

## Variation in and Constraints upon the Decomposition of Woolsour Sludge

S. J. Kroening,\* L. G. Greenfield, and W. M. Williamson

### ABSTRACT

The woolsouring (wool washing) industry has traditionally been viewed as highly polluting and, consequently, effluent treatment systems have been sought. The first stage in the current treatment system for woolsour wastewater, a chemical flocculation process (Sirofan CF), creates a sludge composed of soil and wool grease. We investigated the chemical and biological characteristics of this sludge. The sludge was found to be highly variable on a day to day basis in terms of its chemical composition and biodegradability; 0.8 to 27.8% of sludge total nitrogen was mineralized over 30 d at 37°C. The grease component of sludge (14–40% on a dry weight basis) may retard the decomposition of the sludge but the polyacrylamide flocculant used in its production and its pesticide content had no effect on the rate of decomposition. Our results suggest that variability in substrate quality may translate into variability in treatment performance and have important implications for the biological treatment of industrial wastes, including composting.

THE CLEANING of raw wool (woolsouring) is the most polluting stage of wool processing (Russell, 1996a). Worldwide, the industry has long been regarded as dirty for a variety of reasons, including the use of antiquated equipment, a lack of recycling loops, and the absence of effluent treatment systems (Bateup et al., 1995). The aim of woolsouring is to remove contaminants from wool and leave the wool in a condition fit for further processing such as carding and dyeing (Stewart, 1988). Among these contaminants are wool wax (the solvent-extractable fraction), suint (the water-soluble fraction), soil (including soil particles, fecal matter, and skin and fiber debris), and vegetable matter (Truter, 1956). Wool is washed with hot water and nonylphenol ethoxylate detergent before being rinsed and dried. The effluent load from a typical woolsour (being a 2-m-wide scouring line processing 1 Mg raw wool per hour) is equivalent to the sewage produced by a town of 30 000 people (Christoe, 1996; Jones and Westmoreland, 1998). In the 1999–2000 season, 1.4 million Mg clean wool was produced worldwide (Wool Research Organisation of New Zealand, 2001). Treatment systems must be put into place before wool can be viewed as a “clean green” natural fiber and competitive with synthetic fibers (Russell, 1996a).

Since the woolsouring process removes contaminants from wool and transfers them to the washing liquor, waste minimization is not possible (Bateup et al., 1995). However, if the wastes are viewed as a resource, reuse is

an option (Russell, 1996a). The first stage in the current model for effluent treatment is a chemical flocculation process (Sirofan CF) that transfers contaminants from the wastewater to a sludge. This system is now widely used in countries such as New Zealand, Australia, and the United Kingdom. Effluent from the woolsour wash-bowls is adjusted to pH 3 to 4 using sulfuric acid and then polyacrylamide (PAM), a high molecular weight cationic flocculant, is added. Flocculated solids are then removed by a decanter centrifuge (Jones and Westmoreland, 1999). The sludge contains virtually all of the wool wax, soil, detergent, and pesticide residues, the latter being applied during animal growth to kill sheep parasites. The clarified liquid phase (centrate) contains the suint (Poole et al., 1999), which is largely composed of potassium salts of fatty acids (Truter, 1956; Hoare and Stewart, 1971). The suint undergoes further biological treatment in aerated tanks to reduce the biological oxygen demand and, on evaporation, a concentrate high in potassium is produced. The condensed water is fit for reuse in the scour. A typical single scour line would produce about 10 Mg sludge per day, typically composed of 40% soil, 20% wax, and 40% water (Bateup et al., 1996). This sludge can be further treated by composting or by incineration.

Little laboratory data on the nature and decomposition of this sludge has been reported and only limited findings of composting trials are available in technical reports. Temperatures as high as 70°C were achieved when sludge was mixed with green waste (Bateup et al., 1996), which was considered evidence for the presence of a microbial population that survived the woolsouring and chemical flocculation processes (Jones and Westmoreland, 1999). Using a radish bioassay, the mature product from sludge composting was shown to be as good as a commercial potting mix, as judged by seed germination and root growth (Bateup et al., 1996).

