Chapter 6

Assessment of the maturation process during windrow composting of pulp and paper mill sludge by $^{13}$C CP MAS NMR and FTIR spectroscopy

6.1 Abstract

This study documents the changes in the organic composition of PMS during windrow composting (Chapter 4) by Carbon-13 Cross Polarisation Magic Angle Spinning Nuclear Magnetic Resonance ($^{13}$C CP MAS NMR) and Fourier Transformed Infrared (FTIR) spectroscopy. The study also assessed whether the rate of change in organic composition of the PMS was related to the level of maturity as indicated by direct phytotoxicity tests.

$^{13}$C CP MAS NMR and FTIR spectra revealed that the PMS prior to composting consisted primarily of cellulose polymorph type I with a minor lignin and uronic acid contribution (as reported in Chapter 2). At the end of the thermophilic stage (21 weeks), a marked increase in concentration of aromatic, methoxyl and alkyl moieties occurred, possibly due to selective preservation and/or in-situ synthesis of at least the latter two of these moieties by microorganisms. After the thermophilic stage of PMS composting, ~16% of the carbon originating from cellulose was mineralised with a concomitant increase in concentration of the residual aromatic fraction. An increase in concentration of aromatic quinone and nitrogen-containing amide moieties occurred as well at all stages of decomposition, consistent with the currently held view of humic synthesis from polyphenolic and amide substances. Relatively little structural change occurred during the final maturation or cool down stage, defined as the length of time between the end of the thermophilic phase (>45°C) and the time when windrow temperature returned to ambient (at 37 weeks). However, after the thermophilic phase (at 21 weeks) the material was not phytotoxic, indicating the compost was mature. Evidence suggested that significant structural change to the organic fraction in PMS occurred only during the thermophilic phase of composting and when the material exhibited phytotoxic properties. Thus a cool down phase following the thermophilic stage of composting would not be required prior to sale of the material.

The spectroscopic techniques revealed that when the PMS compost reached maturity, substrate degradation ceased although minor lignin mineralisation continued. However, an incorrect level of maturity may be implied by the spectroscopic techniques when used in this context if cessation of microbial decomposition of the organic substrate was due to
factors other than exhaustion of the available carbon pool, such as low water availability, low nutrient concentration or excessively high temperatures within the composting mass.

These spectroscopic techniques may be useful in other areas of organic waste treatment, such as in the monitoring of biofilter substrate condition, since a gradual reduction in available carbon for microbial growth within the substrate eventually leads to inefficient immobilisation or degradation of malodorous substances.

6.2 Introduction

Evaluation of maturity of composted waste materials has been recognised as one of the most important problems concerning the composting process and the subsequent application of this material to land (Chanyasak et al., 1982). Determination of the point at which a composted material is suitable for application to soil without deleteriously affecting plant growth has been the subject of intensive research and the techniques arising from this work have been reviewed by Jiménez and García (1989), Mathur et al. (1993) and Chen and Inbar (1993). Numerous studies have shown that the most notable effects of immature compost are:

- microbial immobilisation of soil nitrogen, resulting in nitrogen deficiency in crops (Duggan, 1973);
- formation of ammonia (NH$_3$) and volatile fatty acids which are injurious to plant roots at trace amounts (Katayama et al., 1987; Marambe et al., 1993).
- continued respiratory activity and the production of anaerobic or reducing conditions in soil, leading to inhibition of root respiration and formation of phytotoxic substances such as hydrogen sulfide (H$_2$S) and nitrite (NO$_2^-$) by anaerobic transformation of sulfur compounds and incomplete nitrification of NH$_3$ (Mathur et al., 1993);
- production of malodours and fires (Mathur et al., 1993).

Although the problems of oxygen depletion, soil nitrogen immobilisation, and toxicities of NH$_3$, H$_2$S and NO$_2^-$ can be mitigated by spreading the immature compost as a mulch rather than incorporating the material into the soil, no strategy can eliminate the main cause of phytotoxicity of immature compost, namely the organic intermediate products of decomposition (short chain volatile fatty acids) (Patrick, 1970; Lynch, 1977; Marambe et al., 1993; Mathur et al., 1993; Shiralipour et al., 1997). The phytotoxic volatile fatty acids have a chain length of 2 to 22 carbon atoms, and exert their effect on germinating seedlings through the inhibition of α-amylase activity, thereby reducing ATP content and physiological water uptake (Marambe et al., 1993).
Chapter 6 - Spectroscopic assessment of the maturation process during PMS composting

The most reliable method for determining the stability or maturity of compost is through an examination of plant growth in glasshouse pot experiments (Morel et al., 1985). However, due to the length of time required to generate results when using this procedure, more rapid tests have been sought. These include direct phytotoxicity tests (Zucconi et al., 1981; Jorba and Trillas, 1983); biodegradable organic matter content (Morel et al., 1985); reheating ability (Spohn, 1969); C:N ratio in the solid state and in water extracts (Harada and Inoko, 1980; Chanyasak et al., 1982, 1983); concentration and rate of formation of humic substances (Sugahara and Inoko, 1980; Roletto et al., 1985; Riffaldi et al., 1986; Saviozzi et al., 1988; Chen and Inbar, 1993; Forster et al., 1993; Schnitzer et al., 1993); microbial respiration rate (Iannotti et al., 1993, 1994); microbial enzymatic activity (Stutzenberger et al., 1970; Riffaldi et al., 1986; Forster et al., 1993) and others. Although direct phytotoxicity or seed germination tests are the most commonly used, results generated can be misleading, particularly if the composted material is moderately saline, contains herbicide residues or if decomposition was not properly initiated (Mathur et al., 1993). Despite extensive efforts to characterise the maturation process, Jiménez and Garcia (1989) concluded that no parameter by itself was sufficient to establish the degree of maturity of compost, since no single test could assess all parameters responsible for the production of toxic symptoms in plants (e.g. microbial activity, respiration rate, phytotoxic substances and temperature). Further limitations of all these methods have been discussed previously by Jiménez and Garcia, (1989) and Mathur et al., (1993).

Of interest to this study was whether the size of the biodegradable organic fraction during composting could be used as an indicator of maturity. This approach has been identified and studied as an indicator of maturity previously, since the most common polysaccharide carbon sources utilised by microorganisms gradually decline during composting, and the lack of available substrate causes a reduction in microbial respiratory activity, alleviation of anaerobic conditions and a cessation of phytotoxic substance formation (e.g. short chain volatile fatty acids) (Morel et al., 1985; Mathur et al., 1993). Thus, exhaustion of available substrate usually coincides with maturation. Morel et al. (1985), however, noted that although the simple polysaccharide content of urban refuse waste declined from 20% to 4-10% over a 240 day composting period, total extractable polysaccharides, as determined by conventional chemical extraction techniques, were still high. The authors reported that this result could be explained by the fact that polysaccharides are also synthesised by microorganisms during composting (Stevenson, 1982), and if not considered, an incorrect conclusion of incomplete substrate degradation may be drawn. A similar criticism of the use of biodegradable organic matter as an index of maturity has been reported by Mathur et al., (1993). The biodegradable organic matter test of maturity also suffers from further limitations. The efficiency of organic matter
extraction with chemical isolation methods has been questioned (Chen and Inbar, 1993) as these techniques have been shown to result in considerable modifications to covalent bonding which changes the chemical nature of the sample (Worobey and Barrie Webster, 1981). Recent studies, however, have attempted to resolve the difficulties associated with chemical extraction techniques and the problems in determining the true biodegradable organic fraction during composting through the use of solid state $^{13}$C CP MAS NMR and FTIR spectroscopy which can analyse samples in the intact state (Inbar et al., 1989, 1990, 1991, 1992). Furthermore, $^{13}$C CP MAS NMR can structurally characterise the types and forms of carbon present in an organic substance and quantitative determinations of specific organic components can be made (e.g. lignin; Haw et al., 1984). This technique can, therefore, determine the extent of mineralisation of an organic substrate and the extent of microbial synthesis of polysaccharide materials during composting. FTIR is also useful for characterising the principle functional groups in organic substances and can be used in a complementary manner to the structural information provided by $^{13}$C CP MAS NMR spectra (Gerasimowicz and Byler, 1985).

Although solid state $^{13}$C CP MAS NMR and FTIR spectroscopy have been used to characterise changes to the organic fraction during composting, studies have not been conducted to determine whether these changes can be related to the level of maturity as revealed by a direct phytotoxicity test. Despite the fact that NMR and FTIR analyses are not used for practical maturity determinations due to their cost and expertise required for interpretation, these techniques have been used to examine the relationship between the extent of organic matter decomposition and maturity of PMS during composting.

6.3 Materials and Methods

6.3.1 Sample preparation for spectroscopic analysis

A 1 kg composite sample of PMS was obtained from each windrow before nutrient addition, at 21 weeks (end of thermophilic phase) and after 37 weeks (end of mesophilic phase, when the temperature at the centre of the windrow returned to ambient) by removing ~250 g of material from ~20 cm below the peak of each windrow in four different locations. The four sub-samples obtained from a specific windrow were thoroughly mixed to provide a sample of compost representing each windrow. These composite samples were then mixed in equal proportions to provide a sample of compost representing all three windrows. These samples of compost were oven dried for 12 hours at 70°C and ground to < 2 mm particle size in a hammer mill. FTIR samples were prepared by combining ca. 100 mg of KBr with ca. 2 mg of dry PMS which was compressed under vacuum to discs.
6.3.2 $^{13}$C CP MAS NMR spectroscopic conditions

High resolution solid state $^{13}$C CP MAS NMR spectra were acquired with a Bruker MSL 400 spectrometer at a $^1$H frequency of 90.1 MHz, $^{13}$C frequency of 22.6 MHz, spinning rate 7 kHz, contact time 1 ms, spinning angle 54.7° to magnetic field, cycle time 1 s, acquisition time 1024 ms, sweep width 531.11 ppm, line broadening 40 Hz and a scan number of 2 to 3000 (Chapter 2). Difference spectra generated between samples at various decompositional stages were obtained by normalising total signal intensities to 100 so that the relative change in the distribution of carbon could be determined. Difference spectra were inverted about the zero baseline to allow for easier interpretation of spectroscopic changes; signals above the baseline represented a relative increase in signal intensity and signals below the baseline represented a relative loss of signal intensity. The approximate position of the baseline was indicated by a dashed line in all spectra. The $^{13}$C CP MAS NMR spectra were divided into the following regions and assignments were made according to Atalla et al. (1980) and Haw et al. (1984): 6-50 ppm (alkyl C), 50-58 ppm (methoxy C), 58-67 ppm (C-6 of cellulose), 67-78 ppm (C-2, C-3, C-5 of cellulose), 78-95 ppm (C-4 of cellulose), 95-110 ppm (C-1 of cellulose), and 110-165 ppm (aromatic C; lignin). The relative change in the distribution of carbon in samples obtained at various stages of PMS decomposition was determined by integrating signal areas between these chemical shifts. Integrated signal areas representing specific carbon assignments were expressed as a percentage of total spectral area. The distribution of total signal intensity within the delineated chemical shift regions must be considered to be only semi-quantitative since optimal conditions required for acquisition of spectra were not determined.

6.3.3 FTIR spectroscopic conditions

FTIR spectra were obtained at a wavenumber range of 4800-400 cm$^{-1}$ on a Bruker IFS 66 FTIR spectrophotometer. A linear baseline correction function was applied to spectra using 4780 cm$^{-1}$, 3780 cm$^{-1}$, 2300 cm$^{-1}$, 1890 cm$^{-1}$ and 843 cm$^{-1}$ as zero baseline points (Chapter 2). After baseline correction of FTIR spectra, all spectra were rescaled at 3300 cm$^{-1}$ (OH region) to obtain difference spectra, and all peaks were found to rescale accordingly. Difference spectra between samples were prepared as before. The approximate position of the baseline was also indicated by a dashed line in all spectra.

6.3.4 A direct phytotoxicity test of PMS compost maturity

The maturity of PMS at several stages during composting was determined by using a modification of the direct phytotoxicity test described by Keeling et al. (1994). This test
involved the measurement of emerged radicles from germinating *Lepidium sativum* (cress) seeds in aqueous compost extracts. Further descriptions of this test and the actual data obtained during the PMS windrow composting trial are presented in Chapter 4.

### 6.4 Results and Discussion

The $^{13}$C CP MAS NMR spectrum of uncomposted PMS (Figure 6.1a) was similar to the PMS analysed in Chapter 2, though indicating a slightly higher lignin content. The spectrum strongly resembled published spectra of chemically isolated cellulose polymorph type I (Dudley *et al.*, 1983), and indicated little lignin (110-160 ppm) or hemicellulose-like material. The spectrum was dominated by signals characteristic of the C-1 to C-6 carbon atoms of cellulose (Figure 2.2, Chapter 2). The large doublet between 72 and 75 ppm was due to the C-2, C-3 and C-5 carbons of cellulose, and the peak at 65 ppm was due to the cellulose carbon C-6, whereas on the higher shielding region of the 65 ppm shoulder (61 ppm) lie methoxyl signals of 4-O-methyl-α-D-glucuronic acid groups of hemicellulose and possibly lignin. The signal at 89 ppm and the broader high-shielding shoulder at 83 ppm was due to the cellulose carbon C-4, while the sharp signal at 105 ppm was due to cellulose carbon C-1. Signals representing aromatic carbon present in lignin were weak and poorly resolved; a doublet occurred between 148 and 153 ppm, corresponding to C-3 and C-5 of syringyl units having a free phenolic group at C-4 (148 ppm). The signal at 152 ppm was due to the same aromatic carbons but with an ether linkage attached to C-4, as in guaiacyl units of hardwood (Hatcher, 1987); this small doublet is characteristic of hardwood lignin (Nimz *et al.*, 1981). The PMS, therefore, consisted primarily of cellulose type I present in ordinary pulp, in combination with a small quantity of lignin and uronic acid groups present in hemicellulose.

The FTIR spectrum of PMS (Figure 6.2a) complemented the structural information obtained in the $^{13}$C CP MAS NMR spectrum (Figure 6.1a) and was similar to the PMS described in Chapter 2. The FTIR spectrum was dominated with carbonyl (C=O) (1630-1660, 1720 cm$^{-1}$), carboxylic (COOH) (1350 cm$^{-1}$), aliphatic (C-H) (1420, 1470 cm$^{-1}$), alcoholic (C-OH) and hydroxyl (O-H) (1050, 1110, 1185, 1250 cm$^{-1}$) functional group stretches which are characteristic of polysaccharide materials (Stevenson, 1982). Aromatic ring stretches were detected at 1515 and 1300 cm$^{-1}$, although small in intensity relative to those of the polysaccharide functional group stretches. The peak at 1515 cm$^{-1}$ indicated the presence of lignin (Johnston, 1964). A weak absorption peak characteristic of 4-O-methyl-a-D-glucuronic acid present in hemicellulose was located at 1720 cm$^{-1}$ (Marchessault, 1961; Durig *et al.*, 1988). The large absorption peak between peaks at 1630 and 1660 cm$^{-1}$ however were not entirely characteristic of cellulose; usually a carbonyl stretch of cellulose appears at 1630 cm$^{-1}$, although small in intensity relative to
other characteristic cellulosic bands. The peak at 1630 cm⁻¹ may have additionally represented the carbonyl groups of an amide II (due to a combination of NH bending and CN stretching), whereas the peak at 1660 cm⁻¹ may have represented carbonyl stretches of an amide I (Wexler, 1967) or of quinones (Stevenson, 1982). This band could possibly represent carbonyl functional group stretches of the polyacrylamide-based ([H₂C=CH-C(O)NH₂]ₙ) flocculant used during primary clarification. However, given the large intensity of the carbonyl band between 1630 and 1660 cm⁻¹ relative to the remaining bands, the very low rate of addition of the polyacrylamide-based flocculant to the effluent (0.6-1.0 mg L⁻¹), and since inorganic nitrogen comprised the majority of total nitrogen in PMS (Chapter 4), evidence suggested that the peak between 1630 and 1660 cm⁻¹ was primarily due to carbonyl stretches of quinone moieties (originating from lignin) and to cellulose rather than the polyacrylamide-based flocculant. The PMS, therefore, consisted primarily of polysaccharide material, specifically cellulose, in combination with a small quantity of lignin and uronic acid groups present in hemicellulose.

The changes in PMS structural composition after two distinct phases of composting were determined to identify the relative rate of structural change with time. The first phase was defined as the thermophilic phase (>45°C) of composting which lasted approximately 21 weeks, and the second phase was defined as the mesophilic phase (<45°C), which occurred between weeks 21 and 37 (Chapter 4). The cessation of the mesophilic phase occurred when the temperature at the centre of the windrow returned to ambient. Since the PMS did not exhibit any phytotoxic properties after 20-21 weeks composting, the material was considered to be partly matured (Chapter 4). After 37 weeks, the PMS compost was considered fully matured. During the thermophilic phase of composting significant structural change occurred in the PMS according to ¹³C CP MAS NMR (Figure 6.1b) and FTIR spectra (Figure 6.2b), however, during the mesophilic phase of composting, relatively little structural change occurred in the PMS (Figure 6.1c and 6.2c). The net structural change that occurred in the PMS during both phases of composting were identified by generating difference spectra (Figure 6.1d-f and Figure 6.2d-f) and by determining the relative distribution of carbon in samples from ¹³C CP MAS NMR spectra (Figure 6.3).

After the thermophilic phase of composting the average decrease in concentration of cellulose carbon was -15.8%, relative to uncomposted PMS (Figure 6.3). This estimate was determined by averaging the percentage change in integrated signal area representing C-1, C-2,3,5, C-4 and C-6 carbon atoms of cellulose as detected in ¹³C CP MAS NMR spectra (Figures 6.1 and 6.3). Loss of the polysaccharide fraction during the thermophilic stage of composting has been reported frequently (Gerasimowicz and Byler, 1985; Inbare et al., 1989, 1990, 1991, 1992). Mineralisation of some of the polysaccharide
Figures 6.1 and 6.2 $^{13}$C CP MAS NMR (left) and FTIR spectra (right) of (a) uncomposted PMS; (b) PMS after 21 weeks composting (end of thermophilic phase); (c) PMS after 37 weeks composting (end of mesophilic phase); (d) inverted difference spectra, a-b; (e) inverted difference spectra, b-c; (f) inverted difference spectra, a-c.
fraction in PMS during the thermophilic stage of composting was also confirmed in FTIR spectra (Figures 6.2b and 6.2d). Peaks representing 4-O-methyl-α-D-glucuronic acid present in hemicellulose (1720 cm⁻¹; Marchessault, 1961) and alcoholic (C-O)/hydroxyl (O-H) functional groups were partially removed during the thermophilic phase of composting, however, losses of other characteristic cellulosic peaks (OH; 1000-1100 cm⁻¹; Durig et al., 1988) did not occur. A substantial increase in concentration of carbonyl functional groups occurred during the thermophilic phase; an amide II was detected at 1630 cm⁻¹ (Wexler, 1967), and carbonyl stretches of an amide I in benzylamides (Wexler, 1967) or of quinones (Stevenson, 1982) was detected at 1660 cm⁻¹. The increase in amide/aromatic amide and quinone group concentration during the thermophilic phase of composting is consistent with the current theory of humus synthesis from polyphenolic substances (Kononova, 1966; Stevenson, 1982); microorganisms attack lignin and cellulosic substrates, resulting in the synthesis and transformation of existing aromatic moieties into polyphenols which are oxidised to quinones which subsequently react with N-containing compounds to form brown humic substances.

