

Residue Management and Carbon and Nutrient Cycling in Exotic Pine Plantations of Southeast Queensland



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Abstract

In southeast Queensland, Australia, future wood production from exotic pines will rely heavily on second-rotation plantations. This increases the importance of sustaining soil fertility through logging or harvest residue retention for soil organic matter (SOM) maintenance in forest plantations. However, a greater understanding of harvest residues and their impact is essential to fully realise the potential of harvest residue management as an integral component of sustainable production forestry. Therefore, this study examined the nature of harvest residues, their decomposition and nutrient release dynamics, and the short- and long-term impacts of the residues on soil carbon (C), nitrogen (N) and phosphorus (P) pools, tree nutrition, growth and productivity in exotic pine plantations of Toolara State Forest (26° 00'S, 152° 49'E), Maryborough district, southeast Queensland.

The study was carried out at two separate, but nearby, sites in the exotic pine plantations. The first site was a newly logged plantation which was used to study the short-term impacts of residue retention on soil C and nutrient pools under three harvest residue management regimes: (1) residue removal, RR₀; (2) single residue retention, RR₁; and (3) double residue retention, RR₂. The experiment was a randomised complete block design with four blocks. The site was also used to determine the decomposition and nutrient release dynamics, and chemical nature through solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy, of five harvest residue fractions (foliage, branches, twigs, bark and combined harvest residues) incubated inside PVC micro-plots for 900 days. The second site was a 10 year-old F1 hybrid (*Pinus elliottii* var. *elliottii* x *Pinus caribaea* var. *hondurensis*) exotic pine plantation. The plantation was a long-term residue management experiment arranged in a randomised complete block design with three treatments (RR₀, RR₁ and RR₂) and four blocks. In this experiment, I assessed the

long-term impacts of residue management on the nature of SOM through chemical and physical fractionation and ^{13}C NMR spectroscopy. Assessments of the long-term residue management impacts on C and N pools, tree nutrition, growth and productivity were also carried out. Measurements of foliar nutrients, foliar carbon isotope composition ($\delta^{13}\text{C}$) and oxygen isotope composition ($\delta^{18}\text{O}$) and tree growth were carried out 2, 4, 6, 8 and 10 years following the plantation establishment.

Results of this study showed that the foliage and woody fractions (branches and twigs) comprised 42% and 45% of harvest residues, respectively, and that harvest residues contained about 17.0 t C ha^{-1} , 140 kg N ha^{-1} and 9.0 kg P ha^{-1} . The decomposition and nutrient release of the residues were relatively rapid for the foliage and the decomposition rate decreased in the order: foliage > combined residues > twigs > branches > barks. The residue fraction half-lives ranged from 2.5 to 14.5 years. Nitrogen release showed temporary immobilisation while P release closely followed that of mass loss. Solid-state ^{13}C NMR spectra of the residues showed peaks indicating alkyl C (0-45 ppm), O-alkyl C (45-110 ppm), aryl C (110-145 ppm), O-aryl C (145-165 ppm) and carboxyl C (165-190 ppm) functional groups, which continuously changed in composition as decomposition progressed. A rapid decline of the O-alkyl C intensities, especially the carbohydrate C region, and a concomitant increase in the alkyl C and N-alkyl/methoxyl C intensities were consistent with other studies. In addition, significant correlations between N or P and the functional groups among the residue fractions were also observed. The percentage P remaining was negatively related to the alkyl C intensity ($p < 0.05$) of the residue fractions and also positively correlated to the carbohydrate C of the foliage fraction ($r = 0.73$, $p < 0.01$), indicating that nutrient mineralisation was closely linked to the changes in the C chemistry of the residues. In addition, branches and bark contained significantly greater initial N-alkyl/methoxyl C,

aryl C and O-aryl C fractions compared to the foliage fraction, and that these functional groups were significantly correlated with the decomposition rates.

Short-term impacts of harvesting and residue management showed that harvesting decreased soil total C in the first year, but this was returned to or greater than the pre-harvesting levels in the second year under the RR₁ and RR₂ treatments. Soil total N also increased significantly in the RR₁ and RR₂ treatments compared to the RR₀ treatment after 18 and 24 months. Measurements of labile C and N pools showed no clear residue management effects on soil microbial biomass C (MBC) over the 24 month period. The hot water extractable organic C (HWEOC) and N (HWEON), however, were consistently greater in the RR₂ treatment compared to the RR₀ treatment after 12 months following clear-cut harvesting. The mineral N pool (NH₄⁺-N and NO_x-N) was also significantly greater in the RR₁ and RR₂ treatments compared to the RR₀ treatment after 18 and 24 months. Measurements of P pools showed no significant variations in total P, but significantly greater fluoride extractable P (Bray 1_P), sodium bicarbonate extractable P (NaHCO₃_P) and hot water extractable organic P (HWEOP) were observed in the RR₂ treatment compared to the RR₀ treatments. The hot water extractable total P (HWETP) pool, on the other hand, showed significant variations ($p < 0.001$) among the three treatments. Pearson's correlation analyses showed significant positive correlations between the soil total C and N, and between total C and the labile C and N pools. There were also significant correlations between HWEOC and HWEON ($r = 0.95$, $p < 0.001$) or HWEOP ($r = 0.57$, $p < 0.05$), and between HWEOC and the HWETP ($r = 0.69$, $p < 0.05$). A significant positive correlation between microbial biomass N (MBN) and NH₄⁺-N ($r = 0.54$, $p < 0.01$) was also observed. This study suggested a strong linkage between harvest residues and labile C, and that the mineralisation of labile C pools is critical for N and P availability.

The long-term residue management experiment showed that residue management impacts on soil C and N pools were more pronounced in the long term compared to the short-term study. Soil total C and N concentrations were very significantly different among the treatments, increasing in the order $RR_0 < RR_1 < RR_2$. Measurements of labile C and N pools also showed that MBC, HWEOC and HCl hydrolysable C, HWEON, MBN and HCl hydrolysable N were significantly greater in both the RR_1 and RR_2 treatments compared to those in the RR_0 treatment. The recalcitrant C (non-hydrolysable C) fraction was also significantly greater in the RR_1 and RR_2 treatments. Similarly, density fractionation of SOM showed that both the light fraction organic C (LFOC) and heavy fraction organic C (HFOC) were also significantly greater in both the RR_1 and RR_2 treatments compared to those in the RR_0 treatment. However, mineral N pools (NH_4^+ -N and NO_x^- -N) showed no significant variations between the treatments. Solid-state ^{13}C NMR spectroscopy of bulk SOM and LFOM showed greater alkyl C intensities in the RR_0 treatment compared to the RR_2 treatment, while the *O*-alkyl C relative intensities were significantly greater in the RR_2 treatment compared to the RR_1 and RR_0 treatments. Consequently, the *A/O*-*A* ratio also decreased significantly from the RR_0 treatment to the RR_2 treatment in both the bulk SOM and LFOM, indicating significant variations in the degree of SOM decomposition between the treatments. This was consistent with the stable isotope analyses, which showed greater $\delta^{13}C$ of the LF and HF C pools in the RR_0 treatment compared to the RR_1 and RR_2 treatments consistent with the advanced microbial processing of the SOM in the RR_0 treatment. The LFOM spectra, however, showed significantly higher aromatic C in the RR_1 and RR_2 treatments compared to the RR_0 treatment. In addition, there were significant relationships between the measured labile C pools and the *O*-alkyl C intensities of both the bulk SOM and LFOM spectra.

Measurements of litterfall biomass showed that litter production and litter N and P contents were not significantly different among the treatments at age 10 years. Tree growth, however, continued to show greater total growth in the RR₁ and RR₂ treatments compared to the RR₀ treatment after 10 years, consistent with the greater periodic mean annual increments of diameter at breast height (PAID) and basal area (PAIB) in the RR₁ and RR₂ treatments during the early growth phase. However, PAID and PAIB declined significantly after age 4 years to about 68 – 78 % at age 10 years. Declining foliar N and P concentrations accounted for 62 % ($p < 0.05$) of the variation in growth rates after age 4 years, and foliar N and P concentrations were either marginal or below critical concentrations. At age 10 years, PAID and PAIB were significantly greater in the RR₀ treatment compared to the RR₁ and RR₂ treatments, in contrast to the growth trends during the early growth phase. Foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses showed that foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were positively related to the PAID at age 4 years, and there were also significant positive relationships among foliar K, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. These observations were consistent with growth-induced water stress typical of a greater supply of N and P, and therefore growth, to the trees in the RR₁ and RR₂ treatments during the early growth phase. In contrast, foliar and litter needle $\delta^{13}\text{C}$ were negatively related to the PAID at age 10 years, suggesting that stomatal conductance (g_s) largely influenced the long-term PAID. This indicated that long-term tree growth might be influenced by interactions between nutrition and soil water limitation. Overall, while residue management continued to have a significant impact on SOM and nutrient storage, the impact of residue retention on tree nutrition and growth might be limited over a longer period, and that the integration of alternative forest management practices is necessary to sustain the benefits of harvest residues until the end of the rotation.

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Declaration of Originality

The experimentation, analyses, presentation and interpretation of results in this thesis represent original work that has not been previously submitted for a degree or diploma at any university. To the best of my knowledge and belief, this thesis contains no material previously published or written by another person except where due reference is made within the thesis itself.

Shane Sarere Tutua



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CHAPTER ONE

Introduction

1.1 Background

Forest plantations are increasingly becoming the main source of wood products worldwide amidst declining timber supply from natural forest sources and environmental or biodiversity concerns associated with natural forest harvesting (Tomaselli, 2007). In Australia alone, forest plantation production in 2003 was valued at \$1 billion annually, with production levels unable to meet the domestic demands for wood products (Australia's State of the Forests Report, 2003). In sub-tropical southeast Queensland, Australia, the local forest plantation industry also experienced similar trends. At the timber production rate of around 1.61 million m³ per annum as of 2004 (DPI Forestry Yearbook, 2004) the industry is struggling to meet the local demand of more than 2.0 million m³ per annum. This shortfall in supply and the need to increase or maintain production on limited land increases the importance of adopting sustainable forest production systems.

The local plantation estate is largely based on introduced exotic pines, which cover a total area of 181,088 hectares (National Forestry Inventory, 2003). The exotic pine plantations provide softwood products at a shorter rotation of 25 – 30 years compared to the longer rotations of 50-60 years of local conifer species such as hoop pine (*Araucaria cunninghamii*). The exotic pine are dominated by Slash pine (*Pinus ellioti* Engelm. var. *elliottii*) and Honduras Caribbean pine (*P. caribaea* var. *hondurensis* Barr. & Golf.) (Simpson, 1998; Australian Forest Plantations, 2004). The hybrid between these two species (F1 hybrid), however, was recognized as the taxon of first choice across a range of soil conditions in southeast Queensland (Powell and Nikles,

1996), thus has been the main species established in recent second-rotation plantations.

The exotic pine plantations, however, are established on infertile sandy soils derived from Mesozoic sandstones and Quaternary sands in low lying coastal areas (Simpson et al., 2003). These sandy soils have high acidity, with drainage ranging from good on the broad low ridges to poor in lower lying areas (podzols) (Simpson, 1998). The soils are limited in phosphorus (P), and therefore a fertiliser programme that includes a generous application of P maintains plantation productivity (Simpson, 1998).

Forestry Plantations Queensland (FPQ), a state-owned company, manages nearly all the exotic pine plantations in southeast Queensland, Australia. However, FPQ has limited expansion opportunities for new first-rotation plantations, due to environmental concerns regarding new land clearings and competition for land from the burgeoning domestic housing market. Future wood production will, therefore, rely heavily on second-rotation plantations (Simpson et al., 2003). This factor together with the poor soil fertility status of the plantation presents a major challenge in sustaining or expanding production levels to meet increasing demand. Thus, future expansion of production will have to depend on improved silvicultural techniques and sustainable soil fertility maintenance strategies. Furthermore, these strategies will have to reflect FPQ's policies towards environmentally friendly products through enhancing ecosystem benefits of plantations such as the rehabilitation of land and water degradation, carbon sequestration and biodiversity enhancement (Australian Forest Plantations, 2004).

It is widely recognised that soil organic matter (SOM) maintenance is critical for soil fertility and sustainable plantation production in subsequent rotations (Nambiar, 1996; Goncalves et al., 2004b). While SOM is important for maintaining soil physical, chemical and biological properties of soils, it is recognised as an important source of nutrients in tropical forest plantations (Reich et al., 1997; Goncalves et al., 2004a). However, large losses of SOM usually occur during the inter-rotation period as a result of clear-cutting, export of wood biomass, burning of logging or harvest residues and cultivation of the soil. These activities either limit C inputs into the soil from plant biomass or increase SOM mineralization, both of which impact on the quantity and quality of SOM, and therefore the capacity of the soil to support forest plantations in subsequent rotations.

Harvest residue retention during the inter-rotation period is now widely recognised as an important strategy for maintaining SOM in forest plantations. Many studies, mostly in temperate regions and with other timber species, have shown the positive impacts of on-site residue retention following clear-cutting. In southeast Queensland, clear-cut harvesting of slash pines generates between 30 - 46 t ha⁻¹ of logging residues (Simpson et al., 2003; Bubb et al., unpublished). However, residue retention has only been introduced in the last 10 – 15 years and not much is known about its impact on soil and plantation productivity in this sub-tropical climate. Three recent studies of soil and tree growth under different residue management regimes in southeast Queensland, however, have provided valuable insights into the impact of harvest residue retention; showing positive impacts on early tree growth, SOM quantity and quality and soil N content (Mathers and Xu, 2003; Simpson et al., 2003; Chen and Xu, 2005). The three studies were consistent with other residue management studies

conducted in Australia and elsewhere (Jones et al., 1999; Smith et al., 2000; Nzila et al., 2002; Mendham et al., 2003; Mathers et al., 2003a; Tiarks et al., 2003; Goncalves et al., 2004a).

One of the confounding outcomes of these preliminary studies in southeast Queensland was the lack of a significant relationship between soil nutrient content, foliar nutrient concentration and tree growth indices, other than loading rates (Simpson et al., 2003; Chen and Xu, 2005). This brings into question whether the residues impact on nutrition or whether it is the mulching effects, especially soil water retention, that influences tree growth during the establishment and early growth phase of the plantation. In addition, little is known about the nature of slash pine residues and how they release C and nutrients. The study by Mathers and Xu (2003) of SOM using ^{13}C NMR was semi-quantitative and did not fully quantify the impact of residue retention on labile soil C, N and P pools and how these pools changed as residue decomposition progressed. Furthermore, the long-term impact of harvest residues on soil fertility, SOM, tree growth and productivity are unknown and few studies have been conducted in Australia. Thus, this study aimed to provide a much more comprehensive understanding of the nature of the residues, the key processes that would occur following harvest residue retention, and the short- and long-term impacts of the residues on soil C and nutrient pools, long-term soil C storage, tree nutrition, growth and productivity.

1.2 Harvest or Logging Residues

Plant residues, including plantation forest harvest or logging residues retained on-site following clear-cut harvesting, are widely recognised as a source of C and nutrients

(Kumar and Goh, 2000). Many studies have demonstrated the importance of these residues as a source of SOM and nutrients (Goncalves et al., 2004a). Harvest residues, however, are a heterogeneous mixture of foliage, branches of differing sizes, stem and bark. This characteristic variability of harvest residues influences the quality of the residues, how much nutrients they contain, and the dynamics of decomposition and nutrient release. The characterisation of the residues into various fractions and the determination of their biochemical quality are important in understanding their C and nutrient dynamics.

Harvest residue decomposition studies have been conducted in Australia and other parts of the world to understand C and nutrient dynamics (Barber and Van Lear, 1984; King et al., 1997; Jones et al., 1999; Shammass et al., 2003; Palviainen et al., 2004a). In Australia, the decomposition dynamics of plantation species such as eucalypts, radiata pine and hoop pine harvest residues have been documented (Mackensen et al., 2003; Shammass et al., 2003; Blumfield et al., 2004a). However, there is no published information on the decomposition and nutrient dynamics of slash pine, the main exotic pine species in southeast Queensland. In addition, Mackensen et al. (2003) point out that there is insufficient information of decomposition of CWD in Australia, and in particular data on CWD residue quality. The application of ^{13}C nuclear magnetic resonance (NMR) spectroscopy in characterising plant material C chemistry presents an opportunity to determine residue biochemical qualities and residue C chemistry dynamics. ^{13}C NMR have been applied to decomposition studies of woody residues (McColl and Powers, 1998; Preston et al., 1998; Kögel-Knaber, 2002), and in particular, hoop pine residues in southeast Queensland (Mathers et al., 2003b; Blumfield et al., 2004a). It has also been used to study SOM under residues in

southeast Queensland (Mathers et al., 2003b; Mathers and Xu, 2003). The application of ^{13}C NMR spectroscopy to slash pine harvest residues would therefore be expected to provide an insight into the nature of the residues and how these would influence C and nutrient dynamics.

1.3 Soil Organic Matter Pools and Residue Management

Soil organic matter is important for the long-term sustainability and productivity of plantation forest ecosystems (Nambiar, 1996; Ghani et al., 2003; Gonzalez - Prieto and Villar, 2003; Mathers et al., 2003a). Studies have shown that SOM is an important source of nitrogen (N) across a wide range of climatic and soil gradients for both hardwood and softwood production (Reich et al., 1997; Goncalves et al., 2004b). Understanding residue management effects on the nature of SOM and its various fractions during the inter-rotation period is critical in predicting nutrient mineralization or availability. The period from harvesting and plantation establishment to canopy closure represents a significant growth period in stand development, when growth rates are highest for shorter rotation plantations such as slash pine.

Traditionally, chemical fractionation techniques have identified the humic and fulvic acid fractions of SOM (van Hees et al., 2005). However, since these C pools are not biologically meaningful, physical fractionation techniques, based on soil particle size and density, have been used to characterise SOM into the light (LFOM) and heavy fraction (HFOM) organic matter pools. These C pools are deemed to be more biologically meaningful as the LFOM C pools are more accessible to the soil microbial population (Boone, 1994; Post and Kwon, 2000; Cookson et al., 2005). Not

all LFOM are biodegradable and therefore this C pool is limited in explaining C dynamics and biogeochemical processes. This has led to the division of SOM into the labile and non-labile C pools. The labile C pool is defined as the fraction of SOM that is both physically accessible and chemically degradable during microbial growth (Zou et al., 2005). The degradability of labile C plays an important role in biogeochemical processes or nutrient release for plant uptake (van Hees et al., 2005). The proportion of the labile C pools, hence the bioavailability of SOM, is a measure of SOM quality, which in turn determines soil quality.

A number of labile C pools have been proposed recently. These are the water-soluble organic C (WSC) or dissolved organic matter (DOM), microbial biomass C (MBC), hot water-extractable organic C (HWEOC) and HCl-hydrolysable C (Cook and Allan, 1992; Qualls, 2000; Ghani et al., 2003a; Chen et al., 2004; Cookson et al., 2005; Paul et al., 2006). Studies in agricultural and forest soils, however, have shown that HWEOC is the C pool that is most sensitive to land use or management practices, and therefore is a potential biological indicator of soil quality (Ghani et al., 2003; Chen and Xu, 2005). Other studies have also shown that HCl-hydrolysable C is a sensitive indicator of management (Paul et al., 1997). The advantage of using HWEOC to evaluate residue management is that its determination is a relatively simple procedure. There is currently little information on both the immediate and long-term effects of residue retention on labile C, N and P in these sandy soils. Decomposing plant residues are the main source of labile C and nutrients (Homann and Grigal, 1992; Qualls, 2000), and therefore it would be expected that increasing decomposition of harvest residues would be reflected in increasing HWEOC and hot water extractable N and P in the soil.

Plantation ecosystem C sequestration is important for long-term productivity of subsequent rotations, as well as for mitigating increased CO₂ production, and therefore climate change (Brack and Richards, 2002; Tiarks et al., 2004). In southeast Queensland, early results of harvest residue management have indicated significant improvement in SOM quantity and quality (Mathers and Xu, 2003). However, the long-term impact of residue management on SOM quality and C sequestration are unknown. Other long-term studies of residue management have shown little or conflicting results on the long-term benefits of residue retention on soil C and N storage (Olsson et al., 1996; Knoepp and Swank, 1997; Johnson and Curtis, 2001; Johnson et al., 2002). Nonetheless, few long-term studies have assessed the influence of residue management on SOM pools mentioned above. Therefore, an understanding of the long-term impact of harvest residue management on both the forest floor and the soil C and N pools is necessary.

1.4 Tree Nutrition, Growth, Productivity and Residue Management

Harvest residue retention has consistently shown a response in tree growth in plantation ecosystems, ranging from the seedling to the late canopy closure stage in both tropical and temperate regions (Proe et al., 1999b; Nzila et al., 2002; Simpson et al., 2004). Growth responses may be attributed to the combination of mulching and nutrition effects of harvest residues (Proe et al., 1999). Many studies, however, have shown the direct linkage between tree growth and the nutritional effect of residue retention (Proe et al., 1999; Smith et al., 2000; Nzila et al., 2002; Blumfield et al., 2004a). Nonetheless, inconsistencies in results in some trials have been reported (Smith et al., 2000; Simpson et al., 2003; Tiarks et al., 2003). As indicated earlier, a residue management trial in southeast Queensland showed no significant variations in

foliar nutrient concentrations between the different residue management treatments (Simpson et al., 2003), which raises speculations as to whether the mulching effects are more important. The lack of nutritional effects may be related to the confounding effects of variation in soil fertility at the study site (Smith et al., 2000); clear-cutting, which increases soil N mineralization (Piatek and Allen, 2000; Blumfield et al., 2004a), thus providing comparable N supply in all treatments; and time factor relating to residue nutrient immobilisation and release, and therefore availability for tree uptake. It has been noted for radiata pine, Sitka spruce and eucalyptus plantations that foliage nutrient contents declined in the first 1 – 6 years but gradually increased again thereafter (Proe et al., 1999; Smith et al., 2000; Mendham et al., 2003). Thus, nutritional effects may be more clearly linked to tree growth in the medium to long term. This has been supported by studies conducted at approximately 10 years following harvesting, where residue retention has shown higher foliar nutrient concentrations and biomass production or stem sizes (Olsson et al., 2000; Smith et al., 2000; Mendham et al., 2003). Tiarks et al. (2003) also reported higher litterfall of *Pinus taeda* on treatments where harvest residues were retained after 10 years, implying longer-term benefits to subsequent rotations as a source of nutrients and soil C through litter decomposition. Thus, while the nutritional effect of residue retention may not be obvious in the short term, these effects may be expressed in foliar nutrient concentrations in the long term.

1.5 Research Hypotheses and Objectives

Residue decomposition can immobilise and release nutrients important for tree growth and productivity. The retention of harvest residues has the potential to supply or maintain SOM, as well as long-term C storage within the plantation ecosystem.

Based on the above review of literature, it is hypothesized in this study that the retention of slash pine harvest residues as an inter-rotation management practice would release C and nutrients into the soil, which would increase soil C, N and P pools in the short term, and that these nutrient levels will be sustained in the long term. It is also hypothesised that residue retention would have a long-term impact on tree nutrition, growth and productivity. These hypotheses are linked as illustrated by the conceptual model in Fig. 1.1. Based on the above general hypotheses the objectives of this study were to: (1) determine the decomposition, nutrient release and C chemistry of slash pine harvest residues; (2) quantify the impact of residue retention on soil labile C, N and P pools immediately following harvesting; (3) assess the long-term impacts of residue retention on soil C and N pools, tree nutrition, growth and productivity; and (4) explore the nutrition or mulching effects of residues using stable isotope techniques.

This thesis, therefore, reports on the characteristics of slash pine harvest residues, their decomposition and nutrient release dynamics, changing C chemistry as decomposition progressed, and how these are linked to N and P release. The thesis will also report on the impact that residue retention had on soil C and nutrient pools, especially in the first 18-24 months, and will assess the long-term benefits of residue retention on C and N pools, ^{13}C NMR chemistry and C storage, and tree nutrition, growth and productivity. The nutrition or mulching effects of residues on tree growth using stable carbon and oxygen isotope compositions will also be examined.

CHAPTER TWO

Site Description and Methodologies

2.0 Introduction

This chapter describes the study sites, experimental designs, field sampling and analytical procedures employed in this research programme. While the methodologies are also described in the following result chapters, this chapter provides more detailed information on the methodologies, their background and the reasons why they were used. All experiments were field-based with the intention to determine the decomposition and nutrient release dynamics of harvest residues, and the impact of *in situ* residue retention on SOM pools, C storage, tree nutrition, growth and productivity.

2.1 General Site Description

Two experiments were established or used to address the objectives of this research project. The experiments were located within 5 km distance of each other in the exotic pine plantations in Toolara State Forest (26° 00'S, 152° 49'E), Maryborough District, southeast Queensland (see map on Fig. 2.1). Most of the soils in this area are developed from Mesozoic sand stones, and are acidic with deep to shallow sandy soils, and high to moderate drainage. The climate is humid sub-tropical with a mean annual rainfall of 1354 mm, with 56% falling in summer (Simpson et al., 2003). The July to September period is relatively dry, which may extend to November (Xu et al., 2000). The summers are hot and moist with a mid summer mean daily temperature of 24.9 °C and a relative humidity of 70%, while the winters are mild, with a mid winter mean daily temperature of 14.0 °C and a mean relative humidity of 64 %. Plantation trees in this region often experience both well-watered and water-limited conditions in

the same year, even in a wet summer season (Xu et al., 2000). The annual rainfall has been below the mean over the last 10 years as indicated in Fig. 2.2.

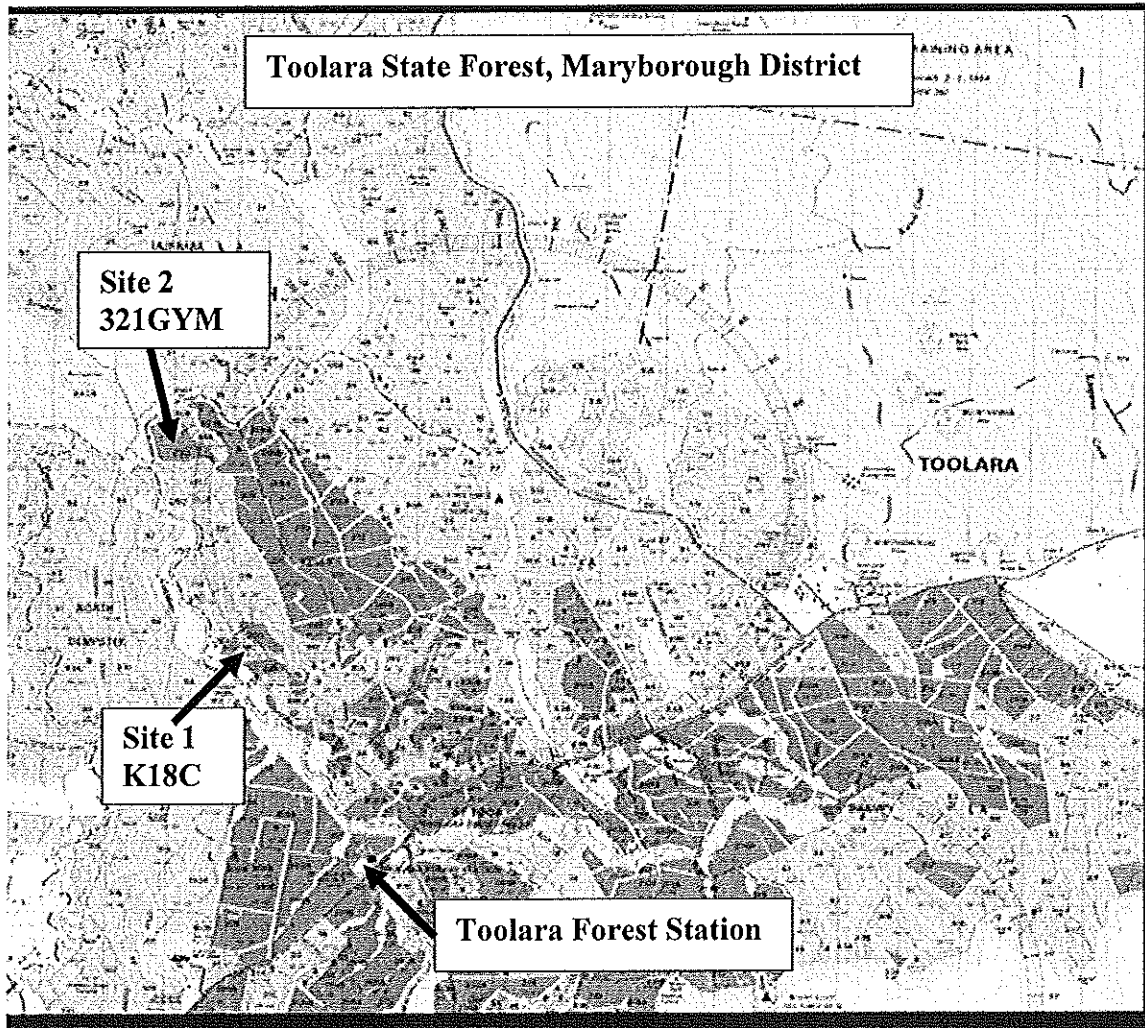


Fig. 2.1. Map showing the relative distance between the experimental sites at Toolara State Forest, Maryborough District, southeast Queensland.

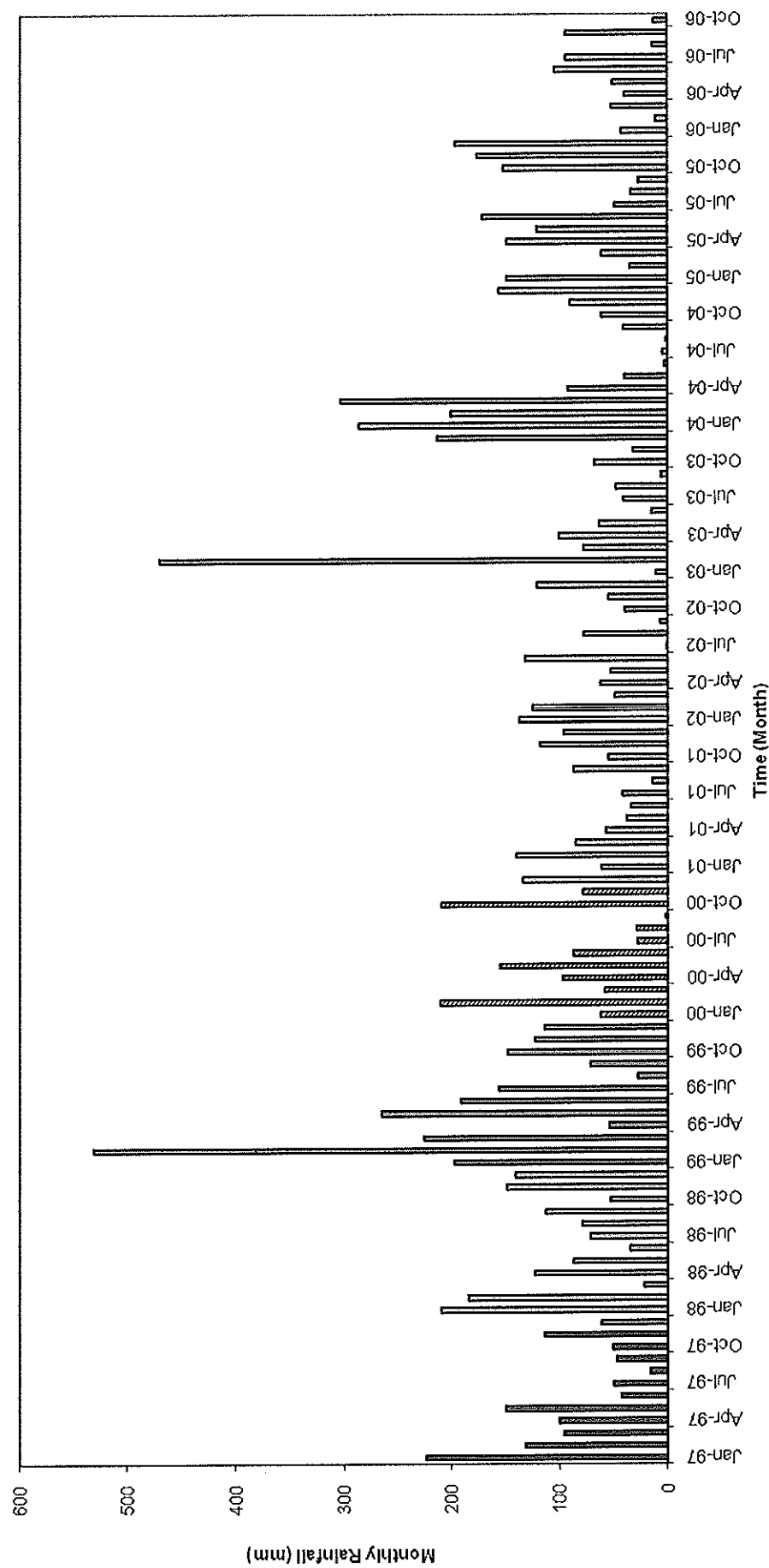


Fig. 2.2. The rainfall history of Toolara State Forest in the last 10 years (Jan 1997 – Oct 2006).

2.2 Site 1 and Experimental Design

This plantation, referred to as experiment K18C or Site 1 (Fig. 2.1), was a newly logged exotic or slash pine plantation located at exactly 25° 58'S, 152° 47'E. The site was used to investigate the short-term effects of harvest residue retention, and the processes involved in C and nutrient cycling following residue retention. It was on a flat land with a gentle slope of less than 2°. The soil was loamy sand developing into a podsol and was classified as a soloth (Isbell, 1996), due to the medium to heavy clay horizon encountered at 70 cm depth.

The experiment on this site was established in late February 2005 on a section of the harvested plantation immediately following clear-cutting. Harvesting operations employed the “at stump” processing method to extract the logs. This method involved the felling and immediate de-branching or processing of the felled trees at the stumps, before the logs were hauled out to the roadside, leaving harvest residues evenly distributed within the plantation area (Fig. 2.3).

For the purpose of this experiment, macro-plots (10 m x 10 m) were established in a randomised complete block design with four blocks and three treatments (Fig. 2.4). The treatments were three residue loading rates or management regimes, which were (1) residue removal (RR_0), (2) single level of residue retention as per the normal operational level (RR_1), and (3) double level of residue retention (RR_2), established by transferring residues from the RR_0 treatments to plots where residues were retained. The RR_2 treatment was not operationally practical, however, it was included to widen the possible treatment effects (Simpson et al., 2003) and represent the uneven residue distribution within the site. The treatment plots were left to fallow, rather than

established with trees, which might compound treatment effects or soil processes during the early establishment period of 6 – 18 months.



Fig. 2.3. The “at stump” harvesting of the exotic pine plantations leaves residues more or less evenly distributed within the exotic pine plantation area.

2.3 Site 2 and Experiment Design

Site 2 (25°53'S, 152°47'E), referred to as experiment 321GYM, was a long-term harvest residue management experiment established in 1996 (Simpson et al., 2003) by Forestry Plantations Queensland (FPQ). The details of this site and experimental design were as described by Simpson et al. (2003). In brief, the site was located at Toolara State Forest (26°00'S, 152° 49'E), Maryborough district, southeast Queensland, Australia. It was generally flat, with a deep sandy soil classified as a grey podsol (Isbell, 1996) or gleyic acrisol (FAO, 1974). Simpson et al. (2003) had reported details of initial soil chemical and physical properties of this site. The experiment was a randomised complete block with six treatments and four blocks. Gross plots were 12 rows by 12 trees at 3 x 3 m

spacing and net plots were 8 rows by 8 trees. The treatments, applied prior to planting, and according to Simpson et al. (2003), were: (1) no harvest residue retained + 50 kg P

BLOCK 1

Plot 1	Plot 2	Plot 3
RR ₁	RR ₀	RR ₂

BLOCK 2

Plot 4	Plot 5	Plot 6
RR ₂	RR ₀	RR ₁

BLOCK 3

Plot 7	Plot 8	Plot 9
RR ₁	RR ₂	RR ₀

BLOCK 4

Plot 10	Plot 11	Plot 12
RR ₀	RR ₂	RR ₁

Key



Macroplots used to install micro-plots for the decomposition experiment
(Section 2.4.9 and chapter 3)

Fig. 2.4. The lay out of macro-plots (10 m x 10 m) at experiment K18C in Toolara State Forest, southeast Queensland, with the residue removal (RR₀), single level residue retention (RR₁) and double residue retention (RR₂) harvest residue management regimes. Each block was separated by 10 m.

ha⁻¹ added (BL₀); (2) harvest residues retained (operational quantity) + 50 kg P ha⁻¹ added (BL₂); (3) double quantities of harvest residues retained + 50 kg P ha⁻¹ added (BL₃); (4) BL₂ + leguminous cover crops established at replanting (BL₂ + L); (5) BL₂ + complete weed control from planting (BL₂ - W); and (6) BL₂ without P fertiliser (BL₂ - P). The present study focussed on treatments 1, 2 and 3 to assess the long-term impacts of residue retention, and therefore these treatments are referred to as RR₀, RR₁ and RR₂, respectively, hereafter, to be consistent with the residue treatment nomenclature in site 1. The double level of residue retention (RR₂) was established by transferring residues from the RR₀ treatments to macro-plots where residues have been retained. The RR₂ treatment was not operationally practical, however, it was included to widen the possible treatment effects (Simpson et al., 2003) and represent the uneven residue distribution within the site. The net plots were planted with stock from 6 different F1 hybrid pine families. Each family was randomly allocated a row, with a double up of 2 families per row to make up the 8 rows.

