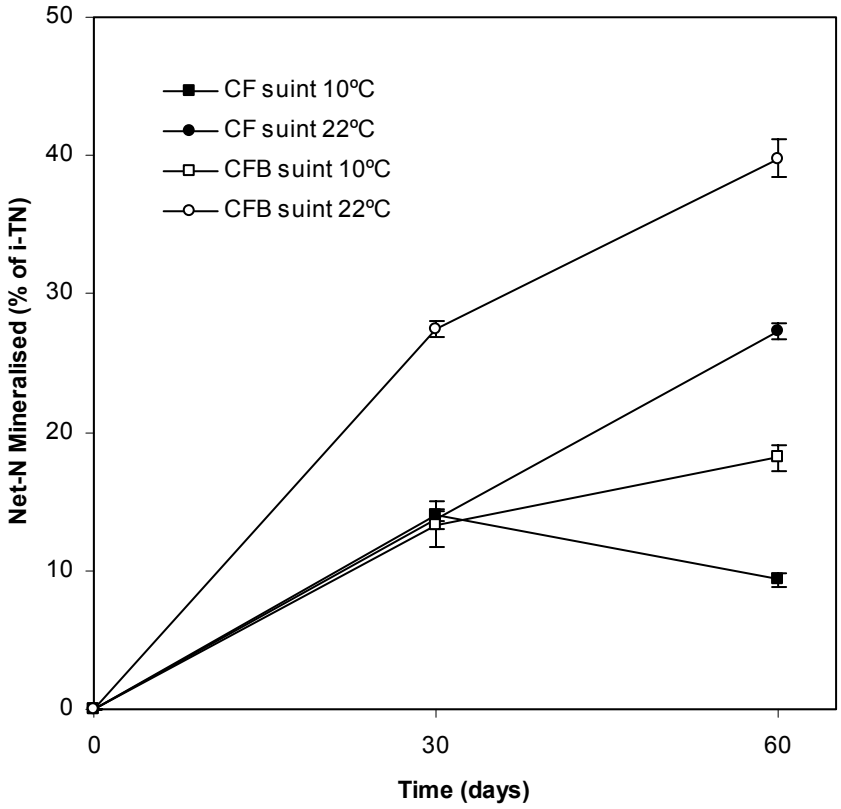
Note: microcosms were incubated at 37°C for 30 days. Numbers in brackets are the standard errors of the means, n=5. Negative net-N mineralisation values indicate N immobilisation.

Extensive microbial growth was observed in diluted (1:10), filtered suint solutions after 3 weeks incubation. In the case of CF suint samples, an increase of 1.5-3.1 pH units, from 4.7-4.8 to 6.2-7.8 was observed as the substrate was utilised, except for the Tuesday sample. All CFB suint samples exhibited a rise in pH of 1.9-2.5 units, from 6.1-6.4 to 8.2-8.6. CFB suint solutions did not have the same large colonies in solution as did CF suint, instead having growth on the bottom and sides of the flasks.

3.3.3. SUINT DECOMPOSITION PROFILE

Except for CF suint incubated at 10°C, an increase in net-N mineralisation over time under aerobic conditions was observed for composite suint samples diluted 1:10 with distilled water (Figure 3–3). CF suint incubated at 10°C showed N immobilisation from 30 to 60 days. CF-B suint showed an effect of temperature on the rate of net-N mineralisation, with the rate at 22°C twice that at 10°C after 30 and 60 days. CFB suint mineralised more N than CF suint at both temperatures examined. After 60 days under anaerobic conditions at 22°C, CF suint mineralised 5.8% of its i-TN (SEM=1.66, n=4) and CFB suint mineralised 49.4% (SEM=1.05, n=4) of its i-TN. Mineral N production under anaerobic (waterlogged) conditions over 7 days at 37°C was 1.4% (SEM=0.13, n=5) and 8.0% (SEM=1.76, n=5) of the i-TN for CF and CFB suint, respectively.

Figure 3–3. Aerobic decomposition profile for CF and CFB suint at the 1:10 dilution as determined by net-N mineralisation.



Note: bars represent standard errors of the means, n=5. A soil matrix was used instead of a sand matrix.

3.3.4. THE EFFECT OF SUINT ON THE TURNOVER OF MODEL ORGANIC COMPOUNDS

Both CF and CFB suint types (at the 1:10 dilution) had no effect on the decomposition of chitin and casein over 30 days aerobic incubation at 37°C and 30% moisture, as determined by net-N mineralisation (Table 3-6). Suint, however, had a large positive effect on Sirolan CF sludge decomposition under the same incubation conditions. Experimental rates of net-N mineralisation were up to three times the rates predicted at the 75:25 sludge:suint ratio and more than twice the rates predicted at the 50:50 sludge:suint ratio.

Table 3-6. Effect of CF and CFB suint at the 1:10 dilution on the turnover of model organic compounds as determined by net-N mineralisation.

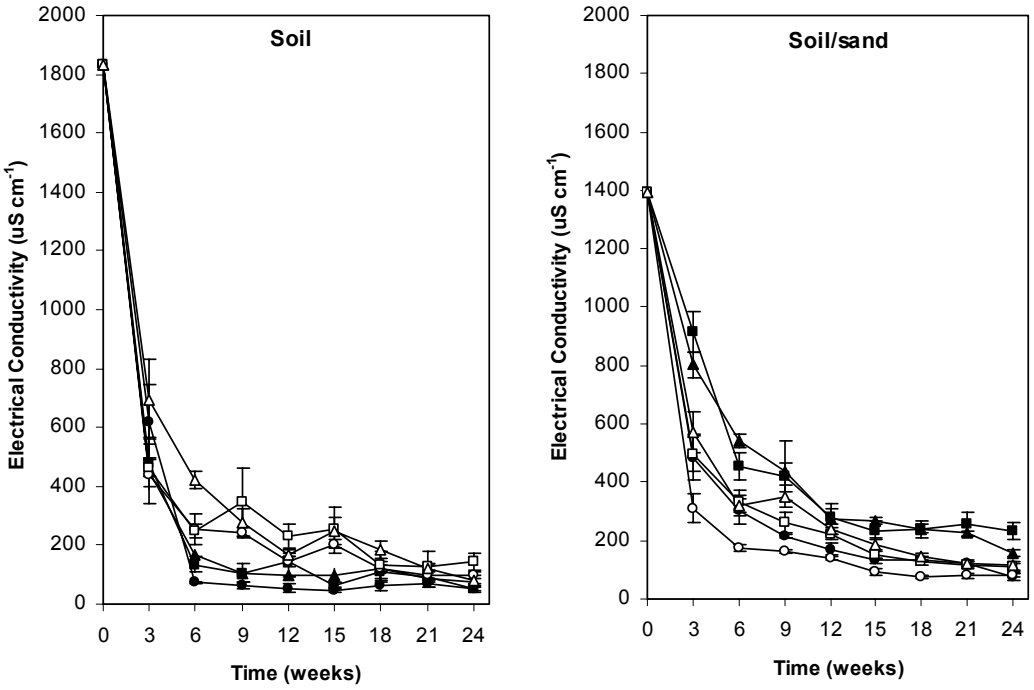
Substrates	Net-N Mineralised (% of i-TN) Observed	Expected
50% Casein – 50% CF Suint	51.2 (1.38) NS	49.0
50% Chitin – 50% CF Suint	17.5 (2.15) NS	16.9
25% Sludge – 75% CF Suint	15.4 (0.82) **	11.5
50% Sludge – 50% CF Suint	24.3 (1.30) ***	9.1
75% Sludge – 25% CF Suint	20.2 (1.16) ***	7.0
50% Casein – 50% CFB Suint	51.7 (1.76) NS	50.3
50% Chitin – 50% CFB Suint	21.5 (1.39) NS	18.2
25% Sludge – 75% CFB Suint	15.3 (0.84) *	12.1
50% Sludge – 50% CFB Suint	26.7 (0.31) ***	9.4
75% Sludge – 25% CFB Suint	21.7 (0.45) ***	7.2

Note: microcosms were incubated at 37°C for 30 days. Substrates were mixed on a total N basis. Numbers in brackets are the standard errors of the means, n=5. *,** and *** indicates experimental values were significantly different to theoretical values at the 0.05, 0.01 and 0.001 levels, respectively, NS = not significant.

3.3.5. The Effect of Suint on Soil Electrical Conductivity, pH and Leaching of Mineral Nitrogen

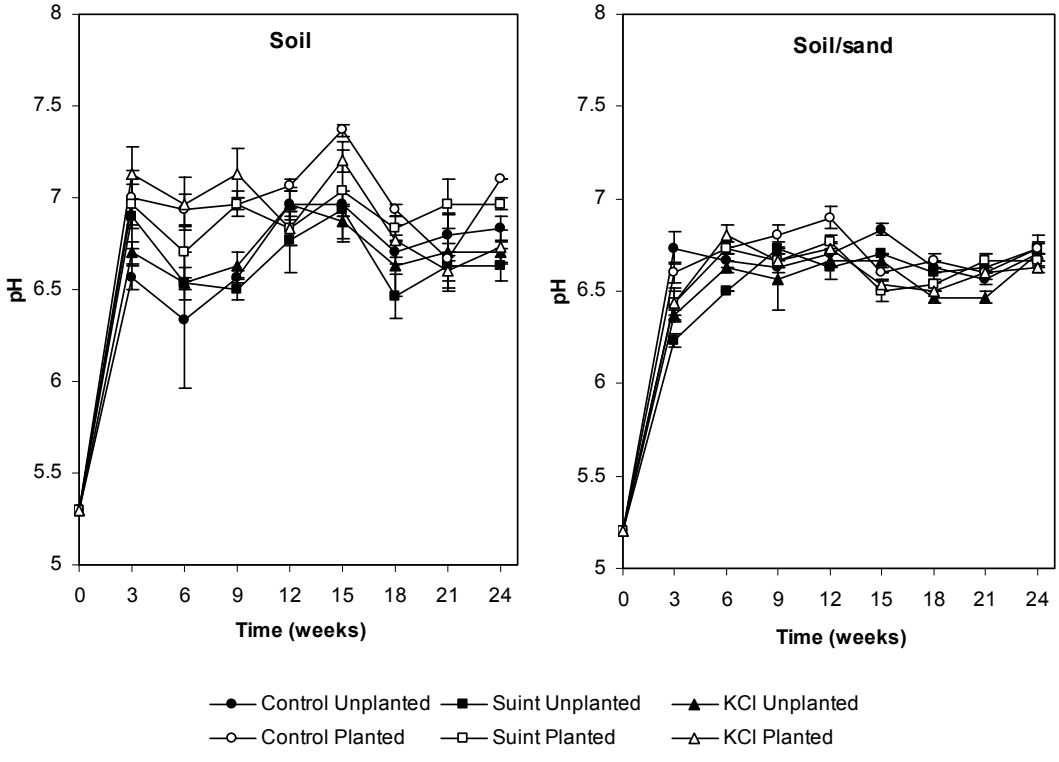
Soil columns initially contained 710 mg TN, including 16 mg mineral N, and soil/sand columns initially contained 400 mg TN, including 9 mg mineral N. The application of CFB suint added 3 mg TN including 0.5 mg mineral N. Over the eight leaching events (every 3 weeks), columns received between 460 mL (in the case of planted soil/sand columns) and 635 mL (in the case of unplanted soil/sand columns) water. The electrical conductivity of soil leachates decreased with each leaching event, with conductivities of control columns decreasing at a slightly faster rate than amended columns in the case of soil/sand columns (Figure 3–4). Amendments had no effect on the pH of soil leachates, which were all in a narrow range between 6.0 and 7.5 (Figure 3–5). Columns planted with ryegrass (10 plants per pot) leached less mineral N than those columns left unplanted, although little mineral N was lost in all cases (Figure 3–6). Statistical analysis showed that, of the cumulative mineral N leached from unplanted columns after 24 weeks, more was leached from soil/sand columns than from soil columns, more was lost from soil/sand columns amended with suint than from those unamended or amended with KCl, and less was leached from soil columns amended with KCl than from soil columns unamended or amended with suint.

Figure 3–4. Electrical conductivity of leachates from soil columns amended with suint or KCl at 100 kg K ha^{-1}.



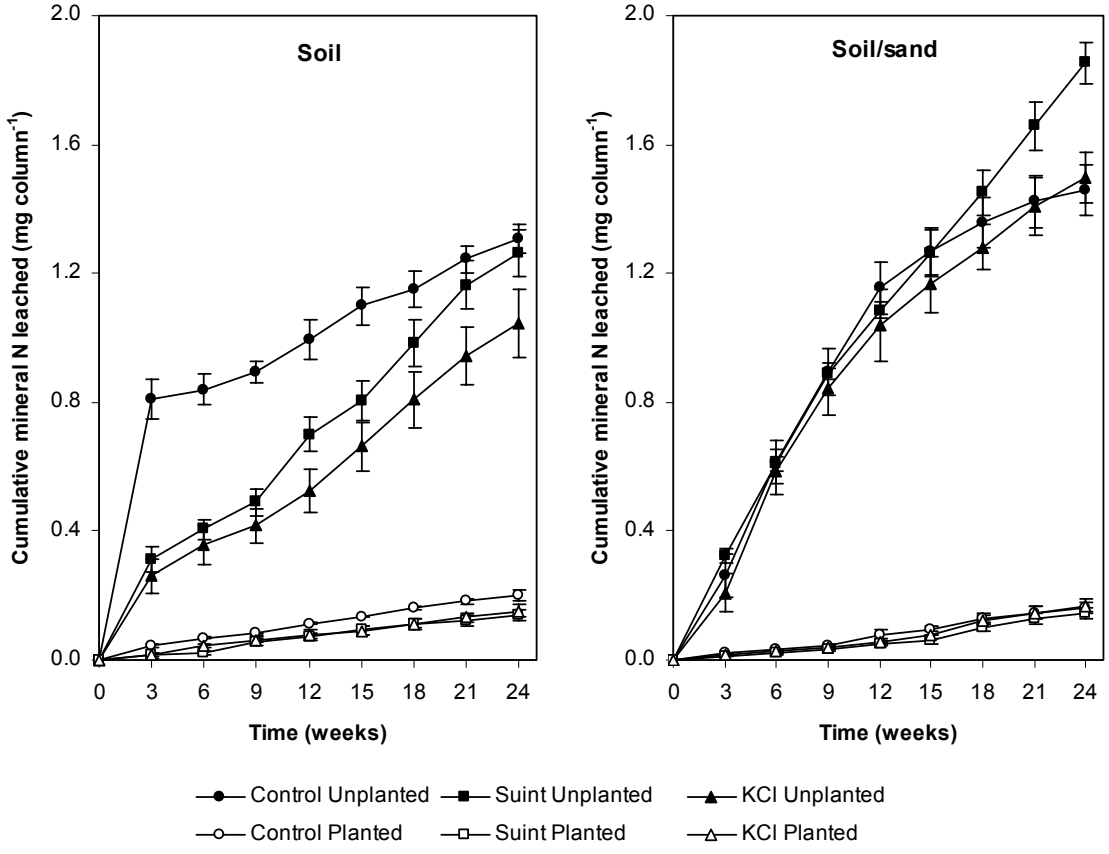
Note: bars represent standard errors of the means, n=3. Refer to Figure 3–5 below for figure legend.

Figure 3–5. pH of leachates from soil columns amended with suint or KCl at 100 kg K ha^{-1}.



Note: bars represent standard errors of the means, n=3.

Figure 3–6. Cumulative mineral nitrogen leached from soil columns amended with suint or KCl at 100 kg K ha^{-1}.

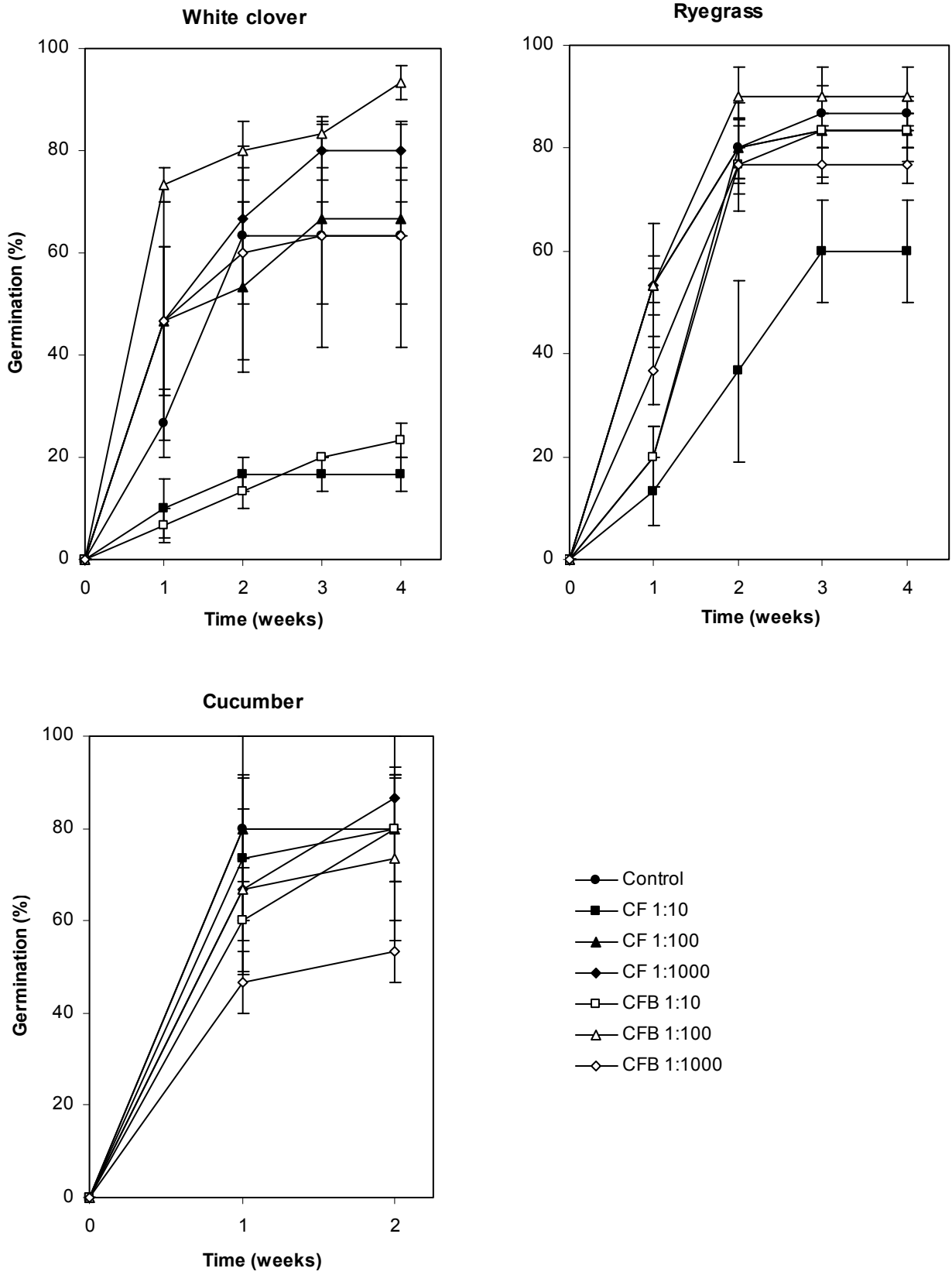


Note: bars represent standard errors of the means, n=3.

3.3.6. PHYTOTOXICITY OF SUINT

When suint was regularly applied to soil, simulating land disposal, germination of cucumber was not affected by the treatments, even at the 1:10 dilution (Figure 3–7). The lower rate of germination with the application of CFB suint at the 1:1,000 dilution appeared to be an anomaly caused by only five seeds being planted per pot. Rates of germination of white clover were not negatively affected by the application of suint, except at the 1:10 dilutions. Ryegrass germination was adversely affected by CF suint at the 1:10 dilution only.

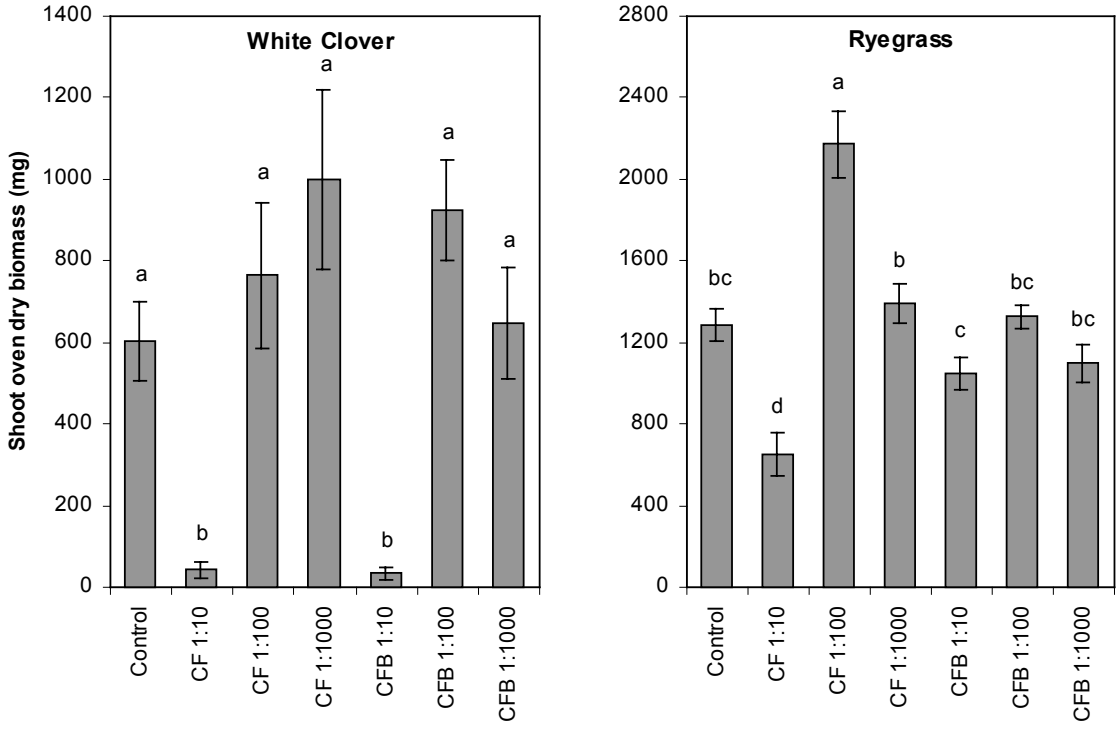
Figure 3–7. Effect of CF and CFB suint on the germination of white clover, ryegrass and cucumber.



Note: bars represent standard errors of the means, n=3.

Total white clover oven-dry shoot biomass produced from pots amended with either suint solution at 1:100 and 1:1,000 dilutions was not statistically different to controls (Figure 3–8). Minimal biomass was produced from plants amended at the 1:10 dilution. A significant enhancement in ryegrass shoot biomass was observed for plants amended with CF suint at the 1:100 dilution, while CF suint diluted 1:10 caused a significant decrease in biomass production. Compared to control plants, root growth of white clover and ryegrass was not affected by 1:100 and 1:1,000 dilutions, with plants utilising the whole soil volume. Plants at the 1:10 dilution exhibited limited root growth. All cucumber plants set flowers, except those in pots amended with CFB suint at the 1:10 dilution, where leaf chlorosis lead to necrosis. Compared to the control plants, those amended with suint showed some leaf yellowing.

Figure 3–8. White clover and ryegrass oven-dry shoot biomass produced from soil amended with suint.



Note: bars represent the standard errors of the means, n=3.
Columns with the same letter for each species were not statistically different at α=0.05.

Aboveground biomass N levels in white clover showed some variation but there was no pattern of increased N content with increased concentration of suint applied (Table 3-7). Ryegrass grown in pots amended with 1:10 dilutions of suint showed elevated levels of biomass N. Potassium levels in biomass were increased by suint additions at all dilutions, except for ryegrass amended with CF suint at the 1:100 dilution.

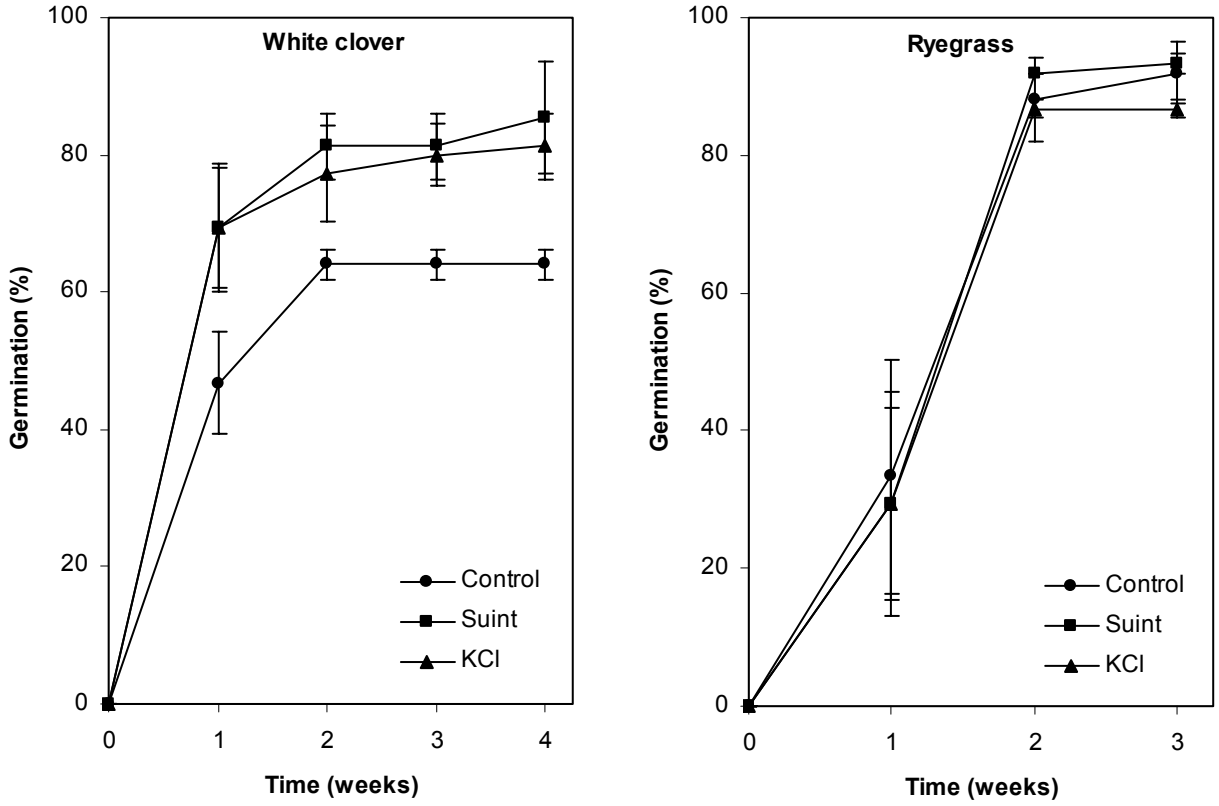
Table 3-7. Effect of CF and CFB suint on aboveground biomass N and K levels in white clover and ryegrass.

	Biomass N (%)		Biomass K (%)	
	White clover	Ryegrass	White clover	Ryegrass
Control	4.5 (0.09)	3.7 (0.02)	3.4	4.3
CF 1:10	4.8	5.2 (0.01)	ND	5.5
CF 1:100	4.6 (0.02)	3.6 (0.21)	5.5	4.4
CF 1:1,000	4.0 (0.02)	3.7 (0.00)	4.6	5.0
CFB 1:10	4.5	4.9 (0.11)	ND	5.4
CFB 1:100	4.3 (0.01)	3.7 (0.06)	5.2	5.7
CFB 1:1,000	4.6 (0.06)	3.8 (0.09)	4.7	5.8

Note: numbers in brackets are the standard errors of the means. No errors are provided for white clover biomass N, nor values for biomass K, at 1:10 dilutions due to the lack of sample. Nutrients are on an oven dry basis. ND = not determined.

When suint or KCl was added to pots at a rate of 100 kg K ha^{-1}, germination of white clover after 4 weeks and ryegrass after 3 weeks was not adversely affected by the suint or KCl treatments at the α=0.05 level (Figure 3–9). Radish germination after one week was between 93 and 100% for all treatments over the three harvests.

Figure 3–9. Germination of white clover and ryegrass in soil amended with suint or KCl at a rate of 100 kg K ha^{-1}.

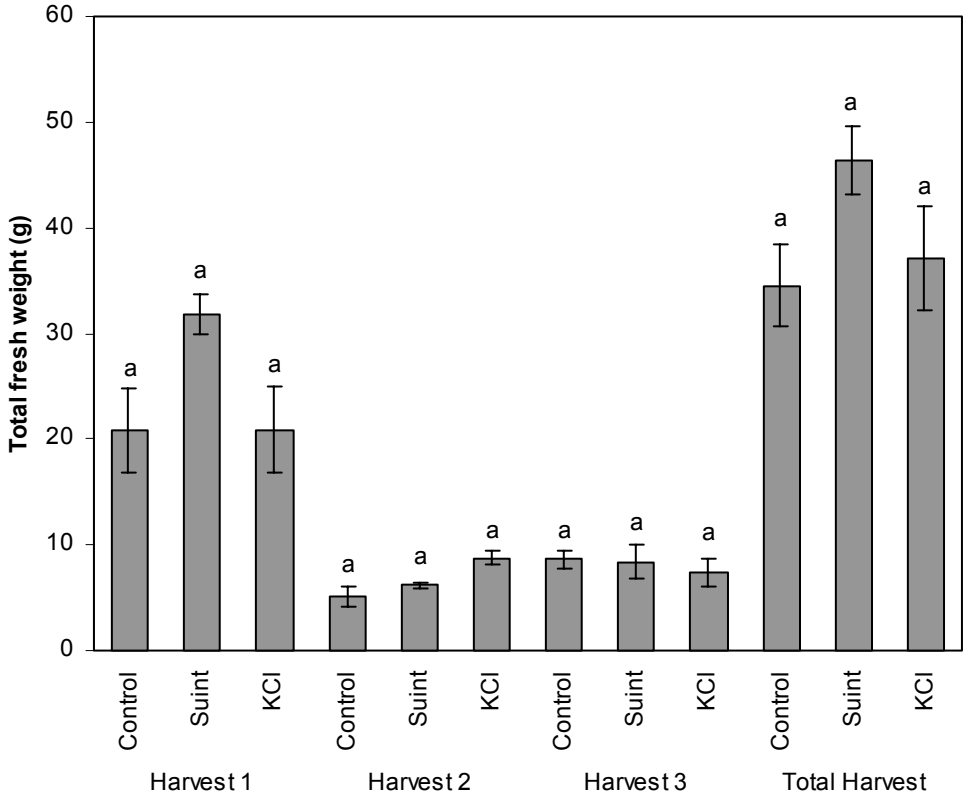


Note: bars represent standard errors of the means, n=3.

Radish fresh weight was not significantly increased ($p>0.05$) by the addition of either suint or KCl to soil for the three harvests, although the first and overall harvest appeared to be increased by suint addition

(Figure 3–10). In this instance, biomass was measured on a fresh weight rather than dry weight basis, since radishes are consumed fresh and thus fresh weight is a measure of quality.

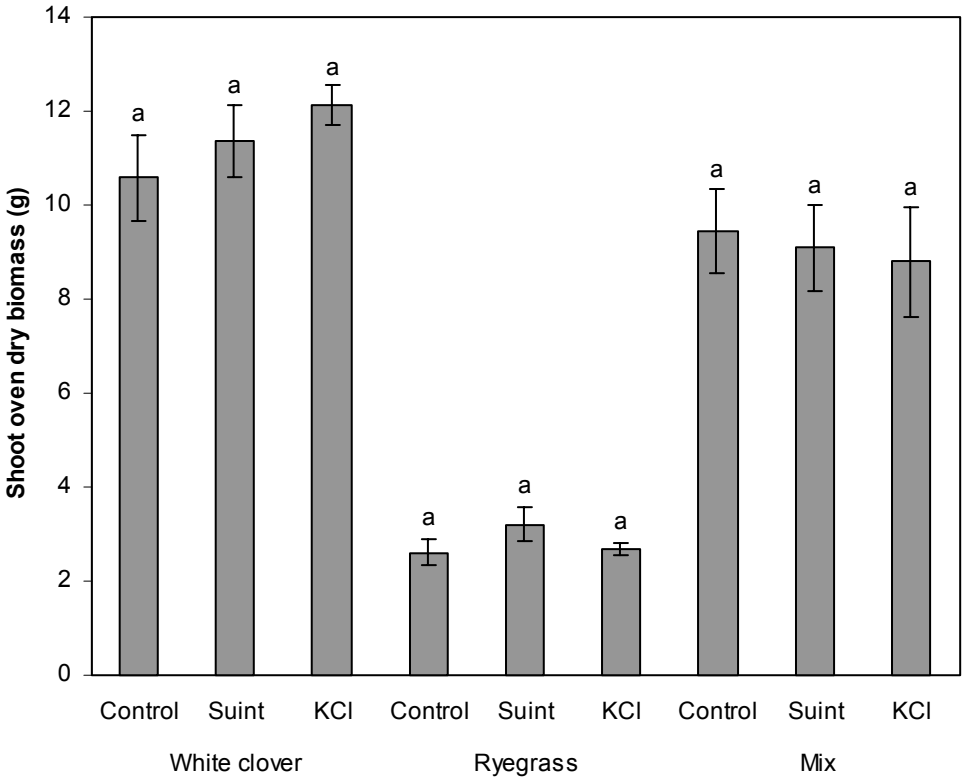
Figure 3–10. Radish fresh weight harvested from soil amended with suint or KCl at a rate of 100 kg K ha^{-1}.



Note: bars represent the standard errors of the means, n=3.
Columns with the same letter for each harvest were not statistically different at α=0.05.

There was no significant effect of treatment ($p>0.05$) on the biomass produced by white clover, ryegrass, or a mixture of the two species, over 27 weeks (Figure 3–11).

Figure 3–11. Shoot oven-dry biomass of white clover, ryegrass, and a mixture of the two species, grown in soil amended with suint or KCl at a rate of 100 kg K ha^{-1}.

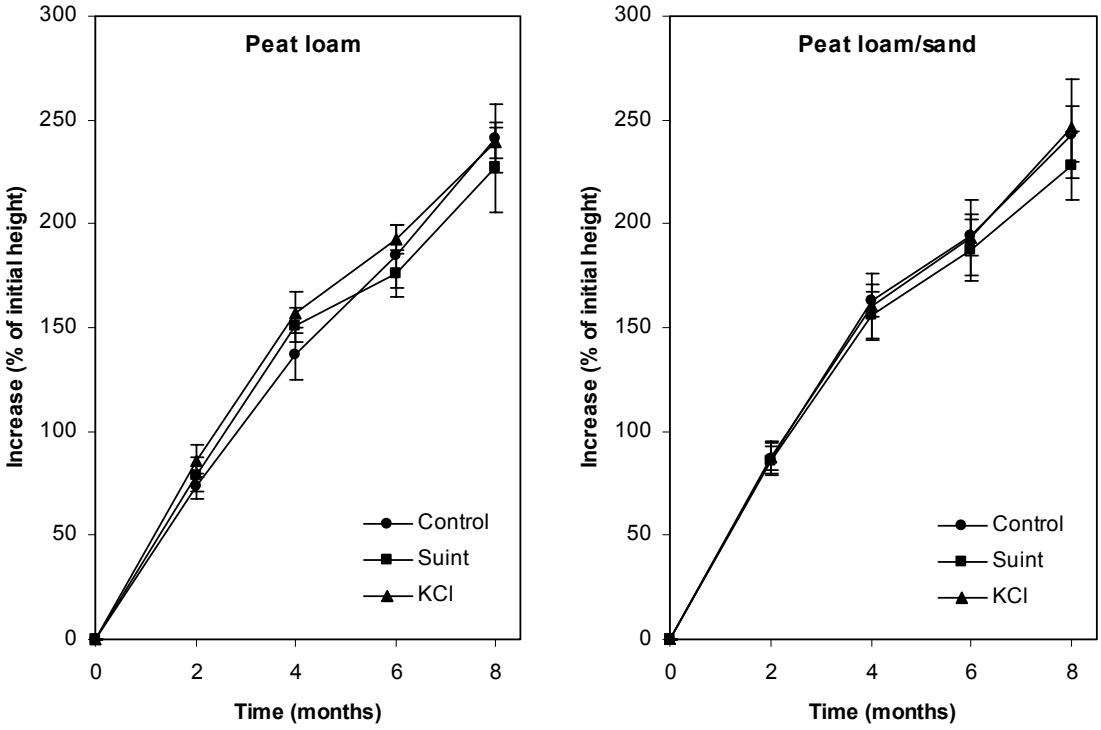


Note: bars represent the standard errors of the means, n=3.
Columns with the same letter for each plant species were not significantly different at α=0.05.

3.3.7. FORESTRY APPLICATIONS OF SUINT

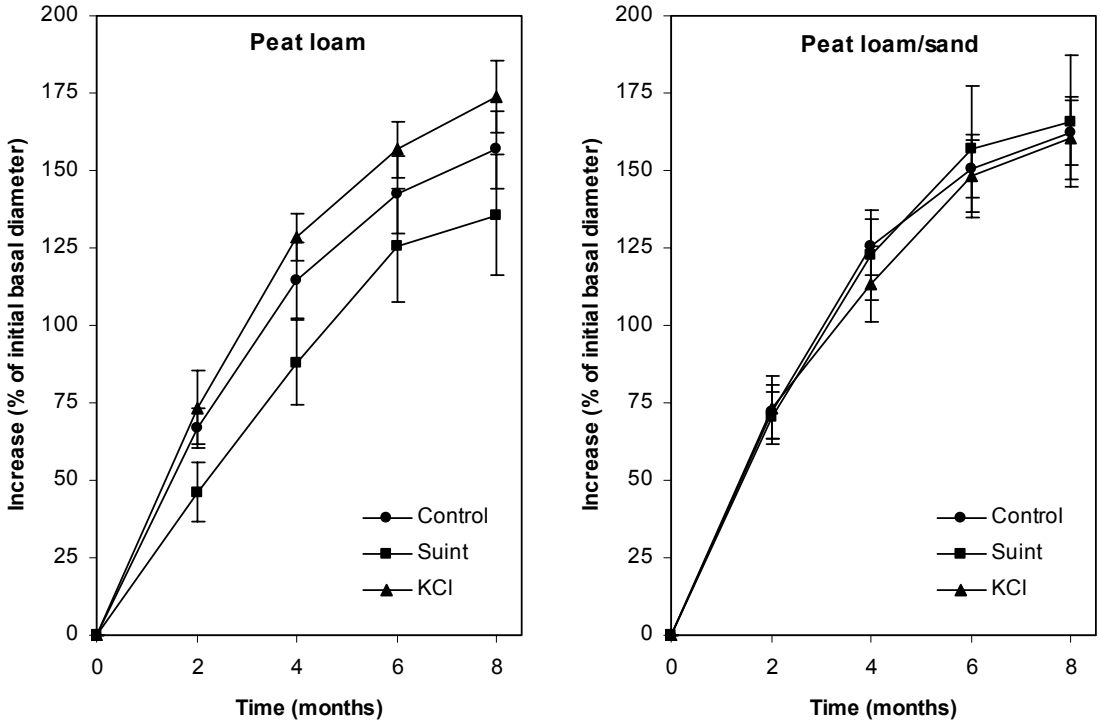
No significant effect ($p>0.05$) of suint or KCl application on the increase in tree height of *Pinus radiata* compared to controls was observed for either the peat loam or peat loam/sand soils (Figure 3–12). In terms of the increase in basal diameter, there was no effect of treatment in the peat loam/sand soil but there was in the peat loam, where suint reduced basal diameter growth compared to the control and KCl-amended trees (Figure 3–13). Very few differences in foliage nutrient levels were observed between treatments (Table 3-8). In the peat loam soil, suint increased the level of aluminium and both suint and KCl increased the levels of iron and zinc. In the peat loam and sand mixture, suint decreased the level of aluminium while KCl increased the level, and suint increased the level of manganese.

Figure 3–12. Increase in seedling height of *Pinus radiata* amended with suint or KCl at 100 kg K ha^{-1}.



Note: bars represent standard errors of the means, n=6.

Figure 3–13. Increase in basal diameter of *Pinus radiata* amended with suint or KCl at 100 kg K ha^{-1}.



Note: bars represent standard errors of the means, n=6.

Table 3-8. Foliage analysis of *Pinus radiata* amended with suint or KCl at 100 kg K ha^{-1}.

Nutrient	Initial	Treatment		
		Control	Suint	KCl
		Peat loam		
Aluminium (ppm)	37	19	27	22
Boron (ppm)	36	23	18	18
Carbon (%)	51.9	51.0	52.1	52.5
Calcium (%)	0.48	0.36	0.37	0.35
Copper (ppm)	4	5	5	5
Iron (ppm)	89	35	46	43
Potassium (%)	1.52	1.19	1.23	1.25
Magnesium (%)	0.08	0.09	0.09	0.09
Manganese (ppm)	24	15	20	15
Nitrogen (%)	2.31	1.19	1.39	1.25
Sodium (%)	0.01	0.01	0.01	0.01
Phosphorus (%)	0.21	0.13	0.15	0.15
Zinc (ppm)	64	42	52	52
		Peat loam/sand		
Aluminium (ppm)	57	113	96	125
Boron (ppm)	41	20	22	23
Carbon (%)	51.7	52.9	51.7	52.3
Calcium (%)	0.46	0.39	0.40	0.37
Copper (ppm)	7	7	9	7
Iron (ppm)	43	47	50	54
Potassium (%)	1.58	1.13	1.13	1.18
Magnesium (%)	0.09	0.10	0.11	0.10
Manganese (ppm)	127	72	80	71
Nitrogen (%)	2.45	1.29	1.30	1.47
Sodium (%)	0.01	0.01	0.01	0.01
Phosphorus (%)	0.19	0.13	0.13	0.14
Zinc (ppm)	66	64	65	62

Note: results are reported on an oven dry basis. Analysis was conducted by New Zealand Forest Research.

3.4. DISCUSSION

3.4.1. CHEMICAL CHARACTERISATION OF SUINT

An average woolscour will discharge 4-5 m^3 h^{-1} high strength effluent and, assuming no significant volume change through the CF and CFB processes, equates to 96-120 m^3 per day of treated effluent (personal communication, Matthew Savage, ANDAR Holdings Ltd.). Evaporation of this treated effluent would reduce this to 2-5% of its original volume, meaning 2-6 m^3 per day of suint concentrate is available for soil application. From another perspective, the scouring of 180,000 t per year greasy wool in New Zealand was calculated to amount to approximately 3,600 t K in the suint concentrate, based on 8% suint on greasy coarse wool and K constituting 25% of the suint. The suitability and sustainability of suint

application to land must be seriously addressed before this method of disposal or fertiliser use is implemented.

The biological treatment of suint (CFB suint) promoted greater compositional consistency and organic matter stabilisation than chemical flocculation alone (CF suint), as observed by a general trend of decreased proportion that the standard errors were of the mean (Table 3-2). For example, the organic matter content of CF suint had a standard error that was 12% of the mean but for the CFB suint samples this decreased to only 2.7%. The moisture content would be more consistent in a full-scale evaporator operating on a continuous basis, where the concentrate would continually be drawn off according to set points. Although the pH of suint from merino wool ranges from 5.5-8.4 and suint from crossbred wools ranges from 6.9-10.0 (Stewart, 1988), the use of sulphuric acid in the Sirolan CF process will negate this pH difference between wool types. The improvement of substrate homogeneity was reported by Parish (1977), who described the positive effect that retaining wastes in holding tanks had in reducing the variation in waste composition for textile and tannery industries. Substrate consistency is critically important if concentrated suint is to be used as a potassium fertiliser. The results presented here strongly support a recommendation that, for fertiliser production, effluent evaporation be carried out after the CFB biological process, as opposed to prior, due to the neutral pH of the CFB suint, its lower grease content, and the N content being composed of more stable forms (Table 3-2; Table 3-3).

The decrease in concentrations of copper and zinc from CF to CFB suint (Table 3-2) suggested that the biomass was being enriched in these metals, providing that initial heavy metal concentrations in the effluent were similar between sampling periods. This cannot be confirmed as the biomass was not analysed; refer to Section 5.2.4 (p.157) for a discussion of heavy metals in the biomass from the Ashburton Woolscour. In addition to potassium, inorganic element analysis indicated high levels of sulphur in both suint types relative to soil (Table 3-4), which is readily explained by the use of sulphuric acid in the Sirolan CF process (Figure 1–8 p.16). Sulphur partitioned into the liquid phase as elevated levels was not found in the sludge (Table 4-3 p.103). The sulphur content of concentrated suint could make it a suitable fertiliser for crops with a high sulphur demand, such as the brassicas (represented by such crops as broccoli, cabbage and cauliflower). The dynamics of suint-sulphur is an area of research that should be investigated in future work.