Despite these findings, only a marginal increase in carbonyl carbon concentration was detected in the ¹³C CP MAS NMR spectrum of PMS after the thermophilic phase of composting (160-190 ppm), although carbonyl/carboxyl groups usually display strong intensity in this region (Hatcher et al., 1981) (Figure 6.1c). However such signals tend to be difficult to resolve due to the occurrence of chemical shift anisotropy (Gerasimowicz and Byler, 1985). Relatively little structural change occurred to the PMS during the mesophilic stage of composting as revealed by the FTIR spectra (Figures 6.2c and 6.2e). A broadening of the peak between 1630 and 1720 cm⁻¹ (C=O of amide I,II and quinones) was consistent with structural changes that occurred during the thermophilic phase of composting. Since mineral nitrogen forms (urea, ammonium sulfate and ammonium nitrate) were added to PMS to lower the C:N ratio and therefore stimulate composting (Chapter 4), the observed increase in absorbance between 1630 and 1660 cm⁻¹ may indicate nitrogen incorporation into organic (amide) forms by the heterotrophic microbiota. This FTIR band may represent a useful indirect, semi-quantitative indicator of compost maturity, since the presence of trace quantities of nitrogen in the form of ammonia, among other microbial metabolites usually imparts strong phytotoxic properties (Zucconi et al., 1981).

A large increase in concentration of aromatic (+108%; 110-165 ppm), methoxyl carbon (lignin) (+46%; 56 and 61 ppm) and alkyl carbon (+41%; 6-50 ppm) occurred after the thermophilic stage of composting, relative to cellulose carbon in the ¹³C CP MAS NMR spectrum (Figures 6.1b and 6.3). Despite a 108% increase in concentration
of aromatic carbon after the thermophilic stage of composting, possibly due to selective mineralisation of cellulose, signals in the $^{13}$C CP MAS NMR spectrum were still poorly resolved. The reason for this is that lignin (unlike cellulose) contains a large number of carbon atoms which have slightly different chemical shifts (Bartuska et al., 1980; Piotrowski et al., 1984). Nevertheless, the large increase in concentration of aromatic carbon suggested that the aromatic ring structures present in lignin were not subject to cleavage during the thermophilic stage of PMS composting. This result was confirmed by a large increase in the peak at 1515 cm$^{-1}$ (aromatic ring stretch) in the FTIR spectrum of PMS after 21 weeks composting (Figures 6.2b and 6.2d). Since bacteria comprise the dominant biota present in thermophilic composts (Finstein and Morris, 1975), the lack of lignin removal from the PMS during this stage was not surprising given that bacterially-mediated lignin mineralisation is poor, relative to that of basidiomycete fungi which persist mainly in mesophilic habitats (Kirk and Farrell, 1987). However, at the end of the mesophilic stage of composting, the concentration of aromatic carbon had decreased by 25% relative to the concentration of aromatic carbon present in the PMS compost after the thermophilic stage (Figures 6.1c and 6.3). Re-invasion of PMS windrows with fungi after the thermophilic phase of composting was observed, and hence fungal mineralisation of lignin may be responsible for the decrease in the concentration of aromatic carbon.

The relative proportion of alkyl carbon detected in $^{13}$C CP MAS NMR and FTIR spectra of PMS increased by 41% after 21 weeks (Figure 6.3). Alkyl groups as detected in the FTIR spectrum (Figure 6.2b) consisted of aliphatic (1420 and 1470 cm$^{-1}$) and carbonyl groups (1630 and 1660 cm$^{-1}$). This may have been due to selective preservation of alkyl carbon derived from both the substrate and microorganisms, and in situ synthesis by microorganisms utilising the carbohydrate and/or aromatic fractions of PMS (Hatcher et al., 1981; Baldock et al., 1992). A further increase in alkyl carbon concentration occurred after the mesophilic stage of composting, although the relative increase (20%) was less than that which occurred after the thermophilic stage of composting (41%). The magnitude of the increase in aromatic and alkyl carbon after the mesophilic stage of PMS composting was small, a result which was very similar to that reported for a cattle manure after 21 weeks composting (Inbar et al., 1989). This indicates that most of the structural change to organic materials occurs during the thermophilic stage. The increase in concentration of aromatic and alkyl carbon with increasing stage of composting relative to uncomposted PMS suggested that the material was displaying increasing similarities to humic acids which have been reported in the literature previously (Hatcher et al., 1981; Gerasimowicz and Byler, 1985).
The spectroscopic techniques clearly demonstrated that PMS compost maturity coincided with an almost complete cessation in substrate decomposition. The techniques were also capable of distinguishing between carbon originating from the substrate and that resynthesised as microbial biomass, which is not achievable with conventional chemical extraction techniques (e.g. Morel et al., 1985). Although it was shown that ~16% of the carbon originating from cellulose was mineralised, a significant proportion of the cellulosic substrate was still present in a non-degraded state. The lack of microbial degradation of cellulose in PMS is consistent with previous reports that cellulose is poorly degraded when it is utilised as a sole source of carbon for microbial growth (Alexander, 1977). Furthermore, the presence of lignin may have also reduced the potential rate of cellulose decomposition during composting as lignin physically inhibits cellulosic enzymes through close structural interlinkages with cellulose (Alexander, 1977).

**Figure 6.3** Distribution of carbon in PMS before composting (week 1), after the thermophilic (21 weeks) and mesophilic (37 weeks) stages as determined by $^{13}$C CP MAS NMR spectroscopy. * Indicates the specific carbon atom in the cellulose repeating unit.

On a practical level, these spectroscopic techniques cannot be used to indicate the maturity of a composted waste (by assessing the point in time in which decomposition ceases) because a cessation of decomposition may be caused by factors other than exhaustion of the available carbon pool (e.g. low water availability, low nutrient content or excessively high substrate temperatures). Furthermore, examination of the carbon
fraction by these methods cannot determine the presence or absence of phytotoxic metabolites produced by microorganisms, such as volatile fatty acids which are the most common phytotoxic metabolites present in unstabilised composts (Lynch, 1977; Marambe et al., 1993). The concentration of volatile fatty acids in the PMS at 21 weeks would, however, be expected to be low as no phytotoxic properties were present at that time. Also, phytotoxic volatile fatty acid metabolites would be difficult to detect with these spectroscopic techniques as their spectroscopic characteristics would be disguised by the remaining unmetabolised organic matrix. Nevertheless, these spectroscopic techniques may be useful in other areas of organic waste treatment, such as in the monitoring of biofilter substrate condition, as a gradual reduction in available carbon for microbial growth within the substrate eventually leads to inefficient immobilisation of malodorous substances (Goldstein, 1996).

Although quantitative estimates of organic components within a material can be achieved with $^{13}$C CP MAS NMR, this is only possible when contact and pulse delay times are optimised to ensure that all carbons are equally excited, the relaxation of protons is homogeneous, all nuclei are fully relaxed and when chemical shift anisotropy is eliminated (Hatcher, 1987; Baldock et al., 1992). Since these spectroscopic conditions are rarely optimised, due to cost, results usually obtained can only be considered as semi-quantitative (as in this study). Furthermore, quantitative determinations of organic components may not be possible in materials with high ash contents (e.g. some PMSs), as the presence of paramagnetic species (e.g. Fe$^{2+}$ and Cu$^{2+}$) in sufficient concentration reduces the efficiency of cross polarisation processes such that $^{13}$C nuclei in close proximity to paramagnetics may be rendered NMR "invisible" (Baldock et al., 1992). Thirdly, although solution state FTIR can yield quantitative information (Wexler, 1967), solid state FTIR cannot, due to uncertainties in the thickness of the particle (path length) in the KBr disk which transmits the infrared frequencies, thereby affecting signal intensity. Nevertheless, both spectroscopic techniques when used in a complementary manner can provide useful semi-quantitative data on structural changes mediated by microbial processes during composting of organic materials.

Probably the best method of establishing the extent of maturation of PMS compost would be a direct phytotoxicity test, carried out as described in Chapter 4. Although this test cannot properly indicate maturity in materials which have excessive salinity, or when herbicides or chlorinated organic compounds (in some PMSs) are present, direct phytotoxicity tests would still be appropriate for the PMS produced by ANM. This is because the material is not contaminated with the former chemical substances which may otherwise indicate an incorrect level of maturity.
Spectroscopic evidence demonstrated that the majority of the structural change to PMS occurred during the thermophilic stage of composting when phytotoxic properties were present. Thereafter, little structural change (apart from minor lignin mineralisation) occurred when phytotoxic properties were absent. When $^{13}$C CP MAS NMR and FTIR were used in a complementary manner, semi-quantitative estimates of the rate of change in cellulose, lignin, alkyl and humus concentration can be determined. These techniques cannot be used to indicate the level of maturity present through an examination of the rate of organic matter decomposition, as cessation of decomposition, which might otherwise indicate a sufficient level of maturation, may be caused by other factors affecting microbial activity. These spectroscopic techniques, however, may be useful in other areas of organic waste treatment, such as in the monitoring of biofilter substrate condition. Given that much of the structural change to the organic fraction ceased when the phytotoxicity of the compost disappeared, evidence suggested that the direct phytotoxicity test was suitable for the characterisation of maturity during PMS composting.
Chapter 7

Structural characterisation of aluminium in pulp and paper mill sludge and the resulting compost

7.1 Abstract

The mechanism of aluminium retention in non-composted and composted PMS was investigated to assess whether aluminium was in a form readily available for plant uptake. Since soluble aluminium is toxic to plants, the potential for aluminium phytotoxicity to occur following the use of PMS compost needed to be determined.

The source of aluminium in the PMS was found to be the use of aluminium sulfate as a flocculating agent in primary clarification and sludge dewatering. Extraction of the non-composted and composted PMS with an unbuffered potassium chloride solution suggested that aluminium was essentially non-exchangeable, even though the pH of PMS (non-composted PMS) was low enough for aluminium to enter the aqueous phase. Further work with wavelength dispersive X-ray analysis revealed that aluminium was evenly distributed over cellulose fibres, and this association did not change following 21 weeks of composting. Before composting, most of the aluminium present in the PMS was still in the monomeric, octahedrally coordinated (AlO6) form as in aluminium sulfate, revealed by solid-state Aluminium-27 Nuclear Magnetic Resonance Spectroscopy with Magic Angle Spinning (27Al MAS NMR). However, a small quantity was present in a penta-coordinate (AlO5) form. This form was found to represent an organo-aluminium complex, possibly with cellulose, uronic acids or lignin which are the major organic components of PMS (Chapter 2). After 21 weeks of composting the aluminium concentration increased from 0.37% to 0.55%, with most of the aluminium still in the monomeric octahedrally coordinated form. The proportion of AlO5 penta-coordinate aluminium decreased in composted PMS, however, the increase in total aluminium concentration was due to contamination with tetrahedrally-coordinated aluminium (clay) from the composting pad, and to mineralisation of the cellulosic fraction. Clay contamination of the PMS was further confirmed by solid state 29Si MAS NMR analyses.

Formation of strong electrostatic bonds between the monomeric octahedrally-coordinated aluminium ions and the cellulose matrix via deprotonable chelation sites was responsible, therefore, for the non-exchangeable nature of the latter in PMS. If the PMS compost was used as a plant growth substrate, the potential for aluminium toxicity would
be very low in the short term. In the long term, however, mineralisation of the cellulose fraction would lead to aluminium deposition in the root zone. Such aluminium may adversely affect plant growth under low pH soil conditions. Therefore, substitution of the aluminium sulfate flocculant with a commercially available iron-based flocculant (e.g., ferric sulfate or ferric chloride) would be advantageous. Since the chemistry of iron-mediated flocculation is analogous to that of aluminium, its use as a flocculant would be compatible with the existing effluent treatment system at ANM, and would not affect the previously described approach to composting.

7.2 Introduction

Aluminium sulfate (alum) is widely used in the physico-chemical treatment of water and waste waters to remove suspended material, to precipitate inorganics such as phosphates and fluorides (Buffle et al., 1985) and to flocculate organic pollutants, being effective within the pH limits of 5.5 and 8.0 (Thébault et al., 1981; Hammer and Hammer, 1996). The use of organic solids from waste water produced through the use of aluminium-based flocculants for agricultural or horticultural purposes may be problematic, as soluble aluminium strongly affects soil chemical and plant growth processes. The possible effects of aluminium in (such) organic wastes on the soil–plant system have not been considered in the literature.

Aluminium toxicity in plants is closely associated with soil acidity, as the soluble form of aluminium increases sharply below pH 5.0 (McLean, 1976). Soluble aluminium at concentrations as low as 1 mg L⁻¹ in the root zone of some plants has been found to inhibit root elongation through its effect on cell division (Fleming and Foy, 1968; Bohn et al., 1985). Aluminium inhibits cell division by reducing the ability of the cell to carry out normal physiological functions, causing the degeneration of the nuclei and cytoplasm (plasmolysis). Soluble aluminium also reduces the uptake and translocation of calcium in plants (Andrew et al., 1973). Since calcium plays a pivotal role in maintaining the selective ion uptake process in roots, loss of calcium by cation exchange with aluminium results in a disruption of membrane function (Viets, 1944). In soils, soluble aluminium can also precipitate with soluble phosphate and cause phosphorus deficiencies in plants (Foy and Brown, 1963). This reaction can also occur at the cell surface or free space of roots (Clarkson, 1966). Soluble aluminium also affects the movement of phosphate in plants. Aluminium has been found to inhibit the esterification of phosphate, a prerequisite to enable the movement of phosphate in the xylem (Loughman, 1966). Since soluble aluminium induces calcium and phosphorus deficiency in plants at low pH, application of lime (calcium carbonate) to raise soil pH and to reduce the concentration of aluminium in solution is widely practiced (Munns, 1965).
The form of aluminium toxic to plants in acid soils include the monomeric species, having a varying number of water ligands and hydroxyl groups (Bohn et al., 1985; Hue et al., 1986). These cations include Al(H2O)63+ (monohexaquoaluminium ion), AlOH(H2O)52+ and Al(OH)2(H2O)4+, all octahedrally-coordinated (six oxygens surrounding a central Al atom, AlO6). The abundance of these aluminium species in soil solution is affected by pH; the Al(H2O)63+ ion is predominant below pH 4.7 and the Al(OH)2(H2O)4+ ion predominates between pH 4.7 and 6.5 (Bohn et al., 1985). The AlOH(H2O)52+ ion, however, is of minor importance as it only forms over a narrow pH range (Bohn et al., 1985). These aluminium cations may exist freely in solution or can be exchangeably bound (i.e. weakly bound and available for release into solution) to negative cation exchange sites on soil colloids. In addition to the soluble aluminium forms, aluminium may also precipitate as solid gibbsite (Al(OH)(H2O)3O) above pH 6.5 or whenever its solubility product is exceeded (Bohn et al., 1985). Since this form of aluminium is insoluble, it is not toxic to plants. Polymeric aluminium forms have also been discovered in solution, forming large, multicharged units of the general formula [Al(OH)x(H2O)6-x(3-x)+]n, where n is the average number of aluminium ions per polymer. These polymers are strongly retained by soil colloid surfaces and normally behave as if they are virtually non-exchangeable (Bohn et al., 1985). Recently, however, laboratory and field evidence suggests that polynuclear species such as the Al13 tridecamer (AlO4Al12(OH)24(H2O)127+) (Bertsch et al., 1986a; Parker and Bertsch, 1992; Thomas et al., 1991, 1993) occurring in partially neutralised solutions is at least 10 times more toxic than the monomeric forms (Parker et al., 1989). The Al13 polycation consists of a symmetrical, cage-like arrangement of 12 octahedrally coordinated aluminium atoms surrounding a single tetrahedral (AlO4) core atom (Akitt and Elders, 1988).

Soluble aluminium has been found to complex with organic ligands such as the carboxylic and hydroxycarboxylic acids in soils, resulting in a reduction in phytotoxicity (Hue et al., 1986). Apparently, these organic ligands reduce aluminium availability and hence toxicity by forming stable 5- or 6-bond ring structures (Hue et al., 1986; Thomas et al., 1991). Humic and fulvic acids in soil also play an important role in complexing monomeric aluminium species in solution (Plankey and Patterson, 1987) and adsorbing solid aluminium hydroxides (McBride and Wesselink, 1988).

The mechanism of aluminium-mediated flocculation during waste water treatment has received much attention, however considerable uncertainty still exists due to the complex reaction of aluminium in solution (Buffle et al., 1985; Parthasarathy and Buffle, 1985; Hammer and Hammer, 1996). Factors which have an important effect on partially hydrolysed aluminium and the formation of cationic polymers which can flocculate
suspended organic solids include pH (or OH/Al ratio), ionic strength and temperature (Parthasarathy and Buffle, 1985). These factors affect the size of the polymer, charge per aluminium atom in the polymer and the ease of dissociation of the polymer (Buffle et al., 1985). Although many models of the aluminium polymer formation have been proposed, formation of the Al\textsubscript{13} polycation (as discussed above) is thought to be responsible for the coagulation and flocculation of solids during waste water treatment (Buffle et al., 1985; Parthasarathy and Buffle, 1985).

The relative distribution of available, complexed or precipitated aluminium species in the root environment of plants will determine whether aluminium phytotoxicity will occur. In order to determine whether the aluminium present in non-composted and composted PMS was available, complexed, or precipitated, high resolution solid state \textsuperscript{27}Al MAS NMR was used. This technique (and variations thereof) has been used with success in the structural characterisation of aluminium in solution (Buffle et al., 1985; Bertsch et al., 1986a; Akitt and Elders, 1988; Thomas et al., 1991, 1993; Parker and Bertsch, 1992), in solid materials such as zeolites (Bertsch et al., 1986b; Corbin et al., 1987; Man and Klinowski, 1988) and in other minerals (Alemany and Kirker, 1986; Cruickshank et al., 1986; Bastow et al., 1994). In addition, \textsuperscript{29}Si MAS NMR analyses was used in a complementary manner to the \textsuperscript{27}Al analysis for the purpose of characterising the complexed aluminium pool (e.g. aluminium in clay minerals). The spatial distribution of aluminium in PMS was also examined by wavelength dispersive X-ray analysis. This technique has been used previously to examine the distribution of aluminium in many mineralogical and biological specimens (Huett and Menary, 1980; Goldstein et al., 1981). Therefore, the purpose of this investigation was to predict whether aluminium toxicity would occur following the use of PMS compost as a substrate for plant growth.

7.3 Materials and Methods

7.3.1 Determination of exchangeable aluminium in PMS and composted PMS

The proportion of the aluminium in PMS and composted PMS (after 21 weeks, Chapter 4) considered exchangeable or available for plant uptake was determined by extraction with an unbuffered 1 M KCl solution at a PMS:solution ratio of 1:10 with end-over-end shaking for 30 minutes (Barnhisel and Bertsch, 1982). Extracts were filtered through a Whatman No. 42 filter and then centrifuged for 10 minutes at 10 000 rev min\textsuperscript{-1}. Aluminium present in the supernatant was quantified with an inductively coupled plasma optical emission spectrometer present in the Central Science Laboratory, University of Tasmania.
7.3.2 Preparation of samples for wavelength dispersive X-ray and multinuclear NMR analysis

A 1 kg representative sample of PMS was sampled from three windrows prior to mineral nutrient addition on day 1 and following composting (21 weeks) as described in Chapter 4. Samples were oven dried at 70°C for 12 hours followed by grinding to < 2mm particle size. Sample homogeneity was ensured by mixing the ground PMS.