2.4 Field Sampling and Measurement Methods

2.4.1 Soil sampling

At experiment K18C, soil sampling was carried out at 0, 6, 12, 18 and 24 months following clear felling of the plantation. Each sampling was carried out at 0 - 10 and 10 - 20 cm depth. For each plot, a composite sample from 5 cores (ca diameter 7.5 cm), each of which was collected from the centre and at four equi-distant positions were collected. These positions were at least 1.0 m from the edge of the plot, to avoid edge effects.

At experiment 321GYM, the long-term experiment, soil sampling was carried out in August 2006, 10 years after the establishment of the experiment. Composite soil

samples were taken at 0 – 10 and 10 – 20 cm depths according to the method described by Simpson et al. (2003) and Chen and Xu (2005) at the same experimental site. The composite samples were taken from five systematically located 1 m quadrats within the net plots. A soil core (ca. 7.5 cm diameter) was taken at each quadrat position. Preliminary results of total soil C and N showed that variations within treatments were the same as those of Chen and Xu (2005) who took two cores within the 1.0 m² quadrat. Therefore, the above sampling regime was adopted for experiment 321GYM.

At each site, fresh composite samples were sub-sampled into two components for chemical and microbial analysis. Sub-samples for microbial C and N pools were stored at 4 °C and processed within 2 weeks of sampling (Chen and Xu, 2005), while sub-samples for chemical analysis were passed through a 2 mm sieve before air-drying and grinding in a Rocklab puck and ring grinder prior to storage in polyethylene vials for chemical analysis.

2.4.2 Soil moisture measurement

At experiment K18C, soil moisture was measured over a 9-month period to determine the influence of harvest residue retention on soil moisture retention. Soil moisture was measured monthly from July 2005 to March 2006 using the Time Domain Reflectometry (TDR). Due to the limited number of probes available, moisture measurement was carried out in one of the four blocks described in section 2.2, in which four probes were installed in each treatment plot, two of which measured soil moisture at 0 – 10 cm depth while the other two at 10 – 20 cm depth.

At experiment 321GYM, soil moisture content was estimated gravimetrically when soil sampling was conducted. Sub-samples of composite soil samples were oven-dried at

105 °C and the difference between soil fresh weight and oven dry weight was considered as the soil moisture content under the three harvest residue treatments. While gravimetric soil moisture content may be under-estimated due to loss during handling and transportation, it was considered as sufficient measure for comparative purposes.

2.4.3 *Estimating soil bulk density*

Soil bulk densities were roughly estimated by a simple method using PVC pipes of 70 mm length and 50 mm diameter, chamfered on one end for easy insertion into the soil. Three soil cores per depth, randomly sampled within each net plot, were collected after clearing the organic layer at each position and inserting the cores into the soil mineral layer at 0 – 10 cm and 10 – 20 cm depths. The cores were carefully removed by digging around them and ensuring the soil mass inside was intact. Soil mass protruding outside of the dimension of the core was cut out and cores cleaned of adhering soil mass on the outside before placed inside sealable plastic bags to prevent loss of soil material, and therefore underestimation of bulk density. The cores were transported to the laboratory and the soil content emptied into trays before being oven dried at 105 °C for 24 hrs to determine dry weight. Since stones were absent in this sandy soil, bulk density was determined purely from the volume of the core and the mass of the soil as follows:

$$\text{Bulk density (g cm}^{-3}\text{)} = \frac{\text{Soil mass (g)}}{\text{Volume of core (cm}^3\text{)}}$$

.....Equation 1

2.4.4 *Estimating harvest residue production and characterisation*

At experiment K18C harvest residue production was determined following clear felling. Fresh harvest residues were sampled inside 11 quadrats (1.0 m²) positioned along a

transect line, and were at least 10 m apart within the plantation area. The residues were placed into large plastic bags and transported to the laboratory where the fresh harvest residues were separated into foliage, branch (ca. 15 – 40 mm diameter), twigs or small branches (ca. <15 mm diameter), bark and stem before fresh weight was determined. Residue dry weight was determined by sub-sampling each type of harvest residues per quadrat and oven dried at 60 °C for 120 hours to constant mass. Sub-sampling involved sawing out thin disc sections of branches and stems to allow quicker drying. Moisture content was determined and the proportion of dry mass was used to calculate the total dry mass of each residue type, and hence the total harvest residue production. Fresh residues of each type were sub-sampled from the 11 quadrats and were used for the decomposition study.

2.4.5 Foliar sampling

Foliar samples were collected from four average trees, representing four genetically separate sets of the 6 families described in section 2.3. Foliage was sampled from the northward facing side of the tree canopy, the side having the longest exposure to sunlight during the day (Xu et al., 1995a; Xu et al., 2000). Fifty fascicles of the most recent, fully expanded needles (approximately 1 year old) were collected from four average trees within a treatment plot and bulked as one sample (Xu et al., 2000; Simpson et al., 2003). These same four trees were sampled in previous years, unless a tree lost its ‘average tree’ status. As in previous sampling, foliar sampling of pine trees was carried out in mid to late winter when growth is minimal and nutrient concentrations are at maximum (Piatek and Allen, 2000; Xu et al., 2000).

2.4.6 Tree growth measurement

At experiment 321GYM, tree height (HT), basal area (BA) and diameter at breast height (DBH) were measured for each tree within the net plots of each treatment. The DBH was measured with a diameter tape at 1.3 m above ground level, while the HT was measured by a hypsometer with a transponder unit (Forestor Vertex 951004), which automatically determined the distance between operator and the tree, and the angle relative to the top of the tree, thus allowing calculation of HT. In each plot the mean for all the trees within each net plot was calculated for each growth index, and expressed as the value for each treatment replicate.

2.4.7 Litterfall sampling

Litterfall was measured to determine the impact of residue retention on plantation productivity. Litterfall was measured every 3 months over 15 months to establish the seasonal dynamics, but also to establish if residue retention influenced litterfall in different seasons. Sixty litter traps (0.81 m^2) were constructed from 100 mm x 5.0 mm timbers with a wire mesh (1.0 cm) on the underside supporting a fine 1.0 mm polyvinyl mesh on the top to trap the litterfall. The traps were propped up 25.0 cm above ground level by wooden legs at each corner. Five traps were systematically laid out in each treatment plot, equally spaced within the net plot to collect the litter.

At each sampling date the fallen litter was collected from the five traps and pooled into a composite sample per plot. The litter samples were oven dried at 60°C for 5 days to ensure all moisture was removed. Litter dry weight was determined and since litter needles comprised more than 95% of the litter biomass, they were presented here as the total litter biomass. The litter samples were then sub-sampled for analytical purposes by carefully mixing the composite sample and then sampling the composite sample at four corners and the inner centre for 50 senescent or litter fascicles. These needles were cut

into 1.0 cm lengths and ground up in a Rocklab puck and ring grinder and stored in sterile 70-ml polyethylene vials for chemical analyses.

2.4.8 *Forest floor biomass sampling*

This sampling was also carried out when soil was sampled (section 2.4.1) to assess the long-term impact of residue management on the total forest floor biomass C in experiment 321GYM. Forest floor was sampled in three of the four blocks (section 2.3) due to time constraints and the large quantity of forest floor materials involved. Five quadrats (1.0 m² each) systematically laid out within the net plot were sampled for each plot, separating the forest floor biomass from the top down into three distinct layers above the mineral soil. These layers or pools of C were: (1) litter layer (new litterfall-light brown/yellowish colour), referred to here as the L horizon; (2) fermenting litter layer (dark brownish in colour), F horizon; and (3) mixture of fermenting litter and organic layer, which was clearly woody remains of harvest residues, H horizon. This horizon nomenclature was adopted from the European system of nomenclature. However, the H horizon was not strictly as defined by the system of nomenclature due to the large quantity of recognisable organic residues under the L and F horizons in the R₁ and R₂ treatments and further treatments as described below.

In each plot, samples from the five quadrats were pooled into a composite sample for each horizon. The samples were oven dried at 60 °C for 5 days before dry weight was determined. Contaminating soil in the H horizon was removed by shaking the organic material through a 2.0-mm sieve, thus the measured biomass in the H horizon was that greater than 2.0 mm.

2.4.9 *Residue mass loss measurement*

Mass loss is the widely used measurement to determine the decomposition rates of plant residues in forest ecosystems. The litterbag method is the most widely used method to study both litter and harvest residue decomposition (Woods and Raison, 1982; Polglase et al., 1992; King et al., 1997; Shammas et al., 2003; Palviainen et al., 2004a). The litterbag method is a simple and inexpensive method of determining mass loss. However, it is criticised for the artificial environment within the contained residues due to the enclosure by the mesh bag. Other limitations of the litterbag are the possibility of over-estimating mass loss through residue loss from bags as well as under-estimating mass loss through soil contamination, and the restriction of soil fauna interactions (Woods and Raison, 1982; Anderson and Ingram, 1998). Thus, to avoid some of these limitations micro-plots were used to incubate residues in the field and mass loss was measured from residues remaining inside the micro-plots. Micro-plots also gave the opportunity to measure the soil within for decomposing residue effect on soil chemical and biological properties.

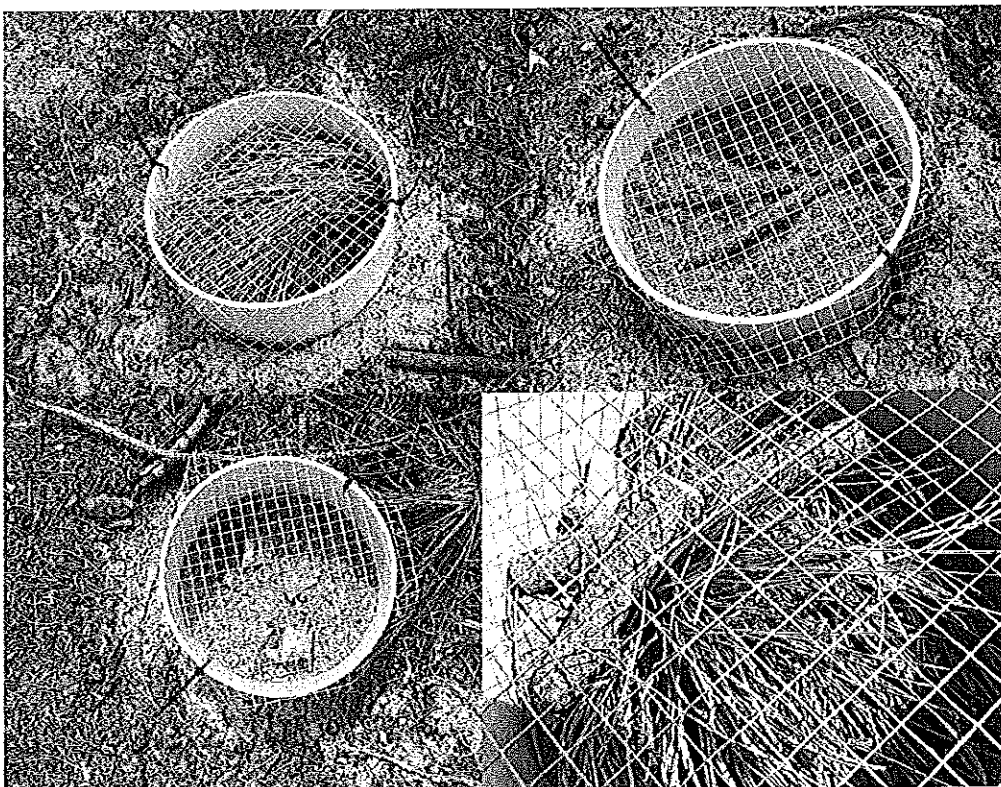
The micro-plots used in this experiment were similar to those described by Blumfield et al. (2004a). They were constructed from 25 cm diameter PVC pipes, which were cut into 30 cm lengths, chamfered at one end for easy insertion into the soil and drilled with 3 mm holes at the opposing end to tie down covers. One hundred and seventy of these micro-plots were divided equally between three of the residue removal macro-plot treatments (RR₀) described in section 2.2 of this chapter, and then inserted 20 cm into the ground using the rear hydraulic arm of a backhoe (Fig. 2.5a). Any layer of decomposing residues inside the micro-plots was removed before the harvest residues were placed inside for maximum contact with the soil mineral layer.

Fresh harvest residues collected immediately after harvesting operations were characterised into foliage, twigs, branches, bark and stems (section 2.4.4), then weighed

on a dry weight basis into sealable plastic bags before transported to the field and transferred into the micro-plots (Fig. 2.5b). The amounts weighed were as follows: (1) foliage (80.0 g); (2) twigs or small branches (30.0 g); (3) branches (15 – 40 mm diameter) (55.0 g); (4) bark (23.0 g); and (5) combined (187.0 g), which is a combination of foliage, twigs, branches and barks. The amount of each residue type was calculated from the actual loading rate of each component calculated in section 2.4.4. Harvest residue mass loss was determined every four months for the first year and every



(a)



(b)

Fig. 2.5. The installation of micro-plots using a backhoe (a) and the incubation of residues inside the micro-plots (b).

6 months subsequently (0, 4, 8, 12, 18, 24 and 30 months). The residues were transferred into sealable plastic bags before transport back to the laboratory, where they were oven dried at 60 °C for 5 days before carefully cleaning sand contaminations and weighing to determine mass loss and decomposition rates. Sub-samples of the residue types were ground for chemical analysis. For the combined residues sample the individual components were ground separately and re-combined according to the relative proportion of the remaining mass of each residue type.

2.5 Laboratory Analytical Procedures

2.5.1 Microbial biomass carbon (C) and nitrogen (N) analyses

Soil microbial biomass C (MBC) and N (MBN) were regarded as a labile C and N pools due to their high turnover rates, and therefore a source of nutrients. The MBC and MBN were determined by the fumigation-extraction method, with 0.5 M K₂SO₄ as the extractant at a soil to K₂SO₄ ratio of 1:4 (Vance et al., 1987; Jenkinson, 1988; Chen and Xu, 2005). In this study, fresh soil samples were cleared of large organic debris, or sieved through 2.0 mm mesh if not too wet, and thoroughly mixed together before two sub-samples of 15.0 g (oven dry weight equivalent) were weighed for direct extraction and fumigation, respectively. Another sub-sample of 10.0 g was weighed into 50 mL beakers and dried at 105 °C for 24 hours to determine soil mass on an oven-dry basis.

Sub-samples for fumigation were weighed into 70 mL beakers, and when soil moisture was < 40 % water holding capacity, it was adjusted to 45 % water-holding capacity

prior to fumigation (Chen and Xu, 2005). The fumigating desiccator was lined with moistened paper towels at its base to minimise drying of samples. Two 50 mL beakers, each containing about 40 mL of purified chloroform, were placed inside the desiccator before it was evacuated under vacuum. Evacuation was discontinued when the chloroform had boiled for 3 – 5 minutes. The desiccator was covered with a black plastic and left for 24 hours. It was then evacuated 8 times (3 minutes duration) to remove residual chloroform from the soil samples prior to extraction.

Both fumigated and non-fumigated (directly extracted) sub-samples were transferred into 100 mL polyethylene tubes and extracted with 60 mL of 0.5 M K₂SO₄. Extraction was carried out by shaking the samples in an end-over-end shaker for 30 minutes, followed by filtering through a Whatman 42 filter paper. All samples were frozen prior to analysis for total organic C (TOC) and total N (TN). The TOC and TN were analysed through high temperature oxidation using a Shimadzu TOC-V_{CSH/CSN} TOC/N analyser (Chen and Xu, 2005). The soil MBC and MBN were calculated as follows taking into account the correction factors:

$$\text{MBC} = (\text{TOC fumigated soil} - \text{TOC non-fumigated soil}) / 0.45 \text{ (Vance et al., 1987)}$$

$$\text{MBN} = (\text{TN fumigated soil} - \text{TN non-fumigated soil}) / 0.57 \text{ (Brookes et al., 1985; Jenkinson, 1988)}$$

2.5.2 Potassium chloride extractable inorganic N

Inorganic N (ammonium, nitrate and nitrite) were determined following extraction of fresh soil with 2.0 M potassium chloride (KCl) (Chen and Xu, 2005). Five grams (oven-dry weight equivalent) was weighed into 50 mL falcon tubes and added with 50 mL KCl solution. The samples were then shaken in an end-over-end shaker for 1 hour

before the extracts were filtered through Whatman 45 filter paper into sterile 70 mL polyethylene vials.

The extracts were determined for ammonium and nitrate concentrations using the SmartChem 200 discrete chemistry analyser (DCA) (Westco Scientific Instruments, Australia). The DCA uses the same colorimetric principles as that of the continuous flow injection analyser (FIA) (Chen and Xu, 2005). However, the DCA injects discrete quantities of the colouring reagent and mixes it in a small quantity of the sample before passing it through the source of UV light for reading the absorbance. Thus, the DCA has the advantage of using very small quantities of the colouring reagents and avoids the use of carrier reagents such as those used by the FIA. Its disadvantage, however, is that it does not distinguish between nitrate and nitrite N, and therefore the oxidised forms of inorganic N were represented as NO_x^- -N.

2.5.3 Soil and plant total C and N and stable isotope compositions

Soil total C can be related to the loss on ignition (LOI) technique at 550 °C, as well as determined through wet oxidation using dichromate (Walkley-Black technique). However, the later method could under-estimate actual C content, while the former could over estimate C content when carbonates, allophane and gibbsite are present (Sollins et al., 1999). Sollins et al. (1999) recommended dry combustion using a CN analyser coupled to a mass spectrometer as a more accurate measure, and which also allows for simultaneous measurement of soil total N. Thus, in this project, soil and plant total C and N were analysed using a Eurovector 3000 elemental analyser (Milan, Italy) coupled to a GVI Isoprime mass spectrometer (Manchester, UK). Forty milligrams of dried and ground soil or 7-10 mg of foliage or woody materials, were packed into tin capsules, which were pelletised and loaded into the auto-sampler, which dropped the

capsule and sample into the combustion column. Samples were determined for total C, N and the $^{13}\text{C}/^{12}\text{C}$ ratio, which was used to calculate the $\delta^{13}\text{C}$ (‰) as:

$$\delta^{13}\text{C} (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \times 1000 \quad \dots\dots\dots \text{Equation 2}$$

where R_{sample} is $^{13}\text{C}/^{12}\text{C}$ ratio of a sample and R_{std} is $^{13}\text{C}/^{12}\text{C}$ ratio of the international PeeDee Belemnite (PDB) standard (Cadisch et al., 1996; Xu et al., 2000).

Foliage samples were also determined for their oxygen-18 compositions ($\delta^{18}\text{O}$) by the VARIO EL III high-temperature elemental analyser (Hanau, Germany) coupled to a Sercon Hydra 20-20 mass spectrometer (Crewe, UK). Samples for $\delta^{18}\text{O}$ analysis were re-dried at 40 °C prior to weighing and pelletising. This was to remove all moisture, a potential source of ^{18}O . The quantity of samples weighed and pelletised was between 1.5 and 2.0 mg. The $\delta^{18}\text{O}$ (‰) was calculated relative to the IAEA Vienna standard mean ocean water for oxygen (VSMOW) as:

$$\delta^{18}\text{O} (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \times 1000 \quad \dots\dots\dots \text{Equation 3}$$

where R_{sample} and R_{std} are $^{18}\text{O}/^{16}\text{O}$ ratios of the sample and standard, respectively (Barbour et al., 2000; Xu et al., 2000).

2.5.4 Hot water extractable organic C and N analyses

Hot water extractable organic C (HWEOC) is a useful measure of labile C, and has been shown to respond to management practices. In this study HWEOC and hot water extractable organic N (HWEON) were analysed using the method of Sparling et al (1998) and modified by Chen and Xu (2005). Air-dried soils, 8.0 g (oven-dried equivalent), were placed into 50 mL polypropylene tubes, added with 40.0 mL of de-ionised water (millipore purified) and incubated at 70 °C for 18 hours. Subsequently, the

samples were shaken for 5 minutes in an end-over-end shaker, followed by centrifuging at 2000 rpm for 20 minutes. The supernatants were then decanted into 40 mL polypropylene tubes, transferred to a high-speed centrifuge and centrifuged at 10,000 rpm for 10 minutes before filtered through 0.45 μ m filter membranes. Samples were frozen until analysis for total organic C (TOC) and total N (TN) in a Shimadzu TOC-V_{CSH/CSN} TOC/N Analyser. The extracted TOC was regarded as the HWEOC, while HWEON was calculated as the difference in TN (HWETN) and hot-water extractable inorganic N (HWEIN) compounds in the same extracts, measured by the DCA (section 2.5.2).

2.5.5 *Hot-water extractable P*

Limited studies have measured hot water extractable organic P (HWEOP). However, this P pool might also be potentially available to plants similar to HWEON. In this study, hot water extracts described in section 2.5.4 were determined for hot water based P pools. A sub-sample (10 mL hot water extract) was added with 5 mL nitric acid (HNO₃), left for 1 hour then added with 2 mL perchloric acid (HClO₄), in a 75 mL tube and digested in an automated block digester for 1 hour at 130 °C and a further 30 minutes at 205 °C to determine the hot water extractable total P (HWETP). After cooling, the tubes were brought to volume with de-ionised water and 20 mL aliquots of the resulting solutions were pipetted into 50 mL volumetric flasks and topped up with 30 mL of de-ionised water. Then the samples were neutralised by adding a drop of para-nitrophenol, followed by drop wise additions of 4.0 M NaOH until the solutions turned slightly yellow, then a further drop wise addition of 2.0 M HCl until the solution just turned colourless. The volumetric flasks were then topped to volume with de-ionised water and total P was determined by the ascorbic acid method (Murphy and Riley, 1962; Sparks, 1996; Lajtha et al., 1999). The concentration of HWETP was calculated

taking into account the dilution in the digestion tubes and also that in the 50 mL volumetric flasks. The hot water extractable organic P (HWEOP) was determined as the difference in total P of digested and total soluble reactive P (SRP) of undigested subsamples of the hot water extract (HWE), which was assumed to be inorganic P in this study.

2.5.6 Bicarbonate extractable P

Bicarbonate extractable P ($\text{NaHCO}_3\text{-P}$) was determined in air-dried soil (<2.0 mm). The $\text{NaHCO}_3\text{-P}$ is commonly extracted in a soil to solution ratio of 1:100 (Rayment and Higginson, 1992; Mendham et al., 2002c). However, initial trials in this study indicated that the P concentration in this soil extract was below the detection limit of the ascorbic acid method (Murphy and Riley, 1962), probably due to the low P levels of the sandy soil in this study. Therefore, this study used a soil to solution ratio of 1:20, similar to that used by Bekunda et al. (1990) for a sandy soil in a radiata pine plantation of southeastern Australia. In this study, 2.5 g soil was added with 50 mL of 0.5 M NaHCO_3 (adjusted to pH 8.5) in a 50 mL falcon (polyethylene) centrifuge tube and shaken end-over-end for 16 hours at 25 °C, centrifuged at 2000 rpm then filtered through a Whatman 42 filter paper into sterile 70 mL vials. Prior to P analysis 10 mL aliquots were pipetted into 50 mL volumetric flasks, added with 25 mL de-ionised water and mixed thoroughly, added with 2 mL 1.0 M H_2SO_4 , mixed again and left to effervesce. After effervescence ceased, a further 3 mL of 1.0 M H_2SO_4 was added, mixed and allowed to stand for 24 hours to complete the removal of CO_2 before the colouring reagent (Murphy and Riley, 1962) was added to the flasks and made up to volume. Standards and blanks were also added 10 mL of the extracting solution and treated

similarly to the sample solutions. The standards contained P concentrations of 0, 12.5, 25, 50, 100, 200 and 300 $\mu\text{g P L}^{-1}$.

2.5.7 Fluoride-extractable P (Bray 1_P)

Fluoride extractable P was carried out according to the Bray 1 P method (Rayment and Higginson, 1992). The preference for Bray 1 P rather than Bray 2 P (Mendham et al., 2002c) was due to the acidity of the soil. Extraction was carried out by shaking 5 g of air-dried soil (<2.0 mm) with 35 mL of the 0.03 M NH_4F /0.025 M HCl extracting solution for 60 s, followed by filtering the extract through a Whatman 42 filter paper. Prior to P determination, 10 mL aliquots of samples were pipetted into 50 mL volumetric flasks and made to volume with deionised water after addition of the colouring reagent. Similarly, 10 mL of the 0.03 M NH_4F /0.025 M HCl extracting solution were added to the secondary standards and blanks to equalise the solution matrix between samples and standards. The standard solutions contained, 0, 50, 100, 200, 300, 400 and 500 $\mu\text{g P L}^{-1}$.

2.5.8 Calcium chloride extractable P

Calcium chloride extractable P ($\text{CaCl}_2\text{-P}$) was determined according to the method of Rayment and Higginson (1992) with some variations. In this study, 8.0 g of air-dried soil was weighed into a 50 mL falcon tube, 40 mL of 5 mM CaCl_2 and 2 drops of chloroform (CHCl_3) were added, and shaken end-over-end for 18 hours at 25 °C. The samples were filtered through Whatman 42 filter papers into sterile 70 mL polyethylene vials before a 30 mL aliquot was pipetted into a 50 mL volumetric flask, the colouring reagent added, and topped up to volume with the extracting solution (5 mM CaCl_2). Similarly, the standards were made up to volume with the extracting solution. The standards contained P concentrations of 0, 25, 50, 100, 200, 300 and 400 $\mu\text{g P L}^{-1}$.

2.5.9 Digestion of plant and soil samples

In order to determine the total P, Ca, Mg and K in a plant sample it is necessary to oxidise the C in the plant material and convert the nutrients to inorganic forms. Two main oxidation methods are dry-ashing and wet oxidation (Sparks, 1996; Sollins et al., 1999). The most common wet-oxidation methods are the tri-acid (nitric/ perchloric /sulphuric acids) digestion, sulphuric acid/hydrogen peroxide digestion and nitric/perchloric acid digestion. The choice of method depends on the availability of appropriate facilities, the element of interest, and the potential of some acids to precipitate the element of interest. In this study, the nitric/perchloric ($\text{HNO}_3/\text{HClO}_4$) acid digestion method (Kalra, 1998; Olsson et al., 2000; Tiarks et al., 2003) was employed with some modifications. The HNO_3 is a more powerful oxidant than sulphuric acid (Harmon and Lajtha, 1999), given that woody samples were also digested along with foliage materials. In addition, Harmon and Lajtha (1999) pointed out that H_2SO_4 could precipitate Ca, one of the elements of interest in this study. A reference plant sample was digested along with the samples to determine the efficiency of the $\text{HNO}_3/\text{HClO}_4$ method. Initial trials in this study indicated that this method had an efficiency of 80 – 100 % for P, Ca, Mg and K, and was sufficient for comparative purposes. Thus, it was used for digesting plant foliage and woody samples in this study.

Ground plant samples, 0.5 g dry weight (60°C), were weighed into digestion tubes and added with 5.0 mL of concentrated HNO_3 and left to froth for at least 1 hour or overnight in the fume cupboard. Prior to digestion, 2 mL of concentrated HClO_4 was added to the tubes and the samples were digested according to the following steps programmed into the digestion controller: initially at 90°C for 30 minutes to allow adequate HNO_3 oxidation, followed by stepping up to 140°C for 1 hour and finally at

205 °C for 2 hours or until white fumes appeared. The tubes were allowed to cool, 10 mL deionised water added, then vortexed, before topping up to volume (75 mL) with deionised water. If the tubes dried out, 5 mL dilute acid was added before topping up to the volume.

Soil samples for total P analyses were digested similarly to the plant samples using the HNO₃/HClO₄ acid method (Sparks, 1996; Chen et al., 2002). Ground soil sample of 0.60 g was added with 5 mL concentrated HNO₃ and left for 1 hour before 2 mL concentrated HClO₄ was added prior to digestion at 130 °C for 1 hour, then the temperature was increased by 5 °C every minute until it reached 205 °C, where it was held for 40 minutes before the process was terminated. The final stage of digestion was shorter than in the method described by Sparks (1996) due to the low organic matter content of the soil. A reference soil sample with known total P was also digested along with the samples of interest to determine the efficiency of this method, and that preliminary results showed total P recoveries of 98-100 %. Thus, this method significantly decreased the turn around time for P analysis.

NB: Where the experiment involved a time series study, e.g decomposition of harvest residues, all the samples for each retrieval time were digested together as one batch so that they were subjected to the same conditions, thus allowing valid comparisons between each residue retrieval time.

2.5.10 Inorganic P (orthophosphate) analysis

Total P was measured following acid digestion by adopting the ascorbic acid method (Murphy and Riley, 1962; Rayment and Higginson, 1992; Lajtha et al., 1999). The ascorbic acid method is effective around pH 5 -7 and therefore neutralisation of the acid

digests was necessary. The colouring reagents were prepared according to the method in Rayment and Higginson (1992) and Lajtha et al. (1999). In this study plant extracts were diluted 20 - 25 times in order for the concentration to be within the concentrations of the standard solutions, which ranged from 0 - 800 $\mu\text{g L}^{-1}$. For plants, 2 mL of extract was pipetted into a 50-mL acid-washed volumetric flask, topped up with 30 ml of de-ionised water, to which was added a drop of para-nitrophenol. The neutralisation of the solution was carried out by adding dropwise 2.0 M NaOH until the solution turned slightly yellow, followed by the dropwise addition of 2 % HCl until the solution just turned colourless. Eight ml of colouring reagent was then added and the solution topped up to the volume. The resulting solution was read on a UV spectrophotometer at 880 nm after 30 minutes, when the colour intensity had stabilised.

The P concentrations of plant materials were expressed in percentage after the following formulae:

$$\text{P concentration (\%)} = \frac{C * DF * VDT * 1000}{M} * 100$$

.....Equation 4

Where

C = concentration of solution ($\mu\text{g P L}^{-1}$)

DF = dilution factor

VDT = volume of digestion tube (L)

M = Mass of digested sample (mg)

Comparisons of the P values derived from this method with that specified for the reference standard sample, and those reported by Simpson et al (2003) for samples of the same years, showed little discrepancy, thus confirming the validity of the above methodology.

Similarly, soil orthophosphate was determined by the ascorbic acid method. For soil total P analyses (section 2.5.9), 10 mL aliquots were pipetted into 50-mL acid-washed

volumetric flasks, and topped up with 30 mL of de-ionised water, before adding a drop of para-nitrophenol. Then 4.0 M NaOH was added dropwise until the solution turned slightly yellow, followed by a further drop wise addition of 2.0 M HCl until the solution just turned colourless to neutralise the solutions. Then 8.0 mL of colouring reagent was added before the solution topped up to the volume. The solution was left to stand for 30 minutes to allow the colour intensity to stabilise before total P was determined at 880 nm.

Other soil P analyses (section 2.5.5 – 2.5.8) were also added 8.0 mL of the colouring reagent and read at 880 nm after 30 minutes after the necessary preparations in the respective sections. Soil P pools were calculated similarly to the plant P but were expressed as mg kg^{-1} air-dried soil (Rayment and Higginson, 1992).

NOTE. All extractions and digestions included duplicated blanks, which contained the extracting solution only. This was to determine the background P in the extracting solution. Digestion tubes and glassware used in the determination of P concentrations were acid washed with 10% HCl prior to use.

2.5.11 *Extraction of soil exchangeable Ca, Mg and K*

Exchangeable bases were extracted by 1.0 M ammonium nitrate (NH_4NO_3) (Phillips and Greenway, 1998). In this method, 5.0 g air-dried soil was weighed into a 50 mL polypropylene centrifuge tube and added with 30 ml 1.0 M NH_4NO_3 before being shaken end-over-end for 2 hours, then centrifuged at 3000 rpm for 15 minutes to obtain clear solution. The supernatant was filtered through a Whatman 42 filter paper into a 100 ml volumetric flask. A further 2 x 30ml additions of 1.0 M NH_4NO_3 , shaking and filtration were carried out on the soil sample, and solutions were bulked into the 100 mL

volumetric flask and made to 100 mL with 1.0 M NH_4NO_3 . This solution was determined for exchangeable Ca^{2+} , Mg^{2+} and K^+ .

2.5.12 Plant and soil Ca, Mg and K analyses

Plant and soil Ca, Mg and K were determined using a flame atomic absorption spectrophotometer (FAAS) (Avanti, GBC Sigma). Plant extracts (acid digested samples) (section 2.5.9) were diluted 10 times in 10 mL centrifuge tubes before analysis to keep concentrations within the limits of those of respective standard solutions. Potassium was diluted with 9 parts de-ionised water, while Ca and Mg extracts were diluted with 5 parts Strontium (Sr) (3000 ppm) (Rayment and Higginson, 1992) and 4 parts de-ionised water in the 10 mL centrifuge tubes, using micropipettes. Soil extracts for Ca and Mg analyses were also diluted with 5 parts strontium. The Sr ion decoupled the Ca and Mg from any organic compounds, which might under-estimate Ca and Mg concentrations. Standards for Ca and Mg were also applied with Sr at the same ratio as the samples.

2.5.13 Density fractionation of soil organic matter

Density fractionation separates SOM into light and heavy fractions, taking advantage of the varying densities of soil particles. The lightest particles are usually organic debris, mostly fragments of dead roots and leaves. The light fraction organic matter (LFOM) is regarded as a relatively labile pool of soil C as it is relatively available for microbial breakdown. LFOM is defined as the pool of OM that is $> 0.45 \mu\text{m}$ in size and with a density of $< 2.0 \mu\text{m}$ (Sollins et al., 1999; Marriot and Wander, 2006a; Yamashita et al., 2006). The LFOM has been a useful indicator of soil management practices.

The LFOM is usually dispersed and separated in a heavy liquid such as sodium iodide (NaI) (Roscoe et al., 2004) or sodium polytungstate (SPT) (Sollins et al., 1999; Yamashita et al., 2006). However, SPT is increasingly preferred as it is less reactive, less viscous and non-toxic compared to NaI (Baldock et al., 1990). Thus in this study SPT was employed as the flotation medium to extract the LFOM. The ratio of soil to SPT solution varies in the literature. When the extraction involved aspirating the floating LFOM the ratio was usually larger to allow enough head space between the soil and the floating LFOM (Sollins et al., 1999). On the other hand, when it involved centrifugation before extraction, the ratio ranged between 2.5 to 4 (Marriot and Wander, 2006b; Yamashita et al., 2006).

The method employed here was adopted from that described by Marriot and Wonder (2006b) and Yamashita et al. (2006) with some modifications to suit the availability of the appropriate equipment. Two 10 g sub-samples of soil from each replicate were weighed into 40 ml falcon tubes and added with 30 mL of SPT (density: 1.75 g mL^{-1}). Preparations of the 1.75 g mL^{-1} SPT solution was as described by Sollins et al. (1999). The samples were gently shaken end-over-end for 12 minutes at 80 rpm before allowed to settle over night. Then the samples were centrifuged at 3500 rpm for 30 minutes, followed by filtering the supernatant through a pre-weighed $0.45 \text{ }\mu\text{m}$ filter paper under vacuum. The collected LFOM were thoroughly rinsed with de-ionised water three times before drying at $50 \text{ }^{\circ}\text{C}$ for 24 hours to determine the dry weight.

2.5.14 HCl – non-hydrolysable SOC

The HCl – insoluble organic C or the non-hydrolysable organic C (NHOC) represents a resistant SOM pool. The HCl acid hydrolysis solubilizes amino compounds, fatty acids, pectins, and most cellulose, including CO_2 through carboxylation, leaving behind long-

chain alkyls, waxes, lignin, and other aromatics. The NHOC gives much older ^{14}C dates compared to the bulk SOC and thus is regarded as a resistant pool of SOM (Paul et al., 1997). However, as pointed out by Sollins et al. (1999), soil could also contain lignin from recent plant residues, therefore acid hydrolysis does not provide complete separation between old and new C. This requires the need to remove recognisable plant materials prior to analysis (Sollins et al., 1999).

The method used in this study was adopted from that of Paul et al. (1997) and Sollins et al. (1999). Ten grams of whole soil was weighed into 50 mL falcon tubes and added with 40 mL NaCl (density: 1.2 g mL^{-1}) to remove identifiable plant materials by flotation (Sollins et al., 1999). The samples were shaken end-over-end for 30 minutes before being centrifuged at 2000 rpm for 20 minutes. The supernatant with identifiable plant materials was discarded, and the remaining soil dried at 50°C for 48 hours. Soil was ground to powder in a puck and ring rock grinder before two grams of soil was weighed into digestion tubes to which was added 20 mL of 6.0 M HCl. The tubes were placed into the block digester and fitted with small glass funnel to minimise loss of acid, allowing it to reflux at 116°C for 16 hours. After hydrolysis, the residues were isolated by vacuum filtration on a pre-weighed $0.45 \mu\text{m}$ nitrocellulose filter membrane, and rinsed with de-ionised water several times. The remaining residues were then dried at 50°C for 48 hours before weighing and analysis for NHOC by the CN analyser/mass spectrometer.