The degree of variability in sludge substrate quality is unknown, as are the constraints that certain sludge components such as grease, pesticide residues, and flocculant (PAM), may place on the decomposition of the sludge. With the use of the Sirofan CF effluent treatment system becoming widespread, it is important to obtain information on the sludge produced by this system. This information is required before the composting potential of the sludge can be assessed. The objectives of this study were to (i) determine the degree of variability in the composition and biodegradability of the sludge produced by the current effluent treatment system for woolsours, (ii) assess various components of the sludge that may retard the decomposition of the sludge, and (iii) discuss the impact of the above findings on the composting potential of the sludge.

S.J. Kroening, School of Biological Sciences, and L.G. Greenfield, School of Biological Sciences, University of Canterbury, Private Bag 4800, Christchurch, New Zealand. W.M. Williamson, Landcare Research New Zealand Limited, PO Box 69, Lincoln 8512, New Zealand. Received 21 Apr. 2003. \*Corresponding author (s.kroening@andarc.co.nz).

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677 S. Segoe Rd., Madison, WI 53711 USA

**Abbreviations:** PAM, polyacrylamide.

## MATERIALS AND METHODS

Woolscour sludge was obtained from a woolscouring plant in Canterbury, New Zealand. The plant consisted of a 2.4-m scouring line and processed a range of wool types, and could be regarded as representative of a typical New Zealand scour. Samples were collected in sterile plastic bags (Whirlpak) immediately after production at the decanter centrifuge and stored at 4°C until use, usually within 5 d. All results are reported on an oven-dry (105°C) weight basis.

### Chemical and Physical Analyses

Sludge pH was determined on the supernatant of a 1:4 (w/v) sludge to distilled water mix after being mixed and allowed to equilibrate for 5 min. Organic matter was determined by weight loss-on-ignition at 560°C for 6 h. Grease content was determined by Soxhlet extraction using petroleum ether (BDH Laboratory Supplies, Poole, England) at 60°C for 3 h, after which the grease was dried at 50°C for 48 h. The petroleum-ether-insoluble fraction was dried at 105°C for 24 h and termed the solvent-insoluble fraction.

Total N was determined by the semi-micro Kjeldahl method followed by steam distillation (Bremner and Mulvaney, 1982). The distribution of N was assessed by reflux hydrolysis in 6 M HCl for 24 h at 110°C (Greenfield, 2001). Mineral N species ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ ) were extracted with 2 M KCl, and 10-mL aliquots of the extract were steam-distilled with MgO for  $\text{NH}_4^+$  and both MgO and Devarda alloy for  $\text{NO}_2^-$  and  $\text{NO}_3^-$  (Keeney and Nelson, 1982).

A composite sample of sludge, consisting of equal amounts (dry weight basis) of five samples collected on consecutive days, was ashed (ignition in a muffle furnace at 800°C for 6 h) for the determination of inorganic elements by standard X-ray fluorescence spectroscopy (PW1400; Philips, Eindhoven, the Netherlands). Samples were supplied to the Christchurch Wastewater Treatment Works for the determination of heavy metals by atomic absorption spectroscopy.

All sludges collected over the period of June 2000 through December 2001 were analyzed for the above chemical properties.

### Biodegradation Assessment

Decomposition of the woolscour sludge was determined by net N mineralization, which was considered an appropriate estimator of decomposition based on two aspects of previous work. First, woolscour sludge weight loss with time, as an estimator of decomposition, significantly underestimated carbon mineralization (Williamson, 1998; Williamson et al., 2000). This artifact was shown to be due to the high grease content preventing water evaporation during sample drying (Williamson, 1998). Second and most importantly, the N in woolscour sludge was significantly more recalcitrant to being mineralized than the chemically determined C to N ratio would suggest (Williamson et al., 2000). Microcosms were set up as described by Williamson et al. (2000) using 125-mL glass conical flasks containing 5 g organic-matter-free sand as a matrix and enough sample to provide 10 mg total N. An inoculum was provided by adding 300  $\mu\text{L}$  of aliquot of soil suspension that was prepared by mixing 20 g soil (a silt loam of pH 6.3 collected from the university campus) in 60 mL distilled water. A vial containing 2 mL of 0.5 M  $\text{H}_2\text{SO}_4$  was suspended in the microcosm to collect evolved  $\text{NH}_3$ . Control microcosms did not include any substrate for decomposition. Microcosms were moistened with distilled water to 30% moisture, covered with plastic film, secured with a rubber band, and incubated. Five replicates were established for each treatment. At the time of