7.3.3 Distribution of aluminium in PMS and composted PMS by wavelength dispersive X-ray analysis

Ground dry PMS and composted PMS specimens were mounted on double sided tape to a perspex base supported by a brass stub to minimise background radiation. Specimens were carbon coated to allow the acquisition of electron images. The analyses were carried out with a Cameca SX 50 electron probe microanalyser with an accelerating voltage of 10-15 kV. The count rate was held constant by varying the electron beam current around 15 nA. Wavelength dispersive X-ray aluminium Ka maps were processed on a Pentium PC workstation with HiMax 38 software (SAMX, France).

7.3.4 27Al and 29Si MAS NMR analysis of PMS and composted PMS

High-resolution solid state 27Al MAS spectra were obtained on a Bruker MSL 400 NMR spectrometer at the CSIRO Division of Materials Science and Technology, Clayton, Victoria, at a 27Al frequency of 104.3 MHz with a magic angle spinning rate of 10 kHz and a spinning angle of 54.7° to the magnetic field. Spectra were acquired with a pulse of 0.75 μs, a repetition time of 0.5 s and a sweep of 416 kHz. The 27Al spectra were referenced to aqueous Al2[SO4]3.18H2O in which the octahedrally coordinated AlO6 peak was set at -0.5 ppm.

29Si MAS spectra were obtained with the same NMR spectrometer at a 29Si frequency of 79.5 MHz with a magic angle spinning rate of 10 kHz and a spinning angle of 54.7° to the magnetic field. Spectra were acquired with a pulse of 2 μs, a repetition time of 2 s and a sweep of 60 kHz. Chemical shifts were referenced to tetramethylsilane.
7.4 Results and Discussion

7.4.1 Determination of exchangeable aluminium in PMS and composted PMS

Given the very high total aluminium contents of PMS (0.37% w/w DW; Chapter 4) and composted PMS (0.55% w/w DW; Chapter 4), and the reasonably low pH values (4.59 and 5.84 respectively; Chapter 4), a large proportion of the total aluminium pool was expected to be in the exchangeable form. However, the exchangeable aluminium concentration in the 1M KCl extracts of the PMS and composted PMS was below the level of detection of the inductively coupled plasma optical emission spectrometer (<0.02 mg L⁻¹). The exchangeable aluminium concentration, therefore, for both PMS samples on a dry matter basis was less than 0.66 mg kg⁻¹. Although this result was surprising, Barnhisel and Bertsch (1982) argued that extraction techniques which employ unbuffered salt solutions (as in this experiment) are probably best suited for estimating truly exchangeable aluminium. Other complexing agents and acidified salt solutions may extract aluminium from both exchangeable and non-exchangeable sources, including structural hydroxyl polymeric interlayers (e.g. as in clay), organically bound species and other non-crystalline metastable forms. Evidence, therefore, suggested that the aluminium in PMS and composted PMS was most likely organically bound in a non-exchangeable form. Given the low concentration of ash in the PMS before composting (1.64% w/w, DW; Chapter 4), it was unlikely that the aluminium present reacted with the inorganic phase to form a stable precipitate, or was present in an aluminosilicate (clay).

7.4.2 Spatial distribution of aluminium in PMS and composted PMS

To further investigate why the aluminium in PMS and composted PMS was non-exchangeable, the spatial distribution of aluminium was determined. The spatial distribution of aluminium over representative cellulose fibre bundles (Figure 7.1) in PMS before composting is shown in Figure 7.2. Clearly, the aluminium present in the PMS was evenly distributed and closely associated with the fibre bundles. Also, there were few localised high concentrations of aluminium (dark regions), which is consistent with the hypothesis that the formation of stable inorganic precipitates were not responsible for the non-exchangeable nature of the aluminium.

The spatial distribution of aluminium over degraded cellulose fibre bundles (Figure 7.3) present in composted PMS was also determined (Figure 7.4). Once again, the pattern of aluminium distribution appeared to follow that of the degraded cellulose matrix. However, in the sample there were many localised high concentrations of aluminium (dark regions), possibly indicating the presence of an inorganic alumino-precipitate.
and/or an aluminosilicate mineral (clay). Contamination of the PMS with clay may have occurred as composting was conducted on an unsealed surface consisting of soil and fly ash.

**Figure 7.1** Electron image of a cellulose bundle in PMS prior to composting and addition of mineral nutrients.

**Figure 7.2** Wavelength dispersive aluminium $K\alpha$ X-ray map (negative image) of the cellulose bundle in PMS as shown in Figure 7.1.
7.4.3 Structural characterisation of aluminium and silicon in PMS and composted PMS by solid state $^{27}$Al and $^{29}$Si MAS NMR spectroscopy

Changes in the chemical state of aluminium before and after composting was studied to determine why the aluminium was non exchangeable. Figure 7.5 shows the solid state $^{27}$Al MAS NMR spectrum of the aluminium sulfate flocculant before addition to the effluent (Figure 7.5a), PMS following dewatering (Figure 7.5b) and PMS after composting (Figure 7.5c). The central peak at -0.5 ppm in the spectrum of aluminium sulfate represented the monomeric, non framework octahedrally coordinated $\text{Al(H}_2\text{O)}_6^{3+}$ cation which forms after aluminium sulfate dissolves in water. Following dewatering of PMS, aluminium was still primarily in the octahedral form, since the spectrum was dominated by the $\text{AlO}_6$ signal at -0.5 ppm (Figure 7.5b). This signal represents a
number of variously hydroxylated aluminium species, including \( \text{Al(H}_2\text{O)}_6^{3+} \), \( \text{AlO}(\text{H}_2\text{O})_5^{2+} \), \( \text{Al}((\text{OH})_2(\text{H}_2\text{O})_2^{3+} \) or \( \text{Al(OH)}_3(\text{H}_2\text{O})_3 \) (gibbsite) (Bertsch et al., 1986a). The absence of a positive shift in the octahedrally coordinated signal centered at -0.5 ppm following dewatering suggested that aluminium in PMS was still in the monomeric form, since previous reports have shown that polymerisation of aluminium, yielding large polycations or precipitated phases, results in a 4-10 ppm positive shift of this signal (Thomas et al., 1991). Furthermore, the absence of a negative shift in the octahedral signal at -0.5 ppm suggested that aluminium present in the PMS after dewatering did not precipitate with a mineral anion, such as phosphate (Alemany et al., 1988).

Although most of the aluminium present in dewatered PMS was octahedrally coordinated (-0.5 ppm), a small proportion was found to be penta-coordinated \( \text{AlO}_5 \) (31 ppm; Figure 7.5b) (Alemany and Kirker, 1986). Penta-coordinated aluminium is relatively rare, since aluminium in most materials is normally either tetrahedrally or octahedrally coordinated (Cruickshank et al., 1986; Alemany and Kirker, 1986; Alemany et al., 1988). Apparently penta-coordination occurs in some organo-aluminium compounds, in which the coordination polyhedra contain other elements along with oxygen (Bonamico, 1966; Cruickshank and Glasser, 1985; Parise, 1984; Cruickshank et al., 1986). Barium aluminium glycolate \( \text{BaAlO}_8\text{C}_6\text{H}_{14.75}\text{O}_{4.75} \) is an example of an organic compound with penta-coordinated aluminium, containing barium and oxygen in the polyhedra. Thus the penta-coordinated signal detected at 31 ppm could represent an organo-aluminium complex with cellulose, uronic acids or lignin, these being the major constituents of PMS (Chapter 2).

The broadening of the signals in the \( ^{27}\text{Al} \) MAS NMR spectrum of PMS (Figure 7.5b) relative to the spectrum of aluminium sulfate (Figure 7.5a) was due to chemical shift dispersion, which usually occurs in non-crystalline (amorphous) samples (Bastow et al., 1994). Furthermore, incomplete removal of quadrupolar interactions with MAS also produces line broadening, sometimes leading to difficulties in separating chemically distinct aluminium sites (Alemany et al., 1988; Bastow et al., 1994).

In solution state \( ^{27}\text{Al} \) NMR, the \( \text{Al}_{13} \) polycation which is thought to be responsible for the flocculation of solids during waste water treatment (Buffle et al., 1985; Parthasarathy and Buffle, 1985) is usually found at 62.5 ppm (Bertsch et al., 1986a). Normally, the \( \text{Al}_{13} \) polycation displays two signals in solution state \( ^{27}\text{Al} \) NMR spectra; a large, sharp signal at 62.5 ppm, representing the core tetrahedral aluminium which exists in a very symmetrical environment; and a second, very broad signal at ~ 0 ppm, representing the remaining 12 octahedral aluminium atoms which do not exist in a symmetrical environment (Bertsch et al., 1986a). Although the \( \text{Al}_{13} \) polycation has been found in
crystals of basic aluminium sulfates precipitated from hydroxy-aluminium solutions (Johansson, 1960), the latter has not been studied by solid state \(^{27}\)Al NMR. The reason for this is that considerable line broadening occurs in the solid state (relative to solution state NMR), owing to specific interactions of the nuclear spins tightly bound in the rigid lattice of the sample, which makes the separation of signals difficult in complex samples.

**Figure 7.5** \(^{27}\)Al MAS NMR spectrum of (a) \(\text{Al}_2(\text{SO}_4)_3\cdot18\text{H}_2\text{O}\) (aluminium sulfate); (b) PMS before composting and mineral nutrient addition; (c) PMS after 21 weeks of composting.
Nevertheless, the very low concentration of soluble aluminium in PMS, coupled with an absence of a distinct signal representing the core aluminium atom of the $\text{Al}_{13}$ polycation at 62.5 ppm, suggested the $\text{Al}_{13}$ polycation was not present in the PMS following dewatering and composting.

The solid state $^{27}\text{Al}$ MAS NMR spectrum of PMS after 21 weeks composting is shown in Figure 7.5c. The spectrum displayed an increased signal to noise ratio compared to the spectrum of PMS before composting (Figure 7.5b), as the former sample had a higher concentration of aluminium (PMS before composting, 0.37% Al w/w OW; PMS after composting, 0.55% Al w/w OW; Chapter 4). Clearly, the octahedrally coordinated aluminium signal at -0.5 ppm still dominated the spectrum, suggesting that the mechanism of aluminium retention did not appreciably change after PMS composting. However, the relative height of the penta-coordinated signal at 31 ppm was reduced, and was partly obscured by a new signal at 53.5 ppm, corresponding to framework, tetrahedral aluminium (Engelhardt and Michel, 1987). The tetrahedral signal detected in composted PMS was highly characteristic of aluminium present as an aluminosilicate mineral, otherwise known as clay (Delpuech, 1983; Fyfe, 1983; Corbin et al., 1987; Engelhardt and Michel, 1987; Man and Klinowski, 1988). The source of the tetrahedral ($\text{AlO}_4$) aluminium (clay) in composted PMS was most likely soil and fly ash from boiler furnaces at ANM, as composting was conducted on an unsealed pad consisting of these two materials.

Clay minerals or aluminosilicates consist of a framework of $\text{SiO}_4$ tetrahedra linked to $\text{AlO}_4$ tetrahedra in a variety of arrangements. Previous work has shown that solid state $^{29}\text{Si}$ MAS NMR is a powerful tool for determining the structure of solid silicates and aluminosilicates (Lippmaa et al., 1980), since $^{29}\text{Si}$ signals are sensitive to the atoms attached to the oxygens of the $\text{SiO}_4$ tetrahedron (Fyfe, 1983). Therefore, to confirm that clay contamination was responsible for the tetrahedral aluminium signal in the composted PMS spectrum (Figure 7.5c), PMS before and after composting was analysed by solid state $^{29}\text{Si}$ MAS NMR. The $^{29}\text{Si}$ MAS NMR spectrum of PMS prior to composting contained no resolvable signals (Figure 7.6a), suggesting the concentration of silicon was extremely low, or absent. After PMS composting, the $^{29}\text{Si}$ MAS NMR spectrum revealed that the material contained a significant quantity of silicon, with signals appearing at -91.5 and -108.5 ppm. A smaller signal (consisting of two peaks) between the two main peaks was detected at -96 ppm, although it was almost completely obscured by the lower frequency side of the signal at -108.5 ppm (Figure 7.6b). The signal at -91.5 ppm corresponded with $\text{SiO}_4$ tetrahedra linked to two $\text{AlO}_4$ tetrahedra, whereas the partially obscured signal at 96 ppm may have represented $\text{SiO}_4$ tetrahedra linked to one $\text{AlO}_4$ tetrahedra (Lippmaa et al., 1980). These two signals were consistent with an
aluminosilicate mineral possessing an Al:Si ratio in the lattice of 1:3 (Lippmaa et al., 1980). The signal at -108.5 ppm, however, represented SiO$_4$ tetrahedra linked with no AlO$_4$ tetrahedra, corresponding to quartz (SiO$_2$) (Lippmaa et al., 1980). Therefore, the evidence obtained in this analysis suggested the tetrahedral aluminium signal in the PMS after composting was due to clay contamination arising from the unsealed composting pad. The small dark regions in the wavelength dispersive K$\alpha$ X-ray map of composted PMS (Figure 7.4), representing localised concentrations of aluminium would most likely be clay particles. In theory, given a 45% reduction in volume after 21 weeks PMS composting, and assuming no aluminium was lost from the system, the concentration should have risen to 0.54% without a clay contribution. Thus the increase in concentration of aluminium in PMS from 0.37% before to 0.55% after composting was mainly attributed to microbial decomposition of the organic fraction, and to minor clay contamination. The presence of quartz in the final PMS may have arisen from the fly ash which was used as a soil cover on the composting pad.

**Figure 7.6** $^{29}$Si MAS NMR spectrum of (a) PMS before composting and mineral nutrient addition; (b) PMS after 21 weeks composting.
From the studies undertaken it became clear that the mechanism of aluminium retention in both the non-composted and composted PMS involved the formation of strong electrostatic interactions between the monomeric aluminium species and the cellulose matrix. Chelation of monomeric aluminium cations within the cellulose matrix is conceivable, given that the polymer contains many functional groups capable of cation exchange (e.g. O-H\(^+\), COO-H\(^+\)). Deprotonation of these chelating sites (hydroxyls and carboxyls) by monomeric aluminium species with the formation of strong electrostatic bonds could possibly explain the non-exchangeable nature of aluminium in both the composted and non-composted PMS. Increased aluminium chelation would be expected during the composting process as well, due to the formation of humic substances (humic and fulvic acids) which are among the most important metal complexing ligands in soil and water (Plankey and Patterson, 1987).

In the large-scale PMS composting study, the PMS appeared to be poorly buffered against pH change, particularly during the final stages of windrow composting, where the pH dropped from ~7.5 at 11 weeks to ~5.8 after 21 weeks (Chapter 4). Although the pH of PMS after composting was within the required range for growing most plants in containers (5.5-6.0), a further decrease in pH would result in sub-optimal nutrient availability and thus poor plant growth (Handreck and Black, 1989). This pH drop could not have been due to Al\(^{3+}\) mediated displacement of H\(^+\) and basic cations from exchange complexes, as Al\(^{3+}\) cations were found to be strongly bound in a non-exchangeable form within the PMS. Given the almost non-reactive nature of aluminium in the PMS compost, a continued reduction in pH mediated by the former mechanism would not occur. In partially neutralised aluminium solutions, however, the highly charged polymeric cations which form often re-polymerise to form more stable polymers, resulting in the consumption of base and a gradual reduction of pH over time (Parthasarathy and Buffle, 1985).

The rapid decline in pH between weeks 11 and 21 was likely due to the nitrification of NH\(_{4}^{+}\) ions, as discussed in Chapter 4. Considerable H\(^+\) release would have occurred during PMS composting as all of the nitrogen sources added (urea, ammonium sulfate and ammonium nitrate) upon hydrolysis and/or dissolution released NH\(_{4}^{+}\) ions. In soil systems, nitrification of NH\(_{4}\)-N fertilisers is one of the major causes of acidification (Tisdale et al., 1993). Sterrett and Fretz (1977) also reported that the use of ammonium-based fertilisers resulted in a much greater fall in pH after 6 weeks composting of hardwood bark compared to when nitrate-based fertilisers were used as nitrogen supplements. The addition of at least 25% of the mineral nitrogen requirement as urea to the PMS, however, would still be required to raise the pH of PMS to within the neutral range required for optimal microbial activity. To prevent a rapid decline in pH during the
later stages of PMS composting, nitrate containing mineral nutrients (e.g. KNO₃) could be used instead of ammonium based mineral nutrients, in a bid to reduce the size of the ammonium pool available for nitrification. Recently, however, it has been shown that diffusion of nitrate to anaerobic zones in manure or to previously aerobic zones which are made anaerobic by high biological oxygen demand during composting, results in microbial denitrification of nitrate to gaseous N₂ and N₂O (Mahimairaja et al., 1995). Loss of nitrogen by microbial denitrification during composting apparently increases with the concentration of nitrate present. The authors reported that denitrification over a 14 week composting period accounted for a loss of ~9% of the total nitrogen initially present. Therefore, given that microbial denitrification can be a significant pathway of nitrogen loss, and that denitrification occurs optimally up to a temperature of 65°C (Keeney et al., 1979), the addition of nitrate mineral nutrients following the first urea amendment to PMS during composting would not be recommended.

The rapid pH decline during the later stages of PMS composting could perhaps be reduced by adding zeolite to PMS. Zeolite has been found to conserve nitrogen in manure presumably by strongly adsorbing NH₄⁺ ions in exchange sites, thereby limiting the availability of adsorbed NH₄⁺ ions for nitrification (Miner, 1984; Mahimairaja et al., 1995). Furthermore, the application of nitrification inhibitors such as nitrapyrin, otherwise known as N-Serve®, has been shown to be effective in improving the efficiency of nitrate fertilisers (Barber, 1984) and may prevent a rapid pH decline caused by nitrification. Since zeolitic minerals and nitrification inhibitors are generally considered expensive (Barber, 1984), their use would not be practicable. Probably simplest may be addition of calcium carbonate (agricultural lime) after PMS composting to neutralise hydrogen ions produced during nitrification.

The availability of aluminium to plants in the composted PMS in the long term could not be determined in this study. Slow mineralisation of the remaining cellulosic fraction in the PMS compost would be expected following application to soil, and this may lead to the deposition of aluminium in the root zone. To overcome the uncertainty regarding the reaction of aluminium in PMS compost in the long term, aluminium sulfate used during primary clarification and sludge dewatering at ANM could be replaced by a non-aluminium based flocculant, such as ferric sulfate (Fe₂(SO₄)₃) or ferric chloride (FeCl₃·6H₂O). Ferric sulfate is available as a commercial flocculant in the form of a reddish-brown granular material that is readily soluble in water, and is particularly effective over a wide pH range (Thébault et al., 1981; Hammer and Hammer, 1996). These iron-based flocculants contain iron in the trivalent form, as in aluminium, and their hydrolysis reactions are analogous to that of aluminium in waste waters (Hammer and Hammer, 1996). The use of iron to assist in the flocculation and dewatering process
would be beneficial in the resulting PMS, as iron is necessary as a micronutrient for plant growth (Salisbury and Ross, 1992). Addition of iron to soils is sometimes required as iron deficiencies often occur if the pH is above 5, due to the formation of precipitates with hydroxyl ions (Tisdale et al., 1993). At pH values less than 5, iron is soluble, however, unlike soluble aluminium, iron does not rapidly accumulate in plants and cause toxicity (Salisbury and Ross, 1992). Although iron is soluble in acidic soils, aluminium in solution actually inhibits iron uptake, often causing iron deficiencies in plants under these conditions (Salisbury and Ross, 1992).