2.5.15 Hydrofluoric (HF) acid pre-treatment of soils

Past studies have recommended hydrofluoric acid (HF) pre-treatment of soil before ^{13}C CPMAS NMR analysis (Skjemstad et al., 1994; Schmidt et al., 1997; Mathers et al., 2002). The HF pre-treatment concentrates the organic matter of a whole soil sample,

thus improving the signal to noise (S/N) ratio and requiring fewer scans, and therefore, reduces NMR analysis time, for better resolution of spectra. In addition, HF pre-treatment removes iron (III) (Fe^{3+}) and other paramagnetic materials present in primary and secondary minerals. The iron acts as a source of both paramagnetism and ferromagnetism (Skjemstad et al., 1994). In this study the soil was sandy and the organic matter content was not more than 2 %, therefore this process was necessary for the direct study of organic structures by solid-state ^{13}C CPMAS NMR.

The method used in this study was adopted from that of Skjemstad et al. (Skjemstad et al., 1994) and Mathers et al. (2002). Five grams of ground air-dried soil was weighed into 50 ml falcon tubes to which was added 45 mL of 2% HF acid and shaken for 4 x 1 hour, 4 x 16 hours, and 2 x 64 hours in that order before extraction to remove the quartz materials. In this study, however, an extra 1 x 64 hours extraction with 3% HF, instead of 2% HF, concentration was carried out due to the large quantity of quartz still remaining. This procedure significantly reduced the NMR run time to just 1.5 hours with improved spectral resolution than those reported by Mathers et al. (2002). Each extraction was carried out following centrifugation at 2000 rpm for 20 minutes. The light fraction between each extraction was retained using Millipore 0.22 μm nitrocellulose membrane filters, and the supernatant discarded into specially labelled dangerous goods waste containers. After the final extraction, the remaining residue and light fraction were washed several times with deionised water and collected on a Millipore 0.2 μm nitrocellulose membrane filter, then dried at 50 $^{\circ}\text{C}$ for 24 hours. For these sandy soils, 4 soil sub-samples of each treatment replicate (total of 20 g) were necessary to extract adequate amounts (>150 mg) of SOM for NMR analysis due to the low C content.

2.5.16 Solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy

This study used solid-state cross-polarisation magic angle spinning (CPMAS) ^{13}C NMR to determine the chemical functional group composition of harvest residues and SOM in the exotic pine plantations (Kögel-Knabner et al., 1991; Baldock et al., 1992; Mathers et al., 2000; Kögel-Knabner, 2002). The CPMAS ^{13}C NMR allows NMR to be used for whole soils, with better resolutions (Mathers et al., 2000). It is non-destructive, does not depend on sample solubility and can analyse solid soil fractions or bulk soil samples and gives reliable information about the structure and composition of SOM (Mathers et al., 2000). The CPMAS ^{13}C NMR spectra have been greatly improved by treating SOM samples with 2% hydrofluoric (HF) acid (Skjemstad et al., 1994; Mathers et al., 2000). The proportion of the functional groups used to assess plant residue and SOM quality in NMR spectra are only estimates and therefore NMR is only semi-quantitative.

In this study, the chemistry of whole SOM were assessed by CPMAS ^{13}C NMR following pre-treatment with HF to remove paramagnetic compounds (Skjemstad et al., 1994; Mathers et al., 2002). The solid-state ^{13}C NMR spectra of both whole SOM and LFOM were obtained from the Varian Unity Inova 400 (Varian Inc., CA) spectrometer operating at a ^{13}C frequency of 100.6 MHz. Samples were packed into a 7 mm silicon nitride rotor and spun at 5000 Hz at the magic angle. A standard cross-polarization pulse sequence was applied, with a single contact time of 2 ms, acquisition time of 14 ms and recycle delay of 2.5 s (Mathers et al., 2007). A total of 2000 transients were collected for each sample over a sweep width of 50 kHz, and chemical shift values were referenced externally to the benzene C resonance of hexamethylbenzene at 132.1 ppm (equivalent to tetramethylsilane at 0 ppm). For decomposing plant residues, a total of 400 transients were collected under the same NMR conditions as whole SOM and LFOM.

The ^{13}C -NMR spectra were divided into the four main chemical shift regions: alkyl C (0 – 45 ppm), *O*-alkyl C (45 – 110), aromatic C (110 – 162) and carbonyl C (162 – 215 ppm). The *O*-alkyl C was further divided into methoxyl C (45 - 60 ppm), carbohydrate C (60 - 90 ppm) and di-*O*-alkyl C (90 -110 ppm) regions, while the aromatic C region was divided into aryl C (110-142 ppm) and phenolic C (142 – 165 ppm) regions. The relative intensities for each region were determined by integration using the Varian NMR software package (Version 6.1c, Varian Inc., CA). The alkyl C to *O*-alkyl C (A/OA) ratio and the aromaticity of SOM (Mathers and Xu, 2003) were also determined as indices of the degree of decomposition or the quality of SOM as a substrate for microbial degradation. The relative intensity or content of the functional groups, however, should be interpreted with caution due to some limitations in the quantitative reliability of solid state ^{13}C NMR (Ussiri and Johnson, 2003; Helfrich et al., 2006). Spinning side bands (SSB) appeared at 225 ppm for some spectra of the whole SOM, and would have appeared in the aromatic region, however, since these would be a small proportion of the aromatic region, and within the intrinsic error of the instrument, they were ignored during integration of the main chemical shift regions.

CHAPTER THREE

Decomposition, Nutrient Release and ^{13}C NMR Carbon Functional Group Changes of Exotic Pine Harvest Residues in Subtropical Australia

3.1 Introduction

Plant residue decomposition is an important ecological process that involves microbial respiration, and residue fragmentation along with chemical leaching. This process results in the gradual loss of mass and the recycling of C and other elements into various pools in the environment. Understanding the dynamics of this process is necessary for understanding the effect on nutrients of harvest residues, nutrient management or fertiliser scheduling, and soil organic matter storage (Anderson and Ingram, 1998; Xu and Chen, 2006). Since about 50 – 70 % of decomposition by-product is carbon dioxide (CO_2), an understanding of decomposition rates is also necessary in CO_2 accounting for greenhouse gas monitoring and estimation of soil and ecosystem C balance (Mackensen et al., 2003; Palviainen et al., 2004a; Xu et al., 2008). Furthermore, an understanding of the interactions between decomposition kinetics, biochemical characteristics and nutrient availability of plant materials is needed for C accounting and land management (Wang et al., 2004; Mathers et al., 2007).

In forest plantation ecosystems, a numbers of decomposition studies have been conducted on logging or harvest residues (Barber and Van Lear, 1984; King et al., 1997; Jones et al., 1999; Shammas et al., 2003; Blumfield et al., 2004a; Palviainen et al., 2004a). These studies consistently showed a negative single exponential decay pattern, indicating a rapid initial phase followed by a slower phase (King et al., 1997), similar to

those conducted in agro-ecosystems (Kumar and Goh, 2000). The double exponential decay model has also been used to describe this process, although some studies showed the single exponential decay model to be satisfactory, especially in predominantly woody residues (Barber and Van Lear, 1984; Shammas et al., 2003; Blumfield et al., 2004a).

Decomposition studies of harvest residues have focussed mainly on foliage, twigs, branches and stems (Barber and Van Lear, 1984; Shammas et al., 2003; Blumfield et al., 2004a). In almost all cases decomposition and nutrient release are fastest for foliage and slowest for branches and stems, and inversely proportional to size classes of branches or stems (Barber and Van Lear, 1984; King et al., 1997; Jones et al., 1999; Shammas et al., 2003; Palviainen et al., 2004b). Foliage half-lives are usually 1 – 2 years, while branches or coarse woody debris (CWD) take much longer with varying lengths of time across space (Lundmark-Thelin and Johansson, 1997; Parfitt et al., 2001; Sanchez, 2001; Blumfield et al., 2004a; Guo et al., 2006). Many studies agree that environmental conditions, residue chemical composition, decomposer community structure, and accessibility to residues largely influence the decomposition of plant residues (Barber and Van Lear, 1984; Carcamo et al., 2000; Marshall, 2000; Parfitt et al., 2001; Sanchez, 2001; Mackensen et al., 2003). Furthermore, the size, volume and density of CWD, unique to plantation or forest residues, have been shown to be important factors (King et al., 1997; Mackensen et al., 2003). Mackensen et al. (2003), however, concluded that mean annual temperature is the main driver of the decomposition of CWD in Australia.

Due to the heterogenous nature of harvest residues, residue fractions usually showed different nutrient release dynamics. In general, the foliage fraction usually showed a net release of nutrients in the first 6-12 months, with release patterns closely following

mass or C loss (Sanchez, 2001; Blumfield et al., 2004a). Foliage, and twigs to some extent, is therefore regarded as important short-term sources of C and nutrients, while branches are important in the long-term (Hyvönen et al., 2000; Parfitt et al., 2001; Laiho and Prescott, 2004). In addition, nitrogen (N) and phosphorus (P) in harvest residues usually show a net increase in the decomposition period, and therefore harvest residues are regarded as a net sink for N and P (Palviainen et al., 2004a). On the other hand, harvest residues are a net source of Ca, Mg and K (King et al., 1997; Sanchez, 2001), with K being the most mobile nutrient and Ca the least mobile (King et al., 1997; Shammass et al., 2003).

In Australia, decomposition studies of plantation species such as eucalypts (Shammass et al., 2003), radiata pine (Mackensen et al., 2003; Guo et al., 2006) and hoop pine (Blumfield et al., 2004a) have been conducted. However, there is no published information on the decomposition and nutrient dynamics of harvest residues of exotic pines such as slash pine and Carribean pine, the main plantation timber species in southeast Queensland, Australia. Harvest residues of these exotic pines had been shown to increase tree growth (Simpson et al., 2003), however, it has not been clearly shown if this effect is due to nutrients released from the residues or the mulching effect of the residues. In addition, Mackensen et al. (2003) pointed out that there is insufficient information on the decomposition of CWD in Australia, and in particular data on CWD residue biochemical composition.

In the past, understanding residue biochemical composition in relation to decomposition was often limited by laborious wet chemistry analyses. The application of solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy in the characterization of plant material carbon (C) chemistry is a step forward in understanding the chemical nature of

harvest residues. ^{13}C NMR has been used successfully in understanding the C transfer pathways and effects of residue quality on decomposition and nutrient release (Baldock et al., 1997; Kögel-Knaber, 2002; Blumfield et al., 2004a; Lorenz et al., 2004; Wang et al., 2004; Mathers et al., 2007). Many of these studies showed that as decomposition proceeds, the O-alkyl C compounds decreased while the alkyl C compounds increased concomitantly. Thus, the ratio of alkyl-to-O-alkyl C (A/O-A) was proposed as a useful indicator of decomposition. Some studies, however, suggests that the carbohydrate C-to-methoxyl C ratio (CC/MC) is a better indicator of the extent of decomposition (Blumfield et al., 2004a; Mathers et al., 2007). Carbon compounds revealed by ^{13}C NMR spectroscopy have also been linked to residue N and P transformations (Gressel et al., 1996; Wang et al., 2004; Ha et al., 2007; Mathers et al., 2007). They proved to be better predictive factors of the mineralisability of C and nutrients in plant materials than molecular level indicators such as lignin and polyphenol contents (Wang et al., 2004). Thus, this study aimed to better understand the C and nutrient dynamics of exotic pine harvest residues in southeast Queensland, as well as gaining a greater understanding of the chemical nature of the residues and how these were linked to N and P mineralisation using ^{13}C NMR. ^{13}C NMR has been used to characterise soil organic matter (SOM) under different residue management regimes in the exotic pine plantations of southeast Queensland (Mathers and Xu, 2003). However, its application to the above ground residues has not been conducted. Studies indicate that the chemical nature of harvest residues, not only influence C pool dynamics, it also has an influence on the chemistry of SOM (Mendham et al., 2002a; Mathers et al., 2003a). Thus, the main objectives of this study were to: (1) quantify the amount of C and nutrient content of slash pine harvest residues; (2) determine the decomposition and nutrient release dynamics of the residues; (3) use ^{13}C NMR spectroscopy to determine the chemical factors controlling slash pine residue decomposition; and (4) use ^{13}C NMR spectroscopy to determine the

changes in residue chemical composition following residue decomposition, and how these chemical changes would be linked to residue N and P dynamics.

3.2 Materials and Methods

3.2.1 *Site description and experimental design*

This experiment was conducted in a newly logged exotic pine plantation in Toolara State Forest described as experiment K18C in Chapter 2. The site description and experimental design were the same as described in Chapter 2. The decomposition experiment, however, was carried out in three of the four residue removal treatment plots of the macro-plots described in Chapter 2 (Fig. 2.4). Residue decomposition was carried out in micro-plots, rather than the litterbag method, to confine and incubate the residues under field conditions. The micro-plots (Fig. 2.5) were constructed from 25 cm diameter PVC pipes, which were cut into 30 cm lengths, chamfered at one end for easy insertion into the soil and drilled with 3 mm holes at the opposing end to tie down 10 mm mesh covers (Blumfield et al., 2004a). One hundred and seventy one of these micro-plots were constructed, divided equally between the three residue-removal treatment plots. The micro-plots were inserted 20 cm into the ground using the rear hydraulic arm of a backhoe around the edges of each plot so as not to disturb the existing macro-plot experiment (Fig. 2.5a). The soil surface inside the micro-plots was brushed clean prior to placement of residues inside micro-plots for maximum contact with the mineral soil.

3.2.2 *Total harvest residue determination and characterisation*

Total harvest residue production was estimated immediately following clear-cutting. The fresh harvest residues were sampled inside 11 quadrats (1.0 m²), positioned along a transect line, and were about 10 m apart within the plantation area. The residues were

transported to the laboratory and characterised into foliage, branch (15 – 40 mm diameter), twigs or small branches (<15 mm diameter), barks and stems (65-100 cm diameter) before fresh weight was determined. Sub-samples of each residue types were oven dried at 60 °C for 120 hours to constant mass to determine the residue dry weight of each quadrat. Twigs, branches and stems were disced before oven drying.

3.4.3 *Harvest residue preparations and incubation*

Fresh residues of each type were sub-sampled from the 11 quadrats for the decomposition experiment, and weighed on a dry weight basis into sealable plastic bags before transport back to the field. The amounts weighed were as follows: (1) foliage (80.0 g); (2) twigs or small branches (30.0 g); (3) branches (15 – 40 mm diameter) (55.0 g); (4) bark (23.0 g); and (5) combined (187.0 g), which is a combination of foliage, twigs, branches and barks in the same proportion as each residue type. The amount of each residue type was determined from the relative proportion of each type in relation to the total harvest residue production. In the field, each residue sample was transferred into the micro-plots described above and the tops of the micro-plots were covered with a 10 mm mesh to prevent entry of other materials or loss of sample.

Residue mass loss was determined every four months for the first year and every 6 months subsequently (0, 0.33, 0.67, 1.0, 1.5, 2.0 and 2.5 years or 0, 120, 240, 360, 540, 720 and 900 days). The residues were carefully removed from the micro-plots and transferred into sealable plastic bags before transport back to the laboratory, where they were oven dried at 60 °C for 120 hours before being thoroughly cleaned of contaminating sand prior to the determination of mass loss. Sub-samples of each residue types were ground in a puck and ring mill prior to chemical analysis. Individual components of the combined residues samples were ground separately and mixed again

according to the relative proportion of the remaining mass of each residue type prior to chemical analysis.

3.4.4 Chemical analyses

Harvest residues were analysed for total C and N concentrations using a Eurovector 3000 elemental analyser (Milan, Italy) coupled to a GVI Isoprime mass spectrometer (Manchester, UK). Residue total P, Ca, Mg and K concentrations were analysed following concentrated nitric/perchloric ($\text{HNO}_3/\text{HClO}_4$) acids digestion of samples (Kalra, 1998; Olsson et al., 2000). Total P was determined by the ascorbic acid method (Murphy and Riley, 1962), while foliar Ca, Mg and K concentrations were determined by flame atomic absorption spectrophotometer (FAAS) (Avanti, GBC Sigma). Samples of all intervals (mass loss measurements) were digested and analysed as one batch so that samples could be subjected to the same analytical conditions, allowing valid comparisons across the time intervals.

Harvest residue chemical composition, especially changes in C functional groups, over time was determined by solid-state cross polarisation magic angle spinning (CPMAS) ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of the decomposing residues were obtained from the Varian Unity Inova 400 (Varian Inc., CA) spectrometer operating at a ^{13}C frequency of 100.6 MHz. Samples were packed into a 7 mm silicon nitride rotor and spun at 5000 ± 10 Hz at the magic angle. A standard cross-polarization pulse sequence was applied, with a single contact time of 2 ms, acquisition time of 14 ms and recycle delay of 2.5 s (Mathers et al., 2007). A total of 400 transients were collected for each sample over a sweep width of 50 kHz, and chemical shift values were referenced externally to the benzene C resonance of hexamethylbenzene at 132.1 ppm (equivalent to tetramethylsilane at 0 ppm).

The ^{13}C -NMR spectra were divided into the four main chemical shift regions: alkyl C (0 – 45 ppm), *O*-alkyl C (45 – 110), aromatic C (110 – 165) and carbonyl C (165 – 215 ppm). The *O*-alkyl C region was further divided into methoxyl C (45 - 60 ppm), carbohydrate C (60 - 92 ppm) and di-*O*-alkyl C (92 -110 ppm) regions, and the aromatic C region was divided into aryl C (110-142 ppm) and *O*-aryl C (142 – 165 ppm) regions. The relative intensities for each region were determined by integration using the Varian NMR software package (Version 6.1c, Varian Inc., CA). The alkyl to *O*-alkyl C (A/OA), carbohydrate/methoxyl C (CCMC), (aryl + *O*-aryl C)/*O*-alkyl C and the (Aryl + *O*-aryl C)/Carbonyl C ratios were also determined as indicators of the extent of decomposition or residue quality (Blumfield et al., 2004a; Mathers et al., 2007).

3.4.5 Calculations and statistical analyses

Nutrient contents of residues at each interval were determined by multiplying the nutrient concentrations with the residue mass remaining for each residue type prior to calculations of the percentage nutrient remaining. The decomposition and nutrient release rates of each residue type were determined by the first order single exponential decay model as follows:

$$M_t = M_0 e^{-kt} \quad \text{.....Equation 5}$$

where M_t is the mass at each interval, M_0 is the initial mass of each residue type and k is the decay constant (Guo et al., 2006). The half-life ($t_{0.5}$) of each residue type was derived from the single exponential decay equation (Guo et al., 2006) as follows:

$$t_{0.5} = -\ln 0.5/k \quad \text{.....Equation 6}$$

Analysis of variance, simple linear correlations, regression and least significant difference (LSD) analyses were carried out on all parameters. The means presented for ^{13}C NMR functional groups were from three field sample replicates, run under the same instrumental conditions (Mathers et al., 2007). The Statistix software (Version 8.0) was

used to carry out all statistical analyses, while the Sigmaplot software (Version 10.0) was used to test the validity of the exponential decay model and calculate the rate constants before residue half-lives were determined.

3.3 Results

3.3.1 Harvest residue quantities and nutrient contents

In general, initial nutrient analyses of harvest residue fractions showed that initial total C concentration were not significantly different between the residue fractions, while N, P and K concentrations were significantly greater in the foliage than other residue fractions (Table 3.1). Bark and branches, on the other hand, contained the lowest nutrient concentrations, while the combined and twig fractions were intermediate. On the other hand, the twigs have significantly greater Ca and Mg concentrations than the foliage. In contrast, the initial C/N ratio was significantly lower for the foliage than the other residues, and highest for the bark fraction (Table 3.1).

Table 3.1. Initial carbon and nutrient concentrations of exotic pine harvest residues

Residue Type	C (%)	N (%)	C/N	P (%)	Ca (%)	Mg (%)	K (%)
Foliage	48.09 a ¹	0.730 a	66.15 d	0.078 a	0.141 bc	0.132 a	0.335 a
Branch	47.23 a	0.147 d	326.08 b	0.008 d	0.113 bc	0.054 bc	0.034 c
Twigs	48.57 a	0.220 c	219.44 c	0.017 c	0.249 a	0.089 ab	0.099 c
Bark	47.91 a	0.113 d	427.29 a	0.006 d	0.055 c	0.029 c	0.036 c
Combined	48.41 a	0.443 b	109.01 d	0.042 b	0.158 ab	0.093 ab	0.238 b

¹Means followed by the same letter in each column are not significantly different (p>0.05).

The quantity of each residue fraction shows that foliage comprised about 42% of the total harvest residue biomass (Table 3.2). The woody components, branches and twigs, made up 45% of the residues, while stems (data not shown) contributed another 3.0 t ha⁻¹ of harvest residue biomass. Therefore, total harvest residue production was estimated to be between 36 - 40 t ha⁻¹. The total residues on site, including litter (10 t ha⁻¹), were estimated to be about 46 – 50 t ha⁻¹. Overall, harvest residues on the plantation surface contained approximately 17.0 t ha⁻¹ C, 140 kg ha⁻¹ N and 9.0 kg ha⁻¹ P, while the other nutrients ranged from 29 kg ha⁻¹ to 60 kg ha⁻¹ (Table 3.2).

Table 3.2. Residue total biomass and initial nutrient content of harvest residues in an exotic pine plantation southeast Queensland.

Residue	Biomass (t ha ⁻¹)	C (t ha ⁻¹)	N (kg ha ⁻¹)	P (kg ha ⁻¹)	Ca (kg ha ⁻¹)	Mg (kg ha ⁻¹)	K (kg ha ⁻¹)
Foliage	14.8 (3.7)*	7.1 (1.8)	108.2 (27.1)	6.7 (1.7)	20.9 (5.2)	16.1 (4.1)	49.7 (12.5)
Branches	10.5 (2.2)	5.0 (1.1)	15.4 (3.3)	0.9 (0.2)	11.8 (2.5)	6.5 (1.4)	3.6 (0.8)
Twigs	5.6 (1.4)	2.7 (0.7)	12.3 (3.2)	1.0 (0.3)	13.9 (3.6)	4.1 (1.1)	5.5 (1.4)
Bark	4.4 (2.1)	2.1 (1.0)	5.0 (2.5)	0.3 (0.1)	2.4 (1.2)	2.3 (1.1)	1.6 (0.8)
Total	35.5 (13.0)	16.9 (4.6)	141 (36)	8.9 (2.3)	51.4 (12.5)	29.0 (7.7)	60.4 (15.5)

*In parenthesis are standard errors for each mean

3.3.2 Residue decomposition and nutrient release

The decomposition and nutrient release patterns of harvest residues are presented in Fig. 3.1. It shows that mass loss over time is greatest in the foliage compared to the other residue fractions, and decreases in the order: foliage>combined>twigs>branches>bark (Fig. 3.1a). The first order single exponential decay model accounted for more than 90%

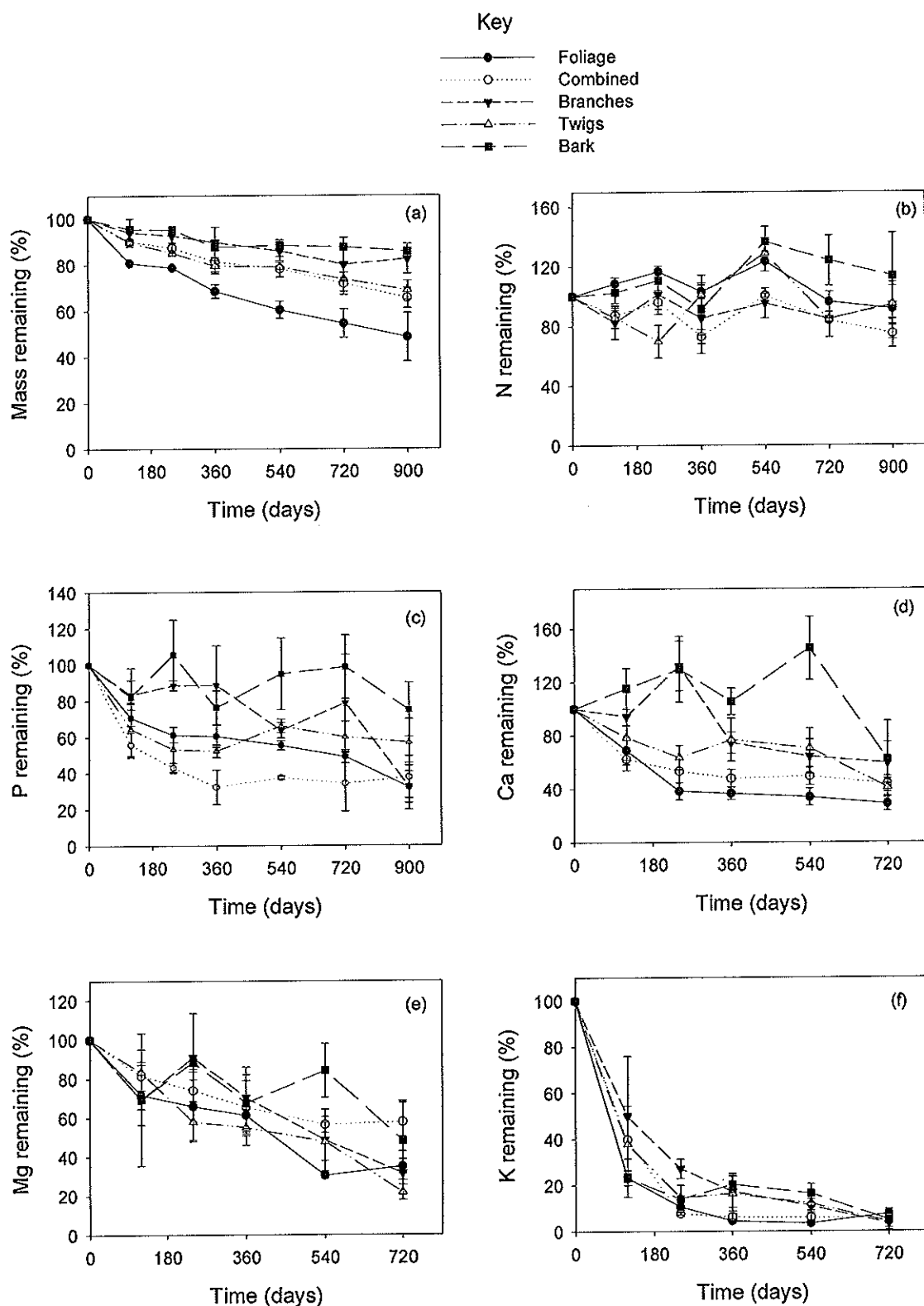


Fig. 3.1. The decomposition and nutrient release patterns of slash pine harvest residues in sub-tropical Australia, where the bars are standard deviations from the means.

of the variation ($p < 0.005$) in mass loss of the residues, except that of the bark where the model could only explain 83% of the variation in mass loss after 2.5 years (Table 3.3).

Rate constants obtained from the regression model showed that the decomposition rate was significantly higher for the foliage than the other residue fractions. The bark and branches had the lowest decomposition rates. Twigs appear to decompose faster than the combined residues, although the LSD analyses suggest that they could be similar.

Table 3.3. Residue decomposition rates and mass half-lives in an exotic pine plantation derived from the exponential decay model (Equations 5 and 6).

Residue type	Decomposition rate, k_e (year^{-1})	Half-life (years)	Decay model fit (r^2 and p values)
Foliage	0.29 (0.05) ^a a ^b	2.5 (0.4) c	0.96, $p < 0.001$
Branch	0.078 (0.04) c	10.8 (5.3) ab	0.92, $p < 0.001$
Twigs	0.15 (0.02) b	4.8 (0.7) bc	0.93, $p < 0.001$
Bark	0.050 (0.01) c	14.5 (3.5) a	0.83, $p < 0.01$
Combined residues	0.10 (0.03) bc	7.5 (2.5) bc	0.98, $p < 0.001$

^a In parenthesis are standard deviations

^b Means followed by the same letter in each column are not significantly different ($p > 0.05$).

The half-life of the residue fractions ranged from 2.5 to 14.5 years (Table 3.3). As expected, foliage had the shortest half-life, while bark had the longest half-life. Branches showed a large variation in half-life, possibly due to the broad class size of 15-40 mm diameter. On the other hand, the combined residues, which reflect field conditions, showed an intermediate half-life (7.5 years).

Nutrients, however, showed varying patterns of release from the residues. Nitrogen appeared to be more mobile in the twigs and branches initially, but increased over time, suggesting N immobilisation (Fig. 3.1b). Interestingly, although foliage has the highest initial N concentration (Table 3.2), it showed a relatively high N immobilisation in the first 1.5 years (540 days). This was reflected in the declining C:N ratio of the foliage (Fig. 3.2b), which reached a C:N ratio of 30:1 on the 540th day, consistent with the decline in percentage N remaining after 540 days (Fig 3.1b).

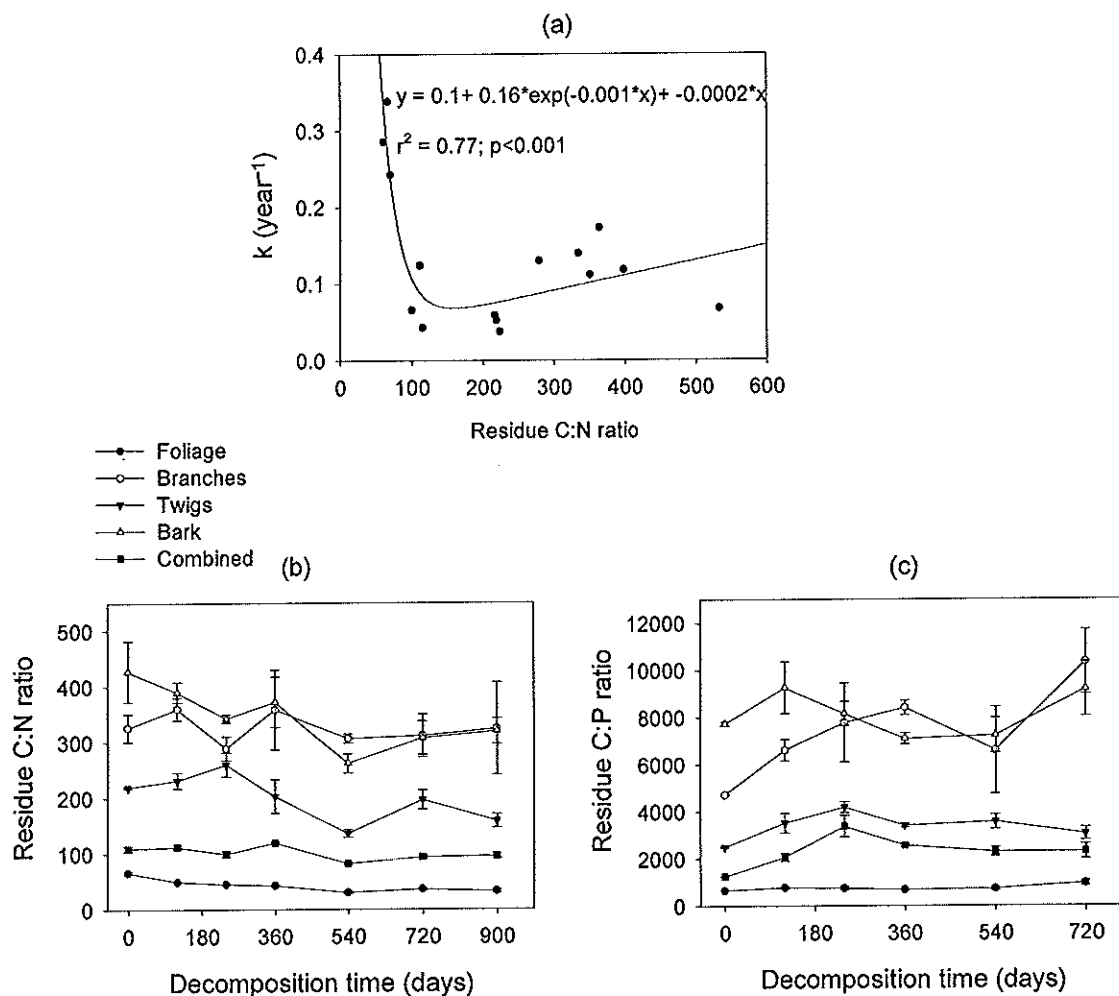


Fig. 3.2. The relationships between the initial C:N ratio and the decomposition rates (a), the C:N ratio (b) and the C:P ratio (c) over the decomposition time of slash pine harvest residues in southeast Queensland.

Phosphorus release patterns, on the other hand, showed a mixture of P mineralisation and immobilisation, depending on the residue fraction (Fig. 3.1c). The foliage and combined fractions showed a steady decline of percentage P remaining. Loss of P from the residues was evident from the increasing or at least steady C:P ratios (Fig. 3.2c), indicating that P loss was either similar to or faster than the C loss. Phosphorus, however, was least mobile in the bark fraction. Similarly, Ca was less mobile in the branches and bark, but highly mobile in the foliage, twigs and combined residues (Fig. 3.1d). Magnesium, showed a relatively faster decline in the bark compared to Ca. However, Mg release in the foliage and combined residues appeared to be slower than Ca release, while K decline was the most drastic of all the nutrients, and was highly mobile in all residue fractions.

Since the N release pattern, and Ca and P in some residue fractions, did not follow either the linear or exponential decay model the rates could not be determined in such cases. However, the determinations of nutrient release rates and half-lives showed that the rate of release was significantly higher for K than for the other nutrients. Thus, K had a significantly shorter half-life (Table 3.4), indicating that 50% of K in all residues would be released in the first 2- 4 months following clear-cut harvesting. On the other hand, the half-life of P in the combined and foliage fractions was between 1 – 2 years (Table 3.4). Overall, nutrient release rates in the foliage decreased in the order: $K > Ca > Mg > P$, while in the combined residue the rates decreased in the order: $K > P > Ca > Mg$ (Table 3.4). This study shows that at the end of 2.5 years 30-70% of P was released. Similarly, at the end of 2 years, 92-97% K, 42-78% Mg and 38-71% Ca were released from the residues, with the largest nutrient release from the foliage fraction.

Table 3.4. Nutrient release rates (k_c) and half-lives ($t_{0.5}$) of exotic pine harvest residues, where k_c and mass at $t_{0.5}$ were derived from the first order single exponential decay model.

Residue type	P	K	Ca	Mg
<u>Rates, K_c ($\times 10^{-4}$ per day)</u>				
Foliage	11 (0.7) ^a	121 (20)	23 (2)	17 (3)
Branch	- ^b	53 (6)	-	13 (6)
Twigs	-	74 (18)	9 (2)	17 (1)
Bark	-	93 (6)	-	7 (4)
Combined residues	16 (0.9)	88 (23)	13 (2)	9 (1)
<u>Half-lives (days)</u>				
Foliage	655 (67)	59 (10)	299 (28)	414 (60)
Branch	-	131 (15)	-	609 (215)
Twigs	-	99 (27)	788 (136)	401 (28)
Bark	-	75 (5)	-	1250 (564)
Combined residues	445 (45)	83 (20)	539 (67)	777 (87)

^a In parenthesis are standard deviations from the mean

^b The exponential decay regression model was not applicable.