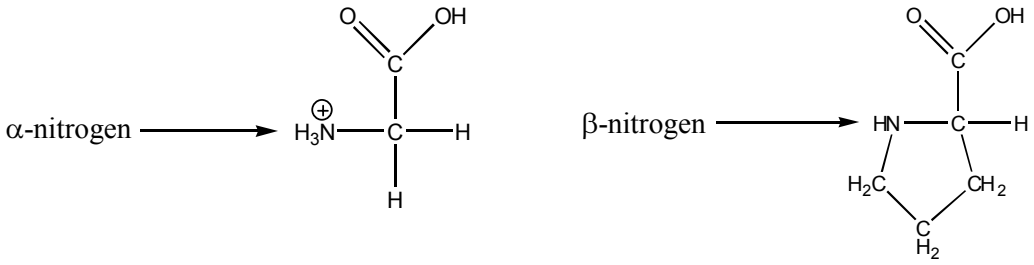
Potassium chloride (KCl) is the most common K fertiliser used in New Zealand, and a comparison of the effects that suint has on soil properties relative to KCl is highly relevant to understanding the impacts that substituting suint for KCl in fertiliser regimes may have. Based on K content, the electrical conductivity of suint dilutions was similar to that for KCl solutions of equivalent concentration (Figure 3–2), suggesting other constituents of suint are unlikely to restrict application to land when applied in a manner

similar to that of KCl. In general, CSIRO reported that suint had a K to Cl ratio of approximately four (Bateup *et al.*, 1996), which is high compared to the less than two found in this study. The CSIRO suint had a K content of about 10% and Cl less than 3%, indicating less chloride in the Australian suint compared to the New Zealand one (Table 3-2). The two principal factors likely to influence the level of chloride in suint are wool type and woolscouring procedure. There are no known differences in suint composition between the fine wools typically scoured in Australia and the coarse wools scoured in New Zealand, pointing to the woolscouring procedure being a strong determinant of chloride in suint. However, an extremely high value of 36% Cl was found for the one CF suint sample produced on a day that slipe wool was processed, while the average for the other four CF suint samples was 11.3%, which suggests that the slipe process contributes to high Cl levels. While sodium chloride is known to be an effective builder (detergent enhancer; (Stewart, 1988)), combined with the data that more sodium relative to K was found in the suint used in this study compared to that in the CSIRO research (Bateup *et al.*, 1996), the suggestion that scouring procedures alone explains the discrepancy between the ratio of K to Cl in New Zealand suint and Australian suint is refuted as the scour from which the suint was produced does not use builders. The ratio of K to Cl in CFB suint (1.6:1) was still better than that of KCl (1.1:1).

In addition to reducing substrate variability, the biological treatment of suint reduced the organic matter content (Table 3-2), explaining the higher K levels in CFB suint compared to CF suint, which were however similar on an ash basis. Organic matter values of the suints used here were lower (ranging from 40 to 50%) than the 59% (dry weight basis) found by Hoare and Stewart (1971) in suint extracted from greasy wool. One of the consequences of biological treatment appeared to be the increase in microbial biomass of the solid fraction of CFB suint, which contained three times the TN that CF suint had. The higher α-amino acid-N in CFB suint compared to CF suint (Table 3-2; Table 3-3) can also be attributed to biological treatment (stabilising substrate N into the microbial biomass), therefore there would be less chance of mineral N being leached following CFB suint application to soil. It is not likely that the protein content (α-amino acid-N) of CFB suint was keratin, since suint represents the principally "soluble" fraction of woolscouring wastes and any intact wool fibres partition preferentially into the sludge fraction, and although there may be some degraded wool fibres in suint, these would be expected to be present in both the CF and CFB suints and therefore do not explain the increase in α-amino acid-N of the CFB suint. The hydrolysable but unidentified N (HUN) fraction is thought to consist of β-amino acid nitrogen, such as in the amino acids proline, hydroxyproline and arginine, and remnants of the hydrolysis procedure (Greenfield, 2001), as shown in Figure 3–14. The TN contents of suint (3.3 and 2.8% on a dry weight basis for CF and CFB suint types, respectively) were slightly lower than the 3.7% reported by Hoare and Stewart (1971) for suint extracted from greasy wool.

The reduction in grease levels in CFB suint compared to CF suint (Table 3-2) could be due to either biological decomposition or partitioning into the biomass phase within the aerated CFB tanks. "Biomass" in this context is defined as the biological flocs settled out of the treated effluent by gravity, which return to the Sirolan CF process while the effluent proceeds to evaporation (Savage, 2002). Biomass analysed from the Ashburton Woolscour showed a grease content of 8.6% on a dry weight basis (Table 5-3). Since the suint samples were collected from the Fairlie Woolscour and the biomass samples from the Ashburton Woolscour, a mass balance cannot be performed. Further confounding understanding the dynamics of the suint-grease, the Fairlie Woolscour processes mainly coarse wools with low grease contents compared to Ashburton where fine wools with higher grease contents are scoured. This suggests that the biomass from the Fairlie Woolscour would presumably have contained less grease than those samples analysed at Ashburton. Therefore, I suggest that at least some part of the grease reduction seen between CF and CFB suint was due to partitioning into the biomass, a physical rather than biological removal process. This distinction is important as the biomass would be returned to Sirolan CF or, alternatively, added to the recipe for the composting of Sirolan CF sludge as water source and inoculum (Section 5.2 p.142), thus "reappearing" in a mass balance sense. Although beyond the scope of this research, future work should conduct a mass balance of trace elements, nutrients and grease through the entire system.

Figure 3–14. Structures of the amino acids glycine and proline illustrating α- and β-amino nitrogen.



Based on CFB suint having a K content of 90 g L^{-1} and the suint being applied at a rate of 100 kg K ha^{-1}, significant quantities of chloride and sodium would also be added to soil (Table 3-9)[1]. Chloride is important for plant nutrition (Adriano and Doner, 1982) and, by not adsorbing to soil minerals, is easily lost by leaching under freely drained conditions (Mengel and Kirkby, 1987). Although most soils contain enough sodium for plant growth, some crops, such as sugar beet, mangolds, and some brassica crops, have a definite sodium requirement (Russell, 1973).

[1] Addition of sodium and chloride would be of concern if suint was applied to soils with an existing salinity problem which, while not a widespread problem in New Zealand, is a real issue in Australia (examiners' comment).

Soils with a high proportion of their exchangeable cations as sodium (the exchangeable sodium percentage) can lose their structure, causing the blockage of pores and a decrease in permeability, in turn leading to waterlogging, poor plant performance, decreased leaching, and salinisation (Russell, 1973; Bond, 1998).

Table 3-9. Theoretical addition of CFB suint components to soil based on a suint application rate of 100 kg K ha^{-1}.

Component	Amount (kg ha^{-1})	Component	Amount (kg ha^{-1})
Total solids	510.9	Calcium (Ca)	4.9
Total N	14.7	Sodium (Na)	43.6
Chloride	61.1	Phosphorus (P)	1.3
Grease	0.9	Sulphur (S)	86.1
Silicon (Si)	14.6	Copper (Cu)	0.007
Titanium (Ti)	0.0	Chromium (Cr)	0.004
Aluminium (Al)	3.9	Nickel (Ni)	0.006
Iron (Fe)	1.3	Zinc (Zn)	0.018
Manganese (Mn)	0.3	Cadmium (Cd)	0.000
Magnesium (Mg)	4.4	Lead (Pb)	0.001

At this application rate, the concentration of sodium and phosphorus in the soil would be increased marginally and the concentration of sulphur in the soil would be increased significantly (Table 3-10). The following calculations were based on (a) a one-off application of CFB suint at a rate of 100 kg K ha^{-1}, (b) a soil density of 1,250 kg m^{-3} in the top 10 cm of the soil profile (within the range published in Borken *et al*. (2002) and Yeates *et al*. (2002)), (c) a soil moisture content of 25% on a wet weight basis, (d) an organic matter content of 10% on a dry weight basis, and (e) the suint application affecting a soil depth of 10 cm. Levels of inorganic elements in a "typical" soil were taken from Williamson (1998). As with the land application of any substance, soils receiving suint should be monitored to ensure their health is maintained. For example, sulphur can contribute to soil acidification in the long term (Russell, 1973).

Table 3-10. Theoretical effect on inorganic element concentrations in soil of CFB suint applied at 100 kg K ha^{-1}.

	Concentration (g kg^{-1} soil dry weight)		
Element	Before application	After application	Change (%)
Silicon	673.6	673.2	-0.05
Titanium	8.3	8.3	-0.05
Aluminium	98.5	98.4	-0.05
Iron	46.3	46.2	-0.05
Manganese	1.6	1.6	-0.04
Magnesium	9.8	9.8	-0.01
Calcium	18.3	18.3	-0.03
Sodium	13.7	13.7	0.29
Phosphorus	0.9	0.9	0.10
Sulphur	0.8	0.9	11.28
Potassium	28.4	28.4	0.32

Note: the inorganic element concentration in soil after application takes into account the weight of solids added with suint.

Ideas for further research offered by Elice-Invaso *et al*. (1997) included reducing the salt content of the suint without affecting the K content, determining how to apply the product and at what dilutions, increasing its potential marketability by the addition of other fertilisers, and comparing the cost of production to that for other K fertilisers. The overall composition of CFB suint relative to its application to soil for K fertilisation is discussed in Section 3.4.4.

3.4.2. THE DECOMPOSITION OF SUINT

Decomposition is the change in state of a substrate due to biological (biotic) and non-biological (abiotic) factors, including: (i) leaching, the removal of soluble matter by water; (ii) catabolism, the transformation of complex organic compounds to simpler molecules by a chain of energy-yielding enzyme-mediated reactions; and (iii) comminution, a reduction in the particle size of organic compounds by physical means (Swift *et al.*, 1979). All three processes occur simultaneously on a substrate. Although microcosm studies are highly artificial, due to the exclusion of many biotic and abiotic factors, they do allow the "resource quality" of substrates to be ascertained. The basis of the term "resource quality" is: different substrates, in terms of their chemical and physical properties, decompose at different rates, even under conditions where all other factors are controlled (Swift *et al.*, 1979).

If suint is to be sustainably applied as a nutrient source to soil, soil microorganisms must readily decompose it. N mineralisation refers to the degradation of organic N, such as proteins, amino sugars, and nucleic acids, to mineral forms such as NH_4^+ and NO_3^- (Paul and Clark, 1996). In the concentrated form, CF suint showed variability in microbial utilisation (Table 3-5), with implications of varying effects on arable land following application. The fate of the N supplied by the suint could therefore not be predicted accurately. Some suint applications may result in the supply of N to the soil system by net-N mineralisation, while other applications may remove soil N, thereby limiting plant growth, as microorganisms immobilise N. Concentrated CFB suint samples mineralised N over the incubation period, although rates were very low and somewhat variable. However, mixing daily inputs in the CFB tanks increased the predictability of the behaviour of suint when applied to soil. The highly hygroscopic nature of suint (Aitken *et al.*, 1994) causing a lack of free moisture may explain its low biodegradability in the concentrated form. However, when suint was diluted 1:10 with distilled water, extensive microbial growth was observed in the solutions, confirming the statement of Truter (1956) that suint is a good medium for the culture of microbes and suggesting that poor growth in the concentrate was due to the high levels of salts in the suint.

Under both aerobic and anaerobic conditions, CFB suint mineralised more N than CF suint when both were applied to soil after being diluted 1:10 with distilled water (Figure 3–3), suggesting that CFB suint is more suitable for soil application. This suggests that the non-mineral N fraction of CFB suint is more available to soil microbes than that of CF suint, since the initial amount of mineral N is subtracted from the final amount during the calculations. High rates of decomposition for CFB suint were observed under both aerobic and anaerobic conditions, both of which could be expected in a heterogeneous soil environment. The effect of incubation temperature on the rate of net-N mineralisation suggests that suint should be applied to land in summer rather than winter months when the soil temperature is higher. A counter to this could be low soil moisture contents during summer months that potentially limit microbial activity in the soil.

3.4.3. THE EFFECT OF SUINT APPLICATION TO SOIL

Applications of suint to soil must not cause detrimental effects on the system. That is, suint must not: (i) disrupt nutrient cycling processes; (ii) increase the rate of nutrient loss due to leaching; or (iii) change soil chemical parameters, such as pH and electrical conductivity.

It appears that suint was neutral or positive towards the rate of decomposition of some organic substrates. Firstly, the co-incubation of either casein or chitin with either suint type, when each substrate contributed an equal amount of TN, caused no change to the rate of net-N mineralisation (Table 3-6). This result can be interpreted as suint having a neutral effect of nutrient cycling and suggests that suint (once diluted) is suitable for land application. Casein and chitin are excellent substrates for microbial growth and can be used as model substrates of different quality against which the impacts of suint on nutrient cycling can be tested. Casein and chitin mineralised 81% and 19% i-TN, respectively, over a 30-day incubation period, which is a sufficient amount for inhibition or synergistic interactions to be quantified. Secondly, a strong beneficial effect was seen when adding either suint type to woolscour sludge, and directly implies that the addition of suint to woolscour sludge during composting will enhance the rate of decomposition (this is discussed in more detail in Section 5.2 p.142). The large positive effect that suint addition had on the rate of mineral N production from woolscour sludge during co-incubation experiments (Table 3-6) suggests that the woolscour sludge was deficient in available nutrients, such as C, N or P, and that suint provided these, with the overall effect of a more balanced substrate for microbial metabolism. The sludge contained 0.3 mg g^{-1} mineral N on a dry weight basis (1.6% of the TN), a typical value for the sludge samples analysed in this thesis. Refer to results in Section 4.3.5 (p.111) on the decomposition of woolscour sludge with the addition of nutrients.

The second and third aspects that must be addressed for suint application to land is the impact that it has on the leachability of soil minerals and soil chemical properties. The application of CFB suint to soil columns did not alter the chemical properties of the soil or increase the rate of leaching of mineral N from the system. Electrical conductivity is a useful estimate of the total salt concentration (Rhoades, 1982b). The electrical conductivity of soil leachates from columns either unamended or amended with CFB suint or KCl at a rate of 100 kg K ha^{-1} decreased with each leaching event (Figure 3–4). The addition of K did not promote the removal of salts from the soil columns, although in the soil/sand columns the electrical conductivity of leachates from amended columns did not decrease as fast as that from control columns initially. Likewise, the relatively neutral pH of CFB suint (6.2), being in the optimum range for pasture soils in the South Island of New Zealand (Appendix Section 8.4 p.197), meant that no disruption to soil pH occurred following CFB suint application (Figure 3–5). Soil pH is an important property in that it affects the solubility of various compounds (including the availability of essential plant elements), the bonding of ions to exchange sites, and the activity of various components of the soil microfauna (McLean, 1982).

The nitrate-N retention capacity of soils in New Zealand is generally low and nitrate is therefore prone to loss by leaching (Cameron *et al.*, 2002). After 24 weeks and eight leaching events, more mineral N was leached from unplanted soil/sand columns than from soil columns (Figure 3–6). For this soil type, the application of suint (which contains mineral N) increased the leaching losses of mineral N in terms of the total amount lost over 24 weeks. The rate of nutrient transport through the soil profile and loss by leaching is dependent on the soil type, the quantity of nutrients present in the soil in soluble forms, and the binding affinity of the nutrients for soil particles (Mengel and Kirkby, 1987). In the soil columns, suint application had no such effect on the amount of mineral N leached. Columns planted with ryegrass showed reduced rates of mineral N leaching compared to unplanted columns. The presence of plants, through their nutrient demands and depending on their planting intensity, reduces the loss of nutrients by leaching (Mengel and Kirkby, 1987). As stated previously, the addition of CFB suint to soil at a rate of 100 kg K ha^{-1} also theoretically adds 15 kg TN ha^{-1} (Table 3-9), of which 18 or 40% could be mineralised over 60 days at 10 or 22ºC, respectively (Figure 3–3), and all of which is potentially mineralisable. In practise, CFB suint would be applied to planted soil as a K fertiliser rather than to unplanted soil, thereby significantly reducing the risk of contamination of groundwater by nitrate, which potentially impacts on human health if the groundwater is then used as a water supply, and nitrate enrichment of groundwater can upset ecological balances if the groundwater discharges to a surface body of water (Bond, 1998).

3.4.4. PHYTOTOXICITY OF SUINT AND ITS USE AS A FERTILISER

The phytotoxicity of suint and its potential use as a fertiliser was evaluated by three experiments involving a range of plant species.

The first of these experiments simulated the regular disposal of suint to soil and showed that, for white clover and ryegrass but not for cucumber, germination was not affected when the suint was diluted 1:100 or 1:1,000 with distilled water (Figure 3–7). At these dilutions, shoot growth of white clover and ryegrass was the same or higher than that of the controls (Figure 3–8). Increased uptake of N in ryegrass plants grown in soil amended with 1:10 suint dilutions, and a general increase in K uptake for both plant species at all suint dilutions, was observed (Table 3-7). The adequate range of N in the shoots of ryegrass is 3.0-4.2% dry weight and for K is 2.5-3.5% dry weight (Marschner, 1986), while McLaren and Cameron (1990) reported an optimum K concentration of 2.0-2.5 and 2.0-2.4% on a dry matter basis for ryegrass and clover, respectively. This experiment evaluated the unsustainable application of suint to soil, as CF suint diluted 1:10 was supplying 49 kg N and 209 kg K ha^{-1} per week, while CFB suint was supplying 43 kg N and 292 kg K ha^{-1} per week. The Ilam soil used in this experiment was also not deficient in exchangeable K (see Appendix Section 8.4 p.197). It should be noted that this experiment did not separate the effects of K addition from the solution and that of other properties of the suint; rather, it evaluated suint solutions as a whole.

The second experiment investigated the measured application of CFB suint to soil and compared this to KCl, allowing the effects of the K content of suint to be separated from that of other components found in suint (Table 3-9). No deleterious effects of suint application to soil were observed. Using a different soil type to that used in the above experiment (Laings soil, refer to Section 8.4 p.197 for properties), germination of white clover, ryegrass and radish was not affected by suint added at a rate of 100 kg K ha^{-1} (Figure 3–9). No benefit or detriment to shoot or radish growth was observed (Figure 3–10; Figure 3–11) and, from visual inspection, no differences in whole plant vigour across treatments were observed. This soil was not deficient in exchangeable K, suggesting that enough K was supplied to allow good plant growth. Therefore, components in suint in addition to K do not affect plant performance and the use of suint as a source of K for plant growth.

The potential for suint applications in forestry was evaluated in a third experiment involving *Pinus radiata* seedlings. With the exception of a slightly decreased rate of basal diameter growth in the case of seedlings grown in peat loam soil (Figure 3–13), suint had no detrimental effect on *Pinus radiata* (Figure 3–12). Combining the above results together, it is a reasonable conclusion that forestry land could be sustainably used for the application of suint. Satisfactory nutrient levels (% dry weight basis) for *Pinus*

radiata are: nitrogen, >1.5; phosphorus, >0.14; magnesium, >0.1; potassium, >0.5; calcium, >0.1; boron, >12 ppm; zinc, 10 ppm; manganese, >6 ppm; and copper, >2 ppm (Will, 1985; Hunter *et al.*, 1991). On this basis, all trees, irrespective of soil type and treatment, were marginal for magnesium and phosphorus, and deficient/restricted for nitrogen (Table 3-8). Therefore, the application of potassium in either suint or KCl did not interfere with the uptake of other nutrients by the seedlings. Forestry land suffering from K deficiencies include podzolised sands in Northland, mineral belt soils near Nelson, and pakihi soils on the West Coast of the South Island, although for the mineral and pakihi soils it is not an absolute deficiency in K but rather very high levels of magnesium preventing adequate uptake of K (Will, 1985). There is increasing interest in applying municipal and industrial residuals, such as biosolids and pulp and paper sludges, to forestry land in New Zealand (Magesan and Wang, 2003).

Results from a 1995 trial conducted by CSIRO and the Victorian Department of Agriculture State Chemical Laboratory showed a pasture crop yield increase of 7 and 26% at two sites following suint application compared to control plots (Bateup *et al.*, 1996). Although Bateup *et al*. reported this research without many important details, such as suint application rate and soil type, and is without peer review, it provides empirical evidence in support of the conclusion in my study that suint can be safely be applied to soil as a K source.

Different results may have been obtained if different plant species or soils were used. Suint should be targeted to crops that have a high demand for K (Table 3-11) or to soils that are known to be deficient in K (Table 3-12). In New Zealand, yellow-brown earths, podzols, and soils from volcanic parent materials have low K reserves (McLaren and Cameron, 1990). If scours are not located in areas where soil K deficiencies feature, the costs associated with transporting the concentrate to such areas may initially seem prohibitive. However, the results I have presented here strongly suggest that suint application to commercially managed soil systems is a viable strategy towards sustainable industry and agriculture. This indicates that addressing transportation difficulties and advancing concentration technology are high priorities.

Sulphur is found in suint at levels approaching that of K. While most of the S found in suint will be a result of the chemical flocculation process, S is also contained in the amino acids cysteine and methionine, in glycosides, several coenzymes and prosthetic groups, in sulfolipids, in oils produced by certain plants, and is involved in the formation of vitamins and some hormones and in reduction-oxidation reactions (Russell, 1973; Bennett, 1993). Plants growing on a well-drained soil source S from sulphate in the soil solution and sulphate absorbed on soil colloids, which is derived from the oxidation of S contained in soil humus (Russell, 1973). A number of soil bacteria reduce sulphates to sulphides whenever anaerobic conditions develop. Most soils retain S poorly and losses can occur via leaching

(During, 1984). Crops have a similar S requirement to their P requirement, between 10-30 kg ha^{-1}, while brassica crops have a high S demand of 40-45 kg ha^{-1} (Russell, 1973). Sulphur deficiency is most widely found on both grain and forage legume crops, and is normally only found in areas at a distance from industrial areas or the sea and only on old deeply weathered land surfaces where soils have been strongly leached over a long period of time. Although sulphur-containing fertilisers have no enduring effect as soil has no mechanism for holding quantities of inorganic S (Russell, 1973), the fate of suint-derived S is an area for further research to better address the sustainability of suint application to soil.

Table 3-11. Removal of potassium by various crops grown in New Zealand.

Crop	Yield	kg K ha^{-1}	Reference(s)
Barley (grain)	2.2 t ha^{-1}	10	McLaren and Cameron (1990), Mengel and Kirkby (1987)
Barley (straw)	2.5 t ha^{-1}	30	McLaren and Cameron (1990), Mengel and Kirkby (1987)
Wheat (grain)	2.7 t ha^{-1}	14	McLaren and Cameron (1990), Mengel and Kirkby (1987)
Wheat (straw)	3.8 t ha^{-1}	33	McLaren and Cameron (1990), Mengel and Kirkby (1987)
Oats (grain)	2.9 t ha^{-1}	14	Mengel and Kirkby (1987)
Oats (straw)	5.0 t ha^{-1}	75	Mengel and Kirkby (1987)
Maize (grain)	9.5 t ha^{-1}	37-41	McLaren and Cameron (1990), Mengel and Kirkby (1987)
Maize (straw)	11.0 t ha^{-1}	110-135	McLaren and Cameron (1990), During (1984), Mengel and Kirkby (1987)
Lucerne	10.0 t ha^{-1}	170-208	McLaren and Cameron (1990), During (1984), Mengel and Kirkby (1987)
Potatoes (tubers)	27.0 t ha^{-1}	140	Mengel and Kirkby (1987)
Tomatoes (fruit)	50.0 t ha^{-1}	150	Mengel and Kirkby (1987)
Cabbage	50.0 t ha^{-1}	120	Mengel and Kirkby (1987)
Stone fruit	Medium	65-96	Mengel and Kirkby (1987), Johnson (1993)
Grapes	Medium (13 t ha^{-1})	85-110	Mengel and Kirkby (1987), Gaertel (1993)
Oranges	Medium	120	Mengel and Kirkby (1987)
Lemons	Medium	115	Mengel and Kirkby (1987)
Corn (grain)	10.0 t ha^{-1}	17	Voss (1993)
Corn (stover)	10.0 t ha^{-1}	42	Voss (1993)
Peanuts	3.4 t ha^{-1}	25	Smith *et al*. (1993)
Onions	35.0 t ha^{-1}	63	Bender (1993)
Apple varieties (fruit)	Not stated	34-120	Hanson (1993)
Pears (fruit)	Not stated	19	Hanson (1993)
Grass-clover pasture	12-14 t ha^{-1} dry wt	300-450	During (1984), McLaren and Cameron (1990)

Table 3-12. Soil groups deficient in potassium in New Zealand.

Soil group	Typical series	Potassium status
Yellow-brown earths (lowland)	Rosedale, Rai, Ohaura, Kaiwera, Waikiwi, Tuturau	Low
Steepland yellow-brown earths	Hurunui	Low
Gley podzols	Okarito, Addison	Deficient
Recent soils	Hokitika, Tasman	Deficient
Yellow-grey earths (Central)	Matapiro, Crownthorpe, Marton, Tokomaru, Halcombe	Adequate-low
Yellow-grey earth/yellow-brown earth intergrades	Wanstead, Atua, Mangaweka, Tinui, Kumeroa, Takapau, Taihape	Adequate-low
Yellow-brown earths	Makotuku, Whetukura, Ngaumu, Te Whatou, Judgeford, Belmont, Taita	Low-deficient
Yellow-brown earth steepland	Mahoenui, Pahiatua, Moumahaki, Tuparua	Adequate-low
Yellow-brown pumice soils	Taupo, Oruanui, Galatea, Tihoi	Deficient
Yellow-brown loams	Egmont, Stratford, Ohaupo, Otorahanga, Te Kuiti, Horotiu, Tirau, Mairoa	Deficient
Yellow-brown sands	Pukepuke, Himatangi	Deficient

Note: adequate = no or small response to fertiliser likely, low = moderate response to fertiliser likely, deficient = large response to fertiliser likely. From McLaren and Cameron (1990).

3.4.5. INDUSTRY PARALLELS

Another industry that generates a by-product with a high K content is the sugarcane industry and, for reference purposes, some discussion is provided here. Sugarcane is grown in tropical and sub-tropical areas of the world, producing sugar that is separated from non-sugar compounds in a series of processes while keeping sucrose destruction to a minimum (Clarke, 1988). There are two stages to traditional processing, the first being the extraction of juice from sugarcane and its conversion to raw sugar, and the second being the refining of the raw sugar to final products. The first stage begins with the extraction of juice, which produces bagasse fibre as a waste product, and results in raw sugar and the by-product molasses. Raw sugar is converted to highly purified products at refineries by further separation of non-sugars from sucrose.

The major inorganic salt in cane juice, syrup and molasses is KCl (Clarke, 1988). Potassium also occurs in sugarbeets at levels three to 20 times higher than sodium (Na), unless the beets were cultivated in very saline soils (Cleary, 1988). Both cations are readily extracted with the sucrose and total 2,500-3,500 ppm in the raw juice. The mineral content of sugarcane tends to increase with plant age or at least remain constant, although K is most abundant in the younger plant parts and decreases in that from the older parts of the stalk (Legendre, 1988).

Bagasse is burnt by the cane factory to provide energy in excess of its requirements (Clarke, 1988). Bagasse ash, which averages 0.3% of the weight of cane processed, is usually spread in the fields as a

fertiliser, with some good results reported due to its K and P content, K_2O being up to 13.4% of the weight of the ash (Paturau, 1989).

Molasses is the final effluent obtained in the preparation of sugar by repeated crystallisation, being the residual syrup from which no crystalline sucrose can be easily obtained (Paturau, 1989). Molasses yield per tonne of cane is approximately 2.7% and its composition can vary widely, with the ash content averaging 12% (fresh weight basis) and K_2O comprising 30-50% of the ash weight. For Australian molasses, inorganic salts are typically in the range of 12-16% by weight, with K comprising 35% of this. In 1988, approximately 37 million tonnes of beet and cane molasses were produced annually worldwide, 70% of which was used in the animal feed industry and much of the remainder used as a fermentation substrate to produce a range of products, including ethanol, of higher value than molasses (Johnson and Lefebvre, 1988). Removal of K and other inorganic ions from molasses will enhance fermentation product yield.

The application of molasses as a fertiliser to cane soils began about 1850 and was common practice at the end of that century when inorganic fertilisers were not available at suitable prices and quantities and there was a lack of manure due to the replacement of animals by machinery (Paturau, 1989). This practice decreased when inorganic fertiliser use became widespread, although the organic matter content of molasses was thought to be beneficial. Excluding its organic matter content, the value of molasses is based on its inorganic nutrients, principally K and N salts. The application of molasses to the fields two weeks before planting was generally at a rate of 10-20 t ha^{-1}, equivalent to 500-1,000 kg K_2O ha^{-1}, although due to leaching concerns, the recommendation in Hawaii was a maximum of 250 kg potash ha^{-1} at any one time. For every one tonne of molasses used as a fertiliser in Mauritius, an average of 51.3 kg K_2O was supplied. The view in 1989 was that molasses used as a fertiliser was not economic, especially for countries that could get a good export price for it.

Since molasses still contains a high level of sugar, methods to extract sugar from the molasses and increase the yield of the process have been investigated (Ramm-Schmidt, 1988). The two main methods are ion exchange, where the aim is to increase the crystallisation yield of the main processes by removal of Na^+ and K^+, and by desugaring of the molasses. Beet molasses contains 66.5% sugars, 10.5% inorganic compounds and 6% K_2O on a dry weight basis, and after processing residual molasses contains 24% inorganic compounds and 14% K_2O (when the sugar content is 21.5%) or 28% inorganic compounds and 16.1% K_2O (when the sugar content is 10%). Residual molasses is used for animal feed (in a mixture of different molasses), mixed with beet pulp, brewer's grain and husks and used as fodder for domestic animals, or as a fertiliser. If the salt content is too high for use as feed, it is possible to crystallise out part of the potassium salts as KCl or K_2SO_4 from the residual molasses. Residual molasses can be used as a

fertiliser and returned to the fields by irrigation since it contains all the minerals and humic matter the plant had taken from the soil in the same proportions. Experiments conducted in Finland, which has the shortest growing season of all countries, have shown that the fertilisation of beet fields increased the beet yield per hectare over general fertilisation. At the Naantali desugaring plant, one of the separations made is the removal of KCl and K_2SO_4 from residual molasses in a forced circulation evaporator.

In Brazil, typical sugarcane mills process approximately 50% of the extracted juice directly to ethanol for fuel purposes (Rossell, 1988). Stillage, also known as dunder, vinasse or slop, is a by-product of the fermentation process and is rich in K (31% on an ash basis) (Gascho *et al.*, 1993). The efficient treatment of stillage from a distillery is a serious problem for any large capacity ethanol producing plant (Paturau, 1989). When ethanol is produced from cane juice, the volume of stillage (8% w/w solids) generated is 8-10 times that of the ethanol and for molasses 13 times that of ethanol. Dried slops contain about 29% mineral matter. Three treatment options are: (1) aerobic treatment, which has a prohibitively high energy cost; (2) anaerobic treatment, which is used successfully although requires a finishing treatment; and (3) evaporation usually followed by incineration. Anaerobic digestion produces methane and fertiliser sludge and this has proved economically feasible on small isolated establishments where the utilisation of methane can be competitive. The evaporation/incineration option is the more efficient process but the capital costs are twice that of anaerobic treatment. However, the surplus steam and potash generated means that the net operation cost is about five times less than the anaerobic option. For example, a 60,000 L per day distillery produces 31.2 t h^{-1} stillage at 8% solids. Concentration of stillage to 60% solids and subsequent combustion generates 0.8 t h^{-1} ash containing 0.33 t h^{-1} K_2O. The condensate can be returned to the distillery for molasses dilution or treated in an aeration pond before discharge. Instead of incineration, the concentrate can be used as a animal feed, when mixed with bagasse and/or cane tops, and directly as a fertiliser on soils with good permeability and humus layer. Important progress has been made in the treatment of stillage through the recycling as a molasses dilutant, which reduces the volume and moisture content such that a smaller evaporator would be required. The stillage produced by the "Biostil" system has a higher solids content such that evaporation is not required, although the incineration will be less efficient.

4. THE CHARACTERISATION AND DECOMPOSITION OF WOOLSCOUR WASTES

4.1. INTRODUCTION

In this section, the primary objectives were to assess the composition of the solid woolscour waste streams, in order to determine their suitability for composting, and assess their rate of decomposition and the effect that each of their individual components had on this rate. Specifically, the hypotheses in Table 4-1 were tested. This section preceded composting trials, which represented applied research, described later in Section 5.

Table 4-1. Hypotheses tested during woolscour waste research.

Hypothesis		Experimental
H4-1 Woolscour wastes will be consistent in their composition	(a)	Analysis of samples for moisture, pH, organic matter, grease, heavy metals, phosphorus, total nitrogen and nitrogen distribution profile (sludge only), pesticides, seeds (opener and scoured wool cleaner wastes only)
H4-2 Woolscour wastes will be consistent in their rate of decomposition	(a)	Decomposition of samples collected on a daily timescale as assessed by net-N mineralisation (in a sand matrix with aerobic incubation at 37ºC for 30 days)
	(b)	Decomposition of samples collected on a weekly timescale as assessed by net-N mineralisation (in a sand matrix with aerobic incubation at 37ºC for 30 days)
H4-3 Woolscour wastes will readily decompose at temperatures expected in a composting process	(a)	Decomposition of samples as assessed by net-N mineralisation (in a sand matrix with aerobic incubation at 43, 50 and 60ºC for 8 days)
	(b)	Decomposition of opener and scoured wool cleaner waste samples as assessed by weight loss (in a centrifuge tube with aerobic incubation at 43, 50 and 60ºC for 8 days)
	(c)	Decomposition of mixtures of woolscour wastes as assessed by net-N mineralisation and weight loss (at 43, 50 and 60ºC for 8 days)
H4-4 The grease content of woolscour sludge will not inhibit the rate of decomposition	(a)	Comparison of the rate of decomposition of intact sludge to the dirt fraction as assessed by net-N mineralisation (in a sand matrix with aerobic incubation at 43, 50 and 60ºC for 8 days)

H4-5 The rate of decomposition of woolscour wastes will respond to inoculation or nutrient addition	(a)	Effect of inocula (soil or keratin-degraders) on the decomposition of keratin as assessed by net-N mineralisation (in a sand matrix with aerobic incubation at 37ºC for 60 days)
	(b)	Effect of inocula (soil, grease degraders, or keratin degraders) on the decomposition of sludge as assessed by net-N mineralisation (in a sand matrix with aerobic incubation at 37ºC for 60 days)
	(c)	Effect of added C, N or P on the decomposition of sludge as assessed by net-N mineralisation (in a sand matrix with aerobic incubation at 37ºC for 60 days)
H4-6 Polyacrylamide will readily decompose and not inhibit the decomposition of organic compounds	(a)	Decomposition of polyacrylamide as assessed by net-N mineralisation (in a sand matrix with aerobic incubation at 20, 37 and 50ºC for 60 days)
	(b)	Net-N mineralisation when polyacrylamide was co-incubated with chitin, casein and woolscour sludge (in a sand matrix with aerobic incubation at 37ºC for 20 days)
H4-7 Diazinon and cypermethrin will not inhibit the decomposition of casein	(a)	Effect of diazinon, cypermethrin, or both, at concentrations of 10, 100 and 1,000 ppm, on the decomposition of casein as assessed by net-N mineralisation (in a sand matrix with aerobic incubation at 37ºC for 30 days)
H4-8 Woolscour sludge is toxic to plants	(a)	Effect of sludge on the germination and growth of white clover, perennial ryegrass and radish compared to potting mix (glasshouse experiment)
H4-9 Woolscour sludge contains an active and consistent microbial population as produced by Sirolan CF	(a)	Plate counts for mesophilic (30ºC incubation) and thermophilic (50ºC incubation) bacteria and fungi from daily sludge samples
	(b)	Microbial activity in daily sludge samples assessed by substrate-induced respiration

4.2. MATERIALS AND METHODS

4.2.1. CHEMICAL CHARACTERISATION OF WOOLSCOUR WASTES

The variability in composition of Sirolan CF sludge, opener waste and scoured wool cleaner waste produced by two Canterbury woolscours was assessed. Samples collected in 2000-2001 were from the Fairlie Woolscour in Timaru, where the trial Sirolan CF module was sited, and those in 2002-2003 were from the Ashburton Woolscour.

Samples analysed for their chemical properties were those collected for composition variability as well as for use in other experiments. Samples were collected as described in Section 2.2, transported to the University in a refrigerated container for immediate analysis, and were tested for moisture content (Section 2.3.1), pH (Section 2.3.2), organic matter content (Section 2.3.3), grease content (Section 2.3.5), heavy metals (Section 2.3.7), phosphorus (Section 2.3.8), and total N (Section 2.4.1). Grease extracted

from samples was analysed for the presence of the organophosphate pesticide residues diazinon and propetamphos, as described in Section 2.3.6. Composite samples composed of equal amounts (dry weight basis) of five daily samples from both woolscours were analysed for inorganic elements (Section 2.3.4). The TN (Section 2.4.1) content of each fraction (the grease fraction and the dirt or fibre fraction produced from the Soxhlet extraction procedure) was determined for a set of five samples of each waste stream collected from the Fairlie Woolscour. The N distribution profiles following acid hydrolysis of a set of five Sirolan CF sludge samples collected from the Fairlie Woolscour were also determined, according to Section 2.4.5.

The number of seeds and seed fragments in five opener and scoured wool cleaner waste samples from the Fairlie Woolscour, and in five opener waste samples from the Ashburton Woolscour, were counted. The viability of the seeds extracted from the Ashburton opener waste samples was assessed by placing 15 seeds, selected at random from the total number, onto a filter paper moistened with distilled water in a Petri dish. Germination was examined over two weeks and compared to triplicate controls, consisting of radish seeds established in the same manner.

4.2.2. Variation in the Biodegradability of Woolscour Wastes

Variation in the biodegradability of woolscour wastes was evaluated on daily and weekly time scales. Decomposition was measured by net-N mineralisation, since weight loss is inappropriate for sludge samples because of interference with drying from the grease content, and there can be difficulties with carbon mineralisation due to partitioning between respired C and biomass C (Williamson, 1998).

To assess daily variation, samples of all three waste streams were collected on five consecutive days in August 2000. To assess weekly variation, samples of all three waste streams were collected on five consecutive Wednesdays during August and September 2000. Decomposition was assessed by net-N mineralisation (Section 2.5.2), with five replicates per sample. Microcosms were incubated under aerobic conditions at 37°C (being a compromise between ambient and composting temperatures) for 30 days.

Variability in the decomposition of sludge was assessed a second time on a daily timescale, which was to directly determine correlations between properties of the sludge and feed to the Sirolan CF module with the biodegradability of the sludge. Samples were collected in August 2001 and decomposition was assessed as described above. Sludge samples were analysed for moisture content (Section 2.3.1), pH (Section 2.3.2), grease content (Section 2.3.5), TN (Section 2.4.1), and mineral N (Section 2.4.2). The

feed to Sirolan CF was analysed for total solids (Section 2.3.1), pH (Section 2.3.2), biological and chemical oxygen demands (Section 2.3.9), TN (Section 2.4.1) and mineral N (Section 2.4.2).

4.2.3. Composting Profiles of Woolscour Wastes

The decomposition of the three woolscour waste streams at temperatures expected during a composting process was evaluated by both net-N mineralisation (Section 2.5.2) and weight loss (Section 2.5.4) methods. For each substrate, composite samples were used, composed of equal amounts (dry weight basis) of five daily samples collected in January 2001. Sirolan CF sludge was not used in weight loss experiments, for reasons discussed previously (Section 4.2.2). Decomposition was assessed at 43, 50 and 60°C. For each substrate, 10 microcosms were established, with five sampled after 4 days and the remaining five after 8 days (8 days being the intended duration of an in-vessel composting stage). Microcosms were incubated under aerobic conditions and at 30% moisture, which was maintained throughout the incubation period.

Mixtures of the wastes were also incubated under the same conditions to examine interaction effects. When two substrates were co-incubated and decomposition assessed by net-N mineralisation, each contributed 5 mg TN, and when three were co-incubated, each contributed 3 mg TN. Using the weight loss method, each substrate contributed 500 mg dry weight. Rates of observed net-N mineralisation or weight loss were compared to theoretical rates based on the decomposition rates of the individual components.

4.2.4. The Decomposition of the Dirt Fraction of Sirolan CF Sludge

To assess the effect of the grease content of woolscour sludge on the rate of decomposition, the decomposition of the dirt fraction (produced by Soxhlet extraction, as described in Section 2.3.5) was compared to that of the intact sludge. The dirt fraction was a composite, made of equal amounts (dry weight basis) of the solvent-insoluble fractions of the sludge samples used in Section 4.2.3 above. Incubation conditions were as described in Section 4.2.3.

4.2.5. The Effect of Inoculation and Nutrient Addition on the Decomposition of Woolscour Wastes

The decomposition of keratin (a composite of five samples of Soxhlet-extracted scoured wool cleaner waste from the Fairlie Woolscour) was compared to that of casein, a storage protein, and haemoglobin, a

transport protein, using net-N mineralisation (Section 2.5.2). For keratin, 10 microcosms were established, with five sampled after 30 days and the remaining five after 60 days. Decomposition of casein and haemoglobin was measured over 30 days only. Microcosms were inoculated with a soil inoculum (Section 2.5.1) and incubated aerobically at 37°C. A second set of 10 microcosms containing keratin was inoculated with a suspension of known microorganisms with keratin-degrading ability (100 μL each of *Trichophyton rubrum*, *T. mentagrophytes*, and *Microsporum gypseum*) instead of a soil inoculum. Each culture was grown in half strength malt extract broth (8.5 g malt extract and 1.5 g peptone L^{-1} distilled water) on an orbital shaker for 3 days.

The selection of grease- and keratin-adapted microbes for sludge decomposition was assessed. A composite sample of sludge was created by mixing four daily sludge samples (equal amounts on a dry weight basis) collected from the Ashburton Woolscour during October 2002. Flasks were inoculated either with the usual soil suspension (Section 2.5.1), a soil suspension adapted to wool grease, or a soil suspension adapted to keratin. The grease inoculum was prepared by adding 5 mL soil inoculum to a 250-mL flask containing 95 mL distilled water, 0.55 g grease (extracted from a sludge sample from the Ashburton Woolscour) and two drops Tween 20. The keratin inoculum was prepared by adding 5 mL soil inoculum to a 250-mL flask containing 95 mL distilled water and 1 g scoured wool cleaner waste (degreased, composite sample from the Fairlie Woolscour). Flasks were placed on an orbital shaker for five days and filtered through muslin before use. For each inoculum, 10 microcosms were incubated under aerobic conditions at 37 °C, five of which were analysed after 30 days and the remaining five after 60 days. Decomposition was assessed by net-N mineralisation (Section 2.5.2).

The effect of nutrient addition on the rate of decomposition of sludge was assessed by net-N mineralisation (Section 2.5.2). Four sludge samples were collected from the Ashburton Woolscour during January-February 2003 and equal amounts (on a dry weight basis) were mixed to form a composite sample. Four treatments were investigated, the first being sludge with no nutrient addition and the remaining were sludge amended with either C, N or P. The C source was glucose, added a rate of 100 mg C to provide a C (glucose):TN (sludge) ratio of 10:1. The N source was ammonium nitrate (NH_4NO_3), providing 5 mg N to the 10 mg TN contained in the sludge. The P source was sodium dihydrogen orthophosphate ($NaH_2PO_4.2H_2O$), added at a rate of 1 mg P to provide a TN (sludge):P (amendment) ratio of 10:1. Nutrients were dissolved in distilled water and each flask received 1 mL of the appropriate solution. For each set, 10 microcosms were incubated under aerobic conditions at 37°C, five of which were analysed after 30 days and the remaining five after 60 days.