sampling, the contents of  $\text{NH}_3$  traps were quantitatively rinsed into analysis flasks and steam-distilled in the presence of 3 mL of 10 M NaOH. The contents of the microcosms were extracted with 2 M KCl and were analyzed for mineral N as described above (Keeney and Nelson, 1982). Net N mineralization (less initial mineral N) as a percentage of the initial total N is reported.

Variation in sludge biodegradability was determined on two sets of samples collected over five consecutive days and on a set of samples collected on the same day of the week for five consecutive weeks. Decomposition was assessed by net N mineralization over 30 d at 37°C, a compromise between ambient and composting temperatures.

To assess the effect of the grease content on decomposition of sludge, the rate of decomposition of the solvent-insoluble fraction (produced by Soxhlet extraction, as described above) was compared with that of the whole sludge. The sludge sample was a composite made of equal amounts (dry weight basis) of five sludge samples collected over consecutive days. The solvent-insoluble fraction was also a composite, made of equal amounts (dry weight basis) of the solvent-insoluble fractions of the sludge samples. Decomposition was assessed by net N mineralization at composting temperatures of 43, 50, and 60°C over 4 and 8 d of incubation (8 d being the intended residence time for an in-vessel composting stage).

The decomposition of the flocculant, polyacrylamide (Profloc CX533; Orica Chemnet, Mt. Maunganui, New Zealand), used in the production of sludge was determined by net N mineralization over 20 and 60 d at 20, 37, and 50°C. The effect of PAM on the decomposition of chitin and casein (Sigma Chemical Co., St. Louis, MO) and woolscour sludge was also determined. The PAM was added at rates of 5 and 20% of the initial total N of the microcosms and decomposition was assessed over 20 d 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 N mineralization were compared with the expected rates, based on the individual decomposition rates of each substrate.

The effect of an organophosphate pesticide diazinon [*O,O*-diethyl 0-2-isopropyl-6-methyl(pyrimidine-4-yl) phosphorothioate] and a synthetic pyrethroid cypermethrin [(*R,S*)- $\alpha$ -cyano-3-phenoxybenzyl(1*RS*)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate] (PestAnal grade; Riedel-de Haën Laborchemikalien GmbH & Co., Seelze, Germany) on the decomposition of casein was determined by net N mineralization over 30 d at 37°C. The pesticides were added at levels of 10, 100, and 1000 mg  $\text{kg}^{-1}$  on a casein weight basis, either separately or together. The pesticides were dissolved in petroleum ether and added to the sand matrix, with excess solvent added to allow the pesticides to be distributed evenly over the matrix by gentle swirling. Casein was added after evaporating the solvent by passing a stream of ambient air over the matrix. The N contributed by the pesticide residues, even at the highest application rates (1000 mg  $\text{kg}^{-1}$  each of diazinon and cypermethrin contributed 12.6  $\mu\text{g}$  total N), was insignificant in terms of the total N content of the microcosms (100 mg casein contributed 13.5 mg total N) and was not included in the calculation of the initial total N.

Statistix 7 (Analytical Software, 2000) was used to perform analysis of variance. When a test gave a *p* value of <0.05, means were compared by least significant differences. Experimental values were compared with expected values using one-sample *t* tests.