3.3.3 ^{13}C NMR spectroscopy of decomposing harvest residues

Solid-state ^{13}C NMR spectra of the harvest residues are presented in Fig. 3.3 and relative intensity obtained through integration of the spectral regions are presented in Fig. 3.4. These results showed that the foliage fraction of harvest residues has significantly greater ($p < 0.001$) relative alkyl C intensity (19 %) than the combined residues (14%), bark (12%), twigs (11%) and branches (9%) (Fig. 3.3), and the intensity increased significantly ($p < 0.001$) with increasing decomposition time (Fig. 3.4). Twigs

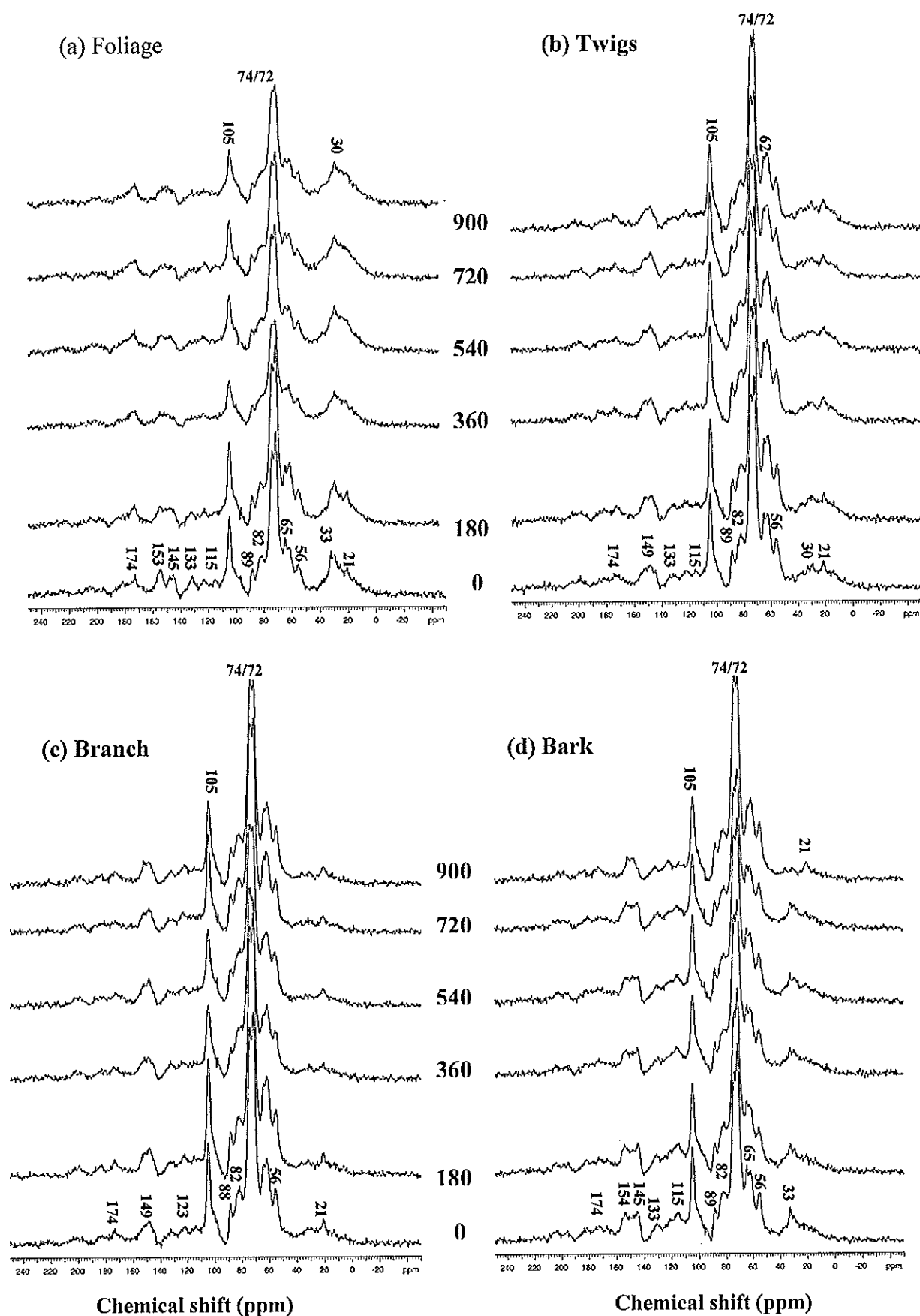
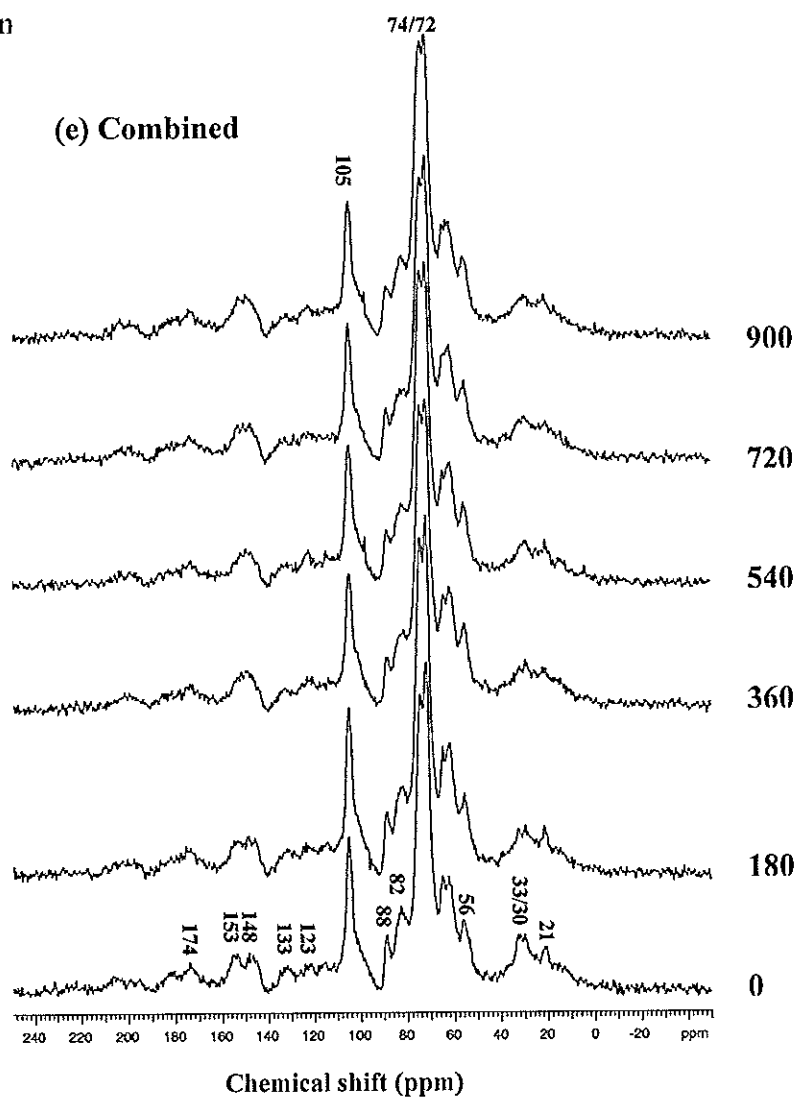


Fig. 3.3. ^{13}C NMR spectra of decomposing slash pine harvest residues: (a) foliage; (b) twigs; (c) branches; (d) barks; and (e) combined residues (next page). The superimposed

spectra for each residue type represented different stages of decomposition determined at 0, 180, 360, 540, 720 and 900 days following sampling.

Fig. 3.3 continuation



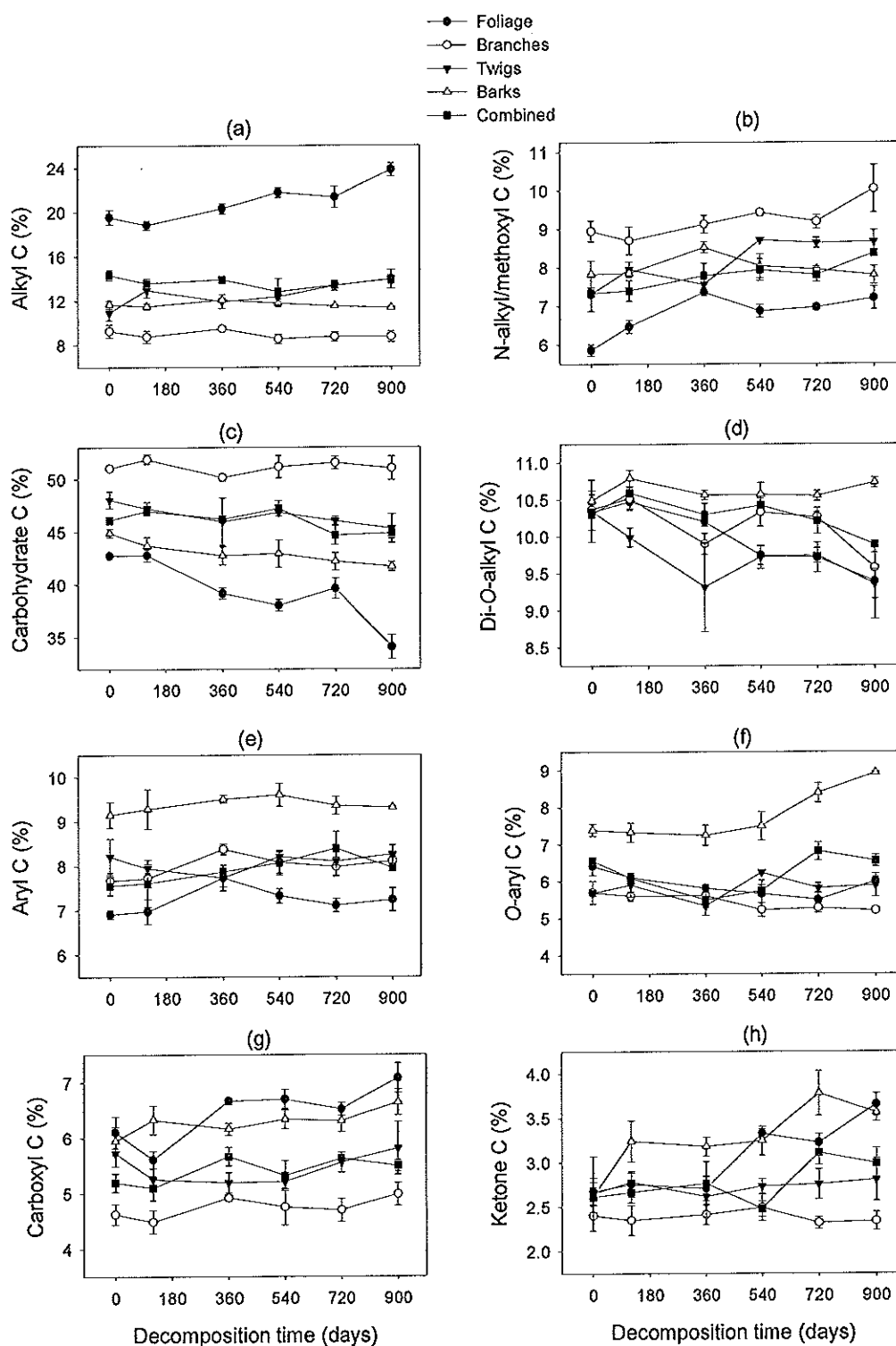


Fig. 3.4. Relative intensities of ^{13}C NMR C functional groups for each residue type over time, where the bars are standard errors of the means.

were the only other residue fraction that showed a significant increase ($p < 0.01$) in alkyl C with increasing decomposition time (Fig. 3.4a). The alkyl C region (0 – 45 ppm) was

broadener for the combined sample (Fig. 3.3e) and the foliage, indicating a greater variety of alkyl C structures (Mathers et al., 2007). Foliage, as well as the bark, twigs and the combined residues indicated the presence of long chain polymethylene structures present in lipids and cutin through the split peak at 30 and 33 ppm (Kögel-Knaber, 2002). The peak at 30 ppm eventually became more dominant over time, especially in the foliage. Peaks between 20-30 ppm are representative of branched polymethylene structures characteristics of lipids and hemicelluloses. The prominent peak at 21 ppm, especially in branches and twigs, indicated the presence of acetate associated with lipids and hemicellulose (Preston et al., 1998; Mathers et al., 2007). This peak eventually became weaker over time in all residue fractions, except in the bark where this peak became evident after 900 days (2.5 years) (Fig. 3.3d).

The O-alkyl C region (45-110 ppm) forms the largest proportion of signal intensity, contributed by the N-alkyl/methoxyl C, carbohydrates and di-O-alkyl C structures. The methoxyl C peak at 56 ppm (Fig. 3.3) indicates the presence of either lignin or N-alkyl C from amino acid groups, while the dominating doublet signal at 72/74 ppm is contributed by the C2, C3 and C5 in hexoses of cellulose and hemicelluloses. The shoulders at 65 ppm, 84 ppm and 89 ppm are largely contributed by celluloses and hemicelluloses, especially the C6 and C5 and C4 of hexoses and pentoses, respectively (Kögel-Knaber, 2002; Mathers et al., 2007). The distinctive signal at 105 ppm is that of the anomeric C1 of polysaccharides in a glycosidic bond (Kögel-Knaber, 2002; Mathers et al., 2007). In contrast to the alkyl C intensity, foliage has a significantly lower ($p < 0.001$) methoxyl C (45-60 ppm) relative intensity (>6%) than the other residue fractions, while the branch fraction has the highest methoxyl C intensity (>9%) of all the residues (Fig. 3.4b). The methoxyl C intensity also increases significantly as the decomposition time increases in all residues, except for the bark fraction. Similarly, the

carbohydrate C region (60-90 ppm), which peaks at 72/74 ppm (Fig. 3.3), was also significantly lower in the foliage and greater in the branches (Fig. 3.4c). However, in contrast to both the alkyl and methoxyl C intensities, the carbohydrate C intensity decreased with increasing decomposition time for foliage ($p<0.001$), bark ($p<0.01$), combined ($p<0.05$) and twigs ($p<0.01$). The di-*O*-alkyl C intensity, however, was not significantly different between the residue fractions initially (Fig. 3.4d). However, the signal intensity gradually became weaker over time, and was significant for the foliage ($p<0.001$), branch ($p<0.05$), twigs ($p<0.01$) and combined ($p<0.01$) fractions.

Initial aryl C (110-142 ppm) also showed significantly lower ($p<0.01$) intensity in the foliage (6.9%) than in the combined (7.6%), branch (7.7%) and twigs (8.2%), and was significantly higher in the bark (9.2%) than the other residue fractions. Aryl C, however, showed no significant increase with decomposition time (Fig. 3.4e). The aryl C region, however, showed three distinct peaks at 115, 123 and 133 ppm in all residue spectra. The peaks at 123 and 133 ppm are probably those attributed to lignin (Mathers et al., 2007). These peaks diminished over time in the foliage but remained prominent in the bark and branches (Fig. 3.3). The broad peak at 149 ppm is that of the *O*-aryl C, which splits up into two peaks at 145 and 153/154 ppm in the initial spectra of the foliage, bark and combined residues (Fig. 3.3). The branches and twigs, on the other hand, did not display this split peak, instead they showed a shoulder at 145/146 ppm. The initial *O*-aryl C intensity was significantly lower in the branch and twigs, and was significantly greater in the bark than the other residues (Fig. 3.4f). The *O*-aryl C intensity continued to increase ($p<0.001$) in the bark, but declined significantly ($p<0.05$) in the foliage and branch, as decomposition time increased. The combined residues showed a decline in *O*-aryl C, but this increased significantly again after 720 days.

The carbonyl C region (165-190 ppm) was dominated by the peak at 174 ppm and was observed in all the residue fractions (Fig. 3.3). Branches (4.6%) showed a significantly lower ($p<0.01$) carbonyl C intensity compared to the combined (5.2%), twigs (5.7%), bark (6.0%) and foliage (6.1%) fractions. Evidence of the presence of ketonic or aldehyde structures in harvest residues was displayed by the broad peak at 190-210 ppm. The ketonic C intensity was not significantly different between the residues initially, but increased significantly in the bark ($p<0.05$) and in the foliage ($p<0.001$) over the decomposition time.

3.3.4 *Relationships between decomposition and harvest residue chemistry*

Examination of relationships between initial residue chemical properties with the decomposition rates was carried out to understand the significant variations of harvest residue fractions' decomposition rates and half-lives. When analysing all the residue fractions together, simple Pearson's linear correlation analyses showed that the initial N concentration was significantly related to the decomposition rate (Table 3.5), and that a non-linear curve fit (Fig. 3.2a) indicated that the initial C:N ratio could explain about 77% of the variation in the decomposition rate. Although Table 3.5 showed that the initial alkyl C and carbohydrate C were positively and negatively related to the decomposition rate, respectively, a stepwise regression analysis eliminated these two factors from the regression model, suggesting the methoxyl C and aryl C compounds better fitted the model, explaining 70% of the variation in decomposition rates. The initial methoxyl C, aryl C and the *O*-aryl C intensities were also positively correlated with the half-life of the harvest residues (Table 3.5), suggesting that these ^{13}C NMR C groups are potential predictors of the decomposition rates or mineralisability of C and nutrients.

Table 3.5. Pearson's correlations between initial C and N concentrations, ^{13}C NMR functional group compositions and ratios, decomposition rate and half-life of each residue.

Chemical parameters (n = 15)	Total N	Rate (yr^{-1})	Half-life (years)
Rate	0.69** ^b		
Half-life	-0.34	-0.83***	
Alkyl C	0.58*	0.78***	-0.56*
Methoxyl C	-0.37	-0.73**	0.56*
Carbohydrate C	-0.31	-0.53*	0.24
Di-O-alkyl C	-0.08	-0.07	0.12
Aryl C	-0.56*	-0.62*	0.63*
O-aryl C	0.00	-0.22	0.54*
Carbonyl C ^a	0.40	0.49	-0.29

^a Carboxyl + ketone C.

^b Asterisks *, ** and *** indicate significance at $p < 0.05$, 0.01 , 0.001 , respectively.

To examine how C fraction compositions change with mass, total C, N and P over time, and to identify which C fraction or parameter is a better indicator of the extent of decomposition, Pearson's correlation analyses were carried out by examining the residue fractions together (Table 3.6) and individually as in the case for foliage (Table 3.7). Table 3.6 and 3.7 showed some inconsistencies in terms of the lack of significant correlation or whether the relationship was positive or negative, however, there were some common trends between the combined analysis and that of the foliage, and these are described in this section. These results showed that the residue total C concentration decreased significantly ($p < 0.001$), consistent with the decrease in residue mass ($p < 0.001$), as decomposition time increased (Table 3.6 and 3.7). In addition, as residue mass remaining decreased, the proportion of alkyl C increased ($p < 0.001$), while the

Table 3.6. Pearson's correlations between selected ^{13}C NMR C functional groups, their ratios, residue mass, total N and P remaining and C, N and P concentrations of slash pine harvest residues over the decomposition time when all residue types were analysed together.

Parameters (n = 72)	Time	C	N	P	N remaining	P remaining	Mass remaining
C	-0.43*** ^c						
N	0.81***	-0.40***					
P	-0.03	-0.18	0.93***				
N remaining	0.17	0.21	0.23	0.15			
P remaining ^a	-0.48***	0.27*	-0.38**	-0.21	0.26*		
Mass remaining	-0.86***	0.28*	-0.72***	-0.51***	-0.15	0.72***	
Alkyl C	0.73***	-0.32**	0.93***	0.94***	0.22	-0.26*	-0.66***
N-alkyl/methoxyl C	-0.28*	0.20	0.61***	-0.76***	-0.28*	-0.07	0.18
Carbohydrate C	-0.67***	0.23**	0.72***	-0.65***	-0.44***	0.06	0.56***
Aryl C	0.09	0.33**	-0.61***	-0.65***	0.20	0.36**	0.35**
Carboxyl C	0.22	-0.13	0.54***	0.49***	0.39**	0.06	-0.41***
A/O-A ratio ^b	0.79***	-0.36**	0.93***	0.92***	0.24	-0.28*	-0.70***
CC/MC	-0.37**	0.03	0.03	0.37**	-0.07	0.19	0.39***
AO/C ratio	-0.75***	0.31**	-0.87***	-0.82***	-0.20	0.34**	0.69***

^aAll correlations with P are obtained from a n = 60 data set.

^bA/O-A = alkyl/O-alkyl C ratio; CC/MC = carbohydrate/methoxyl C; and AO/C = (Aryl + O-aryl C)/Carboxyl C

^cAsterisks *, ** and *** indicate significance at $p < 0.05$, 0.01, 0.001, respectively.

Table 3.7. Pearson's correlations between selected ^{13}C NMR C functional groups, their ratios, residue mass, total N and P remaining and C, N and P concentrations of slash pine foliage over the decomposition time.

Parameters (n = 18)	Time	C	N	P	N remaining	P remaining	Mass remaining
C	-0.55* ^c						
N	0.84***	-0.59*					
P	-0.22	-0.11	-0.16				
N remaining	-0.23	-0.22	0.23	-0.23			
P remaining ^a	-0.90***	-0.42	-0.86***	-0.30	-0.23		
Mass remaining	-0.94***	0.45	-0.86***	0.17	0.22	0.97***	
Alkyl C	0.80***	0.62**	0.66**	0.58*	-0.31	-0.55*	-0.77***
N-alkyl/methoxyl C	0.68**	-0.27	0.64**	-0.32	-0.09	-0.81***	-0.71***
Carbohydrate C	-0.84***	0.59**	-0.70***	-0.15	0.27	0.73**	0.83***
Aryl C	0.20	0.07	0.26	-0.09	-0.08	-0.39	-0.37
Carboxyl C	0.68**	-0.60**	0.62**	0.10	-0.22	-0.65*	-0.69**
A/O-A ratio ^b	0.84***	-0.60**	0.68**	0.23	-0.32	-0.73**	-0.84***
CC/MC	-0.86***	0.49*	-0.77***	0.18	0.18	0.86***	0.88***
AO/C ratio	-0.86***	0.61**	-0.79***	-0.11	0.18	0.65**	0.82***

^aAll correlations with P are obtained from a n = 15 data set.

^bA/O-A = alkyl/O-alkyl C ratio; CC/MC = carbohydrate/methoxyl C; and AO/C = (Aryl + O-aryl C)/Carboxyl C

^cAsterisks *, ** and *** indicate significance at $p < 0.05$, 0.01, 0.001, respectively.

carbohydrate C decreased with increasing decomposition time ($p < 0.001$). This analysis showed no significant correlations between mass remaining and the N-alkyl/methoxyl C intensity when examining the residue fractions together (Table 3.6). However, individual analyses of the residues showed that mass of both foliage (Table 3.7) and twigs (data not provided) was significantly negatively related to the N-alkyl/methoxyl C intensity ($r = -0.71$, $p < 0.001$ and $r = -0.61$, $p < 0.01$, respectively). Table 3.6, on the other hand, indicated a significant positive correlation between mass remaining and the aryl C fraction ($p < 0.01$), perhaps indicating lignin compound degradation.

Total N concentration significantly increased with increasing decomposition time and mass loss ($p < 0.001$) (Table 3.6 and 3.7). Total N was also positively related ($p < 0.001$) to the alkyl C, methoxyl C and carboxyl C functional groups when residues are examined together (Table 3.6) or when the foliage was examined individually (Table 3.7). The percentage P remaining, on the other hand, was positively related to the mass remaining ($p < 0.001$) and negatively related to the alkyl C intensity ($p < 0.05$) (Table 3.6). The P concentration, however, was positively related to the alkyl C ($p < 0.05$) (Table 3.6 and 3.7) and carboxyl C (Table 3.6) compositions. In addition, while P remaining did not show a positive relationship with the carbohydrate C (Table 3.6), the correlation analysis of the foliar fraction did show a significant positive correlation of P remaining with the carbohydrate C ($r = 0.73$, $p < 0.01$) (Table 3.7) and the O-alkyl C region ($r = 0.60$, $p < 0.05$) (correlation analysis data not included in Table 3.7).

Four decomposition indicators (alkyl C/O-alkyl C [A/O-A] ratio, carbohydrate C/methoxyl C [CC/MC] ratio, (aryl + O-aryl C)/O-alkyl C [AO/O-A] ratio and (aryl + O-aryl C)/carbonyl C [AO/C] ratio) suggested in the literature were also examined in this study. The A/O-A ratio showed a significant positive correlation ($p < 0.001$), while

the CC/MC ($p < 0.01$) and AO/C ($p < 0.001$) ratios were negatively correlated with the decomposition time in both the combined analysis (Table 3.6) and the foliage fraction (Table 3.7). While these decomposition indicators showed significant relationships with decomposition and mass loss (Table 3.6 and 3.7), a closer analysis (Fig. 3.5), however, showed that the relationship between the A/O-A ratio and decomposition time was only

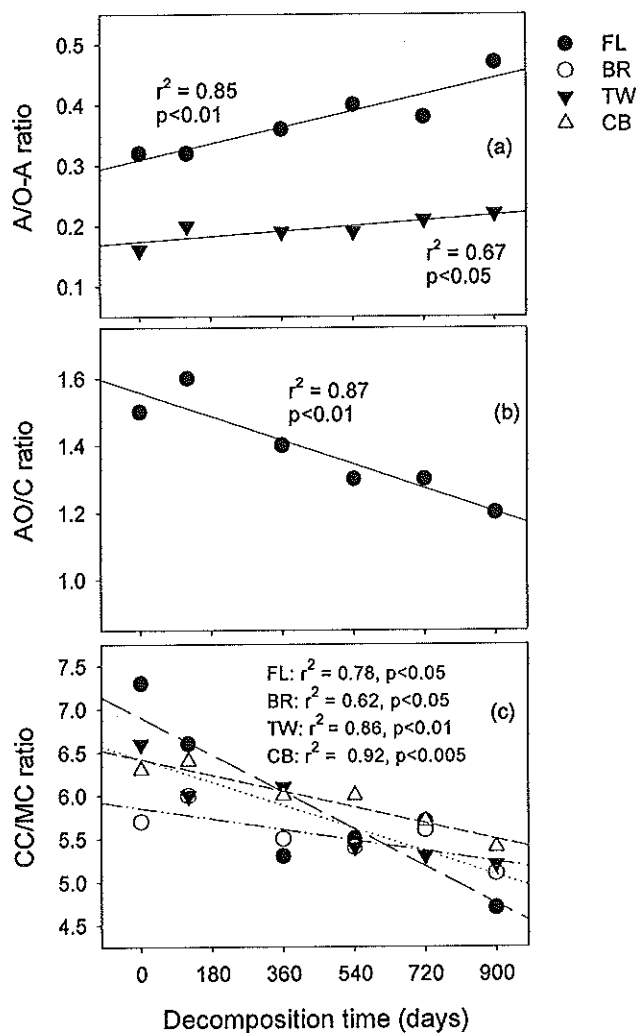


Fig. 3.5. The relationships between time and solid-state ^{13}C NMR decomposition indicators for the slash pine foliage (FL), branches (BR), twigs (TW), and combined (CB) harvest residues in southeast Queensland, where A/O-A = alkyl/O-alkyl C (a); AO/C = (Aryl + O-aryl C)/Carbonyl C (b); and CC/MC = carbohydrate C/methoxyl C (c).

significant for the foliage and twigs fractions (Fig. 3.5a). Similarly, the trend in the AO/C ratio was only significant for the foliage (Fig. 3.5b). The relationship between CC/MC ratio and decomposition time, however, was significant for all residue fractions, except for the bark (Fig. 3.5b). The AO/O-A ratio (data not shown), on the other hand, showed no significant changes with time for the individual residues, consistent with the overall Pearson's correlation analyses in Table 3.6.

3.3.5 Comparisons between current and long-term decomposition

Since the branch and bark in general showed no significant changes in alkyl C, carbohydrate C, aryl C, the current decomposition indicators (A/O-A, AO/C and CC/MC ratios) for branch and bark fractions were compared to those of 10-year-old slash pine harvest residues in a nearby exotic pine plantation (experiment 321GYM) (assuming identical environmental conditions). This analysis showed significantly lower carbohydrate C, and significantly greater alkyl C, aryl C and carboxyl C intensities in the 10 year old than the 2.5 year old harvest residues (data not shown), which resulted in greater A/O-A and AO/C, and lower CC/MC ratios for 10 year old branch and bark residues (Table 3.8). Thus, the increasing trend in the A/O-A and decreasing CC/MC were consistent with the short-term changes in these decomposition indicators.

3.4 Discussion

The characterisation of slash pine harvest residues in this study provided a valuable insight into how residues contribute to C storage and plant nutrition. While other studies in southeast Queensland, Australia, have determined the impact of harvest residues on SOM and tree growth (Mathers and Xu, 2003; Simpson et al., 2003; Chen and Xu, 2005; Xu et al., 2008), this study for the first time gave a detailed analysis of the

residues, the quantity of C and nutrients and their dynamics. This study showed that slash pine residues contain a considerable amount of C (17.0 t ha^{-1}) and N (140 kg ha^{-1}).

Table 3.8. ^{13}C NMR decomposition indicators of slash pine branch and bark residues determined at 2.5 years after clear-cutting and in comparison to 10 year-old branch and bark residues in a nearby exotic pine plantation in southeast Queensland.

^{13}C NMR decomposition indicators	Branch (2.5 yrs)	Branch (10 years)	Bark (2.5 yrs)	Bark (10 yrs)
A/O-A ratio	0.12 (0.00)	0.25 (0.02)	0.19 (0.00)	0.27 (0.02)
AO/C ratio	1.8 (0.1)	5.0 (0.3)	1.8 (0.0)	5.2 (0.1)
CC/MC ratio	5.1 (0.4)	3.1 (0.0)	5.4 (0.2)	4.3 (0.5)

^a In parentheses are standard errors of the means.

The amount of C on the plantation surface could be at least $20.0 - 30.0 \text{ t ha}^{-1}$ considering the contribution of litterfall. A significant quantity of this C will be stored in the soil as SOM through residue decomposition (Coûteaux et al., 1995; Mackensen et al., 2003; Mathers et al., 2007). The large quantity of C and N in the residues supports other work in southeast Queensland and elsewhere that residue retention increases the quantity and quality of SOM, as well as soil and foliar N (Nzila et al., 2002; Mathers and Xu, 2003; Mendham et al., 2003; Simpson et al., 2003). Thus, harvest residue retention has significant implications for both climate change mitigation, through C storage from the atmosphere, and plantation productivity.

3.4.1 *Residue decomposition dynamics*

Many studies used the exponential decay model to describe the change in the mass of logging harvest residues or coarse woody residues over time (Barber and Van Lear, 1984; King et al., 1997; Jones et al., 1999; Shammass et al., 2003; Blumfield et al.,

2004a; Palviainen et al., 2004a). In this study, the use of this model explained more than 90% of the variation in mass loss or the percentage mass remaining, and therefore its usage is justified. This pattern of mass loss indicated the initial rapid loss of water soluble C and other easily degradable C compounds followed by a slower decay of less degradable compounds (Kumar and Goh, 2000). This sequence of events is clearly demonstrated by the changes in ^{13}C NMR C functional groups in this study.

The fastest decomposition of the foliage compared to the other residue fractions (Table 3.3) is consistent with those of other conifer species (Lundmark-Thelin and Johansson, 1997; Parfitt et al., 2001; Blumfield et al., 2004a). Foliage half-life of 2.5 years in this study is similar to that of field incubated hoop pine needles in southeast Queensland (Blumfield et al., 2004a). Exotic pine needle decomposition was apparently much slower than for eucalyptus foliage in Western Australia, where a half-life of 20 weeks was reported (Shammas et al., 2003). Differences in the decomposition rates of foliar materials are probably related to residue biochemical quality and environmental factors.

The twig fraction decomposed faster than branches in this study, and this was probably size-related, as size (diameter) is inversely related to the decomposition rate (Harmon et al., 1986; Guo et al., 2006). The half-lives of branches (Table 3.3), however, were much shorter than those of similar sized *P. radiata* branches in south-eastern Australia, where *P. radiata* half-lives ranged from 19 – 62 years (Guo et al., 2006). Even the combined residue half-life of 7.5 years was shorter than those of fresh *P. radiata* thinning slash (combined) in New Zealand, where the half-life was about 13.3 years (Ganjegunte et al., 2004). The large variation in branch half-life of this study, however, was indicative of the wide range of branch sizes (15-40 mm diameter) in this class.

The slower decomposition of bark, on the other hand, was probably due to its quality. The ^{13}C NMR signals in this study indicate that bark contains significant amounts of lignin as well as tannin compounds, which will be discussed later. Ganjegunte et al. (2004) reported slow *P radiata* bark decomposition due largely to the large polyphenol and lignin content of the bark. These results are consistent with studies showing that residue decomposition is affected by both climate and resource quality (Swift et al., 1979; Laiho and Prescott, 2004; Guo et al., 2006). Although the physical dimension of the logging residues may play a part in determining the decomposition rate of residues, residue biochemical quality has been regarded as an important factor in the decomposition of harvest residues. The greatest decomposition rate and shortest half-life of the foliage fraction is consistent with the initial N content of the residues. In this study, N concentration (<1.0%) largely affected the C:N ratios of the residue fractions, and it appeared to be the major controlling factor of the decomposition of the harvest residues (Wang et al., 2004). The non-linear relationship between initial C:N ratio and decomposition rate constant, k , was consistent with that of a study by Guo et al. (2006). Many studies have shown a consistently strong correlation between the initial C:N ratio and C and N mineralisation across a wide range of residues (Tian et al., 1992; Seneviratne, 2000; Goh and Tutua, 2004). Nonetheless, the warmer Queensland climate obviously increased the decomposition rate of logging harvest residues compared to the other parts of the world. Mackensen et al. (2003) concluded that mean annual temperature is the main driver of the decomposition of CWD. However, the relatively slower decomposition rates and therefore longer half-lives of branches and bark show that they are an important sink of C and longer-term source of nutrients in the exotic pine plantations. This agrees with other studies which regard CWD as important structural and functional components of forest ecosystems (Harmon et al., 1986; Ganjegunte et al., 2004; Guo et al., 2006).

3.4.2 *Residue nutrient dynamics*

This study demonstrated that nutrients in the residues are released over time, most likely into the soil, and that this process is largely influenced by the quality of the residue fractions. The general trend of increasing N content of the residue fractions in the first 18 months (540 days) was consistent with other nutrient release studies of coniferous forests showing increased N concentrations over time (Staaf and Berg, 1982; Lundmark-Thelin and Johansson, 1997; Hyvönen et al., 2000; Ganjegunte et al., 2004; Palviainen et al., 2004a). The decreasing C:N ratio in nearly all residue fractions indicated that C loss was faster than N loss or that N immobilisation through fungal uptake occurred (King et al., 1997). This is an indication that N is probably the limiting factor to decomposition (Shammas et al., 2003). Nonetheless, while the C:N ratio of the residues, except foliage, remained well above the critical C:N ratio (30:1) for N mineralisation (King et al., 1997; Palviainen et al., 2004a), the decreasing percentage N remaining in all residue fractions after 18 months indicated the onset of N mineralisation from the residues. This observation was consistent with studies showing logging residues being net sources of N even when the C:N ratio is well above 30:1 (King et al., 1997). Furthermore, the onset of N release on the 18th month was supported by soil analyses of harvest residue treatment plots (Simpson et al., 2003; Chen and Xu, 2005). A number of studies recognise that the microbial immobilisation and subsequent slow release of N from logging residues is a mechanism to minimise leaching losses, and residues play an important role as a long-term N source (Shammas et al., 2003; Guo et al., 2006).

The consistent decline in percentage P remaining over time in residue fractions other than bark is in contrast to the N release. This was reflected in the increasing or steady C:P ratio, indicating that P loss closely followed, or was decreasing faster than C loss.

Released P may come from both soluble inorganic P compounds and organically bound P in the residues (Ha et al., 2007). However, the fact that P release closely followed mass or C loss indicates that P release was from the mineralisation of organic P compounds, and that P may be associated with easily degradable C compounds in the slash pine logging residues. The net release of P from the residues was consistent with P release from *P. radiata* thinning slash (Ganjegunte et al., 2004), although this was in contrast to P release in other woody residues, which have been shown to act as sinks of P and N (Staaf and Berg, 1982; O'Connell, 1988; Shammas et al., 2003; Palviainen et al., 2004a). This study, therefore, suggests that slash pine residues are an important source of P immediately after clear-cutting, consistent with a study showing harvest residues as the source of soil solution and surface water P immediately after clear-cutting (Palviainen et al., 2004a).

The rapid release of K in all residue fractions, even in the bark and branches, agrees with other studies indicating the mobility of K relative to other nutrients. However, while the literature indicated K loss of 80-90% in 3-4 years in other conifer species (Palviainen et al., 2004b), this study of slash pine residues showed K losses of 92-97 % in just two years. The faster release of K relative to N and P is due to its presence in plants as water-soluble salts, rather than being structurally bound to organic tissues (Shammas et al., 2003; Ganjegunte et al., 2004; Palviainen et al., 2004b). The highest initial K release of the foliage fraction compared to the other residue fractions is consistent with other studies showing that the higher the initial K concentration (see Table 3.2), the faster the quantitative release of K (Laskowski et al., 1995; Palviainen et al., 2004b).

Many studies reported that Ca generally accumulates in woody residues, especially branches and bark (King et al., 1997; Shammas et al., 2003; Palviainen et al., 2004b). Shammas et al. (2003) reported accumulation of Ca in *E. globulus* residues to be large in the first year, especially for branches and bark, consistent with that of the bark of this study. The accumulation of Ca is thought to be from external sources, through wet and dry deposition or adsorption from exchange sites (Staaf and Berg, 1982). Some studies have shown that Ca is transferred by fungi to the residues from the surrounding soil and deposited as oxalate salts (O'Connell et al., 1983; Connolly and Jellison, 1995; Shammas et al., 2003). Calcium is believed to stimulate some species of white rot fungi involved with lignin decomposition (Johansson, 1994), which might explain Ca immobilisation in the bark rather than the foliage (Fig 3.1). This study shows that slash pine foliage is an immediate source of Ca, followed by twigs and branches, consistent with the studies showing foliage and twigs as important short-term sources of nutrients, while branches are important long-term sources of nutrient (King et al., 1997; Hyvönen et al., 2000; Laiho and Prescott, 2004). In contrast to Ca, Mg showed a net release in all residue fractions over time, similar to those reported for *P. radiata* slash thinnings in New Zealand (Ganjegunte et al., 2004) and for *E. globulus* in southwestern Australia (Shammas et al., 2003). Studies of *E. globulus*, showed that Mg and P releases tend to follow mass loss of residues (Shammas et al., 2003). The subsequent decreases in N, P, K, Ca, Mg and K content from slash pine harvest residues were consistent with soil analyses conducted in residue treatment plots in southeast Queensland, showing higher concentrations of these nutrients (Mathers and Xu, 2003; Simpson et al., 2003).

3.4.3 ¹³C NMR spectroscopy of slash pine harvest residues

This study again demonstrated that organic matter is continuously transformed into different chemical compounds during decomposition (Baldock and Preston, 1995;

Gregorich et al., 1996; Kögel-Knaber, 2002). These changes in chemical compounds provide a greater understanding of C dynamics, and a number of studies have also shown that these compounds are linked to N and P mineralisation (Gressel et al., 1996; Wang et al., 2004; Ha et al., 2007; Mathers et al., 2007).

The ^{13}C NMR spectra presented in this study were similar to those of hoop pine and eucalypt harvest residues (Mathers et al., 2003b; Mathers et al., 2003a). Many studies agree that the chemical shift region of 0-45 ppm represents the alkyl C compounds, which constitutes long chain aliphatic structures such as lipids (Kögel-Knaber, 2002; Mathers et al., 2007). The loss of signal intensity at 21 ppm over time seen in this study had been attributed to the loss of hemicellulose by Mathers et al (2003b) in a study of hoop pine harvest residues. Other studies have also shown that amino acid groups may also contribute to the signal intensity of the alkyl C region (Kögel-Knaber, 2002; Ha et al., 2007). This is consistent with the greater initial alkyl C intensity of the foliage, which has a higher N concentration compared to the other residue fractions. The increasing alkyl C intensity during decomposition, however, is believed to be the accumulation of recalcitrant microbial by-products or selective preservation of resistant, or insoluble aliphatic macromolecules such as cutan and suberin (Ussiri and Johnson, 2003; Winkler et al., 2005; Mathers et al., 2007). It has also been attributed to increasing cross-linking of long-chain alkyl compounds (Kögel-Knabner et al., 1992). The degradation of O-alkyl C, especially carbohydrates, and lignin structures into aliphatic hydroxy acids and alcohols (Wershaw et al., 1996) may also have contributed to the increase in alkyl C intensity as decomposition progressed.