4.2.6. THE DECOMPOSITION OF POLYACRYLAMIDE AND ITS EFFECT ON THE TURNOVER OF MODEL ORGANIC COMPOUNDS

The decomposition of the flocculant used in the Sirolan CF process, high molecular weight (1-5x10^6 g $mole^{-1}$) and moderately cationic (10-30 mole %) polyacrylamide (Profloc CX533, Orica Chemnet, Mt. Maunganui, New Zealand), was determined by net-N mineralisation (Section 2.5.2) over 60 days at 20, 37 and 50°C. These temperatures were judged to represent ambient, a compromise between ambient and composting, and composting conditions, respectively. The effect of polyacrylamide (PAM) on the decomposition of chitin, casein, and woolscour sludge (from the Ashburton Woolscour) was also determined. The PAM was added at rates of 5 and 20% of the i-TN of the microcosms and decomposition was assessed over 20 days at 37°C. A rate of 5% PAM corresponded to 5 mg PAM added to 70, 155 and 300 mg of casein, chitin and sludge (dry weight), respectively, and 20% PAM corresponded to 20 mg PAM added to 60, 130 and 250 mg of casein, chitin and sludge (dry weight), respectively. The observed rates of net-N mineralisation were compared to the expected rates, based on the individual decomposition rates of each substrate.

4.2.7. THE EFFECT OF PESTICIDE RESIDUES ON THE DECOMPOSITION OF CASEIN

The effect of the organophosphate pesticide diazinon (O,O-diethyl 0-(2-isopropyl-4-methyl-pyrimidine-6-yl) phosphorothioate) and the synthetic pyrethroid cypermethrin ((R,S)-alpha-cyano-3-phenoxybenzyl(1RS)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate) (PestAnal grade, Riedel-deHaën Laborchemikalien GmbH & Co., Germany) on the decomposition of casein was determined by net N mineralisation (Section 2.5.2) over 30 days at 37°C. The pesticides were added at levels of 10, 100, and 1,000 ppm on a casein weight basis, either separately or together. The pesticides were dissolved in petroleum spirit and added to the sand matrix of the microcosms, with excess solvent added to allow the pesticides to be distributed evenly through the matrix by gentle swirling. Once the solvent had been evaporated, by passing a stream of ambient air over the matrix, casein was added. Control microcosms contained no pesticide but petroleum spirit was added to the matrices, as described above. The N contributed by the pesticide residues, even at the highest application rates (1,000 ppm each of diazinon and cypermethrin contributed 12.6 μg TN), was insignificant in terms of the TN of the microcosms (100 mg casein contributed 13.5 mg TN) and was not included in the calculation of the i-TN.

4.2.8. PHYTOTOXICITY OF SIROLAN CF SLUDGE

The phytotoxicity of Sirolan CF sludge collected from the Ashburton Woolscour was determined by investigating the germination of white clover, perennial ryegrass, and radish seeds and subsequent growth of the seedlings. Equal volumes of sludge were collected over five consecutive days and homogenised by hand. Seeds were planted in 1-L pots containing either potting mix (control, obtained from supplies held by the university glasshouses), sludge, or a 50:50 v/v mixture of sludge and potting mix. Each pot was sown with either 10 ryegrass or white clover seeds or five radish seeds. Treatments were set up in triplicate and pots were placed in a glasshouse under conditions of 16 h light and 8 h dark in a randomised fashion. After weeks one to five, the pots were re-randomised and germination was recorded. After six weeks, the final germination was recorded and, for white clover and ryegrass, the oven dry weight (after 48 h at 105ºC) of shoot biomass was determined, and for radish the fresh weights of radishes were recorded.

To identify the cause of any observed phytotoxicity, a second assay was employed using potting mix (as a control), sludge, air-dried sludge (50°C for 48 h to remove any volatile components) and the dirt fraction of the sludge after the grease had been removed (by Soxhlet extraction using petroleum spirit followed by oven drying at 105°C for 24 h). Five radish seeds were added to each of triplicate petri dishes containing one of the above materials and dishes were placed in the laboratory under natural lighting. Germination was recorded over 7 days. To assess the effect of PAM solutions on radish germination, 10 seeds were germinated in triplicate on Whatman No. 1 filter paper soaked with 3 mL of either distilled water or PAM solutions of varying concentration (0.5, 1.0, 1.5 and 2.0 g L^{-1}). Petri dishes were placed in the laboratory under natural lighting and germination was recorded after 7 days.

4.2.9. MICROBIAL COUNTS AND ACTIVITY IN SIROLAN CF SLUDGE

Numbers of culturable microorganisms and microbial activity in freshly produced Sirolan CF sludge from two woolscours were determined by plate counts and substrate-induced respiration, respectively.

Samples of sludge were collected over five consecutive days in sterile plastic bags from the Ashburton Woolscour during May 2002 and twice from the Kaputone Woolscour in Christchurch during December 2002 and August 2003. Samples were stored at 4°C before and during transport to the laboratory. Samples from Ashburton and the second set from Kaputone were collected when the scour allowed the wastewater feeding Sirolan CF to become anaerobic prior to treatment, by holding the wastewater in tanks for in excess of 12 h. (This step was thought to improve flocculation and reduce chemical use.) The

type of wool scoured on the day of sludge production was recorded, and the moisture content of each sample was determined in duplicate (Section 2.3.1) to correct colony forming units (CFU) to an oven dry basis. Heterotrophic bacteria and fungi were estimated by the pour plate method, with bacteria grown on 0.3% yeast extract agar and fungi on a modified dichloran rose bengal media (refer to Appendix Section 8.5 p.198 for media recipes) at temperatures of 30°C (for mesophilic microbes) and 50°C (for thermophilic microbes). For bacteria, 1 mL of the 10^{-6} to 10^{-4} dilutions was used, and for fungi 1 mL of 10^{-4} to 10^{-2} dilutions was used. Uninoculated plates were used as controls. Colonies were counted after 7 days in the case of bacteria and 21 days for fungi.

The active microbial population of sludge and sawdust (used as the bulking agent in composting trials; refer to Section 5.2 p.142) was assessed by substrate-induced respiration. A set of sludge samples was collected from the Ashburton Woolscour during July 2002 and untreated rimu sawdust was collected from a Timaru furniture manufacturer at the same time. Sludge samples were also collected from Kaputone during February and August 2003. Samples from Ashburton and the second set from Kaputone were collected when the scour allowed the feed to Sirolan CF to go anaerobic before treatment, as described above. Sawdust, adjusted to a moisture content of 50% (wet weight basis) by the addition of distilled water, and the sludge, at its existing moisture content, was pre-incubated at 20°C for 48 h.

On the day of analysis, 10 g (dry weight equivalent) of sludge samples (5 g in the case of sawdust) was added to each of three 100-mL Schott bottles that had a rubber septum in the lid. For the Ashburton Woolscour sludge samples, 4.5 and 0.5 g (dry weight) of each sludge sample and sawdust, respectively, was added to each of three Schott bottles. For each set of three bottles, one was unamended for basal respiration (control), one received 0.5% glucose and the third 2% glucose on a dry weight basis. After each bottle was amended, the contents were thoroughly mixed and the lids firmly tightened, and the bottles were incubated at 25°C. After 1 and 4 h, the CO_2 in the headspace of each bottle was analysed by an infra-red gas analyser (ADC-225-Mk3, The Analytical Development Co. Ltd., Hoddesdon, England). Using a syringe, 1 mL of gas (or less if required) was removed from the headspace and injected into the machine and the value (in volts) was recorded.

Gas standards of known CO_2 concentration were used to convert readings (in volts) to ppm CO_2. Since 1 mol CO_2-C equals 12 g C and occupies 22.4 L at standard temperature and pressure, the Schott bottles used (0.13 L) would contain 70,000 μg CO_2-C if filled only with CO_2.

The recorded value (in ppm) was converted to μg CO_2-C using Equation 4-1:

$$\mu g\, CO_2\text{-}C = \left(\frac{\text{recorded value (ppm)}}{1{,}000{,}000} \right) * 70{,}000$$

Equation 4-1

Respiration (as μg CO_2-C h^{-1} g^{-1}) over 3 h was calculated using Equation 4-2:

$$\text{Respiration } (\mu g\, CO_2\text{-}C\ h^{-1}\ g^{-1}) = \left(\frac{\text{4 h reading - 1 h reading } (\mu g\, CO_2\text{-}C)}{24 * \text{sample weight (g)}} \right)$$

Equation 4-2

4.3. RESULTS

4.3.1. CHEMICAL CHARACTERISATION OF WOOLSCOUR WASTES

Variation in the composition of woolscour wastes was observed, especially for Sirolan CF sludge (Table 4-2). The moisture content of the sludge was highly variable, depending on how efficient the Sirolan CF module was operating. The moisture content of the fibrous wastes was more consistent, and similar between scours (Fairlie compared to Ashburton) for opener waste. Sludge pH differed between scours; this was not observed for opener waste. The pH of scoured wool cleaner waste differed by only 1 pH unit. All three waste streams had a high organic matter content, although the amount varied considerably. The opener waste, and especially the scoured wool cleaner waste, had a high TN content. Phosphorus levels were low in all three waste streams. Levels of heavy metals in the woolscour wastes were similar to those found in two soil types analysed for comparison (see Appendix Table 8-4 p.197), except for high zinc levels in the sludge produced at Ashburton. It was noted by the testing laboratory that it was extremely difficult with the opener and scoured wool cleaner waste samples to get a representative sub-sample for analysis, as the fibre made homogenising impossible.

Sludge produced at the Ashburton Woolscour contained more grease than that produced at the Fairlie Woolscour. The efficiency of the grease extraction process (the weights of the grease and dirt or fibre fractions as a percentage of the initial sample weight) ranged from 96-101%, indicating that the Soxhlet extraction procedure was efficient. Grease extracted from samples from the Fairlie Woolscour contained 0.1-0.3% TN on a dry weight basis and therefore, based on the grease content of the samples and the TN content of the solvent-insoluble fractions (2.4, 5.1 and 7.9% for sludge, opener waste and scoured wool

cleaner waste, respectively), the grease fraction contributed 3.3, 0.6 and 0.1% of the TN of sludge, opener waste, and scoured wool cleaner waste, respectively. The N distribution profiles of five sludge samples collected from the Fairlie Woolscour showed little variation on a daily basis, the sludge N being principally in the α-amino acid form, with the HUN fraction the second largest pool.

Table 4-2. Chemical properties of woolscour wastes collected from the Fairlie and Ashburton Woolscours.

Property	Fairlie Woolscour			Ashburton Woolscour	
	Sirolan CF sludge	Opener waste	Scoured wool cleaner waste	Sirolan CF sludge	Opener waste
Moisture (%)	44.8 (1.49)	10.5 (0.48)	13.4 (0.61)	48.7 (1.21)	10.3 (0.97)
pH	3.6 (0.15)	8.5 (0.40)	8.4 (0.18)	5.1 (0.18)	8.5 (0.15)
Organic matter (%)	55.2 (7.02)	55.2 (3.12)	76.9 (6.02)	60.7 (6.46)	62.7 (1.93)
Total N (%)	2.1 (0.09)	5.0 (0.34)	10.7 (0.59)	1.8 (0.22)	3.9 (0.27)
Phosphorus (%)	0.08 (0.01)	0.14 (0.00)	0.08 (0.01)		
Grease (%)	27.7 (2.90)	12.7 (1.57)	1.7 (0.26)	38.0 (2.07)	14.3 (0.80)
Diazinon (ppm)	43 (7.7)	15 (10.3)		119 (17.6)	14 (6.4)
Propetamphos (ppm)	13 (7.8)	25 (13.3)		53 (18.8)	11 (5.4)
Arsenic (mg kg^{-1})	3.3 (0.27)	2.4 (0.17)	1.3 (0.31)	3.2 (0.20)	
Cadmium (mg kg^{-1})	1.1 (0.57)	0.5 (0.21)	0.5 (0.31)	0.1 (0.02)	
Chromium (mg kg^{-1})	10.9 (1.27)	6.7 (0.28)	3.6 (0.38)	7.8 (1.16)	
Copper (mg kg^{-1})	9.0 (0.72)	8.5 (0.77)	6.4 (1.05)	10.4 (0.51)	
Lead (mg kg^{-1})	9.5 (3.07)	9.7 (2.34)	3.2 (1.94)	6.5 (0.26)	
Nickel (mg kg^{-1})	12.9 (3.75)	7.2 (1.45)	2.8 (1.90)	10.4 (2.38)	
Zinc (mg kg^{-1})	152.6 (36.01)	131.7 (16.47)	104.3 (9.01)	664.6 (84.80)	
Total N (mg g^{-1})	20.5 (1.00)				
Acid-insoluble N (% of TN)	9.6 (0.31)				
NH_4-N (% of TN)	12.6 (0.31)				
Hexosamine-N (% of TN)	2.8 (0.38)				
α-Amino Acid-N (% of TN)	47.0 (0.68)				
HUN (% of TN)	28.0 (0.83)				

Note: numbers in brackets are the standard errors of the means. All analyses (except moisture and pH) are on an oven dry basis. TN = total N, HUN = hydrolysable but unidentified N. Hexosamine-N values have been corrected for decomposition. For heavy metal analysis, n=5.

Inorganic elements in the woolscour waste samples collected from the Fairlie Woolscour were in similar proportions to those typically found in soil (Table 4-3). For reference, elemental values for sludge from a previous study (although produced by a different process) are given. All three wastes contained more sodium and potassium than typical soil, while the opener and scoured wool cleaner wastes also contained more sulphur.

The number of seeds in opener waste and scoured wool cleaner waste samples collected from the Fairlie and Ashburton Woolscours were both high and very variable, depending on the relative amounts of dirt and fibre in the case of opener waste, and wool dust and fibre in the case of scoured wool cleaner waste (Table 4-4). Approximately 40% of the seeds contained in opener waste from Ashburton germinated within 2 weeks on filter paper moistened with distilled water.

Table 4-3. Inorganic elements in woolscour wastes collected from the Fairlie and Ashburton Woolscours.

Element (% of ash)	Fairlie Woolscour Sirolan CF sludge	Fairlie Woolscour Opener waste	Fairlie Woolscour Scoured wool cleaner waste	Ashburton Woolscour Sirolan CF sludge	Woolscour sludge[#]
Silicon	62.66	54.97	64.38	62.54	65.79
Titanium	0.84	0.69	0.54	0.83	0.61
Aluminium	15.10	12.65	11.57	14.98	12.13
Iron	5.46	5.09	4.31	5.54	4.07
Manganese	0.08	0.13	0.12	0.09	0.08
Magnesium	1.43	1.51	1.39	1.50	1.10
Calcium	2.34	3.70	4.66	3.15	6.66
Sodium	4.47	4.09	4.21	4.81	4.99
Potassium	7.15	14.85	6.93	5.90	3.10
Phosphorus	0.34	0.61	0.60	0.35	0.21
Sulphur	0.14	1.72	1.30	0.30	1.26

Note: #Sludge used in the study by Williamson (1998). Refer to Table 3-4 p.65 for inorganic elements typically found in soil.

Table 4-4. Numbers of seeds in woolscour wastes collected from the Fairlie and Ashburton Woolscours.

	Fairlie Woolscour		Ashburton Woolscour
	Opener waste	Scoured wool cleaner waste	Opener waste
Seeds (per kg fresh weight)	20,397 (9,220)	21,861 (5,875)	17,647 (4,154)
Germination (%)	ND	ND	41 (3.9)
Viable seeds (per kg fresh weight)	ND	ND	7,544 (2,170)

Note: numbers in brackets refer to the standard errors of the means, n=5. ND = not determined.

4.3.2. VARIATION IN THE BIODEGRADABILITY OF WOOLSCOUR WASTES

Large variations in the biodegradability of wastes collected from the Fairlie Woolscour, particularly for Sirolan CF sludge, was observed on a daily time scale after a 30 day incubation period (Table 4-5). This variation was statistically significant at α=0.05. Of the i-TN, the amount mineralised ranged from 0.8 to 27.8% for the sludge, from 10.0 to 18.6% for the opener waste, and from 10.9 to 26.5% for the scoured wool cleaner waste.

Table 4-5. Daily variation in woolscour waste biodegradability as determined by net-N mineralisation.

Day	Net-N Mineralised (% of i-TN)		
	Sirolan CF sludge	Opener waste	Scoured wool cleaner waste
Monday	3.6 (0.09) abc	18.3 (1.56) ab	26.5 (1.19) a
Tuesday	27.8 (2.45) a	11.0 (0.91) bc	11.2 (1.11) c
Wednesday	21.2 (0.74) ab	10.0 (0.49) c	10.9 (0.74) c
Thursday	0.8 (0.03) c	13.4 (0.16) abc	19.0 (0.87) b
Friday	2.4 (0.42) bc	18.6 (1.07) a	23.7 (1.55) a

Note: microcosms were incubated at 37°C for 30 days. Numbers in brackets are the standard errors of the means, n=5. Samples with the same letter in a column are not significantly different at α=0.05.

On a weekly time scale, the decomposition of Sirolan CF sludge collected from the Fairlie Woolscour was more uniform, ranging from 0.8 to 5.6% of the i-TN mineralised over 30 days (Table 4-6). The range for opener and scoured wool cleaner wastes were similar to that on a daily time scale, being 9.1 to 19.6% and from 10.6 to 25.2% for opener and scoured wool cleaner wastes, respectively. Significant variation in decomposition was found for all three waste streams. Note that, for the week five opener and scoured wool cleaner waste samples, the machines had been shut down for three days prior and the material analysed was that cleaned from the machines.

Table 4-6. Weekly variation in woolscour waste biodegradability as determined by net-N mineralisation.

Week	Net-N Mineralised (% of i-TN)		
	Sirolan CF sludge	Opener waste	Scoured wool cleaner waste
1	2.5 (0.88) b	9.1 (0.68) c	13.7 (1.03) c
2	3.7 (0.73) b	13.4 (0.51) b	22.0 (0.73) a
3	5.6 (1.01) a	9.7 (0.83) c	10.6 (2.41) c
4	0.8 (0.53) c	9.4 (0.68) c	25.2 (0.89) a
5	2.7 (0.65) b	19.6 (1.79) a	18.0 (0.65) b

Note: microcosms were incubated at 37°C for 30 days. Numbers in brackets are the standard errors of the means, n=5. Samples with the same letter in a column are not significantly different at α=0.05.

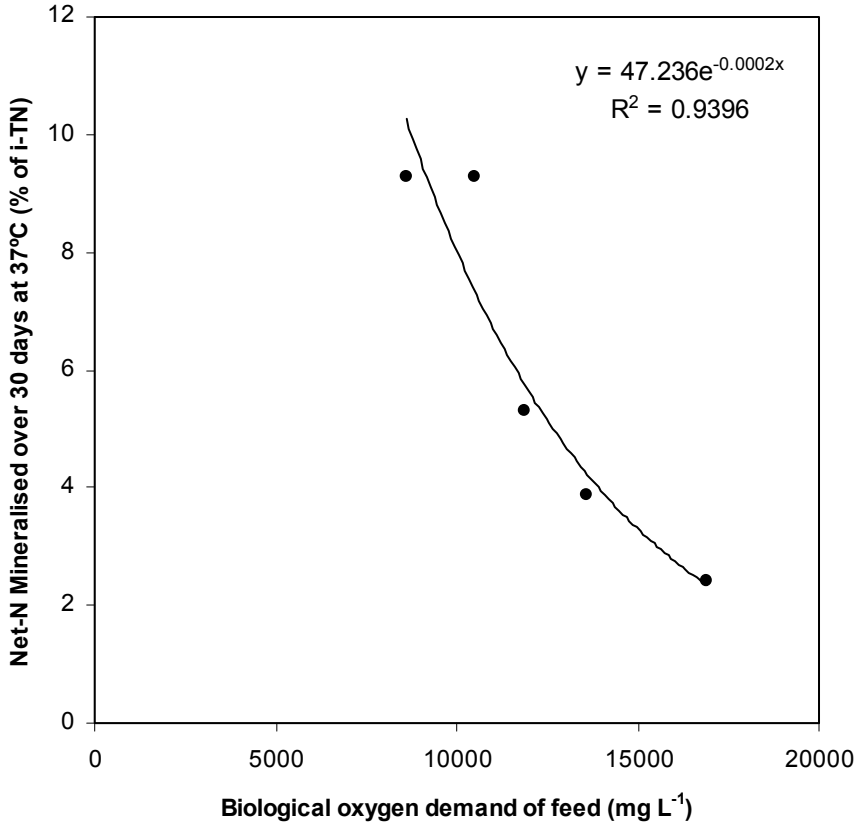
A second set of Sirolan CF sludge samples collected from the Fairlie Woolscour over five consecutive days showed a range of 2.4 to 9.3% of the i-TN mineralised over 30 days (Table 4-7). The best linear correlation involving net-N mineralised was with the biological oxygen demand of the feed to the Sirolan CF unit. The best equation for explaining sludge decomposition involved the biological oxygen demand of the feed (Figure 4–1). Caution must be exercised though, since only five data points were used.

Table 4-7. Daily variation in woolscour sludge biodegradability as determined by net-N mineralisation correlated to feed and sludge properties.

Property	Monday	Tuesday	Sample Wednesday	Thursday	Friday	Linear r^2
Net-N Mineralised (% of i-TN)	2.4 (0.38)	9.3 (0.72)	9.3 (2.14)	3.9 (0.45)	5.3 (0.88)	
			Sirolan CF feed properties			
Wool type	X-bred	Half-bred	X-bred	Half-bred	Half-bred	
BOD_5 (mg L^{-1})	16,900	8,600	10,500	13,600	11,900	0.87
COD (mg L^{-1})	100,000	130,000	94,000	130,000	110,000	0.00
pH	7.6	8.0	8.2	8.9	8.2	0.00
TS (mg mL^{-1})	0.07 (0.00)	0.08 (0.00)	0.07 (0.00)	0.09 (0.00)	0.08 (0.00)	0.18
TN (mg mL^{-1})	2.0 (0.02)	2.2 (0.05)	2.0 (0.03)	2.3 (0.02)	2.0 (0.03)	0.00
Min N (mg mL^{-1})	0.80 (0.03)	0.46 (0.01)	0.61 (0.02)	0.52 (0.02)	0.49 (0.01)	0.26
			Sludge properties			
pH	3.1 (0.00)	3.2 (0.00)	3.7 (0.00)	3.7 (0.05)	3.6 (0.05)	0.05
Moisture (%)	50.3 (0.23)	44.9 (0.98)	46.6 (2.96)	43.3 (0.13)	46.7 (1.22)	0.14
TN (mg g^{-1})	24.6 (0.15)	20.8 (0.49)	21.9 (0.22)	20.8 (0.16)	18.9 (0.26)	0.10
Min N (mg g^{-1})	0.24 (0.01)	0.23 (0.01)	0.28 (0.02)	0.26 (0.01)	0.26 (0.00)	0.05
Grease (%)	15.6	40.0	21.3	30.7	24.0	0.25

Note: microcosms were incubated at 37°C for 30 days. Numbers in brackets are the standard errors of the means, n=5.
BOD = biological oxygen demand, COD = chemical oxygen demand, TS = total solids, TN = total nitrogen, X-bred = cross-bred.
TN, Min N and grease content is expressed on a dry weight basis for sludge.

Figure 4–1. Correlation between the rate of Sirolan CF sludge decomposition and the biological oxygen demand of the feed to the Sirolan CF unit.



4.3.3. COMPOSTING PROFILES OF WOOLSCOUR WASTES

Sirolan CF sludge was very slow to decompose at all incubation temperatures studied, the highest rate being 1.3% of the i-TN mineralised at 50°C after 8 days, with decomposition faster at 50 and 60°C than at 43°C and increasing with time (Figure 4–2; Table 4-8). The fibrous wastes decomposed more readily than woolscour sludge. Decomposition of opener waste was faster at 50 and 60°C than at 43°C and did not significantly increase from 4 to 8 days incubation. Temperature had no effect on the decomposition of scoured wool cleaner waste, but the degree of decomposition increased from 4 to 8 days incubation.

When decomposition was assessed by weight loss, there was no effect of temperature on the decomposition of opener waste or scoured wool cleaner waste, but decomposition increased with increasing length of incubation (Figure 4–3; Table 4-8). As stated earlier, Sirolan CF sludge was not used in these weight loss experiments, based on the research findings of Williamson (1998) that the grease content of the sludge interfered with water removal during drying.

The decomposition of Sirolan CF sludge was enhanced in the presence of either opener waste or scoured wool cleaner waste, as the rates of net-N mineralisation observed were up to three times that of the expected rates, which were calculated from the individual rates of decomposition for each incubation temperature and time (Figure 4–4; Table 4-9). After 8 days incubation, the observed rates of net-N mineralisation for sludge co-incubated with either opener waste or scoured wool cleaner waste were significantly higher ($p<0.01$) than the expected rates for all three incubation temperatures. Rates of decomposition were also significantly enhanced ($p<0.01$) at all temperatures when all three woolscour wastes were co-incubated.

Decomposition, as measured by net-N mineralisation, was also enhanced when the two fibrous wastes, opener waste and scoured wool cleaner waste, were co-incubated (Figure 4–4). After 8 days incubation, the observed rates of net-N mineralisation were significantly higher ($p<0.05$) than the expected rates at all temperatures. In contrast, there were no effects observed on a weight loss basis, with the rates of weight loss observed in close agreement to the calculated theoretical rates (Figure 4–3). After 8 days incubation, the observed rates of weight loss were not significantly higher ($p>0.05$) than the expected rates for all three incubation temperatures.

Table 4-8. Significance of temperature and time on the decomposition of woolscour wastes as judged by analysis of variance.

Method	Substrate	Temperature	Time	Temp*Time
Net-N mineralisation	Sirolan CF sludge	***	***	NS
	Opener waste	***	NS	NS
	Scoured wool cleaner waste	NS	*	NS
Weight loss	Opener waste	NS	***	NS
	Scoured wool cleaner waste	NS	***	***

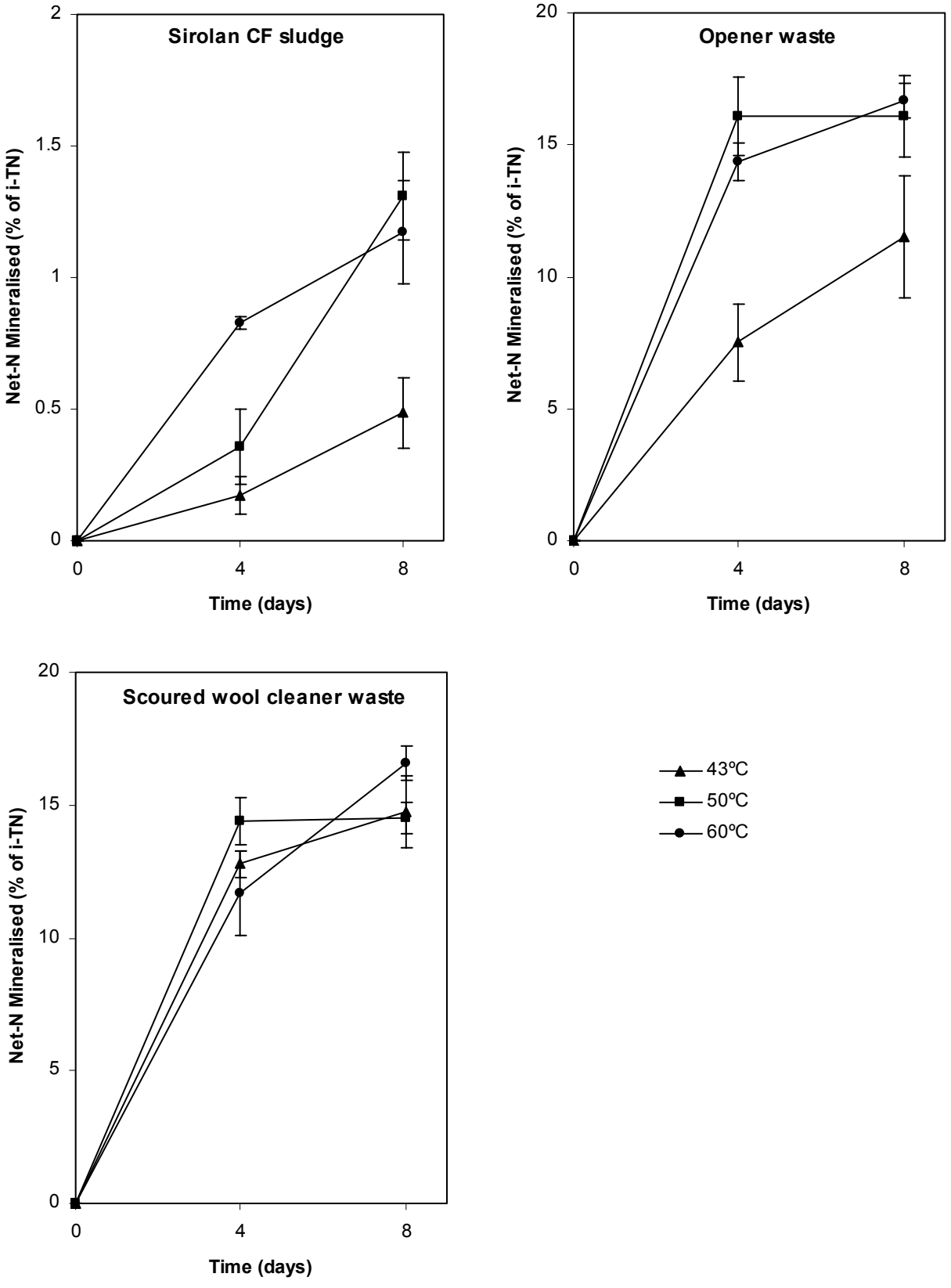
Note: *,** and *** refer to significant effects at the 0.05, 0.01 and 0.001 levels, respectively. NS = not significant.

Table 4-9. Significance of temperature and time on the decomposition of mixtures of woolscour wastes, as assessed by net-N mineralisation and judged by analysis of variance.

Substrates	Temperature	Time	Temp*Time
Sludge-Opener waste	NS	***	*
Sludge-Scoured wool cleaner waste	NS	***	*
Opener waste-Scoured wool cleaner waste	*	***	NS
Sludge-Opener waste-Scoured wool cleaner waste	***	***	**

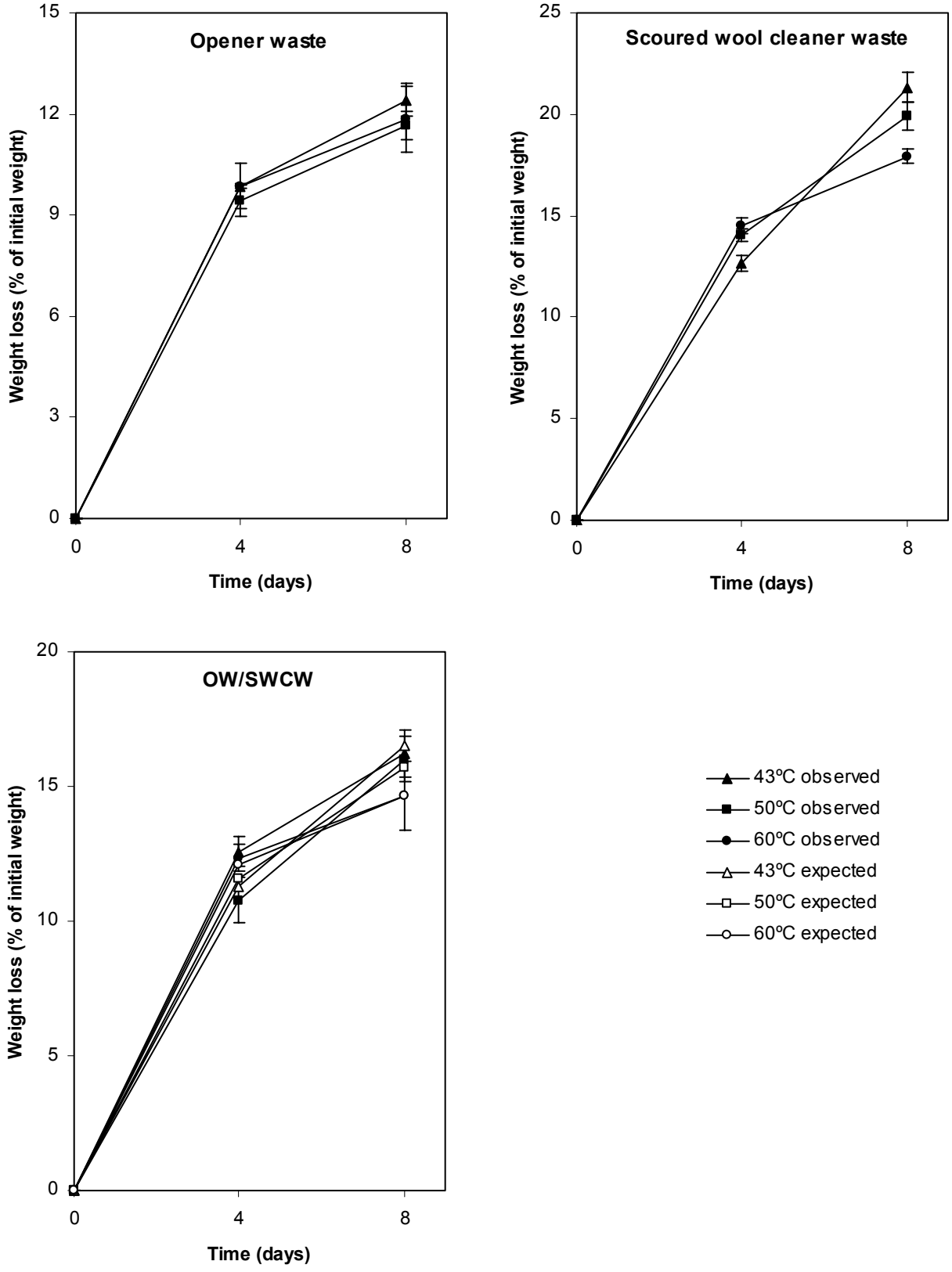
Note: *,** and *** refer to significant effects at the 0.05, 0.01 and 0.001 levels, respectively. NS = not significant.

Figure 4–2. Composting profiles of woolscour wastes as determined by net-N mineralisation.



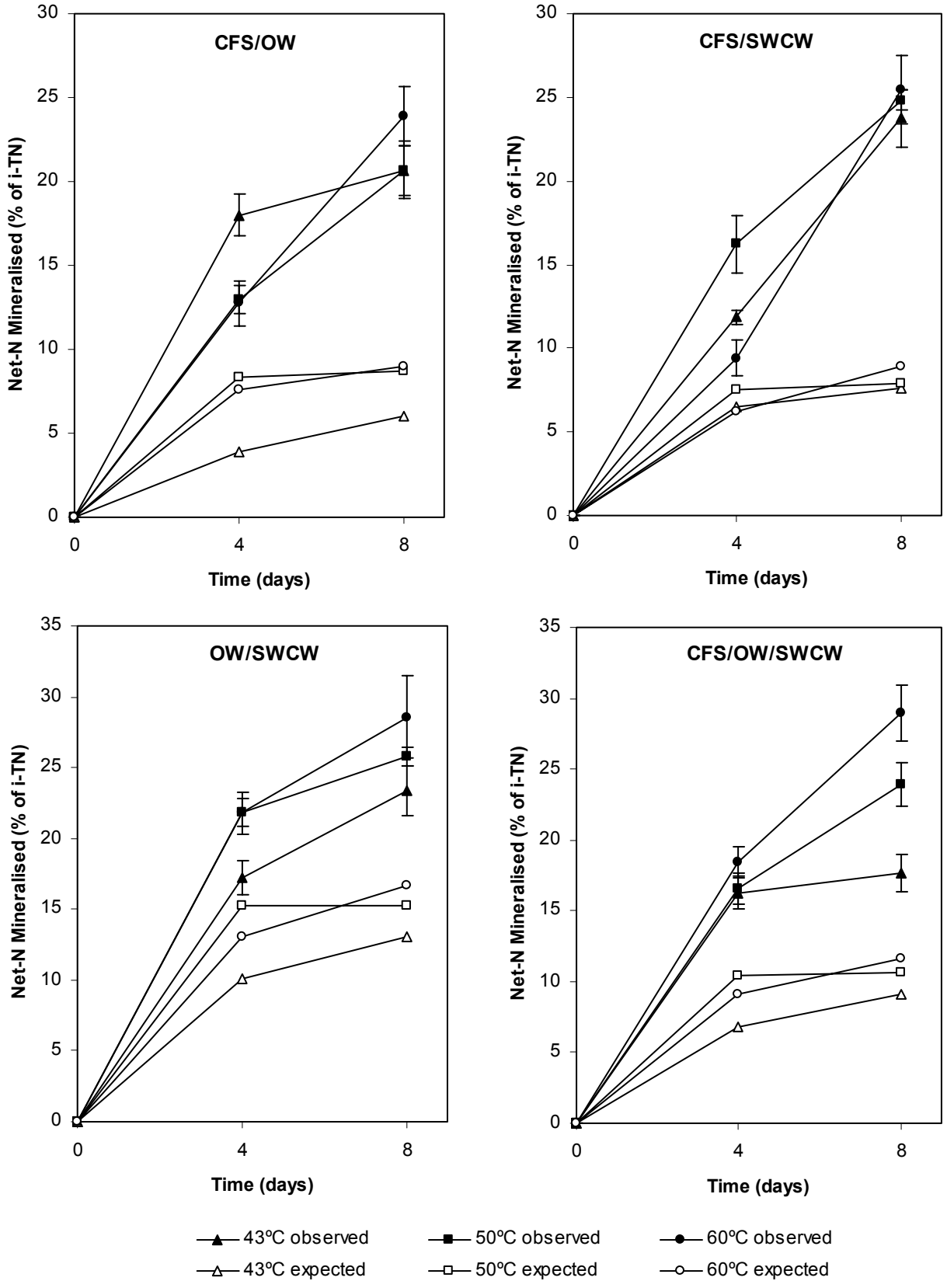
Note: bars represent standard errors of the means, n=5.

Figure 4–3. Composting profiles of woolscour wastes and mixtures as determined by weight loss.



Note: bars represent standard errors of the means, n=5. OW = opener waste, SWCW = scoured wool cleaner waste.

Figure 4–4. Composting profiles of mixtures of woolscour wastes as determined by net-N mineralisation.

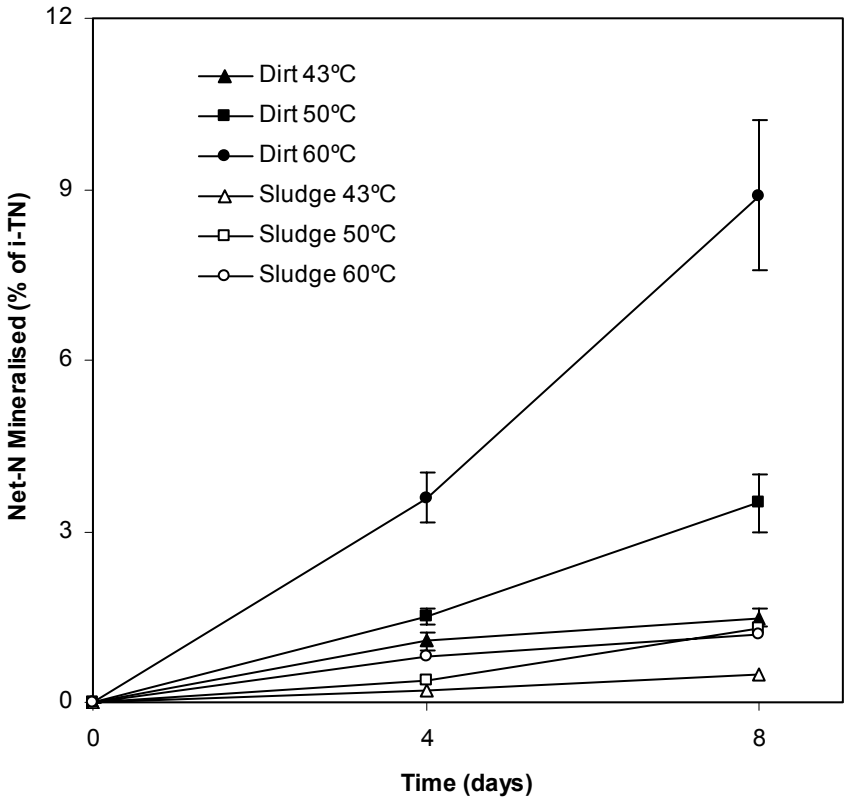


Note: bars represent standard errors of the means, n=5.
CFS = Sirolan CF sludge, OW = opener waste, SWCW = scoured wool cleaner waste.

4.3.4. THE DECOMPOSITION OF THE DIRT FRACTION OF SIROLAN CF SLUDGE

After the removal of the grease fraction from sludge, the remaining (dirt) fraction decomposed more readily than sludge (Figure 4–5). The dirt fraction showed an increase in the rate of decomposition with increasing temperature, which was more pronounced than was the case for the sludge, and the rate of decomposition increased with the length of incubation. As a fraction of the mineral N detected at the end of 8 days incubation, less than 10% was released as NH_3 and detected in the acid trap for all dirt samples, irrespective of incubation temperature. The data for Sirolan CF sludge decomposition is repeated from Figure 4–2.

Figure 4–5. Decomposition of sludge and the dirt fraction of sludge as determined by net-N mineralisation.



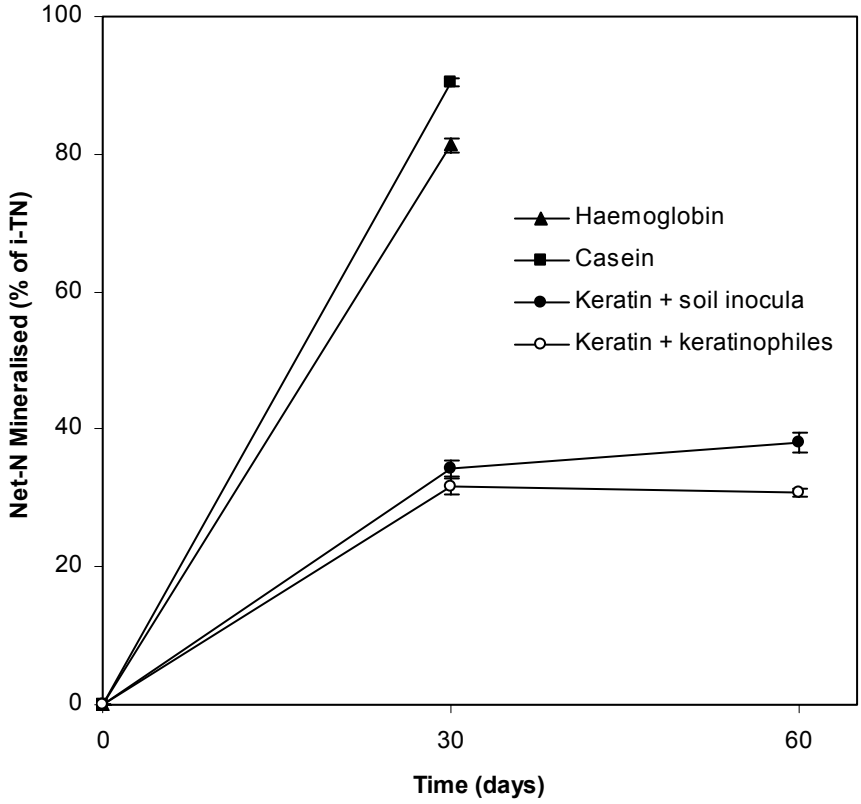
Note: bars represent standard errors of the means, n=5.

4.3.5. THE EFFECT OF INOCULATION AND NUTRIENT ADDITION ON THE DECOMPOSITION OF WOOLSCOUR WASTES

Compared to casein and haemoglobin, keratin (degreased scoured wool cleaner waste) decomposed at a much slower rate over 30 days (Figure 4–6). Inoculation of the keratin with three keratinophilic species

did not increase the rate of decomposition over that provided by a soil inoculum; in fact, the soil inocula provided a significantly higher ($p<0.01$) rate of decomposition. There was no effect of time ($p>0.05$) on the rate of decomposition of keratin.