Other relatively new non-aluminium based flocculants that could be used for primary clarification and dewatering include magnesium oxide (MgO) or magnesium hydroxide (Mg(OH)$_2$). Unlike the acidic aluminium and iron-based flocculants discussed previously, magnesium oxide and magnesium hydroxide are alkaline, and buffer between pH 9 and 9.5 (ICI Watercare, 1996). As magnesium is a macronutrient required for the growth of plants, use of such flocculants may be beneficial in the resulting PMS. However, use of magnesium oxide or magnesium hydroxide as a flocculant would result in the formation of a dewatered PMS with a very high pH. If pH of the resulting PMS was above 7.5, the addition of mineral nitrogen to stimulate composting would result in rapid NH$_3$ volatilisation (Chapter 3). Composting could therefore not proceed until the pH of the PMS was reduced by acidification to a level not conductive to NH$_3$ volatilisation. Therefore, as the chemistry of iron-mediated flocculation is analogous to aluminium, use of the former would be preferred as it would be compatible with the existing effluent treatment system at ANM and would not affect the previously developed approach to composting. Furthermore, if an iron-based flocculant replaced aluminium sulfate, the use of composted PMS as a plant growth substrate would not be accompanied by the potential of aluminium toxicity. Currently, ferric chloride retails at AU$410 t$^{-1}$, which is approximately twice as expensive as aluminium sulfate (AU$190 t^{-1}$) (Orica Watercare, Australia).

7.5 Conclusions

Aluminium in PMS and composted PMS was characterised by chemical extraction and by multi-nuclear NMR to determine whether this element was present in a form readily available for uptake in plants. Since soluble aluminium is toxic to plants, it was necessary to determine the potential of aluminium in PMS compost to deleteriously affect plant growth. The source of aluminium in the PMS was due to the use of aluminium sulfate as a flocculating agent during primary clarification and in sludge dewatering. In both forms of PMS, extraction with unbuffered potassium chloride solution revealed that aluminium was essentially non-exchangeable, even though the pH (of the non-composted PMS) was
low enough for aluminium to enter the aqueous phase. After composting, aluminium was present in a monomeric, octahedrally coordinated form, as in the PMS before composting. The non-exchangeable nature of monomeric aluminium was due to the strong chelating properties of the cellulose matrix. Therefore, if the PMS compost was used as a plant growth substrate the potential for aluminium toxicity would be low in the short term. In the long term, however, gradual mineralisation of the remaining cellulose fraction may lead to aluminium deposition in the root zone. Substitution of the aluminium sulfate flocculant with a commercially available iron-based flocculant (e.g. ferric sulfate or ferric chloride) would eliminate the uncertainty regarding the reaction of aluminium in composted PMS in the long term. Since the chemistry of iron mediated flocculation is analogous to aluminium, use of an iron-based flocculant would be compatible with the existing effluent treatment system at ANM, and would not affect the previously developed approach to composting.
Chapter 8

Application of composted pulp and paper mill sludge to a young radiata pine plantation

8.1 Abstract

A field experiment was conducted to determine the effects of composted PMS on the growth, nutrition, water relations and weed suppression in a 3 year old plantation of radiata pine (*Pinus radiata*) on an infertile, acidic podosol soil in southern Tasmania. PMS compost was applied in a 0.5 m band within rows of trees at rates of 0, 20, 40 and 60 t ha\(^{-1}\) (dry matter) to the surface without incorporation. Compost applied at the high rate (60 t ha\(^{-1}\) dry matter) had a fertiliser value of 864 kg N and 264 kg P, with 47% of the total nitrogen (406 kg N) and 2% of the total phosphorus (5 kg P) being in forms available for plant uptake.

The growth of radiata pine after 6 months was significantly better in plots which received PMS compost; the percentage increase in stem diameter was 22 to 37% greater than that achieved in untreated plots (mean control stem diameter prior to application was 29.5 mm), with significantly better growth at the highest compost application rate. After 12 months, the growth of radiata pine in plots treated with PMS compost increased further; the percentage increase in stem diameter was 40 to 66% above that made in control plots. There was a linear tree growth response to increasing rates of PMS compost, suggesting that larger application rates could result in further yield improvements. The significant improvement in growth of radiata pine 11 months after application of PMS compost was primarily attributable to a 17 to 37% increase in the concentration of nitrogen in the foliage, and to decreased water stress in amended plots.

An improvement in nitrogen uptake in radiata pine following compost application was due to the release of soluble nitrogen from the PMS compost, much of which was released from the material within the first 2 months following application. After this, the PMS compost slowly released nitrogen. Nitrogen released from the PMS compost was rapidly assimilated by plant roots within the first 20 cm of the soil profile, with no significant movement beyond this depth range. The concentration of aluminium in the foliage of radiata pine significantly decreased following application of PMS compost, possibly due to dilution in the additional biomass formed. The PMS compost released little phosphorus, due to the insoluble nature of the phosphorus present. As a result, phosphorus uptake in radiata pine did not improve following application. The PMS
compost did not increase the foliar concentration of any other elements, except for sulfur after 6 months, however, this effect disappeared after 11 months.

The PMS compost suppressed the growth of weeds for -3 months, however, this effect diminished, largely due to the re-emergence of bracken fern (*Pteridium esculentum*). The PMS compost had a major effect on the water relations of radiata pine, but not on the availability of water in the soil profile. Trees which received PMS compost experienced significantly less water stress than trees which did not, possibly due to increased root growth, resulting in more extensive exploration of the soil profile for water, and/or due to better stomatal control of water loss. Application of PMS compost to young stands of radiata pine was found to be an environmentally acceptable method of improving plantation productivity, capable of utilising large quantities of this material.

8.2 Introduction

The agricultural use of composts prepared from agricultural, domestic and industrial organic wastes is widely advocated as an environmentally preferable alternative to incineration and landfilling. This is because composts can significantly improve the productivity of agricultural soils through the provision of nutrients and organic matter (Epstein *et al.*, 1976; Bonmati *et al.*, 1985; Gallardo-Lara and Nogales, 1987; García *et al.*, 1991, 1994; Shiralipour *et al.*, 1993; Maynard and Hill, 1994; Turner *et al.*, 1994). However, the use of composts on plantation soils has largely been overlooked (Bengtson and Cornette, 1973; Jokela *et al.*, 1990), although significant work on the use of municipal sewage effluent and sludge has been reported during the last two decades (Sopper and Kerr, 1979; Lutrick *et al.*, 1986; Turner *et al.*, 1996).

Reports on the use of compost in plantation forestry have shown that significant yield improvements can be achieved, particularly on unproductive soils. Bengtson and Cornette (1973) reported that a nutrient-poor garbage compost, applied at a rate of 4.4 to 44.4 t ha⁻¹ improved the growth of slash pine when disced into the soil. However, the authors indicated that the growth response may have been due to the effect of discing on weed competition. Jokela *et al.* (1990) also reported that a compost prepared from municipal garbage and sewage sludge applied at rates of between 112 and 448 t ha⁻¹ significantly improved the wood yield of a slash pine plantation from 55.7 t ha⁻¹ to 94.7 t ha⁻¹ sixteen years after application, a 1.7 fold increase over the control for the heaviest compost application rate.

The effects of raw primary and secondary PMSs on the growth of young hybrid cottonwood trees (*Populus deltoides* x *P. trichocarpa*) in plantation forestry has been
studied (Henry et al., 1993; Lo et al., 1996). Henry et al. (1993) found that surface applications of primary and secondary sludges at rates of between 22 and 67 t ha\(^{-1}\) significantly improved the growth of hybrid cottonwood cuttings (1 year old at planting) after a period of 3 years. Average tree height and stem diameter increases following the addition of secondary sludge were 256 and 281% greater than that achieved in untreated plots, respectively. The average increase in tree height and stem diameter following the application of nutrient-poor primary sludge, however, was smaller, but still significantly greater than that achieved in untreated plots (94 and 92%, respectively). The authors suggested that the increase in tree growth following the application of secondary sludge was due to the release of nitrogen, whereas the growth response following the application of primary sludge was due to weed suppression. Good weed suppression following surface applications of primary sludge to young plantations of cottonwood has also been reported by Lo et al. (1996). The authors found that between 75 and 90% of weeds were suppressed by the primary sludge for more than 2 years when applied at a thickness of between 10 and 20 cm, with no significant effect on nutrient availability or tree growth. These studies, therefore, suggest that raw primary PMSs can be beneficially utilised in plantation forestry. However, the effects of composted PMS on the growth of various plantation species, or on weed suppression, has not been documented.

The stimulation of plantation growth following application of raw organic materials and composts to soils is mainly through the provision of nutrients, much of which is released slowly over time. Slow nutrient release occurs because much of the nutrient pool is present in organic forms, being slowly converted into soluble forms through the action of microorganisms (Bengtson and Cornette, 1973; Smith and Evans, 1977; Jokela et al., 1990; Slivka et al., 1992; Bauhus and Meiwes, 1994; Turner et al., 1996). Slow nutrient release with time may be advantageous in plantation forestry, because the nutritional demands of trees need to be met over a long period of time (Smith and Evans, 1977; Bauhus and Meiwes, 1994). Recent predictions suggest that in central Europe, fertilisation of alpine forest stands with slow nutrient releasing composts will become increasingly important. This is because alpine forests cover some of the most important water supply areas, and ground water quality must not be endangered through leaching of mineral fertiliser nutrients (e.g. nitrate) (Katzensteiner et al., 1995; Insam and Merschak, 1997).

As many countries possess vast areas of plantation forests, the silvicultural industry could be a potentially large market for compost. Composts produced from reclaimed organic wastes could be used to improve plantation growth rates and assist in areas of reforestation. Estimates in the United States suggest that plantation forests near the major population centres could easily accommodate all of the compost produced in the country.
Chapter 8 - Application of composted PMS to a young radiata pine plantation

(46 million tonnes) (Slivka et al., 1992). Use of composts in plantation forestry, however, is believed to be significantly less than the maximum potential (Slivka et al., 1992). Reasons for the under-utilisation of composts in the silvicultural industry are: limited accessibility to compost supplies, problems with application on steep or rough terrain, the presence of contaminants (e.g. plastics, glass and heavy metals, particularly in municipal composts), large transportation costs; and the lack of knowledge regarding the potential benefits of composts (Bengtson and Cornette, 1973; Smith and Evans, 1977; Slivka et al., 1992).

The purpose of this study was to investigate the effect of PMS compost on the growth of a young radiata pine plantation on a relatively unproductive soil in southern Tasmania, as such plantations respond well to nutrient applications (e.g. Lutrick et al., 1986; Turner et al., 1996). The effects of PMS compost on the nutrition of radiata pine, water uptake, soil water availability, soil nutrient status and weed suppression were also assessed. The feasibility of applying PMS compost to radiata pine plantations on a large-scale is discussed.

8.3 Materials and Methods

8.3.1 Description and preparation of the field site

The radiata pine plantation site used in this experiment was located in the Plenty Valley, Tasmania (E 489706, N 251072), with an elevation of 425 m above sea level, a slope angle of 2-7% and an aspect of 010. The soil was classified as a humose humic semiaquic podosol according to The Australian Soil Classification Handbook (Isbell, 1996). The soil profile consisted of a sandy-loam A1 horizon (0-20 cm), a sandy A2 (20-50 cm), a thin sandy-loam B horizon (50-52 cm), and a moderately heavy sandy loam-clay B2 (52-75 cm), beneath which was sandstone bedrock (75+ cm).

Root systems of the 3 year old stand of radiata pine were mainly restricted to the A1 horizon, with some roots being present in the A2 and B. Soil texture was found to be reasonably consistent over all plots. Dominant weed species (% coverage) on the site were Oxylobium ellip hicum (40%), Pteridium esculentum (bracken fern) (20%), Amperea xiphodada (10%), Monotoca glauca (5%) and Phebalium squameum (5%). Most radiata pine trees displayed varying degrees of chlorosis and twisting of needles and apical shoots, possibly indicating nitrogen and copper deficiency, respectively. Tree growth was relatively poor on the site.
One week before application of PMS compost, the site was slashed at ~10 cm above ground level (August 13, 1996), with the slashed residue being left *in-situ*. This was done to assist in the application of the PMS compost.

### 8.3.2 Treatments and experimental design

PMS compost was applied at 0, 50, 100 and 150 t ha⁻¹ (wet weight) in a randomised block design with four replications of each treatment. These rates were chosen to provide a range of mulch thicknesses capable of being applied to plantations on a large-scale. Rectangular plots consisted of 20 trees, with 5 trees in 4 parallel rows. Trees were spaced 2 m apart within rows, with each row being separated by a distance of 4 m. A buffer zone of 2 to 4 m within rows, and 4 m between rows existed between plots. The gravimetric water content of the PMS compost at application was 60%, and equivalent dry rates were 0, 20, 40 and 60 t ha⁻¹. Further references to the treatments will be made to the weight of dry material (DM) applied. The PMS compost was applied on August 20, 1996.

PMS compost was applied in a 0.5 m band within each row, such that the band extended 0.25 m to either side of the trees. PMS compost was also applied 0.25 m before the first and after the last tree in each plot. The volume of PMS compost required for each plot to achieve a given application rate was calculated by determining the bulk density of the material prior to transportation. A 20 L polythene pail was filled with a representative sample of PMS compost, dropped 5 times from a height of 5 cm to ensure even packing density, then weighed (~800 kg m⁻³). The volume of material, and thus the required depth of application for each treatment was calculated on the basis that each plot contained 34 m of rows with the width of application being 0.5 m. Approximate PMS compost application depths were calculated to be 0 cm (control), 4.8 cm (20 t ha⁻¹ DM), 9.6 cm (40 t ha⁻¹ DM) and 14.4 cm (60 t ha⁻¹ DM). In order to accurately apply the PMS compost to achieve a certain depth, two 5 m long wooden templates (20 cm in width) with sliding holding pegs were used. The templates were positioned 0.25 m either side of the trees within the rows. The sliding pegs were then inserted into the soil to fix the template at right angles to the soil surface. The templates were also hinged at the centre to account for surface undulations. PMS compost was then applied to the soil surface between the templates to the required height as indicated by a fixed string on the inner surface. The PMS compost was then evenly packed to the required height (at approximately the same packing density as in the piled compost). Once the length of the template was filled with PMS compost, the sliding pegs were removed from the soil and the template was repositioned further along the row. As the actual packing density of the
compost within the templates could not be determined, the application rates specified can only be considered approximate.

8.3.3 Changes in soil chemical properties following application of PMS compost

Chemical changes in the PMS compost, the A1 (0-20 cm) and A2 (20-50 cm) soil horizons were monitored before application of PMS compost and bi-monthly thereafter for a period of between 8 and 12 months. Available NH$_4^+$-N, NO$_3^-$-N (including NO$_2^-$), available phosphorus and pH analyses were performed. The position of PMS compost and soil sampling was randomly chosen. In treated plots, one sample of PMS compost (~100 g) was removed from the soil surface and bagged. Once all the PMS compost was removed from a 100 cm$^2$ region of the soil surface, sampling of the two soil horizons was achieved with an auger. Soil removed from the individual horizons were then mixed on plastic sheeting, sampled (~100 g) then bagged. pH determinations on the PMS compost and soils were carried out following air drying in a 1:10 sample:distilled water slurry with a pH electrode (Orion Research, USA) following shaking at 100 rev min$^{-1}$ for 1 hour (Rayment and Higginson, 1992).

The concentration of available NH$_4^+$ and NO$_3^-$ (including NO$_2^-$) in the PMS compost and soil samples was determined by the method reported by Rayment and Higginson, (1992). Briefly, air dried samples were extracted with 2 M KCl at a 1:10 sample:solution ratio with shaking at 100 rev min$^{-1}$ for 1 hour. Solutions were then passed through a Whatman No. 1 filter. Heavy magnesium oxide was used for the distillation of NH$_4^+$-N to NH$_3$ in a Tecator 1002® distillation unit. Subsequently, finely ground Devarda's alloy was added for the reduction of NO$_3^-$-N and NO$_2^-$-N to NH$_3$. Ammonia present in the distillates containing a 2% H$_3$BO$_3$ solution was determined by titration with standardised HCl.

The concentration of available phosphorus in the PMS compost and soil samples was determined colorimetrically with the vanadomolybdate method (Olsen and Sommers, 1982). Briefly, air dried samples were extracted with 0.5 M NaHCO$_3$ at a 1:10 sample:solution ratio with shaking at 100 rev min$^{-1}$ for 0.5 hours. Extracts were passed through a Whatman No. 1 filter then clarified with ~2 g of carbon black to remove humic acids. The carbon black amendment was leached with 6 M HCl, washed and tested for the absence of phosphorus prior to use. Extracts containing carbon black were clarified by filtration through a 25 mm diameter, 0.45 µm pore size nitrocellulose filter membrane (Sigma®, USA). Following colour development, phosphorus present in extracts was then quantified by spectrophotometric analysis at 882 nm with a Spectronic 20® (Bausch
and Lomb, USA). All nutrient determinations were expressed on a mg kg\(^{-1}\) dry weight basis.

8.3.4 Effect of PMS compost on soil water availability

The effect of PMS compost on the availability of water in the A1 soil horizon (0-20 cm) was determined monthly for a period of 12 months. A soil moisture characteristic curve of a representative sample of the A1 horizon was established to permit the conversion of soil water content measured gravimetrically (% water, w/w) on disturbed samples taken directly from the field with a soil auger (oven drying at 105°C to constant weight) to an equivalent soil water potential (MPa). A representative sample of the A1 soil horizon was prepared by combining ~100 g of soil sampled from each plot prior to application of PMS compost. Gravimetric water contents of the disturbed A1 sample over a range of soil water potentials between saturation (0 MPa) and the permanent wilting point (-1.52 MPa or -15 bar) was achieved with a Haines apparatus (Haines, 1930) and a pressure plate apparatus (Richards and Fireman, 1943). The Haines apparatus was used to provide soil water potentials between 0 and -0.02 MPa, whereas the pressure plate apparatus was used to achieve soil water potentials between -0.05 and -1.52 MPa. Once the soils were equilibrated at the specific soil water potentials, a sub-sample of soil was taken and gravimetric water content determined as before. Three replicate determinations were made for every soil water potential. The soil moisture characteristic curve of the A1 soil horizon can be seen in Figure A2.1 (Appendix 2).