**Table 1. Chemical and physical characteristics of wooldscour sludge used in this experimental work.†**

Property	Mean	Range
Moisture, % fresh wt.	44.8	32.4–54.9
Organic matter, % dry wt.	55.2	27.5–64.5
pH	3.6	3.0–4.3
Grease, % dry wt.	27.7	13.8–40.0
Total nitrogen, % dry wt.	2.1	1.2–2.8
Insoluble nitrogen, % of total N	9.6	8.5–10.3
Ammonium nitrogen, % of total N	12.6	11.7–13.3
Hexosamine nitrogen, % of total N	2.8	1.5–3.8
$\alpha$ -Amino acid nitrogen, % of total N	47.0	45.7–49.5
Hydrolyzable unidentified nitrogen, % of total N	28.0	25.8–29.9
Arsenic, mg kg <sup>-1</sup> dry wt.	3	2–4
Cadmium, mg kg <sup>-1</sup> dry wt.	1	0–3
Chromium, mg kg <sup>-1</sup> dry wt.	11	8–14
Copper, mg kg <sup>-1</sup> dry wt.	9	7–11
Lead, mg kg <sup>-1</sup> dry wt.	10	3–19
Nickel, mg kg <sup>-1</sup> dry wt.	13	3–26
Zinc, mg kg <sup>-1</sup> dry wt.	153	55–240
SiO <sub>2</sub> , g kg <sup>-1</sup> dry wt.	310.7	
TiO <sub>2</sub> , g kg <sup>-1</sup> dry wt.	3.2	
Al <sub>2</sub> O <sub>3</sub> , g kg <sup>-1</sup> dry wt.	66.1	
Fe <sub>2</sub> O <sub>3</sub> , g kg <sup>-1</sup> dry wt.	18.1	
MnO, g kg <sup>-1</sup> dry wt.	0.2	
MgO, g kg <sup>-1</sup> dry wt.	5.5	
CaO, g kg <sup>-1</sup> dry wt.	7.6	
Na <sub>2</sub> O, g kg <sup>-1</sup> dry wt.	14.0	
K <sub>2</sub> O, g kg <sup>-1</sup> dry wt.	20.0	
P <sub>2</sub> O <sub>5</sub> , g kg <sup>-1</sup> dry wt.	1.8	
SO <sub>3</sub> , g kg <sup>-1</sup> dry wt.	0.8	

† For moisture and total N analysis,  $n = 20$ ; for pH and grease analysis,  $n = 10$ ; and for organic matter, N fractions, and heavy metal analysis,  $n = 5$ . A composite sample was used for the determination of inorganic elements, hence no range is provided.

## RESULTS

### Chemical and Physical Characteristics of Wooldscour Sludge

Considerable variation in the composition of the sludge was observed (Table 1). With the grease fraction containing only 0.2% N on a dry weight basis, 97% of the N in the sludge was contributed by the solvent-insoluble fraction. Consistently, almost 50% of the total N was in the  $\alpha$ -amino acid form, mainly in peptides and not free amino acids. Concentrations of heavy metals and inorganic elements were similar to two local pasture

**Table 2. Variation in the biodegradability of wooldscour sludge collected on different days of the week (daily variation) and on different weeks (weekly variation). Incubation was at 37°C over 30 d in sand-based microcosms.**

Sample	Net N mineralized† % of initial total N
<u>Daily variation</u>	
Set 1 Day 1	3.6 (0.09)
Set 1 Day 2	27.8 (2.45)
Set 1 Day 3	21.2 (0.74)
Set 1 Day 4	0.8 (0.03)
Set 1 Day 5	2.4 (0.42)
Set 2 Day 1	2.4 (0.38)
Set 2 Day 2	9.3 (0.72)
Set 2 Day 3	9.3 (2.14)
Set 2 Day 4	3.9 (0.45)
Set 2 Day 5	5.3 (0.88)
<u>Weekly variation</u>	
Week 1	2.5 (0.88)
Week 2	3.7 (0.73)
Week 3	5.6 (1.01)
Week 4	0.8 (0.53)
Week 5	2.7 (0.65)

† Means from five replicates followed by standard errors in parentheses.

**Table 3. Net N mineralization during the decomposition of wooldscour sludge and the solvent-insoluble fraction of wooldscour sludge in sand-based microcosms.**

	Temperature °C	Net N mineralized†	
		4 d	8 d
Whole sludge	43	0.2 (0.07)	0.5 (0.14)
Solvent-insoluble fraction	43	1.1 (0.16)	1.5 (0.17)
Whole sludge	50	0.4 (0.14)	1.3 (0.17)
Solvent-insoluble fraction	50	1.5 (0.14)	3.5 (0.51)
Whole sludge	60	0.8 (0.03)	1.2 (0.20)
Solvent-insoluble fraction	60	3.6 (0.44)	8.9 (1.31)

† Means from five replicates followed by standard errors in parentheses.

soils (data not shown). The grease content, which contained any detergent and pesticide residues, ranged from 14 to 40% of the dry weight of the sludge.