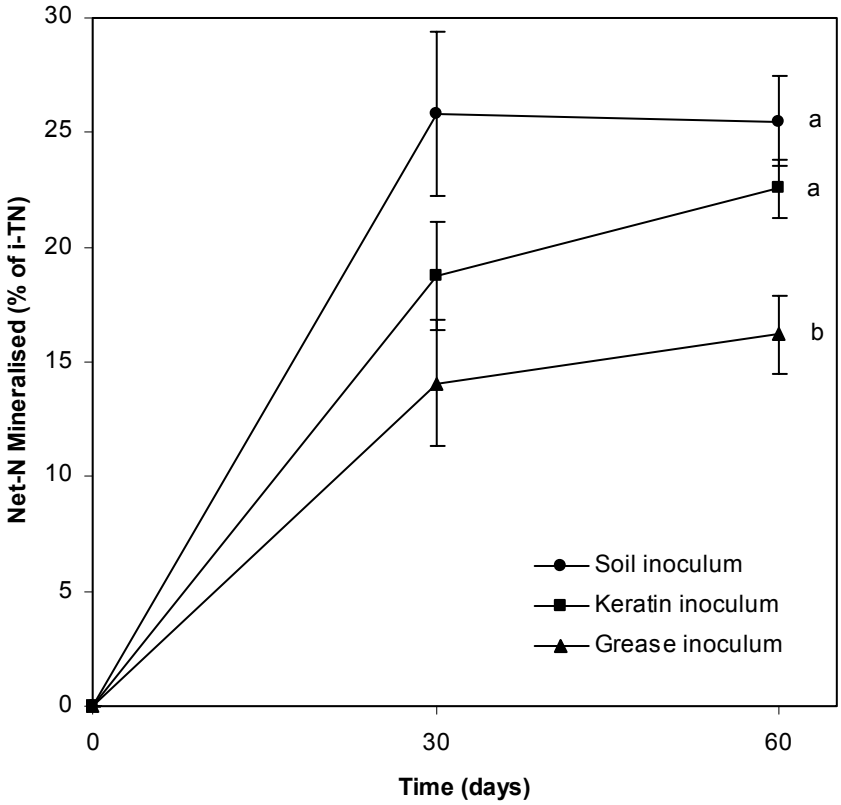
Figure 4–6. Decomposition of keratin, casein and haemoglobin as determined by net-N mineralisation.



Note: microcosms were incubated at 37°C. Bars represent standard errors of the means, n=5.

The choice of inocula significantly ($p<0.01$) affected the rate of net-N mineralisation from sludge, but there was no significant effect ($p>0.05$) of time of incubation (Figure 4–7). The inoculum selected from wool grease provided a lower rate of decomposition than the soil inocula or that selected from keratin. It was noted that the sludge decomposed in a similar fashion to that observed for keratin (Figure 4–6).

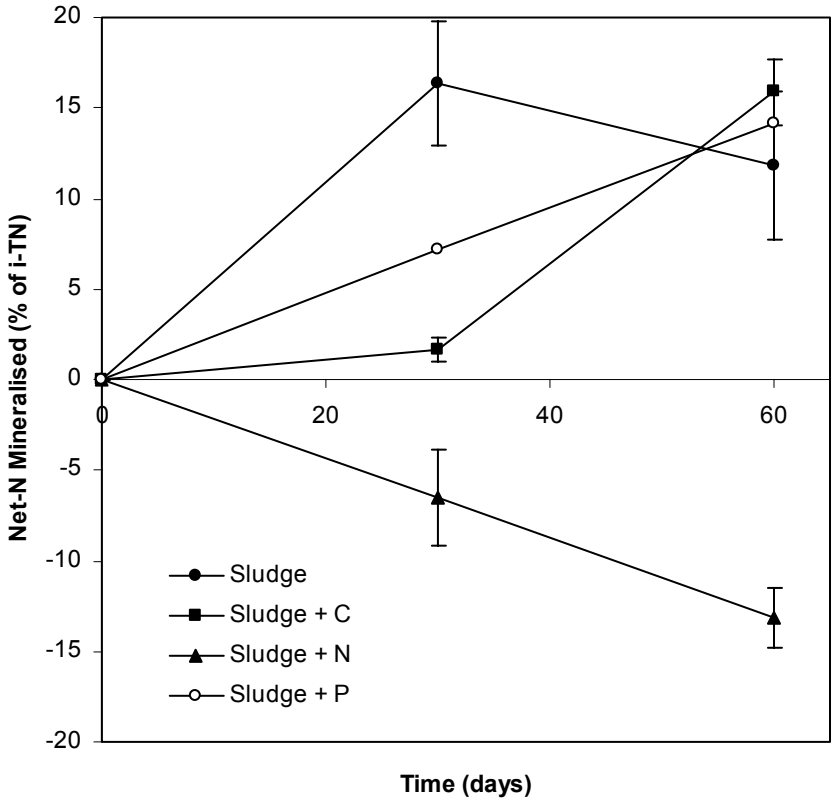
Figure 4–7. Effect of inocula on the decomposition of Sirolan CF sludge as determined by net-N mineralisation.



Note: microcosms were incubated at 37°C. Bars represent standard errors of the means, n=5.
Inocula with the same letter are not significantly different (least significant difference, α=0.05).

The addition of C (100 mg as glucose), N (5 mg as ammonium nitrate) or P (1 mg as sodium dihydrogen orthophosphate) to woolscour sludge had varying effects on the rate of decomposition (Figure 4–8). There was a significant effect of nutrient amendment ($p<0.0000$) but not time ($p=0.1151$), with a significant ($p=0.0001$) interaction between treatment and time. The addition of N caused mineral N to be immobilised. Carbon initially suppressed the rate of net-N mineralisation but after 60 days had increased the rate above that of the control. A linear increase in mineral N was observed with the addition of P.

Figure 4–8. Effect of C, N or P addition on the decomposition of Sirolan CF sludge as determined by net-N mineralisation.

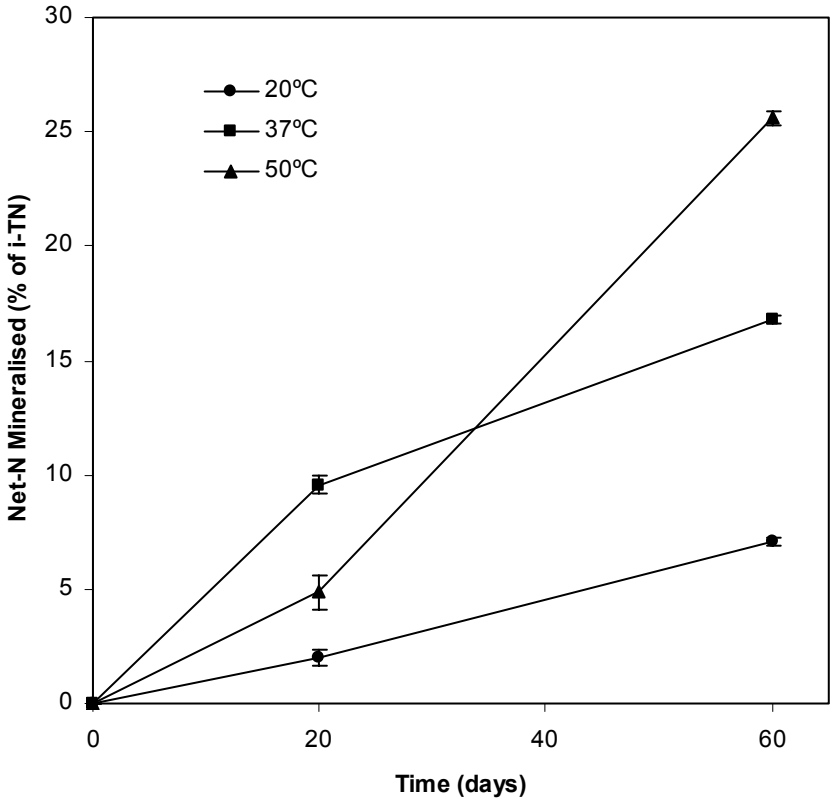


Note: microcosms were incubated at 37°C. Bars represent standard errors of the means, n=5.

4.3.6. THE DECOMPOSITION OF POLYACRYLAMIDE AND ITS EFFECT ON THE TURNOVER OF MODEL ORGANIC COMPOUNDS

Polyacrylamide (PAM), containing 10.2% TN by weight, a typical value for commercially-available polyacrylamides (Adam, 2003), released increasing amounts of mineral N with both increasing time and temperature when the PAM contributed all nutrients for microbial growth, except for those added with the inocula (Figure 4–9). No effect of PAM on the decomposition of either casein, chitin or woolscour sludge was observed, even at levels higher than those found in woolscour sludge (being 0.35% on a dry weight basis), with observed rates of decomposition matching the expected rates based on the individual decomposition rates of the substrates (Table 4-10). Note that the rate of decomposition of the sludge sample was considerably higher than the average rate of samples analysed for variation analysis (Section 4.3.2).

Figure 4–9. Decomposition of polyacrylamide as determined by net-N mineralisation.



Note: bars represent standard errors of the means, n=5.

Table 4-10. Effect of polyacrylamide on the decomposition of casein, chitin, and woolscour sludge as determined by net-N mineralisation.

	Net-N mineralised (% of i-TN)	
Substrate	Observed	Expected
Chitin	41.6 (2.27)	
95% Chitin – 5% Polyacrylamide	36.9 (2.27) NS	39.7
80% Chitin – 20% Polyacrylamide	31.6 (2.06) NS	34.9
Casein	81.8 (0.46)	
95% Casein – 5% Polyacrylamide	77.7 (1.15) NS	77.6
80% Casein – 20% Polyacrylamide	68.8 (1.49) NS	67.1
Sirolan CF Sludge	31.5 (0.83)	
95% Sludge – 5% Polyacrylamide	29.3 (0.96) NS	30.3
80% Sludge – 20% Polyacrylamide	27.4 (1.02) NS	27.2

Note: microcosms were incubated at 37°C for 20 days. Numbers in brackets are the standard errors of the means, n=5. Ratios of substrates are on a TN basis. NS = observed values not significantly different from expected values, $p>0.05$.

4.3.7. THE EFFECT OF PESTICIDE RESIDUES ON THE DECOMPOSITION OF CASEIN

The pesticides diazinon and cypermethrin were shown to have no effect (p=0.22) on the rate of decomposition of casein, even at very high levels (Table 4-11). When both these pesticides were added to casein together, there was no effect on the rate of casein decomposition.

Table 4-11. Effect of diazinon and cypermethrin on the decomposition of casein as determined by net-N mineralisation.

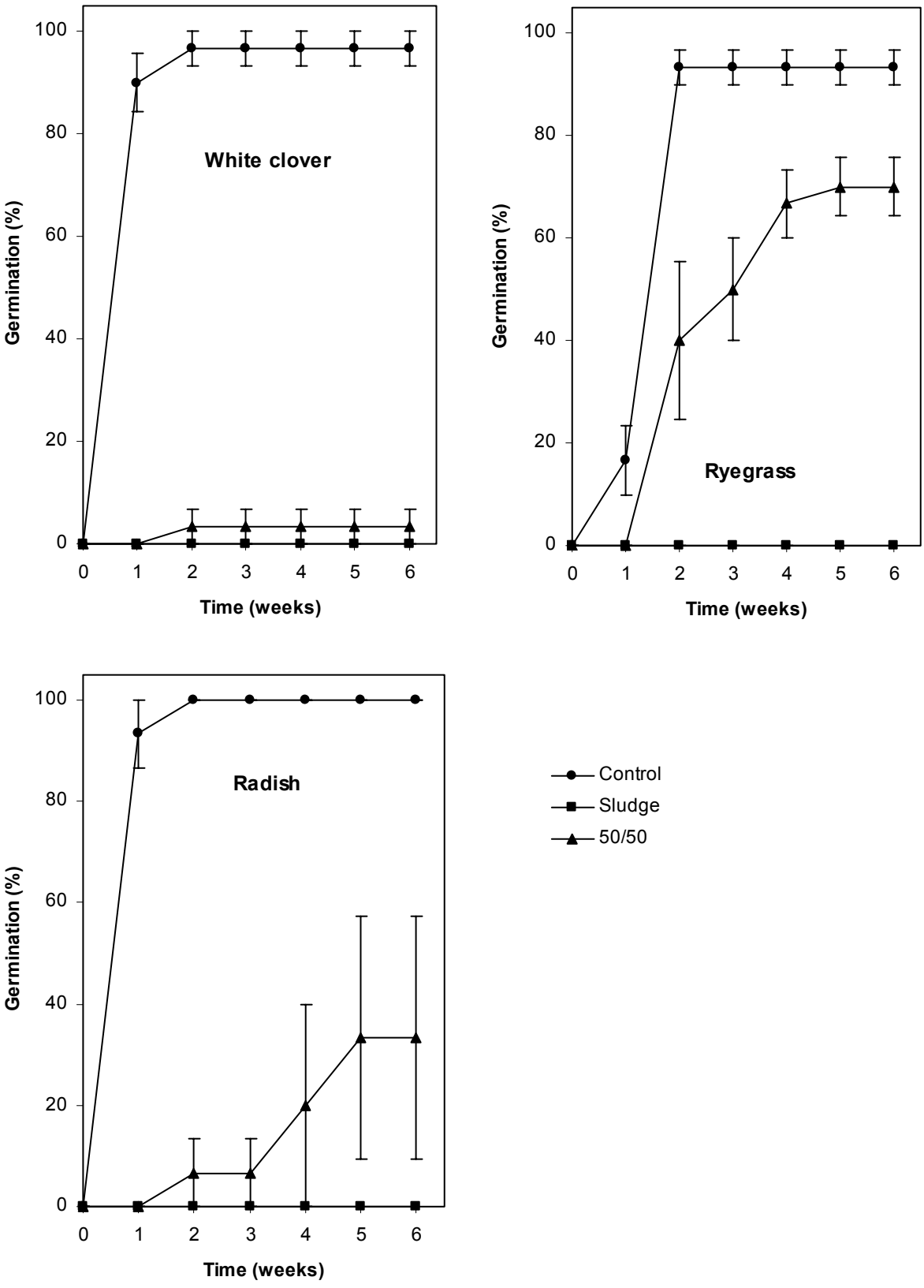
Substrate	Net-N mineralised (% of i-TN)
Casein	91.0 (1.63) ab
Casein + 10 ppm diazinon	89.9 (1.54) ab
Casein + 100 ppm diazinon	88.0 (1.56) b
Casein + 1,000 ppm diazinon	88.0 (0.52) b
Casein + 10 ppm cypermethrin	93.1 (2.06) a
Casein + 100 ppm cypermethrin	90.4 (2.63) ab
Casein + 1,000 ppm cypermethrin	94.5 (0.89) a
Casein + 10 ppm diazinon + 10 ppm cypermethrin	90.1 (1.67) ab
Casein + 100 ppm diazinon + 100 ppm cypermethrin	90.2 (1.92) ab
Casein + 1,000 ppm diazinon + 1,000 ppm cypermethrin	90.5 (1.15) ab

Note: microcosms were incubated at 37°C for 30 days. Numbers in brackets are the standard errors of the means, n=5. Substrates with the same letter are not significantly different (least significant difference, α=0.05).

4.3.8. PHYTOTOXICITY OF SIROLAN CF SLUDGE

Sirolan CF sludge inhibited seed germination and subsequent growth of radish, white clover, and ryegrass in a glasshouse assay (Figure 4–10 and Table 4-12). Germination was greater than 90% for all controls. There was no germination of white clover in sludge and only 3% germination in a 50/50 mixture of sludge and potting mix. Ryegrass seed also did not germinate in sludge, and in the 50/50 mixture 70% germination was achieved after six weeks, although germination took longer than in potting mix. Likewise, there was no radish germination in sludge and poor germination (33%) in the mixture of sludge and potting mix. The seeds that did not germinate had not absorbed water and had not increased in size. The total shoot biomass produced by ryegrass in the mixture of sludge and potting mix was only 29% of that of the controls. Radishes (as a root crop) did not develop even in the case of the controls, presumably due to bad seed, therefore no data are presented here. The sludge, and also the mixture of sludge and potting mix, was observed to have a hard surface, almost like concrete, after 2 weeks. All pots containing sludge had a band of white fungal growth below the surface of the sludge.

Figure 4–10. Germination of white clover, ryegrass and radish in woolscour sludge.



Note: bars represent standard errors of the means, n=3.

Table 4-12. Effect of sludge on ryegrass and white clover shoot biomass production over six weeks.

	Oven dry shoot biomass (mg)	
Treatment	Ryegrass	White clover
Control (potting mix)	109 (27.7)	73 (14.0)
Sludge	0	0
50/50 potting mix/sludge	32 (5.5)	0.3 (0.3)

Note: numbers in brackets are the standard errors of the means, n=3.

Radish seeds did not germinate in undiluted sludge, in sludge that had any volatile components removed by air drying, or when the sludge was free of volatile components and wool grease (removed by Soxhlet extraction). In potting mix (the control), 87% germination was observed after 6 days. It was very difficult to rehydrate the dirt fraction of the sludge after Soxhlet extraction and subsequent oven drying; water tended to bead on the surface and was absorbed very slowly. Radish germination was not affected by solutions of PAM on filter paper soaked with distilled water or PAM solutions at up to 2 g PAM L^{-1}. Minimum germination was 93% after 7 days.

4.3.9. Microbial Counts and Activity in Sirolan CF Sludge

Numbers of culturable heterotrophic bacteria and fungi in sludge samples collected from the Ashburton and Kaputone Woolscours were very low compared to typical values for soil and were highly variable on a daily basis (Table 4-13). Only two of the five samples from Ashburton Woolscour contained culturable fungi, and none contained thermophilic fungal species. The sample collected on Friday supported no microbial growth. Mesophilic bacterial numbers in Kaputone Woolscour sludge without anaerobic treatment were consistent, and all but one sample contained thermophilic species of the same order of magnitude. Three of the samples contained culturable fungi, two of which were enumerated at 30ºC and the third at 50ºC. Samples taken from Kaputone Woolscour with the anaerobic treatment stage in place showed consistent bacterial numbers at both mesophilic and thermophilic temperatures, with very low numbers of fungi observed. Only one sample contained culturable thermophilic fungi. Note that plate counts give a conservative estimate of total numbers, due to unculturable microorganisms. Control plates showed no microbial growth, indicating that the media was free of contamination.

Microbial activity in sludge, in sawdust (the bulking agent to be used in composting), and in a mixture of sludge and sawdust (90% sludge and 10% sawdust w/w – the intended ratio for composting) was determined by measuring the basal respiration and the substrate-induced respiration (Table 4-14). Respiration was induced by the presence of a readily degradable carbon source, glucose, added at 0.5% or 2.0% of the dry weight of substrate. Basal respiration varied widely between the five sludge samples and

between the sludge samples co-incubated with sawdust. There was little variation between the five sawdust sub-samples. The sludge samples taken on Wednesday and Friday showed a small response to the added glucose, with and without co-incubation with sawdust. The sawdust sub-samples did not differ markedly in their response to the input of glucose.

Table 4-13. Numbers of heterotrophic bacteria and fungi isolated from Sirolan CF sludge samples.

		CFU g^{-1} oven dry sludge			
		Mesophilic (30ºC)		Thermophilic (50ºC)	
Woolscour	Day	Bacteria	Fungi	Bacteria	Fungi
Ashburton (anaerobic treatment)	Monday	$6.2x10^4$	$2.1x10^2$	0	0
	Tuesday	$9.0x10^5$	0	$4.0x10^4$	0
	Wednesday	$1.3x10^6$	0	$2.3x10^5$	0
	Thursday	$1.1x10^6$	$2.1x10^2$	$1.1x10^6$	0
	Friday	0	0	0	0
Kaputone (no anaerobic treatment)	Monday	$3.8x10^5$	0	0	$2.1x10^2$
	Tuesday	$1.2x10^5$	$1.7x10^2$	$1.0x10^5$	0
	Thursday	$4.5x10^5$	$2.3x10^2$	$5.4x10^5$	0
	Friday	$2.6x10^5$	0	$2.0x10^5$	0
Kaputone (anaerobic treatment)	Monday	$9.5x10^5$	76	$8.6x10^4$	0
	Tuesday	$9.2x10^5$	69	$1.2x10^5$	23
	Wednesday	$3.5x10^5$	20	$3.9x10^4$	0
	Thursday	$3.1x10^5$	$1.2x10^2$	$1.4x10^5$	0
	Friday	$5.6x10^4$	68	$7.9x10^4$	0

Note: a typical value for soil would be $2x10^7$ CFU g^{-1} (Greenfield, personal communication). CFU = colony-forming units.

Table 4-14. Microbial activity in Sirolan CF sludge from the Ashburton Woolscour and sawdust as measured by substrate-induced respiration.

	Respiration (μg CO_2-C h^{-1} g^{-1} over 3 h incubation)			Efficiency (SIR/BR)	
Sample	BR	SIR-0.5%	SIR-2.0%	SIR-0.5%	SIR-2.0%
Monday sludge	34.88	21.89	19.84	0.63	0.57
Tuesday sludge	21.55	21.20	18.13	0.98	0.84
Wednesday sludge	1.71	2.39	1.71	1.40	1.00
Thursday sludge	1.03	0.68	0.68	0.67	0.67
Friday sludge	0.34	2.05	0.68	6.00	2.00
Monday + Sawdust	25.31	24.62	4.79	0.97	0.19
Tuesday + Sawdust	19.84	18.47	13.00	0.93	0.66
Wednesday + Sawdust	2.05	2.05	2.74	1.00	1.33
Thursday + Sawdust	2.05	0.68	0.68	0.33	0.33
Friday + Sawdust	1.37	1.71	1.37	1.25	1.00
Sawdust 1	18.47	19.84	17.10	1.07	0.93
Sawdust 2	17.78	19.15	19.84	1.08	1.12
Sawdust 3	16.42	19.15	19.15	1.17	1.17
Sawdust 4	12.31	14.36	17.78	1.17	1.44
Sawdust 5	16.42	17.78	19.15	1.08	1.17

Note: BR = basal respiration, SIR = substrate-induced respiration (glucose added at 0.5 and 2.0% w/w basis).

Sludge treatment for samples collected from the Kaputone Woolscour had no effect ($p>0.05$) on basal respiration (Table 4-15), the averages being 18 and 11 μg CO_2–C h^{-1} g^{-1} over 3 h for no anaerobic and anaerobic treatment, respectively, compared to 12 μg CO_2–C h^{-1} g^{-1} for Ashburton Woolscour samples (Table 4-14). As for the Ashburton samples, there was considerable variation in basal respiration rates. Only three samples showed a definite response to the added glucose in terms of an increased respiration rate, being the aerobic sample collected on Monday (at both the 0.5 and 2.0% glucose levels, although levels of respiration were very low in all cases) and anaerobic samples collected on Tuesday and Friday.

Table 4-15. Microbial activity in Sirolan CF Sludge from the Kaputone Woolscour as measured by substrate-induced respiration.

		Respiration (μg CO_2-C h^{-1} g^{-1} over 3 h incubation)			Efficiency (SIR/BR)	
Treatment	Sample	BR	SIR-0.5%	SIR-2.0%	SIR-0.5%	SIR-2.0%
No anaerobic treatment	Monday	0.23	0.80	0.63	3.43	2.71
	Tuesday	19.21	19.01	13.13	0.99	0.68
	Wednesday	18.35	15.32	9.97	0.84	0.54
	Thursday	22.73	15.12	12.80	0.67	0.56
	Friday	26.72	27.82	9.61	1.04	0.36
Anaerobic treatment	Monday	5.74	5.74	4.83	1.00	0.84
	Tuesday	9.47	25.11	27.53	2.65	2.91
	Wednesday	25.15	15.24	16.82	0.61	0.67
	Thursday	6.98	8.49	3.76	1.22	0.54
	Friday	5.77	7.76	8.43	1.34	1.46

Note: BR = basal respiration, SIR = substrate-induced respiration (glucose added at 0.5 and 2.0% w/w basis).

4.4. DISCUSSION

4.4.1. CHEMICAL CHARACTERISATION OF WOOLSCOUR WASTES

In terms of effluent treatment at woolscours, the quality of the sludge produced is only a secondary concern, with the quality of the centrate (liquid fraction) to CFB for further biological treatment being of paramount importance. Centrate quality is determined with a turbidity sensor. This view of the effluent treatment process may impact negatively on the composting potential of woolscour sludge, the effect of which must be thoroughly assessed before sludge is composted. In this section, the characterisation of Sirolan CF sludge will be discussed before the fibrous wastes, reflecting the priorities of this project.

Despite the woolscour sludge being produced from a single process (aqueous scouring) utilising a single material (raw wool), considerable variation in the composition of the sludge was observed. Sludge pH depends on the pH at which Sirolan CF is run, which is determined by optimum flocculation. The anaerobic stage prior to Sirolan CF affects the pH of the sludge, as shown by the difference in sludge pH

between the Fairlie and Ashburton woolscours (Table 4-2). This anaerobic stage aids natural (biological) flocculation processes, thus minimising acid dosage and therefore producing a sludge with a more neutral pH.

Moisture content is dependent on the extent to which flocculation is occurring (and the flocs not being destroyed in the decanter centrifuge). With a moisture content of about 50%, the sludge is relatively dry, which reduces the need for the addition of bulking agents that are often used to bring the moisture content and bulk density into the range acceptable for composting, which keeps the overall volume of material down (Spinosa *et al.*, 1994; Lowe and Buckmaster, 1995). This woolscour sludge had a solids content greater than most other industry sludges described in the literature. For example, dewatering brewery sludge using a flocculant and decanter centrifuge produced sludge with a maximum solids content of 25%, at double the recommended dose of flocculant (Stocks *et al.*, 1999). Sludges produced from pulp and paper industry wastewaters have a solids content ranging from 25 to 60% (Jackson and Line, 1997a; Jackson and Line, 1997b; Sesay *et al.*, 1997; Rantala *et al.*, 1999). Dewatered sewage sludge may have a solids content of between 15 and 20% (Wong *et al.*, 1997; Fang and Wong, 1999).

Variation in the TN of the sludge has implications for composting in terms of the calculation of a suitable initial C:N ratio; a ratio of 25-40:1 is usually considered optimal (Anderson, 1990). Almost 50% of the woolscour sludge TN was in the α-amino acid form and would be expected to be readily decomposed; the proteins casein and haemoglobin (both of which are dominated by α-amino acids) mineralised 90 and 81% of the i-TN over 30 days aerobic incubation at 37°C, respectively (Figure 4–6). As stated in Section 3.4.1 (p.78), the hydrolysable but unidentified N (HUN) fraction is thought to consist of non-α-amino acid N, such as that contained in proline, hydroxyproline and arginine, and N contained in remnants of the hydrolysis procedure. The HUN fraction of sludge (28%) is remarkably similar to the proline and hydroxyproline content of keratin (20-30% of keratin TN).

Levels of heavy metals (Table 4-2) and inorganic elements (Table 4-3) found in the sludge would not limit its use as a substrate for composting, even with the high levels of zinc (up to 834 mg kg^{-1}) found in the Ashburton Woolscour sludge. The source(s) of the zinc could be impurities in fertilisers applied to grazing land, faeces entrained in the dirty wool, from the application of pesticides, and from corrosion of metals (Kiekens, 1995). Although not applicable to the limits set for biosolids in New Zealand (New Zealand Water and Wastes Association, 2003), all waste streams analysed met the grade B ("restricted use") and the more stringent grade A ("unrestricted use") limits for all heavy metals, except for the sludge from Ashburton, which met the 1,250 mg kg^{-1} grade B but not the 600 mg kg^{-1} grade A limit for zinc. International limits for zinc in composts ranges from 150 to 2,800 mg kg^{-1} dry weight (Haug, 1993). Zinc is essential for plants and animals and not usually toxic to even sensitive crops (Epstein, 1997). Adam

(2003) showed that the decomposition of casein, as measured by net-N mineralisation in soil-based microcosms over 60 days at 20ºC, was not affected when 50 mg casein was co-incubated with 50 mg ash from Christchurch City Council biosolids. However, when decomposition was measured by CO_2 evolution, although there was no difference in evolution rates after 10 and 30 days, a significant decrease from 92 to 86% after 60 days was found As the biosolids used were reported to have an average zinc content of 1,479 mg kg^{-1} (levels of other heavy metals were not given), which is well above that of woolscour sludge, it suggests nutrient cycling is unlikely to be negatively affected by sludge application, nor should the sludge be deleterious to composting processes. The distribution of inorganic elements in the sludge was very similar to that typically found in soil (Williamson, 1998), which is not surprising considering the origin of most of these elements is soil particles that become entrained in the fleece as the sheep grazes. Sulphur from the use of sulphuric acid was shown to partition into the suint and not the sludge (Section 3.4.1 p.78). Products containing the sludge must be analysed for their heavy metal content, as these components will accumulate during composting due to the decomposition of organic matter (Gomez, 1998).

The effect heavy metals have on soil microorganisms was summarised by Wuertz and Mergeay (1997). Heavy metals can affect the abundance and diversity of microbes in the soil environment, with fungi more tolerant than bacteria, and gram negative and high-GC (guanine and cytosine) gram positive bacteria more resistant than low-GC gram positive bacteria. Heavy metals can affect important microbial processes in the soil, such as the decomposition of litter and xenobiotic compounds, soil respiration, the nitrogen cycle (both positively and negatively), specific and general enzyme activities, and the effect of mycorrhizal associations on their host plants. Microbes can adapt to heavy metals in the soil environment through intrinsic properties, such as the structure of the cell wall, extracellular polymeric substances, and binding/precipitation of metals inside or outside the cell, or through mechanisms developed after exposure to the metal, such as active efflux, methylation, reduction and oxidation, alkylation and dealkylation, and intracellular compartmentalisation and sequestration. Resistance to many heavy metals is often conferred by plasmids.

On a dry weight basis, the average grease content of sludge from the Fairlie Woolscour, where mainly crossbred wool was scoured, was 28%, compared to 38% for sludge from the Ashburton Woolscour, where merino wool was scoured (Table 4-2). The grease content of the sludge will depend on the type of wool scoured, since the grease content of the fleece generally increases as fibre diameter decreases (Truter, 1956). This may mean that the time required for composting will not be consistent on a day to day basis at a scour and will differ between scours, which will be especially true if the sludge is composted using static piles or windrows, where there is little opportunity for the mixing of sludge batches from different days. While commercial scale composting is not widely practiced in New Zealand

yet, the example from the United States where approximately 90% of composting facilities use the static pile approach and the remainder use windrows (Gerba, 2000) may suggest that, without significant research and development input, New Zealand may focus on static pile methods. These methods are unlikely to promote effective and efficient composting of woolscour wastes. Wool grease has a high C:N ratio, which may limit biotic degradation. Detergent residues will be contained in the grease fraction of woolscour sludge. Alcohol ethoxylate-type detergents are thought to degrade faster than nonylphenol ethoxylates (Jones and Westmoreland, 1998), but are more expensive and are not as good with fine wools (personal communication, Graeme Wood, ANDAR Holdings Ltd.). All these contributing factors will affect the decomposition and nutrient cycling dynamics of the sludge and add to the biological variability, making it necessary to analyse the wastes from scours on an individual basis.

A comparison of the composition of sludge utilised in this study to that of a previous study (Williamson *et al.*, 2000), where woolscour sludge was produced by crude clarification of the effluent, allows the effect of technology development to be assessed. Major differences in sludge properties between studies include the pH (3.6-5.1 compared to 7.0) and TN (1.8-2.1% compared to 4.5%, on a dry weight basis) for the current study and that by Williamson *et al*. (2000), respectively. The pH of the sludge utilised in this study was lower due to the use of sulphuric acid in the flocculation process, and the TN was lower since wool fibre, which contains approximately 18% N on an elemental basis (Truter, 1956), was absent from the sludge. As identified by Williamson *et al*. (2000), more efficient effluent treatment systems will transfer more material, such as grease, pesticides, and heavy metals, into the sludge, possibly to its detriment. Treating the pesticide residues in the sludge phase is considered easier than in the wastewater (Russell, 1996c).

In New Zealand, approximately 3,300 t of active ingredients (pesticidal compounds in overall products) are currently used in the agriculture, horticulture and forestry sectors, of which 8% are insecticides and 25% are used in pastoral agriculture (Cameron *et al.*, 2002). The fate of pesticide residues during scouring has not been studied to date. Residues may simply partition into the quality grease recovered for refinement and the grease found in sludge (Figure 1–8 p.16), or may undergo degradation during scouring, either by biological or physical/chemical processes. The pesticides examined in this thesis, cypermethrin, diazinon, and propetamphos, are slightly to moderately toxic (Table 4-16), based on the likely acute toxicity to humans, potential for eye or skin damage to applicators, ecological effects or potential to contaminate ground or surface water. Diazinon is contained in products including Topclip 40, Diazinon 40 and Flystrike powder, propetamphos in Maggo, Seraphos, and Seraphos 500, and cypermethrin in Cypercare, Flypel and Banish. Pesticide effects on decomposition are further discussed in Section 4.4.3.

Based on a daily sludge production of 10 t (fresh weight), the total amounts of sludge components were calculated based on average values for all data collected from the Fairlie Woolscour in Timaru (Table 4-17). The production of sludge includes a large amount of organic matter, which includes a significant quantity of wool grease, that could be returned to the land from which it came rather than "disappearing" into landfill.

Table 4-16. Properties of diazinon, propetamphos, and cypermethrin pesticides.

Property	Diazinon	Propetamphos	Cypermethrin
Chemical class	Organophosphate	Organophosphate	Synthetic pyrethroid
EPA toxicity class	Moderately toxic Slightly toxic	Moderately toxic	Moderately toxic Slightly toxic
Water solubility (mg L^{-1})	40-60 (slightly)	110 (soluble)	0.004-0.01 (insoluble)
Solvent solubility(mg L^{-1})	> 10,000 (very)	> 10,000 (very)	> 10,000 (very)
Toxicological effects			
Acute	Varies with formulation and species	Oral – moderate Dermal – slightly to practically nontoxic Inhalation – slightly toxic	Dermal – moderate Ingestion – moderate Oral – variable
Chronic	Data inconclusive Not considered carcinogenic	No repoductive, teratogenic, mutagenic, or carcinogenic effects Affects nervous system	No reproductive, teratogenic, or mutagenic effects Possible carcinogen Toxic to central nervous system
Ecological effects			
Birds	Very highly toxic Highly toxic	Moderately toxic	Practically nontoxic
Aquatic organisms	Highly toxic	Highly toxic	Very highly toxic
Non-target species	Highly toxic to bees	No data	Highly toxic to bees
Breakdown			
In soil and groundwater	Low persistence in soil May contaminate groundwater	No data	Moderate persistence in soils Photodegrades rapidly Undergoes aerobic microbial degradation Not water soluble
In water	Low persistence at low pH, high persistence at neutral	Rapid at extreme pH or in presence of sunlight.	Moderate persistence
In vegetation	Rapid	No data	Fast

From Robinson (1993), EXTOXNET (1996), Kamrin (1997) and Robinson (1999).

Any variation in the composition of the two fibrous waste streams would depend on the source and type of the wool and the ratio of wool to non-wool components (see Figure 1–10 p.18). In the case of opener waste, this refers to wool and dirt/seeds, and in the case of scoured wool cleaner waste, wool fibre/dust and seeds. Moisture, pH and TN were very consistent (Table 4-2). The higher TN value for opener waste

from the Fairlie Woolscour compared to that from Ashburton suggests a higher dirt fraction in the dirty wool received at Ashburton. In fact, TN could be used as a measure of the non-wool component since TN values for wool (18% (Truter, 1956)) and soil (see Appendix Table 8-4 p.197) are very different. The grease content of the opener waste depends on the type of wool received. Levels of pesticide residues depends entirely on the source of the wool received by the scours. As scoured wool cleaner waste has been produced by the scouring process, grease levels should be very low and therefore will have a biological decomposition profile different from non-scoured wool, such as opener waste or wool on a sheep that dies in the field.

Table 4-17. Amounts of sludge components produced each day by a typical New Zealand woolscour.

Component	Amount (kg)	Component	Amount (kg)
Water	4,700	Calcium (Ca)	42.2
Solids	5,300	Sodium (Na)	80.5
Organic Matter	3,498	Potassium (K)	128.8
Inorganic Matter	1,802	Phosphorus (P)	6.1
Grease	1,643	Sulphur (S)	2.5
Total Nitrogen	117	Copper (Cu)	0.048
Diazinon + Propetamphos	0.6	Chromium (Cr)	0.058
Silicon (Si)	1,129	Nickel (Ni)	0.068
Titanium (Ti)	15.1	Zinc (Zn)	0.809
Aluminium (Al)	272.1	Cadmium (Cd)	0.006
Iron (Fe)	98.4	Lead (Pb)	0.050
Manganese (Mn)	1.4	Arsenic (As)	0.017
Magnesium (Mg)	25.8		

Both fibrous waste streams contained high numbers of seeds, with numbers being highly variable, again depending on the relative amounts of wool to non-wool fractions (Table 4-4). Rates of germination from seeds contained in opener waste from the Ashburton Woolscour suggest that, should the waste stream be composted with the sludge, there is a significant number of viable seeds that the composting process must destroy for the product to meet criteria for propagule destruction. These numbers would have been an underestimate of total viable seeds, which includes seeds that germinate and those that did not germinate but were respiring (Larney and Blackshaw, 2003). Respiration could be detected by a tetrazolium test, where seeds are placed in a petri dish containing filter paper moistened with a 1% tetrazolium solution. Respiration is shown by red staining at the growing point.

4.4.2. THE DECOMPOSITION OF WOOLSCOUR WASTES

Before the composting of solid woolscour waste streams is attempted, an analysis of the rate of decomposition, and variation within, must first be assessed. In this section, the variation in rate of

decomposition of individual woolscour wastes (sludge, opener waste, and scoured wool cleaner waste) will be discussed first, followed by the composting profiles of the wastes and mixtures thereof.

Sirolan CF sludge was found to be highly variable in its rate of decomposition, with a range of 0.8 to 27.8% of the i-TN mineralised over 30 days (Table 4-5; Table 4-6; Table 4-7). Sources of variability would include the type of wool being scoured (influencing the fibre diameter and the grease content), the source of that wool (influencing the non-wool component and the levels of pesticides applied), the operation of the scour (influencing operating parameters such as the rate of detergent use), and the timing of cleaning procedures to remove accumulated material from scour bowls. Material cleaned from the machines after shutdown would have been exposed longer to degradation. Sludge was produced from the scouring of cross-bred, half-bred and slipe wools, and mixtures thereof, but there was no correlation between decomposition and wool type. The minimum and maximum decomposition were both obtained from the scouring of the same wool type (cross-bred). Of all the properties of the feed used to produce sludge and of the sludge itself, the biological oxygen demand of the feed correlated best with the rate of decomposition of a set of five sludge samples (Table 4-7; Figure 4–1). Previous research by Savage (2002) on the biological treatment of the liquid phase separated from the sludge showed that the waste stream was toxic to the microorganisms used to treat it, i.e., results showed substrate-inhibition kinetics. It is possible that the same was true for the sludge.

The wool grease content of the sludge may limit the rate of decomposition due to the inhibition of oxygen transfer. From previous trials conducted in Australia, however, it was suggested that the grease content of sludge was good for composting due to its calorific value (personal communication, Brian Jeffrey, Geelong Wool Combing Ltd.). This would only be true, however, if N deficiencies in the grease were corrected by the presence of a readily-available N source. Variability in woolscour sludge in terms of substrate quality for microbial activity has implications for the composting of this waste stream. A consistent final material must be produced for the compost to gain commercial acceptance (Paul and Clark, 1996), and this may be difficult to achieve with material of such potentially variable composition.

Variation in the biodegradability of the fibrous wastes was also detected (Table 4-5; Table 4-6), although the range was less than that found for the sludge. Proteins are readily decomposed by soil organisms via proteolytic enzymes that hydrolyse the peptide links between amino acids (Paul and Clark, 1996). Keratin is quite resistant to attack by normal proteolytic enzymes and chemical and physical means due to its super-coiled helical structure, high degree of cross-linking by disulphide bonds, hydrogen bonds, and hydrophobic interactions, and its insolubility in water (Noval and Nickerson, 1959; Mathison, 1964). Treatments such as autoclaving, ball milling, and microbial action make the molecule more susceptible to proteolytic enzymes. Wool quality will also undergo seasonal variation. For example, wool from pregnant

ewes shorn in summer will break more easily due to irregular growth of the fibre during lactation. In terms of mineral N, up to 10% of the N is contained between keratinised cells (in the matrix) and becomes biologically available as the fibre disintegrates, whereas the N within the cells is unavailable. Variation in the biodegradability of the fibrous wastes may be explained by the degree of physical damage to the wool fibres, as well as the amount and nature of the non-wool component in the case of opener waste. The use of keratinophilic species such as *Streptomyces fradiae* (Noval and Nickerson, 1959; Katuzewska *et al.*, 1991) and *Thermoactinomyces candidus* (Ignatova *et al.*, 1999) may aid the decomposition of the fibrous wastes, providing that conditions for their growth and proliferation are suitable.

The form of N in the woolscour sludge may explain the slow decomposition of this material. With almost 50% of the TN of the sludge in the α-amino acid form (Table 4-2), and wool being composed of more than 90% protein (Wools of New Zealand, 1997), the N probably originated from wool proteins (keratin). This is discussed further in Section 4.4.3.

Slipe wool for scouring will contain depilatory (sodium sulphide and lime) and damaged fibres and, due to the higher yield and absence of suint, will require the addition of about 50% more detergent than usual (Stewart, 1988). If the detergent (surfactant) content of sludge inhibited its decomposition, sludge produced from slipe wool would be expected to decompose at a slower rate than that produced from the processing of half- or cross-bred wools. Although a limited number of sludge samples were used for analysis of the variation in the rate in decomposition, no such link was observed. Of the sets of scoured wool cleaner waste samples collected for daily and weekly variation analysis, the sample that decomposed at the highest rate from each set (Monday and week four, respectively) was from days when slipe wool was scoured. This suggests that the presence of damaged fibres increased the biodegradability of the waste stream.

The effect of detergents on the decomposition of woolscour sludge was not specifically investigated during this work. Although several different detergents are used in the woolscouring industry, surfactants all have a similar two-component form. Surfactants are amphiphilic structures; the polyethoxylate chain is hydrophilic and the alkylphenol is hydrophobic (Thiele *et al.*, 1997). Alkylphenol ethoxylates are one of the main non-ionic surfactant groups produced since the 1950s and, in recent years, have been the most intensively discussed of all the surfactant groups due to the possible threat they pose to the environment (Jonkers *et al.*, 2003). Despite this, production is increasing in some areas such as Japan (Maruyama *et al.*, 2000), presumably due to their good performance and low production costs (Jonkers *et al.*, 2001). Although alkylphenol ethoxylates are generally believed to biodegrade beginning with shortening of the ethoxylate chain (Thiele *et al.*, 1997), some researchers have suggested that, under aerobic conditions,

degradation begins with ω-carboxylation of the ethoxylate chains, resulting in short-chain carboxylated ethylene oxides. The nonyl chain is oxidised at the same time, resulting in metabolites with both a carboxylated ethoxylate and an alkyl chain of varying lengths (Jonkers *et al.*, 2001). Thiele *et al*. (1997) provides a review of the behaviour of alkylphenol ethoxylates.

In terms of resource quality, using the average decomposition rate from the variability studies, the woolscour waste streams could be ordered: scoured wool cleaner waste > opener waste >> woolscour sludge.

Direct comparisons of rates of net-N mineralisation between the sludge used in this study and that used in previous research (Williamson *et al.*, 2000) are not possible since identical incubation conditions (time, temperature, and moisture content) were not employed, due to the different objectives of the two studies (land application compared to composting). However, since the moisture content was shown to have no effect on the rate of decomposition in the previous study and there was a linear relationship between incubation temperature and the rate of net-N mineralisation (Williamson *et al.*, 2000), a rate of 0.54% i-TN per day mineralised at 37°C could be calculated from their study. The mean rate of 6.8% i-TN mineralised over 30 days at 37°C in this study equates to 0.23% i-TN per day mineralised. However, both these calculations assume that decomposition proceeded in a linear fashion over time (30 days), which, while not necessarily true, permits a general comparison between these studies. It can be tentatively suggested, therefore, that the chemically flocculated woolscour sludge examined in this study decomposed at approximately half the rate of the sludge produced by clarification in the mid 1990s.

Composting profiles for woolscour sludge showed that, although rates of decomposition were low at all incubation temperatures, there was a significant effect of increasing temperature and time (Table 4-8; Figure 4–2). For the composting of this sludge, temperatures in excess of 50ºC should be aimed for. This is also true for opener waste, although there was no significant increase in decomposition from 4 to 8 days. However, incubation temperature had no effect on mineral N release from scoured wool cleaner waste, or from either fibrous waste when measured by weight loss (Figure 4–3). There was some lack of agreement between the two methods used to assess the decomposition of the fibrous wastes. Although both are valid methods for assessing decomposition, weight loss may be more relevant when considering the composting of these materials, where a weight or volume reduction figure is useful. Although analysis of variance showed a significant effect of time on the decomposition of the fibrous wastes in general, there appears to be a levelling out from 4 to 8 days incubation. This suggests there may be an easily available N pool that is released quickly, followed by the slow release of N from wool fibres, as discussed in the previous section.

The effect of temperature on the rate of decomposition of sludge and opener waste could be due to the wool grease content. Since wool grease melts at 35-40ºC (Truter, 1956), temperatures in excess of this will melt the grease fraction and change the physical properties of the wastes, allowing microorganisms to attack the substrate with a higher surface area to volume ratio.