8.3.5 Effect of PMS compost on the water relations of radiata pine

The effect of PMS compost on the water relations of radiata pine was determined by monitoring pre-dawn xylem water pressure potential of excised needles with a pressure chamber (Ritchie and Hinckley, 1975). Xylem water pressure potentials were measured pre-dawn since at this time of the day, stomata are closed and minimal water loss occurs (Ritchie and Hinckley, 1975), thereby ensuring that the plant is in equilibrium with the soil solution. Young, fully expanded needles approximately 1 m above ground level were sampled and analysed within ~5 minutes in the field. Care was exercised to ensure that the amount of needle outside the chamber was minimised, needles sampled were of comparable developmental stage and the correct balancing pressure was noted. The correct balancing pressure occurred when fluid was observed to exit the xylem trace from the cut needle. Two trees per plot were selected prior to treatment allocation and were consistently sampled once per month for a period of 12 months following application of PMS compost.
8.3.6 Effect of PMS compost on the growth and nutrition of radiata pine

Tree height (from ground level to apex) and stem diameter (at ground level) of all 20 trees within each plot was measured just after application of PMS compost (August 20, 1996), after 6 months (February 25, 1997) and after 12 months (August 15, 1997). Tree height and stem diameter measurements were taken at ground level by removing the PMS compost surrounding the base of each tree. Tree heights were measured with a height stick (± 0.01 m) and stem diameters were measured with vernier callipers (± 0.1 mm).

The nutrient status of radiata pine was assessed before application of PMS compost (August 20, 1996), after 6 months during a period of rapid growth (February 18, 1997; Summer) and after 11 months during a period of dormancy (July 15, 1997; Winter). The nutrient status of trees in all plots was determined by sampling two fascicles per tree with fully extended needles in the upper whorl of branches. Thus, a total of 40 fascicles per plot was sampled for nutrient analyses. Needles of similar size were collected within plots in order to minimise sampling bias. Collection of fascicles instead of whole shoots was considered more appropriate for this type of experiment since it was less destructive and hence suited for time course monitoring of tree nutrition. Following collection, fascicles were stored in plastic bags and frozen at -18°C. Samples were sent to the Centre for Forest Tree Technology, Heidelberg, Victoria in refrigerated transport for analysis. Samples were thawed then dried at 70°C, ground to <0.2 mm particle size then digested in nitric/perchloric acid and analysed for total P, K, S, Ca, Mg, Na, Zn, B, Al, Fe, Cu and Mn by inductively coupled plasma optical emission spectroscopy. Total N was determined by Kjeldahl distillation.

8.3.7 Effect of PMS compost on weed suppression

The incidence of weeds in untreated plots and in plots where compost was applied was determined after application (August 20, 1996), and once every three months thereafter. A region within a row within each plot was randomly selected at the start of the trial for the time course monitoring of weed incidence. Weed incidence within a 0.40 m by 1 m rectangular quadrat was determined by counting the total number of weeds, species composition and percentage cover (visually estimated). Care was exercised to ensure that weeds under the edge of the quadrat were either categorised as falling within or outside the area of the quadrat. Slashing of the site at ~10 cm above ground level one week prior to application of PMS compost did not noticeably affect weed survival.
8.3.8 Statistical analysis of results

Analysis of variance (Systat® 5.2.1, USA) tables for changes in stem diameter, increases in tree height, nutrient uptake, nutrient release from the PMS compost, soil water availability, tree water potential and weed suppression were computed to compare the different PMS compost application rates at each analysis time for a 12 month period.

8.4 Results and Discussion

8.4.1 Fertiliser value of PMS compost

The fertiliser value of PMS compost applied at varying rates on a per hectare basis is shown in Table 8.1. The concentration of nitrogen, phosphorus and potassium in the PMS compost was reasonable (compared to composts prepared from sewage sludge and other materials [e.g. Jokela et al., 1990]), but a significant proportion of these nutrients were present in organic and/or insoluble forms unavailable for immediate release: ~47% of the total N pool and 2.2% of total P pool were considered available, based on the concentration of available N and P determined after 21 weeks composting (Chapter 4). Thus, the immediate fertiliser value of PMS compost at the high rate (60 t ha⁻¹ DM) was 406 kg N and only 5 kg P. Most of the potassium present in the PMS compost, however, would be available for immediate release, because K⁺ ions do not usually undergo conversion into organic forms and/or precipitate as insoluble minerals as readily as nitrogen and phosphorus (Bohn et al., 1985).

Table 8.1 Fertiliser value of PMS compost at various application rates.

<table>
<thead>
<tr>
<th>PMS compost application rate (t dry matter ha⁻¹)</th>
<th>Total N (kg ha⁻¹)</th>
<th>Total P (kg ha⁻¹)</th>
<th>Total K (kg ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>288</td>
<td>88</td>
<td>31.3</td>
</tr>
<tr>
<td>40</td>
<td>576</td>
<td>176</td>
<td>62.7</td>
</tr>
<tr>
<td>60</td>
<td>864</td>
<td>264</td>
<td>94.0</td>
</tr>
</tbody>
</table>

The fertiliser value of PMS compost was considerably less than that of a sewage sludge applied to a slash pine plantation in a previous study. When the sewage sludge was applied at 60 t ha⁻¹ DM, it supplied 2190 kg N (total), 860 kg P (available) and 69 kg K (available) (Lutrick et al., 1986). Although the growth of slash pine improved following application, due to uptake of nitrogen and phosphorus from the sludge,
applications at this rate could lead to ground water contamination through leaching of nitrate (Lutrick et al., 1986). The risk of nitrate leaching from the PMS compost applied at the high rate, however, would be low because the concentration of available nitrogen was considerably less. Release of the soluble nitrogen pool present in the PMS compost would probably occur rapidly with leaching, but release of the remaining organic nitrogen pool would occur slowly over time. Release of phosphorus from the PMS compost would possibly occur slowly over time too, as the form of phosphorus added during composting (partially acidulated phosphate rock) was only partially soluble (Chapter 4).

8.4.2 Nutrient status and growth of radiata pine before and after application of PMS compost

Radiata pine growth on the site after 3 years was poor, due to low soil fertility (Table 8.2). The soil was sandy, acidic, and the availability of nitrogen and phosphorus was low (Table 8.2). Under these low soil pH conditions, plant growth is usually limited by poor availability of phosphorus, calcium and magnesium, or excessive concentrations of aluminium and manganese (Bohn et al., 1985). Clearly, application of lime to these soils would neutralise acidity and increase nutrient availability.

An analysis of the foliage prior to application of PMS compost indicated that the trees were indeed subject to mild nitrogen, calcium, magnesium and copper deficiencies (Table 8.3). The concentration of aluminium and manganese were high in the foliage, but not excessive, and levels of the remaining elements were generally sufficient (Table 8.3). The tissue nutritional requirements of radiata pine are given in Table 8.4 (Will, 1985). Plate 8.1 shows replicate block 1 of the trial site with various levels of PMS compost applied within the rows of the radiata pine stand.

Table 8.2 Characteristics of the humose humic semiaquic podosol soil before application of PMS compost.

<table>
<thead>
<tr>
<th>Soil horizon and depth range</th>
<th>Texture</th>
<th>pH a</th>
<th>Available N a (mg kg$^{-1}$ DM b)</th>
<th>Available P a (mg kg$^{-1}$ DM b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 (0-20 cm)</td>
<td>sandy loam</td>
<td>4.0 ± 0.1</td>
<td>90.2 ± 47.0</td>
<td>7.0 ± 2.2</td>
</tr>
<tr>
<td>A2 (20-50 cm)</td>
<td>sand</td>
<td>4.1 ± 0.1</td>
<td>60.4 ± 35.5</td>
<td>5.1 ± 2.7</td>
</tr>
</tbody>
</table>

aData represents the mean of samples from four replicate plots ± standard error; b Dry matter.
Six months after application of PMS compost, the percentage increase in stem diameter of radiata pine was 22 to 37% greater than that achieved in untreated plots (mean control stem diameter prior to application was 29.5 mm), with significantly better growth at the highest compost application rate (P<0.05) (Table 8.5). The mean increase in stem diameter of radiata pine in response to PMS compost was not significant because of the large variability in stem diameter between plots prior to application (P>0.05) (Table 8.5).

After 12 months, the growth of radiata pine in plots treated with PMS compost increased further; the percentage increase in stem diameter was 40 to 66% above that made in untreated plots (Table 8.5). The difference was significant at all application rates.

Table 8.3 Foliar nutritional status of radiata pine at different times following application of PMS compost.

<table>
<thead>
<tr>
<th>Macronutrients</th>
<th>PMS Compost Application Rate (t ha⁻¹ DM a)</th>
<th>0 months b</th>
<th>6 months c</th>
<th>11 months d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>20</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>15.5</td>
<td>15.9a</td>
<td>21.1b</td>
<td>22.0c</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.1</td>
<td>1.1a</td>
<td>1.5b</td>
<td>1.5b</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>1.7</td>
<td>1.5a</td>
<td>1.4a</td>
<td>1.5a</td>
</tr>
<tr>
<td>Potassium</td>
<td>7.9</td>
<td>8.6a</td>
<td>8.5a</td>
<td>8.5a</td>
</tr>
<tr>
<td>Calcium</td>
<td>1.3</td>
<td>1.1a</td>
<td>0.9a</td>
<td>0.9a</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.9</td>
<td>0.8a</td>
<td>0.7a</td>
<td>0.7a</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.1</td>
<td>0.1a</td>
<td>0.1a</td>
<td>0.1a</td>
</tr>
<tr>
<td>Micronutrients</td>
<td>(mg kg⁻¹ DM a)</td>
<td>311</td>
<td>315c</td>
<td>216b</td>
</tr>
<tr>
<td>Aluminium</td>
<td>50</td>
<td>46a</td>
<td>50a</td>
<td>50a</td>
</tr>
<tr>
<td>Iron</td>
<td>168</td>
<td>141a</td>
<td>110a</td>
<td>130a</td>
</tr>
<tr>
<td>Manganese</td>
<td>23</td>
<td>24a</td>
<td>21a</td>
<td>22a</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.2</td>
<td>3.3c</td>
<td>2.4b</td>
<td>2.1ab</td>
</tr>
<tr>
<td>Copper</td>
<td>12</td>
<td>10a</td>
<td>8.8a</td>
<td>8.8a</td>
</tr>
</tbody>
</table>

a PMS compost application rates and elemental data are expressed on a dry matter (DM) basis; b Mean data obtained over all plots (n=16) before application of PMS compost (August 20 1996; Winter). No significant differences (P>0.05) in elemental concentration were present between the four replicate blocks prior to the start of the trial; c Sampling conducted within a period of rapid growth (February 18, 1997; Summer) or d dormancy (July 15, 1997; Winter); Treatment data in a row at a sampling date followed by a different letter are significantly different at the 0.05 probability level (bold text).
Table 8.4 Foliar tissue nutritional requirements of radiata pine according to Will (1985).

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Low (&lt;)</th>
<th>Satisfactory (&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (g kg(^{-1}))</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>P (g kg(^{-1}))</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>K (g kg(^{-1}))</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Ca (g kg(^{-1}))</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Mg (g kg(^{-1}))</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>B (mg kg(^{-1}))</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>Cu (mg kg(^{-1}))</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Zn (mg kg(^{-1}))</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Mn (mg kg(^{-1}))</td>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>

Plate 8.1 Replicate block 1 of the trial site just after application of PMS compost (at varying rates) within rows of the three year old stand of radiata pine.

(P<0.05), though again, a better growth response occurred at the highest PMS compost application rate. Since the increase in stem diameter increased linearly with the PMS compost application rate, this indicated that the optimum rate for increasing the growth of radiata pine had not been reached. No significant differences in tree height or percentage
increase in tree height were recorded between treatments after 6 or 12 months (P>0.05). This result was consistent with a previous report which demonstrated that tree height is not a sensitive indicator of growth response of radiata pine growth to fertiliser treatments (Table A2.1, Appendix 2) (Turner, 1982).

Table 8.5 Effect of PMS compost on stem diameter of radiata pine over a 12 month period.

<table>
<thead>
<tr>
<th>Application rate (t ha⁻¹ DM)</th>
<th>0 b</th>
<th>6 b</th>
<th>12 b</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>29.5 ± 2.1</td>
<td>43.3 ± 2.9</td>
<td>50.1 ± 3.4</td>
</tr>
<tr>
<td>20</td>
<td>26.4 ± 4.6</td>
<td>45.2 ± 6.7</td>
<td>55.3 ± 6.9</td>
</tr>
<tr>
<td>40</td>
<td>27.8 ± 0.78</td>
<td>46.9 ± 0.7</td>
<td>57.9 ± 1.0</td>
</tr>
<tr>
<td>60</td>
<td>24.0 ± 2.5</td>
<td>42.4 ± 2.7</td>
<td>54.6 ± 3.5</td>
</tr>
</tbody>
</table>

LSD₀.₀₅ c  ns  ns  ns

Percentage increase in stem diameter of radiata pine following application of PMS compost (% of initial stem diameter at ground level)

<table>
<thead>
<tr>
<th>Application rate (t ha⁻¹ DM)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>48.5 ± 1.6</td>
<td>76.2 ± 4.9</td>
<td>70.2 ± 5.3</td>
<td>85.2 ± 10.0</td>
</tr>
<tr>
<td>20</td>
<td>72.2 ± 1.6</td>
<td>119.6 ± 10.8</td>
<td>112.2 ± 7.3</td>
<td>137.9 ± 11.7</td>
</tr>
<tr>
<td>40</td>
<td>ns</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>ns</td>
<td>ns</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a PMS compost application rate is expressed on a dry matter (DM) basis; b Data represented is the mean of four replicate plots containing 20 trees per plot ± standard error; c Least significant difference at the 0.05 probability level; ns Not significant.

Increased growth of radiata pine 6 months after application of PMS compost could be explained by significantly improved nitrogen and sulfur accumulation, and possibly due to a reduction in the concentration of foliar aluminium (P<0.05) (Table 8.3). The application of PMS compost also significantly reduced the concentration of copper in the foliage of trees (P<0.05) (Table 8.3). The concentration of nitrogen in the foliage of radiata pine increased by 33 to 47% above untreated plots, this being proportional to the compost application rate. An increase in the concentration of sulfur in the foliage was probably due to the release of sulfate from the PMS compost. The PMS compost contained a reasonable level of sulfur (0.82%; Chapter 4), due to the use of ammonium sulfate as a nitrogen source during composting. Although sulfur accumulation improved,
its contribution to the growth response could not be determined as the requirement for
this nutrient in radiata pine has not been established. A decrease in the concentration of
aluminium and copper in the foliage may have been due to dilution of these elements in
the additional biomass formed. Dilution of aluminium, among other elements (also
potassium and magnesium) in newly formed biomass of slash pine following application
of a raw sewage sludge has been reported previously (Lutrick et al., 1986).

A reduction in the concentration of copper (as a result of compost treatments) in the
foliage was expected to increase the severity of deficiency symptoms (twisting of apical
shoots and branches) (Will, 1985; Turvey et al., 1992), but this did not occur. Application of copper sulfate to such soils may improve copper uptake, and possibly tree
growth. Application of this micronutrient is often necessary to improve plant growth on
many Australian soils because this element is usually extremely limiting (Turvey et al.,

Eleven months after application of PMS compost, differences in the concentration of
nitrogen in the foliage between untreated and treated plots were still significant (P<0.05),
although the concentration of nitrogen was slightly less than in the previous analysis
conducted during a period of active growth (at 6 months) (Table 8.3). The concentration
of nitrogen in the foliage of radiata pine increased by 17 to 37% above untreated plots,
the increase in nitrogen concentration being proportional to the compost application rate
(Table 8.3). The concentration of foliar sulfur, however, was not significantly different
between treated and untreated plots (P>0.05). After 11 months, the concentration of
aluminium in the foliage of radiata pine was still reduced (P<0.05), but differences in the
concentration of copper between treated and untreated plots became non-significant
(P>0.05). PMS compost significantly reduced the concentration of foliar boron (P<0.05)
after 11 months (Table 8.3), but the concentration of this element in the foliage was still
sufficient for adequate growth (Table 8.4) (Will, 1985).

The moderate concentration of aluminium in the foliage of radiata pine was due to the
acidic nature of the podosol soil, and under such conditions, the growth of some plants
may be inhibited due to the high availability of aluminium which has an adverse effect on
root growth and phosphorus availability (Clarkson, 1966). Radiata pine, however, is
generally tolerant of high levels of foliar aluminium, and growth occurs normally up to a
concentration of 500 mg kg⁻¹ (P. Hopmans, Pers. Com., 1997). Since the concentration
of foliar aluminium was below this level during the trial (Table 8.3), the improvement in
growth of radiata pine following application of PMS compost was not due to an
alleviation of aluminium toxicity. More importantly, the PMS compost did not increase
the concentration of aluminium in the foliage of radiata pine, despite the fact that the pH
of PMS compost (4 to 4.5 twelve months after application) and the underlying soil (3.3 to 3.7 twelve months after application) were sufficiently low for aluminium to become mobile. This suggested that aluminium present in the PMS compost remained strongly bound and unavailable for plant uptake (Chapter 7).

An important nutritional criterion for radiata pine is the ratio of nitrogen to phosphorus in the foliage (Raupach et al., 1969). For a given foliar phosphorus concentration, adequate levels of foliar nitrogen can be predicted. In general, a foliar N:P ratio of 10:1 is required for good growth of radiata pine (Raupach et al., 1969). Eleven months after application of PMS compost, the N:P ratio improved from 8.46 in untreated plots to between 9.25 and 10.29 in treated plots. A significantly better N:P ratio was established in plots subject to the highest compost addition (60 t ha\(^{-1}\) DM), due to an increase in the concentration of foliar nitrogen (Table 8.3). However, if PMS compost was applied in excess of 60 t ha\(^{-1}\) DM to the radiata pine plantation, a further yield improvement may not occur because this would raise the foliar N:P ratio above the optimum ratio, possibly leading to a deficiency in phosphorus. This possibility is favoured because the PMS compost was found to increase the concentration of nitrogen in the foliage much more effectively than the concentration of phosphorus. Under these conditions, a further growth response of radiata pine might be achieved by adding a phosphatic fertiliser directly to the soil.

8.4.3 Effect of PMS compost on soil nutrition

The growth of radiata pine improved significantly following application of PMS compost, largely due to the release of ammonium and nitrate (including nitrite) into the root zone (Figures 8.1 and 8.2). Within the first 2 months, the concentration of available NH\(_4^+\) and NO\(_3^-\) in the PMS compost decreased by ~77% and 66% of their original levels respectively, suggesting that the rapid growth response of radiata pine may be attributed to an initial flush of soluble nitrogen from the PMS compost. Movement of these soluble nitrogen forms out of the surface applied compost was due to the leaching effect of relatively high amount of rainfall experienced during this period (225 mm). For the subsequent 6 months, NH\(_4^+\) and NO\(_3^-\) was released slowly from the PMS compost (Figures 8.1 and 8.2).

The rate of NH\(_4^+\) and NO\(_3^-\) accumulation in the A1 (0-20 cm) and A2 (20-50 cm) soil horizons depended on the rate of PMS compost addition (Figures 8.1 and 8.2). The highest PMS compost application rate generally released more soluble nitrogen into the root zone (P<0.05), and continued for a longer period relative to the lower rates of application. PMS compost significantly raised the concentration of NH\(_4^+\) and NO\(_3^-\) in the
A1 soil horizon (P<0.05), but this generally did not occur in the underlying A2 soil horizon, possibly due to high within-treatment variability. This suggested that as NH$_4^+$ and NO$_3^-$ were leached from the PMS compost, these nutrients were rapidly assimilated by plant roots in the first 20 cm of the soil profile, probably because the majority of plant roots were located in this region. Thus, leaching loss of NH$_4^+$ and NO$_3^-$ was not significant, suggesting that the PMS compost was effective in releasing these nutrients at a rate which did not exceed plant demand.