The strong signal of the O-alkyl C region (45-110 ppm) demonstrates the dominance of carbohydrate compounds such as cellulose and hemicellulose in plant materials. In other

^{13}C NMR decomposition studies the signal at 56 ppm, which has been assigned to the N-alkyl and methoxyl C, is largely contributed by the methoxyl C of lignin (Mathers et al., 2003b; Mathers et al., 2007). The contribution of lignin methoxyl C to the peak at 56 ppm was supported by the increasing methoxyl C intensity over time in this study. The increase in lignin is most likely due to discrimination during microbial degradation. The decreasing O-alkyl C signal of the fractions is linked to the ease at which these carbohydrate compounds are degraded by micro-organisms. Therefore, this study is consistent with many studies showing a decrease in O-alkyl C over time and a concomitant increase in the alkyl C intensity (Mathers et al., 2007).

The aryl C region (110-142 ppm) has been predominantly assigned to C atoms associated with lignin (Kögel-Knaber, 2002; Mathers et al., 2007). The peaks at 115, 123/124 and 133 ppm in the present study are most likely those contributed by the C3, C5 in p-hydroxyphenyl units, C6 of guaiacyl units and C1 of guaiacyl units of lignin, respectively (Kögel-Knaber, 2002). The lack of change in the composition of aryl C region with time, when all residues were regressed together or individually was consistent with a study of hoop pine logging residues, where the aryl and O-aryl C intensities were not related to decomposition (Mathers et al., 2003b). This is in contrast to studies of other more decomposable plant materials which showed a negative relationship between aryl C and decomposition time (Mathers et al., 2007). The duration of this study may have been too short to reveal the changes in aryl C intensity, considering the slow rate of change in the O-alkyl C region in the branches and bark. The foliage fraction indicated an increase in the aryl C in the first year but decreased subsequently (Fig. 3.4), probably due to lignin degradation.

The signal at 145 ppm, which is more prominent for bark and foliage, is highly indicative of tannins (Preston et al., 1997; Kögel-Knaber, 2002). Tannins slow down microbial attack due to their ability to bind and therefore protect protein molecules (Kögel-Knaber, 2002; Mathers et al., 2007). The dominant peak at 149 ppm in the O-aryl C region of the twigs and bark is consistent with the C3 and C4 of guaiacyl units of lignin common in gymnosperms (Kögel-Knaber, 2002). However, the splitting of the O-aryl C region of the foliage and combined fraction at 148 ppm and 153 ppm has been frequently found in lignin from angiosperms, which contains both guaiacyl and syringyl units of lignin (Kögel-Knaber, 2002). This splitting of the O-aryl C region was also noted for *P. radiata* needles (Parfitt and Newman, 2000), and may indicate that gymnosperm foliage might contain equal proportions of these lignin units. Except for the twigs, the lack of significant change in the O-aryl C intensity was consistent with that of the aryl C. However, as shown in the results the initial aryl C and O-aryl C intensities were significantly related to the decomposition rates and half-lives of residues, and therefore are potentially important regulators of the decomposition of slash pine logging residues. This is consistent with studies showing a negative correlation between C mineralisation and initial aryl C and O-aryl C (Wang et al., 2004). These compounds are indicative of lignin compounds, which have inhibitory effects on the decomposition of logging residues (Kögel-Knaber, 2002; Mathers et al., 2003b; Ganjegunte et al., 2004; Mathers et al., 2007). This study suggests that the methoxyl C and aryl C concentrations are potentially useful predictors of residue decomposition rates. In fact, Wang et al. (2004) reported that initial aryl C and O-aryl C better correlated with C mineralisation than did lignin or polyphenol. They recommended that classification of organic C based on NMR C types, rather than in molecular level composition, would provide a better assessment of the mineralisability of C. The use of ^{13}C NMR C types is further advantageous since it eliminates the need

to carry out lengthy wet chemical extractions involved in determining lignin or polyphenol contents.

Carboxyl groups and amides, especially from proteins, contribute to the peak at 174 ppm (Kögel-Knaber, 2002). In contrast to aryl C and O-aryl C, the carboxyl C intensity increased significantly over time (Fig. 3.4). This is especially so for the foliage fraction as indicated in the regression with time (Table 6). This increase in the carboxyl C intensity is consistent with a study by Wershaw et al. (1996) showing increasing carboxylate C from stage 1 to stage 4 of decomposition, using ^{13}C NMR and FTIR spectroscopy. They suggested that the increase is attributed to the oxidative degradation or ring-fission of lignin components, which led to the formation of carboxylic acids on the cleaved ends of the phenolic rings. The lack of a significant increase in aryl C and O-aryl C in most residue fractions indicates the degradation of lignin and therefore supports the above proposition.

3.4.4 Relationships between decomposition and harvest residue chemistry

A number of studies have linked residue chemistry as revealed by ^{13}C NMR spectroscopy to C, N and P mineralisation (Gressel et al., 1996; Wang et al., 2004; Ha et al., 2007; Mathers et al., 2007), in contrast to other studies showing no useful predictive ^{13}C NMR C chemistry to mass loss (Preston and Trofymow, 2000). This study examined these linkages through simple Pearson's correlation. Although, there were some discrepancies in correlations between the combined examination (Table 3.6) and that of the foliage (Table 3.7) there are some common trends, which appeared to be biologically meaningful and therefore are discussed here.

The significant positive correlation between the alkyl C and carboxyl C (the main component of the carbonyl C region) to the total N and P concentrations is consistent with those studies mentioned immediately above. It indicated that N was associated with amino acids, proteins, cutins and suberins (Mathers et al., 2007), and with proteins and amides in the carbonyl C regions (Ha et al., 2007), which increased with the decomposition in the present study. The significant negative relationship between foliage P remaining and carboxyl C (Table 3.7) is also consistent with studies showing a significant positive correlation between carbonyl C and soil solution P (Gressel et al., 1996; Ha et al., 2007). This, however, may be related to the ability of carboxylates to increase soil solution P by displacing P from anion sorption sites and/or chelating Fe (Iyamuremye et al., 1996; Ha et al., 2007). The association of P with the alkyl C supports work showing strong correlation of monoester P with alkyl C, and suggest that the mineralisation of monoester P is linked to the breakdown of structural components (cutin and suberin) of plant materials (Gressel et al., 1996). Ha et al. (2007) further suggest P association with the lipids in the alkyl C region. The increase in alkyl C with decreasing mass remaining or increasing mass loss, is consistent with the increase in the cross-linking of long-chain alkyl compounds during humification or the selective preservation of resistant or insoluble aliphatic biomacromolecules such as cutan or suberin (Kögel-Knabner et al., 1992; Winkler et al., 2005; Mathers et al., 2007).

The O-alkyl C components (carbohydrate C and N-alkyl/methoxyl C) also showed a negative relationship with N content for the foliage. This inverse relationship suggests that the immobilisation of N is necessary for the mineralisation of readily decomposable compounds such as carbohydrates. The positive relationship between carbohydrate C and mass remaining (Table 3.6), suggests that mass loss is due to the loss of relatively decomposable biopolymers such as cellulose. Furthermore, the positive relationship

between carbohydrate C, P remaining and mass loss of the foliage (Table 3.7) indicates that P mineralisation is associated with these compounds or at least the decomposition of the residues, and explains the significant decline in P over time (Fig. 3.2). This is supported by the work of Gressel et al. (1996) which showed a significant negative correlation ($r = -0.76$) between soil inorganic P and the O-alkyl C of decomposing litter. This study clearly demonstrates that the behaviour of P in the foliage and to some extent in the other residue fractions is closely linked to the changes in C chemistry of the residues over time, and that initial C chemistry has a greater influence on the release of N and P.

The A/O-A ratio has been proposed as an indicator of the extent of decomposition of plant residues or organic matter (Mathers et al., 2007). However, its lack of correlation with time in the decomposition of branches is consistent with other studies suggesting its unsuitability for branches (Baldock et al., 1997). This is probably due to the slow decomposition of branches, and therefore little variation of the A/O-A ratio. The time factor involved is demonstrated by the much higher A/O-A ratio of 10 year old woody and bark materials relative to the 2.5 year old materials of the present study (Table 3.8). The significant relationship between the CC/MC ratio and decomposition time in all residue fractions, except the bark, however, suggested that it might be a better decomposition indicator compared to the other parameters in the shorter term. Studies by Blumfield et al. (2004a) and Mathers et al. (2007) have also reported the usefulness of the CC/MC ratio as an indicator of the extent of decomposition. On the other hand, the aryl + O-aryl C/carbonyl C (AO/C) ratio used by Matthers et al. (2003b) and McColl and Powers (1998) showed significant variation over time in the foliage only, while the (aryl + O-aryl C)/O-alkyl C ratio (Mathers et al., 2007) was not useful in this study.

3.5 Conclusion

This study shows that exotic pine harvest residues contained significant amounts of nutrients, which are released at varying rates into the soil. It shows that while N release is slow, P release is faster and closely follows mass loss, indicating that exotic pine residues are an immediate source of P during the establishment of subsequent rotations. The rapid release of K, Ca and Mg explained increased concentrations of these nutrients in the soil as reported by other studies. In general, the decomposition and nutrient release of exotic pine residues in southeast Queensland are comparatively faster than those reported by other studies. The ^{13}C NMR studies of the harvest residues revealed the heterogenous nature of the quality of the residues, which influenced the varying rates of decomposition of the residue fractions. It also showed that the C chemistry composition of the residues changes over time, with the CC/MC ratio being a better decomposition indicator across a number of residue fractions in the short-term. Changes in ^{13}C NMR functional groups were also strongly linked to the mineralisation of C, N and P from the residues.

CHAPTER FOUR

Short-term Changes in Labile Carbon, Nitrogen and Phosphorus Pools under Different Residue Management Regimes Following Clear-cut Harvesting of an Exotic Pine Plantation in Subtropical Australia

4.1 Introduction

Many studies have shown that harvest residue retention is an important strategy for soil organic matter (SOM) maintenance and nutrient availability for plantation trees through residue decomposition. In southeast Queensland, Australia, harvest residue retention is a relatively new management practice and recent assessments of the impact of residue retention in a second rotation exotic pine plantation showed increased soil total C and N in residue retention treatments (Mathers and Xu, 2003; Simpson et al., 2003; Chen and Xu, 2005). Furthermore, a ^{13}C nuclear magnetic resonance (NMR) study of SOM under residues also revealed improved quality of SOM at age two years (Mathers and Xu, 2003).

However, while these within-rotation studies provided valuable insight into the impact of the residues, there are currently little inter-rotation studies, especially on the impact of clear-cut harvesting on carbon (C) and nitrogen (N) dynamics in southeast Queensland (Blumfield and Xu, 2003). The inter-rotation period represents an important phase in the establishment of subsequent rotations, especially for seedling establishment, therefore, understanding the impacts of clear-cut harvesting and residue management on labile C and N pools during the inter-rotation period are critical in predicting nutrient availability for the seedling establishment to canopy closure phases. Studies in the northern hemisphere, however, reported significant mineralisation of C

and N during this period, and their subsequent decline due to leaching losses (Olsson et al., 1996; Carter et al., 2002). Similar observations were reported for *Pinus radiata* plantations in south-eastern Australia, where net N mineralisation increased threefold following clear-cutting, leading to an increased loss of both SOM and N through CO₂ evolution and N leaching (Smethurst and Nambiar, 1990b). A number of studies showed that clear-cutting had a much greater impact on C and N pools than residue retention resulting from different harvesting intensities (Olsson et al., 1996; Carter et al., 2002).

Decomposition studies of harvest residues showed that phosphorus (P) release was relatively faster than N, and that harvest residues were the main source of soil solution P immediately after clear-cutting (Bekunda et al., 1990; Palviainen et al., 2004a). However, the impact of harvest residues on soil P has not been clearly established in the exotic pine plantations of southeast Queensland due to compounding effects of residual P from past P fertiliser applications (Simpson et al., 2003). Difficulties with the assessment of P and its availability, however, are an universal problem due to the complex chemistry and spatial variability of P in soils (Guo et al., 2000). Extraction methods that release adsorbed labile P are likely to compound the assessment of labile P directly released from the residues. Thus, there is a need to identify suitable soil P fractions that may be useful indicators of residue management in situations such as those in southeast Queensland. Bekunda et al. (1990) have used bicarbonate (NaHCO₃) extractable inorganic and organic P as labile P pools to assess the impact of clear-cutting and residue management in a sandy soil in South-eastern Australia. However, quantity-based P analyses such as NaHCO₃ and Bray P may extract inorganic P adsorbed onto solid phases (Mendham et al., 2002c) with potential contributions from residual P. Calcium chloride (CaCl₂) extractable P has been reported to measure P

immediately available in soil solution (Rayment and Higginson, 1992; Mendham et al., 2002c), and may be potentially useful in assessing soil P response to residue management. Furthermore, since decomposing plant residues are the main source of labile C (Homann and Grigal, 1992; Qualls, 2000), measurements of labile organic P associated with labile C pools could potentially be suitable indicators of soil P response to residue management.

Labile C is defined as the fraction of SOM that is both physically accessible and chemically degradable during microbial growth (Zou et al., 2005). The degradability of labile C pools plays an important role in biogeochemical processes or nutrient release for plant uptake (van Hees et al., 2005). The proportion of labile C pools, hence the bioavailability of SOM, can be a measure of its quality, which in turn may determine soil quality. A number of labile C pools have been proposed recently, including microbial biomass C (MBC) (Sparling, 1992; Bauhus et al., 1998; Pérez-Batallón et al., 2001) and hot water-extractable organic C (HWEOC) (Ghani et al., 2003; Chen and Xu, 2005) as indicators of management practices. Labile C pools have been assessed recently in a 6 year old exotic plantation under different residue management regimes (Chen and Xu, 2005). However, there is currently little information on P pools in these sandy soils of southeast Queensland. This study therefore tested the hypotheses that clear-cut harvesting would cause large changes in C and nutrient pools leading to a reduction in these pools during the inter-rotation period and that retaining residues would increase soil C, N and P pools through residue decomposition. Labile C and N pools are also important process indicators whose dynamics can indirectly point to a particular soil process. For instance, the increase or decrease in the mineral N pool over time is indicative of mineralisation or immobilisation, respectively. While past studies have assessed the impact of clear-cutting on total C and N and the on the immediate effects of

clear-cut harvesting and residue management retention on labile C, N mineral N pools (Blumfield and Xu, 2003), as well as on water soluble C (WSOC) (Pirainen et al., 2002), there is a paucity of understanding of the dynamics of hot water-extractable organic C (HWEOC) and N (HWEON), which are regarded as labile organic C and N pools, respectively, during the establishment of subsequent rotations. Therefore the objectives of this study were to: (1) quantify soil C and N pools and determine their dynamics following clear-cut harvesting under different residue management regimes; (2) assess the impact of residue management on P pools by a number of extraction methods; and (3) examine the relationships among soil C, N and P pools.

4.2 Materials and Methods

4.2.1 Site description and experimental design

This study was located in a newly logged slash or exotic pine plantation at Toolara State Forest (26° 00'S, 152° 49'E), Maryborough District, southeast Queensland. Detailed site description has been given in Chapter 2. Briefly, the soil is an acidic loamy sand, developing into a podsol, and classified as a soloth (Isbell, 1996). In February 2005, the plantation was harvested using the “at stump” processing method (see Chapter 2) to extract the logs. Immediately following clear-cutting, macro-plots (10 m x 10 m) were established on a section of the plantation in a randomised complete block design with four blocks (each block being separated by 10 m) and three treatments. The treatments were three residue loading rates: (1) residue removal (RR_0), (2) single level of residue retention, which is the operational level, (RR_1), and (3) double level of residue retention (RR_2), established by transferring residues from the RR_0 treatments to macro-plots where residues have been retained. The RR_2 treatment was not operationally practical, however, it was included to widen the possible treatment effects (Simpson et al., 2003) and represent the uneven residue distribution within the site. The macro-plots were left

to fallow rather than established with trees to minimise compounding effects on soil processes on such small-sized plots.

4.2.2 Soil sampling and soil moisture measurements

Soil sampling was carried out at 0, 6, 12, 18 and 24 months following clear-cutting at the 0 – 10 cm and 10 - 20 cm depth using a soil auger (ca diameter 7.5 cm). For each macro-plot, five soil cores were systematically sampled within the plot and bulked into a composite sample. The fresh composite samples were then sub-sampled for chemical and microbial analysis. Sub-samples for microbial C and N pools were stored at 4 °C and processed within 2 weeks of sampling (Chen and Xu, 2005), while sub-samples for chemical analyses were passed through a 2 mm sieve before air-drying and grinding in a Rocklab puck and ring grinder prior to storage in polyethylene vials for chemical analysis.

Monthly soil moisture measurement was also carried out for 10 months using the time domain reflectometry (TDR) to determine the impact of residue retention on soil moisture content. Due to the limited number of probes available, moisture measurements were carried out in one of the four blocks described above. Four probes were installed in each treatment plot, two of which measured soil moisture at 0 – 10 cm depth while the other two at 10 – 20 cm depth. This arrangement provided two pseudo-replicates for each treatment.

4.2.3 Soil total C, N and P analyses

Soil total C and N were determined by combustion in a Eurovector 3000 elemental analyser (Milan, Italy) coupled to a GVI Isoprime mass spectrometer (Manchester, UK). Soil total P was determined by the ascorbic acid method (Murphy and Riley, 1962;

Lajtha et al., 1999) following concentrated nitric/perchloric ($\text{HNO}_3/\text{HClO}_4$) acid digestion (Sparks, 1996; Chen et al., 2002). Initial soil pH was determined in a soil: solution ratio of 1:5 using a pH meter, while initial exchangeable Ca, Mg and K were determined by the flame atomic absorption spectrophotometer (FAAS) (Avanti, GBC Sigma) following extraction with 1.0 M NH_4NO_3 (Phillips and Greenway, 1998).

4.2.4 Labile C and N pool analyses

Labile C and N pools were determined on soils sampled at 6, 12 18, and 24 months following clear-cutting. Soil microbial biomass C (MBC) and N (MBN) were determined by the fumigation-extraction method (Brookes et al., 1985; Vance et al., 1987). Two sub-samples of fresh soil (15.0 g oven dry basis each) were prepared for direct extraction and fumigation, respectively. Fumigated samples were adjusted to 45 % water-holding capacity prior to the 24-hour exposure to ethanol-free chloroform (Chen and Xu, 2005). Both fumigated and non-fumigated sub-samples were extracted with 60 ml of 0.5 M K_2SO_4 for 30 minutes, and the extracts filtered through Whatman 42 filter papers. The total organic C (TOC) and total N (TN) in the extracts were analysed by a Shimadzu TOC- $\text{V}_{\text{CSH/CSN}}$ TOC/N analyser (Chen and Xu, 2005), and the MBC and MBN were calculated as the difference in extractable TOC and TN before and after fumigation, divided by the correction factors $K_{\text{ec}} = 0.45$ and $K_{\text{en}} = 0.54$, respectively (Brookes et al., 1985; Vance et al., 1987).

Hot water extractable organic C (HWEOC) and hot water extractable organic N (HWEON) were determined by the method of Sparling et al (1998) and modified by Chen and Xu (2005). Eight grams (oven-dried equivalent) of air-dried soil were incubated at 70 °C for 18 hours in 40.0 ml of de-ionised water (Millipore purified), shaken in an end-over-end shaker at 87 revs/min for 5 minutes, centrifuged at 10,000

revs/min then filtered through a 0.45 µm filter membrane. The TOC and total N (TN) in the extracts were determined by the Shimadzu TOC-V_{CSH/CSN} TOC/N analyser, from which the measured TOC was regarded as the HWEOC, while the HWEON was obtained as the difference in TN (HWETN) and hot water-extractable inorganic N (HWEIN) compounds as determined by the SmartChem 200 discrete chemistry analyser (DCA) (Westco Scientific Instruments, Australia). The inorganic NH_4^+ -N and NO_x^- -N pools were extracted from fresh soils with 2.0 M KCl (Chen and Xu, 2005). Five grams (oven dry equivalent) of fresh soil were extracted in 40 ml of 2.0 M KCl by shaking in an end-over-end shaker for 1 hour, centrifuging at 2000 rpm and then filtering through a Whatman 42 filter paper. The extracts were analysed for NH_4^+ -N and NO_x^- -N by the DCA. The DCA, however, does not discriminate between nitrate and nitrite therefore NO_x -N in this study is the sum of these oxidised forms of mineral N.

4.2.5 Labile P pool analyses

Labile P pools were determined from air-dried (<2 mm) soil sampled at 24 months after clear-cut harvesting of the plantation. A number of methods were used to evaluate residue retention impacts on labile P pools. Bicarbonate extractable P (NaHCO_3 _P) was determined in a soil to solution ratio of 1:20 (Bekunda et al., 1990) after shaking end-over-end 2.5 g soil in 50 ml of 0.5 M NaHCO_3 (pH 8.5) for 16 hours at 25 °C. Bray 1 P (Bray1_P) was determined after shaking 5 g of soil with 35 ml of 0.03 M NH_4F /0.025 M HCl solution for 60 s (Rayment and Higginson, 1992). Calcium chloride extractable P (CaCl_2 _P) was determined in soil extracts after shaking 8 g of soil in an end-over-end shaker for 18 hours in 40 ml of 5 mM CaCl_2 (Rayment and Higginson, 1992). Hot water-extractable P (HWEOP) was determined from soil extracts described above, and hot water-extractable total P (HWETP) was determined after nitric/perchloric acid digestion of the hot water extracts. Hot water-extractable organic P (HWEOP) was the

difference between P determined in undigested and that of digested hot water soil extracts. Phosphorus concentrations in all extracts were determined colorimetrically at 880 nm using the ascorbic acid method (Murphy and Riley, 1962; Lajtha et al., 1999), and expressed per kg of air-dried soil (Rayment and Higginson, 1992).

4.2.6 Statistical analyses

Analyses of variance (ANOVA) were carried out on all measured parameters to determine residue management effects. Where there was a significant treatment effect at $p < 0.05$, the data were subjected to the least significant difference (LSD) test. A repeated measure ANOVA was also carried out on C and N pools to determine both treatment and time effects. Correlation and regression analyses of labile C, N and P pools at 18 or 24 months were also carried out to determine relationships among the labile C, N and P pools.

4.3 Results

4.3.1 Initial soil chemical properties and soil moisture measurements

Initial soil properties measured immediately following clear-cut harvesting are presented in Table 4.1. These measurements indicated that the soil was acidic, at pH 4.8, and generally low in C and N, as well as in exchangeable bases, while total P was around 33 mg kg⁻¹. Except for soil pH, soil chemical properties were greater in the 0-10 cm than the 10 – 20 cm soil depth.

I acknowledge that the ANOVA from the pseudo-replication of soil moisture measurements are not statistically valid. However, it did indicate some trends in soil moisture content between the residue retention treatments in the 0 – 10 cm soil depth (Fig. 4.1), suggesting that from September 2005 to February 2006, soil moisture content might be greater in the RR₁ and RR₂ compared to the RR₀ treatments. Fig. 4.1 also

showed that although rainfall influenced the total monthly soil moisture content, greater variation in soil moisture between the treatments seems to occur during the months with higher daily temperatures.

Table 4.1. Some initial soil chemical properties of the sandy soil at the experimental site of Toolara State Forest, Queensland, Australia.

Soil properties	Soil depth	
	0 – 10 cm	10 – 20 cm
Bulk density (g cm^{-3})	1.46 (0.12)*	1.52 (0.10)
Soil pH	4.78 (0.15)	4.82 (0.25)
Electrical conductivity (mSm^{-1})	1.63 (0.07)	1.29 (0.16)
Total carbon (g kg^{-1})	10.0 (1.0)	5.00 (1.5)
Total nitrogen (g kg^{-1})	0.26 (0.02)	0.17 (0.03)
Total phosphorus (mg kg^{-1})	33.40 (6.50)	17.80 (3.30)
Soil C:N ratio	38.04 (5.90)	29.61 (5.25)
Exchangeable Ca (cmol kg^{-1})	2.05 (0.74)	1.33 (0.19)
Exchangeable Mg (cmol kg^{-1})	1.35 (0.41)	0.65 (0.21)
Exchangeable K (cmol kg^{-1})	0.55 (0.44)	0.20 (0.06)

*In brackets are standard deviations.

4.3.2 Soil C and N pools following clear-cut harvesting

Soil total C and N measured after 12, 18 and 24 months following clear-cutting are presented in Table 4.2. The total C (0-10 cm) was lowest after 12 months especially in the RR_0 treatment (Table 4.2), which was a reduction of around 30% compared to the initial soil total C of 1.0 ± 0.10 % (Table 4.1). This was in contrast to total N, which remained unchanged in the RR_0 treatment during the same period. Nonetheless, residue management effects were observed after 18 months, when total C and N were

significantly greater in the RR_1 and RR_2 than the RR_0 treatment in both depths (Table 4.2). Similar treatment effects were also observed after 24 months in the 0-10 cm depth. Overall, a repeated measure ANOVA showed that residue retention increased total C and N by 45% ($p < 0.001$) and 32% ($p < 0.001$) over the 12-24 months, with no significant time effect and treatment x time interactions for both parameters at this stage. No significant variations among the treatments were detected for the C:N ratio,

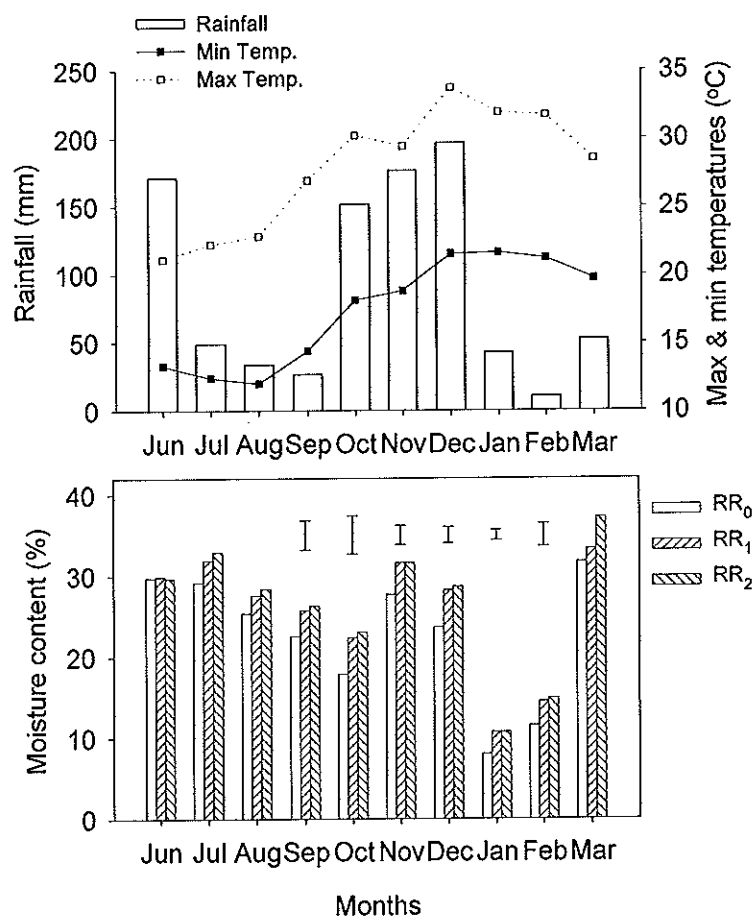


Fig. 4.1. Influence of residue retention on soil moisture content in relation to ambient temperature and rainfall in a clear-cut slash pine plantation in southeast Queensland.

Table 4.2. Soil total C and N concentrations (%) under three harvest residue management regimes as sampled after 12, 18, and 24 months following clear-fall harvesting. The residue treatments are: (1) residue removal, RR₀; (2) single residue retention, RR₁; and (3) double residue retention, RR₂.

Treatments	12 months			18 months			24 months		
	C (%)	N (%)	C:N	C (%)	N (%)	C:N	C (%)	N (%)	C:N
<u>0–10 cm depth</u>									
RR ₀	0.69 ^b *	0.026 ^a	27.10 ^a	0.83 ^b	0.025 ^b	33.53 ^a	0.87 ^b	0.022 ^b	40.15 ^a
RR ₁	1.02 ^a	0.032 ^a	31.77 ^a	1.27 ^a	0.033 ^a	38.58 ^a	1.29 ^a	0.029 ^a	44.78 ^a
RR ₂	0.85 ^{ab}	0.030 ^a	28.90 ^a	1.28 ^a	0.035 ^a	36.80 ^a	1.33 ^a	0.031 ^a	42.48 ^a
<u>10–20 cm depth</u>									
RR ₀	0.36 ^a	0.018 ^b	20.58 ^a	0.41 ^c	0.015 ^b	28.42 ^a	0.39 ^a	0.013 ^a	29.92 ^a
RR ₁	0.50 ^a	0.020 ^a	24.72 ^a	0.54 ^b	0.018 ^a	31.67 ^a	0.43 ^a	0.013 ^a	34.24 ^a
RR ₂	0.40 ^a	0.017 ^b	23.51 ^a	0.62 ^a	0.018 ^a	34.40 ^a	0.39 ^a	0.013 ^a	30.78 ^a

* Means followed by the same letter in each column, and for each depth, are not significantly different ($p > 0.05$).

and except on the 12th month, the C:N ratio remained well above the critical C:N ratio of 20-30 for N mineralisation (Pérez-Batallón et al., 2001).

Measurements of soil microbial biomass C (MBC) after 6–24 months showed relatively higher levels of MBC after 6 months than for the other sampling dates (Fig. 4.2a). A seasonal pattern was observed for MBC, although MBC was also declining with time

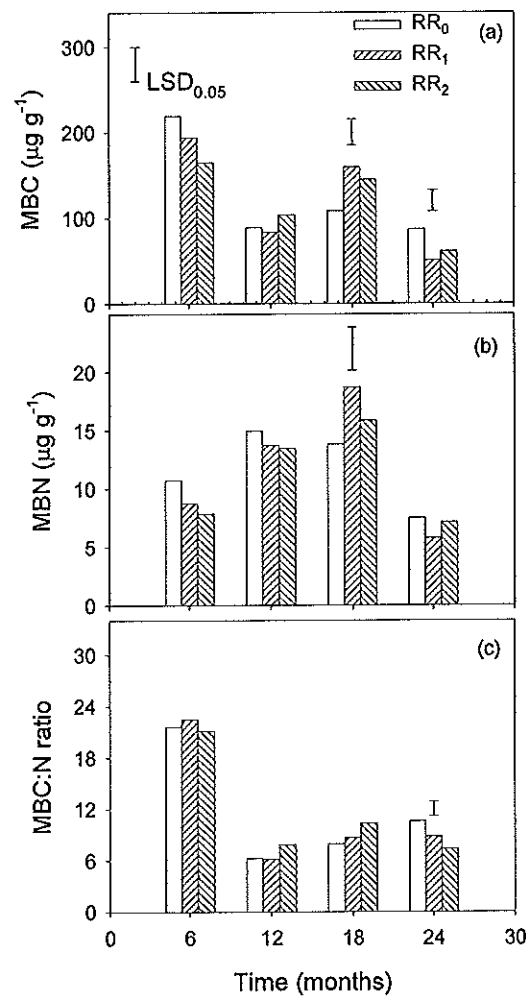


Fig. 4.2. Changes in soil microbial biomass C (MBC) (a), microbial biomass N (MBN) (b) and the microbial biomass C:N ratio (c) under (1) residue removal, RR₀; (2) single residue retention, RR₁; and (3) double residue retention, RR₂, treatments over 24 months following clear-cutting of a slash pine plantation of Southeast Queensland.

regardless of residue management. Significant residue management effects on MBC were observed after 18 months, with greater MBC in both the RR₁ and RR₂ treatments compared to the RR₀ treatment. This trend, however, was reversed after 24 months when MBC was significantly greater in the RR₀ treatment than in both the RR₁ and RR₂ treatments (Fig. 4.2a). On the other hand, the MBN pool increased ($p < 0.001$) from the 6th to the 18th month following clear-cut harvesting (Fig. 4.2b). Nonetheless, no significant residue management effects were observed, except after 18 months. Similarly, the microbial biomass C:N ratio, MBC:N, also showed no significant residue treatment effects except after 24 months when it was highest in the RR₀ treatment compared to the RR₁ and RR₂ treatments (Fig. 4.2c). The MBC:N ratio, however, declined significantly over time ($p < 0.001$), and in the opposite direction to MBN, especially in the first 18 months, when the decreasing MBC:N ratio had some correlation to the increasing MBN ($r = -0.73$, $p < 0.001$).

In contrast to the MBC and MBN pools, the HWEON showed significant temporal variations ($p < 0.05$), treatment effects ($p < 0.01$) and treatment x time interaction ($p < 0.01$) overall. This analysis reflects the initial peak in HWEON in all three treatments on the 6th month (Fig. 4.3a), followed by a significant drop especially in the RR₀ and RR₁ treatments on the 12th month, then an increase ($p < 0.05$) in HWEON in the RR₁ and RR₂ treatments subsequently. Fig. 4.3a showed that, except for the first 6 months, HWEON was consistently greater in the RR₂ treatments compared to the RR₀ treatment, and intermediate in the RR₁ treatment. Significant variations in HWEON among the three treatments were observed after 18 months.

Similar to the HWEON, an initial surge in HWEON was observed in the first 6 months (Fig. 4.3b), which was significantly greater in the RR₀ treatment compared to both the

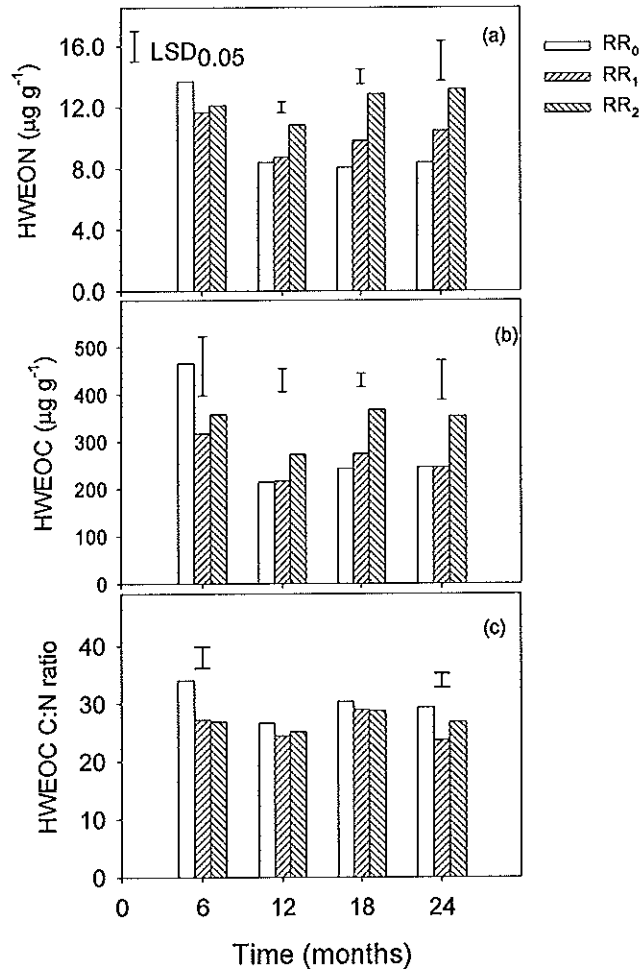


Fig. 4.3. Changes in hot water-extractable organic N (HWEON) (a) and hot water-extractable C (HWEOC) (b) and their C:N ratio (c) under (1) residue removal, RR₀; (2) single residue retention, RR₁; and (3) double residue retention, RR₂, treatments over 24 months following clear-cutting of a slash pine plantation of Southeast Queensland.