The increase in the rate of decomposition when sludge was co-incubated with either fibrous waste stream (Figure 4–4) suggests that composting of the sludge with other substrates will give much improved performance. This enhancement was observed when each substrate contributed equal amounts of TN to the microcosm. On a dry weight basis, this equated to 560 g opener waste or 245 g scoured wool cleaner waste to 1,000 g sludge. The resource quality of the overall substrate mixture was improved, either chemically or physically, as described previously from Swift *et al*. (1979). From the chemical properties of the waste streams (Table 4-2; Table 4-3); the fibrous wastes did not supply any element not present in the sludge, except for sulphur. Nutrient deficiencies in woolscour sludge are discussed further in Section 4.4.3. The fibrous wastes may have improved the physical properties of the overall mixture, by having a much higher surface area to volume ratio compared to the sludge. The enhancement in decomposition when the two fibrous wastes were co-incubated suggested that, overall, a microbial population with a broader metabolism was provided for the decomposition of the waste mixtures. Differences in interaction effects between weight loss (Figure 4–3) and net-N mineralisation methods when opener waste and scoured wool cleaner waste were co-incubated may be due to the different ratios of the two components used in each experiment. In the weight loss experiment, each substrate was added at equal amounts on an oven dry weight basis. In the net-N mineralisation experiment, the ratio was 440 g scoured wool cleaner waste to 1,000 g opener waste on a dry weight basis.

4.4.3. CONSTRAINTS ON SLUDGE DECOMPOSITION

Woolscour sludge contains a mixture of compounds, including detergent, flocculant (polyacrylamide), wool grease, and pesticides, all of which may impact on the decomposition of the sludge. For complex substrates, such as woolscour sludge, the overall decomposition rate is a reflection of the rate of decomposition of the individual fractions of the substrate (Swift *et al.*, 1979). Resource quality is continually changing as decomposition proceeds, by regulation of further decomposition in a feed-back manner. Substrates include different groups of compounds, including: (i) carbon and energy sources; (ii) source of nutrients other than carbon, such as N and P; and (iii) molecules that either inhibit or stimulate decomposition activity (Swift *et al.*, 1979). It is for this reason that the effect of various sludge components on the rate of decomposition must be elucidated.

A faster rate of decomposition for the dirt fraction of woolscour sludge compared to the intact sludge indicated that the wool grease may retard sludge decomposition (Figure 4–5). This is consistent with the results of Williamson *et al*. (2000), who observed a higher rate of net-N mineralisation from the sludge fibre-dirt fraction (37% of the i-TN) compared to the sludge as a whole (9%) over 162 days at 22ºC. Grease could cause both oxygen- and moisture-limited conditions to occur within the sample. It is also a poor substrate, being deficient in nitrogen (C:N ratio of 400:1). However, Williamson *et al*. (2000) also showed that wool grease did not inhibit the decomposition of casein, as measured by net-N mineralisation over 116 days at 22ºC, when mixed at a rate up to 35% grease to casein, w/w. The suggestion was made that the Soxhlet extraction procedure to remove the grease increased the availability of the N contained in the non-solvent extractable fraction to microorganisms. Certainly, conditions of the extraction (petroleum spirit at 60ºC) could be expected to affect the nature of the sample remaining after the extraction.

Simple attempts to select for microorganisms that could increase the rate at which keratin (degreased scoured wool cleaner waste) and woolscour sludge decomposed were unsuccessful. Compared to haemoglobin and casein, keratin decomposed at a much slower rate and there was little change in the mineralisation of TN from 30 to 60 days (Figure 4–6). This keratin decomposition curve shows the importance of looking past 30 days and not just extrapolating initial data. The decomposition curve for sludge (Figure 4–7) showed the same trend as for keratin. Both keratin and sludge contained two pools of N, each differing in their ability to be mineralised.

The aqueous scouring of wool could be expected to cause some damage to the wool fibres, including modification of the outer surface, destruction of disulphide bonds, and breakage of polypeptide chains (Peters, 1967). Scoured wool cleaner waste, being short wool fibre and dust, is damaged keratin that may decompose faster than intact wool. Noval and Nickerson (1959) reported that treatments such as autoclaving and ball milling will denature and physically degrade keratin, as evidenced by a decrease in the cysteine and sulphur content, allowing microorganisms to degrade it that would be otherwise unable to. Extraction with chloroform at room temperature was considered to have negligible effect of keratin. Whether the extraction of grease from scoured wool cleaner waste with petroleum spirit in the Soxhlet apparatus was more harsh is not known. The use of polar solvents, such as ethanol, to extract dirt and grease from wool can increase the susceptibility of wool to chemical digestion, possibly due to the extraction of a fatty acid-protein complex important for the integrity of the keratin structure (Mathison, 1964). Non-polar solvents, such as ether and benzene, do not increase the susceptibility to digestion. Ball milling reduces the cysteine content of wool, thereby denaturing the γ-keratin. Scoured wool cleaner waste has been pre-treated by the scouring process and can therefore be regarded as denatured keratin.

Soil is a reservoir for keratin-decomposing microorganisms (Mukhopadhyay and Chandra, 1992) that could be employed for the decomposition of woolscour wastes. Keratinophilic fungi can be isolated from soil by the keratin-baiting technique (Simpanya and Baxter, 1996). In that study, which investigated soils from Palmerston North in New Zealand, keratinophilic fungi were found to be abundant in soils. Successful inoculation of substrates with keratinophilic species in the laboratory would be much harder to employ at the industrial scale. During in-vessel composting, the inocula may be retained within the composting vessel. Added keratinophilic species must tolerate the temperature and pH profile of the composting mix and compete with indigenous microorganisms for inoculation to be effective. *Trichophyton mentagrophytes* has a proteinase system with a double pH optimum on hide powder at pH 6.5-7.0 and 10, and a single optimum on casein and gelatin at pH 8-9 (Mathison, 1964). Optimum pH for *Microsporum gypseum* proteinase on casein and gelatin is 7.5-8.1. *Trichophyton rubrum* may be capable of proteolytic activity over a wide range of pH in the skin (Mathison, 1964).

Keratinophilic fungi will degrade different keratin substrates, such as human hair, wool, and feathers, at different rates (Muhsin and Hadi, 2002). The inoculation of chicken feathers with *Bacillus licheniformis* and *Streptomyces* spp. was found to increase the rate of degradation during composting, as evidenced by scanning electron microscopy (Ichida *et al.*, 2001). Composting temperatures peaked at 60°C, suggesting that microorganisms were active at thermophilic temperatures. It was suggested that inoculation could improve the efficiency of keratin decomposition and pathogen inactivation. Brady *et al*. (1990) used electron microscopy to show wool fibre degradation.

The addition of C, N or P to woolscour sludge had varying effects on the rate of decomposition (Figure 4–8). It appeared that, initially, the biomass was limited by available nutrients. Results in Section 4.3.9, which are discussed in the next section, showed low levels of microbial activity in the sludge. After 30 days incubation, all nutrient additions decreased mineral N production compared to the unamended control, suggesting that mineral N was incorporated into microbial biomass. However, for N to be incorporated into microbial biomass, other nutrients, such as C and P, must also be available. In this experiment, one nutrient was added at a time so, for example, it is not clear where the C came from when the addition of mineral N resulted in N immobilisation. After 60 days incubation, the biomass was in a better state (either in terms of size or activity) than it was initially and the additions of C and P increased the rate of decomposition. The control showed the same decomposition curve as seen in other experiments (Figure 4–7), being a levelling off in mineral N production from 30 to 60 days, except in this study the production of mineral N was actually less at 60 days than at 30 days. There is a discrepancy in the context of sludge decomposition in that its chemical properties (such as a good C:N ratio) do not match its biological properties (poor rate of decomposition). The use of the ratio of total C to total N

when judging the suitability of a substrate to be treated by composting is therefore limited and any appraisal of a waste stream should include biological aspects.

The decomposition of polyacrylamide (PAM) showed a definite response to increasing temperature, with 25% of the i-TN mineralised after 60 days at 50°C (Figure 4–9). In contrast, using the cationic polyacrylamides Percol 292 and Zetag 7653, Adam (2003) showed a decomposition rate of only 1% of the i-TN mineralised after 30 days in soil-based microcosms at 20ºC. After 60 days, N immobilisation (12% of the i-TN) was observed. CO_2 evolution showed the same trend; after 10 days, more CO_2 was produced from soils amended with PAM than from control (unamended) soils, and after 30 and 60 days, CO_2 evolution from amended soils was below that from control soils. It was suggested by Adam (2003) that, since PAM is used as a soil conditioner, a low decomposition rate (indicating stability) is not surprising. The binding of mineral N by PAM, causing N immobilisation, was discounted and it was therefore suggested that PAM effects a reduction in the activity of soil microorganisms. The different matrices used in the microcosms (sand and soil) would certainly have influenced the results obtained. While the use of soil is more natural than organic matter-free sand, and there would have been different interactions between the PAM and the different matrices, the use of sand means that the added PAM provided all the nutrients for microbial growth, except that provided with the soil inoculum. The effect of temperature on the rate of decomposition may have been due to abiotic decomposition occurring, or the high temperatures altering the structure of the molecule and making it more amenable to microbial decomposition. Therefore, PAM would readily decompose in a composting environment but not in soil, where temperatures would be unlikely to reach 50ºC in New Zealand.

The addition of PAM to chitin, casein, or woolscour sludge, did not affect their rates of decomposition of these materials (Table 4-10), a results in agreement with Adam (2003). While biosolids (dewatered sewage sludge to which PAM was added) decomposed at a slower rate than sewage sludge, as measured by net-N mineralisation and CO_2 evolution over 60 days at 20ºC, the addition of PAM (5 mg Zetag 7653) to sewage sludge (1,000 mg) did not cause a significant reduction in the rate of decomposition as measured by net-N mineralisation (Adam, 2003). It was concluded that the dewatering procedure and not the addition of PAM caused the decrease in biodegradability. This finding was confirmed when 5 mg PAM added to 50 mg casein did not significantly affect the rate of N mineralisation or CO_2 evolution over 60 days at 20ºC. The PAM content of woolscour sludge therefore did not limit the rate of decomposition of the sludge.

Polyacrylamides were developed by the oil industry for use in enhanced oil recovery (King and Noss, 1989), and are now used for a variety of applications in addition to its use as a soil conditioner (Table

4-18). Cationic polyacrylamides are used for flocculation of sewage sludge and other industrial wastes, as well as retention aids in paper industry (Barvenik, 1994).

Polymers of acrylamide are considered non-biodegradable as judged by CO_2-C release, although hydrolysis reactions release N from amide groups, with a rate of biotic and abiotic degradation in soil systems of about 10% per year (King and Noss, 1989; Barvenik, 1994; Grula *et al.*, 1994). The higher rate of decomposition observed in this study was probably due to the higher incubation temperatures used, since the decomposition of PAM during sludge composting was the focus in this study, compared to those referred to above, which investigated soil systems. Cationic polymers, such as the PAM used in this study, have a high affinity for solids (Barvenik, 1994) and PAM should therefore be present entirely in the sludge, unless the flocculation process is not optimal and the centrate (liquid fraction) still contains high amounts of solids. Polymers will become irreversibly bonded if the soil is dried (Seybold, 1994), since the probability that all of the polymer simultaneously detaches from the soil surface, moves away from the surface, and moves into solution, is very small (Nadler and Letey, 1989). PAM is not soluble in petroleum spirit and therefore remained in the dirt fraction after Soxhlet extraction to remove wool grease, which may explain the tacky nature of the dirt fraction after all grease had been removed.

Table 4-18. Industrial uses for anionic polyacrylamides.

Industry	Applications
Mineral and coal processing	Thickening and dewatering of concentrates and tailings; separation of coal fines and clay; purifying aluminium ores (Bayer process); clarification of process steams; dispersants and antiscalants
Petroleum production	Tertiary oil recovery; reservoir profile modification; well cementing; drilling muds
Paper making	Retention aids; dry strength aids (with alum); dispersants; drainage and dewatering aids
Water treating	Clarification, thickening and dewatering of wastewaters and sludges (commonly as flocculant aids to primary coagulants); raw/potable water clarification (flocculant aid); alum sludge dewatering; dispersants and antiscalants; boiler and cooling applications; desalinisation; heavy metals removal (with pH adjustment)
Food processing	Washing fruits and vegetables; clarification of sugar juice and liquor; scale control in sugar production
Miscellaneous applications	Super-absorbers (cross-linked polyacrylamides); chemical grouting; textile additives; friction reduction; adhesives; viscosity enhancement/gelling applications; laboratory applications; cosmetics

From Barvenik (1994).

The acrylamide monomer, which is a neurotoxin that causes behavioural disorders, nervous system damage, and cellular abnormalities (Abdelmagid and Tabatabai, 1982; King and Noss, 1989), may be contained within the flocculant at trace (less than 0.15%) levels. Scour workers must manually transfer the powder from the bags in which it is supplied to a hopper that feeds the mixing system, with no safety

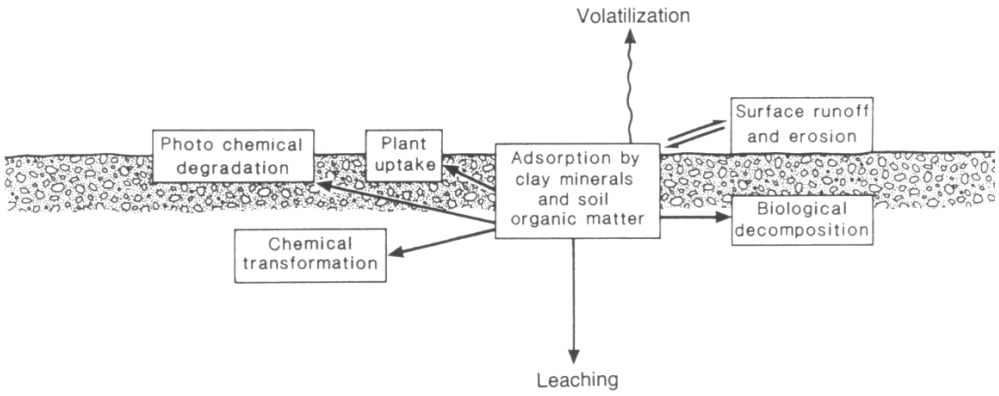
precautions currently recommended or employed. This situation should be remedied. Due to its high solubility in water and its tendency not to be adsorbed by sediments and sludges (Brown *et al.*, 1980; King and Noss, 1989), any acrylamide contained in the flocculant would therefore partition to the centrate and not the sludge. Brown *et al*. (1980), using high performance liquid chromatography and ultraviolet absorption, showed that acrylamide completely degraded over 1 to 31 days in a range of natural and polluted water samples at 25°C when added at rates of 0.5 and 5.0 mg L^{-1}, with degradation occurring generally after a lag period. Little abiotic degradation occurred. Although the concentrations of acrylamide used were very low, they are similar to levels that could be found in the centrate. If the monomer is present at the maximum allowable level in the flocculant (0.15%) and is found exclusively in the centrate, it would be found at a level of 0.35 mg L^{-1}. Any acrylamide would be expected to degrade rapidly during biological treatment of the centrate, where temperatures (30°C) and levels of biological activity are high. Acrylamide has also been observed to degrade (to acrylic acid and ammonia) in soil systems (Abdelmagid and Tabatabai, 1982; Shanker *et al.*, 1990).

The grease fraction of woolscour sludge will contain any pesticide residues originating from the greasy wool being scoured. Diazinon, an organophosphate (OP), and cypermethrin, a synthetic pyrethroid, were shown to have no effect on the rate of decomposition of casein (Table 4-11), which indicated that the pesticide content of woolscour sludge did not limit its rate of decomposition. This also implies that, when present in soil systems, these residues will not inhibit protein decomposition and organic matter turnover.

The fate of pesticides in soil systems is difficult to predict even when information on the pesticide and the receiving soil is available, therefore woolscour sludge should not be applied to land while still containing pesticide residues. Since the 1940s, pesticide use has changed from a situation where non-selective and persistent pesticides used at high concentrations is now one where more selective chemicals are used at lower effective concentrations (Topp *et al.*, 1997). As shown in Figure 4–11, synthetic pesticides applied to soil can be (i) degraded by biotic or abiotic means, (ii) adsorbed by organic matter, clay minerals, and iron and aluminium sesquioxides, (iii) washed into water bodies through leaching and runoff, and (iv) volatilised (Ross, 1989). Their presence may disrupt soil biological processes through their effect on non-target organisms. Pesticide persistence depends on the type of pesticide, the amount and method of application, soil properties, and environmental factors; OP pesticides are classified as non-persistent. Abiotic degradation processes include hydrolysis (acid and/or alkaline), oxidation and reduction reactions, and photodecomposition, catalysed by soil components. Biological degradation proceeds after an adaptation period by a microbial consortia under the influence of soil properties. Microorganisms can also acquire new degradative capabilities through the exchange of plasmids and transposons in soil and water (Topp *et al.*, 1997).

Pesticide adsorption onto soil constituents is influenced by their surface charge and solubility in water, which is in turn influenced by the pH of the soil solution and temperature (Ross, 1989). The sorption of pesticides to the surfaces of minerals and organic matter found in soil affects its ability to be degraded by soil microorganisms, with the extent of adsorption and the rate of desorption affecting its bioavailability (Novak *et al.*, 1995; Morra, 1996). Sorption is via a range of chemical and physical processes and can lead to the formation of a bound (unextractable) fraction and, in time, "aged" residues. Pesticide transport in soil is via leaching, surface runoff/erosion (typically on soil particles rather than in solution), and volatilisation (largely dependent on the vapour pressure of the compound) (Ross, 1989). Most pesticides cause only a temporary impact on the soil system, in terms of its biological population and microbial processes.

Figure 4–11. Fate of pesticides in soil.



From Ross (1989).

An insecticide should not be expected to be toxic to soil microorganisms since they lack the targets for the chemical (Topp *et al.*, 1997). Insecticides applied at normal field rates are generally harmless to the soil microflora (Ross, 1989). OPs are toxic to nematodes and diazinon is more toxic to predaceous soil mites than to other types of mites, which subsequently flourish after the removal of predaceous species. Insecticides are toxic to earthworms, may suppress or enhance levels of soil respiration, and do not appear to inhibit denitrification when applied at normal field rates (Ross, 1989). This scenario may have non-target flow-on effects, however, as the various groups of soil organisms are not independent of each other but form an interdependent system in equilibrium with the environment (Russell, 1973). Nematodes and mites belong to the mesofaunal population, while earthworms belong to the macrofauna (Coleman and Crossley, 1996). Nematodes can be grouped into bacterial feeders, fungal feeders, plant feeders, and predators and omnivores. Many species of mites also feed on fungi, while earthworms play an important role in soil formation, organic litter decomposition, and the redistribution of organic matter in the soil through their burrowing activity and soil ingestion. In terms of nutrient cycling, they regulate bacterial and fungal populations. Although microbes are responsible for litter decomposition, fauna condition litter

and aid microbial actions, and strongly influence the decomposition of more resistant substrates (Coleman and Crossley, 1996). Soil structure may also control decomposition processes by its effect on the grazing intensity of the soil fauna on microbes, due to physical separation of microorganisms and fauna through their occupation of different pore sizes (Hassink *et al.*, 1997).

Ragnarsdottir (2000) suggested that OPs, in general, are relatively soluble in water (10-10,000 ppm), and residues can be transported into water bodies where they undergo hydrolysis, a reaction highly dependent on pH and temperature. Different OP pesticides undergo different abiotic hydrolysis reactions, diazinon undergoing acid hydrolysis (Ross, 1989). Hydrolysis can be catalysed by basic amino acids and amino acid functional groups, as well as copper (II) ions and clay minerals. Residues are sorbed by soil particulate matter by physical means and tends to be irreversible, with desorption inversely related to the soil organic matter content (Ragnarsdottir, 2000). This sorption means that volatilisation does not readily occur, despite the relatively high vapour pressure of OPs. OPs are adsorbed by both clay and organic matter fractions, but show a greater affinity for organic matter in aqueous solution (Ross, 1989). After an acclimatisation period, microbes will degrade OP residues at a rate dependent on the soil microbial biomass (specifically the mass of degraders and not the total microbial biomass) and the concentration of the OP (Ragnarsdottir, 2000). A major product from the microbial hydrolysis of the P-O bond in diazinon is diethyl 2-isopropyl-4-methyl-6-hydroxypyrimidine (IMHP). *Arthrobacter* spp., *Flavobacterium* spp., *Pseudomonas melophtora*, *Trichoderma viride* and *Streptomyces* spp. are known to be involved in the degradation of diazinon. Alloway (1997) reported that the principle metabolites from the decomposition of diazinon are diethyl thiophosphate and diethyl phosphate. It was reported in Ross (1989) that, of 4.9 kg ha^{-1} ^{14}C-labelled diazinon applied to turf in a microcosm study, 47% remained in diazinon, 22% was mineralised to CO_2 , 28% remained in soil as a metabolite, 2% was volatilised, and 1% was leached from the soil (incubation time and soil properties not given). Another reported study showed that diazinon applied to the leaves of bean plants initially decreased microbial numbers followed by an increase in numbers to levels higher than that found initially, due to selective enrichment of one type of bacterium. Repeat exposure to OPs enhances degradation due to the evolution of new metabolic capabilities (Ragnarsdottir, 2000).

From the pesticide data in Table 4-16 and applying the principles from Ragnarsdottir (2000), it can be suggested that diazinon residues in soil will be predominantly adsorbed onto soil particles, where it will degrade rapidly, although the fraction in the soil solution will persist unless the pH is low. A greater fraction of propetamphos will be found in the soil solution and will persist if the pH is neutral. Cypermethrin will not be found in the soil solution but will sorb onto soil particles where it will undergo biotic and abiotic degradation. Any diazinon or cypermethrin residues taken up by plants would be degraded rapidly. The rate and frequency of application, properties of the plant surface, and weather

conditions influence the effect OPs have in plants (Kamrin, 1997). Plants absorb OPs mainly through the roots and translocate residues to other parts of the plant where they do not accumulate.

The fate of pesticides during composting is discussed in Section 5.2.4 (p.157).

4.4.4. PHYTOTOXICITY OF SIROLAN CF SLUDGE

Sirolan CF sludge produced from the woolscouring process did not support the germination (Figure 4–10) and subsequent growth (Table 4-12) of various plant species, indicating that some component, or components, of the sludge were phytotoxic, and therefore necessitating the processing of the sludge into a less toxic form suitable for land application or horticultural use. Plant assays subsequently showed that volatile compounds removed by air drying and the grease content were not responsible for the observed toxicity. Since PAM would not be extracted by petroleum spirit in the Soxhlet apparatus, as it is insoluble in almost all organic solvents (King and Noss, 1989), an observation confirmed in the laboratory, PAM in the dirt fraction was considered to be the phytotoxic component of the sludge. However, radish seeds were shown to germinate in PAM solutions up to 2 g L^{-1}, the concentration used in the effluent treatment process. Adam (2003) suggested that the cationic PAM Zetag 7653 did not have a toxic effect on the germination of radish seeds when added at rates up to 1 g PAM per 100g soil, although seeds did not germinate in areas where the PAM prevented water entering the dry soil. Seeds that did not germinate had not increased in size, an observation that seems to indicate a lack of water uptake by the seeds. Therefore, I conclude that a combination of grease and PAM in the bulk sludge prevented enough water being available to the seeds for germination to occur.

Polyacrylamide applied to soils at various rates to improve the physical properties of the soils has been shown to improve seedling emergence and growth in the case of wheat (Wallace and Wallace, 1986a; Wallace *et al.*, 1986a; Stern *et al.*, 1992), lettuce and cotton (Wallace and Wallace, 1986c; Wallace, 1987; Helalia and Letey, 1989), sweet corn and alfalfa (Cook and Nelson, 1986), soybean (Wallace *et al.*, 1986b), tomato (Wallace and Abouzamzam, 1986; Wallace and Wallace, 1986c; Wallace and Wallace, 1986b; Wallace and Wallace, 1986a; Wallace *et al.*, 1986a; Wallace, 1987; Helalia and Letey, 1989), and grass species (Rubio *et al.*, 1989). In some of these studies, however, PAM was added to improve soils prone to crusting or to soils with poor aggregate stability, so control rates may have been poor compared to a healthy control soil. Reasons for the improvements to seedling emergence and growth have been attributed to the prevention of soil crusting and increased pore space leading to improved soil aeration and water infiltration and retention (Wallace and Wallace, 1990). Of all the above studies where the charge of the PAM used were reported, only one (Wallace and Wallace, 1986b) used cationic PAM. This PAM type

improved seedling emergence and growth compared to the control, but was not as effective as anionic PAM. A slight reduction in seedling emergence was reported for sugar beet grown in a silt loam amended with high MW anionic PAM (Lehrsch *et al.*, 1996) but, with the rate of germination for the control being only 33%, a more drastic reduction may have been masked. In liquid culture, tomato growth was improved by the addition of anionic PAM at 100 mg L^{-1} but decreased by cationic PAM added at the same concentration (Wallace, 1986). The charge and MW of the polyacrylamide used, and its application rate, would certainly influence its effect on plant performance.

4.4.5. MICROBIAL COUNTS AND ACTIVITY IN SIROLAN CF SLUDGE

The impacts of the woolscouring and effluent treatment processes on the numbers and activity of microorganisms in the sludge produced were investigated in order to assess the need for inoculation of sludge with other materials for successful composting to proceed.

Results showed that woolscour sludge typically contained mesophilic microbes at a level an order of magnitude less than that typically found in soil (Table 4-13). As a benchmark, numbers of culturable microorganisms determined recently in soil collected from the University campus were $4.2x10^6$ and $8.3x10^3$ CFU g^{-1} on an oven dry basis for bacteria and fungi, respectively, after 4 days incubation at 30ºC (Kroening, 2000). The scouring of wool at temperatures of 60-65ºC, followed by the addition of 98% sulphuric acid into the effluent to allow flocculation to occur during the Sirolan CF process, would eliminate the growth of many microorganisms and could be expected to select for thermophilic and acid-tolerant (acidophilic) microorganisms, respectively. It was not surprising, therefore, that high numbers of thermophilic bacteria relative to the numbers of mesophilic bacteria were found. It appeared that the anaerobic stage prior to sludge making did not affect the numbers of microorganisms in the resulting sludge. It should be noted that plate counts have limitations in that only culturable microbes able to grow on the one media type used are counted. However, plate count methods are still used in recent studies, including Kay-Shoemake *et al*. (1998a) and Guerin (2001), where the effect of PAM on the soil microbial community and the composting of soil contaminated with pharmaceuticals were studied, respectively, indicating that they still have scientific merit.

Woolscour sludge also contained a very low level of microbial activity (Table 4-14; Table 4-15). The anaerobic stage prior to Sirolan CF did not affect the basal respiration rate of the sludge produced from the effluent. Low microbial activity was probably due to a lack of readily available nutrients to support the microbial biomass, as discussed previously in Section 4.4.3, as well as the low pH. The addition of sawdust to the sludge increased the basal respiration rate, albeit marginally, in some cases, possibly due to

allowing better aeration of the sludge mass. Most sludge samples did not respond to the addition of glucose, a readily available source of C, suggesting that the microbes present were not in an active state. It was very difficult to evenly incorporate the added glucose into the sludge due to its grease content, therefore some of the variation between samples may be explained by differences in the success of this mixing process (although this was due to properties of the sludge itself).

Combining the plate count and respiration results, it could be suggested that inoculation of the sludge (addition of other organic substrates or soil) for successful composting may be required, otherwise there may be a significant lag period before thermophilic temperatures, indicative of a high level of biological activity, are attained. However, no issues with limited biological activity of sludge composting mixtures have been reported in the literature (Bateup *et al.*, 1996; Jones and Westmoreland, 1998; Jones and Westmoreland, 1999). The issue of inoculation in relation to the composting trials conducted as part of this thesis is further discussed further in Section 5.2.4 (p.157).

5. THE COMPOSTING OF WOOLSCOUR WASTES

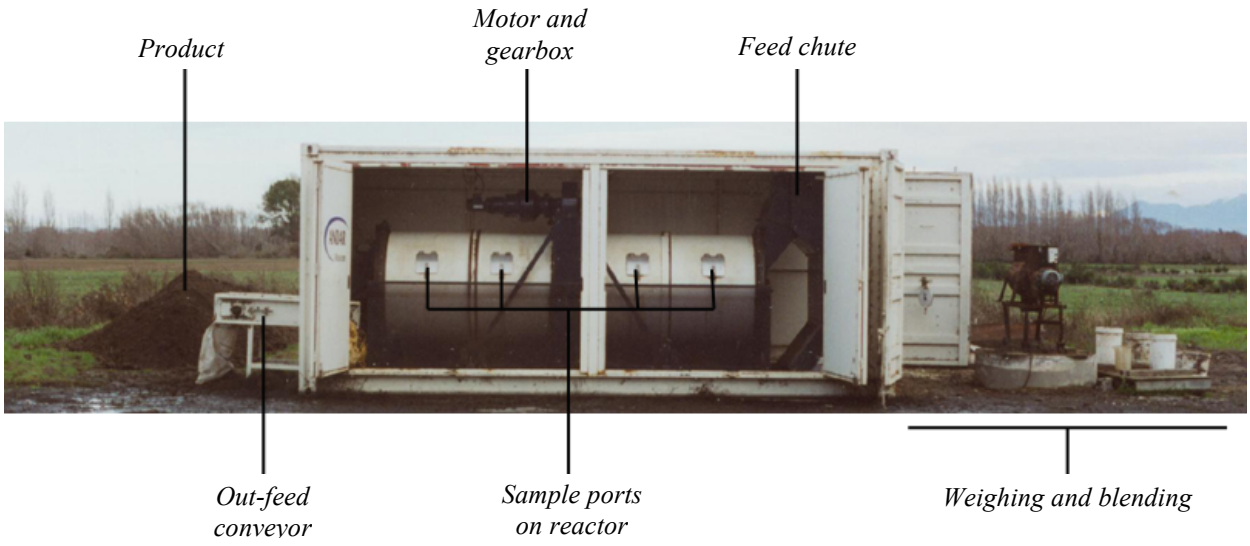
The primary objective of composting trials was the treatment of Sirolan CF sludge produced by the current effluent treatment system for woolscours. This section represents the applied part of this research and merges both microbiological and engineering aspects of the composting process.

5.1. THE ROTOCOM COMPOSTING SYSTEM

5.1.1. OVERVIEW OF THE ROTOCOM COMPOSTING SYSTEM

The Rotocom composting system manufactured by ANDAR Holdings Ltd. is an example of a rotary drum horizontal flow reactor (Haug, 1993). The small-scale machine used during this project, which was installed in a standard 20-foot shipping container so that it could be moved with relative ease, had drum dimensions of 1.2 m diameter by 4 m length and a total capacity of 4.4 m^3 (Figure 5–1).

Figure 5–1. Photograph of the Rotocom in-vessel composting system manufactured by ANDAR Holdings Ltd.



A tube of 0.2 m diameter ran through middle of drum, supporting the temperature probes and two vanes designed to push material through the drum. At an operating capacity of about 70% of total, and taking into account the volume of the central tube, the Rotocom capacity was approximately 3.1 m^3. Sludge was mixed with other substrates with a ribbon blender prior to being added to the Rotocom.

5.1.2. OPERATION OF THE ROTOCOM COMPOSTING SYSTEM

A ribbon mixer was used to blend components prior to composting, as within the Rotocom unit, mixing of the contents with normal drum rotation could not be expected to mix substrates thoroughly enough to achieve the homogeneity required for successful composting. In the ribbon mixer, between 50 and 60 L of material could be blended and homogenised in approximately 30 seconds. Blended material was added to the Rotocom via a 0.1 m^3 bucket tipper mounted inside the container. A motor and chain system lifted and tilted the bucket so that the material fed into the drum via a chute. Material was released from the Rotocom by an opening at the "out" end that fed onto a conveyor belt.

The frequency and speed of the turning of the drum (clockwise as viewed from the "in" end) was controlled by on-off timers and a variable frequency drive, respectively. Residence time in the drum could be set by adjusting the angle of the vane and the speed and frequency of the turning of the drum. Markers (200 mL plastic bottles) could be filled with material of the same density as that being composted and added to the Rotocom to confirm the residence time. Aeration of the composting materials was achieved using a blower installed at the "out" end of the drum, providing an airflow counter-current to the direction of the material being composted. A valve allowed the airflow into the drum to be controlled, the maximum being 5 m^3 air per minute. Samples could be taken from the drum using four ports located 0.5 m in from each end of the drum and spaced 1 m apart.

5.1.3. TEMPERATURE RECORDING

Five PT100 temperature probes providing a 4-20 milliamp (mA) output connected to a data logger recorded the temperature in the composting mass at four points (0.5 m in from the ends of the drum and at 1 m intervals, as for the sampling ports) as well as providing an ambient reading from inside the container. A current of 4 mA corresponded to a temperature of 0ºC, while 20 mA corresponded to a temperature of 100ºC. The logging interval could be set from 1 to 255 seconds. Data was retrieved from the logger using a laptop computer and imported into a Microsoft Excel spreadsheet.

5.2. COMPOSTING TRIALS AT THE ASHBURTON WOOLSCOUR

5.2.1. INTRODUCTION

Although composting woolscour sludge with other industrial wastes provides the ability to treat more than one waste stream and allows the selection of the best possible wastes for blending, in this case

materials to be composted with the sludge were sourced on a local scale, otherwise transport costs would have been prohibitive. The scope of research in this section was to determine a recipe that would maximise the rate of grease decomposition in the woolscour sludge and assess that composting process. Analysis of final products and conformity of the process to all applicable standards was regarded as future work, although some aspects of this were covered as part of the trials. Research in this section is a logical and necessary progression from the laboratory work carried out in the previous section. Specifically, the hypotheses in Table 5-1 were tested.

Trials were conducted at the Ashburton Woolscour as the plant had the necessary effluent treatment systems installed, was conveniently located midway between the University in Christchurch and ANDAR Holdings Ltd. in Timaru, and the owners were prepared to have the composting unit on site for the duration of the trials.

Table 5-1. Hypotheses tested during composting trials.

Hypothesis	Experimental
H5-1 Woolscour sludge mixed with sawdust will not successfully compost	Evaluation of the composting process; specifically: (a) Temperatures reaching 55ºC for 3 days (b) High rate of grease breakdown
H5-2 Addition of opener waste to the sludge blend will improve composting performance	Evaluation of the composting process; specifically: (a) Higher temperatures compared to the control (above) (b) Higher rate of grease breakdown compared to the control
H5-3 The composition of CFB biomass will not prevent its addition to the blend of sludge for composting, and will act as an inoculum thus improving composting performance	(a) Laboratory analysis of moisture, pH, organic matter, grease, pesticides, heavy metals, electrical conductivity and total nitrogen (b) Improved composting performance when biomass included in the blend (as outlined for hypothesis H5-2 above)

5.2.2. MATERIALS AND METHODS

Three recipes were evaluated during trials at the woolscour (Table 5-2): the first composted sludge with sawdust, and was used as a control to assess baseline composting performance; the second included opener waste in the mix, and was used to confirm laboratory results that suggested that sludge would decompose faster in the presence of fibrous wastes (as shown in Section 4.3.3 p.106); and the third included opener waste and replaced water (for moisture adjustment) with biomass from the CFB system, and was used to test the hypothesis that the biomass (previously defined as the biological flocs settled out of the treated effluent by gravity) may act as an inoculum to increase the rate of sludge decomposition.

Opener waste (from the short wool processor) was included at a rate that reflected the relative amounts of sludge and opener waste produced daily by the scour. Water (or biomass) was added to increase the initial overall moisture content to 50% on a wet weight basis. The sawdust (rimu free of chemical treatments) used as the bulking agent was obtained from a furniture manufacturer adjacent to the woolscour and was added at a rate of twice the volume of sludge.

Due to the moisture losses observed in the three trials evaluated above, a moisture addition system was subsequently installed to assess the rate of organic matter and grease decomposition under conditions where moisture was not limiting to microbial activity (using the recipe of trial 3). During this fourth trial, the moisture addition system consisted of a 200 L water tank with a submersible pump to add water into the composting vessel when the drum was rotating through a pipe and spray nozzle inside the drum. The nozzle was located prior to port 3 (after 13 days composting), where moisture had decreased to about 25% (Figure 5–7). A flow rate was set to bring the moisture content up to 50% at the third sampling port. During this trial, the scour used a new detergent that was thought to remove more grease through the grease recovery plant and consequently lower the amount found in the sludge. Five sludge samples were analysed to determine new organic matter and grease contents for the subsequent determination of mass and grease reductions during composting.

Table 5-2. Recipes evaluated during composting trials at the Ashburton Woolscour.

	Fresh weight (kg)			
Substrate	Trial 1	Trial 2	Trial 3	Trial 4
Sirolan CF sludge	15.1	13.9	13.9	13.9
Sawdust	4.8	4.5	4.5	4.5
Opener Waste	-	2.9	2.9	2.9
Water	3.1	5.2	-	#
CFB Biomass	-	-	5.6	5.6

Note: #Water added during composting to maintain an optimum moisture content.

Biomass was analysed for moisture (Section 2.3.1), pH (Section 2.3.2), organic matter (Section 2.3.3), grease (Section 2.3.5), pesticides (Section 2.3.6), heavy metals (Section 2.3.7), electrical conductivity (Section 2.3.11) and total N (Section 2.4.1). Chemical properties of Sirolan CF sludge and opener waste from the Ashburton Woolscour was described in Section 4.3.1 (p.101). Bulk densities were determined for all components.

The Rotocom was set on a 12 h cycle, being on for 1.5 h and making half a revolution, then off for 10.5 h, such that the drum made one revolution per day and provided a residence time of 21 days. The residence time was confirmed with a series of markers that were added with blended sludge. The fan for aeration was set on full, and temperatures were logged every 255 seconds. For the construction of temperature

graphs, peak temperatures attained when the drum was turning was used, since this corresponded to the heat released from the material when the drum was turning.

Waste streams were typically blended twice per week by the author, with enough material blended to supply the Rotocom for 4 days. On days when wastes were blended, the author fed material into the Rotocom. On other days, a woolscour employee assumed this duty.

Before samples were taken for analysis, the Rotocom was allowed to reach steady state conditions. This was checked by firstly adding markers to the first mixes added for each recipe and waiting for the markers to be discharged (the drum was therefore full of a consistent recipe), and secondly, waiting for the recorded temperatures to be steady (indicating a settled level of biological activity). Once the composting process was at a steady state, five samples were taken on random days over a 3 week period from material mixed for composting, from all four sampling ports, and from material discharged from the drum. Over this sampling period, amounts added to the composter were recorded. Samples were analysed for moisture content (Section 2.3.1), pH (Section 2.3.2), organic matter and carbon (Section 2.3.3), grease content (Section 2.3.5), pesticides (Section 2.3.6), TN (Section 2.4.1) and mineral N (Section 2.4.2), and mesophilic and thermophilic microbial counts (Section 4.2.9). The material mixed for composting was analysed for mineral N, pH and microbial counts; other properties (as listed above) were calculated from data obtained for the individual substrates (Table 4-2 p.102 and Table 5-3). Fungal species in the samples taken for plate counts during the third trial were isolated from conidia and incubated at 20ºC for 4 weeks in a moist chamber for identification purposes. Phytotoxicity was determined by recording the germination of ten radish seeds placed on samples incubated in covered petri dishes for 7 days. Controls consisted of seeds placed on filter paper moistened with distilled water. The destruction of plant seeds that contaminated the feed materials was determined by placing 10 g (fresh weight) of samples in petri dishes and recording the germination of any seeds after 7 days.

Mass reduction (on an oven dry basis) was calculated from the organic and inorganic matter contents of the samples compared to that of the initial material (Equation 5-1). If the equation yielded a negative value (i.e. a gain in mass) due to the sample having a higher organic matter content than the initial material, the mass reduction was set to 0%.

$$\text{Mass reduction (\%)} = 100 - \left(\frac{\text{Initial Inorganic Matter (\%)} * 100}{\text{Sample Inorganic Matter (\%)}} \right)$$

Equation 5-1

Grease reduction (also on an oven dry basis) was calculated from the grease content of samples, compared to the initial material, and the degree of mass reduction (Equation 5-2). If the equation yielded a negative value (i.e. a gain in grease) due to the sample having a higher grease content than the initial material, the grease reduction was set to 0%.

$$\text{Grease reduction (\%)} = 100 - \left(\frac{\text{Sample grease (\%)} * (100 - \text{Mass reduction (\%)})}{\text{Initial grease (\%)} * 100} \right)$$

Equation 5-2

5.2.3. RESULTS

The general characteristics of the CFB biomass are in Table 5-3 and indicate a near neutral pH, a high TN content (equivalent to 1.2 g L^{-1}), and it contained wool grease. The biomass had an electrical conductivity half that of seawater and equivalent to CFB suint diluted 1:10 with distilled water (Section 3.3.1 p.63); for comparison, the electrical conductivity of the water used at the scour was 660 μS cm^{-1} (24 July 2003). Heavy metals in the biomass were comparable to levels found in the sludge (Table 4-2 p.102). Bulk densities of sludge and opener waste were 965 and 250 kg m^{-3}, respectively. The sawdust, used as a bulking agent in the compost, was almost entirely organic and had a low N content.

Table 5-3. Properties of the substrates composted during trials at the Ashburton Woolscour.

Property	Sawdust	CFB Biomass
Moisture (%)	20.8 (2.18)	96.2 (0.90)
pH	5.8 (0.16)	6.3 (0.60)
Bulk density (kg m^{-3})	208 (24.7)	1,013 (3.3)
Organic Matter (%)	97.8 (0.20)	34.1 (1.75)
Total N (%)	0.2 (0.01)	5.1 (0.25)
Grease (%)		8.6 (1.65)
Diazinon (ppm)		11 (11)
Propetamphos (ppm)		8 (8)
Electrical conductivity (mS cm^{-1})		20.2 (0.81)
Arsenic (mg kg^{-1})		3.4 (0.51)
Cadmium (mg kg^{-1})		0.2 (0.05)
Chromium (mg kg^{-1})		7.4 (1.72)
Copper (mg kg^{-1})		10.2 (2.48)
Lead (mg kg^{-1})		3.7 (0.72)
Nickel (mg kg^{-1})		5.8 (2.58)
Zinc (mg kg^{-1})		525.0 (98.44)

Note: all results except moisture, pH and bulk density are on an oven dry basis. Numbers in brackets are the standard errors of the means, n ≥ 5 except for pesticides (n=2). Properties of Sirolan CF sludge and opener waste were described in Table 4-2.

The average residence time for material in the Rotocom was 21 days (n=12); residence times were fairly uniform, with results in the 19-24 day range with few exceptions. Therefore, 21 days was used for calculating the residence times for samples removed from each of the ports on a linear scale, such that ports 1, 2, 3 and 4 equated to 2.6, 7.9, 13.1 and 18.4 days, respectively. A linear scale may not have been entirely appropriate, because the reduction in mass during composting would have meant that material would have occupied less linear length of the drum (as the fullness of the drum would not have changed) as composting proceeded.

For trial 1, a total of 1,057 kg (fresh weight) material was added to the composting unit over the three week period of analysis, of which 664 kg (63%) was sludge. For trial 2, a total of 1,710 kg of material was composted, of which 862 kg (50%) was sludge. A total of 936 kg material, including 459 kg (49%) sludge, was composted during trial 3. The difference in the amounts composted between trials 2 and 3 suggested that problems with keeping materials dry due to the rainfall that occurred during trial 3 may have affected throughput, as the blended materials, having a higher moisture content than intended at certain times, may not have fed through the chute and into the Rotocom as freely as otherwise expected. Sludge was converted from a sticky, grey coloured material to a dark brown, friable product during the composting process (Figure 5–2).

Figure 5–2. Appearance of the sludge-sawdust blend before and after composting.