Figure 8.1 Changes in the concentration of available nitrogen as ammonium (NH$_4^+$) ions in (i) PMS compost, (ii) A1 (0-20 cm) and (iii) A2 (20-50 cm) soil horizons over a period of 8 months. Data shown are the mean of samples from four replicate plots, and numbers in parentheses are LSDs (when significant at P<0.05) between treatments.

The release of phosphorus from the PMS compost was also studied over an eight month period following application (Figure 8.3). Unlike the available pool of NH$_4^+$ and NO$_3^-$ in the compost, the concentration of available phosphorus actually increased, with little being released to the underlying soil. The increase in concentration of available phosphorus within the PMS compost with time was unexpected as the pH of the material decreased from ~5.5 before application to ~ 4 to 4.5 after twelve months (Figure 8.4). Usually, soluble phosphate precipitates with iron and aluminium within this pH range,
Figure 8.2 Changes in the concentration of available nitrogen as nitrate and nitrite (NO$_3^-$ and NO$_2^-$) ions in (i) PMS compost, (ii) A1 (0-20 cm) and (iii) A2 (20-50 cm) soil horizons over a period of 8 months. Data shown are the mean of samples from four replicate plots, and numbers in parentheses are LSDs (when significant at P<0.05) between treatments.

making it unavailable for plant uptake (Bohn et al., 1985). The increase in the concentration of available phosphorus in the PMS compost may have been due to microbially mediated mineralisation of the insoluble phosphorus pool. Compost applied at the high rate did significantly improve the level of available phosphorus in the A1 horizon in the first two months (P<0.05), but not in the A2 horizon. Since little phosphorus was released from the PMS compost into the root zone, it was not surprising that phosphorus uptake in radiata pine did not improve over the time span studied (P>0.05) (Table 8.3). However, if significant phosphorus release did in fact occur from the PMS compost, the acidic nature of the soil would result in rapid fixation of this nutrient into insoluble aluminium and iron compounds, thereby decreasing the efficiency of compost as a source of phosphorus. Previous work with sewage sludge on acidic soils has shown that phosphorus does indeed become fixed into forms unavailable for plant uptake, and this can only be reduced with liming (Lutrick et al., 1986).

As stated previously, the pH of the PMS compost decreased initially from 5.5 to between 4 and 4.5 twelve months after application (Figure 8.4). Gradual acidification of
the PMS compost could have been due to nitrification of the NH$_4^+$ pool. Although the pH of the PMS compost decreased with time, acidification of the underlying A1 (0-20 cm) and A2 (20-50 cm) soil horizons, in general, did not occur (P>0.05) (Figure 8.4). Proton release and soil acidification has been reported previously during the use of a sewage sludge on a plantation of slash pine (Lutrick et al., 1986). The authors similarly suggested that proton release and soil acidification was due to microbially mediated nitrification of reduced forms of nitrogen.

Figure 8.3 Changes in the concentration of available phosphorus in (i) PMS compost, (ii) A1 (0-20 cm) and (iii) A2 (20-50 cm) soil horizons over a period of 8 months. Data shown are the mean of samples from four replicate plots, and numbers in parentheses are LSDs (when significant at P<0.05) between treatments.
Figure 8.4 Changes in pH of (i) PMS compost, (ii) A1 (0-20 cm) and (iii) A2 (20-50 cm) soil horizons over a period of 12 months. Data shown are the mean of samples from four replicate plots, and numbers in parentheses are LSDs (when significant at P<0.05) between treatments.

8.4.4 Effect of PMS compost on weed suppression

Application of PMS compost at the high rate (60 t ha\(^{-1}\) DM) following slashing was found to cover weeds well, including bracken fern ("Pteridium esculentum") and "Oxyllobium ellipicum" (Figure 8.5). These weeds were difficult to cover at the lower compost application rates (20 and 40 t ha\(^{-1}\) DM). The suppressive effect of the compost, as a result, only lasted for approximately 3 months at the highest application rate. Although "Oxyllobium ellipicum" continued to be suppressed after this period of time, an increase in weed coverage in areas where PMS compost was applied was observed, initially due to the emergence of new bracken fern fronds from beneath the PMS compost. In fact, newly formed fronds were only formed where the PMS compost was applied, suggesting that this weed may have been stimulated by the release of soluble nitrogen from the compost and/or the increased presence of moisture (Plate 8.2). Bracken fern is particularly problematic on these poor soils because it is very resistant to drought stress, even in dry summers, and competes well with radiata pine for water and nutrients.
Chapter 8 - Application of composted PMS to a young radiata pine plantation (Nambiar and Zed, 1980). After approximately 2 months, many aerially-sown weeds also established on the surface of the compost, possibly due to the availability of nutrients and water for growth (Plate 8.2). Since the PMS compost had only a temporary effect on the weed populations present in the plantation studied, it was unlikely that this contributed to the growth of radiata pine.

Figure 8.5 - Weed coverage following application of PMS compost within rows of radiata pine. Data shown are the mean of four replicate plots, and numbers in parentheses are LSDs (when significant at P<0.05) between treatments. Arrow indicates the plots were slashed at ~10 cm above ground level prior to the start of the experiment.

Although the PMS compost had little effect on the fully established weeds present in the 3 year old stand of radiata pine, it may be effective on developing weed populations, particularly in areas recently planted with radiata pine. Weed control during the early establishment phase of radiata pine is particularly important, as previous work has shown that mortality rates of up to 40% can occur, largely due to the effect of weeds on water and nutrient availability (Nambiar and Zed, 1980). Reduced weed competition during the establishment phase of radiata pine would not only decrease mortality rates, but also promote early, rapid tree growth. Nutrient release from the PMS compost would also encourage strong radiata pine growth during the establishment phase, and would no doubt increase the ability of the trees to compete with subsequent weed populations for water and nutrients. However, the effect of compost on weed suppression would not be long-lasting, due to the possibility of extensive weed growth on the surface from aerially-deposited weed seeds.
Chapter 8 - Application of composted PMS to a young radiata pine plantation

Plate 8.2 Emergence of bracken fern fronds (*Pteridium esculentum*) through the PMS compost applied at 40 t ha\(^{-1}\) DM four months after application. The weed suppressive effect of the PMS compost reduced with time, primarily due to the growth of bracken fern (as shown). The development of newly established weeds on the compost surface occurred to a small extent in some plots. The newly established perennial rosette weed on the surface of PMS compost shown below is *Hypochoeris radicata* (Flat Weed).

Long-lasting weed suppression in cottonwood plantations has been achieved following surface applications of nutrient-poor, raw primary PMS in Canada (Lo et al., 1996). These workers showed that primary sludge applied at a thickness of between 10 and 20 cm was effective in suppressing between 75 and 90% of total weed growth for more than 2 years. This indicated that herbicide usage could be substantially reduced. The long-lasting effect of the primary sludge on weed suppression, unlike that achieved with compost in this study, was possibly due to the fact that the material was applied prior to planting when weeds were not fully established on the site. Furthermore, as the sludge was nutrient-poor (C:N > 200:1), this probably inhibited the establishment of aerially-sown weeds. The long-lasting effect of the primary sludge on weed suppression was also due to very slow decomposition of the material on the soil surface. Lo et al. (1996) found that surface applications of primary sludge did not deleteriously effect nutrient availability or tree growth within a two year period. Henry et al. (1993) also reported that surface applications of primary sludge at rates of between 22 and 67 t ha\(^{-1}\) significantly improved the growth of cottonwood cuttings (1 year old at planting) after a period of 3 years, due to a reduction in weed competition. Average tree height and stem diameter increases following the addition of primary sludge were 94 and 92% greater than that achieved in untreated plots, respectively. These studies, therefore, suggest that primary sludge can be
beneficially used in plantation forestry when surface applied, without the need for composting.

As composted PMS can promote tree growth through the release of soluble nitrogen, and since raw primary sludge can reduce weed competition, use of these two materials could reduce the fertiliser and herbicide requirements of radiata pine in plantation forestry. Reductions in fertiliser and herbicide usage could be achieved by applying PMS compost to the soil surface in a 0.5 m band within rows of trees after planting (as done in this study), with the remainder of the site being covered with primary sludge. Alternatively, PMS compost could be ploughed into the root zone prior to planting. Following planting, the whole site could be covered with primary sludge to act as a weed suppressing mulch. Given that the use of raw and composted PMS could markedly improve the productivity of radiata pine in plantation forestry, the practical and economic feasibility of this sludge recycling option should be determined.

8.4.5 Effect of PMS compost on soil water availability

The incorporation of composts and other organic matter sources into soils often increases their ability to retain water, an effect which may be attributed to their colloidal properties (Bengtson and Cornette, 1973; Horst and Rothwell, 1972; Gallardo-Lara and Nogales, 1987). As composts and other organic wastes can increase the ability of a soil to retain water, and hence increase its water holding capacity, the effectiveness of rainfall can be increased, thus reducing the likelihood of plant water stress (Epstein et al., 1976; Kladivko and Nelson, 1979; Turner et al., 1994). The increased ability of soils to retain water following application of compost can also reduce the rate of leaching, and hence the loss of soluble nutrients during periods of high rainfall (Turner et al., 1994). Surface applied composts, however, have little effect on water holding capacity (Bengtson and Cornette, 1973), but can insulate a soil against large temperature increases which may lead to excessive moisture losses. Given the potential of surface applied composts to conserve soil water, the effect of PMS compost on soil water availability was studied.

The moisture characteristic curve of the A1 soil horizon (0-20 cm) was determined prior to application of PMS compost, to examine the ability of the soil to supply water to radiata pine (Figure A2.1, Appendix 2). Due to its sandy texture, the amount of water available for plant uptake between field capacity (-10 kPa or -0.01 MPa) and the permanent wilting point (-1.52 MPa) was low; only 12% by weight (Figure A2.1, Appendix 2). This suggested that radiata pine grown on these soils may be susceptible to drought stress during periods of low rainfall. However, as the plantation site received
significant amounts of rainfall during the 12 months of the trial (904.4 mm), exceeding
the annual rainfall requirement for good growth of radiata pine in Tasmania (850 mm yr
1; Neilsen and Crane, 1977), the water potential of the A1 soil horizon remained at or
slightly below field capacity (Figure 8.6). As a consequence, at no time during the trial
was soil water availability significantly different between plots which received or did not
receive PMS compost (P>0.05) (Figure 8.6). During mid-summer (January), the mean
soil water potential in plots which did not receive PMS compost was much more negative
than in plots which did, but this result was not significant at the 0.05 probability level.
This may have indicated that the PMS compost, to a small degree, reduced the rate of
water loss from the soil surface via evaporation.

Figure 8.6 Effect of PMS compost on water potential of the A1 soil horizon (0-20 cm),
and total monthly precipitation over a 12 month period. Data shown are the mean of
samples from four replicate plots. No significant differences at the 0.05 probability level
were detected between treatments at any time during the trial.
Incorporation of the PMS compost into the soil would have markedly improved the level of water retention of the sandy podosol, but this would not be practicable in established plantations. However, incorporation of PMS compost into soil may be achievable prior to planting of radiata pine. On sandy soils, an improvement in water retention would no doubt assist in the growth of radiata pine during the establishment phase.

8.4.6 Effect of PMS compost on the water relations of radiata pine

Two months after the application of PMS compost, trees in plots which received compost possessed a significantly less negative pre-dawn needle water potential than those in plots which did not receive compost (P<0.05) (Figure 8.7). This suggested that the PMS compost stimulated the uptake of water and/or resulted in better control of water loss in radiata pine, causing an apparent decrease in water stress. Radiata pine in plots which received PMS compost maintained lower levels of water stress relative to untreated plots during the 12 months of the trial, except for the months of May and June. During this time of the year, no significant differences in water potential were recorded between treated and untreated plots because the needles at sampling were partially frozen. Poor water availability under such conditions (Zahner, 1968) was probably responsible for the high degree of water stress experienced by trees during these months. In general, the level of water stress experienced by radiata pine reduced as the rate of PMS compost application increased (P<0.05) (Figure 8.7).

The cumulative water deficit of radiata pine was calculated by summing the pre-dawn needle water potential of radiata pine, determined every month for 12 successive months, to compare the overall effect of the treatments on the level of water stress experienced by radiata pine. The cumulative water deficit of radiata pine after 12 months can be seen in Table 8.6. Clearly, trees which did not receive surface applications of PMS compost experienced significantly more water stress than trees which did (at all rates) (P<0.05); the level of water stress was reduced as the PMS compost application rate increased (P<0.05) (Table 8.6). This, therefore, suggested that improved water uptake and/or better control of water losses could have contributed to the significant improvement in growth of radiata pine following application of PMS compost. This is likely, as previous work has shown that water deficits during the middle of the season have a dominant influence on the growth of forest trees, determining how much and when new tissues can be formed (Zahner, 1968). The effect of cumulative water deficits on the growth of radiata pine has also been demonstrated (Linder et al., 1987). This study showed that the cumulative water deficit experienced by radiata pine subjected to various irrigation and fertiliser treatments was responsible for 93% of the variation in mean needle length.
Similarly, Myers (1988) reported that the cumulative water deficit experienced by radiata pine could account for 91% of the variation in annual basal area increment (annual increment in stem cross-sectional area at breast height). Thus, the cumulative water deficit experienced by forest trees has a large effect on long term growth and productivity.

**Figure 8.7** Effect of PMS compost on the pre-dawn needle water potential of radiata pine, and total monthly precipitation over a 12 month period. Data shown are the mean of samples from four replicate plots, and numbers in parentheses are LSDs (when significant at P<0.05) between treatments.

The improvement in growth of radiata pine following application of PMS compost could have been due in part to increased water uptake through enhanced root growth, resulting in more extensive exploration of the soil profile for water. Previous work has shown that tree nutrition does indeed markedly affect root growth, exploration of soil for water and the level of water stress experienced (Viets, 1972; Turner and Lambert, 1987). Myers (1988) demonstrated that during a trial in which the level of irrigation and
Table 8.6 Cumulative water deficit of radiata pine 12 months after the application of PMS compost.

<table>
<thead>
<tr>
<th>Application rate (t ha(^{-1}) DM (^{a}))</th>
<th>Cumulative water deficit (MPa) (^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.495 ± 0.177</td>
</tr>
<tr>
<td>20</td>
<td>8.040 ± 0.250</td>
</tr>
<tr>
<td>40</td>
<td>7.797 ± 0.226</td>
</tr>
<tr>
<td>60</td>
<td>7.483 ± 0.174</td>
</tr>
<tr>
<td><strong>LSD(_{0.05}^{c})</strong></td>
<td><strong>0.311</strong></td>
</tr>
</tbody>
</table>

\(^{a}\) PMS compost application rate expressed on a dry matter (DM) basis;

\(^{b}\) Data is the mean of four replicate plots ± standard error; Cumulative water deficit was calculated by summing the pre-dawn needle water potential of radiata pine assessed monthly over 12 successive months;

\(^{c}\) Least significant difference at the 0.05 probability level.

Fertilisers applied to radiata pine was varied, the level of water stress was significantly less in plots which received fertilisers, relative to those which were not fertilised but were irrigated instead. Likewise, work with Douglas-fir has demonstrated that nitrogen fertilised trees experienced lower water stress relative to their unfertilised counterparts, achieved through better stomatal control of water loss (Brix and Mitchell, 1986). Since nitrogen uptake improved following application of PMS compost, treated trees experienced significantly less water stress relative to untreated trees possibly due to the combined effect of nitrogen on root growth and water uptake, and better stomatal control of water losses. Thus, the PMS compost not only improved the nutrition of radiata pine, but also reduced the level of water stress experienced; both of which have an important effect on its growth (Zahner, 1968; Viets, 1972; Myers, 1988).

In summary, application of PMS compost to a relatively infertile podosol soil in southern Tasmania significantly improved the growth of radiata pine, mainly through the release of nitrogen. Use of nitrogenous fertilisers on these soils mulched with PMS compost would, therefore, be unnecessary. However, the longevity of tree responses to compost would need to be determined to establish how long this material lasts as a nutrient source. This could be determined by measuring the height and stem diameter of treated and untreated trees yearly following compost application. Although the concentration of phosphorus within the PMS compost was relatively high, little was released for plant uptake over the period of the study, due to the relatively insoluble nature of the partially acidulated phosphate rock added during the composting process, and to the phosphorus-fixing nature of the acidic soil studied. Thus, substitution of the
Chapter 8 - Application of composted PMS to a young radiata pine plantation

partially acidulated phosphate rock with a relatively more soluble phosphorus form (e.g. calcium orthophosphate [superphosphate]; Chapter 4) during the composting process could increase the potential fertiliser value of the resulting compost. This would not only increase the concentration of phosphorus potentially available for release from the material, but would also reduce the total weight of the final compost because significant quantities of partially acidulated phosphate rock had to be added during the composting process to achieve the desired C:P ratio, due to its low total phosphorus content (11.9%; Chapter 3). The total phosphorus content of the calcium orthophosphates, for comparative purposes, can be up to 53% (Tisdale et al., 1993). A reduction in the final weight, and an increase in the phosphorus fertiliser value of the PMS compost could, therefore, assist in the phosphorus nutrition of radiata pine. Application of PMS compost as a source of phosphorus to plantation soils where this nutrient is limiting would be advantageous, as previous work has shown that in many cases, the growth of radiata pine can be significantly improved following application of phosphatic fertilisers (Raupach et al., 1969; Turner, 1982; Turner and Lambert, 1987).

Application of PMS compost to relatively young plantations of radiata pine is preferable to older plantations as other work has shown that such plantations respond well to nutrient applications, particularly in circumstances where soil nutrients may be limiting (Turner, 1982; Turner et al., 1996). PMS compost may also be beneficially used in very young plantations, just after transplanting, because this material could reduce tree mortality by suppressing weeds, preventing excessive moisture loss from the soil surface and by encouraging strong growth through the provision of nutrients. The mortality rates of radiata pine on some sites can be up to 40%, due to competition with weeds for water and nutrients (Nambiar and Zed, 1980). If weed cover could be reduced by the application of PMS compost as a nutrient releasing weed suppressant, the yield of radiata pine on some sites could be substantially improved. The need for routine applications of herbicide sprays may also be reduced in this instance. The use of PMS compost as a slow nutrient releasing mulch on younger, rather than older plantations is preferable because the nutritional requirements of trees following canopy closure reduces. This is because the rate of biomass formation is relatively slow, and because nutrient cycling often meets the nutritional demands of trees (Bauhus and Meiwes, 1994). Therefore, the benefits associated with the use of PMS compost as a slow nutrient releasing mulch could be maximised during use on young radiata pine plantations, as these, in general, are responsive to nutrient applications (Turner, 1982; Turner et al., 1996).

The ability of PMS compost to suppress established weed populations on the 3 year old radiata pine plantation was low, even when applied up to a depth of -15 cm (60 t ha\(^{-1}\) DM). Better weed suppression may be achieved at even higher application rates, although
this would only occur where the compost was applied. Alternatively, better weed suppression over the entire site could be achieved by surface applying the compost within rows of trees, or by ploughing the compost into the root zone prior to planting (as a nutrient source), with the remainder of the site being covered with primary sludge. This would result in long term weed suppression, as previous work has shown that nutrient-poor primary sludge can suppress established and aerial-sown weeds for more than 2 years, without deleteriously affecting nutrient availability or tree growth (Lo et al., 1996). As the use of primary and composted PMS (in this manner) could significantly reduce the need for regular herbicide and fertiliser treatments normally associated with the management of radiata pine in plantation forestry, the feasibility of this approach may warrant further investigation.