### Variation in Sludge Decomposition

Considerable variation was observed in the rate of biodegradation of wooldscour sludge collected on either different days of the week (daily timescale) or over different weeks (weekly timescale) (Table 2). The mean rate of decomposition of the 15 samples recorded below was 6.8% of the initial total N mineralized over 30 d, with the range from 0.8 to 27.8%. Excluding values for Days 2 and 3 of the first set of samples collected for daily variation analysis, all rates of decomposition were very low.

### Constraints upon Sludge Decomposition

After the removal of the grease fraction from sludge, the remaining (solvent-insoluble) fraction decomposed more readily than sludge (Table 3). This fraction showed increased decomposition with increasing temperature, which was more pronounced than for the whole sludge. Decomposition of the sludge was higher at 50 and 60°C than at 43°C, although net N mineralization was very low at all temperatures.

Polyacrylamide (10.2% total N) was observed to release increasing amounts of mineral N with both increasing time and temperature when incubated in sand-based microcosms where the PAM contributed all nutrients for microbial growth, except for those added with the inocula (Table 4).

There was no evidence that PAM affected the decomposition of casein, chitin, or wooldscour sludge, even at levels higher than those found in wooldscour sludge (0.35% on a dry weight basis). Net N mineralization of the individual components (used to calculate an expected amount of decomposition for the substrate mixture)

**Table 4. Net N mineralization during the decomposition of polyacrylamide in sand-based microcosms.**

Temperature °C	Net N mineralized†	
	20 d	60 d
	% of initial total N	
20	2.0 (0.34)	7.1 (0.20)
37	9.5 (0.39)	16.8 (0.17)
50	4.9 (0.76)	25.6 (0.30)

† Means from five replicates followed by standard errors in parentheses.

**Table 5. Effect of polyacrylamide on the decomposition of casein, chitin, and wooldour sludge. Incubation was at 37°C over 20 d in sand-based microcosms.**

Substrate <sup>†</sup>	Net N mineralized <sup>‡</sup>	
	Observed	Expected
	% of initial total N	
Polyacrylamide (PAM)	9.5 (0.39)	
Casein	81.8 (0.46)	
95% Casein-5% PAM	77.7 (1.15) NS <sup>§</sup>	77.6
80% Casein-20% PAM	68.8 (1.49) NS	67.1
Chitin	41.6 (2.27)	
95% Chitin-5% PAM	36.9 (2.27) NS	39.7
80% Chitin-20% PAM	31.6 (2.06) NS	34.9
Wooldour sludge	31.5 (0.83)	
95% Sludge-5% PAM	29.3 (0.96) NS	30.3
80% Sludge-5% PAM	27.4 (1.02) NS	27.2

<sup>†</sup> Ratios of substrates are expressed on a total N basis.

<sup>‡</sup> Means from five replicates are presented followed by standard errors in parentheses.

<sup>§</sup> NS = observed values not significantly different from expected values ( $p > 0.05$ ).

was similar to the amount of decomposition observed (Table 5). Note that the rate of sludge decomposition (percent of mineralized N per day) was considerably higher than the average rate of samples analyzed for variation analysis (Table 2).

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 6). When both these pesticides were added to casein together, there was no effect on the rate of casein decomposition.

## DISCUSSION

### Chemical and Physical Characteristics of Wooldour Sludge

Despite the wooldour sludge being produced from a single process (aqueous scouring) utilizing a single material (raw wool), considerable variation in the composition of the sludge was observed. Variation in the total N of the sludge has implications for composting in terms of the calculation of a suitable initial C to N ratio, a ratio of 25 to 40 being considered optimal (Anderson, 1990). Almost 50% of the total N was in the  $\alpha$ -amino acid form and would be expected to be readily decomposed; the proteins casein and hemoglobin mineralized 90 and 81% of the initial total N over 30 d of aerobic incubation at 37°C, respectively (data not shown). The hydrolyzable but unidentified nitrogen fraction is thought to consist of non- $\alpha$ -amino acid N, such as that contained in proline and arginine, and remnants of the hydrolysis procedure (Greenfield, 2001).