Sludge-sawdust blend in ribbon mixer

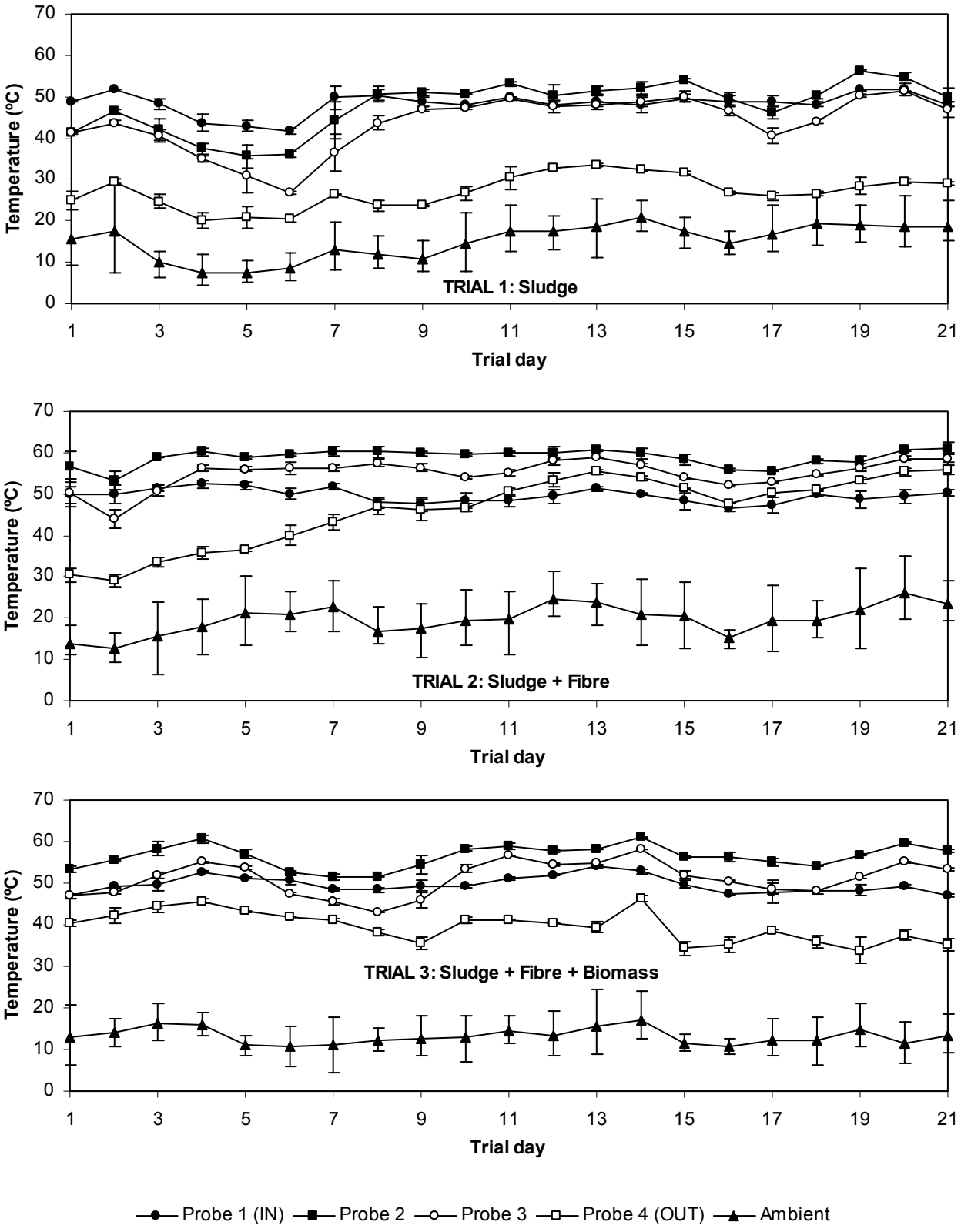
After 21 days composting

In Figure 5–3, the average peak temperatures are shown for all four probes for each recipe over the 21 day sampling period of each trial. In general, temperatures from the probes were stable over the three week period, although, during trial 2, the temperature from probe 4 increased over the first half of the trial period. Figure 5–4 provides the temperature profiles for each of the recipes evaluated. All three recipes showed a similar initial temperature rise. Sludge and sawdust (trial 1) did not meet pasteurisation

requirements, being 55°C for 3 days (Standards Australia, 1999), with a very early temperature peak. The addition of opener waste (with or without biomass) gave good temperature profiles, with a later temperature peak at 7 days, and a slightly better profile with water (trial 2) rather than biomass (trial 3) as the moisture source.

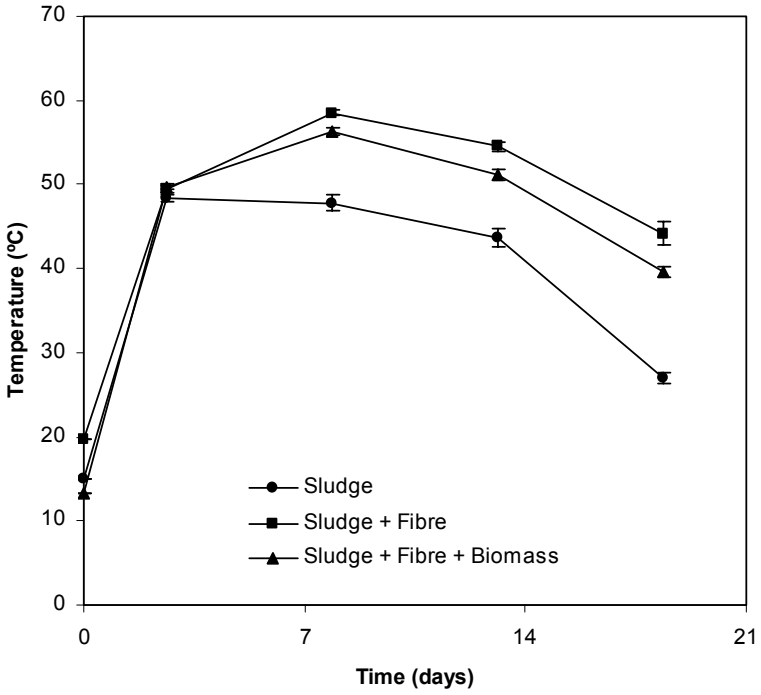
The highest mass reduction was achieved by the sludge and sawdust mixture (31% over 21 days), while the addition of fibre with or without biomass gave a mass reduction of 23-24% over the same duration (Figure 5–5). The rate of organic matter decomposition slowed from 13 to 21 days. Due to small sample sizes, these values should be taken as indicative only, and repeat sampling over a long time frame would give more accurate results.

Figure 5–3. Daily temperature profile for trials composting Ashburton Woolscour sludge.



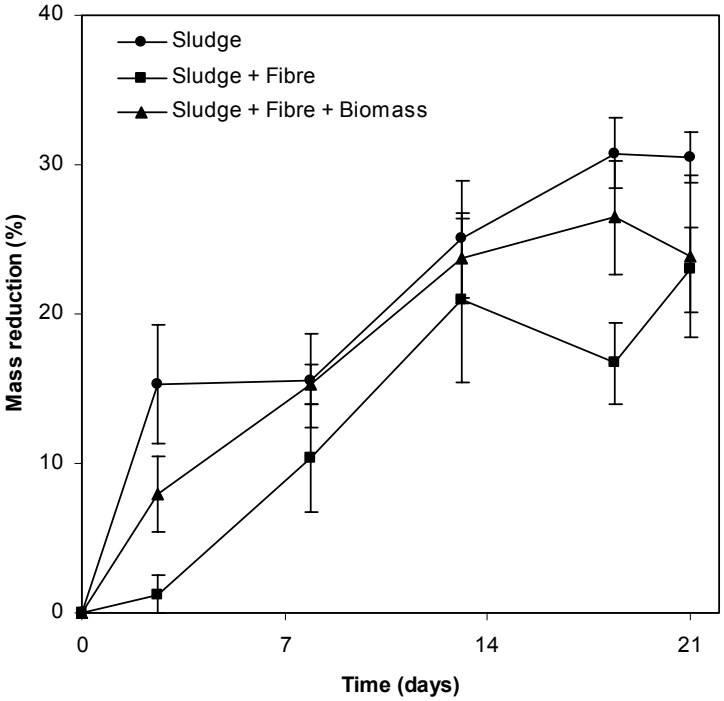
Note: for each probe, points are the average of two peak temperatures and bars represent standard errors of the means. For ambient temperatures, points are the daily averages and bars represent minimum and maximum values for the day.

Figure 5–4. Rotocom temperature profile for trials composting Ashburton Woolscour sludge.



Note: initial temperature (t=0) is the mean ambient temperature of the 21 day trial period. Other temperatures are the mean peak temperatures (n=42, being 2 readings per day for 21 days) from the 4 probes, bars represent standard errors of the means.

Figure 5–5. Reduction in mass during the composting of Ashburton Woolscour sludge.

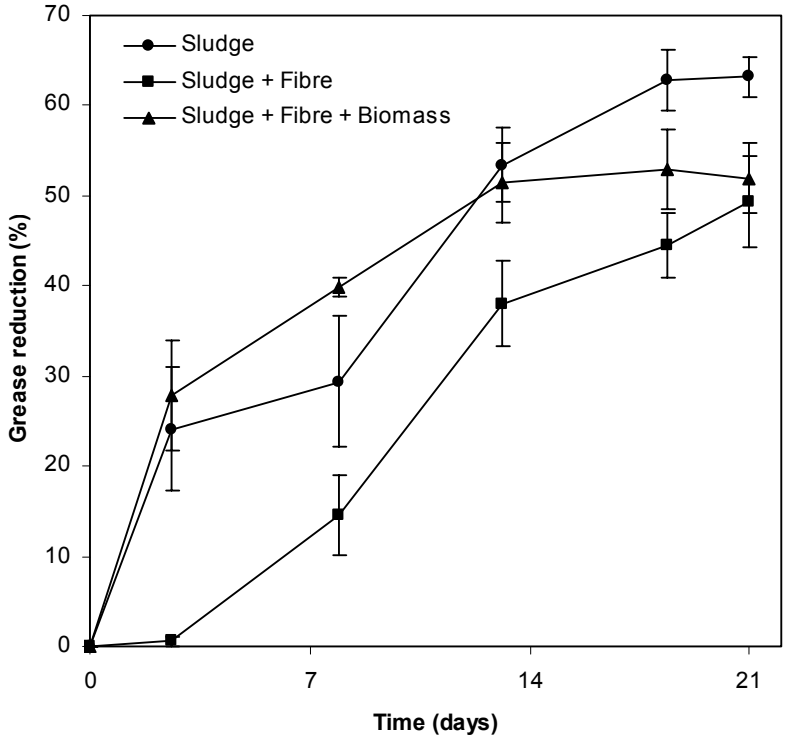


Note: bars represent standard errors of the means, n=5.

The highest grease reduction was achieved by sludge and sawdust (63%), with a grease reduction of 49-52% observed with the addition of fibre (Figure 5–6). Grease percentages (on dry weight bases) were reduced from 24.2 to 12.8% for sludge and sawdust, from 21.9 to 14.3% with the addition of opener waste, and from 21.1 to 13.3% with the addition of opener waste and biomass. The rate of grease reduction also slowed with time.

The organophosphate pesticides diazinon and propetamphos appeared to decompose at a rate faster than that of the grease fraction. Propetamphos was calculated to be at initial levels of 133 ppm in the grease fraction for the sludge and sawdust mixture, and at 127 ppm in the grease fraction for the two mixtures containing fibre. No propetamphos residues were detected in the grease fractions extracted from compost samples taken from port 3 (after 13 days) or from the out-feed chute (after 21 days) for all of the three recipes. Diazinon was reduced from a calculated 310 ppm in the grease fraction initially to 204 ppm after 13 days and 177 ppm after 21 days for the sludge and sawdust mixture. With the addition of fibre, diazinon was reduced from a calculated level of 285 ppm to 30 and 52 ppm in the grease fraction after 13 and 21 days, respectively. With the addition of fibre and biomass, diazinon was reduced from a calculated level of 285 ppm to 0 and 65 ppm in the grease fraction after 13 and 21 days, respectively. These results give an indication only, due to the small number of samples analysed.

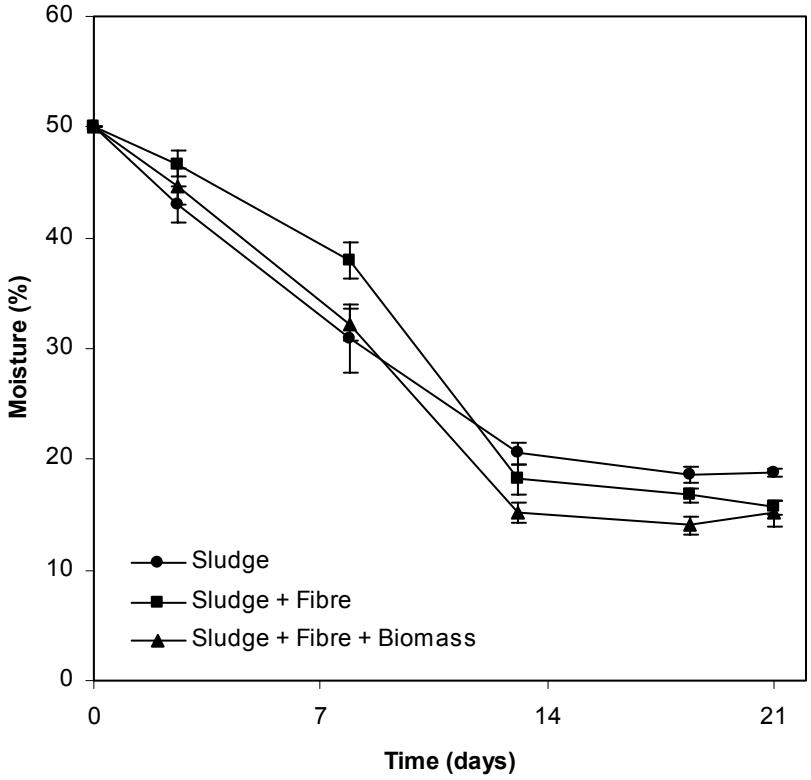
Figure 5–6. Reduction in grease during the composting of Ashburton Woolscour sludge.



Note: bars represent standard errors of the means, n=5.

All three recipes lost a significant amount of water over the three-week residence time such that microbial activity would have been inhibited after about 10 days of composting (Figure 5–7).

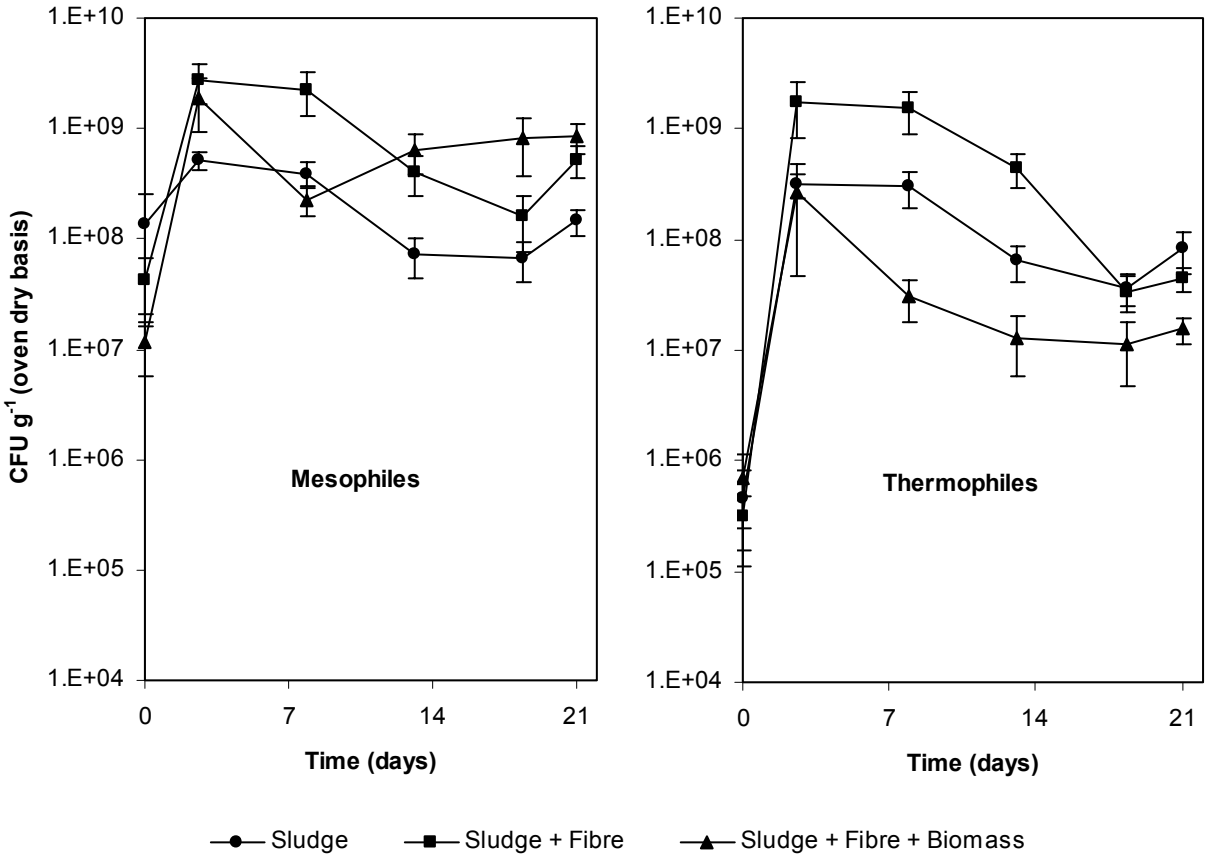
Figure 5–7. Changes in moisture content during the composting of Ashburton Woolscour sludge.



Note: bars represent the standard errors of the means, n=5.

Heterotrophic microorganisms were counted after four days incubation at 30°C for mesophilic organisms and 50°C for thermophilic organisms (Figure 5–8). The addition of fibre and biomass did not increase initial counts in the feed. Counts of mesophilic organisms rapidly increased with the addition of fibre. Thermophilic organism counts were higher with the addition of fibre compared to the sludge-sawdust mix, but the addition of fibre and biomass decreased counts. Thermophilic counts decreased as the temperature decreased. Sludge, as produced or after blending with sawdust, was often observed to have white to yellow growth on its surface after two to three days. Species were identified as *Aspergillus fumigatus* and *Malbranchea pulchella*. Dominant fungal species in the samples taken for plate counts during the third trial were *A. fumigatus*, *Cephaliophora* spp., *Penicillium* spp., and *Scopulariopsis brevicaulis*.

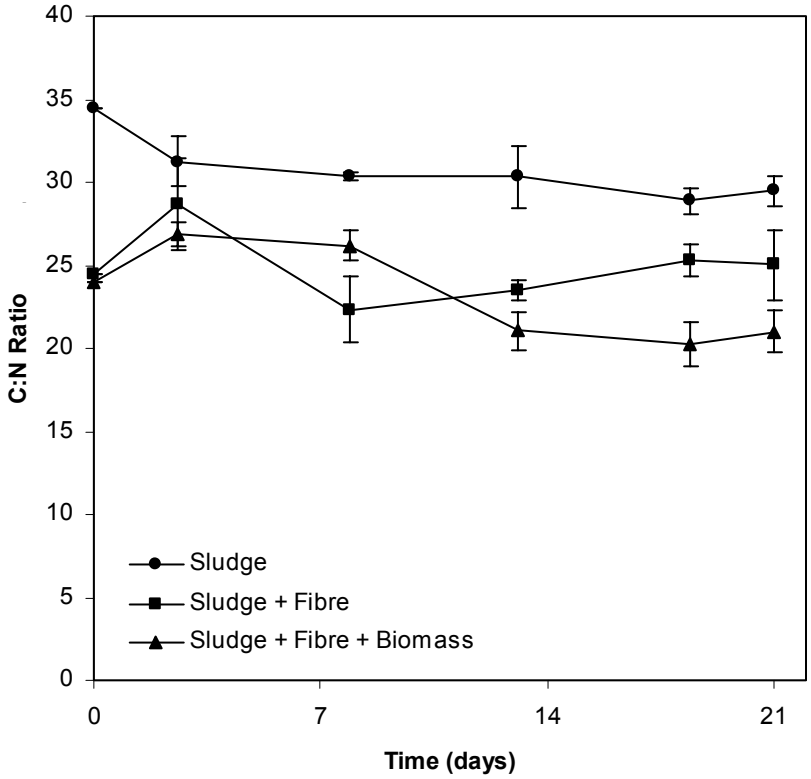
Figure 5–8. Culturable microbial numbers during the composting of Ashburton Woolscour sludge.



Note: bars represent the standard errors of the means, n=5. CFU = colony-forming units.

Generally, there were slight decreases in C:N ratios during composting: from 35:1 to 30:1 for sludge and sawdust; from 24:1 to 25:1 with the addition of fibre; and from 24:1 to 21:1 with the addition of fibre and biomass (Figure 5–9). One sample *t*-tests showed that the final C:N ratio was significantly different from the theoretical initial ratio for only the sludge and sawdust blend ($p=0.0052$, for other blends $p>0.05$). Final TN amounts (on dry weight bases) were 1.3% (sludge and sawdust), 1.6% when fibre was included, and 1.7% when fibre and biomass was included. Mass balance calculations showed that 19%, 25%, and 17% of the i-TN for recipes 1, 2 and 3, respectively, was lost during the composting process.

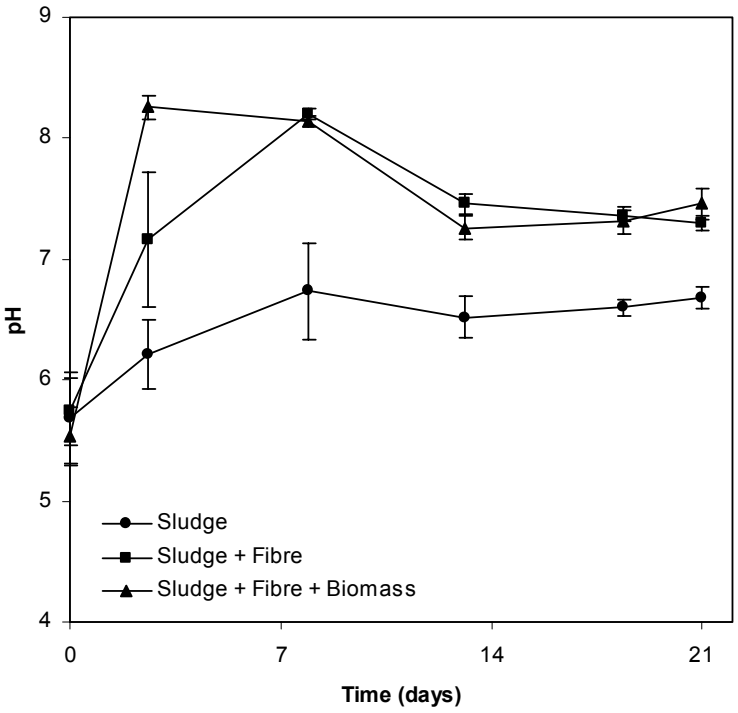
Figure 5–9. Changes in C:N ratio during the composting of Ashburton Woolscour sludge.



Note: bars represent the standard errors of the means, n=5. Carbon was estimated from the organic matter content.

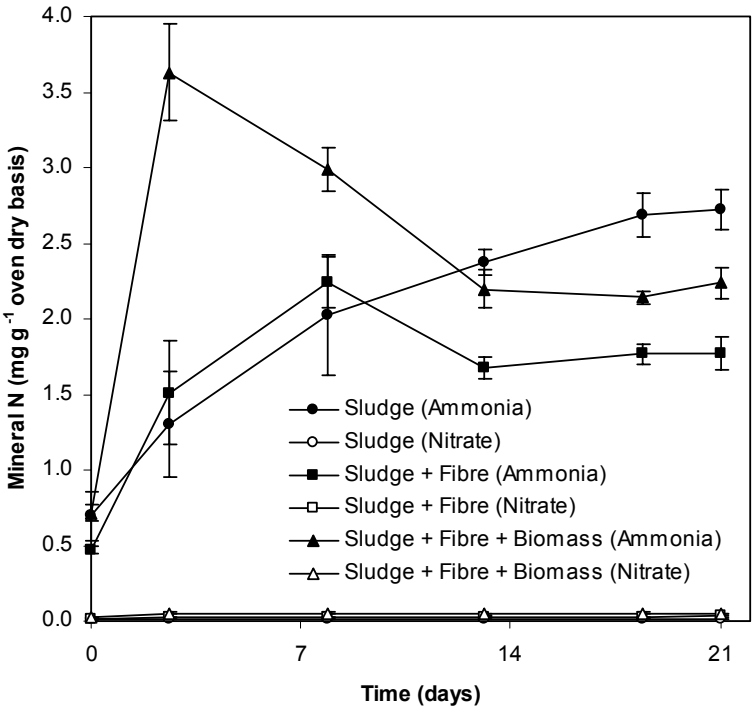
The pH did not increase above 7.0 when composting sludge with sawdust (Figure 5–10), therefore there appeared to be no issues with odours caused by ammonia volatilisation. The pH increased above 8.0 when fibre was added and, together with higher composting temperatures, caused ammonia to be lost by volatilisation and thus odour to be detected and flies to be attracted (especially with warm ambient temperatures during trial 2). Ammonia volatilisation was confirmed by passing the exhaust air over a container of concentrated hydrochloric acid; white fumes qualitatively showed the presence of ammonia. Ammonia was rapidly produced during composting from the breakdown of nitrogenous substances (Figure 5–11). There was a steady increase in ammonia production over time when sludge was composted with sawdust. A rapid increase was observed when sludge was composted with fibre and biomass. The addition of fibre and/or biomass did not increase the initial levels of available N. Little nitrate was produced from all three blends during composting.

Figure 5–10. Changes in pH during the composting of Ashburton Woolscour sludge.



Note: bars represent the standard errors of the means, n=5.

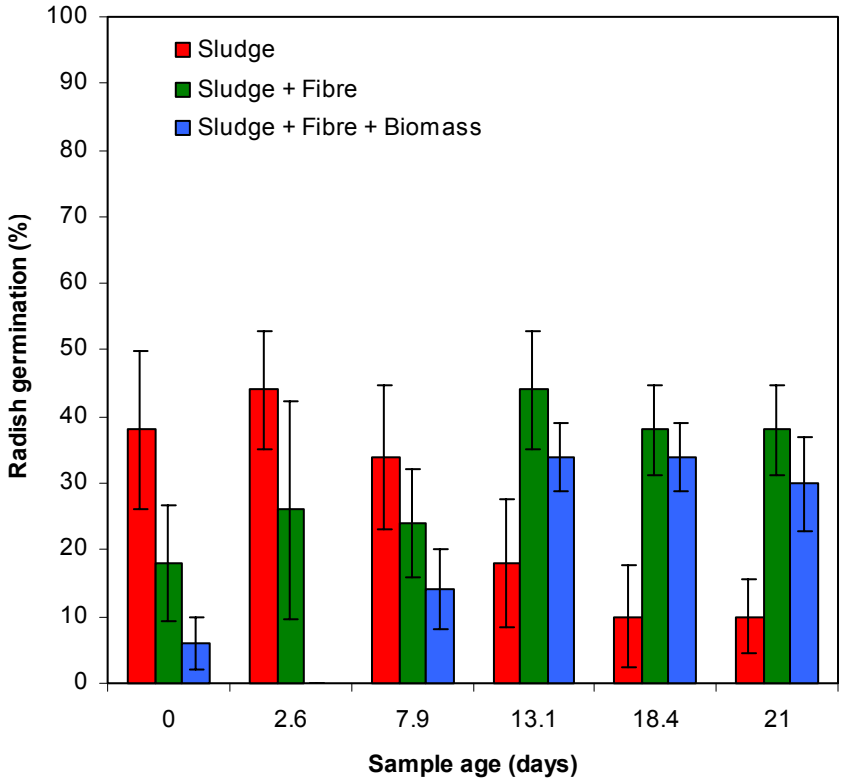
Figure 5–11. Changes in mineral N levels during the composting of Ashburton Woolscour sludge.



Note: bars represent the standard errors of the means, n=5.

Germination after 7 days was assessed using radish seeds in Petri dishes containing compost samples; average control germination (on filter paper) was at least 96% for each trial. Germination was low for all recipes in the feed (t_0) and at all sampling times, indicating immature compost (Figure 5–12). No seeds that contaminated the feed materials germinated in any of the samples taken from various stages of the composting process for all three trials.

Figure 5–12. Changes in phytotoxicity during the composting of Ashburton Woolscour sludge.



Note: bars represent the standard errors of the means, n=5.

The fourth trial used the same recipe as the third trial together with the installation of a moisture addition system to maintain optimal moisture levels in the composting material. This system proved temperamental, however, with the moisture content increased to 56% (1.3) at port 3 and material exiting the vessel after 21 days composting at 53% (1.4) moisture (mean values from five sampling dates reported, with standard errors of the means in brackets). The sludge produced when the experimental detergent was used during this trial period contained 33% (2.6) grease, which was less than that contained in the sludge during previous trials (38%), and had 63% (3.4) organic matter, on a dry weight basis. The temperature profile was down on that observed during trial 3; the temperature peaked at 54ºC after 8 days composting. The average ambient temperature during the sampling period was 9.0ºC. Mass reduction was

30% (0.9) over the 21 day composting period. On a dry weight basis, the product contained 2.6% (0.33) grease, equating to a grease reduction of 91% (1.2).

5.2.4. DISCUSSION

To reuse woolscour sludge and other waste streams produced by the industry, viable alternatives to landfilling must be available. Composting of these materials to produce a saleable product offers a real alternative.

CFB biomass did not appear to accumulate heavy metals from the incoming feed to the tanks (Table 5-3) and, on a dry weight basis, metals were found at concentrations similar to that in the sludge (Table 4-2). Therefore, biomass could be added to the blends for composting without affecting the likely levels of heavy metals in the product. The biomass also contained wool grease, indicating that some of the reduction in grease content observed between CF and CFB suint types at the Fairlie Woolscour (discussed in Section 3.4.1 p.78) was due to the grease partitioning into the biomass phase during the biological treatment stage. The conductivity of the biomass was similar to that reported by Becker *et al*. (1999) for woolscouring wastewater (18 mS cm^{-1}). While the biomass may supply microorganisms and N to the mixture of wastes to be composted, its salt content (as measured by electrical conductivity) may negate some or all of this benefit. The conductivities of the composts produced during each trial was not measured. The optimum ratio of biomass to water should be determined in future work to maximise any benefit to the composting process from the inclusion of biomass.

Soil quality can be defined as the capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality, and promote plant and animal health (Doran and Parkin, 1994). Although pressures on soils in New Zealand are not as great as those in many regions, due to factors such as a small population and relatively recent settlement, other factors that have led to agricultural intensification have increased the risk of soil degradation such as erosion, organic matter depletion, and compaction (Lilburne *et al.*, 2002). Water use is increasing exponentially, with most of the demand for agricultural production, and water scarcity will be a real issue facing many countries over the next 20 years (Grommen and Verstraete, 2002). There is a need, therefore, to return organic materials, such as compost derived from woolscour sludge, to agricultural land, and thus promote sustainable agriculture.

While there was some variation in the residence time of material inside the Rotocom vessel during trials at the Ashburton Woolscour, the compost unit generally operated in a stable fashion. Over the three trials,

an average of 32 kg sludge per day was composted and, based on an estimated daily sludge production of 1,500 kg, represented 2% of the total sludge produced by the scour.

Although it was suggested in Section 4.4.5 (p.138) that there may be a need for inoculation since the sludge was essentially devoid of microbial activity, composting trials suggested otherwise, with a large increase in temperature during the first three days of composting (Figure 5–4). Temperature profiles were also relatively stable during trial evaluation (Figure 5–3), indicating a consistent process. Organic matter is the organic fraction of a sample, including plant, animal, and microbial residues, fresh and at all stages of decomposition (Nelson and Sommers, 1982; Schnitzer, 1982), with heat as a product of the microbial decomposition of this organic matter. A rapid temperature increase was observed in previous studies (Bateup *et al.*, 1996; Jones and Westmoreland, 1998; Jones and Westmoreland, 1999), all of which used greenwaste as the bulking agent. Epstein (1997) suggested that there is no evidence in the literature to support the use of inoculants or enzymes to accelerate the composting process and correct preparation of the feedstock would provide for successful composting. It would appear that the addition of a bulking agent to decrease the bulk density of the sludge and thus increase the aeration of the substrate improved the sludge as a substrate for microbial activity. Sawdust or water was not expected to add appreciable numbers of microorganisms to the blend. For agitated composting systems, a particle size of about 12.5 mm is regarded as suitable (Anderson, 1990).

The addition of opener waste improved the temperature profile during composting, but the substitution of CFB biomass for water reduced this benefit. The effect of ambient temperature on the profiles was unknown; the increase above ambient was greater for fibre and biomass than fibre alone. It could be suggested that, with a composting unit of the trial size, ambient temperatures affected heat loss from the composting materials, as temperatures attained when the moisture addition system was in place (August, being the Southern Hemisphere winter) were less than that attained during trial 3 (April, being autumn). This was despite the same recipe being evaluated, although the sludges did contain different amounts of grease. The container did provide some insulation to the composting vessel, as the minimum ambient temperature logged inside the container was 2ºC.

Thus, with the trial composting unit, sludge alone failed to reach 55ºC and would suggest insufficient pasteurisation of the material was likely to have occurred. The temperature-time requirement for effective compost pasteurisation varies amongst countries (Brinton, 2001). For example, in Germany, the requirement is 55°C for 2 weeks or greater than 65°C for 1 week for open windrow systems, and more than 60°C for 1 week for closed/in-vessel systems. In Austria, the requirement is more than 60°C for 6 days, or more than 65°C for 3 days. In Denmark, more than 55°C for 2 weeks is required. The Australian standard requires three consecutive days at a minimum temperature of 55°C (Standards Australia, 1999).

New Zealand does not, as yet, have composting standards, and general practice is to adopt the Australian standard. Based on this standard, when sludge was supplemented with fibre, compost pasteurisation was likely to have been achieved.

The addition of opener waste and/or biomass did not increase the initial numbers of culturable microbes in the blend for composting, although mesophilic organisms (those cultured at 30ºC) peaked at higher levels with the addition of fibre and generally persisted at higher levels (Figure 5–8). Opener waste did not increase initial levels of available N either (as discussed below); the benefit from fibre addition was unclear. It was previously noted (Section 4.4.2 p.125) that fibre provided only one element, sulphur, that was not present in the sludge, and while it was suggested that fibre may improve the physical properties of the mixture, observations from the composting trials (discussed later in this section) refuted this. The fibre may have supplied a different set of microbes to that contained in the sludge, thus providing for a more robust microbial population in the mix. The fact that their levels did not significantly decrease during composting suggests that thermophilic conditions did not penetrate the entire composting mass. Numbers of thermophilic microbes were enhanced during the process with the addition of fibre, but the inclusion of biomass decreased numbers, possibly due to the salt content increasing the conductivity.

Aspergillus fumigatus was found on sludge and on partially composted material containing sludge. *Aspergillus* species are commonly found in soil from warmer climates and in various composted products, with *A. fumigatus* able to grow between 12 and 57ºC, with an optimum between 37 and 43ºC, suggesting a potential human pathogen (Domsch *et al.*, 1980). *A. fumigatus* is the main etiological agent of aspergillosis, with the acute pulmonary and invasive infection forms serious concerns for people with impaired natural immunity (de Hoog *et al.*, 2000). *A. fumigatus* and endotoxins have been identified as the bioaerosols (organisms or biological agents dispersed through the air and affecting human health) most affecting worker health and the surrounding environment at composting facilities (Epstein, 1997). However, *A. fumigatus* causes losses in tensile strength of woollen fabrics, can grow slowly on hair, and produces lipases of modest activity, making it an important member of the wool composting community (Domsch *et al.*, 1980). Of the other fungal species associated with the composting of wool, *Cephaliophora* spp. cannot grow at temperatures exceeding 35ºC, while *Penicillium* spp. are ubiquitous saprophytes predominating in soils in temperate regions, with most species not able to grow at temperatures exceeding 37ºC (Domsch *et al.*, 1980; de Hoog *et al.*, 2000). Most *Scopulariopsis* species are soil fungi, with *S. brevicaulis* the most common species of its genus, having a worldwide distribution, and has been isolated from compost (Domsch *et al.*, 1980; de Hoog *et al.*, 2000). *S. brevicaulis* cannot tolerate temperatures above 37ºC, but can grow on keratin and degrade hairs, and can be pathogenic to humans.

Actinomycetes, many of which are thermophilic and are important in composting due to their ability to degrade complex and recalcitrant molecules, can cause occupational respiratory diseases due to the release of spores to levels as high as 10^6-10^7 CFU m^{-3} air in the vicinity of composting operations when compost is turned (Lacey, 1997). Future work should quantify levels of potentially disease-causing microbial agents in the exhaust air.

The highest rate of reduction in organic matter (Figure 5–5) and wool grease (Figure 5–6) was achieved when sludge was composted with sawdust alone (trial 1), although this blend did not achieve temperatures above 55ºC. The addition of fibre with (trial 3) or without (trial 2) biomass, although improving the temperature profile, reduced the rate of decomposition of organic matter and wool grease. Blends containing fibre were observed to be more clumped than recipes without, suggesting that the addition of fibre may have caused aggregation of particles, thus reducing surface area and potentially causing formation of anaerobic microsites. Future research should investigate the rate of fibre breakdown if fibre is to be added to sludge for composting. Loss of moisture during the composting process in trials 1, 2 and 3 (Figure 5–7) was predicted to have decreased the rates of mass and grease reduction, to have limited temperature elevation (and thus thermophilic CFU) and reduced ammonification. This prediction was confirmed during the fourth trial where the installation of a moisture addition system maintained conditions more optimal for microbial activity. Enhanced mass reduction, but particularly a grease reduction of almost 91%, by optimising moisture indicated the strong influence that environment has on microbial metabolism in composting systems.

Various studies have shown wool grease to decompose under composting conditions, with rates ranging from a 90% reduction in wool grease by 9 weeks, to a 70% reduction in 14 weeks in two different static heaps, although recipes and process conditions were not detailed (Bateup *et al.*, 1996). Similarly, static pile composting of Sirolan CF sludge blended with green waste over 14 weeks showed 80% and 96% degradation of the wool grease and detergent, respectively (Jones and Westmoreland, 1998). While, in a subsequent study, Jones and Westmoreland (1999) showed that during 100 days of composting 2 m^3 sludge with 4 m^3 greenwaste the rate of wool grease decomposition increased with the maximum initial temperature rise, with 95% of the wool grease and 100% of the detergent decomposed. Placed in context with the above studies, a grease reduction of 50-91% in 3 weeks during the four trials conducted in this project compares well, especially as sawdust rather than greenwaste was used as the bulking agent. The in-vessel composting approach may have enhanced grease reduction due to the frequent mixing and aeration of the composting mass, thus reducing the time required for the production of a usable material and the area required for the establishment of a composting operation.

The decomposition of substrates containing fats and oils is expected to be enhanced under thermophilic conditions, since physical properties of these substrates, such as accessibility to microorganisms and their lipolytic enzymes, diffusion coefficients and solubility, improve as they change into the liquid state with increasing temperature (Becker *et al.*, 1999). The bulk density of wool grease at 15ºC was reported to be 0.94-0.97 g cm^{-3}. Bateup *et al*. (1996) suggested that woolscour sludge could be pelletised to improve its handling and transport and subsequently burned as a fuel or applied to land as a slow release soil improver. This scenario, however, would return the grease fraction to its bulk, and therefore unavailable, form where it would not melt and readily decompose under low soil temperatures.

The organophosphate pesticides diazinon and propetamphos decomposed at a rate faster than that of the solvent-extractable (grease) fraction as a whole, as observed by decreasing concentrations in the grease fraction following Soxhlet extraction and gas chromatographic analysis. This result agrees with previous data: cypermethrin, propetamphos and diazinon present in the wool grease fraction was shown not to accumulate during the composting of woolscour sludge; diazinon decomposed at a faster rate than that of the solvent-extractable fraction, while propetamphos decomposed marginally faster and cypermethrin marginally slower than that of the solvent-extractable fraction (Bateup *et al.*, 1996). During the composting of 2 m^3 sludge with 4 m^3 greenwaste, diazinon had a half life of 6-11 days and cypermethrin 31-36 days (Jones and Westmoreland, 1999). While organophosphate residues (such as diazinon) degraded two to three times faster than the wool grease, synthetic pyrethroid residues (such as cypermethrin) degraded at half the rate of the wool grease.

There are a variety of mechanisms affecting the degradation of pesticides in a composting system, including: adsorption to organic matter; leaching; volatilisation; abiotic transformations (such as hydrolysis, photolysis, and advanced oxidation processes); and biological transformations (detoxification, activation, cometabolism, and conjugation) (Büyüksönmez *et al.*, 1999). Adsorption is the binding of chemicals to the surfaces of solid particles by weak, reversible bonds, which reduces the rate of decomposition and movement. This is an important mechanism due to the high organic matter of composting substrates. Leaching, the movement of chemicals with percolating water through soil, is not a major factor as composting materials are not saturated, have a high organic content (and thus adsorption capacity), and many pesticides have low solubility in water. Volatilisation is the transformation of a pesticide to the gas phase and is affected by the management of the composting system, due to competing factors that either promote (high temperatures, moist conditions, aeration) or inhibit (adsorption, mass of material) vaporisation. The most important abiotic transformation processes is hydrolysis (breaking of bonds by water), but also includes photolysis (transformations involving ultra-violet light) and advanced oxidation processes (generation of free radicals). Biological transformations include detoxification (a change that renders the compound less harmful), activation (production of a toxic compound),

cometabolism (no energy derived from the transformation), and conjugation (combination of pesticides with other compounds). Photolysis would not occur inside a composting vessel, however.

Decomposition of detergent residues were not analysed in this research. Nonylphenol ethoxylate detergents, usually used in New Zealand and specifically at the Ashburton Woolscour, are one of a number of "potentially toxic elements" and, as such, are limited to 50-100 mg kg^{-1} total solids in organic wastes applied to land in the European Union (Brinton, 2000).

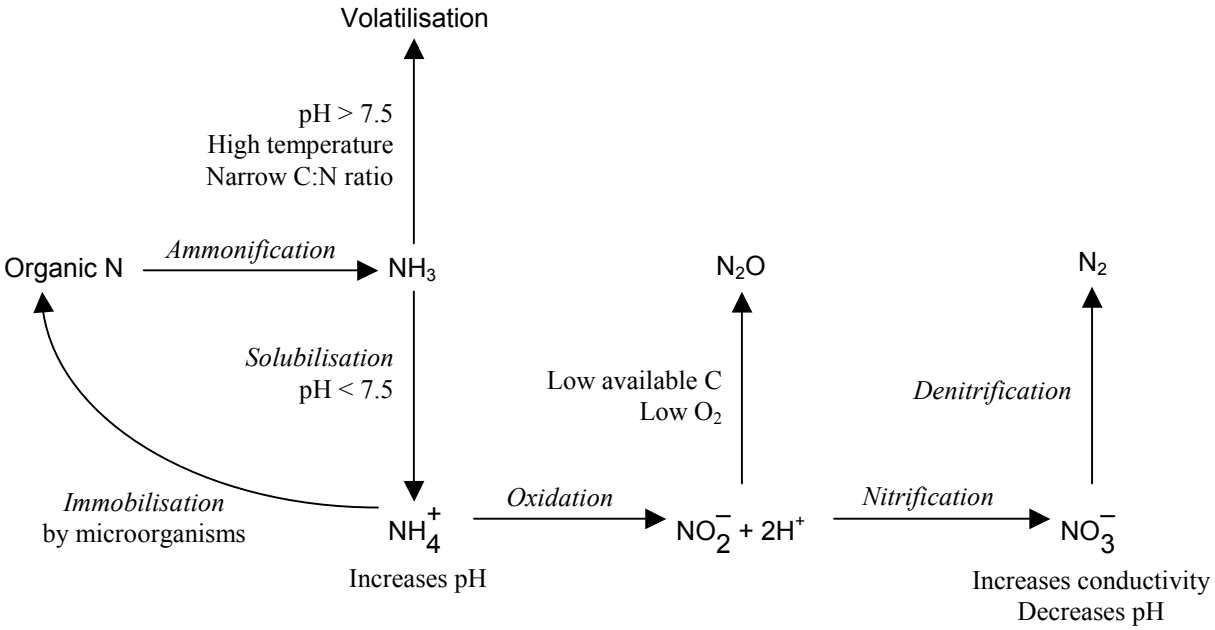
Although the initial pH of the blends (Figure 5–10) was at the low end of the optimum range, being 5.5-8.0 (de Bertoldi *et al.*, 1983), adjustment is not usually required due to the buffering capacity and "self-correcting" nature of the process (Haug, 1993; Miller, 1993). The pH decreases at the start of the composting process due to acid-forming bacteria that decompose complex carbonaceous materials to organic acid intermediates (de Bertoldi *et al.*, 1983). The pH increases rapidly to about 8.5 as the decomposition process proceeds, due to ammonification (Figure 5–13) and its role as a proton sink, before the pH settles to 7.5-8.0 as ammonification decreases (Miller, 1993). The pH can decrease under anaerobic conditions due to the production of potentially toxic volatile organic acids (Miller, 1993). Changes in pH values were not given in previous reports composting Sirolan CF sludge (Bateup *et al.*, 1996; Jones and Westmoreland, 1998; Jones and Westmoreland, 1999).