Since the growth response of radiata pine over the PMS compost application rates tested was linear, and leaching losses of $\text{NH}_4^+$ and $\text{NO}_3^-$ did not occur, higher application rates could probably be beneficially used without the risk of ground water contamination. As stated previously, however, the addition of PMS compost above a rate of 60 t ha$^{-1}$ DM would result in the establishment of a foliar N:P ratio in excess of 10:1, indicating that a soluble phosphatic fertiliser would need to be applied to ameliorate any phosphorus deficiency.

Surface applications of PMS compost to an entire site containing radiata pine could be a viable alternative to applying the material within rows (or bands) as done in this study. In young plantations, or in areas recently planted with radiata pine, this would not be recommended, because nutrients released from the compost would not be efficiently utilised by trees, due to a lack of root development relative to older stands. Furthermore, surface applications of compost to an entire site could encourage the development of aerially-sown weeds, which could compete with radiata pine for water, nutrients and light. Thus, in younger plantations it is recommended that the benefits associated with the use of PMS compost could be maximised by applying the material in rows where the root systems of these trees are likely to be present.

Incorporation of PMS compost within the root zone prior to the planting of radiata pine, as stated previously, could be a practicable alternative to the application of this material to the surface. Addition of compost to the root zone where nutrients are absorbed could assist in the establishment and early growth of radiata pine. However, as radiata pine transplants are usually planted in the field during winter, to minimise shock, nutrients released from the compost may not be efficiently utilised by the trees because rapid root growth does not occur until the following spring (Nambiar and Zed, 1980). Furthermore, the ploughing of compost into soil may not be possible just before planting,
because of the difficulty in gaining vehicular access to some sites which are often subject
to extremely wet conditions during this time of year. Therefore, the benefits of using
PMS compost as a nutrient releasing mulch in young radiata pine plantations may be
maximised when the material is applied after planting, to the soil surface within rows
during periods of active tree growth (i.e. spring).

In older plantations of radiata pine, surface applications of PMS compost to the entire
site would be beneficial because root development, or the network of root systems
capable of absorbing nutrients is much more extensive than that in younger stands.
Application of compost would be possible prior to canopy closure, but not after, due to
the difficulties in gaining vehicular access. However, application of compost to such
plantations may be possible after thinning. Previous work has shown that large radiata
pine growth responses to fertiliser treatments can be obtained following thinning (Turner,
1982), suggesting that the application of compost at this stage may be beneficial. Growth
responses usually occur following thinning because the effectiveness of incident rainfall
is increased (Turner and Lambert, 1987). On sites which receive little rainfall (< 600 mm
yr\(^{-1}\)), the magnitude of the growth response of radiata pine to compost following thinning
may be small, because growth may be limited by the availability of moisture (Turner and
Lambert, 1987). Nevertheless, the ability of PMS compost to increase the growth of
older radiata pine stands prior to canopy closure, or after thinning may be worthy of
further study.

The use of PMS compost as a slow nutrient releasing mulch in plantation forestry has
two main problems: the first is an economic one, associated with the cost of compost
transport relative to mineral fertilisers. Several studies have indicated that the use of raw
organic materials and composts in plantation forestry as nutrient releasing mulches is
costly, due to the large transportation costs involved (Bengtson and Cornette, 1973;
Slivka et al., 1992; Turner et al., 1996). This is because the concentration of nutrients in
composts relative to mineral fertilisers is low, necessitating the application of significantly
more material to achieve a target nutrient application rate. The large transportation costs
associated with the use of compost is probably why compost utilisation on plantation
soils in the United States, for example, is less than 1% of the maximum potential (Slivka
et al., 1992). Application of PMS compost may, therefore, only be economic on
plantations located relatively near the source of compost production (i.e. near the mill).

The second problem associated with the use of PMS compost in plantation forestry is
a practical one. At present, there is no universally accepted method of applying compost
to plantations, although manure spreaders have been successfully used in some cases
when the terrain is not steep and rough (Bengtson and Cornette, 1973; Lutrick et al.,
Manure spreaders can be truck mounted or tractor drawn, having a capacity of between 2.5 and 18 m$^3$ (Miner and Hazen, 1977). Application of compost via truck mounted manure spreaders which are sometimes used in agricultural operations, probably could not be employed in plantations, since trucks cannot navigate variable or steep terrain. Manure spreaders which are towed by all-terrain vehicles, such as large tractors or small bulldozers may provide a means of applying compost to plantations in these conditions.

Although an assessment of the economic feasibility of applying PMS compost to radiata pine plantations was beyond the scope of this study, use of this material as a slow nutrient releasing mulch, capable of weed suppression in intensive agricultural operations located near the mill may warrant further investigation. Some examples of intensive agricultural operations located near the mill which could beneficially utilise PMS compost include growers of hops (Bushy Park), wine grapes (Granton), blackcurrants / raspberries (New Norfolk), potatoes and radiata pine transplants (Westerway).

Despite the existence of some economic and logistic problems, application of PMS compost to young stands of radiata pine was found to be an environmentally acceptable method of improving plantation productivity, capable of utilising large quantities of PMS compost.

8.5 Conclusions

This study reported the effect of a PMS compost on the growth, nutrition, water relations and weed suppression in a 3 year old plantation of radiata pine. PMS compost was applied in a 0.5 m band within rows of trees at rates of 0, 20, 40 and 60 t ha$^{-1}$ dry matter to the surface of the soil without incorporation. Six months after application of PMS compost, the percentage increase in stem diameter was 22 to 37% greater than that achieved in untreated plots (mean control stem diameter prior to application was 29.5 mm). After 12 months, the percentage increase in stem diameter of trees in treated plots increased to between 40 and 66% above that made in untreated plots, with growth response being proportional to the PMS compost application rate. The large growth response of radiata pine following application of PMS compost was due to an increase in the concentration of foliar nitrogen, caused by the release of soluble nitrogen from the PMS compost, and to a reduction in water stress. The PMS compost released little phosphorus to the underlying soil, possibly due to the insoluble nature of the phosphorus present in the compost. Better phosphorus release could be achieved if some of the partially acidulated phosphate rock used during PMS composting was substituted with a more soluble phosphorus form.
Chapter 8 - Application of composted PMS to a young radiata pine plantation

The PMS compost suppressed the growth of weeds for ~3 months, but after this period of time, re-growth of bracken fern (*Pteridium esculentum*) from beneath the compost occurred. The PMS compost had a major effect on the water relations on treated radiata pine trees, but not on the availability of water present in the underlying soil. Trees which received PMS compost experienced significantly less water stress than those that did not, possibly due to increased root growth, resulting in more extensive exploration of the soil profile for water, and/or to better stomatal control of water loss.
Chapter 9

Use of composted pulp and paper mill sludge as a component in horticultural growing media

9.1 Abstract

The germination and growth of lettuce (*Lactuca sativa* 'Green mignonette'), foxglove (*Digitalis purpurea* 'Excelsior hybrid'), broccoli (*Brassica oleracea* 'Jewel F1') and English marigold (*Calendula officinalis* 'Greenheart orange') in growing media formulated with composted PMS and perlite was assessed. The two most important physical properties required for plant growth in containers, air-filled porosity and total water holding capacity, were excellent in media containing between 60 and 90% compost by volume. In the mix containing 90% compost, air filled porosity was 22.9% and total water holding capacity was 65.4% at container capacity. This mix was physically stable, as shrinkage did not occur after 15 weeks of plant growth.

Germination of all plant varieties in the tested media, containing between 60 and 90% compost, was very high. The moderately high electrical conductivity of these mixes (2.46 to 2.77 dS m⁻¹) did not affect the germination rate of the plant varieties tested. Significantly more biomass was produced at the highest compost additions for lettuce and foxglove, but this was not the case with broccoli and English marigold. Although the PMS compost contained a high concentration of aluminium, there was no evidence of aluminium toxicity symptoms, as root growth was good for all the tested plant varieties. The amount of biomass produced after 15 weeks by the different plant varieties on all media formulated with PMS compost and perlite was reasonable. However, significantly better growth could be achieved by increasing the pH of the mixes from -4.8-5.3 to -6, and by decreasing the calcium to magnesium ratio by adding magnesium carbonate. The addition of trace elements, particularly iron and copper, could also improve growth. The concentrations of macronutrients in the media were generally sufficient, however, continued growth over a growing season would require the addition of a slow release fertiliser. If these measures are taken, a high quality, high value growing medium could be prepared with PMS compost.

9.2 Introduction

The use of peat as a cost-effective substitute for soil in horticultural growing media was widely adopted during the 1970's (Yates and Rogers, 1981). Continued use of peat
in horticultural growing media, however, has lead to the exhaustion of natural peat reserves in some countries. Although large peat reserves still exist in Germany, Scandinavia and Canada, its high price in other regions of the world has encouraged horticulturists to search for quality, low cost alternatives for use in horticultural growing media (De Boodt and Verdonck, 1972; Gouin, 1982; Chen et al., 1988). Today, a variety of composted organic waste products are used for this purpose.

The use of composted hardwood bark as a growing medium for container-grown ornamentals has been found to be an acceptable, cheap substitute for peat while alleviating some of the disposal problems of the paper and veneer industries (Verdonck et al., 1976; Sterrett and Fretz, 1977; Hoitink and Poole, 1980; Yates and Rogers, 1981; Daudin and Michelot, 1985). Other composted materials successfully used in soil-less growing media include leaf moulds (De Boodt and Verdonck, 1972; Verdonck et al., 1976); sewage sludge mixtures (Sanderson, 1980); municipal compost (Daudin and Michelot, 1985; Fitzpatrick, 1989; Sawhney et al., 1994, 1996); tobacco waste (Verdonck et al., 1985); cattle manure and grape marc (Chen et al., 1988), and composted green waste (Hartz et al., 1996). Composts are an effective substitute for peat because the organic fraction absorbs and releases water, slowly releases nutrients, provides cation exchange capacity and nutrient retention, and can inhibit the growth of pathogenic microorganisms such as Pythium and Phytophthora root rots (Hoitink et al., 1977, 1991; Daft et al., 1979; Hoitink, 1980; Hoitink and Fahy, 1986; Hardy and Sivasithamparam, 1991). The suppressive effects of compost-amended substrates are thought to involve the presence of antagonistic biota, including some fungi (e.g. *Trichoderma* spp. and *Gliocladium virens*) and bacteria (e.g. *Flavobacterium balustinum, Pseudomonas putida* and *Xanthomonas maltophilia*) which recolonise compost heaps after peak heating (Kuter et al., 1983; Hoitink and Fahy, 1986). These organisms are not usually found in peat (as peat is resistant to decomposition), possibly explaining why it is not normally suppressive to plant pathogens (Hoitink et al., 1991). Recent work has shown that composts may also activate genes associated with systemic acquired resistance in plants, apparently responsible for the suppression of Pythium root rot of cucumber (Zhang et al., 1996). Thus, most compost-amended growing media do not require steam sterilisation or fungicidal treatments to remove plant pathogens prior to use, as do most peats for example (Logsdon, 1993).

Growing media formulated with compost are often combined with an inert material to improve structural stability and porosity. This is because some composts tend to decompose rather quickly, and for this reason, Handreck and Black (1989) recommend that composts should not comprise more than 30% by volume of a mix. The following support materials may be combined with compost to improve stability and porosity:
coarse sand, gravel, perlite, vermiculite, plastic foams, clay pellets, rockwool, scoria, pumice, diatomite and lignite (Handreck and Black, 1989). The choice of a particular material depends on cost, continuity of supply and properties of the material (e.g. particle size and bulk density). In some cases, the percentage of compost in a growing medium may be limited due to high salinity or heavy metals, such as in municipal solid waste composts. Nevertheless, composts should be fully matured before incorporation into growing media to prevent plant damage through nitrogen immobilisation or oxygen starvation in the root zone. In some cases, where compost quality and continuity of supply has been inconsistent, use of compost in growing media has not been a favourable option (Handreck and Black, 1989).

The use of raw PMS as a component in growing media has been reported. Pridham and Cline (1988) studied the effect of various ratios of primary to secondary sludge in combination with a constant volume of vermiculite (50%) on the growth of corn, pepper and tomato with nutrients applied with irrigation twice-weekly (100 ppm solution of 20N-20P-20K). Growth of all three plants was proportional to the concentration of nitrogen present in the secondary sludge mixtures, and germination was constant over all the mixtures tested. The primary sludge apparently inhibited growth due to nitrogen immobilisation. Chong and Cline (1993) also tested the response of four deciduous ornamental shrubs to mixtures consisting of up to 30% by volume of primary and secondary sludge, with the remainder consisting of sand, peat and pine bark. Nutrients were added via trickle irrigation three times weekly (200 ppm solution of 20N-8.7P-16.6K). Again, the results obtained from this study suggested that plant growth was related to the concentration of nitrogen present in the secondary sludge.

The use of composted rather than uncomposted materials is preferable in a growing medium as uncomposted organic materials usually undergo rapid decomposition after formulation, they compact and reduce the air-filled porosity of the medium with time, they may immobilise nitrogen and cause nitrogen deficiencies in plants, they can reduce the tension of oxygen in the root zone, and they may not be sufficiently colonised by antagonistic microorganisms capable of inhibiting plant pathogens (Hoitink and Fahy, 1986). A composting phase is also neccessary for fresh hardwood bark to remove allelopathic toxins (Hoitink and Fahy, 1986). Composts can also supplement plant nutrient requirements through microbially-mediated mineralisation of nutrients bound in organic complexes (Poincelot, 1974).

The purpose of this chapter was to investigate whether PMS compost combined with an inert material could be used for the growth of container plants. The chemical and physical attributes of the mixes formulated with PMS compost were also evaluated.
Measures required to improve plant growth in the PMS compost media are discussed as well.

9.3 Materials and Methods

9.3.1 Materials

PMS compost was collected after 37 weeks of composting (Chapter 4), and stored indoors for a further 10 months in field condition in open, 100 L polythene bags. The PMS compost was passed through a 5 mm sieve to remove gravel picked up from the composting pad. The gravimetric water content of the PMS compost was ~60% at the time of mix preparation. Horticultural grade coarse perlite (2-5 mm) was combined with PMS compost at varying proportions (on a volumetric basis) to produce mixes with contrasting levels of air-filled porosity and total water holding capacity. Perlite is a porous, siliceous material produced by rapidly heating natural volcanic glass to 1200°C. It has a low bulk density, is inert and is often used to improve porosity in media (Handreck and Black, 1989). Horticultural grade crushed zeolite was also used as a constant in all media. This silicate mineral was used to reduce the loss of ammonium ions, thereby improving the efficiency of nitrogen added during the composting process (Handreck and Black, 1989).

9.3.2 Formulation of experimental growing media with PMS compost

PMS compost and perlite were mixed together at the following volumetric ratios to provide a range of mixes with contrasting physical properties: 0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0. Materials were loosely packed into a 2 L polythene volumetric cylinder and then dropped from a height of 0.05 m five times to obtain a constant packing density. The weight of either material required to fill the 2 L volumetric cylinder to a constant packing density was determined so subsequent volume measurements could be done on a gravimetric basis. Measured volumes of PMS compost and perlite were then combined in a cement mixer for 2 minutes. Crushed zeolite was added at a rate of 20 g L⁻¹ during the third minute of mixing. Addition of water during mixing was required to ensure proper incorporation of the perlite with the PMS compost. Mixes were stored in a moist condition (near field capacity) for one week prior to physical and chemical assessment.
9.3.3 Physical properties of media formulated with PMS compost and perlite

Air filled porosity at container capacity (volume percent at -1 kPa) and total water holding capacity (volume percent of water released between -1 kPa and oven drying) were determined with a modified method reported by Goh and Maas (1980). This procedure involved the assembly of 5 tension funnels connected individually with polythene tubing (10 mm i.d.) to a 2 m long common tube, with all funnels being mounted at the same level on a 1.2 m high stand (Figure 9.1). Borosilicate sintered glass filter funnels were used as tension funnels (95 mm i.d., porosity 4, Duran®, Germany) instead of Buchner funnels filled with plaster of paris as the latter tended to disintegrate under suction. All connections were made gas tight to prevent air entering the water filled tension system. The tension system was filled with water by immersing the tension funnels in water which had been boiled previously for 30 minutes to remove dissolved gases. Water was drawn into the funnels and through the tubing system by applying negative pressure to the common tube. Once the tension system was water filled, tension funnels were installed on the stand again. A glass pipette bent at 90° was inserted into the end of the common tube so that the water column could be accurately lowered to a certain level.

Two open-ended plastic cylinders (diameter 10.0 cm, height 7.0 cm) were used to contain the growing media. The two cylinders were joined and taped together to contain the growing media, with the bottom of the lower cylinder being covered with cheesecloth, held in place with rubber bands. These double cylinders were then pre-wetted and left overnight. Each growing medium was then transferred to the weighed double cylinders immersed in water at room temperature, gravity drained and re-immersed in water two times. The double cylinder was then left flooded for 24 hours, followed by gravity drainage. The double cylinder was again re-immersed and gravity drained two more times to consolidate the sample. The double cylinders were then transferred to the tension cylinders for drainage at -30 cm (-3 kPa) for 4 hours. The two cylinders were then separated with a knife and the sample in the bottom cylinder was retained for analysis.

The top of the bottom cylinder was levelled and covered with a close fitting plastic lid having a 1 cm hole near the centre. The cylinder was then submerged gradually in water, and once flooded, the lid was pushed down firmly to remove all air from the growing medium. After 1 hour soaking, a finger was placed over the hole in the lid and the cylinder was removed from the water. The sides of the cylinder were dried, then the cylinder was transferred to a weighed dish. To determine the air filled porosity of the growing media, the cylinder was again transferred to a tension funnel and drained at -10
cm (-1 kPa) for 24 hours. The cylinder was again removed and weighed. The volume of water released from the growing media between saturation and drainage at -1 kPa divided by the volume of the cylinder corresponded to the air-filled porosity of the growing medium at container capacity (or after free drainage). To determine the total water holding capacity, or the total volume percentage of water held in the growing media after free drainage, the contents of the cylinder was transferred to a weighed aluminium tray and oven dried at 105°C for two days. The total amount of water released after oven drying when divided by the volume of the cylinder before drying corresponded with the total water holding capacity of the growing medium. Although this method for determining air-filled porosity and total water holding capacity was time consuming, Goh and Maas (1980) found that this procedure closely represented actual conditions associated with settling of growing media in pots occurring under normal nursery conditions.