The concentrations of heavy metals in the wooldour sludge were low and, when compared with those for the New Zealand guidelines for the application of biosolids to land (New Zealand Water and Wastes Association, 2003), are not expected to be inhibitory to microbially mediated processes such as composting. The distribution of inorganic elements in the sludge was very similar to that typically found in soil (Williamson, 1998), while heavy metal concentrations were similar or less than those for a peat loam and a silt loam, both of which were obtained locally (data not shown). This was not

**Table 6. Effect of diazinon and cypermethrin on the decomposition of casein. Incubation was at 37°C over 30 d in sand-based microcosms.**

Substrate	Net N mineralized <sup>†</sup>
	% of initial total N
Casein	91.0 (1.63) ab
Casein + 10 mg kg <sup>-1</sup> diazinon	89.9 (1.54) ab
Casein + 100 mg kg <sup>-1</sup> diazinon	88.0 (1.56) b
Casein + 1000 mg kg <sup>-1</sup> diazinon	88.0 (0.52) b
Casein + 10 mg kg <sup>-1</sup> cypermethrin	93.1 (2.06) a
Casein + 100 mg kg <sup>-1</sup> cypermethrin	90.4 (2.63) ab
Casein + 1000 mg kg <sup>-1</sup> cypermethrin	94.5 (0.89) a
Casein + 10 mg kg <sup>-1</sup> diazinon + 10 mg kg <sup>-1</sup> cypermethrin	90.1 (1.67) ab
Casein + 100 mg kg <sup>-1</sup> diazinon + 100 mg kg <sup>-1</sup> cypermethrin	90.2 (1.92) ab
Casein + 1000 mg kg <sup>-1</sup> diazinon + 1000 mg kg <sup>-1</sup> cypermethrin	90.5 (1.15) ab

<sup>†</sup> Means from five replicates are presented followed by standard errors in parentheses. Substrates with the same letter are not significantly different (least significant difference,  $\alpha = 0.05$ ).

surprising considering the origin of most of these elements is soil particles that become entrained in the fleece as the sheep grazes. Products containing the sludge must be analyzed for their heavy metal content, as these components will accumulate during composting due to the decomposition of organic matter (Gomez, 1998).

The grease content of the sludge will depend on the type of wool scoured, since the grease content of the fleece generally increases as fiber diameter decreases (Truter, 1956). This may mean that the time required for composting will not be consistent on a day to day basis, 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. Approximately 90% of composting facilities in the USA use the static pile approach, with the remainder using windrows (Gerba, 2000).

A comparison of the composition of sludge used in this study (Table 1) to that of a previous study (Williamson et al., 2000), where wooldour 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 compared to 7.0) and total N (2.1% compared with 4.5%, on a dry weight basis) for the current study and Williamson et al. (2000), respectively. The pH of the sludge used here is lower due to the use of sulfuric acid in the flocculation process, and the total N is lower since wool fiber, which contains approximately 18% N on an elemental basis (Truter, 1956), is 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, 1996b).

### Variation in Sludge Decomposition

Sources of variability in sludge biodegradation would include the type of wool being scoured, the source of that wool, the operation of the scour, and the timing of

cleaning procedures to remove accumulated material from scour bowls. However, neither wool type nor scour operation was readily identifiable as explaining the high rates of N mineralization from samples collected on Days 2 and 3 of the first daily variation set. Variability in woollscour 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 acceptance (Paul and Clark, 1996), and this may be difficult to achieve with material of such potentially variable composition.

Direct comparisons of rates of N mineralization 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 with 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 N mineralization (Williamson et al., 2000), a rate of 0.54% initial total N  $d^{-1}$  mineralized at 37°C could be calculated from their study. The mean rate of 6.8% initial total N mineralized over 30 d at 37°C in this study equates to 0.23% initial total N  $d^{-1}$  mineralized. However, both these calculations assume that decomposition proceeded in a linear fashion over time (30 d), which, while not necessarily true, permits a general comparison between these studies. It can be tentatively suggested, therefore, that the chemically flocculated woollscour sludge examined in this study decomposed at approximately half the rate of the sludge produced by clarification in the mid-1990s.