RR₁ and RR₂ treatments. This was followed by a significant decline ($p < 0.001$) in HWEOC in the RR₀ treatment in subsequent months to levels below $250 \mu\text{g g}^{-1}$ soil. On the other hand, HWEOC was consistently significantly greater in the RR₂ treatment, while no significant differences were observed between the RR₀ and RR₁ treatments (Fig 4.3b). Thus, overall, the HWEOC showed significant temporal ($p < 0.001$) and residue management ($p < 0.01$), as well as a significant treatment x time interactions ($p < 0.001$) over the 24 months. Similarly, significant temporal variations ($p < 0.001$),

treatment effects ($p < 0.001$) and treatment x time interactions ($p < 0.05$) were also observed for the HWEOC:N ratio. There appeared to be consistently greater HWEOC:N ratio in the RR_0 treatment compared to the RR_1 and RR_2 treatments, although this was only significant on two occasions (Fig 4.3c). Labile inorganic N pools (NH_4^+ -N and NO_x -N) also showed significant temporal variation, with levels of NH_4^+ -N being the dominant mineral N pool (Fig. 4.4). The NH_4^+ -N pool decreased over time ($p < 0.001$) to

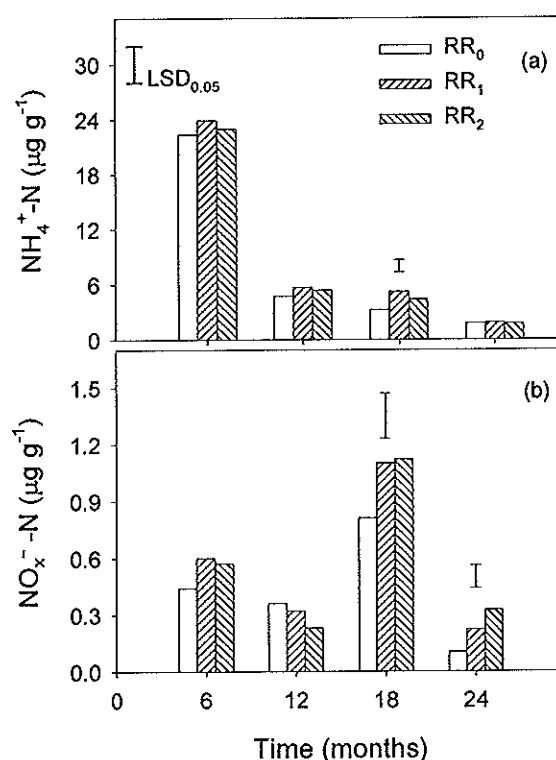


Fig. 4.4. Changes in soil ammonium-N (NH_4^+ -N) (a) and nitrate/nitrite – N (NO_x -N) (b) under (1) residue removal, RR_0 ; (2) single residue retention, RR_1 ; and (3) double residue retention, RR_2 , treatments over 24 months following clear-cutting of a slash pine plantation of Southeast Queensland.

levels below $5\ \mu g\ g^{-1}$ soil after 6 months, while the NO_x -N appeared to be increasing, peaking after 18 months ($p < 0.05$). The repeated measure ANOVA indicated significant residue treatment effects on the mineral N pool, and this was apparent after 18 months, and 24 months for NO_x -N (Fig. 4.4), where inorganic N pools were greater in the RR_1

and RR₂ treatments relative to the RR₀ treatment. In contrast to HWEON or MBN, no significant treatment x time interactions were observed for the mineral N pools.

Since significant variations among the treatments were consistently observed after 18 months following clear-cutting for most of the soil C and N pools, Pearson's correlation analyses were carried out for this month's data in the 0-10 and 10-20 cm depths. Results (Table 4.3) showed significant positive correlations between the soil total C and N, and

Table 4.3. Pearson's correlation coefficients between soil total C (TC), total N (TN), NH₄⁺-N, NO₃⁻-N, hot water extractable organic C (HWEOC) and total N (HWETN), and microbial biomass C (MBC) and N (MBN) in the 0-10 cm and 10-20 cm depth under different residue management regimes as measured at 18 months following clear-cutting of a slash pine plantation.

Variables	HWEOC	HWEON	MBC	MBN	NH ₄ ⁺ -N	NO ₃ ⁻ -N	TC
HWEON	0.95 ^{***a}						
MBC	0.61 ^{**}	0.58 ^{**}					
MBN	0.84 ^{***}	0.80 ^{***}	0.55 ^{**}				
NH ₄ ⁺ -N	0.52 ^{**}	0.57 ^{**}	0.31 ^{ns}	0.54 ^{**}			
NO ₃ ⁻ -N	0.44 [*]	0.50 [*]	0.22 ^{ns}	0.53 ^{**}	0.48 [*]		
TC	0.83 ^{***}	0.84 ^{***}	0.60 ^{**}	0.86 ^{***}	0.63 ^{***}	0.65 ^{***}	
TN	0.84 ^{***}	0.79 ^{***}	0.52 ^{**}	0.87 ^{***}	0.62 ^{***}	0.73 ^{***}	0.96 ^{***}

^aAsterisks *, **, and *** indicate significance at p<0.05, 0.01 and 0.001, respectively, and ns = not significant (p>0.05).

between these two parameters and the labile C and N pools. HWEOC was also significantly correlated with the MBC and the labile N pools, with the highest

correlation between HWEOC and HWEON ($r = 0.95$, $p < 0.001$). There was also a highly significant correlation between HWEON and MBN ($r = 0.80$, $p < 0.001$). Significant positive correlations between MBN and $\text{NH}_4^+\text{-N}$ ($r = 0.54$, $p < 0.01$) and between MBN and $\text{NO}_x\text{-N}$ ($r = 0.53$, $p < 0.01$) were also observed. In addition, regression analyses also showed significant relationships between soil total C and HWEOC and between soil total N and HWEON in the 0 – 10 cm depth over the 12 – 24 months period (Fig. 4.5), indicating the linkages of HWEOC and HWEON with total C and N, respectively, across time. Similarly, regression analyses combining data from the 12 – 24 month

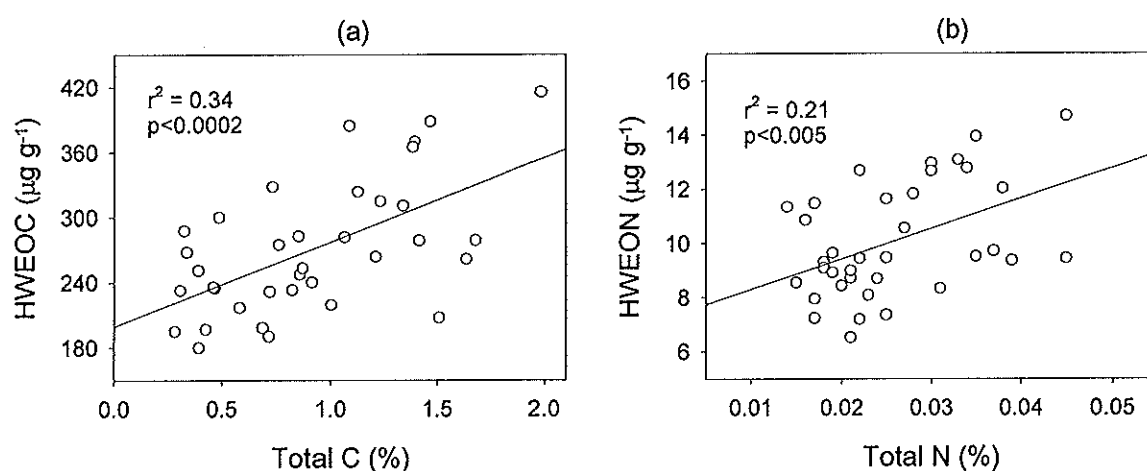


Fig. 4.5. The relationships between (a) soil total C and hot water-extractable C (HWEOC) and (b) between soil total N and hot water-extractable organic N (HWEON) under different residue management regimes over a period of 12-24 months following clear-cut harvesting of a slash pine plantation of Southeast Queensland.

period also showed a significant relationship between MBN and the inorganic N pools (Fig. 4.6), with a slightly more significant relationship with $\text{NH}_4^+\text{-N}$ than the $\text{NO}_x^-\text{-N}$ (Fig. 4.6a-b). The MBC, however, was more closely related to the $\text{NO}_x^-\text{-N}$ than to the $\text{NH}_4^+\text{-N}$ (Fig. 4.6c-d).

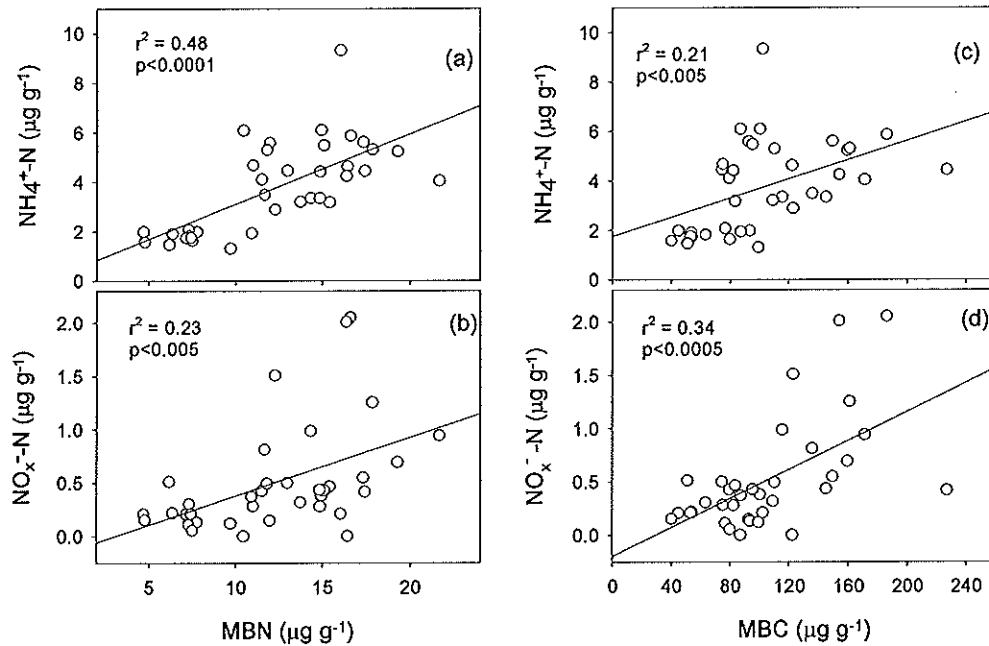


Fig. 4.6. The relationships between microbial biomass N (MBN) and ammonium-N ($\text{NH}_4^+\text{-N}$) (a) or nitrate/nitrite-N ($\text{NO}_x^-\text{-N}$) (b), and between microbial biomass C (MBC) and $\text{NH}_4^+\text{-N}$ (c) or $\text{NO}_x^-\text{-N}$ (d) under different residue management regimes over a period of 12-24 months following clear-cutting of a slash pine plantation of Southeast Queensland.

4.3.3 Soil P pools under different residue management regimes

Seven P pool parameters were measured to assess the effect of residue management on soil P. The results in Table 4.4 show no significant variations in total P among the treatments. Similarly, no significant variations among the treatments were observed for the $\text{CaCl}_2\text{-P}$ and HWEOP pools. The Bray1_P pool, however, was significantly greater in the RR_2 treatment compared to both the RR_1 and RR_0 treatments, while the HWEOP and $\text{NaHCO}_3\text{-P}$ were significantly greater in the RR_2 treatment than the RR_0 treatment, and intermediate in the RR_1 treatment (Table 4.4). The HWETP pool was the only P pool that showed significant differences among the treatments, with P concentration in

Table 4.4. Soil total P, Bray 1 extractable P (Bray1_P), calcium chloride extractable P (CaCl₂_P), bicarbonate extractable P (NaHCO₃_P), hotwater extractable P (HWEOP), hotwater extractable organic P (HWEOP) and hotwater extractable total P (HWETP) under the no residue retention (RR₀), single residue retention (RR₁) and double residue retention (RR₂) treatments obtained for the 0-10 cm soil depth after 24 months following clear-cut harvesting.

Treatments	Total P mg kg ⁻¹	Bray1_P mg kg ⁻¹	CaCl ₂ _P µg kg ⁻¹	NaHCO ₃ _P mg kg ⁻¹	HWEOP mg kg ⁻¹	HWETP ^a mg kg ⁻¹
RR ₀	33.88a ^b	1.74b	213a	1.87b	1.54a	2.11c
RR ₁	42.19a	1.84b	378a	3.21ab	2.39a	3.36b
RR ₂	44.95a	2.81a	265a	3.62a	2.46a	4.38a

^a Hot-water extractable total P (HWETP) is the P measured following acid digestion of hot-water extracts and that the HWEOP is the difference between HWETP and HWEOP.

^b Means followed by the same letter in each column are not significantly different (p>0.05).

the RR₂ treatment being twice the magnitude of that in the RR₀ treatment. Overall, the quantities of labile P pools were less than 5 mg kg⁻¹ soil.

Pearson's correlation analyses of P pools are shown in Table 4.5. There was no significant correlation between total P and the labile P pools, except CaCl₂_P. The CaCl₂_P, on the other hand, was positively correlated to HWEP and HWETP, although the correlation was much stronger with HWEP ($r = 0.85$, $p < 0.001$). The HWETP was

Table 4.5. Pearson's correlation coefficients between soil total P, Bray 1 extractable P (Bray1_P), calcium chloride extractable P (CaCl₂_P), bicarbonate extractable P (NaHCO₃_P), hot water extractable P (HWEP), hot water extractable organic P (HWEOP) and hot water extractable total P (HWETP) under different harvest residue management regimes measured after 24 months following clear-cut harvesting of a slash pine plantation of southeast Queensland.

	Bray1_P	CaCl ₂ _P	HCO ₃ _P	HWEP	HWEOP	HWETP
CaCl ₂ _P	0.00 ^{ns b}					
HCO ₃ _P	0.49 ^{ns}	0.50 ^{ns}				
HWEP	0.37 ^{ns}	0.85 ^{***}	0.61 [*]			
HWEOP	0.40 ^{ns}	-0.26 ^{ns}	0.29 ^{ns}	-0.16 ^{ns}		
HWETP ^a	0.58 [*]	0.59 [*]	0.72 ^{**}	0.78 ^{**}	0.49 ^{ns}	
Total P	0.35 ^{ns}	-0.65 [*]	-0.06 ^{ns}	-0.52 ^{ns}	0.55 ^{ns}	-0.11 ^{ns}

^a Hot water extractable total P (HWETP) is the P measured following acid digestion of hot water extracts and that the HWEOP is the difference between HWETP and HWEP.

^b Asterisks *, **, and *** indicate significance at $p < 0.05$, 0.01 and 0.001, respectively, and ns = not significant ($p > 0.05$).

also significantly correlated to the Bray1_P and $\text{NaHCO}_3\text{-P}$. Interestingly, the HWEOP showed no significant correlation with total P or the other labile P pools. On the other hand, regression analyses showed that HWEOP was significantly related to soil total C and HWEOC determined from the same soil samples (Fig. 4.7). Other Pearson's correlation analyses (data not presented) also show a very significant relationship between HWEOP and HWEON ($r = 0.94$, $p < 0.001$) and between HWEOC and HWETP ($r = 0.69$, $p < 0.05$). In addition, unlike a significant relationship between soil total C and N ($r = 0.96$, $p < 0.001$) (Table 4.3), no significant correlation between total C and total P was observed.

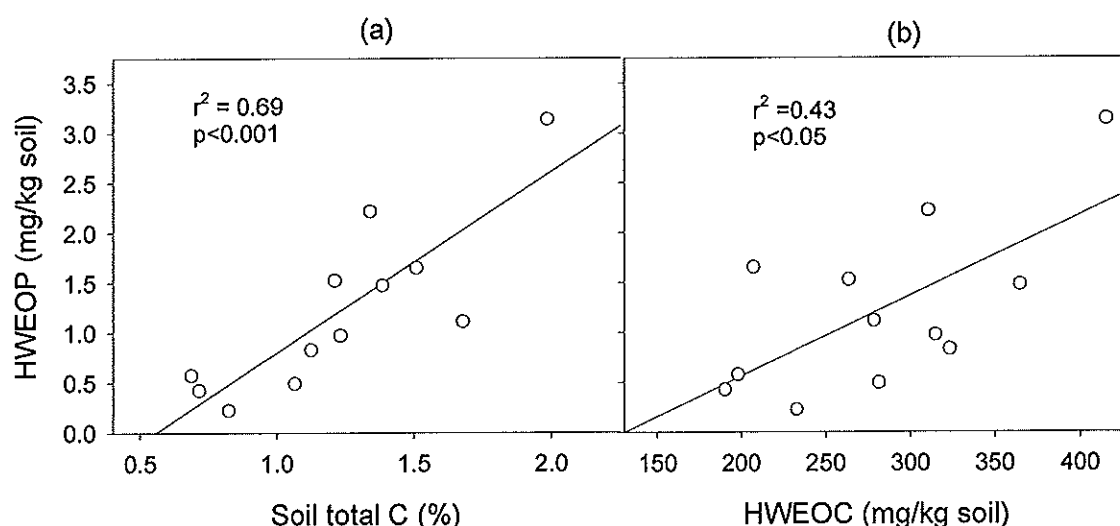


Fig. 4.7. The relationships between (a) hot water extractable organic P (HWEOP) and soil total C and (b) between HWEOP and hot water extractable organic C (HWEOC) under three different residue management regimes in an exotic pine plantation of Southeast Queensland.

4.4 Discussion

4.4.1 Soil C and N pools following clear-cutting and residue retention

Many studies reported significant reductions in SOM following clear-cut harvesting due to the changing abiotic environment favouring microbial growth and activity, thus

increased mineralisation of SOM (Smethurst and Nambiar, 1990b; Carlyle et al., 1998; Chatterjee et al., 2008). Although soil processes were not determined directly in this study, increased mineralisation of SOM and associated nutrients following clear-cutting can be inferred from the initial surge in $\text{NH}_4^+\text{-N}$, HWEOC, HWEON and MBC in the first 6 months irrespective of residue management. Increased MBC is indicative of increased microbial population, including the decomposer community, consequently increasing the mineralisation of SOM and labile organic C and N pools. The depletion of soil total C after 12 months (Table 4.2) relative to the initial total C (Table 4.1), especially in the RR_0 and RR_2 treatment, clearly demonstrated the impact of clear-cutting on soil C and therefore was consistent with studies showing clear-cutting to have a large effect on SOM, in some cases over the long-term (Smethurst and Nambiar, 1990b; Olsson et al., 1996; Carter et al., 2002; Chatterjee et al., 2008). However, the significant increase in soil total C and N under residue retention to levels similar to or greater than those prior to clear-cutting, showed that residue management can have a significant effect on soil total C and N in the short-term. The faster decomposition of slash pine residues in this subtropical region compared to the decomposition of other harvest residues in the northern hemisphere (Chapter 3), and the low soil C content of this sandy soil, might be the reasons for the significant recovery of soil C under residue retention in this study.

In contrast to C loss in the first 12 months, the similarities in the initial soil total N (Table 4.1) and total N after 12 months in the RR_0 treatment (Table 4.2) suggested that total N loss might be negligible compared to the reductions in total C in the same period. This indicated that loss of N through leaching might be minimised by N immobilisation due to the increase in the microbial population regardless of residue management as is evident in this study. The case for increased N immobilisation

following clear-cutting is supported by the increasing trend of MBN, and the significant reduction in microbial C:N ratio and $\text{NH}_4^+\text{-N}$, irrespective of residue management. The significant variations in soil total N among the treatments after 18 months, however, indicated the influence of residue retention on soil total N. The study of harvest residue decomposition (Chapter 3) showed that N release from the residues coincided with the onset of significant variations in soil total N observed after 18 months.

While clear-cut harvesting had some influence on the dynamics of HWEOC and HWEON, this study showed that residue management had a larger influence than clear-cutting on the variations in HWEOC and HWEON pools after 12 months. The higher levels of HWEOC and HWEON in the RR_1 and RR_2 treatments compared to those in the RR_0 treatments indicated the leaching of WSOC from decomposing residues, which typically occurs during the early stage of residue decomposition (Kumar and Goh, 2000). Although HWEOC may contain both microbial C and WSOC (Sparling et al., 1998; Chen and Xu, 2005), the differences in the pattern and magnitude of MBC and HWEOC indicated that WSOC from decomposing residues might have influenced the variations in HWEOC and HWEON among the treatments. This study, therefore, complemented a previous ^{13}C NMR study in these plantations which showed greater SOM quality, as indicated by higher O-alkyl C functional groups, under residue retention after 2 years (Mathers and Xu, 2003). Other studies have established a significant relationship between HWEOC and the labile O-alkyl C functional group (Chen et al., 2004; Huang et al., 2008), the first C group to lose signal intensity as decomposition proceeds (Mathers et al., 2000; 2003b). In addition, this study also showed higher C:N ratio of HWEOC under the RR_0 treatment, which indicated the quality of SOM as a source of nutrients under residue removal practices. Thus, HWEOC is a simple measure of SOM quality, and a number of studies have used it as an

indicator of management impacts on soil quality (Ghani et al., 2003; Chen and Xu, 2005; Huang et al., 2008).

The consistent significant variations in HWEON among the treatments in this study suggested that HWEON might be a more sensitive indicator of residue management than HWEOC. The significant relationship between HWEOC and HWEON or $\text{NH}_4^+\text{-N}$ observed after 18 months indicated the role of HWEOC as not only a source of energy but also as a source of nutrients in plantation ecosystems. The greater HWEON under the residue treatments may have contributed to the increased early tree growth observed in an exotic pine plantation under different residue management regimes (Simpson et al., 2003) through the uptake of mineralised HWEON.

In contrast to HWEOC, MBC showed a strong seasonal pattern consistent with other studies (Wardle, 1998; Pérez-Batallón et al., 2001; Jiang et al., 2006). The relatively lower autumn measurements (12 and 24 months) compared to the spring measurements might be related to soil moisture limitation (Pérez-Batallón et al., 2001). Nonetheless, an overall decline in MBC was apparent in the first 2 years. Soil MBC is a measure of the microbial population and can be a sensitive indicator of change in soil quality (Sparling, 1992; Webster et al., 2001) or management practices (Bauhus et al., 1998; Chen and Xu, 2005). Plantation harvesting and management have been shown to affect the microbial biomass population and community structure (Chatterjee et al., 2008). The overall decline in MBC in the first 2 years in this study agrees with those studies showing a decrease in microbial biomass following harvesting (Fratterigo et al., 2006), although forest harvesting effects on microbial biomass showed varying results (Entry et al., 1986; Li et al., 2004; Chatterjee et al., 2008). Studies examining the effects of residue retention resulting from different harvesting intensities also found no effect on

MBC and soil respiration (Carter et al., 2002; Li et al., 2004). In contrast, studies by Mendham et al. (2002b) and Pérez-Batallón et al. (2001) showed significantly higher MBC and MBN following residue retention early in the rotation, consistent with the MBC and MBN measured after 18 months in the present study. The differences in results discussed here could be due to different degrees of residue incorporation into the mineral soil during harvesting, therefore affecting C and N dynamics differently (Powers et al., 2005; Tan and Chang, 2007).

The decline in MBC from the 18th to the 24th month after clear-cutting in this study, however, could not be related to decline in available substrates (Mendham et al., 2002b), as labile C and N remained high, especially in residue retention plots. The significantly higher MBN under the residues after 18 months in this study was consistent with those reported under *Eucalyptus globulus* residues (Mendham et al., 2002b). Although, the influence of residue retention on MBN was not directly evident on the 24th month, the lower microbial C:N ratios in the RR₁ and RR₂ treatments (Fig. 4.2c) indicated greater microbial immobilisation of N, consistent with studies showing greater N immobilisation in residue retention sites (Pérez-Batallón et al., 2001; Blumfield et al., 2004b). The increase in MBN across the treatments from the 6th to the 18th month may be related to the increase in labile substrate (Mendham et al., 2002b).

The large flux of NH₄⁺-N in the first 6 months regardless of residue retention was consistent with increased N mineralisation as measured by other studies (Smethurst and Nambiar, 1990b; Pérez-Batallón et al., 2001) following clear-cutting. The declining trend in NH₄⁺-N after the 6th month was similar to other inter-rotation studies (Pérez-Batallón et al., 2001; Blumfield and Xu, 2003; Blumfield et al., 2004b). Blumfield and Xu (2003) showed that NH₄⁺-N declined from about 60 kg ha⁻¹ to <10 kg ha⁻¹ within a

year in a hoop pine plantation in southeast Queensland. The NH_4^+ -N concentrations after 12 months in this study were also very low compared to those reported by Chen and Xu (2005) in a 6-year-old exotic plantation under different residue management regimes. The subsequent low NH_4^+ -N concentration, however, may be due to high N immobilisation, which is supported by the increasing MBN, decreasing microbial C:N ratio and the lack of a reduction in soil total N discussed earlier. Pérez-Batallón et al. (2001) showed that N immobilisation was favoured by a soil C:N ratio greater than 30, which was the case in this study regardless of residue management.

The lower NO_x -N concentrations compared to NH_4^+ -N concentrations in this study were consistent with past studies in the exotic pine plantation (Chen and Xu, 2005). The peak NO_x -N of $1.2 \mu\text{g g}^{-1}$ soil in this study was much lower than those reported by Blumfield and Xu (2003) and Pérez-Batallón et al. (2001). Many factors have been proposed to inhibit nitrification, including low pH, low populations of nitrifying bacteria or low soil NH_4^+ -N availability (Vitousek and Matson, 1985). Mathers et al. (2007) also highlighted the importance of tannins from residues in inhibiting nitrification. Nonetheless, the temporal variation of NO_x -N in this study was similar to those reported by Blumfield and Xu (2003) and Pérez-Batallón et al (2001). The late increase in NO_x -N in all treatments, however, could not be related to the apparent NH_4^+ -N concentrations. The study by Stark and Hart (1997) reported that in some cases increasing NO_3 -N could be due to a reduction in NO_3 -N assimilation by micro-organisms, rather than a temporal increase in NH_4^+ -N.

Like HWEOC and HWEON, the significant variation in NH_4^+ -N and NO_x -N among the treatments in the later part of this study, and the lack of a treatment x time interaction, were further evidence of the influence of residue management on soil C and N pools.

The relatively greater $\text{NH}_4^+\text{-N}$ production in the RR_1 and RR_2 treatments than in the RR_0 treatment was consistent with N release from the harvest residues (Chapter 3) after 18 months. The concomitant increase in $\text{NO}_x\text{-N}$ could therefore now be due to increased nitrification triggered by the increase in soil $\text{NH}_4^+\text{-N}$ across the treatments (Pérez-Batallón et al., 2001). This is supported by the significant correlation between $\text{NH}_4^+\text{-N}$ and $\text{NO}_x\text{-N}$ in the soil after 18 months (Table 4.3). Furthermore, soluble organic N has been reported to enhance nitrification (Killham, 1990), consistent with the significant relationship between $\text{NO}_x\text{-N}$ and HWEON (Table 4.3). The lack of significant variation in $\text{NH}_4^+\text{-N}$ in the 24th month therefore might be due to the greater rate of conversion of $\text{NH}_4^+\text{-N}$ to $\text{NO}_x\text{-N}$ in the RR_1 and RR_2 treatments, consequently causing a significant increase in $\text{NO}_x\text{-N}$ under these treatments after 24 months.

4.4.2 Labile P pools under different residue management regimes

Conclusive results on the influence of residue management on soil P have been difficult to achieve under the exotic pine plantations due to confounding effects of residual P from past P fertiliser applications (Simpson et al., 2003). This study, however, showed that harvest residue management did have a significant influence on labile P as demonstrated by the significant variations in NaHCO_3P , HWEOP and HWETP among the treatments. Similar results using $\text{NaHCO}_3\text{-P}$ as a measure of labile P have been reported in a sandy soil in south-eastern Australia (Bekunda et al., 1990). In addition, the concentrations of labile inorganic P from bicarbonate extraction in this study were within the lower range of those reported by Bekunda et al. (1990) when converting to kg ha^{-1} P in the 0-10 cm depth, which in this study ranged from 2.7-5.2 kg ha^{-1} for $\text{NaHCO}_3\text{-P}$. Rapidly growing radiata pine require between 1 – 2 kg ha^{-1} P per year in the first 2 years, with a critical foliar concentration of 0.12% (Bekunda et al., 1990). In southeast Queensland, the critical foliar concentration of exotic pines is between

0.093% and 0.11% P (Xu et al., 1995a). Therefore, it is possible that labile soil P from harvest residue retention, or following clear-cutting, may be sufficient to meet the demands of exotic pine plantations especially during the early growth phase.

Comparison of labile P pools indicated that $\text{NaHCO}_3\text{-P}$, HWEOP and HWETP were sensitive measures of labile P pools reflecting management impacts. While $\text{NaHCO}_3\text{-P}$ had been used in the past (Bekunda et al., 1990), this study proposed that HWEOP and HWETP might also be useful indicators of residue management on soil P, and have the advantage of a relatively simple extraction method. The highly significant variations in HWETP among the treatments suggest that HWETP is the more sensitive indicator. This might be because HWETP encompasses both the inorganic and organic P released from the residues. On the other hand, the lack of a significant variation in $\text{CaCl}_2\text{-P}$ among the treatments may be due to the high leaching potential of this P pool, which has been linked to drainage water P (McDowell et al., 2003).

The significant positive relationships between HWEOP or HWETP and total C with increasing residue-loading rate indicated that the residues largely contributed to the increase in the HWEOP and HWETP pools in the RR_1 and RR_2 treatments. Nonetheless, since HWEOP and HWETP have not been assessed in the past in forest soils, the use of these measures of labile P needs further evaluation due to the one-off measurement employed in this study. In addition, further evaluation may be necessary for HWEOP given its significant relationship and similar magnitude to those of $\text{NaHCO}_3\text{-P}$, as well as the simple analytical procedure involved.

4.4.3 Relationships among C, N and P pools

The significant correlations between various C and N pools were consistent with those established by other studies in plantation ecosystems (Chen et al., 2004; Chen and Xu, 2005; Huang et al., 2008). These relationships indicated that the labile C and N pools represented similar pools or parts of the same pool as indicated by the magnitude of HWEOC and MBC. The significant correlations of all labile C and N pools with total C also indicated their contribution to the total C pool or vice versa, and that their concentration in the soil was dependent on the intensity of SOM made available through residue decomposition. This was demonstrated in Fig. 4.5, where the relationship between total C and HWEOC or between total N and HWEON holds true even when pooling data over the 12 - 24 months period. The significant relationship between HWEOC and HWEON or HWEOP supports the view that labile C fractions are not only a readily available energy source, they are an important source of nutrients. The significant relationships among MBC, MBN and NH_4^+ -N also support the proposition that MBC is a source of NH_4^+ -N through microbial turnover and mineralisation of MBN. This was demonstrated by the stronger relationship between MBN and NH_4^+ -N ($r^2 = 0.48$, $p < 0.001$) compared to the NO_x -N ($r^2 = 0.23$, $p < 0.01$) (Fig. 4.6a-b). On the other hand, the relatively more significant relationship between MBC and NO_x -N ($r^2 = 0.34$, $p < 0.001$) compared to that between MBC and NH_4^+ -N ($r^2 = 0.21$, $p < 0.01$) (Fig. 4.6c-d) suggests that these soil microbes are probably more important in regulating nitrification than just as a source of NH_4^+ -N. This was consistent with reports suggesting that nitrate production is dependent on the nitrifier population (Meiwes et al., 1998; Pérez-Batallón et al., 2001). These relationships also hold true across the seasons as demonstrated by the significant relationships between these C and N pools when pooling data obtained from the top 10 cm of soil from the 12- 24 months period (Fig. 4.6).

The lack of a significant relationship between total P and HWEOP or HWETP indicated that these P pools might be independent of the residual P pool represented by the total P. This was further supported by the highly significant relationship between HWEOP or HWETP and soil total C instead. The significant relationship between HWEOP and HWETP and between HWEON and HWEOP further supports the proposition that the labile P pools measured in this study were likely to be influenced by residue retention. The significant relationship between HWEP and $\text{CaCl}_2\text{-P}$ may be explained by the similarities in the extraction method, although the HWEP extracted more inorganic P or at least more soluble reactive P, and may be a substitute for $\text{NaHCO}_3\text{-P}$, given their significant correlation and similarity in magnitude.

4.5 Conclusions

This study shows that residue management can increase soil C and nutrient pools or at least alleviate the impact of clear-cut harvesting. The effects of clear-cutting on C and N pools were limited to the first year while residue management had a significant influence in the second year, returning total C on the residue retention plots to concentrations similar to or greater than those prior to clear-cutting. Residue management also influenced labile C and N pools such as HWEOP and HWEON, which consistently showed residue treatment effects after 12 months. The effect of residue management on MBC could not be clearly established due to inconsistencies in the treatment effects over the 2 years. Microbial biomass N showed significant residue management effect on at least one occasion. However, the dynamics of MBN indicated microbial immobilisation of N, which was supported by the declining $\text{NH}_4^+\text{-N}$ but a lack of a decline in soil total N. This study, therefore, indicated that residue retention increased soil C and N pools following clear-cut harvesting in the short term. Similarly, residue management has significant impact on labile P pools with significantly

increased labile P in the residue retention treatments. Measurements of HWETP showed greater sensitivity of residue management effects on soil P, with magnitudes similar to or greater than that of NaHCO_3P , thus had great potential as a sensitive indicator of soil P response to residue management. This study recommends further evaluation of hot water-based labile P pools.

CHAPTER FIVE

Long-term Impact of Residue Management on Carbon and Nitrogen Pools in an Exotic Pine Plantation of Subtropical Australia as Revealed by Chemical and Density Fractionations and ^{13}C NMR Spectroscopy

5.1 Introduction

Soil organic matter (SOM) is important for the long-term sustainability and productivity of plantation forest ecosystems due to its influence on soil physical, chemical and biological properties (Nambiar, 1996; Ghani et al., 2003; Mathers et al., 2003a; Xu and Chen, 2006). Studies have shown that SOM is an important source of nitrogen (N) across a wide range of climatic and soil gradient for both hardwood and softwood species production (Reich et al., 1997; Goncalves et al., 2004b). Furthermore, SOM is an important store of C, improves water quality and restores degraded soils and ecosystems (Lal, 2004; Quénéa et al., 2006). Harvest residue management can maintain or improve SOM following clear-fell harvesting of plantations and lessens the long-term impact of harvesting on soil fertility (Cromer, 1996; Mendham et al., 2003; Lal, 2005). Quantifying the size of SOM pools and characterising their nature are important in understanding the long-term impact of residue management on SOM dynamics and nutrient cycling.

Soil organic matter is a heterogenous mixture of compounds with varying chemical characteristics and physical availability, which influence C and nutrient cycling and stability of SOM (Oades, 1988; Rovira and Vallejo, 2007). Fractionating SOM into biologically meaningful pools such as the recalcitrant and labile C pools is useful for understanding SOM dynamics and nutrient cycling or biogeochemical processes (McLauchlan and Hobbie, 2004; van Hees et al., 2005; Paul et al., 2006). Paul et al.

(2006) also highlighted the usefulness of SOM fractionation in understanding the influence of management on SOM storage and dynamics. While the recalcitrant C pool is less biodegradable, the labile C fraction is defined as the SOM fraction that is both physically accessible and chemically degradable during microbial growth (Zou et al., 2005; Rovira and Vallejo, 2007).

Many methods have been used to separate labile and recalcitrant SOM pools (Doran et al., 1999; McLauchlan and Hobbie, 2004). Physical fractionation of SOM, based on soil particle size and density, has been used to separate SOM into the light fraction (LF) and the heavy fraction (HF) C pools (Gregorich and Janzen, 1996; Six et al., 1998; McLauchlan and Hobbie, 2004; Yamashita et al., 2006). The labile SOM component can also be chemically fractionated into microbial biomass C (MBC), the smallest but most labile C pool, and hot water extractable organic C (HWEOC) (Cook and Allan, 1992; Qualls, 2000; Ghani et al., 2003; Chen et al., 2004; Cookson et al., 2005). Studies in agricultural and forest soils show that HWEOC and MBC C pools are sensitive to land use or management practices, and therefore are potential indicators of soil quality (Bauhus et al., 1998; Ghani et al., 2003; Chen and Xu, 2005). Furthermore, SOM can also be separated into the acid hydrolysable C and non-hydrolysable, recalcitrant C pools (Paul et al., 1997; McLauchlan and Hobbie, 2004). While the MBC, HWEOC, LF C and hydrolysable C indicate the quality of SOM, the recalcitrant pools are a measure of the size of SOM stabilised by microbial processing and adsorption onto mineral surfaces, which have important implications for C sequestration.

In southeast Queensland, Australia, early results of harvest residue management indicated significant improvement in SOM quantity and quality (Mathers and Xu, 2003). However, the long-term impact of residue management on SOM quality and C

sequestration are unknown. Other long-term studies of residue management, however, showed little or conflicting results on the long-term benefits of residue retention on soil C and N storage (Olsson et al., 1996; Knoepp and Swank, 1997; Johnson and Curtis, 2001; Johnson et al., 2002). Furthermore, few long-term studies have assessed the influence of residue management on the various SOM fractions mentioned above. Therefore, this study aimed to understand the long-term impact of harvest residue management on both the forest floor and the soil C and N pools. Earlier studies of residue management impact on SOM storage and quality in southeast Queensland were based on ^{13}C NMR analyses, total C and N, HWEOC and microbial properties (Mathers and Xu, 2003; Chen and Xu, 2005). However, the HWEOC and MBC pools were not as sensitive indicators as expected in differentiating between the residue removal and single residue retention (the operational residue loading rate) treatments on this site. Thus, in order to identify the most sensitive parameters, this study included density and acid hydrolysis fractions as potential indicators of long-term residue management impacts. Since the LF C, MBC and hydrolysable C fractions have been related to each other and to the total soil C (McLauchlan and Hobbie, 2004), this study intended to relate these SOM fractions to the ^{13}C NMR functional groups of SOM, in understanding long-term residue management impacts. Land-use studies have shown that it can influence the chemistry of SOM, and therefore functional SOM pools (Leiffield and Kogel-Knaber, 2005; Helfrich et al., 2006). Thus, the main objective of this study was to combine the use of chemical and physical fractionation techniques with ^{13}C NMR spectroscopy to better understand C and N storage on the forest floor and soil, as well as on the size and nature of SOM pools after 10 years of subjecting an exotic pine plantation to three residue management regimes.