Figure 9.1 Custom-built tension funnel apparatus used in this study to assist in the determination of air-filled porosity and total water holding capacity of various growing media formulated with PMS compost and perlite. Five funnels were used so that five replicate determinations could be carried out at any one time.
9.3.4 Chemical properties of PMS compost and the formulated growing media

pH and electrical conductivity measurements of the various media formulated with PMS compost and perlite were conducted according to standard procedures for the assessment of potting mixes (Standards Australia AS3743, 1993). The available concentration of $\text{NH}_4^+$, $\text{NO}_3^-$, $\text{P}$, $\text{K}$, $\text{S}$, $\text{Ca}$, $\text{Mg}$, $\text{Na}$, $\text{Cl}$, $\text{Fe}$, $\text{Cu}$, $\text{Zn}$ and $\text{Mn}$ in PMS compost were determined according to standard procedures for the assessment of potting mixes (Standards Australia AS3743, 1993) by Sydney Environmental and Soil Laboratory, Thornleigh, New South Wales. Briefly, the PMS compost was extracted with a 2 mM solution of DTPA (1,7-diamo-4-azapentane-$\text{N,N,N',N''}$,N'-pentaacetic acid), and the concentration of $\text{P}$, $\text{K}$, $\text{S}$, $\text{Ca}$, $\text{Mg}$, $\text{Na}$, $\text{Cl}$, $\text{Fe}$, $\text{Cu}$, $\text{Zn}$ and $\text{Mn}$ in the extract was determined by ICPOES. The concentration of $\text{NH}_4^+$ and $\text{NO}_3^-$ in the PMS compost, following extraction with distilled water, was determined by Kjeldahl distillation (Standards Australia AS3743, 1993). The concentration of these nutrients in the media formulated with PMS compost and perlite were calculated on the percentage of PMS compost present in the mix (as perlite is inert and does not contribute to the chemical properties of growing media [Handreck and Black, 1989]).

9.3.5 Plant growth response to selected media formulated with PMS compost and perlite

Germination and growth of lettuce (*Lactuca sativa* 'Green mignonette'), foxglove (*Digitalis purpurea* 'Excelsior hybrid'), broccoli (*Brassica oleracea* 'Jewel F1') and English marigold (*Calendula officinalis* 'Greenheart orange') in media formulated with PMS compost and perlite was assessed. Black polythene pots (125 mm diameter) (Plant-It-Rite, Australia) were filled with media containing a PMS compost to perlite volumetric ratio of 6:4, 7:3, 8:2 or 9:1. Five seeds of each plant variety were sown at a constant depth of 1 cm in each of the 5 replicate pots, organised in a randomised block design in a glasshouse under natural daylight conditions heated to a constant temperature of 22°C. Automatic watering was provided via sprinklers twice daily. No fertiliser nutrients were added to the pots at any time during the experiment. The percentage germination was calculated after seeds had fully emerged from the media. Following this, all but one seedling was removed from the pots to assess plant growth after a 15 week period (from sowing). At harvest, compost was gently removed from the root system of each plant variety by agitation in water. The amount of foliar and root dry matter produced by each plant variety was determined following oven drying at 70°C for 1 week.
9.4 Results and Discussion

The most important physical properties of container growing media relate to their ability to supply oxygen and water to plant roots (Handreck, 1983). This ability is most simply described by measurements of air-filled porosity (the volume percent of the medium that is air at container capacity, taken as 1 kPa suction), and water released between 1 and 10 kPa suctions (De Boodt and Verdonck, 1972; Handreck, 1983). The physical properties are determined by the shape, size and density of individual particles (Handreck, 1983; Handreck and Black, 1989). Adequate pore space is required for gas exchange and the removal of waste gases produced by respiring plant roots, and the retention of water for plant uptake. Therefore, a balance between air-filled porosity and plant available water is necessary to obtain good growth in soil-less media (Handreck, 1983; Inbar et al., 1993).

For convenience, this study used total water holding capacity of the growing media as a measure of the capacity to supply water to growing plants. This is the amount of water held at container capacity, and includes both easily available, readily available and residual water, the latter being unavailable for plant uptake.

The air-filled porosity and total water holding capacity of various growing media formulated with PMS compost and perlite is shown in Figure 9.2. Without perlite, the air-filled porosity (22.3%) and total water holding capacity (71.1%) (at container capacity) of PMS compost were both very high. At container capacity, only 6.6% of the volume was occupied by solids. Thus, the PMS compost particles were capable of absorbing large amounts of water, without severely compromising air-filled porosity. Since the volume of air retained in the PMS compost at container capacity was higher than the desirable level of media for general nursery use (15-25%) (Handreck, 1983), or that required for potting media according to the Australian Standard for potting media (≥13%) (Standards Australia AS3743, 1993), the addition of perlite to improve porosity appeared to be unnecessary. However, perlite was still added to provide structural stability to the mixes, as composted materials tend to compact with time (Handreck and Black, 1989). Compaction normally leads to a reduction in air filled porosity, and could potentially reduce plant growth. Perlite retails at ~AU$30 per 100 L.

As expected, the level of air-filled porosity increased and total water holding capacity decreased, at container capacity, with an increasing proportion of perlite in the mixes (Figure 9.2). Perlite increased the volume of air retained in the mixes at container capacity because it consisted of particles which are effective at increasing pore volume (0.5 to 5.0 mm) (Handreck, 1983). Similarly, perlite reduced the total water holding capacity of the
PMS compost mixes as this particle size range (0.5 to 5 mm) does not significantly contribute to water retention in growing media (Handreck, 1983). Given that the media consisting of 60 to 90% compost by volume had an air-filled porosity and total water holding capacity in excess of that required for a good growing medium (air-filled porosity ≥ 13%; total water holding capacity ≥ 50%) (Standards Australia AS3743, 1993), their ability to support plant growth was tested.

Figure 9.2 Air-filled porosity (AFP) and total water holding capacity (TWHC) of various media formulated with PMS compost and perlite. Bars represent the standard error of three replicate determinations.

The chemical properties of the four growing media formulated with PMS compost and perlite are shown in Table 9.1, together with the Australian Standard AS3743 (1993) for potting mixes. The nutrient levels specified by the Standard for potting mixes are sufficient to provide nutrients for approximately one month's plant growth. Thereafter, the standard specifies that a slow-nutrient releasing fertiliser may have to be added to maintain good plant growth. The pH of the PMS compost alone was low (4.4), and increased proportionally with an increasing volume of perlite (Table 9.1). Clearly, nitrification of NH$_4^+$ ions was responsible for the decrease in pH of PMS compost from ~5.8 (after 21 weeks composting) to ~4.4 (after another 13 months storage), as the concentration of NH$_4^+$ decreased from ~5000 ppm (Chapter 4) to 5.2 ppm during this time (Table 9.1). This drop in pH was also responsible for lowering the concentration of
soluble phosphorus from ~98 ppm (after 21 weeks composting) to less than 10 ppm after another 13 months storage. Given that a soluble phosphorus concentration of more than 8 ppm (or mg L⁻¹) is required for good plant growth in containers, phosphorus deficiencies may be expected if these media formulated with PMS compost and perlite are used as growing media. Nevertheless, the concentration of soluble nitrogen, potassium, magnesium, sodium and chloride were all within the required range for good plant growth.

A consistent problem with the media formulated with PMS compost was the moderately high electrical conductivity (2.46 to 2.77 dS m⁻¹), exceeding the Australian Standard AS3743 (1993) for potting mixes (≤ 2.2 dS m⁻¹) (Table 9.1). The electrical conductivity, again, was dependent on the volume of PMS compost present in the mixes. The reason why excessive soluble salts are problematic in growing media is because they can damage developing seedlings and young plants by inducing osmotic water stress, or physiological drought (Flowers et al., 1977). The high electrical conductivity level was due to the presence of soluble calcium and sulfate (Table 9.1). The large increase in concentration of calcium and sulfate was possibly due to the use of partially acidulated phosphate rock (as a source of phosphorus) and ammonium sulfate (as a source of nitrogen) added as nutrient supplements to initiate composting (Chapter 4). On a practical level, however, the moderately high soluble salt concentration in the PMS would probably not adversely affect plant growth, as previous work has shown that plant growth on such materials is more related to nitrogen content, even up to an initial electrical conductivity level of 7.6 dS m⁻¹ (Chong and Cline, 1993). Furthermore, the electrical conductivity level usually decreases rapidly, as much of the potentially toxic soluble salts are leached from the medium during irrigation (Chong and Cline, 1993).

Another problem with the media formulated with PMS compost was the high calcium to magnesium ratio (Table 9.1). In agricultural soils, Ca²⁺ usually dominates the cation exchange complex; it is required as a macronutrient by plants and microorganisms, and is normally associated with highly productive soils. However, in circumstances where there is a large surplus of Ca²⁺ over Mg²⁺ cations, calcium can antagonise the uptake of magnesium because calcium has more affinity for negative sites on soil colloids than does magnesium (Bohn et al., 1985). Thus, it is possible that plants grown in PMS compost amended media may experience slight magnesium deficiency. This could be easily overcome by adding a source of magnesium to the media, such as magnesium carbonate. This addition would also neutralise the acidity, and increase the concentration of soluble phosphorus. In this trial, initially, the ability of the PMS compost media to support plant growth was tested without such amendments.
The concentrations of soluble micronutrients (Fe, Cu and Mn) were moderately low in the media formulated with PMS compost, suggesting that the material may need to be supplemented with a trace element mix to ensure good plant growth (Table 9.1). The concentration of soluble zinc on the other hand was high in all media because the PMS compost contained ~100 mg kg$^{-1}$ total Zn (Chapter 4), this possibly being a contaminant in the mineral nutrients used to initiate composting (Chapter 4).

Table 9.1 Chemical analysis of selected growing media formulated with PMS compost and perlite.

<table>
<thead>
<tr>
<th>Property</th>
<th>PMS compost : Perlite ratio (v/v)</th>
<th>Premium potting mixes (AS 3743) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6:4</td>
<td>7:3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8:2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9:1</td>
</tr>
<tr>
<td>pH</td>
<td>5.27</td>
<td>4.94</td>
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<tr>
<td>EC (dS m$^{-1}$)</td>
<td>2.46</td>
<td>2.64</td>
</tr>
<tr>
<td>NH$_4^+$.N (mg L$^{-1}$)</td>
<td>3.1</td>
<td>3.6</td>
</tr>
<tr>
<td>NO$_3^-$.N + NH$_4^+$.N (mg L$^{-1}$)</td>
<td>60.7</td>
<td>70.8</td>
</tr>
<tr>
<td>Phosphate-P (mg L$^{-1}$)</td>
<td>6.3</td>
<td>7.4</td>
</tr>
<tr>
<td>Potassium (mg L$^{-1}$)</td>
<td>53.5</td>
<td>62.4</td>
</tr>
<tr>
<td>Sulfate-S (mg L$^{-1}$)</td>
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<td>135.3</td>
</tr>
<tr>
<td>Calcium (mg L$^{-1}$)</td>
<td>262.4</td>
<td>306.1</td>
</tr>
<tr>
<td>Magnesium (mg L$^{-1}$)</td>
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<td>14.5</td>
</tr>
<tr>
<td>Calcium / Magnesium ratio</td>
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<td>21.1</td>
</tr>
<tr>
<td>Potassium / Magnesium ratio</td>
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<td>4.3</td>
</tr>
<tr>
<td>Sodium (mg L$^{-1}$)</td>
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<td>32.8</td>
</tr>
<tr>
<td>Chloride (mg L$^{-1}$)</td>
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<tr>
<td>Iron (mg L$^{-1}$)</td>
<td>8.7</td>
<td>10.2</td>
</tr>
<tr>
<td>Copper (mg L$^{-1}$)</td>
<td>$&lt; 0.2$</td>
<td>$&lt; 0.3$</td>
</tr>
<tr>
<td>Zinc (mg L$^{-1}$)</td>
<td>18.1</td>
<td>21.1</td>
</tr>
<tr>
<td>Manganese (mg L$^{-1}$)</td>
<td>1.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$^a$ All data except the pH and electrical conductivity measurements were calculated on the percentage of PMS compost in the mix; $^b$ Analysis performed according to the methods as specified by Standards Australia AS 3743, (1993).

The germination of all plant species in all growing media was excellent, at 100% for lettuce and foxglove, and only slightly lower for broccoli and English marigold 13 days after sowing (Table 9.2). There were no significant differences in the germination percent between different growing media for all four plant varieties tested, suggesting that the
moderate salt content of the mixes did not affect germination (P>0.05) (Table 9.2). The growth of all plants was rapid for the first six weeks, but after this period the rate of plant growth slowed, and visible signs of phosphorus deficiency were present (red and purple colour development in older leaves).

After 15 weeks of growth in the glasshouse, plants were harvested, and the amount of root, foliar and total biomass was determined (Figure 9.3). Significantly more biomass was produced at the highest compost additions for lettuce and foxglove (P<0.05), however, this was not the case with broccoli or English marigold. There were no significant differences in the biomass produced by broccoli in the different growing media, suggesting that this plant variety was not sensitive to the different chemical and/or physical attributes of the mixes. English marigold produced significantly more biomass on the growing medium consisting of 70% compost by volume. Greater biomass production of lettuce and foxglove in media with an increasing proportion of compost may have been due to the higher concentration of soluble nutrients available for uptake.

Table 9.2 Germination percent of lettuce, foxglove, broccoli and English marigold on various growing media formulated with PMS compost and perlite.

<table>
<thead>
<tr>
<th>PMS compost : perlite ratio (v/v)</th>
<th>Lettuce b</th>
<th>Foxglove b</th>
<th>Broccoli b</th>
<th>English marigold b</th>
</tr>
</thead>
<tbody>
<tr>
<td>6:4</td>
<td>100 ± 0</td>
<td>100 ± 0</td>
<td>92 ± 5</td>
<td>68 ± 8</td>
</tr>
<tr>
<td>7:3</td>
<td>100 ± 0</td>
<td>100 ± 0</td>
<td>88 ± 5</td>
<td>92 ± 5</td>
</tr>
<tr>
<td>8:2</td>
<td>100 ± 0</td>
<td>100 ± 0</td>
<td>92 ± 5</td>
<td>76 ± 4</td>
</tr>
<tr>
<td>9:1</td>
<td>100 ± 0</td>
<td>100 ± 0</td>
<td>88 ± 8</td>
<td>88 ± 5</td>
</tr>
</tbody>
</table>

LSD0.05 c ns ns ns ns

a Germination percent determined 13 days after sowing; b Data represents the mean of five replicate pots containing 5 seeds per pot ± standard error; c Least significant difference at the 0.05 probability level. ns Not significant.

After 15 weeks of growth of plants in containers, no shrinkage of media occurred, suggesting that the PMS was physically stable, even when it comprised up to 90% of the mix by volume.

Clearly, since root growth was extensive in all tested plant species, there was no evidence to suggest that aluminium toxicity occurred, even though the PMS compost was
found to contain a large concentration of aluminium (Chapter 4). This result, therefore, confirmed the previous finding that aluminium in PMS compost was non-exchangeably bound, and the potential for aluminium phytotoxicity to occur (in the short term) was considered to be low (Chapter 7).

Figure 9.3 Growth (dry matter, DM) of (a) lettuce, (b) foxglove, (c) broccoli and (d) English marigold in growing media formulated with PMS and perlite for a 15 week period with no nutrient supplementation. Bars show the standard error of total biomass produced in five replicate pots. Different letters above each column represent significant differences (P<0.05) in total biomass between different growing media.

Although the media formulated with PMS compost and perlite could support excellent plant growth over a 6 week period, continued growth would require the addition of a slow nutrient releasing fertiliser (e.g. Osmocote®). Incorporation of magnesium carbonate into the media before planting would increase pH, improve the calcium to magnesium ratio and phosphorus availability, thereby assisting in the nutrition of plants.
Chapter 9 - Use of PMS compost as a component in horticultural growing media

The addition of a balanced mix of trace elements would also assist in the nutrition of plants grown in these media. If these measures were taken, media consisting of between 60 and 90% PMS compost would be excellent for the growth of most horticultural plants over an entire growing season.

The cost to produce growing media consisting of PMS compost and perlite has been estimated (Table 9.3). The cost of PMS compost was estimated to be AU$16.84 m\(^{-3}\) (Chapter 4), perlite at AU$300 m\(^{-3}\) and zeolite at AU$13.50 per 20 kg. As only 70% of the produced compost (by volume) could be used for the preparation of growing media (due to the presence of gravel and large consolidated aggregates of compost), the actual cost of the useable fraction of compost was estimated to be AU$24.06 m\(^{-3}\). The cost to supplement 1 m\(^3\) of media with zeolite was estimated to be AU$13.50, given that this is normally added at a rate of 20 g L\(^{-1}\) (or 20 kg per m\(^3\)). If the compost is supplemented with magnesium carbonate, trace elements and a slow nutrient releasing fertiliser (estimated at AU$30 m\(^{-3}\) of compost), the cost to produce growing media formulated with varying proportions of compost and perlite was estimated to be between AU$92 and AU$166 m\(^{-3}\) (Table 9.3). Clearly, the cost to produce growing media from compost and perlite was highly dependent on the volume of perlite used in the mix, due to the high cost of this material (relative to compost). Consequently, the least expensive growing medium that could be formulated with PMS compost and perlite from the combinations examined in this study was one which consisted of 90% compost and 10% perlite. Given that plant growth generally improved as the proportion of compost in the mix increased, the most

Table 9.3 Estimated cost to produce various growing media formulated with PMS compost and perlite.

<table>
<thead>
<tr>
<th>Component</th>
<th>PMS compost : perlite ratio (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6:4</td>
</tr>
<tr>
<td>PMS compost a</td>
<td>14.43</td>
</tr>
<tr>
<td>Perlite b</td>
<td>120.00</td>
</tr>
<tr>
<td>Zeolite c</td>
<td>13.50</td>
</tr>
<tr>
<td>Mineral supplements d</td>
<td>18.00</td>
</tr>
<tr>
<td>Total cost (AU$ m(^{-3}))</td>
<td>165.93</td>
</tr>
</tbody>
</table>

\(^a\) Estimated cost of PMS compost is AU$24.06 m\(^{-3}\); \(^b\) Cost of perlite is AU$300 m\(^{-3}\); \(^c\) Cost of zeolite is AU$13.50 per 20 kg (added at a rate of 20 kg m\(^{-3}\) of media); \(^d\) Estimated cost of magnesium carbonate, slow release fertilisers and trace elements is AU$30 m\(^{-3}\) of PMS compost.
suitable mix for use by domestic users would be one consisting of 90% compost and 10% perlite. Commercial nurseries, however, would not require a medium containing slow nutrient releasing fertilisers, as nutrients are usually supplied through the application of nutrients via irrigation and watering systems. The cost to produce the growing medium consisting of 90% compost and 10% perlite (−AU$92 m⁻³) compares very well with other commercially available bark-based media (retailing at AU$5 to AU$10 per 20 L bag, or AU$250 to AU$500 m⁻³). Thus, use of PMS compost as the major component in horticultural growing media is considered to be an environmentally acceptable and an economically viable method of recycling this organic waste.

9.5 Conclusions

PMS compost and perlite mixed at various ratios was assessed for their ability to support the growth of lettuce, foxglove, broccoli and English marigold. The two most important physical properties required for plant growth of plants in containers: air filled porosity and total water holding capacity, were excellent in media containing between 60 and 90% compost. These mixes were physically stable over a 15 week growing period.

Germination of all plant species was very high in the tested media, containing between 60 and 90% compost, suggesting that the moderately high salt content did not affect plant germination. Significantly more biomass was produced at the highest compost additions for lettuce and foxglove, however, this was not the case with broccoli or English marigold. Better plant growth should be achieved by increasing the pH of the mixes from −4.8−5.3 to −6, and by decreasing the calcium to magnesium ratio by adding magnesium carbonate. The addition of trace elements would also improve growth. The concentration of the macronutrients in the media were generally sufficient, however continued growth over an extended period would require the addition of a slow nutrient releasing fertiliser. The cost to produce a growing medium consisting of 90% compost and 10% perlite (−AU$92 m⁻³) compared very well with other commercially available bark-based media, retailing at AU$5 to AU$10 per 20 L bag, or AU$250 to AU$500 m⁻³.