### Constraints upon Sludge Decomposition

A faster rate of decomposition for the solvent-insoluble fraction of woollscour sludge compared with the sludge indicated that the wool grease may retard sludge decomposition. This is consistent with the results of Williamson et al. (2000), who observed a higher rate of N mineralization from the sludge fiber-inorganic fraction compared with the sludge as a whole. However, Williamson et al. (2000) also showed that wool grease did not inhibit the decomposition of casein when mixed at a rate up to 35% grease to casein (w/w).

Various studies have shown wool wax to decompose under composting conditions, with rates ranging from a 90% reduction in wool wax by 8 wk to a 70% reduction in 14 wk in two different heaps (Bateup et al., 1996). Similarly, static pile composting of Sirolan CF sludge blended with green waste over 14 wk showed 80 and 96% degradation of the wool wax and detergent, respectively (Jones and Westmoreland, 1998). In a subsequent study, Jones and Westmoreland (1999) showed that the rate of wool grease decomposition increased with the maximum initial temperature rise during the composting of 2 m<sup>3</sup> sludge with 4 m<sup>3</sup> greenwaste and, after 100 d, 95% of the wax and 100% of the detergent had decomposed.

Polymers of acrylamide are considered non-biodegradable as judged by CO<sub>2</sub>-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 with 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 is very small that all of the polymer simultaneously detaches from the soil surface, moves away from the surface, and moves into solution (Nadler and Letey, 1989).

The acrylamide monomer, which is a neurotoxin that causes behavioral 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. 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 d in a range of natural and polluted water samples at 25°C when added at rates of 0.5 and 5.0 mg L<sup>-1</sup>, 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<sup>-1</sup>. 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 degradation of cypermethrin, propetamphos, and diazinon present in the wool grease was shown to follow a similar trend to the breakdown of the wool grease in which it was contained (Bateup et al., 1996). During the composting of 2 m<sup>3</sup> sludge with 4 m<sup>3</sup> greenwaste, diazinon had a half-life of 6 to 11 d and cypermethrin 31 to 36 d (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.

The form of N in the woollscour sludge may explain the slow decomposition of this material. With almost

50% of the total N of the sludge in the  $\alpha$ -amino acid form (Table 1), and wool being composed of more than 90% protein (Wools of New Zealand, 1997), the N probably originated from wool proteins (keratin). 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 disulfide bonds, hydrogen bonds, and hydrophobic interactions, and its insolubility in water (Noval and Nickerson, 1959; Mathison, 1964). If this is indeed the case, 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 sludge, providing that conditions for their growth and proliferation are suitable.

### CONCLUSIONS

During this study into the decomposition of wool-scour sludge, several aspects have been identified that are likely to have important implications for the biological treatment of industrial wastes. First, the woolscour sludge was quite variable in composition and substrate quality. Inconsistent resources for microbially mediated processes, such as composting, could compromise the successful production of a consistent commercial product. Second, the grease content of the sludge directly influenced the rate of sludge decomposition, whereas pesticides and the flocculant polyacrylamide did not inhibit net N mineralization. The implication of this finding for other industries is that components of industrial wastes need to be assessed individually (wherever possible) to identify the probable order of their impact on decomposition processes. Individual component assessment may contribute to the rationalization of in-house waste treatments, with a positive feedback reducing waste stream variability. Finally, our data support the suggestion by Williamson et al. (2000) that new technology (in this case Sirolan CF system) designed to partition more material from the effluent into the sludge phase produced a sludge that decomposed more slowly than an earlier woolscour sludge produced by significantly less advanced technology. Further research is required to determine whether low available N contributes to the slow decomposition of woolscour sludge. In woolscour sludge, N is principally derived from the recalcitrant wool protein keratin, and therefore we suggest that a sludge pretreatment such as composting may denature keratin and ultimately make wool N more bioavailable for plant growth.

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