5.2 Materials and Methods

5.2.1 Site description and experimental design

The experimental site is located at Toolara State Forest (26° 00'S, 152° 49'E), Maryborough district, southeast Queensland, and referred to as experiment 321GYM. As described in Chapter 2, Forestry Plantations Queensland (FPQ) established the experiment in July 1996 as a long-term residue management trial. Detailed site description has been provided in Chapter 2 and by previous investigators (Mathers and Xu, 2003; Simpson et al., 2003; Chen and Xu, 2005). In brief, the site has a deep, acidic sandy soil classified as Gleyic Acrisol (FAO, 1974) and was comprised of 5.3 % clay, 7.3% silt, 33.8% sand and 53.9% coarse sand (Mathers and Xu, 2003). Other soil properties had been reported by Mathers and Xu (2003), Simpson et al. (2003) and Chen and Xu (2005).

The experiment is a randomised complete block design with six treatments and four blocks (Simpson et al., 2003). The gross plots were 12 rows by 12 trees at 3 x 3 m spacing and net plots were 8 rows by 8 trees (0.058 ha). The present study focussed on the three residue-loading rate treatments, which are: (1) residue removal; (2) residues retained (50.8 to 73.8 t ha⁻¹); and (3) double quantities of residues retained (140 t ha⁻¹). The three treatments are referred to as RR₀, RR₁ and RR₂, respectively. The plots were planted with the F1 hybrid between slash pine (*Pinus elliottii* var. *elliottii*) and Carribean pine (*Pinus caribaea* var. *hondurensis*).

5.2.2 Forest floor sampling

Forest floor biomass and soil samplings were carried out in August 2006, 10 years after the establishment of the experiment. The forest floor was sampled in three blocks of the three residue treatments with five quadrats (1.0 m² each) systematically laid out within the net plot of each plot. From the top down to the mineral soil, the forest floor biomass

was separated into three distinct layers or horizons representing C pools of varying bioavailability. These were the (1) L horizon, comprised of fresh litterfall characterised by their light brownish colour; (2) F horizon, comprised of fermenting litter characterised by their dark brownish colour; and (3) H horizon, comprised of a mixture of fermenting litter and a thick organic layer which were clearly the woody or bark remains of harvest residues. The H horizon in the RR₁ and RR₂ treatments is not strictly an H horizon according to the European system since the thick organic layer contained varying debris sizes from recognisable plant parts to highly amorphous materials.

In each plot, samples from the five quadrats were pooled into a composite sample for each horizon. The samples were oven dried at 60 °C for 5 days before dry weight was determined. Contaminating soil in the H horizon was removed by shaking the organic material in a 2.0-mm sieve. Therefore, the measured biomass in the H horizon was greater than 2.0 mm in size. The litter horizons were sorted into fruiting bodies and needles before dry weight was determined. Since litter needles comprised more than 95% of the litter biomass, they are presented here as the total litter biomass. Sub-samples of dried forest floor biomass were ground to powder for chemical analyses.

5.2.3 Soil sampling

Composite soil samples were collected at 0 – 10 and 10 – 20 cm depths, respectively, from five soil cores (ca. 7.5 cm diameter) systematically positioned within the net plots (Simpson et al., 2003; Chen and Xu, 2005). The fresh composite samples were passed through a 2.0 mm sieve to remove large debris before being divided into two sub-samples for chemical and microbial biomass analyses. Sub-samples for microbial C and N pools were stored at 4 °C and processed within 2 weeks of sampling (Chen and Xu, 2005), while sub-samples for chemical analysis were air-dried and ground to powder in a puck and ring mill (Rocklab) before chemical analyses.

5.2.4 Soil chemical analyses

Total C and N for plant materials, whole soil and SOM fractions were determined by combustion with Eurovector 3000 elemental analyser (Milan, Italy) coupled to a GVI Isoprime mass spectrometer (Manchester, UK), and the C and N concentrations are expressed as g per kg of soil. The SOM fractionation scheme is presented in Fig. 5.1.

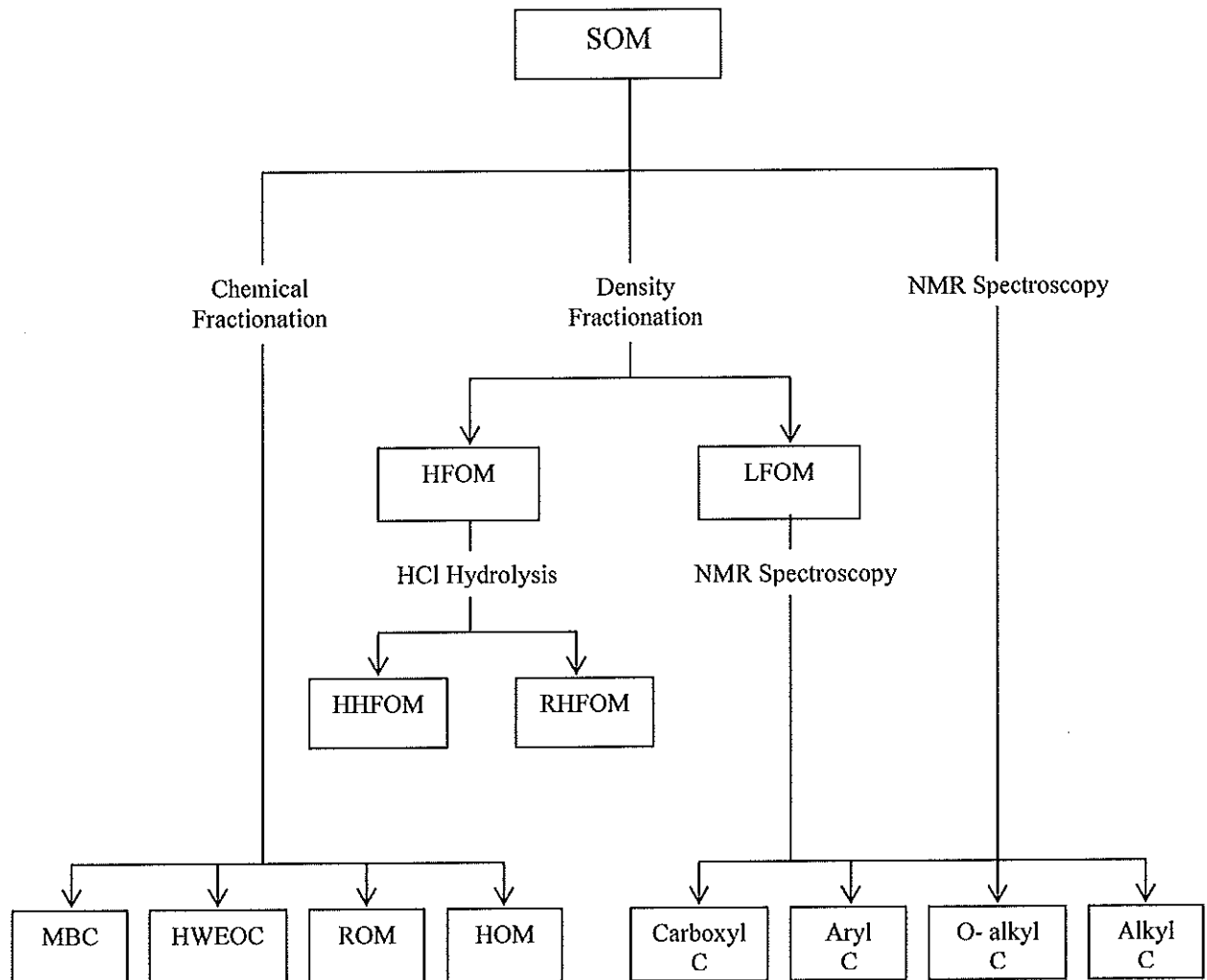


Fig.5.1. The fractionation scheme for soil organic matter in a 10-year-old exotic pine plantation

Soil microbial biomass C (MBC) and N (MBN) were determined by the fumigation-extraction method (Brookes et al., 1985; Vance et al., 1987). Two sub-samples of fresh soil (15.0 g oven dry basis each) were prepared for direct extraction and fumigation,

respectively. Fumigated samples were adjusted to 45% water-holding capacity prior to the 24 hour exposure to ethanol-free chloroform (Chen and Xu, 2005). Both fumigated and non-fumigated sub-samples were extracted with 60 ml of 0.5 M K_2SO_4 for 30 minutes, and the extracts filtered through Whatman 42 filter papers. The total organic C (TOC) and total N (TN) in the extracts were analysed by a Shimadzu TOC-V_{CSH/CSN} TOC/N analyser (Chen and Xu, 2005), and the MBC and MBN were calculated as the difference in extractable TOC and TN before and after fumigation, divided by the correction factors $K_{ec} = 0.45$ and $K_{en} = 0.54$, respectively (Brookes et al., 1985; Vance et al., 1987).

5.2.5 *Hot water extractable organic C and N*

Hot water extractable organic C (HWEOC) and hot water extractable organic N (HWEON) were determined by the method of Sparling et al. (1998) and modified by Chen and Xu (2005). Eight grams (oven-dried equivalent) of air-dried soil was incubated at 70 °C for 18 hours in 40.0 ml of de-ionised water (Millipore purified), shaken in an end-over-end shaker for 5 minutes, centrifuged then filtered through a 0.45 µm filter membrane. The TOC and TN in the extracts were determined by the Shimadzu TOC-V_{CSH/CSN} TOC/N Analyser, where the measured TOC was regarded as the HWEOC, while the HWEON was obtained as the difference in TN (HWETN) and hot-water extractable inorganic N (HWEIN) compounds as determined by a discrete chemistry analyser (DCA).

5.2.6 *Hydrolysable and non-hydrolysable C*

The SOM was separated into hydrolysable and non-hydrolysable or recalcitrant C fractions through hydrochloric acid digestion (Paul et al., 1997; Sollins et al., 1999; Paul et al., 2006). Identifiable plant materials were removed from the air-dried soil according

to Sollins et al. (1999), and ground to powder in a puck and ring grinder. Soil samples (2.0 g) were refluxed at 116 °C for 16 hours in 20 ml of 6.0 M HCl (Paul et al., 2006). The remaining residue was isolated, rinsed with de-ionised water several times, dried at 50 °C for 48 hours, weighed and analysed for total C and N. The hydrolysable C was determined by subtracting the recalcitrant C from the soil total C. We acknowledge the contribution of inorganic C to the hydrolysable C, however, this is assumed to be negligible due to the low pH of the soil.

5.2.7. *Light and heavy fraction organic C density fractionation*

The light fraction organic matter (LFOM) was separated from the heavy fraction organic matter (HFOM) by flotation with aqueous sodium polytungstate (SPT) adjusted to 1.75 g cm⁻³ (Sollins et al., 1999; Marriot and Wander, 2006a; Yamashita et al., 2006). Two 10 g sub-samples of air-dried soil from each replicate were added with 30 ml of SPT, shaken in an end-over-end shaker for 12 minutes at 80 rpm, allowed to settle overnight, and then centrifuged at 3500 rpm for 30 minutes prior to isolation on a pre-weighed 0.45 µm nitrocellulose filter paper. The isolated LFOM and HFOM were rinsed with de-ionised water, dried at 50 °C for 24 hours, weighed and analysed for total C and N by the mass spectrometer. Sub-samples of the HFOM were further fractionated by acid hydrolysis as described above. The remaining recalcitrant heavy fraction (RHFOM) was, rinsed, dried, weighed and analysed for total C and N by mass spectrometer. The hydrolysable heavy fraction C and N pools were obtained by subtracting the C and N concentrations of the RHFOM from that of the C and N concentration of the HFOM.

5.2.8 KCl extractable ammonium-N and nitrate-N

The inorganic NH_4^+ -N and NO_3^- -N pools were extracted from fresh soils with 2.0 M KCl (Chen and Xu, 2005). Five gram (oven dry equivalent) of fresh soil were extracted in 40 ml of 2.0 M KCl by shaking in an end-over-end shaker, centrifuging at 2000 rpm and then filtering through a Whatman 42 filter paper. The extracts were analysed for NH_4^+ -N and NO_3^- -N by the DCA.

5.2.9 Nuclear magnetic resonance (NMR) spectroscopy

The chemistry of whole SOM was assessed by solid-state cross polarisation magic angle spinning (CPMAS) ^{13}C NMR following pre-treatment with 2% HF to remove paramagnetic compounds (Skjemstad et al., 1994; Mathers et al., 2002). The solid-state ^{13}C NMR spectra of both whole SOM and LFOM were obtained from the Varian Unity Inova 400 (Varian Inc., CA) spectrometer operating at a ^{13}C frequency of 100.6 MHz. Samples were packed into a 7 mm silicon nitride rotor and spun at 5000 Hz at the magic angle. A standard cross-polarization pulse sequence was applied, with a single contact time of 2 ms, acquisition time of 14 ms and recycle delay of 2.5 s (Mathers et al., 2007). A total of 2000 transients were collected for each sample over a sweep width of 50 kHz, and chemical shift values were referenced externally to the benzene C resonance of hexamethylbenzene at 132.1 ppm (equivalent to tetramethylsilane at 0 ppm).

The ^{13}C -NMR spectra were divided into the four main chemical shift regions: alkyl C (0 – 45 ppm), *O*-alkyl C (45 – 110), aromatic C (110 – 162) and carbonyl C (162 – 215 ppm). The *O*-alkyl C was further divided into methoxyl C (45 - 60 ppm), carbohydrate C (60 - 90 ppm) and di-*O*-alkyl C (90 -110 ppm) regions, while the aromatic C region was divided into aryl C (110-142 ppm) and *O*-aryl C (142 – 165 ppm) regions. The relative intensities for each region were determined by integration using the Varian NMR software package (Version 6.1c, Varian Inc., CA). The alkyl C to *O*-alkyl C

(A/OA) ratio, carbohydrate C to methoxyl C (CC/MC) ratio and the aromaticity of SOM or decomposing residue layers were also determined as indices of the degree of decomposition or the quality of SOM as a substrate for microbial degradation.

The relative intensity or content of the functional groups should be interpreted with caution due to some limitations in the quantitative reliability of solid state ^{13}C NMR (Ussiri and Johnson, 2003; Helfrich et al., 2006). Spinning side bands (SSB) appeared at 225 ppm for some spectra of the whole SOM, and would have appeared in the aromatic region, however, since these would be a small proportion of the aromatic region, and within the intrinsic error of the instrument, they were ignored during integration of the main chemical shift regions.

5.2.10 Statistical analysis

Analysis of variance (ANOVA) was carried out on C and N pool sizes and chemical composition of SOM and LFOM under the different treatments. Least significant difference (LSD) analysis at $p < 0.05$ was carried out to determine significant differences between treatments. Linear regression analyses were carried out to determine relationships between each C fraction, and between C fractions and the chemical composition of SOM. All statistical analyses and graphing were carried out using Statistix (Version 8.0) and Sigmaplot (Version 10).

5.3 Results

5.3.1 Forest floor total C and N pools

Forest floor biomass horizons represent different stages of residue decomposition. The H horizon contained the largest C and N pools compared to the F and L horizons (Table 5.1). This is due to the fact that harvest residues retained previously largely comprised

the H horizon, especially in the RR₁ and RR₂ treatments, while the L and F horizons are mainly litter horizons. While total C in the RR₂ treatment was significantly greater in the L and H horizons, no significant differences were detected between the RR₀ and

Table 5.1. Forest floor C pools of the L, F and H horizons in a 10-year-old exotic pine plantation under different residue management treatments. Means followed by the same letter in each column, and for each parameter, are not significantly different ($p > 0.05$).

Residue treatments	L Horizon ^a	F horizon	H Horizon ^b	Total
<u>Total C (kg ha⁻¹)</u>				
Residue removal (RR ₀)	1466b	1720a	2145b	5331b
Single residue retention (RR ₁)	1320b	1555a	3706b	6581b
Double residue retention (RR ₂)	1701a	1978a	7226a	10904a
<u>Total N (kg ha⁻¹)</u>				
Residue removal (RR ₀)	10.7b	15.9b	25.3b	51.9b
Single residue retention (RR ₁)	10.4b	17.5b	52.6ab	80.4b
Double residue retention (RR ₂)	12.7a	24.4a	87.8a	124.8a

^a L and F horizons are mainly litter needle horizons.

^b The H horizon represents mostly decomposing woody and bark materials (> 2.0 mm size) originating from harvest residues in the RR₁ and RR₂ treatments.

RR₁ treatments in these litter horizons. Similarly, total forest floor C content was not significantly different between the RR₀ and RR₁ treatments (Table 5.1). Forest floor N pool also increased from the L to the H horizon by 48 % and 144% in the RR₀ and RR₂ treatments, respectively. Total N was consistently higher in the RR₂ treatment but was not significantly different between the RR₀ and RR₁ treatments even though the difference between the means was large.

5.3.2 Soil C and N pools

The largest C fraction was the whole soil recalcitrant C, comprising 55 - 58% of the soil total C. The hydrolysable C consisted of about 43 – 45 % of the soil total C (Table 5.2), while the HWEOC and MBC were about 2.3-2.4 % and 1.1–1.2 % of the soil total C, respectively. The proportion of each C fraction in relation to soil total C, however, was

Table 5.2. Effect of residue retention on the 0 – 10 cm depth soil total C, hot water extractable organic C (HWEOC), microbial biomass C (MBC), recalcitrant C (RC) and hydrolysable C (HC) under the (1) residue removal, RR₀; (2) single residue retention, RR₁; and (3) double residue retention, RR₂, treatments in the 10-year old exotic pine plantation.

Treatments	Total C (g kg ⁻¹)	HWEOC (mg kg ⁻¹)	MBC (mg kg ⁻¹)	RC (g kg ⁻¹)	HC (g kg ⁻¹)	HC ^a (%)
RR ₀	10.6 ^c	255.7 ^c	110.4 ^b	5.8 ^b	4.8 ^c	44.5 ^a
RR ₁	16.0 ^b	365.8 ^b	185.0 ^a	9.2 ^a	6.8 ^b	42.8 ^a
RR ₂	19.4 ^a	458.4 ^a	223.0 ^a	11.0 ^a	8.3 ^a	42.8 ^a

^a Hydrolysable C as a percentage of soil total C.

^b Means followed by the same letter in each column are not significantly different ($p > 0.05$).

not significantly different between the treatments. On the other hand, soil total C, HWEOC and hydrolysable C were significantly different between the treatments and increasing in the order: RR₀ < RR₁ < RR₂ treatments (Table 5.2). The MBC and recalcitrant C were also significantly higher in both the RR₁ and RR₂ treatments compared to those in the RR₀ treatment.

Soil total N in this plantation ranged from a mean of 362.5 mg kg⁻¹ to 575 mg kg⁻¹, with the HWEON and MBN consisting of 3.0% to 3.2% and 3.4% to 4.5% of the total N (Table 5.3). Mineral N ((NH₄⁺-N and NO₃⁻-N) was the smallest pool of N (1.5%-2.2%).

Table 5.3. Total soil N, hot water extractable organic N (HWEON), microbial biomass N (MBN), ammonium N ($\text{NH}_4^+\text{-N}$), nitrate N ($\text{NO}_3^-\text{-N}$), recalcitrant N (RN) and hydrolysable N (HN) in different residue treatments obtained from the 0 – 10 cm soil depth of a 10-year old exotic pine plantation.

Residue treatment	Total N (mg kg^{-1})	HWEON (mg kg^{-1})	MBN (mg kg^{-1})	$\text{NH}_4^+\text{-N}$ (mg kg^{-1})	$\text{NO}_3^-\text{-N}$ (mg kg^{-1})	RN (mg kg^{-1})	HN (mg kg^{-1})	HN ^a (%)
Residue removal (RR_0)	362.5 ^b	11.4 ^c	16.2 ^b	9.8 ^a	0.26 ^a	45.0 ^b	307.7 ^b	84.8 ^a
Single residue retention (RR_1)	507.5 ^a	14.8 ^b	19.2 ^a	10.9 ^a	0.36 ^a	70.0 ^a	426.6 ^a	84.5 ^a
Double residue retention (RR_2)	575.0 ^a	17.3 ^a	19.8 ^a	10.9 ^a	0.36 ^a	77.5 ^a	486.5 ^a	84.2 ^a

^a Hydrolysable N as a percentage of soil total N.

^b Means followed by the same letter in each column are not significantly different ($p > 0.05$).

While the mineral N pool showed no significant variations between the treatments, all the other N pools consistently showed the lowest N content in the RR₀ compared to either RR₁ or RR₂ treatments. The HWEON, similar to the HWEONC (Table 5.2), showed significant variation between the treatments, indicating its sensitivity to each of the three treatments. In contrast to hydrolysable C (Table 5.2), hydrolysable N represented 84-85% of total soil N. However, the proportions of hydrolysable N relative to total N were not different across the treatments. Similar lack of significant variation in the proportion of HWEON and MBN relative to total N between treatments were observed. Interestingly, the proportion of mineral N relative to total N was significantly higher ($p < 0.05$) in the RR₀ treatment (2.8 %), intermediate in the RR₁ (2.2%) and lowest in the RR₂ treatments (1.9%), suggesting higher mineralisation rates per unit of total N in the RR₀ treatments.

5.3.3 Density fractionation of SOM

Density fractionation of the whole SOM showed that the HF C pool was larger (54 – 59 % of total C) compared to the extracted LFC pool (29-39 %) (Table 5.4a). The impact of residue management on the LF C and HF C was also significant with both fractions showing greater mean pool sizes in the RR₁ or RR₂ treatments compared to the RR₀ treatment (Table 5.4a). Acid hydrolysis of the HF C pool showed that about 28-30% of the HF C is hydrolysable, contributing towards 15.4 – 17.8 % of the total hydrolysable C (Table 5.4a). Consistent with other labile fractions, the relative proportion of each pool size in relation to total C was not significantly different between the treatments. Nonetheless, the hydrolysable HF C and the recalcitrant HF C pool sizes were significantly higher in the RR₁ and RR₂ treatments compared to the RR₀ treatment (Table 5.4a).

Table 5.4. The long-term impact of residue retention on the C pools: light fraction C (LFC), heavy fraction C (HFC), recalcitrant HFC (RHFC) and hydrolysable HFC (HHFC) (a), and N pools: light fraction N (LFN), heavy fraction N (HFN), recalcitrant HFN (RHFN) and hydrolysable HFN (HHFN) (b) in a 10-year-old exotic pine plantation under different residue management treatments. Means followed by the same letter in each column are not significantly different ($p>0.05$).

<i>Table 4a</i> Residue treatments	LFC ^a (g kg ⁻¹)	LFC ^b (g kg ⁻¹)	Recovery efficiency (%)	HFC (g kg ⁻¹)	RHFC (g kg ⁻¹)	HHFC (g kg ⁻¹)	HHFC ^c (%)
Residue removal (RR ₀)	3.08 ^b	4.33 ^c	70.20 ^a	6.22 ^b	4.35 ^b	1.97 ^b	17.7 ^a
Single residue retention (RR ₁)	5.50 ^a	6.51 ^b	83.40 ^a	9.52 ^a	6.73 ^a	2.79 ^a	17.4 ^a
Double residue retention (RR ₂)	7.50 ^a	8.83 ^a	85.00 ^a	10.52 ^a	7.53 ^a	2.99 ^a	15.4 ^a

<i>Table 4b</i> Residue treatments	LFN ^a (mg kg ⁻¹)	LFN ^b (mg kg ⁻¹)	Recovery efficiency (%)	HFN (mg kg ⁻¹)	RHFN (mg kg ⁻¹)	HHFN (mg kg ⁻¹)	HHFN ^c (%)
Residue removal (RR ₀)	68.17 ^c	117.50 ^b	59.82 ^a	245.00 ^b	32.50 ^b	212.50 ^b	59.10 ^a
Single residue retention (RR ₁)	118.12 ^b	147.50 ^b	79.32 ^a	360.00 ^a	52.50 ^a	307.50 ^a	60.54 ^a
Double residue retention (RR ₂)	166.03 ^a	202.50 ^a	83.26 ^a	372.50 ^a	60.00 ^a	312.50 ^a	54.19 ^a

^a LFC and LFN extracted with 1.75 g cm⁻³ sodium polytungstate

^b LFC or LFN calculated as the difference between the total C and HFC or HFN, respectively.

^c Hydrolysable HFC and HFN as a percentage of total soil C and N, respectively.

Density fractions of N pools also showed similar results to the C pools, where the HF organic matter contained the largest N pool compared to the LF (Table 5.4b). In contrast to the hydrolysable HFC (Table 5.4a), the proportion of hydrolysable N in the HF pool represented between 54% and 60% of the total N (Table 5.4b), which is 64% to 72 % of the total hydrolysable N. This indicated that the bulk of the whole soil hydrolysable N (Table 5.3) came from the HF N pool. The LF and HF N pools were consistently lower in the RR₀ treatment compared to the RR₁ and RR₂ treatments. However, no significant variation in the proportion of hydrolysable N relative to total N was found between the treatments.

5.3.4 *SOM pool CN ratio and $\delta^{13}\text{C}$*

The C:N ratios and $\delta^{13}\text{C}$ were determined as an index of the extent of decomposition or SOM dynamics (Table 5.5). Results showed that $\delta^{13}\text{C}$ enrichment increased from the LF to the HF C pools consistent with the degree of microbial processing. In addition, both C pools showed significant differences between the treatments, where the LF and HF C pools in the RR₀ treatment were more enriched compared to the RR₁ and RR₂ treatments. The HF $\delta^{13}\text{C}$, however, was particularly sensitive to the treatments as indicated by the significant variation between each of the three treatments (Table 5.5). Interestingly, the recalcitrant HF C or recalcitrant whole soil C $\delta^{13}\text{C}$ showed no significant variation across the treatments. No significant variation in the C:N ratio of all SOM fractions were observed across the treatments. However, the decreasing C:N ratio from the LF C pool to the HF C pool was consistent with the $\delta^{13}\text{C}$ data, indicating the extent of decomposition of the SOM fractions.

Table 5.5. The $\delta^{13}\text{C}$ and C:N ratios of SOM pools obtained in the 0–10 cm depth soil of a 10-year-old exotic pine plantation subjected to the residue removal (RR_0), single residue retention (RR_1) and double residue retention (RR_2) treatments.

Treatment	Bulk soil	LFOM ^a	HFOM	RHFOM	ROM	H-HFOM	HOM
<u>$\delta^{13}\text{C}$</u>							
RR_0	-27.25 ^a _b	-27.71 ^a	-26.40 ^a	-27.95 ^a	-28.00 ^{ab}	-	-
RR_1	-27.25 ^a	-28.01 ^b	-26.80 ^b	-27.73 ^a	-27.85 ^a	-	-
RR_2	-27.50 ^a	-28.01 ^b	-27.20 ^c	-27.90 ^a	-28.15 ^b	-	-
<u>C:N ratio</u>							
RR_0	29.24 ^a	44.46 ^a	25.22 ^a	134 ^a	133 ^a	8.76 ^a	10.98 ^a
RR_1	31.72 ^a	45.38 ^a	26.59 ^a	137 ^a	134 ^a	9.03 ^a	12.18 ^a
RR_2	33.73 ^a	46.40 ^a	28.25 ^a	127 ^a	142 ^a	9.62 ^a	12.00 ^a

^a The SOM pools are the light fraction organic matter (LFOM), heavy fraction organic matter (HFOM), recalcitrant HFOM (R-HFOM), hydrolysable HFOM (H-HFOM), and the whole soil recalcitrant organic matter (ROM) and whole soil hydrolysable organic matter (HOM).

^b Means followed by the same letter in each column, and for each parameter, are not significantly different ($p > 0.05$).

5.3.5 ^{13}C CPMAS NMR Spectroscopy

The bulk SOM and LFOM spectra (Fig. 5.2) show distinctive differences in the intensities of the peaks, especially in the alkyl C (30 ppm), carbohydrate C (75 ppm) and di-*O*-alkyl C (105 ppm) regions between the treatments. The spectra clearly showed a decline in the carbohydrate C intensity and an increasing alkyl C intensity relative to the carbohydrate C intensity, from the RR_2 treatment to the RR_0 treatment (Fig. 5.2). Integration of the four major chemical shift regions showed that the alkyl C was significantly greater in the RR_0 treatment compared to the RR_2 treatment, while the RR_1 treatment had an intermediate intensity (Fig. 5.3). In contrast, the *O*-alkyl C relative

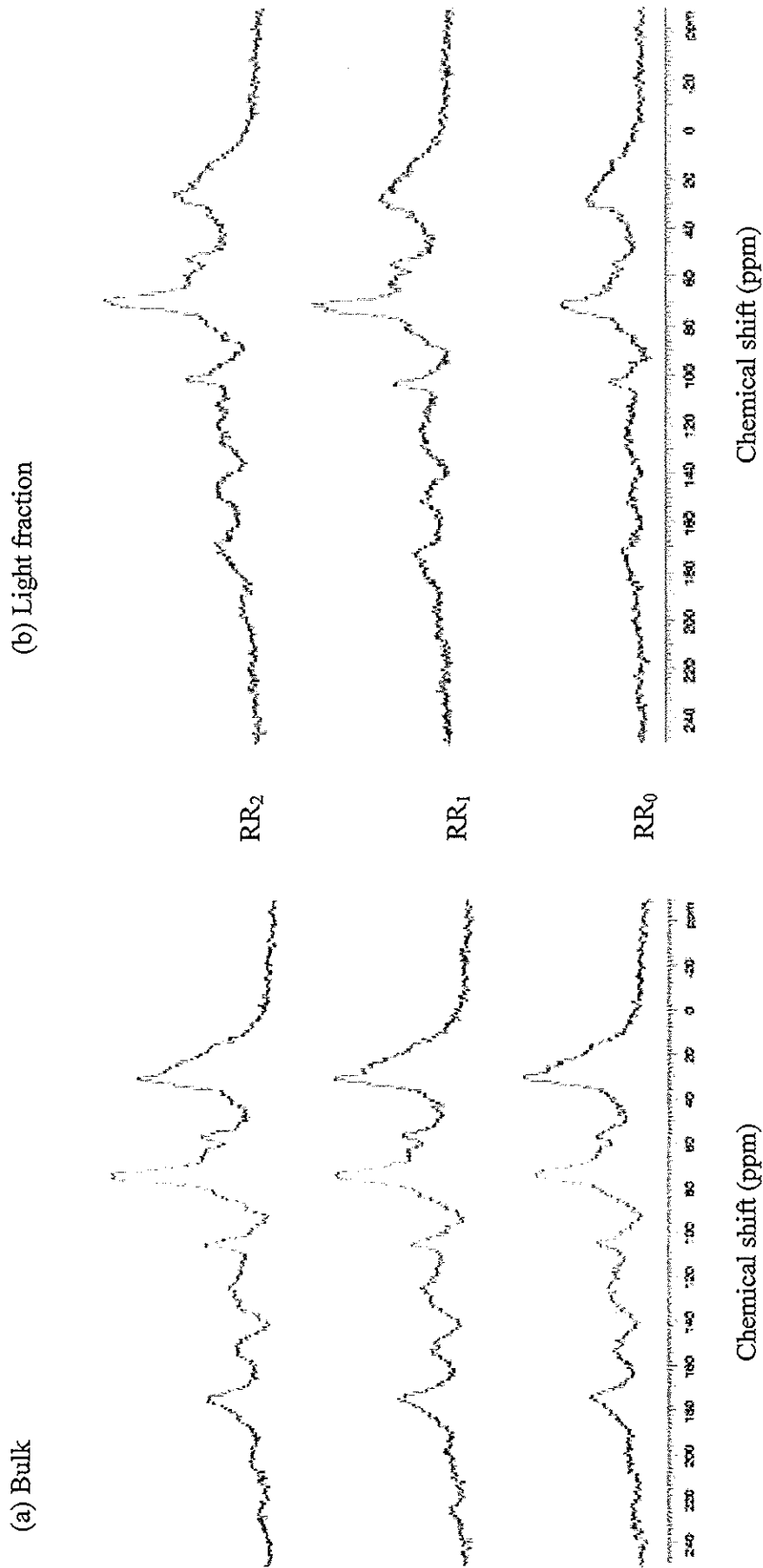


Fig. 5.2. ¹³C NMR spectra of the bulk SOM (a) and light fraction organic matter (LFOM) (b) obtained from the 0 – 10 cm soil depth under the residue removal (RR₀), single residue retention (RR₁), and double residue retention (RR₂) treatments of a 10-year-old exotic pine plantation.

intensities were significantly greater in the RR₂ treatment compared to the RR₁ and RR₀ treatments, which were similar in O-alkyl C intensities. The bulk SOM spectra showed no significant differences between the treatments for the aromatic and carbonyl C groups (Fig. 5.3a). On the other hand, relative intensities obtained from the LFOM spectra showed significantly higher aromatic C in the RR₁ and RR₂ treatments (Fig. 5.3b). Further division of the major chemical shift regions into their subregions (Table 6.6), showed significantly higher methoxyl C and O-aryl (phenolic) C intensities in the bulk SOM of the RR₂ treatment compared to the RR₁ and RR₀ treatments, while the LFOM only showed significant differences in the phenolic C region, which was also greater in the RR₁ and RR₂ treatments. The A/O-A ratio also decreased significantly from the RR₀ treatment to the RR₂ treatment in both the bulk SOM and LFOM (Table 5.6), indicating significant variations in the degree of SOM decomposition between the treatments.

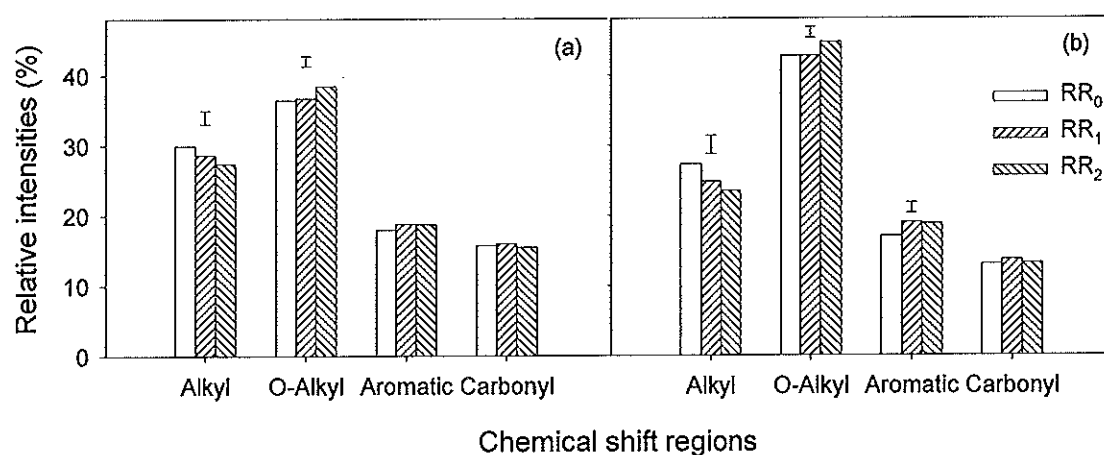


Fig. 5.3. Relative intensities of the major functional groups obtained from the NMR spectra of the bulk SOM (a) and the light fraction organic matter (LFOM) (b) in the 0 – 10 cm soil depth of a 10-year-old exotic pine plantation under three residue management regimes. The bars represented the least significant differences (LSD), and the mean relative intensities were obtained from three replicates.

Comparisons of the LFOM and whole SOM spectra showed significant differences in their chemical composition, especially those marked with an asterisk in Table 5.6. It showed that the LFOM has a relatively low proportion of alkyl C, higher O-alkyl C, especially carbohydrate C and methoxyl C, and a lower proportion of aryl C and carbonyl C compared to the whole SOM. However, as indicated above, the variation in the aromatic C region among the treatments was significant in the LFOM (Fig. 5.3). The *A/O-A* ratio was also significantly lower in the LFOM compared to the bulk SOM (Table 5.6), indicating that the degree of decomposition of this C fraction was less compared to the bulk SOM.

Given the greater aromaticity of LFOM in the RR₁ and RR₂ treatments compared to the RR₀ treatment, the H horizon residues (2.0 – 9.5 mm sizes) of the RR₀ and RR₂ treatments were assessed for their chemical composition. The relative intensities of the functional groups (Table 5.7) indicate higher proportions of aromatic C, both the aryl and phenolic compounds, and consequently a higher proportion of aromaticity in the 2.0 – 9.5 mm sized residues of the RR₂ treatment compared to the RR₀ treatment. In addition, higher alkyl C and O-alkyl C intensities in the residues of the RR₀ treatment compared to the RR₂ treatment were observed. However, the methoxyl C intensity was greater in the RR₂ compared to the RR₀ treatment, while the di-O-alkyl C intensity was lower in the RR₂ treatment compared to the RR₀ treatment. Residues in both treatments, however, have identical *A/O-A* ratios. Comparisons of the H horizon residues and SOM chemical shift regions in the RR₀ and RR₂ treatments (Table 5.6 and 5.7), suggest that residue chemistry may influence SOM chemistry, and therefore its quality.

Table 5.6. Relative intensities (%), A/O-A ratios and aromaticities obtained from the ^{13}C CPMAS NMR spectra of bulk SOM and LFOM of the 0 – 10 cm depth soil in a 10-year-old exotic pine plantation under the residue removal (RR_0), single residue retention (RR_1) and double residue retention (RR_2) treatments. Means followed by the same letter in each column are not significantly different between the treatments ($p>0.05$).