The carbon to nitrogen ratio (C:N) did not decrease to any large extent during the three trials (Figure 5–9), which suggested that C (as CO_2) and N (mainly as NH_3 – see Figure 5–13) were lost in relatively equal amounts since there was mass loss (Figure 5–5). Composting normally lowers the C:N ratio as more C is lost than N (de Bertoldi *et al.*, 1983). If grease (a substrate high in C) was decomposing fast (as shown in Figure 5–6), the sludge and fibre (thought to contain largely keratinous N) must have also decomposed rapidly for the ratio not to change. The unchanging ratio of C to N may be due to the method by which C was estimated (Section 2.3.3 p.46), which states that 56% of organic matter is C. Using the average C content from the chemical structures of typical acids in each series found in wool wax (74%; Figure 1–3 p.9) as representative of the acidic fraction of wool wax and the C content of cholesterol (84%; Figure 1–4 p.9) as representative of the alcoholic fraction (Table 1-2 p.8), we can suggest that 79% of wool wax is C. This figure was confirmed when the total organic C content of four wool grease samples collected from the Kaputone Woolscour was found to be 81% using the Walkley-Black method as described in Hesse (1971). Therefore, especially for samples high in grease (and noting that the grease content of samples decreased with composting time), the method described in Section 2.3.3 may have underestimated the C content of the compost samples collected early in the process and been more accurate for samples collected at the end of the process. If this were the case, then there was an effective

decrease in the C:N ratio during composting of woolscour wastes, consistent with the composting of other materials such as straw (Eiland *et al.*, 2001) and paper pulp sludge (Sesay *et al.*, 1997).

Decreasing levels of ammonia in the compost (Figure 5–11) in the latter half of the composting period when fibre was blended with the sludge could have been due to a release of ammonia caused by the low moisture content of the mix. Ammonia was not undergoing nitrification, since levels of nitrate did not increase (Figure 5–11), due to the high temperatures. The detection concentration for ammonia in air is approximately 17 ppm (Lau *et al.*, 1996). The volatilisation of ammonia is positively correlated with the percent of compost mass reaching temperatures exceeding 60°C. Ammonia and other volatile components temporarily dissolve in the film of moisture that surrounds organic matter before they are metabolised (Grebus *et al.*, 1994). It should be noted that CO_2 produced during composting does not contribute to greenhouse gas emission equations. The cycling of carbon, or carbon equivalents, in the environment via composting is considered a non-anthropogenic source of carbon entering global biogeochemical cycles and is therefore neither a loss nor gain in regard to carbon inputs or off-sets from the system as a whole (Zeman *et al.*, 2002). Methane and nitrous oxide trap 21 and 270 times more heat per molecule than carbon dioxide, respectively (United States Environmental Protection Agency, 2002).

Figure 5–13. Nitrogen dynamics during the composting process.



From Liao *et al.* (1995), Paul and Clark (1996), Liao *et al.* (1997), Tiquia and Tam (2000), He *et al.* (2001) and Sánchez-Monedero *et al.* (2001).

Germination of radish in samples (Figure 5–12) after various composting periods correlated well with levels of ammonia in the samples (Figure 5–11). With low rates of radish germination after 21 days of

composting, the product could not be regarded as a mature compost. Avnimelech *et al*. (1996) suggested an ammonium level of 50 mg kg^{-1} or less represents a stable compost, while Sánchez-Monedero *et al*. (2001) suggested that the ratio of ammonium-N to nitrate-N should be less than 1, with ammonium-N at levels less than 0.04%. Here, ammonia levels after 21 days composting ranged between 1,770 and 2,724 mg kg^{-1} on an oven dry basis, providing ammonium-N to nitrate-N ratios between 46 and 178, consistent with the radish assay and the recommendations qualifying the compost as immature.

Approximately 40% of the seeds present in the opener waste were viable initially (Table 4-4 p.103), and although no seeds germinated in the product resulting from 21 days composting, these seeds may have still been viable since, as described above, levels of ammonia were phytotoxic. The requirements for the destruction of seed viability, in terms of temperature and the length of exposure to the temperature, is very species-dependent, and it appears that other factors, such as phytotoxic leachates produced during the early stages of composting, also contribute to the loss of seed viability (Larney and Blackshaw, 2003).

During these composting trials, odorous compounds in the exhaust air were not quantified or treated. As one of the main advantages of in-vessel composting systems over other types is the minimisation and easy treatment of odours (Table 1-5 p.30), odour treatment will be briefly discussed. In a full-scale installation, odours could be treated by either chemical means, such as a scrubber, or biologically, such as a biofilter. Ammonia is produced from N-containing compounds irrespective of the feedstock, and is volatilised due to high composting temperatures at pH values above neutral in large amounts that can mask more offensive odours (Lau *et al.*, 1996; Sánchez-Monedero *et al.*, 2001). Ammonia, which was qualitatively identified as being present in the exhaust air from woolscour waste composting trials, could be trapped in a dilute sulphuric acid solution, using acid already present on woolscouring sites for the chemical flocculation process, in a similar (albeit on a much larger scale) fashion to the method employed in microcosm studies (Section 2.5.2 p.54).

Biofilters are a low cost and effective means of removing odours and volatile organic compounds from air streams, providing that factors such as water content, nutrient concentration, pH, inlet air relative humidity, and temperature are controlled (van Lith *et al.*, 1997; Morales *et al.*, 2003). The moisture content of the biofilter material is the most important operating parameter affecting the performance and consistency of the biofilter. Excess water affects the porosity of the biofilter, causing a reduction in mass transfer and increasing in the pressure drop, and decreases the colonisation of these pores by microorganisms. A low moisture content affects the formation of a biofilm on the filter particles, microbial activity, and can lead to the formation of preferential flow channels within the filter. If the off-gas entering the biofilter is at less than 100% relative humidity, moisture will be evaporated from the

media until the off-gas reaches full saturation. Media compaction, temperature, nutrient availability, and pH must also be monitored and controlled.

Biofilters can be composed of organic or inorganic substrates such as compost, bark and wood chips, pelletised peat, polystyrene spheres, lime, shells, zeolite and sludge (Lau *et al.*, 1996). Immature compost can also be used (Park *et al.*, 2002). Breakdown of odorous compounds is due to sorption followed by biological oxidation (Lau *et al.*, 1996). Advantages over physical and chemical odour treatment systems include the generation of only a small amount of residues, its simple operation, its applicability for a range of compounds, and its low capital and operating costs. Disadvantages include the area of land required (to allow a residence time typically between 30 and 60 seconds), the necessity of moisture (between 40-70%) and pH control, and the ageing of the filter media causing the development of channels in the filter.

Future work should include a thorough analysis of the compost produced by the chosen recipe to test for adherence to the relevant standards. Levels of heavy metals in the compost could be predicted based on the composition of the substrates and the level of organic matter decomposition. For example, assuming (i) woolscour sludge had a bulk density of 975 kg m^{-3}, a moisture content of 50%, and heavy metals at levels found in sludge from Ashburton Woolscour (Table 4-2 p.102), (ii) sawdust had a bulk density of 200 kg m^{-3}, a moisture content of 20%, contained no heavy metals, and was added at a rate of two times the volume of sludge, and (iii) during composting a 30% reduction in organic matter was achieved, heavy metal levels in the product could be calculated (Table 5-4). Standards for heavy metal limits in compost vary widely depending on country, use and source materials (Table 5-5). Some countries have different classes of composts each with their own allowable levels of heavy metals. There are also standards in Europe and North America for maximum annual heavy metal loading of soils and absolute soil concentrations (Brinton, 2000). Expected levels in woolscour sludge-based composts would be marginally lower than those in the sludge and only zinc levels would be higher than some of the limits imposed by certain countries, such as Austria (class 2) and Canada.

Table 5-4. Predicted changes in heavy metal levels during the composting of woolscour sludge and sawdust.

		mg kg^{-1}	
Heavy metal	Sludge	Before composting	After composting
Arsenic	3.2	1.9	2.8
Cadmium	0.1	0.1	0.1
Chromium	7.8	4.7	6.7
Copper	10.4	6.3	9.0
Lead	6.5	3.9	5.6
Nickel	10.4	6.3	9.0
Zinc	664.6	401.2	573.2

Table 5-5. A comparison of international standards for heavy metal levels in compost.

	Heavy metal limit (mg kg^{-1})								
Country	As	Cd	Cr	Co	Cu	Pb	Hg	Ni	Zn
Austria	-	4	150	-	400	500	4	100	1000
Austria class 2	-	1	70	-	100	150	1	60	400
Belgium (AG)	-	5	150	10	100	600	5	50	1000
Belgium (HO)	-	5	200	20	500	1000	5	100	1500
Canada	10	3	50	25	60	150	0.15	60	500
Denmark	25	1.2	-	-	-	120	1.2	45	-
France	-	8	-	-	-	800	8	200	-
Germany	-	1.5	100	-	100	150	1	50	400
Italy	10	1.5	100	-	300	140	1.5	50	500
Netherlands A	25	2	200	-	300	200	2	50	900
Netherlands B	15	1	70	-	90	120	0.7	20	280
Spain	-	40	750	-	1750	1200	25	400	4000
Switzerland	-	3	150	25	150	150	3	50	500
USA (SS)	41	39	1200	-	1500	300	17	420	2800

Note: AG = agricultural use, HO = horticultural use, SS = for sewage sludge-based products. Not all regulated heavy metals are shown in this table. The difference between Netherlands A and B was not specified. From Haug (1993) and Brinton (2001).

In addition to national standards already mentioned, levels of compost contamination, including stones and man-made foreign matter (glass, plastic, and metal) are also regulated (Brinton, 2000). With woolscour sludge (and fibrous wastes) free of such contamination, these standards should be easily achieved, providing that the bulking agent used is also contaminant-free and contaminants are not introduced during the process. The use of concrete bunkers (or similar) for material storage prior to composting and for product curing would be desirable.

An alternative treatment option for the sludge produced by the woolscouring process is incineration or pyrolysis (incineration in the absence of air) but, although this avenue has been tentatively investigated by the industry, only one paper (Lu *et al.*, 2000) was found on this subject. Those authors considered incineration one of the most economically viable and environmentally friendly options for the disposal of woolscour sludge and a process that could destroy all hazardous substances safely and completely without producing new hazardous substances. They also suggested that incineration could reduce the weight and volume of the sludge to less than 20% of the original amount. While this is true, the incineration of 10 t per day sludge (wet weight) would result in 1.8 t ash (Table 4-17 p.125) that would still require disposal. This option also does not allow for the recycling of the organic matter contained within the sludge. Therefore, Lu *et al*. (2000) concluded that all four sludges tested (produced using different treatments) could be incinerated in a vertical-axis-rotating fluidised bed. For comparison, the use of microorganisms in environmental technology is due to their cost efficiency; the incineration of 1 kg waste (dry weight basis) costs an estimated €0.5, whereas biological mineralisation costs a factor of ten less (Grommen and Verstraete, 2002). Microbiological processes are also flexible and adaptable and are perceived as being "green."

5.3. CASE STUDY: COMPOSTING OF KAPUTONE WOOLSCOUR SLUDGE

5.3.1. INTRODUCTION

The installation of a complete effluent treatment system, involving Sirolan CF, CFB, and evaporation, at the Kaputone Woolscour in Belfast, Christchurch, and the use of the installation as a reference site by ANDAR Holdings Ltd., permitted full-scale composting of Sirolan CF sludge to be evaluated. This case study served to illustrate the reasons behind why the research in this thesis was carried out.

Canterbury Landscape Supplies is an established company based at Bridgend, on the northern edge of Christchurch City, and supplies a range of landscaping products to customers across much of the South Island. Being located close to the Kaputone Woolscour, they were approached by the woolscour to compost their sludge.

5.3.2. MATERIALS AND METHODS

As part of the initial discussions between the two companies, the author acted as a consultant and offered expertise learnt through the research conducted during this project. Chemical analysis of the sludge produced by the Kaputone Woolscour, both prior to and after the anaerobic tank (designed to improve flocculation and reduce chemical use) was installed, was carried out as for the composting trials at Ashburton (Section 5.2.2); the results were provided to both Kaputone Woolscour and Canterbury Landscape Supplies.

The design and manufacture of a suitable mixer of 4 m^3 capacity for blending sludge with bulking agents was carried our by ANDAR Holdings Ltd.

At the time of printing, windrow composting of Sirolan CF sludge had not begun due to delays in commissioning the ANDAR sludge mixer, and thus no composting performance data was available for discussion. The composting operation is ultimately under the direction of Canterbury Landscape Supplies who will, for example, add water to the windrows based on visual determination and turn the windrows at a frequency based upon their experience. The following suggestions were made by the author, based on research findings previously discussed in this work:

- Mix the sludge with a bulking agent, such as sawdust, wood chips or greenwaste, at a ratio of at least 1:1 bulking agent to sludge, so that the bulk density of the blend is below 700 kg m^{-3}.

- The initial moisture content of the blend may be limited to 50% (depending on the chosen bulking agent) due to the water holding capacity of the sludge.
- CFB biomass could be added with water for moisture control during composting, to act as an inoculum and provide nutrients such as K, providing that the electrical conductivity of the compost produced is not increased beyond acceptable values.
- Add scour fibrous wastes to the blend to increase the initial pH, provide for a higher level of microbial activity (which would be shown by higher temperatures), and increase the N content of the compost produced. However, if opener waste is chosen over scoured wool cleaner waste, adding too much fibre may bind particles in the blend and reduce composting performance.

5.3.3. RESULTS AND DISCUSSION

Installation of the ANDAR effluent treatment system at the Kaputone Woolscour resulted in the production of approximately 16 t per day Sirolan CF sludge available for composting. At the current disposal cost of \$31.82 t^{-1}, Kaputone faces a yearly cost of \$150,000, excluding goods and services tax (GST) and transport costs. Disposal charges were expected to increase beyond \$80 t^{-1} once the Kate Valley regional landfill opens and existing landfills close. Chemical properties of the sludge (Table 5-6) were similar to those of sludges produced at other woolscours examined in this thesis (Table 4-2 p.102). Average moisture content was the highest of the three scours, while pH was the same as that at Ashburton. The grease content of the sludge produced before the anaerobic tank was installed was very low. Heavy metal levels were similar to samples collected from the other scours, with levels of zinc between those found at the Fairlie and Ashburton Woolscours. It appears that zinc is the only heavy metal whose level in sludge varies between woolscours.

While limited samples were taken, and although parameters such as flowdown rates and the types of wool scoured on days when samples were collected were not recorded, comparisons can still be made to provide an indication of the effect of the anaerobic tank on sludge properties. The anaerobic stage had no effect ($p>0.05$) on the moisture or pH of the resulting sludge, but significantly affected the organic matter ($p=0.0000$), total N ($p=0.0455$) and grease ($p=0.0072$) contents. The pH of the "anaerobic" sludge was marginally higher, indicating that acid consumption in the Sirolan CF process was reduced. Higher organic matter levels could have been due to better flocculation (biologically-mediated) of small micron organic materials in the anaerobic tank. Likewise for grease, it appeared that biological flocculation processes partitioned more grease into the sludge from the wastewater entering the tank, implying that levels entering the CFB process would have been reduced. An increase in sludge TN levels suggested that

nutrients were incorporated from the wastewater into microbial biomass. Microbial counts and activity in sludge from Kaputone were described in Section 4.3.9 (p.118).

Table 5-6. Chemical properties of Sirolan CF Sludge from the Kaputone Woolscour.

	Treatment	
Property	No anaerobic stage	Anaerobic stage
Moisture (%)	50.3 (1.27)	51.9 (1.82)
pH	5.1 (0.18)	5.3 (0.10)
Organic matter (%)	54.7 (1.72)	67.7 (1.68)
Total N (%)	1.4 (0.25)	2.2 (0.08)
Grease (%)	15.6 (3.02)	34.9 (0.37)
Arsenic (mg kg^{-1})		5.2 (0.97)
Cadmium (mg kg^{-1})		0.1 (0.00)
Chromium (mg kg^{-1})		8.4 (0.51)
Copper (mg kg^{-1})		12.4 (0.40)
Lead (mg kg^{-1})		5.2 (0.39)
Nickel (mg kg^{-1})		3.6 (0.24)
Zinc (mg kg^{-1})		265 (17.31)

Note: organic matter, total N, grease and heavy metals are reported on an oven dry basis.
Numbers in brackets are the standard errors of the means, n≥4.

The composting of 16 t sludge per day (approximately 16 m^3) is not a small operation. If bulking agent was added at a rate of 1.5 times the volume of sludge, a total of 40 m^3 material per day would require mixing. A volume reduction of 20% during mixing would result in 32 m^3 blended material per day for composting. Based on a total composting duration of 16 weeks, 3,584 m^3 material would be at various stages of composting at any one time. This equates to a windrow of 1,195 m length, assuming a cross-sectional area of 3 m^2 (3 m base and 2 m height).

This case study shows real life application of university research in a commercial setting which, based on a sludge production of 16 m^3 per day for 365 days per year, diverts 5,840 m^3 sludge (equivalent to 90 standard 40-foot shipping containers) from landfill to the composting operation each year.

6. CONCLUSIONS

6.1. CONCLUSIONS

Tightening environmental regulations and increasing environmental awareness around the world means it is increasingly difficult for industry to legally and responsibly dispose of wastes into water sources or landfills. An example of a highly polluting industry, and one that has realised the importance of effluent treatment to its future, is the woolscouring (wool washing) industry.

The woolscouring process aims to remove contaminants, such as wax (the solvent-insoluble fraction), suint (sheep sweat; the water-soluble fraction), dirt (soil particles, faecal matter and skin and fibre debris) and vegetable matter, from the fleece, and therefore waste minimisation is not possible. A state of the art effluent treatment system for woolscouring plants is being increasingly adopted (Figure 6–1), which involves the use of recovery loops and treatment components for various fractions of woolscour wastes to produce only two streams that move off site. Both of these are viewed as a resource rather than a waste. The philosophy behind the multi-stage treatment process is that components can be optimised for the individual waste streams to provide a better overall result.

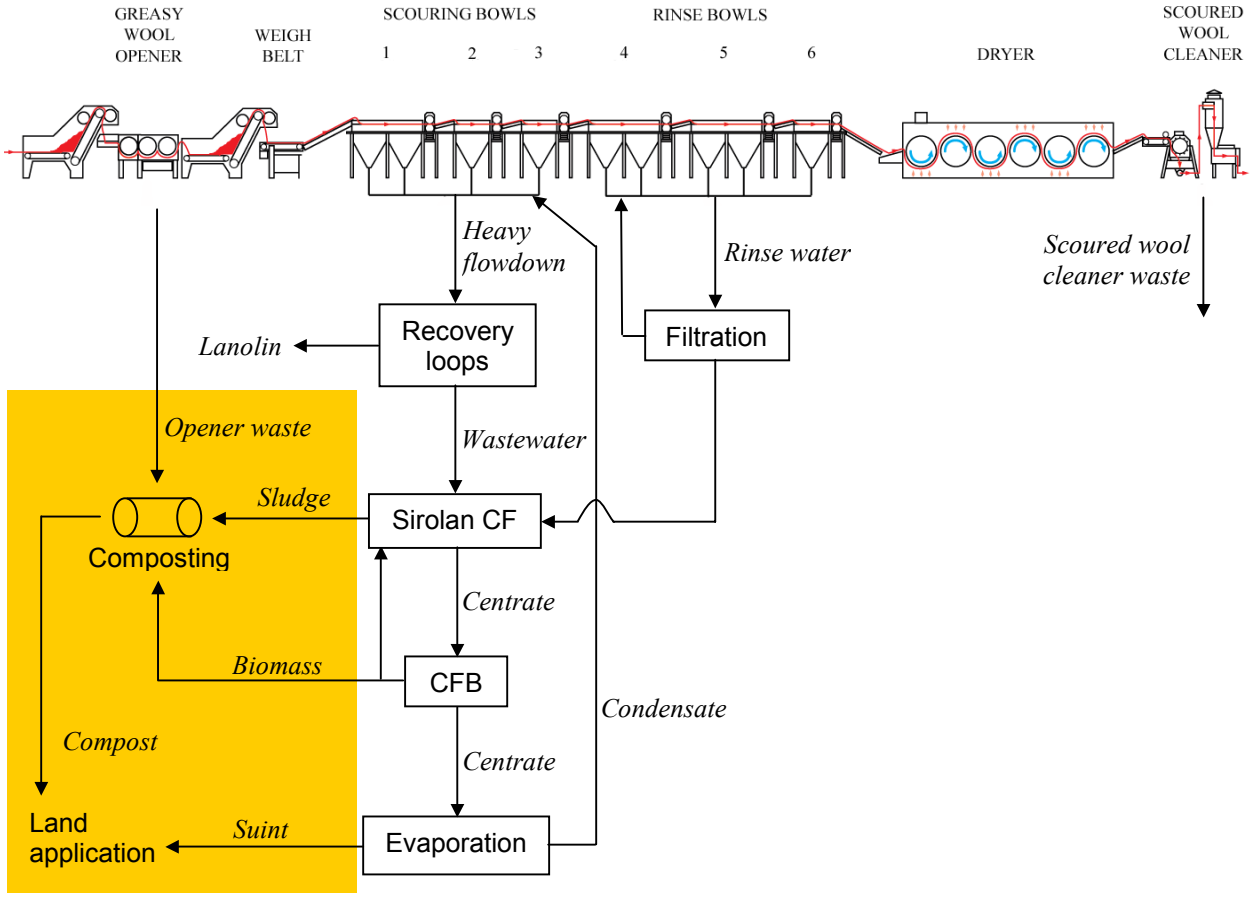
As part of this overall effluent treatment system, the objectives of research in this thesis (shown in the shaded area of Figure 6–1) were an evaluation of the potential for concentrated suint to be applied to land as a potassium fertiliser, and the composting of Sirolan CF sludge with other waste streams to return organic matter to agricultural land. Both concentrated suint and sludge had not previously been thoroughly characterised.

For the product from the evaporator, concentrated suint, to be suitable as a potassium fertiliser for use on arable land, it must not contain any components that could negatively affect the soil system, it must be able to be applied in a sustainable way without causing detrimental effects on the normal functioning of the soil system, and must be either neutral or positive to plant growth. Based on the work here, it can be concluded that suint is suitable for use as a potassium fertiliser for land application when applied at realistic rates such as 100 kg K ha^{-1}.

My research findings recommended that suint be produced by evaporation of the centrate after the CFB process (as shown in Figure 6–1), rather than before, as the post-CFB product had a more consistent composition on a daily basis, contained less wool grease, had a more neutral pH, and had been stabilised (more of the TN being in organic forms). Residual wool grease could reduce the water infiltration into the soil on which the suint had been applied, while a neutral pH would be unlikely to change the soil pH. A

smaller fraction of the TN of CFB suint was in the readily-leachable mineral form. Concentrated CFB suint was shown to have a high potassium content (20% on a dry weight basis) and would also add appreciable quantities of sulphur, chlorine and sodium to soil.

Figure 6–1. Effluent treatment diagram for woolscouring plants.



CFB suint in the dilute form (1:10 in distilled water) was a resource of good quality as judged by rates of net-N mineralisation, more so than the suint produced prior to the biological stage. Decomposition occurred under both aerobic and anaerobic conditions, both of which can occur simultaneously in soils. Aerobic decomposition was enhanced as incubation temperature increased, suggesting seasonal variation in decomposition rates could occur. Both suint types were either neutral (in the case of casein and chitin) or positive (in the case of woolscour sludge) to the turnover of model organic compounds, as judged by comparing observed rates of net-N mineralisation to expected rates. Soil pH and electrical conductivity (a measure of the salt concentration) were not adversely affected by the application of suint, although monitoring the effects of repeat suint applications in the long term is recommended.

Assays showed that suint was not phytotoxic to pasture plants (white clover and ryegrass), cucumber, radish or *Pinus radiata* when applied at a rate of 100 kg K ha^{-1} over growth periods ranging from six

weeks to eight months, being neutral or positive to seed germination and seedling growth. Suint should therefore be applied to areas used for pasture or forestry. Suint could be regarded as an unbalanced fertiliser and, for best use, should be targeted to crops that require large amounts of the nutrients found in suint in high amounts, or to soil types deficient in these elements.

For woolscour sludge, and scour fibrous wastes, composting should be performed prior to land application to reduce grease, pesticide and detergent residues. Woolscour sludge was phytotoxic, probably due to the wool grease and polyacrylamide preventing the uptake of adequate water required by seeds for germination. Composting must therefore degrade these components. From laboratory research, and trials involving a small-scale in-vessel composter established at a New Zealand scour, it was concluded that sludge and other woolscour waste streams could be successfully composted to allow the return of organic material to agricultural land from which it was derived.

Industrial waste streams are thought to be more consistent in composition than wastes derived from municipal sources, but considerable variation, such as in levels of organic matter and TN, was detected in the composition of Sirolan CF sludge. Fibrous wastes were more uniform in composition, although the grease content of opener waste varied depending on the wool type. Sludge variability may be due to the importance placed on the quality of the wastewater that goes to CFB. Some of the variability, such as the wool grease content, was due to the inherent nature of wool and was thus beyond the control of the plant operators. The moisture content of the sludge, typically between 45 and 50%, means that the sludge is dry in comparison to other industrial sludges, which keeps the volume of bulking agent required for composting low. No components in the sludge, such as heavy metals, were found at levels that would preclude the use of sludge in composting processes. The anaerobic tank that is part of Sirolan CF (immediately prior to acid and flocculant dosing) is recommended to maximise biological flocculation and therefore reduce the rate of acid addition, thus ensuring the sludge pH is as close to neutral as possible.

Results of decomposition studies showed the variable nature of woolscour sludge, with sludge generally regarded as a substrate of poor resource quality. This was thought to be due to the sludge N being derived mainly from wool proteins (keratin) that are quite resistant to decomposition. The sludge also contained very low numbers of microorganisms and low microbial activity, both due to scouring factors leading to the production of the sludge (scouring at 65ºC followed by sulphuric acid injection) and the low levels of available nutrients in the sludge. While the grease content of the sludge was shown to retard the mineralisation of N, its pesticide and flocculant (polyacrylamide) contents had no effect on the rate of decomposition. Under composting temperatures, polyacrylamide exhibited high rates of decomposition. Sludge decomposition was enhanced when co-incubated with fibrous wastes, such as opener and scoured

wool cleaner wastes, possibly due to the presence of a more metabolically-diverse microbial community. In the case of sludge, chemical properties, such as a good C:N ratio (being 17:1), did not correlate well with its biological properties, illustrating the limited use of selected chemical properties in determining its biodegradability. The results suggest that the use of new technology that partitions more material from the effluent into the sludge phase produced a sludge that decomposed at a slower rate than sludges produced in the past.

The variability in sludge composition and substrate quality has important implications for the biological treatment of industrial wastes. In using a process such as composting for the treatment of waste streams, a consistent final product is required for it to have future use as a soil conditioner. Despite laboratory results suggesting that woolscour sludge was a poor substrate from a resource quality perspective, composting trials were successful, as judged by rates of wool grease and organic matter decomposition and temperature profiles. Although Figure 6–1 showed no end use for scoured wool cleaner waste, this stream could also be composted with sludge, either as a substitute for or additional to opener waste, depending on the amounts of fibrous wastes produced when compared to sludge. The addition of a bulking agent, in this case untreated sawdust, improved the physical properties of the sludge and allowed for a high rate of organic matter decomposition and a grease reduction of 90% in three weeks when moisture was maintained at optimum levels. An increase in microbial activity occurred immediately following blending. The grease fraction melts at temperatures above 40ºC, improving its physical properties and thus its ability to be degraded. The addition of fibrous wastes to the sludge, although reducing rates of grease decomposition, was recommended to meet temperatures high enough for effective compost pasteurisation (greater than 55ºC for three days).

Overall, a closed-loop effluent treatment process for the woolscouring industry was shown to be feasible, with research in this thesis showing that the final products from the system could be safely applied to land for sustainable agriculture. The implementation of such a system is shown by the development at the Kaputone Woolscour. A similar methodology could, and should, be applied to other industries to minimise their impacts on the environment.

6.2. RECOMMENDATIONS

Based on these research conclusions and observations made while at woolscour factories, recommendations can be made to both the woolscouring industry and regulatory bodies regarding the handling and land application of woolscour wastes. Woolscour sludge should not be allowed to accumulate on the scouring site due to the potential production of odours resulting from anaerobic microbial activity within the sludge. Storage in exposed locations could involve two scenarios. Firstly, if

sludge were stockpiled when it was raining, the sludge would become waterlogged and leach nutrients. Secondly, warm conditions would result in the formation of a hard, hydrophobic, crust similar to concrete on the sludge surface, potentially causing runoff following subsequent rainfall events. These scenarios would complicate the future handling of the sludge.

CFB suint, but not suint produced prior to the CFB process, is suitable for land application, providing that resource consents specify a maximum application rate which, in this case, should be based on the potassium content of the suint (whether the suint is applied direct in the dilute form or after evaporation followed by dilution). Woolscour sludge application to land should not be permitted unless the sludge has been processed, such as by composting, to reduce both the grease content and phytotoxicity. Woolscour sludge, with a high grease content, would likely decompose slowly in a soil environment and reduce water infiltration into soil and potentially reduce soil productivity. There may, however, be a beneficial application for non-processed sludge: incorporation into soil in situations where erosion and soil stability is a problem, as the grease component would act as a binder of soil particles, thus stabilising the site. As the grease would likely contain pesticide and detergent residues, sludge incorporation should only be practiced in areas with no public access and where no crops are harvested, in order to meet health and safety requirements.

6.3. FUTURE RESEARCH

Following the completion of this project, recommendations for future work can be made:

- The source(s) of chloride in suint should be determined.
- Reducing the salt content of suint without affecting its K content should be investigated, as suggested by Elice-Invaso *et al*. (1997).
- The use of suint as a sulphur fertiliser should be investigated.
- Long term monitoring of soil health following suint application to land should be conducted.
- A mass balance on the fate of the wool grease and heavy metals entering the CFB system (biological decomposition or partitioning into the biomass phase) should be conducted.
- Research into whether the slow decomposition of the sludge is due to a shortage of available N resulting from the slow decomposition of wool proteins (keratin) should be made.
- The amount of CFB biomass added as an inoculant instead of water to the composting blend should be optimised, with the electrical conductivity of the products determined.
- The rate of detergent breakdown during in-vessel composting should be determined to allow comparisons to windrow composting to be made.

- A complete analysis of the compost produced from woolscour sludge should be made to ensure the requirements of the relevant standard (e.g. Australian Standard AS4454) are met.
- The effluent treatment demonstration site at the Kaputone Woolscour offers an excellent opportunity for a mass balance of the entire system to be performed.

7. REFERENCES

Abdelmagid, H. M. and Tabatabai, M. A. (1982). Decomposition of acrylamide in soils. *Journal of Environmental Quality*, **11,** 701-704.

Adam, K. (2003). The environmental and health implications of the decomposition of biosolids. M.Sc. thesis (Microbiology), University of Canterbury, Christchurch, New Zealand, 98 pp.

Adriano, D. C. and Doner, H. E. (1982). Bromine, chlorine and fluorine. In *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*, Page, A. L., Miller, R. H. and Keeney, D. R. (eds.). American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, pp. 449-483.

Aitken, F. J., Cottle, D. J., Reid, T. C. and Wilkinson, B. R. (1994). Mineral and amino acid composition of wool from New Zealand merino sheep differing in susceptibility to yellowing. *Australian Journal of Agricultural Research*, **45,** 391-401.

Allison, F. E. and Murphy, R. M. (1963). Comparative rates of decomposition in soil of wood and bark particles of several species of pines. *Soil Science Society of America Proceedings*, **27,** 309-312.

Alloway, B. J. (1995a). Cadmium. In *Heavy metals in soils*, Alloway, B. J. (ed.). Blackie Academic and Professional, London, pp. 122-151.

Alloway, B. J. (1995b). The origin of heavy metals in soils. In *Heavy metals in soils*, Alloway, B. J. (ed.). Blackie Academic and Professional, London, pp. 38-57.

Alloway, B. J. and Ayres, D. C. (1997). *Chemical principles of environmental pollution.* Chapman and Hall, London, 395 pp.

Anderson, C. A. (1983). Mechanisms of raw wool scouring - the role of the protein contaminant layer. *Textile Research Journal*, **53,** 741-750.

Anderson, J. G. (1990). Treatment of wastes by composting. In *Microbiology of Landfill Sites*, Senior, E. (ed.). CRC Press Inc., Boca Raton, pp. 59-79.

Anon (1994). Brown gold or trouble? *Compressed Air Magazine*, **April/May,** 22-31.

Atlas, R. M. (1993). *Handbook of microbiological media.* CRC Press, Inc., Boca Raton, 1079 pp.

Atlas, R. M. (1998). *Microbiology: fundamentals and applications.* Macmillan Publishing Company, New York, 807 pp.

Avnimelech, Y., Bruner, M., Ezrony, I., Sela, R. and Kochba, M. (1996). Stability indices for municipal solid waste compost. *Compost Science and Utilization*, **4,** 13-20.

Badr EL-Din, S. M. S., Attia, M. and Abo-Sedera, S. A. (2000). Field assessment of composts produced by highly effective cellulolytic microorganisms. *Biology and Fertility of Soils*, **32,** 35-40.

Baker, D. E. and Senft, J. P. (1995). Copper. In *Heavy metals in soils*, Alloway, B. J. (ed.). Blackie Academic and Professional, London, pp. 179-205.

Barry, G. A., Gardner, E. A., Rayment, G. E. and Bloesch, P. M. (1999). Recycling organic materials on agricultural lands. Available at: http://www.recycledorganics.com.au (5.09.2001).

Barvenik, F. W. (1994). Polyacrylamide characteristics related to soil applications. *Soil Science*, **158,** 235-243.

Bateup, B. O. (1986). Optimisation of the aqueous scouring process. *Wool scouring and worsted carding: new approaches*, Geelong, Australia, 5-7 November 1986, CSIRO Division of Textile Industry, pp. 8-16.

Bateup, B. O., Christoe, J. R., Jones, F. W., Poole, A. J., Skourtis, C. and Westmoreland, D. J. (1996). Effluent management. *Top-Tech '96*, Geelong, Australia, 11-14 November 1996, CSIRO Australia, IWS International Wool Secretariat, pp. 388-407.

Bateup, B. O., Christoe, J. R. and Russell, I. M. (1995). Scouring wastes: a resource, not a problem. *Proceedings of the 9th International Wool Textile Research Conference***,** 171-179.

Becker, P., Köster, D., Popov, M. N., Markossian, S., Antranikian, G. and Märkl, H. (1999). The biodegradation of olive oil and the treatment of lipid-rich wool scouring wastewater under aerobic thermophilic conditions. *Water Research*, **33,** 653-660.

Bender, D. A. (1993). Onions. In *Nutrient deficiencies and toxicities in crop plants*, Bennett, W. F. (ed.). American Phytopathological Society, St. Paul, pp. 131-135.

Bennett, W. F. (1993). Plant nutrient utilization and diagnostic plant symptoms. In *Nutrient deficiencies and toxicities in crop plants*, Bennett, W. F. (ed.). American Phytopathological Society, St. Paul, pp. 1-7.

Bhamidimarri, S. M. R. and Pandey, S. P. (1996). Aerobic thermophilic composting of piggery solid wastes. *Water Science and Technology*, **33,** 89-94.

Bond, W. J. (1998). Effluent irrigation - an environmental challenge for soil science. *Australian Journal of Soil Research*, **36,** 543-555.

Borken, W., Muhs, A. and Beese, F. (2002). Changes in microbial and soil properties following compost treatment of degraded temperate forest soils. *Soil Biology and Biochemistry*, **34,** 403-412.

Brady, D., Duncan, J. R., Cross, R. H. M. and Russell, A. E. (1990). Scanning electron microscopy of wool fibre degradation by *Streptomyces* bacteria. *South African Journal of Animal Science*, **20,** 136-140.

Bremner, J. (1985). *Woolscours of New Zealand.* New Zealand Woolscourers Association Inc., Christchurch, 136 pp.

Bremner, J. M. and Mulvaney, C. S. (1982). Nitrogen - total. In *Methods of soil analysis, part 2. Chemical and microbiological properties*, Page, A. L., Miller, R. H. and Keeney, D. R. (eds.). American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, pp. 595-624.

Brinson, S. E., Jr., Cabrera, M. L. and Tyson, S. C. (1994). Ammonia volatilization from surface-applied, fresh and composted poultry litter. *Plant and Soil*, **167,** 213-218.

Brinton, W. F. (2000). *Compost quality standards and guidelines: an international viewpoint.* Woods End Research Laboratory, Inc., New York, 44 pp.

Brinton, W. F. (2001). An international look at compost standards. *BioCycle*, **42,** 74-76.

Brown, J. E., Dangler, J. M., Gilliam, C. H., Porch, D. W. and Shumach, R. L. (1994). Comparison of broiler litter and inorganic nitrogen, phosphorous, and potassium for double-cropped sweet corn and broccoli. *Journal of Plant Nutrition*, **17,** 859-867.

Brown, L., Rhead, M. M., Bancroft, K. C. C. and Allen, N. (1980). Model studies of the degradation of acrylamide monomer. *Water Research*, **14,** 775-778.

Butler, T. A., Sikora, L. J., Steinhilber, P. M. and Douglass, L. W. (2001). Compost age and sample storage effects on maturity indicators of biosolids compost. *Journal of Environmental Quality*, **30,** 2141-2148.

Büyüksönmez, F., Rynk, R., Hess, T. F. and Bechinski, E. (1999). Occurrence, degradation and fate of pesticides during composting - part 1: composting, pesticides, and pesticide degradation. *Compost Science and Utilization*, **7,** 66-82.

Büyüksönmez, F., Rynk, R., Hess, T. F. and Bechinski, E. (2000). Occurrence, degradation and fate of pesticides during composting - part 2: occurrence and fate of pesticides in compost and composting systems. *Compost Science and Utilization*, **8,** 61-81.

Cameron, K. C., Di, H. J. and Condron, L. M. (2002). Nutrient and pesticide transfer from agricultural soils to water in New Zealand. In *Agriculture, hydrology and water quality*, Haygarth, P. M. and Jarvis, S. C. (eds.). CAB International, Wallingford, pp. 373-393.

Campbell, A. G., Folk, R. L. and Tripepi, R. R. (1994). Amended and composted log yard fines as a growth medium for crimson clover and red top grass. *Communications in Soil Science and Plant Analysis*, **25,** 2439-2454.

Charles, W., Ho, G. and Cord-Ruwisch, R. (1996). Anaerobic bioflocculation of wool scouring effluent: the influence of non-ionic surfactant on efficiency. *Water Science and Technology*, **34,** 1-8.

Chiampo, F., Antonielli, M. and Conti, R. (1995). Composting solid wastes from wool industry. *Proceedings of the 9th International Wool Textile Research Conference***,** 293-299.

Chong, C. (1999). Experiences with the utilization of wastes in nursery potting mixes and as field soil amendments. *Canadian Journal of Plant Science*, **79,** 139-148.

Christian, G. (1998). Making sure our wool industry doesn't dip out. *Wool*, **8,** 9-10.

Christoe, J. R. (1996a). Early stage processing of the future: wool scouring. *Top-Tech '96*, Geelong, Australia, 11-14 November 1996, CSIRO Australia, IWS International Wool Secretariat, pp. 448-451.

Christoe, J. R. (1996b). Environmental issues in wool scouring. *Top-Tech '96*, Geelong, Australia, 11-14 November 1996, CSIRO Australia, IWS International Wool Secretariat, pp. 105-112.

Clarke, M. A. (1988). Sugarcane processing: raw and refined sugar manufacture. In *Chemistry and processing of sugarbeet and sugarcane*, Clarke, M. A. and Godshall, M. A. (eds.). Elsevier Science Publishers B. V., Amsterdam, pp. 162-175.

Cleary, M. (1988). Carbonatation process in beet sugar manufacture. In *Chemistry and processing of sugarbeet and sugarcane*, Clarke, M. A. and Godshall, M. A. (eds.). Elsevier Science Publishers B. V., Amsterdam, pp. 20-34.

Clesceri, L. S., Greenberg, A. E. and Eaton, A. D. eds. (1998). *Standard methods for the examination of water and wastewater.* American Public Health Association, American Water Works Association, Water Environment Federation, Washington.

Coleman, D. C. and Crossley, D. A., Jr. (1996). *Fundamentals of soil ecology.* Academic Press, Inc., San Diego, 205 pp.

Cook, D. F. and Nelson, S. D. (1986). Effect of polyacrylamide on seedling emergence in crust-forming soils. *Soil Science*, **141,** 328-333.

Craft, C. M. and Nelson, E. B. (1996). Microbial properties of composts that suppress damping-off and root rot of creeping bentgrass caused by *Pythium graminicola*. *Applied and Environmental Microbiology*, **62,** 1550-1557.

Davies, B. E. (1995). Lead. In *Heavy metals in soils*, Alloway, B. J. (ed.). Blackie Academic and Professional, London, pp. 206-223.

de Bertoldi, M., Vallini, G. and Pera, A. (1983). The biology of composting: a review. *Waste Management Research*, **1,** 157-176.

de Hoog, G. S., Guarro, J., Gené, J. and Figueras, M. J. (2000). *Atlas of clinical fungi.* Centraalbureau voor Schimmelcultures/Universitat Rovira i Virgili,, 1126 pp.

De, S. and Chandra, A. L. (1982). A keratin-decomposing streptomycete. *Enzyme and Microbial Technology*, **4,** 158-160.

Domsch, K. H., Gams, W. and Anderson, T.-H. (1980). *Compendium of soil fungi Volume 1.* Academic Press, London, 859 pp.

Doran, J. W. and Parkin, T. B. (1994). Defining and assessing soil quality. In *Defining soil quality for a sustainable environment*, Doran, J. W., Coleman, D. C., Bezdicek, D. F. and Stewart, B. A. (eds.). Soil Science Society of America, Inc., American Society of Agronomy, Inc., Madison, pp. 3-21.

During, C. (1984). *Fertilisers and soils in New Zealand farming.* P. D. Hasselberg, Government Printer, Wellington, 355 pp.

Dynes, R. A., Baker, S. K., Hirst, N. A. L. and Martin, S. B. (2000). Composting earthworms grow well on paunch material. *Asian-Australasian Journal of Animal Sciences*, **13 (Supplement C),** 107.

Eiland, F., Klamer, M., Lind, A.-M., Leth, M. and Bååth, E. (2001). Influence of initial C/N ratio on chemical and microbial composition during long term composting of straw. *Microbial Ecology*, **41,** 272-280.

Elice-Invaso, A., Maheswaran, J., Rogers, S. and Peverill, K. (1997). *Utilisation of wool scour waste on agricultural land.* CSIRO Division of Wool Technology, International Wool Secretariat, Department of Natural Resources and Environment, Melbourne, Australia, 38 pp.

Epstein, E. (1997). *The science of composting.* Technomic Publishing Company, Inc., Lancaster, 487 pp.

Evanylo, G. K. and Daniels, W. L. (1999). Paper mill sludge composting and compost utilization. *Compost Science and Utilization*, **7,** 30-39.

Everett, J. G. (1977). Sludge treatment and disposal. In *Treatment of industrial effluents*, Callely, A. G., Forster, C. F. and Stafford, D. A. (eds.). Hodder and Stoughton, London, pp. 103-128.

EXTOXNET (1996). Extension toxicology network pesticide information profiles. Available at: http://ace.ace.orst.edu/info/extoxnet/pips (6.12.2001).

Fang, M. and Wong, J. W. C. (1999). Effects of lime amendment on availability of heavy metals and maturation in sewage sludge composting. *Environmental Pollution*, **106,** 83-89.

Ferrier, D. A. (1960). *Woolscour and woollen mill wastes.* Ministry of Works, Wellington, 23 pp.

Feughelman, M. (1997). *Mechanical properties and structure of alpha-keratin fibres: wool, human hair and related fibres.* University of New South Wales Press, Sydney, 164 pp.

Fürhacker, M. and Haberl, R. (1995). Composting of sewage sludge in a rotating vessel. *Water Science and Technology*, **32,** 121-125.

Gaertel, W. (1993). Grapes. In *Nutrient deficiencies and toxicities in crop plants*, Bennett, W. F. (ed.). American Phytopathological Society, St. Paul, pp. 177-183.

Garrett, R. H. and Grisham, C. M. (1995). *Biochemistry.* Saunders College Publishing, Fort Worth, 1100 pp.

Gascho, G. J., Anderson, D. L. and Bowen, J. E. (1993). Sugarcane. In *Nutrient deficiencies and toxicities in crop plants*, Bennett, W. F. (ed.). American Phytopathological Society, St. Paul, pp. 37-42.

Gauch, H. G. (1972). *Inorganic plant nutrition.* Dowden, Hutchinson and Ross, Inc., Stroudsburg, 488 pp.

Gerba, C. P. (2000). Domestic wastes and waste treatment. In *Environmental Microbiology*, Maier, R. M., Pepper, I. L. and Gerba, C. P. (eds.). Academic Press, San Diego, pp. 505-534.

Gomez, A. (1998). The evaluation of compost quality. *Trends in Analytical Chemistry*, **17,** 310-314.

Gray, S. R., Le, N. P., Dixon, D. R., Jones, F. W. and Bateup, B. O. (1996). Supercritical carbon dioxide extraction of wool wax from wool scour sludges. *Environmental Technology*, **17,** 1131-1138.

Grebus, M. E., Watson, M. E. and Hoitink, H. A. J. (1994). Biological, chemical and physical properties of composted yard trimmings as indicators of maturity and plant disease suppression. *Compost Science and Utilization*, **2,** 57-71.

Greenfield, L. G. (2001). The origin and nature of organic nitrogen in soil as assessed by acidic and alkaline hydrolysis. *European Journal of Soil Science*, **52,** 575-583.

Grommen, R. and Verstraete, W. (2002). Environmental biotechnology: the ongoing quest. *Journal of Biotechnology*, **98,** 113-123.

Grula, M. M., Huang, M.-L. and Sewell, G. (1994). Interactions of certain polyacrylamides with soil bacteria. *Soil Science*, **158,** 291-300.

Guerin, T. F. (2001). Co-composting of pharmaceutical wastes in soil. *Letters in Applied Microbiology*, **33,** 256-263.

Gutiérrez, S., Hernández, A. and Viñas, M. (1999). Mechanism of degradation of wool wax in the anaerobic treatment of woolscouring wastewater. *Water Science and Technology*, **40,** 17-23.

Hanson, E. (1993). Apples and pears. In *Nutrient deficiencies and toxicities in crop plants*, Bennett, W. F. (ed.). American Phytopathological Society, St. Paul, pp. 159-163.

Hart, P. B. S. and Speir, T. W. (1992). Agricultural and industrial effluents and wastes as fertilisers and soil amendments in New Zealand. In *The use of wastes and byproducts as fertilisers and soil amendments for pastures and crops*, White, R. E. and Currie, L. D. (eds.). Fertiliser and Lime Research Centre, Massey University, Palmerston North, pp. 69-90.

Hassink, J., Matus, F. J., Chenu, C. and Dalenberg, J. W. (1997). Interactions between soil biota, soil organic matter, and soil structure. In *Soil ecology in sustainable agricultural systems*, Brussaard, L. and Ferrera-Cerrato, R. (eds.). CRC Press LLC, Boca Raton, pp. 15-35.

Haug, R. T. (1993). *The practical handbook of compost engineering.* Lewis Publishers, Boca Raton, USA, 717 pp.

He, Y., Inamori, Y., Mizuochi, M., Kong, H., Iwami, N. and Sun, T. (2001). Nitrous oxide emissions from aerated composting of organic waste. *Environmental Science and Technology*, **35,** 2347-2351.

Hearle, J. W. S. (2000). A critical review of the structural mechanics of wool and hair fibres. *International Journal of Biological Macromolecules*, **27,** 123-138.

Heathman, G. C., Sharpley, A. N., Smith, S. J. and Robinson, J. S. (1995). Land application of poultry litter and water quality in Oklahoma, USA. *Fertilizer Research*, **40,** 165-173.

Helalia, A. M. and Letey, J. (1989). Effects of different polymers on seedling emergence, aggregate stability, and crust hardness. *Soil Science*, **148,** 199-203.

Hellmann, B., Zelles, L., Palojärvi, A. and Bai, Q. (1997). Emission of climate-relevant trace gases and succession of microbial communities during open-windrow composting. *Applied and Environmental Microbiology*, **63,** 1011-1018.

Herbert, T. L. (1997). Paunch composting methods. *BioCycle*, **38,** 71.

Herman, D. C. and Maier, R. M. (2000). Consequences of biogeochemical cycles gone wild. In *Environmental Microbiology*, Maier, R. M., Pepper, I. L. and Gerba, C. P. (eds.). Academic Press, San Diego, pp. 347-361.

Hesse, P. (1971). *A textbook of soil chemical analysis.* John Murray Ltd., London, 520 pp.

Hoare, J. L. and Stewart, R. G. (1971). Some aspects of suint composition and yellow discoloration in New Zealand wools. *Journal of the Textile Institute*, **62,** 455-464.

Hoare, J. L., Stewart, R. G. and Sweetman, B. J. (1969). New Zealand woolscouring liquors - treatment and potassium recovery. *New Zealand Journal of Science*, **12,** 237-251.

Hoffmann, R. and Timmer, G. (1996). Environmentally-friendly production of worsted tops: experiences at BWK. *Top-Tech '96*, Geelong, Australia, 11-14 November 1996, CSIRO Australia, IWS International Wool Secretariat, pp. 492-500.

Horwath, W. R. and Paul, E. A. (1994). Microbial biomass. In *Methods of soil analysis, part 2. Microbiological and biochemical properties*, Weaver, R. W., Angle, J. S. and Bottomley, P. S. (eds.). Soil Science Society of America, Inc., Madison, pp. 753-773.

Hunter, I. R., Rodgers, B. E., Dunningham, A., Prince, J. M. and Thorn, A. J. (1991). *An atlas of radiata pine nutrition in New Zealand.* Forest Research Institute, Rotorua, 24 pp.

Hynd, P. I. (2000). The nutritional biochemistry of wool and hair follicles. *Animal Science*, **70,** 181-195.

Ichida, J. M., Krizova, L., LeFevre, C. A., Keener, H. M., Elwell, D. L. and Burtt, E. H., Jr. (2001). Bacterial inoculum enhances keratin degradation and biofilm formation in poultry compost. *Journal of Microbiological Methods*, **47,** 199-208.

Ignatova, Z., Gousterova, A., Spassov, G. and Nedkov, P. (1999). Isolation and partial characterisation of extracellular keratinase from a wool degrading thermophilic actinomycete strain *Thermoactinomyces candidus*. *Canadian Journal of Microbiology*, **45,** 217-222.

Imbeah, M. (1998). Composting piggery waste: a review. *Bioresource Technology*, **63,** 197-203.

Jackson, M. J. and Line, M. A. (1997a). Composting pulp and paper mill sludge - effect of temperature and nutrient addition method. *Compost Science and Utilization*, **5,** 74-81.

Jackson, M. J. and Line, M. A. (1997b). Windrow composting of a pulp and paper mill sludge: process performance and assessment of product quality. *Compost Science and Utilization*, **5,** 6-14.

Jenkinson, D. S. and Ladd, J. N. (1981). Microbial biomass in soil: measurement and turnover. In *Soil Biochemistry*, Vol. 5, Paul, E. A. and Ladd, J. N. (eds.). Marcel Dekker, New York, pp. 415-471.

Johnson, R. A. and Lefebvre, M. S. (1988). Desalting of molasses by counter diffusion in the fermentation industry. In *Chemistry and processing of sugarbeet and sugarcane*, Clarke, M. A. and Godshall, M. A. (eds.). Elsevier Science Publishers B. V., Amsterdam, pp. 340-348.

Johnson, R. S. (1993). Stone fruit: peaches and nectarines. In *Nutrient deficiencies and toxicities in crop plants*, Bennett, W. F. (ed.). American Phytopathological Society, St. Paul, pp. 171-175.

Jones, F. W. (1996). Multiresidue analysis of pesticides in wool wax and lanolin using gel permeation and gas chromatography. *Journal of Agricultural and Food Chemistry*, **44,** 3197-3201.

Jones, F. W. (1997). Supercritical fluid extraction as a cleanup technique for gas chromatographic analysis of pesticides in wool wax. *Journal of Agricultural and Food Chemistry*, **45,** 2569-2572.

Jones, F. W. and Westmoreland, D. J. (1998). Degradation of nonylphenol ethoxylates during the composting of sludges from wool scour effluents. *Environmental Science and Technology*, **32,** 2623-2627.

Jones, F. W. and Westmoreland, D. J. (1999). Removal of wool wax, nonylphenol ethoxylates and pesticide residues from wool scour effluent. *Water Research*, **33,** 1775-1780.

Jonkers, N., Knepper, T. P. and De Voogt, P. (2001). Aerobic biodegradation studies of nonylphenol ethoxylates in river water using liquid chromatography-electrospray tandem mass spectrometry. *Environmental Science and Technology*, **35,** 335-340.

Jonkers, N., Laane, R. W. P. M. and De Voogt, P. (2003). Fate of nonylphenol ethoxylates and their metabolites in two Dutch estuaries: evidence of biodegradation in the field. *Environmental Science and Technology*, **37,** 321-327.

Kamrin, M. A. (1997). *Pesticide profiles - toxicity, environmental impact, and fate.* Lewis Publishers, Boca Raton, 676 pp.

Katuzewska, M., Wawrzkiewicz, K. and Lobarzewski, J. (1991). Microscopic examination of keratin substrates subjected to the action of the enzymes of *Streptomyces fradiae*. *International Biodeterioration*, **27,** 11-26.

Kay-Shoemake, J. L., Watwood, M. E., Kilpatrick, L. and Harris, K. (2000a). Exchangeable ammonium and nitrate from different nitrogen fertiliser preparations in polyacrylamide-treated and untreated agricultural soils. *Biology and Fertility of Soils*, **31,** 245-248.

Kay-Shoemake, J. L., Watwood, M. E., Lentz, R. D. and Sojka, R. E. (1998a). Polyacrylamide as an organic nitrogen source for soil microorganisms with potential effects on inorganic soil nitrogen in agricultural soil. *Soil Biology and Biochemistry*, **30,** 1045-1052.

Kay-Shoemake, J. L., Watwood, M. E., Sojka, R. E. and Lentz, R. D. (1998b). Polyacrylamide as a substrate for microbial amidase in culture and soil. *Soil Biology and Biochemistry*, **30,** 1647-1654.

Kay-Shoemake, J. L., Watwood, M. E., Sojka, R. E. and Lentz, R. D. (2000b). Soil amidase activity in polyacrylamide-treated soils and potential activity toward common amide-containing pesticides. *Biology and Fertility of Soils*, **31,** 183-186.

Keeney, D. R. (1982). Nitrogen - availability indices. In *Methods of soil analysis, part 2. Chemical and microbiological properties*, Page, A. L., Miller, R. H. and Keeney, D. R. (eds.). American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, pp. 711-733.

Keeney, D. R. and Nelson, D. W. (1982). Nitrogen - inorganic forms. In *Methods of soil analysis, part 2. Chemical and microbiological properties*, Page, A. L., Miller, R. H. and Keeney, D. R. (eds.). American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, pp. 643-698.

Kiekens, L. (1995). Zinc. In *Heavy metals in soils*, Alloway, B. J. (ed.). Blackie Academic and Professional, London, pp. 284-305.

King, D. J. and Noss, R. R. (1989). Toxicity of polyacrylamide and acrylamide monomer. *Reviews on Environmental Health*, **8,** 3-16.

Kirkman, J. H., Basker, A. and MacGregor, A. N. (1994). Potassium in the soils of New Zealand - a review. *New Zealand Journal of Agricultural Research*, **37,** 207-227.

Kitson, R. E. and Mellon, M. G. (1944). Colorimetric determination of phosphorus as molybdivanadophosphoric acid. *Industrial and Engineering Chemistry Analytical Edition*, **16,** 379-383.

Kroening, S. J. (2000). Bioremediation of diesel oil contamination of soil. M.Sc thesis (Microbiology), University of Canterbury, Christchurch, New Zealand, 154 pp.

Lacey, J. (1997). Actinomycetes in composts. *Annals of Agricultural and Environmental Medicine*, **4,** 113-121.

Lande, S. S., Bosch, S. J. and Howard, P. H. (1979). Degradation and leaching of acrylamide in soil. *Journal of Environmental Quality*, **8,** 133-137.

Laos, F., Mazzarino, M. J., Walter, I. and Roselli, L. (1998). Composting of fish waste with wood by-products and testing compost quality as a soil amendment: experiences in the Patagonia region of Argentina. *Compost Science and Utilization*, **6,** 59-66.

Lapsirikul, W., Cord-Ruwisch, R. and Ho, G. (1994a). Anaerobic bioflocculation of wool scouring effluent. *Water Research*, **28,** 1743-1747.

Lapsirikul, W., Ho, G. and Cord-Ruwisch, R. (1994b). Mechanisms in anaerobic bioflocculation of wool scouring effluent. *Water Research*, **28,** 1749-1754.

Larney, F. J. and Blackshaw, R. E. (2003). Weed seed viability in composted beef cattle feedlot manure. *Journal of Environmental Quality*, **32,** 1105-1113.

Lau, A. K., Bruce, M. P. and Chase, R. J. (1996). Evaluating the performance of biofilters for composting odor control. *Journal of Environmental Science and Health*, **31,** 2247-2273.

Legendre, B. L. (1988). Varietal differences in the chemical composition of sugarcane. In *Chemistry and processing of sugarbeet and sugarcane*, Clarke, M. A. and Godshall, M. A. (eds.). Elsevier Science Publishers B. V., Amsterdam, pp. 176-185.

Lehrsch, G. A., Kincaid, D. C. and Lentz, R. D. (1996). PAM spray effects on sugarbeet emergence. *Managing irrigation-induced erosion and infiltration with polyacrylamide*, Twin Falls, USA, 6-8 May, University of Idaho, pp. 115-118.

Lewis, J. (1975). The biodeterioration of wool by microorganisms - its causes, effects and prevention. In *Microbial aspects of the deterioration of materials*, Gilbert, R. J. and Lovelock, D. W. (eds.). Academic Press, London, pp. 153-185.

Liao, P. H., Jones, L., Lau, A. K., Walkemeyer, S., Egan, B. and Holbek, N. (1997). Composting of fish wastes in a full-scale in-vessel system. *Bioresource Technology*, **59,** 163-168.

Liao, P. H., May, A. C. and Chieng, S. T. (1995). Monitoring process efficiency of a full-scale in-vessel system for composting fisheries wastes. *Bioresource Technology*, **54,** 159-163.

Lilburne, L. R., Hewitt, A. E., Sparling, G. P. and Selvarajah, N. (2002). Soil quality in New Zealand: policy and the science response. *Journal of Environmental Quality*, **31,** 1768-1773.

Lo, K. V. and Liao, P. H. (1992). Composting of salmon farm mortalities. *Canadian Agricultural Engineering*, **34,** 401-404.

Lowe, E. D. and Buckmaster, D. R. (1995). Dewatering makes big difference in compost strategies. *BioCycle*, **36,** 78-82.

Lu, Y., Wong, W. Y., Nasserzadeh, V., Swithenbank, J., Shaw, T. and Madden, M. (2000). Incineration of wool-scouring sludge in a vertical-axis-spinning fluidised-bed incinerator. *Journal of the Institute of Energy*, **73,** 149-159.

Magesan, G. N. and Wang, H. (2003). Application of municipal and industrial residuals in New Zealand forests: an overview. *Australian Journal of Soil Research*, **41,** 557-569.

Maheswaran, J., Meehan, B., Peverill, K. and Dziedzic, A.-M. (1999). Potential for agri-industry wastes as soil ameliorants. Available at: http://www.recycledorganics.com.au (5.09.2001).

Marr, J. B. and Facey, R. M. (1994). Agricultural waste. *Water Environment Research*, **66,** 387-394.

Marr, J. B. and Facey, R. M. (1995). Agricultural waste. *Water Environment Research*, **67,** 503-507.

Marschner, H. (1986). *Mineral nutrition of higher plants.* Academic Press Inc., London, 674 pp.

Maruyama, K., Yuan, M. and Otsuki, A. (2000). Seasonal changes in ethylene oxide chain length of poly(oxyethylene)alkylphenyl ether nonionic surfactants in three main rivers in Tokyo. *Environmental Science and Technology*, **34,** 343-348.

Mathison, G. E. (1964). The microbiological decomposition of keratin. *Annales de la Societe Belge de Medecine Tropicale*, **44,** 767-792.

McGrath, S. P. (1995). Chromium and nickel. In *Heavy metals in soils*, Alloway, B. J. (ed.). Blackie Academic and Professional, London, pp. 152-178.

McLaren, R. G. and Cameron, K. C. (1990). *Soil science: an introduction to the properties and management of New Zealand soils.* Oxford University Press, Auckland, 294 pp.

McLean, E. O. (1982). Soil pH and lime requirement. In *Methods of soil analysis, part 2. Chemical and microbiological properties*, Page, A. L., Miller, R. H. and Keeney, D. R. (eds.). American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, pp. 199-224.

Mengel, K. and Kirkby, E. A. (1987). *Principles of plant nutrition.* International Potash Institute, Bern, 687 pp.

Mercz, T. I. and Cord-Ruwisch, R. (1997). Treatment of wool scouring effluent using anaerobic biological and chemical flocculation. *Water Research*, **31,** 170-178.

Michel, F. C., Jr., Reddy, C. A. and Forney, L. J. (1997). Fate of carbon-14 diazinon during the composting of yard trimmings. *Journal of Environmental Quality*, **26,** 200-205.

Mickelson, C. A., Smith, G. C. and Bateup, B. O. (1990). Biological degradation of pesticides in wool scouring effluent. *8th International Wool Textile Research Conference*, Christchurch, New Zealand, 7-14 February 1990, Wool Research Organisation of New Zealand, pp. 61-70.

Miller, F. C. (1993). Composting as a process based on the control of ecologically selective factors. In *Soil Microbial Ecology: Applications in Agricultural and Environmental Management*, Metting Jr., F. B. (ed.). Marcel Dekker, New York, pp. 515-544.

Moody, P. (1999). Sustainable agriculture, soil health, and soil organic matter. Available at: http://www.recycledorganics.com.au (5.09.2001).

Morales, M., Hernández, S., Cornabé, T., Revah, S. and Auria, R. (2003). Effect of drying on biofilter performance: modeling and experimental approach. *Environmental Science and Technology*, **37,** 985-992.

Morra, M. J. (1996). Bioremediation in soil: influence of soil properties on organic contaminants and bacteria. In *Bioremediation: principles and applications*, Crawford, R. L. and Crawford, D. L. (eds.). Cambridge University Press, New York, pp. 35-60.

Muhsin, T. M. and Hadi, R. B. (2002). Degradation of keratin substrates by fungi isolated from sewage sludge. *Mycopathologia*, **154,** 185-189.

Mukhopadhyay, R. P. and Chandra, A. L. (1992). Application of a Streptomycete in the removal of waste keratinous materials. In *Industrial biotechnology*, Polasa, H., Malik, V. S., Sridhar, P. and Sharma, M. C. (eds.). Oxford & IBH Publishing Company, pp. 595-597.

Nadler, A. and Letey, J. (1989). Adsorption isotherms of polyanions on soils using tritium labeled compounds. *Soil Science Society of America Journal*, **53,** 1375-1378.

Nakasaki, K. and Ohtaki, A. (2002). A simple numerical model for predicting organic matter decomposition in a fed-batch composting operation. *Journal of Environmental Quality*, **31,** 997-1003.

Ndiaye, M., Yamoah, C. F. and Dick, R. P. (2000). Fish by-product as a soil amendment for millet and groundnut cropping systems in Senegal. *Biological Agriculture and Horticulture*, **17,** 329-338.

Nelson, D. W. and Sommers, L. E. (1982). Total carbon, organic carbon and organic matter. In *Methods of soil analysis, part 2. Chemical and microbiological properties*, Page, A. L., Miller, R. H. and Keeney, D. R. (eds.). American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, pp. 539-579.

New Zealand Water and Wastes Association (2003). *Guidelines for the safe application of biosolids to land in New Zealand.* New Zealand Water and Wastes Association, Wellington, 177 pp.

Nicholson, G. (1984). *Methods of soil, plant, and water analysis.* Forest Research Institute, New Zealand Forest Service, Rotorua, 17-19 pp.

Nogueira, W. A., Nogueira, F. N. and Devens, D. C. (1999). Temperature and pH control in composting of coffee and agricultural wastes. *Water Science and Technology*, **40,** 113-119.

Novak, J. M., Jayachandran, K., Moorman, T. B. and Weber, J. B. (1995). Sorption and binding of organic compounds in soils and their relation to bioavailability. In *Bioremediation: science and applications*, Skipper, H. D. and Turco, R. F. (eds.). Soil Science Society of America, American Society of Agronomy, Crop Science Society of America, Madison, pp. 13-28.

Noval, J. J. and Nickerson, W. J. (1959). Decomposition of native keratin by *Streptomyces fradiae*. *Journal of Bacteriology*, **77,** 251-263.

O'Neill, P. (1995). Arsenic. In *Heavy metals in soils*, Alloway, B. J. (ed.). Blackie Academic and Professional, London, pp. 105-121.

Papadimitriou, E. K., Chatjipavlidis, I. and Balis, C. (1997). Application of composting to olive mill wastewater treatment. *Environmental Technology*, **18**.

Papadimitriou, E. K. and Diaz, L. F. (2000). Report: ORBIT 99: biological processing of waste. Putting innovation and information channelling into perspective. *Waste Management Research*, **18,** 293-295.

Parish, G. J. (1977). Textile and tannery wastes. In *Treatment of industrial effluents*, Callely, A. G., Forster, C. F. and Stafford, D. A. (eds.). Hodder and Stoughton, London, pp. 229-244.

Park, K. J., Choi, M. H. and Hong, J. H. (2002). Control of composting odor using biofiltration. *Compost Science and Utilization*, **10,** 356-362.

Parkinson, D. and Paul, E. A. (1982). Microbial biomass. In *Methods of soil analysis, part 2. Chemical and microbiological properties*, Page, A. L., Miller, R. H. and Keeney, D. R. (eds.). American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, pp. 821-830.

Paturau, J. M. (1989). *By-products of the cane sugar industry.* Elsevier Science Publishers B. V., Amsterdam, 435 pp.

Paul, E. A. and Clark, F. E. (1996). *Soil microbiology and biochemistry.* Academic Press, Inc., San Diego, 340 pp.

Perrenoud, S. (1977). *Potassium and plant health.* International Potash Institute, Bern, 218 pp.

Peters, R. H. (1963). *Textile chemistry volume 1: the chemistry of fibres.* Elsevier Publishing Company, Amsterdam, 477 pp.

Peters, R. H. (1967). *Textile chemistry volume 2: impurities in fibres; purification of fibres.* Elsevier Publishing Company, Amsterdam, 374 pp.

Pittaway, P. (1999). Getting the right mix - composting from the microbiological viewpoint. Available at: http://www.recycledorganics.com.au (5.09.2001).

Poggi-Varaldo, H. M. and Estrada-Vázquez, C. (1997). Agricultural wastes. *Water Environment Research*, **69,** 575-603.

Poggi-Varaldo, H. M., Estrada-Vázquez, C. and Rinderknecht-Seijas, N. (1998). Agricultural wastes. *Water Environment Research*, **70,** 601-620.

Poole, A. J., Cord-Ruwisch, R. and Jones, F. W. (1999). Biological treatment of chemically flocculated agro-industrial waste from the wool scouring industry by an aerobic process without sludge recycle. *Water Research*, **33,** 1981-1988.

Pryor, S. W., Hay, A. G. and Walker, L. P. (2002). Nonylphenol in anaerobically digested sewage sludge from New York State. *Environmental Science and Technology*, **36,** 3678-3682.

Ragnarsdottir, K. V. (2000). Environmental fate and toxicology of organophosphate pesticides. *Journal of the Geological Society, London*, **157,** 859-876.

Rai, M. K. and Qureshi, S. (1994). Screening of different keratin baits for isolation of keratinophilic fungi. *Mycoses*, **37,** 295-298.

Ramm-Schmidt, L. H. (1988). Ion exchange for desugaring of molasses and byproduct isolation. In *Chemistry and processing of sugarbeet and sugarcane*, Clarke, M. A. and Godshall, M. A. (eds.). Elsevier Science Publishers B. V., Amsterdam, pp. 111-126.

Rankin, D. A. (1985). Free fatty acids and soaps in New Zealand woolgreases. *New Zealand Journal of Technology*, **1,** 91-99.

Rantala, P.-R., Vaajasaari, K., Juvonen, R., Schultz, E., Joutti, A. and Mäkelä-Kurtto, R. (1999). Composting of forest industry wastewater sludges for agricultural use. *Water Science and Technology*, **40,** 187-194.

Rhoades, J. D. (1982a). Cation exchange capacity. In *Methods of soil analysis, part 2. Chemical and microbiological properties*, Page, A. L., Miller, R. H. and Keeney, D. R. (eds.). American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, pp. 149-157.

Rhoades, J. D. (1982b). Soluble salts. In *Methods of soil analysis, part 2. Chemical and microbiological properties*, Page, A. L., Miller, R. H. and Keeney, D. R. (eds.). American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, pp. 167-179.

Riva, M. C., Cegarra, J. and Crespi, M. (1993). Effluent ecotoxicology in the wool-scouring process. *The Science of the Total Environment*, **Supplement,** 1143-1150.

Robinson, P. W. (1993). *A review of the toxicology of pesticides used for the control of external parasites on sheep*. Report No. C124, Wool Research Organisation of New Zealand (Inc.), Christchurch, 40 pp.

Robinson, P. W. (1999). The toxicity of pesticides and organics to mysid shrimps can be predicted from *Daphnia* spp. toxicity data. *Water Research*, **33,** 1545-1549.

Ross, S. (1989). *Soil processes: a systematic approach.* Routledge, London, 444 pp.

Rossell, C. E. V. (1988). Sugarcane processing to ethanol for fuel purposes. In *Chemistry and processing of sugarbeet and sugarcane*, Clarke, M. A. and Godshall, M. A. (eds.). Elsevier Science Publishers B. V., Amsterdam, pp. 349-366.

Rubio, H. O., Wood, M. K., Cardenas, M. and Buchanan, B. A. (1989). Effect of polyacrylamide on seedling emergence of three grass species. *Soil Science*, **148,** 355-360.

Russell, E. W. (1973). *Soil conditions and plant growth.* Longman Group Limited, London, 807 pp.

Russell, I. M. (1996a). Clean green wool: development of environmental regulations. *Top-Tech '96*, Geelong, Australia, 11-14 November 1996, CSIRO Australia, IWS International Wool Secretariat, pp. 96-104.

Russell, I. M. (1996b). Clean green wool: managing environmental issues. *Top-Tech '96*, Geelong, Australia, 11-14 November 1996, CSIRO Australia, IWS International Wool Secretariat, pp. 408-418.

Russell, I. M. (1996c). Meeting the needs on-farm: Australian program to produce low-pesticide wool. *Top-Tech '96*, Geelong, Australia, 11-14 November 1996, CSIRO Australia, IWS International Wool Secretariat, pp. 125-129.

Sabine, J. R. (1999). Waste is a verb, not a noun. Available at: http://www.recycledorganics.com.au (5.09.2001).

Sánchez-Monedero, M. A., Roig, A., Paredes, C. and Bernal, M. P. (2001). Nitrogen transformation during organic waste composting by the Rutgers system and its effects on pH, EC and maturity of the composting mixtures. *Bioresource Technology*, **78,** 301-208.

Sangali, S. and Brandelli, A. (2000). Feather keratin hydrolysis by a *Vibrio* sp. strain kr2. *Journal of Applied Microbiology*, **89,** 735-743.

Savage, M. J. (2002). Integrated treatment processes for primary wool scouring effluent. Ph.D. thesis (Chemical and Process Engineering), University of Canterbury, Christchurch, New Zealand, 250 pp.

Schnitzer, M. (1982). Organic matter characterisation. In *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*, Vol. 2nd, Page, A. L., Miller, R. H. and Keeney, D. R. (eds.). American Society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, pp. 581-594.

Sesay, A. A., Lasaridi, K., Stentiford, E. and Budd, T. (1997). Controlled composting of paper pulp sludge using the aerated static pile method. *Compost Science and Utilization*, **5,** 82-96.

Seybold, C. A. (1994). Polyacrylamide review: soil conditioning and environmental fate. *Communications in Soil Science and Plant Analysis*, **25,** 2171-2185.

Shanker, R., Ramakrishna, C. and Seth, P. K. (1990). Microbial degradation of acrylamide monomer. *Archives of Microbiology*, **154,** 192-198.

Shehu, Y., Alhassan, W. S., Mensah, G. W. K., Aliyu, A. and Phillips, C. J. C. (1997). The effects of green manuring and chemical fertiliser application on maize yield, quality and soil composition. *Tropical Grasslands*, **32,** 139-142.

Simpanya, M. F. and Baxter, M. (1996). Isolation of fungi from soil using the keratin-baiting technique. *Mycopathologia*, **136,** 85-89.

Smith, D. H., Wells, M. A., Porter, D. M. and Cox, F. R. (1993). Peanuts. In *Nutrient deficiencies and toxicities in crop plants*, Bennett, W. F. (ed.). American Phytopathological Society, St. Paul, pp. 105-110.

Smith, E. A., Prues, S. L. and Oehme, F. W. (1996). Environmental degradation of polyacrylamides. 1. Effects of artificial environmental conditions: temperature, light, and pH. *Ecotoxicology and Environmental Safety*, **35,** 121-135.

Smith, E. A., Prues, S. L. and Oehme, F. W. (1997). Environmental degradation of polyacrylamides. 2. Effects of environmental (outdoor) exposure. *Ecotoxicology and Environmental Safety*, **37,** 76-91.

Spinosa, L., Kempa, E. S., Okuno, N. and Vesilind, P. A. (1994). Global sludge management: a status report and perspective. *Water Science and Technology*, **30,** 73-80.

Standards Australia (1999). *AS4454-1999: composts, soil conditioners and mulches.* Standards Australia, Homebush, 49 pp.

Stanford, K., Larney, F. J., Olson, A. F., Yanke, L. J. and McKenzie, R. H. (2000). Composting as a means of disposal of sheep mortalities. *Compost Science and Utilization*, **8,** 135-146.

Statistics New Zealand (1998). *Agriculture Statistics 1996.* Statistics New Zealand, Wellington, pp.

Stern, R., Van Der Merwe, A. J., Laker, M. C. and Shainberg, I. (1992). Effect of soil surface treatments on runoff and wheat yields under irrigation. *Agronomy Journal*, **84,** 114-119.

Sterrett, S. B., Chaney, R. L., Gifford, C. H. and Mielke, H. W. (1996). Influence of fertiliser and sewage sludge compost on yield and heavy metal accumulation by lettuce grown in urban soils. *Environmental Geochemistry and Health*, **18,** 135-142.

Stewart, R. G. (1988). *Woolscouring and allied technology.* Wool Research Organisation of New Zealand, Christchurch, 284 pp.

Stocks, C., Barker, A. J. and Guy, S. (1999). Dewatering of brewery sludge produced from a dedicated aerobic effluent treatment plant. *Journal of the Institute of Brewing*, **105,** 279-285.

Swift, M. J., Heal, O. W. and Anderson, J. M. (1979). *Decomposition in terrestrial ecosystems.* Blackwell Scientific Publications, Oxford, 372 pp.

Taylor, D. and Taylor, Y. (1998). *The compost book.* New Holland Publishers (Australia) Pty Ltd.,, 85 pp.

Thiele, B., Günther, K. and Schwuger, M. J. (1997). Alkylphenol ethoxylates: trace analysis and environmental behavior. *Chemical Reviews*, **97,** 3247-3272.

Tiquia, S. M., Richard, T. L. and Honeyman, M. S. (2000). Effect of windrow turning and seasonal temperatures on composting of hog manure from hoop structures. *Environmental Technology*, **21,** 1037-1046.

Tiquia, S. M. and Tam, N. F. Y. (2000). Fate of nitrogen during composting of chicken litter. *Environmental Pollution*, **110,** 535-541.

Topp, E., Vallaeys, T. and Soulas, G. (1997). Pesticides: microbial degradation and effects on microorganisms. In *Modern soil microbiology*, van Elsas, J. D., Trevors, J. T. and Wellington, E. M. H. (eds.). Marcel Dekker, Inc., New York, pp. 547-575.

Truter, E. V. (1956). *Wool wax: chemistry and technology.* Cleaver-Hume Press Ltd., London, 368 pp.

United States Environmental Protection Agency (2002). Global warming - emissions. Available at: http://www.epa.gov/globalwarming/emissions/index.html (18/02/2003).

van Lith, C., Leson, G. and Michelsen, R. (1997). Evaluating design options for biofilters. *Journal of the Air and Waste Management Association*, **47,** 37-48.

Ver Vers, L. M. (1999). Determination of acrylamide monomer in polyacrylamide degradation studies by high-performance liquid chromatography. *Journal of Chromatographic Science*, **37,** 486-494.

Voss, R. D. (1993). Corn. In *Nutrient deficiencies and toxicities in crop plants*, Bennett, W. F. (ed.). American Phytopathological Society, St. Paul, pp. 11-14.

Wallace, A. (1986). Effect of polymers in solution culture on growth and mineral composition of tomatoes. *Soil Science*, **141,** 395-396.

Wallace, A. (1987). Anionic polyacrylamide treatment of soil improves seedling emergence and growth. *HortScience*, **22,** 951.

Wallace, A. and Abouzamzam, A. M. (1986). Interactions of soil conditioner with other limiting factors to achieve high crop yields. *Soil Science*, **141,** 343-345.

Wallace, A. and Wallace, G. A. (1986a). Additive and synergistic effects on plant growth from polymers and organic matter applied to the soil simultaneously. *Soil Science*, **141,** 334-342.

Wallace, A. and Wallace, G. A. (1986b). Effect of polymeric soil conditioners on emergence of tomato seedlings. *Soil Science*, **141,** 321-323.

Wallace, A. and Wallace, G. A. (1986c). Effects of soil conditioners on emergence and growth of tomato, cotton, and lettuce seedlings. *Soil Science*, **141,** 313-316.

Wallace, A. and Wallace, G. A. (1990). Soil and crop improvement with water-soluble polymers. *Soil Technology*, **3,** 1-8.

Wallace, A., Wallace, G. A. and Abouzamzam, A. M. (1986a). Effects of excess levels of a polymer as a soil conditioner on yields and mineral nutrition of plants. *Soil Science*, **141,** 377-380.

Wallace, A., Wallace, G. A., Abouzamzam, A. M. and Cha, J. W. (1986b). Effects of polyacrylamide soil conditioner on the iron status of soybean plants. *Soil Science*, **141,** 368-370.

Walsh, J. L., Jr., Ross, C. C. and Valentine, G. E., Jr. (1994). Food processing waste. *Water Environment Research*, **66,** 409-413.

Walsh, J. L., Jr., Ross, C. C. and Valentine, G. E., Jr. (1995). Food processing waste. *Water Environment Research*, **67,** 522-527.

Warman, P. R. and Cooper, J. M. (2000). Fertilization of a mixed forage crop with fresh and composted chicken manure and NPK fertilizer: effects on dry matter yield and soil and tissue N, P and K. *Canadian Journal of Soil Science*, **80,** 337-344.

Watson-Craik, I. A. and Sinclair, K. J. (1995). Co-disposal of industrial wastewaters and sludges. In *Microbiology of Landfill Sites*, Senior, E. (ed.). CRC Press Inc., Boca Raton, pp. 91-130.

Wen, G., Winter, J. P., Voroney, R. P. and Bates, T. E. (1997). Potassium availability with application of sewage sludge, and sludge and manure composts in field experiments. *Nutrient Cycling in Agroecosystems*, **47,** 233-241.

White, R. E. (1997). *Principles and practice of soil science: the soil as a natural resource.* Blackwell Science Ltd., Oxford, 348 pp.

Will, G. (1985). *Nutrient deficiencies and fertiliser use in New Zealand exotic forests.* Forest Research Institute, New Zealand Forest Service, Rotorua, 53 pp.

Williamson, M. E. (1995). Pesticide residues in New Zealand wool; reducing the levels. *Wool*, **8,** 58-60.

Williamson, W. M. (1998). The decomposition of woolscour and fellmongery sludges. Ph.D. thesis (Microbiology), University of Canterbury, Christchurch, New Zealand, 223 pp.

Williamson, W. M., Greenfield, L. G. and Beare, M. H. (2000). Biodegradation assessment of woolscour sludge and fellmongery sludge. *Journal of Environmental Quality*, **29,** 1998-2006.

Winder, L. M., Rea, A., Scobie, D. R. and Bray, A. R. (1998). Unravelling the causes of wool yellowing part I: involvement of a water soluble component. *Proceedings of the New Zealand Society of Animal Production*, **58,** 274-276.

Wong, J. W. C., Fang, M., Li, G. X. and Wong, M. H. (1997). Feasibility of using coal ash residues as co-composting materials for sewage sludge. *Environmental Technology*, **18,** 563-568.

Wool Record (1994). *Wool trade directory of the world.* World Textile Publications Ltd., Bradford, pp.

Wools of New Zealand (1997). *The New Zealand wool industry manual.* Wools of New Zealand, Christchurch, 129 pp.

WRONZ (2001). *Introduction to wool and the wool industry.* Wool Research Organisation of New Zealand, Christchurch, 80 pp.

Wu, L. and Ma, L. Q. (2001). Effects of sample storage on biosolids compost stability and maturity evaluation. *Journal of Environmental Quality*, **30,** 222-228.

Wu, N. (1995). Composting coffee pulp in El Salvador. *BioCycle*, **36,** 82-83.

Wuertz, S. and Mergeay, M. (1997). The impact of heavy metals on soil microbial communities and their activities. In *Modern soil microbiology*, van Elsas, J. D., Trevors, J. T. and Wellington, E. M. H. (eds.). Marcel Dekker, Inc., New York, pp. 607-642.

Yeates, G. W., Ross, C. W., Dando, J. L. and Speir, T. W. (2002). Some effects of incorporation of compost including sewage biosolids into a dairy pasture on Foxton sandy loam. *New Zealand Soil News*, **50,** 5-8.

Zeman, C., Depken, D. and Rich, M. (2002). Research on how the composting process impacts greenhouse gas emissions and global warming. *Compost Science and Utilization*, **10,** 72-86.

8. APPENDICES

8.1. PESTICIDE ANALYSIS CALIBRATION CURVES

Calibration curves for the organophosphate pesticides diazinon and propetamphos were constructed from the data contained in Table 8-1, from which Equation 8-1 and Equation 8-2 were calculated. It was noted that, for both pesticides, the retention time increased as the concentration of pesticide increased.

Table 8-1. Data for the construction of calibration curves for organophosphate pesticides.

Diazinon			Propetamphos		
Concentration ($mg\ L^{-1}$)	Peak area	Retention time (min)	Concentration ($mg\ L^{-1}$)	Peak area	Retention time (min)
0	0		0	0	
2.14	18.459	7.488	2.51	18.499	7.194
5.36	68.438	7.496	6.28	66.747	7.213
10.72	116.730	7.508	12.56	112.659	7.221
21.44	198.078	7.519	25.12	196.570	7.228
64.32	567.103	7.548	75.36	558.234	7.258
107.20	928.638	7.542	125.60	930.857	7.264
379.20	2901.273	7.598	251.20	1874.359	7.304

$$\text{Diazinon concentration } (mg\ L^{-1}) = \left(\frac{\text{Peak area}}{7.7617} \right)$$

Equation 8-1

$$\text{Propetamphos concentration } (mg\ L^{-1}) = \left(\frac{\text{Peak area}}{7.4557} \right)$$

Equation 8-2

The R^2 values of 0.9973 and 0.9997 for diazinon and propetamphos, respectively, indicate that the equations were highly linear.

8.2. PHOSPHORUS ANALYSIS CALIBRATION CURVE

Table 8-2 provides the absorption values for a range of phosphorus solutions of known concentrations as described by Kitson and Mellon (1944). Excluding the data for 0 ppm phosphorus, an equation was formulated for the calculation of ppm phosphorus in solution (Equation 8-3).

Table 8-2. Data for the construction of a calibration curve for phosphorus.

ppm Phosphorus	Reading (A_{465})	Adjusted Reading[#]
0	9.825	0
4	9.840	0.015
8	9.930	0.105
10	9.950	0.125
12	9.990	0.165
16	10.085	0.260
20	10.160	0.335
32	10.413	0.588

Note: #Adjusted reading is the observed reading less that for 0 ppm phosphorus.

$$\text{ppm P} = \left(\frac{\text{Adjusted absorbance} + 0.0706}{0.0205} \right)$$

Equation 8-3

The R^2 value of 0.9983 indicated that the equation was highly linear.

8.3. CHLORIDE ANALYSIS CALIBRATION CURVE

Table 8-3 provides the absorption values for a range of chloride (NaCl) solutions of known concentrations using the methodology of Adriano and Doner (1982), from which an equation was formulated (Equation 8-4).

Table 8-3. Data for the construction of a calibration curve for chloride.

ppm Chloride	Reading (A_{460})
0	0
1	0.022
2	0.036
3	0.042
4	0.053
6	0.067
8	0.076
10	0.089
16	0.118

$$\text{ppm Chloride} = \left(\frac{\text{Absorbance} - 0.0193}{0.0068} \right)$$

Equation 8-4

The R^2 value of 0.9374 indicated that the equation was highly linear.

8.4. ANALYSIS OF SOILS USED

Chemical properties of the various soils used in this thesis are described in Table 8-4 below. Soil texture, Olsen P and P retention, and cation exchange capacity and exchangeable cations were tested through Lincoln University. Heavy metals were analysed at the Christchurch Wastewater Treatment Works, Christchurch City Council. Clay particles are those less than 2 μm, silt particles 2-20 μm, and sand particles greater than 20 μm in size.

Table 8-4. Chemical properties of soils used in this project.

Property	Coarse sand (Laings)	Marshlands soil	Ilam soil	Soil (Laings)
Sand (%)	99.7	24.3	38.7	53.5
Silt (%)	0.1	45.8	43.8	29.0
Clay (%)	0.2	29.9	17.5	17.5
Bulk density (kg m^{-3})	1,620	770	1,010	1,080
pH	6.0	5.7	6.3	5.3
Organic matter (%)	0.8	27.5	10.7	5.3
Total N (%)	0.02	0.9	0.4	0.2
K (%)		0.2	0.1	
Olsen P (μg ml^{-1})	9	120	23	26
P Retention (% w/w)	5	29	13	21
CEC (me $100g^{-1}$)	2	46	18.4	12
Potassium (me $100g^{-1}$)	0.27	2.06	0.70	0.50
Calcium (me $100g^{-1}$)	0.9	32.1	11.8	3.3
Magnesium (me $100g^{-1}$)	0.42	4.27	2.74	0.93
Sodium (me $100g^{-1}$)	0.05	0.24	0.19	0.13
Arsenic (mg kg^{-1})		6.1	3.8	
Cadmium (mg kg^{-1})		1.0	0.5	
Chromium (mg kg^{-1})		16	11	
Copper (mg kg^{-1})		26	12	
Lead (mg kg^{-1})		50	51	
Nickel (mg kg^{-1})		15	14	
Zinc (mg kg^{-1})		140	110	

Note: analysis of Ilam soil (except heavy metals) was reported in Kroening (2000). CEC = cation exchange capacity.

In terms of the suitability of the soils for pasture use in the South Island of New Zealand, the optimum ranges are: pH, 5.8-6.2; Olsen P, 20-30 μg mL^{-1}; P retention, 30-60%; cation exchange capacity, 12-25 me $100g^{-1}$; potassium, 0.5-0.8 me $100g^{-1}$; calcium, 6-12 me $100g^{-1}$; magnesium, 1-3 me $100g^{-1}$; sodium, 0.1-0.3 me $100g^{-1}$. These optimum ranges were reported by the testing laboratories.

8.5. MICROBIOLOGICAL MEDIA USED

Yeast Extract Agar (Atlas, 1993) pp. 1003.

Yeast extract	3 g
Bacto peptone	5 g
Agar	15 g
Distilled water	1,000 mL

The pH was adjusted to 7.0 before autoclaving.

Modified Dichloran Rose Bengal (DRB) Media (Atlas, 1993) pp. 311.

DRB		31.5 g, containing
	Peptone	5 g
	Glucose	10 g
	KH_2PO_4	1 g
	$MgSO_4$	0.5 g
	Dichloran	0.002 g
	Rose Bengal	0.025 g
	Agar	15 g
Yeast extract		0.5 g
Distilled water		1,000 mL

After autoclaving, 0.2 μm filter sterilised streptomycin (200 μg mL^{-1}) and chlortetracycline (50 μg mL^{-1}) was added to suppress bacterial growth.