Residue treatment	Chemical shift regions							A/O-A ratio	Aromaticity
	Alkyl C	O-alkyl C					Carbonyl C		
		Aromatic C							
		Methoxyl C	Carbohydrate C	Di-O-alkyl C	Aryl C	O-aryl C			
<u>Bulk soil</u>									
RR ₀	29.9a	6.9b	23.1a	6.5a	12.1a	5.8b	15.7a	0.83a	21.3a
RR ₁	28.6ab	6.8b	23.3a	6.6a	12.6a	6.2ab	16.0a	0.78ab	22.3a
RR ₂	27.4b	7.6a	24.0a	6.8a	12.3a	6.4a	15.0a	0.71b	22.2a
	*	*	*		*		*	*	
<u>LFOM</u>									
RR ₀	27.3a	7.3a	28.1a	7.2a	10.9a	6.1b	13.0a	0.64a	19.6b
RR ₁	24.8ab	7.5a	28.1a	7.0a	11.6a	7.3a	13.6a	0.58ab	21.9a
RR ₂	23.5b	8.3a	28.6a	7.8a	11.9a	6.9ab	13.1a	0.53b	21.6a

* Asterisks denote significant differences ($p<0.05$) between the bulk SOM and LFOM for each chemical shift region or parameter.

Table 5.7. Relative intensities (%), A/O-A ratios and aromaticities obtained from the ^{13}C CPMAS NMR spectra of the H horizon residues (2.0 - 4 mm and 4.0 - 9.5 mm size residues) of the residue removal (RR_0) and double residue retention (RR_2) treatments in a 10-year-old exotic pine plantation. The spectral intensities were the result of pooling three replicates into one sample for each residue size and treatment, therefore no statistical analyses was carried out with these data.

Residue treatments	Chemical Shift Region							A/O-A ratio	Aromaticity (%)	CC/MC ratio
	Alkyl C		O-alkyl C			Aromatic C				
		Meth C ^a	CHO C	D-O-A C	Aryl C	O-aryl C				
<u>RR₀</u>										
2.0-4.0 mm	22.85	6.29	34.00	9.69	9.19	6.54	11.44	0.46	17.76	5.41
4.0-9.5 mm	20.55	7.76	37.84	10.16	8.17	6.14	9.38	0.37	15.79	4.88
<u>RR₂</u>										
2.0-4.0 mm	21.45	9.03	29.75	8.24	10.99	7.78	12.76	0.46	21.52	3.29
4.0-9.5 mm	18.83	8.99	33.75	8.46	10.23	7.85	11.89	0.37	20.52	3.75

^a Meth C = methoxyl C; CHO C = carbohydrate C; D-O-A C = di-O-alkyl C; and CC/MC ratio = CHO C/Meth C ratio

5.3.7 Relationships between C pools

Correlation and regression analyses were carried out on the C and N pools to assess their relationships with each other. Significant correlations were observed between HWEOC and MBC, and between the HWEON and MBN (data not shown), consistent with an earlier study on this site (Chen and Xu, 2005). The LFC, which was determined for the first time in this sandy forest soil, was also significantly related to both the MBC and HWEOC, although the relationship between the LFC and HWEOC was much stronger (Fig. 5.4). Similarly, the hydrolysable C pool was significantly related to the MBC, HWEOC and LFC (Fig. 5.5). However, like the LFC pool, the hydrolysable C pool could only account for 42% of the variation in MBC, compared with the 71% and

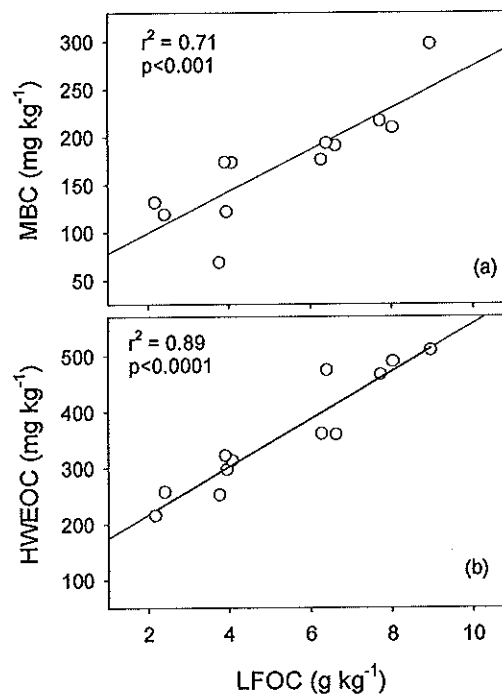


Fig. 5.4. The relationships between light fraction organic C (LFOC) and microbial biomass C (MBC) (a) or hot-water extractable organic C (HWEOC) (b) in the 0–10 cm soil depth of a 10-year-old exotic pine plantation under different harvest residue management regimes.

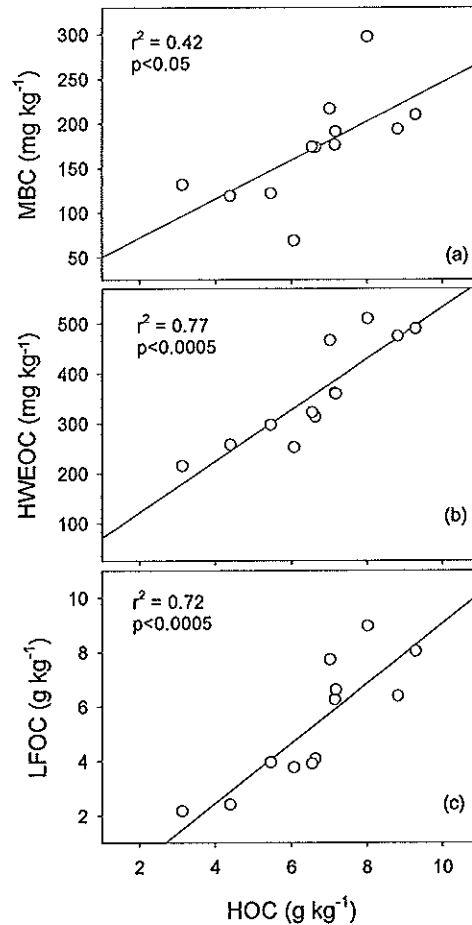


Fig. 5.5. The relationships between hydrolysable organic C (HOC) and microbial biomass C (MBC) (a), hotwater extractable organic C (HWEOC) (b) or light fraction organic C (LFOC) (c) of the 0 – 10 cm soil depth in a 10-year-old exotic pine plantation under different harvest residue management regimes.

77% for the LFC and HWEOC, respectively. The non-hydrolysable C of the whole soil and that of the HFOM were also significantly related ($r^2 = 0.93$; $p < 0.0001$), as were the recalcitrant HF N pool and the recalcitrant whole soil N ($r^2 = 0.75$; $p < 0.0005$). All C or N pool sizes, including the recalcitrant C and N pools, increased with the increasing size of soil total C or N, factors related to the residue loading rates (Table 5.1).

Regression analyses were carried out between the C pools isolated by the chemical and physical fractionation techniques and the chemical shift regions or functional group intensities obtained from the NMR spectra of the whole SOM and the LFOM. Significant relationships between the *O*-alkyl C intensities or the *A/O*-A ratios obtained from the whole SOM spectra and the labile C fractions were established (Fig. 5.6). Similarly, except for MBC vs *O*-alkyl C, significant relationships were found between the labile C fractions and the *O*-alkyl C intensities or the *A/O*-A ratios obtained from the extracted LFOM spectra (Fig. 5.7). The HWEOC pool size explained a greater proportion of the variations of the *O*-alkyl C intensities or *A/O*-A ratio of the whole

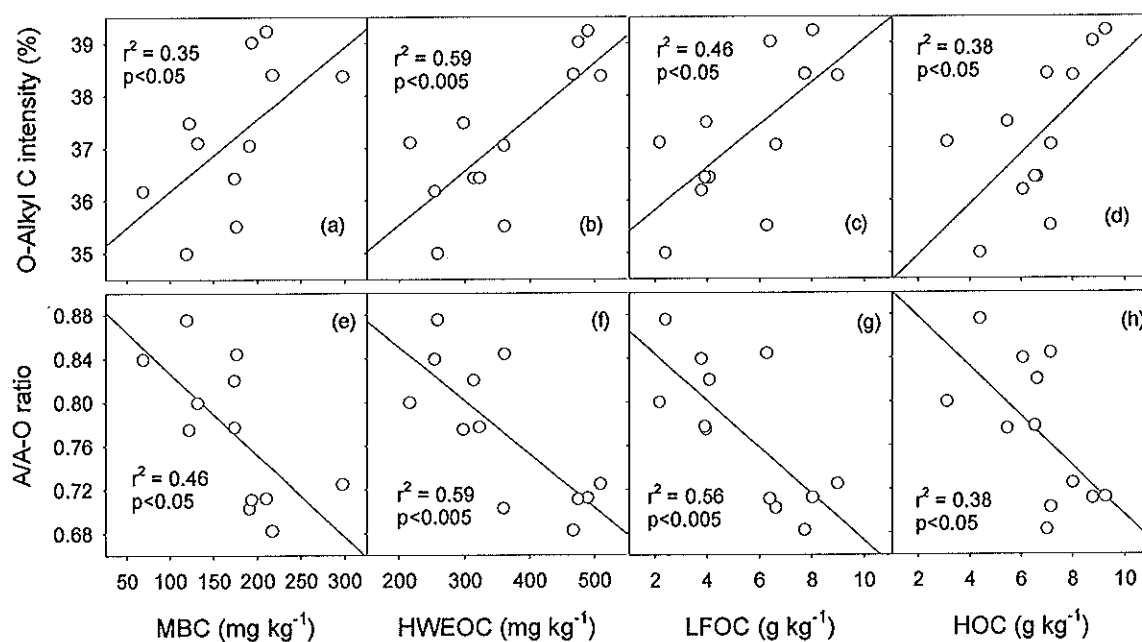


Fig. 5.6. Relationships between the labile C fractions and the *O*-Alkyl C intensities (a-d) or the *A/O*-A ratio (e-h) obtained from the bulk SOM in the 0 – 10 cm soil depth of the 10-year-old exotic pine plantation.

SOM spectra (Fig. 5.6b and 5.6f) compared to the other C fractions. In contrast, LFC and hydrolysable C explained a greater proportion of the variations in the *O*-alkyl C intensities and the *A/O*-A ratios obtained from the extracted LFOM spectra (Fig. 5.7).

This study also found a significant relationship between the LFC and the aromaticity of the LFOM, in contrast to the whole SOM (Fig. 5.8). In contrast, no significant relationship between the recalcitrant fractions or HF C pool and the aromatic or alkyl C intensities of the whole SOM, presuming similarities in biochemical composition and therefore recalcitrance, could be established. However, the non-hydrolysable C pools from the whole SOM and the HFOM showed significant relationships with the methoxyl C (50-60 ppm) ($r^2 = 0.35$; $p < 0.05$ and $r^2 = 0.37$; $p < 0.05$, respectively). The non-hydrolysable HFOM was also related to the di-O-alkyl C intensity, although only weakly ($r^2 = 0.32$; $p < 0.06$).

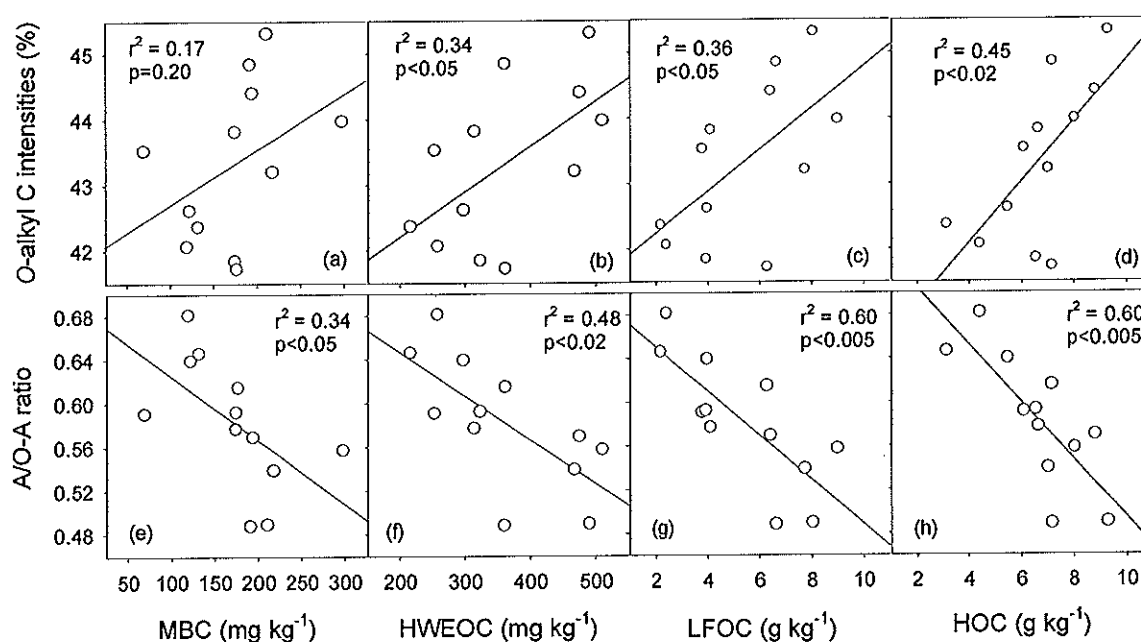


Fig. 5.7. Relationships between the labile C fractions and the O-alkyl C intensities (a-d) or the A/O-A ratios (e-h) obtained from the spectra of the LFOM extracted from the 0 – 10 cm soil depth of the 10-year-old exotic pine plantation.

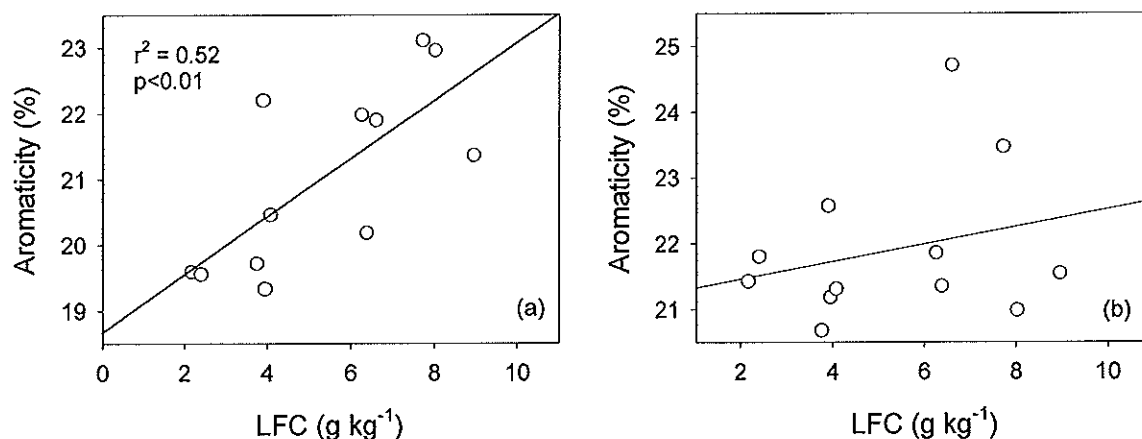


Fig. 5.8. The relationships between the LFC and the aromaticity obtained from the NMR spectra of the extracted LFOM (a) and the aromaticity of the spectra obtained from the bulk SOM (b) of the 0 – 10 cm soil depth in the 10-year-old exotic pine plantation.

5.4 Discussion

5.4.1 Total C and N storage

Harvest residues have the potential to maintain or increase SOM for the purpose of sustaining soil quality, and therefore soil fertility and productivity, as well as the potential to store C in forest plantations. This study demonstrated that residue retention during the inter-rotation had a significant impact on soil total C and N pools as demonstrated by the significant variation between the control treatment, RR₀, and the operational residue retention level, RR₁. The result was in contrast to other studies, showing little or no long term effect of harvest residue retention following clearfall harvesting (Olsson et al., 1996; Knoepp and Swank, 1997; Johnson and Curtis, 2001; Johnson et al., 2002). However, this study was consistent with a meta analysis of published data which showed that, on average, residue retention caused an 18 % increase in C and N in the A horizon, although the impact of retaining residues was

limited to coniferous species (Johnson and Curtis, 2001). This study found that residue retention in the sandy soil of this site increased soil total C by 50% and N by 40 % in the RR₁ treatment, the operational residue retention level, relative to the RR₀ treatment. However, no significant temporal change in soil total C and N was noted after 10 years relative to the measurements conducted in the 2nd (Mathers and Xu, 2003) and 6th (Chen and Xu, 2005) years following establishment in each treatment. Other studies, in contrast, showed a temporary increase, up to 4 years in C and N concentrations (Smethurst and Nambiar, 1990b), while others showed a longer lasting increase in soil C over time following residue retention (Knoepp and Swank, 1997). This result, therefore, suggests that harvest residue management, rather than harvesting *per se* or time, is the critical factor in maintaining SOM C and N. It also suggests that the rate of C and N input is in equilibrium with the rate of loss from as early as 2 years after harvesting in each treatment.

The L and F horizons C pools, which results from litter production, and which were supposed to be responsive to the H horizon residues through residue decomposition, nutrient release and foliar production, however, only showed significant treatment effects in the RR₂ treatment. The quantity of C and N in the H horizons, nonetheless, suggested that *in situ* remnants of harvest residues are still an important source of C and N after 10 years in the RR₁ and RR₂ treatments. The H horizon C and N stocks are an integral component of the plantation ecosystem C stock, thus, these results suggest that harvest residues, given their nature, can increase and maintain forest floor C and N stocks over extended periods. The influence of residue management on forest floor C stock merits further assessment of the total ecosystem C stock, as other studies have shown significant treatment effects on the total ecosystem C rather than the soil C stock (Johnson et al., 2002).

5.4.2 *Labile and recalcitrant C and N pools*

Limited studies have assessed the long-term impact of residue retention on labile C and N pools. Studies of land use change have shown that the structure and stability of SOM can be altered (Helfrich et al., 2006), thus it was a matter of great interest in this study to assess the residue management impact on labile SOM pools. SOM pools can also serve as useful indicators of management practices or sustainability (Sparling et al., 1998; Ghani et al., 2003; McLauchlan and Hobbie, 2004; Paul et al., 2006). The present study showed that residue management not only impacted on the soil C and N stock, it also had significant impacts on the size of the labile C and recalcitrant C fractions in this sandy forest soil.

Studies have shown that MBC can be a sensitive indicator of management in forest soils (Bauhus et al., 1998). An earlier study by Chen and Xu (2005) at the same site as the present study, however, showed no significant differences in MBC between the residue treatments. They attributed the lack of significant differences to high spatial variability. This was in contrast to the significantly higher MBC in the RR₁ and RR₂ treatments compared to the RR₀ treatment (Table 5.2) in the present study, suggesting that time could be an important factor in expressing treatment effects. Nonetheless, the MBC in the present study appeared to be lower than that reported by Chen and Xu (2005) when comparing the means and the standard errors of their work and this present study. This decrease in MBC in all treatments at age 10 years may be reflective of resource quality. However, other factors such as soil moisture, rainfall and temperature could affect the temporal variation in MBC (Chen et al., 2003). The MBN (Table 5.3) showed similar treatment effects and temporal variation as those observed for the MBC.

The significant differences in HWEOC between the treatments (Table 5.2) were consistent with studies showing HWEOC as a sensitive indicator of management on the labile C fraction, and therefore SOM quality (Ghani et al., 2003; Haynes, 2005; von Lutzow et al., 2007). While the earlier study by Chen and Xu (2005) showed significant differences in HWEOC between the RR₀ and RR₂ treatments only, the present study was able to show significant variations in HWEOC between the RR₀ and RR₁ as well, indicating that HWEOC may become more sensitive to the treatments over the longer term. The variation in HWEON between treatments was also in contrast to the lack of variation reported in the 6th year for HWETN (Chen and Xu, 2005). In addition, the HWEON in the present study (Table 5.3) was greater than the hot-water extractable total N (HWETN), which also included inorganic N, reported in the 6th year (Chen and Xu, 2005). This suggests a higher N mineralisation potential at age 10 years compared to that at age 6 years in the residue treatments. However, similar to the earlier study by Chen and Xu (2005) in the same plantation, no significant variation in mineral N concentrations was detected across the treatments after 10 years. Furthermore, mineral N concentration declined by more than 50% compared to those reported in the 6th year (Chen and Xu, 2005). The lack of variation between treatments and the declining mineral N over time, contradicts the likely N mineralisation predicted from the HWEON at age 10 years old. This result could be due to soil moisture limitation, which could limit microbial mineralisation of SOM N. Plant uptake could also influence soil mineral N concentrations (Chen and Xu, 2005), but foliar N concentrations were marginal compared to age 2 years as discussed in chapter 6.

Acid hydrolysis was used for the first time in this plantation to assess the impact of residue management on the size of the labile and non-labile C pools. The sensitivity of hydrolysable C to management is reflected in the significant variation between the

treatments. This study indicated that hydrolysable C is as sensitive as HWEOC to residue management, showing a clear separation between the means in the RR₀ and RR₁ treatments. The large differences in the proportion of hydrolysable C (42% to 45%) and hydrolysable N (84% to 85%) (Tables 5.2 & 5.3), indicate that N is associated mostly with the hydrolysable or labile C pool. This was consistent with studies suggesting that the hydrolysable C contains labile amino acids and amides (Sollins et al., 1999). However, von Lutzow et al. (2007) pointed out that the hydrolysable C could represent more than one C pool if acid hydrolysis is applied to whole soils. This is because acid hydrolysis indiscriminately solubilizes SOM fractions stabilised by different mechanisms, such as occluded SOM (POM), complexed SOM and sorption by polyvalent cation bridges. In the sandy soils of this study, the hydrolysis of the whole soil might have hydrolysed both the LF and stabilised C and N pools in the HFOM as indicated by the hydrolysis of the HF C and N pools (Tables 5.3 & 5.4). Thus, the hydrolysable C pool could be representing both the active and slow pools of SOM of a three-pool model (McLauchlan and Hobbie, 2004). Nonetheless, acid hydrolysis is useful in demonstrating the stability of SOM as well as the impact of management.

According to ¹⁴C studies, the non-hydrolysable C fraction is, on average, about 1200 to 1400 years older than the whole SOM in surface soils, and therefore a meaningful estimate of the passive or recalcitrant C pool (Paul et al., 1997; 2006). However, a recent review by Paul et al. (2006), showed that the non-hydrolysable C may not be as recalcitrant as previously thought, and that it is a dynamic pool sensitive to management, rapidly increasing or declining after retention or removal of organic residues, respectively. This observation is consistent with the significantly greater recalcitrant fraction in the RR₁ and RR₂ treatments compared to the RR₀ treatment of this exotic pine plantation. In addition, the significant relationship between the

recalcitrant fraction and total C is also consistent with other studies (Paul et al., 2006). Thus, residue retention, through the accumulation of the non-hydrolysable C pool, has significant implications for C sequestration due to the lengthy turnover time of this C pool.

5.4.3 *Light and heavy fraction C*

The LF C pool is the most labile fraction compared to the heavy fraction, with a turnover time of <10 years or a couple of decades (Golchin et al., 1995; Baisden et al., 2002). Studies have shown that the LF C pool responds to management more readily than the stabilised heavy fraction (Cambardella and Elliott, 1992; Gregorich and Janzen, 1996; Six et al., 1998). In addition, LF N could be a potential predictor of N availability from labile SOM due to its significant correlation with potentially mineralisable N (Curtin and Wen, 1999). In this study, the significant variation in the sizes of the LF C and N pools between the treatments were consistent with previous studies (Cambardella and Elliott, 1992; Gregorich and Janzen, 1996; Six et al., 1998). The similar response by the HF C and N pools to residue management was also consistent with studies where straw incorporation induced C and N immobilisation and eventual stabilisation into SOM fractions by the microbial biomass (Bird et al., 2001). In addition, the greater proportion of hydrolysable N within the HF pool, indicated that residue retention could lead to increased stabilisation of C and N compounds onto the mineral surfaces of this sandy soil, consistent with studies showing stabilisation of hydrolysable proteins and amino acids, including polysaccharides within fine size mineral fractions in the long term (Knicker, 2004; Sollins et al., 2006; von Lutzow et al., 2007). This study indicated that although the clay and silt size mineral fractions of this soil are small in proportion (5.3% and 7.3%, respectively) (Mathers and Xu, 2003), they could play an important

role in the stabilisation of organic N as indicated by the significant differences between treatments in the hydrolysable N of the whole soil and the HF C pools.

The significant variation in $\delta^{13}\text{C}$ of the LF and HF C pools across the treatments also suggests the influence of residue management on the degree of microbial processing of SOM. The $\delta^{13}\text{C}$ enrichment either indicates more advanced decomposition in the RR_0 treatment compared to the RR_1 and RR_2 treatments or that continuous additions of new organic matter in the RR_1 and RR_2 treatments diluted the $\delta^{13}\text{C}$ enrichment. The decline in the C:N ratio from the LF to the HF C pool is also a reflection of the N stabilisation in the HFOM. These observations were consistent with studies showing lower C:N ratio and higher enrichment of ^{13}C and ^{15}N isotopes during the stabilisation of C in mineral associated SOM (Bird et al., 2001; Baisden et al., 2002). Interestingly, the non-hydrolysable, recalcitrant HF C pool did not show any variation in $\delta^{13}\text{C}$, such as those for LF and HF C pools, across the treatments, and therefore failed to indicate residue management impacts on the relative age or degree of decomposition of the recalcitrant C pool. It is probable that ^{13}C -containing compounds were less resistant to acid hydrolysis, demonstrating the uncoupling of biodegradation and laboratory chemical degradation in this situation. Trumbore and Zheng (1996) reported similar results for tropical soils using the ^{14}C tracer, suggesting the exchange of young for old C on functional groups of the non-hydrolysable C pool during acid hydrolysis as the cause of the lack of variation in the age of whole SOM and the recalcitrant fraction. On the other hand, it could just be that the recalcitrant HF C pool is too isolated to be influenced by additions of new SOM and therefore the dilution effect mentioned above.

5.4.4 SOM chemistry as revealed by ^{13}C NMR

CPMAS ^{13}C NMR spectroscopy is an advanced technique that provides useful information on the structure of SOM, which could be related to SOM functional pools with different stages of decomposition or turnover rates (Helfrich et al., 2006). The chemistry of SOM can be influenced by the type of litter inputs, degree of decomposition, and the type of micro-organisms, therefore microbial products (Ussiri and Johnson, 2003; Helfrich et al., 2006). The alkyl C region, resonance at 30 ppm, is assigned to recalcitrant long chain aliphatic structures such as waxes, lipids, cutins and resins, which increase in proportion as decomposition of SOM proceeds (Kögel-Knabner et al., 1992; Baldock and Preston, 1995; Dai et al., 2001; Mathers and Xu, 2003; Ussiri and Johnson, 2003; Helfrich et al., 2006). The increase is attributed to microbial synthesis of alkyl C structures and increased cross-linking of the long-chain alkyl compounds during humification (Baldock et al., 1990; Kögel-Knabner et al., 1992; Mathers and Xu, 2003). In this study, the significant increase in the alkyl C intensity obtained from the SOM and LFOM spectra of the RR_0 treatment relative to the RR_2 treatment is consistent with the above studies, where the paucity of new C sources, and therefore a likely greater proportion of decomposition products were present in the RR_0 treatment. An earlier study by Mathers and Xu (2003) on this same plantation at age 2 years old, also reported a slightly higher, although not statistically significant, alkyl C intensity in the RR_0 treatment in comparison to the RR_2 treatment. The significant variation in alkyl C intensity in the present study demonstrates a gradual differentiation between the two treatments over time, thus stressing the importance of long-term studies in assessing the impact of residue management on the nature of SOM.

Carbohydrate C, the principal component of the *O*-alkyl C region (Kögel-Knabner et al., 1992), is usually the first region to lose intensity due to the preferential degradation of

carbohydrates (Skjemstad et al., 1997; Mathers and Xu, 2003; Ussiri and Johnson, 2003). This situation is clearly demonstrated in Fig. 5.5, where the carbohydrate peak intensity (60 – 110 ppm) is lower in the RR₀ treatment. In contrast, the relatively higher *O*-alkyl C intensities in the RR₁ and RR₂ treatments were due to the continuous input of labile C from the residue retention treatments, thus the bulk SOM and LFOM fractions have a lesser degree of decomposition or decomposition products. This was supported by the *A/O*-A ratio (Table 5.6), which decreased significantly from the RR₀ to the RR₂ treatment, again indicating greater decomposition of SOM fractions in the RR₀ relative to the RR₁ and RR₂ treatments or the dilution of ‘old’ SOM with ‘new’ organic matter rich in carbohydrates in the RR₁ and RR₂ treatments.

The significantly greater proportion of methoxyl C in the bulk SOM of the RR₂ treatment compared to the RR₀ treatment was consistent with the study by Mathers and Xu (2003) on the same plantation at age 2 years old. The methoxyl C peak (45-60 ppm) arises from the O-CH₃ bond common in lignin and tannin compounds, and from the N-CH₂ bond of amino acids (Mendham et al., 2002a). The significantly higher *O*-aryl C intensity of the whole SOM and LFOM in the RR₂ treatment compared to the RR₀ treatment suggests that lignin and tannin compounds made a large contribution to the methoxyl peak. However, the contribution of amino compounds, which were presumably a major component of the hydrolysable C and N, and greatest in the RR₂ treatment (Table 5.4b) could not be ruled out. Nonetheless, the greater proportion of methoxyl C, and *O*-aryl C intensities in the H horizon residues and the LFOM spectra of the RR₂ treatment compared to the RR₀ treatment was also reflective of the dilution of ‘old’ SOM with ‘new’ organic matter or decomposing residues rich in lignin and tannin as evidenced by the methoxyl and *O*-aryl C peaks. This result was also consistent with the reported presence of condensed tannin structures in decaying bark, small wood and

foliage of hoop pines (Mathers et al., 2003b). The significant variation of di-*O*-alkyl C at age 2 years old of the same site also indicated the presence of lignin and tannin structures in the decomposing harvest residues (Mathers and Xu, 2003).

The lack of significant variations in di-*O*-alkyl C obtained from both the whole SOM and LFOM in contrast to the significant variations at age 2 years of the plantation (Mathers and Xu, 2003) was probably due to the increasing intensity of di-*O*-alkyl C in the RR₀ treatment (48% increase), while the di-*O*-alkyl C in the RR₂ treatment was relatively unchanged over time. The increase in the di-*O*-alkyl C intensity in the RR₀ treatment (Table 5.6), however, could be attributed to the recent input of decomposing litterfall C. This was apparent in the ¹³C NMR analysis of the H horizon residues in the RR₀ treatment, where a larger proportion of carbohydrates and di-*O*-alkyl C was present in the RR₀ treatment compared to the RR₂ treatment (Table 5.7). The higher carbohydrate to methoxyl C ratio (Blumfield et al., 2004a) in the H horizon residues of the RR₀ treatment relative to the RR₂ treatment (Table 5.7) suggests recent inputs of *O*-alkyl C sources in the RR₀ treatment, most likely from litterfall that came in direct contact with the soil. This is in contrast to the RR₁ and RR₂ treatments where these recent inputs of C sources were unlikely to be detected due to the thick harvest residue layers which prevented the litterfall C from coming in contact with the soil matrix.

Comparisons of the SOM chemistry at age 2 (Mathers and Xu, 2003) and the present study also showed that while the aryl C intensity remains unchanged, the *O*-aryl C intensity had increased by 32% and 23% in the RR₀ and RR₂ treatments, respectively, possibly due to increased input of decomposing woody residues in the RR₂ treatments and decomposing litter needles in the RR₀ treatment. In addition, while SOM chemistry at age 2 years revealed a relatively lower proportion of aromaticity in the RR₂ treatment

compared to the RR₀ treatment, the present study, in contrast, showed that the aromaticity appeared to be higher in the RR₁ and RR₂ treatments. This was supported by the NMR analysis of the LFOM where a significantly higher aromaticity was found in the RR₁ and RR₂ treatments compared to the RR₀ treatment (Table 5.6). These findings support the proposition that lignin and tannin content of the decomposing woody residues influenced the aromaticity of SOM in the present study.

The differences in chemical composition, especially the alkyl C, methoxyl C, carbohydrate C and aryl C intensities and the A/O-A ratio of the whole SOM and LFOM demonstrate the different stages in decomposition of SOM fractions. By deduction, a larger proportion of the alkyl C intensities in the bulk SOM spectra (Fig. 5.5a) might have come from the stabilised HFOM, which include microbial products and humified C fractions. In addition, higher carbohydrate intensities in the LFOM suggest that LFOM is a relatively young input into the SOM. This was consistent with the $\delta^{13}\text{C}$ data. Furthermore, the lower aryl C intensity and A/O-A ratio in the LFOM compared to the whole SOM is consistent with studies showing increasing decomposition from free LFOM to fine particle size OM (von Lutzow et al., 2007). These differences in the chemical structure of LFOM and whole SOM explain the labile nature of the LF C.

5.4.5 *Relationships between SOM fractions*

The relationships between MBC, HWEOC, LF and hydrolysable C fractions (Figs. 5.3 & 5.4) were consistent with those reported by McLauchlan and Hobbie (2004) in arable soils and Chen and Xu (2005) at the same site as this study. The significant relationship between LFC and MBC was consistent with studies suggesting LF C as having a substantial microbial component (Paul and Clark, 1996). The stronger relationships

between LFC and HWEOC and between LFC and hydrolysable C suggest that they are probably parts of the same labile pool of C (McLauchlan and Hobbie, 2004). As indicated earlier, the hydrolysable C may include some stabilised SOM, which would explain its larger size relative to the LF C. The significant relationship between the HF C pool and the whole soil recalcitrant C pool suggests that they represent the same pool of stabilised SOM. Overall, the significant relationship between all the SOM fractions and the total soil C was consistent with other studies (McLauchlan and Hobbie, 2004; Paul et al., 2006), indicating the impact of residue retention on total C also influenced the size of SOM fractions.

The significant relationships between labile C fractions and the *O*-alkyl C intensity of the whole SOM and LFOM explains that the *O*-alkyl C structures are the most labile components of SOM, reflective of carbohydrates, cellulose, hemicelluloses, polysaccharides, alcohols and amino sugars (Skjemstad et al., 1997; Ussiri and Johnson, 2003; Mathers et al., 2007). This was consistent with pyrolysis mass spectrometry analysis of HWEOC, which is largely composed of carbohydrates, amino-N and amides (Leinweber et al., 1995; von Lutzow et al., 2007). The hydrolysable C fraction also contained amino compounds, pectins and most cellulose (Sollins et al., 1999). The stronger relationship between hydrolysable C and the *O*-alkyl C intensity obtained from the LFOM spectra (Fig. 5.7) compared to that of the whole SOM spectra (Fig. 5.6) suggests that the hydrolysable C fraction largely came from the light fraction C pool, consistent with the small proportion of hydrolysable C in the HFOM pool (Table 5.4a). Furthermore, the decrease in labile C fractions with increasing A/O-A ratio (Figs. 5.6 & 5.7) was also consistent with the decreasing *O*-alkyl C compounds with increasing decomposition.

The lack of a significant relationship between MBC and *O*-alkyl C in the LFOM was unexpected, as a significant relationship between the LF C pool and MBC was established in this study, and other studies have shown that the LFOM has a significant microbial component (Bird et al., 2002). Thus the significant relationship between MBC and the *O*-alkyl C of the whole SOM, rather than the LFOM, is difficult to explain.

Interestingly, while the labile C fractions could be related to the *O*-alkyl C structures, the same could not be demonstrated for the non-hydrolysable, recalcitrant fractions and the corresponding aromatic or alkyl C structures, presuming similarities in biochemical composition and therefore recalcitrance. However, the significant relationship between the non-hydrolysable whole SOM (Table 5.2) and either the methoxyl or di-*O*-alkyl C of the whole SOM spectra indicated that the non-hydrolysable C at this site probably consisted of lignin and tannin structures, which increased with increasing input of harvest residues containing these compounds. Although the non-hydrolysable C pool is composed of more than just lignin and tannins, the significant relationship between the LFC pool and the aromaticity obtained from the LFOM spectra (Fig. 5.8) further supported this proposition. The relationship between LFC and the aromaticity obtained from the LFOM spectra was consistent with the presence of lignin and tannin structures, which in turn influenced the aromaticity of whole SOM. These findings have significant implications for nutrient mineralisation as studies have shown that tannins can form complexes with labile C pools, therefore affecting their mineralisation (Halvorson and Gonzalez, 2008).

5.5 Conclusion

This study demonstrated that residue management can have long-term impacts on the C and N stocks of a plantation as indicated by the size of the forest floor and soil total C and N concentrations of this exotic pine plantation, with a potential for C sequestration.

It showed that residue management impacts were more pronounced in the soil C and N concentrations than on the forest floor C pools, as indicated by the sizes of all the labile and recalcitrant soil C pools measured. This study indicated that HWEOC, HWEON, heavy fraction $\delta^{13}\text{C}$, and hydrolysable C were more suitable indicators of long-term residue retention, and perhaps requires further assessments in a wide range of soils. The relationship between labile C pools and their relative sizes within a sample indicated that they were parts of the same labile C pool. This study also showed that the sizes of labile C pools were related to the SOM chemistry as revealed by the ^{13}C NMR spectroscopy analyses, and that residue chemical composition influences the chemistry of SOM, which can change over time as the sizes of the C pools changes. Thus, these results signify that harvest residue retention is an important management strategy with long-term impacts on C sequestration and on both the quantity and quality of SOM in plantation ecosystems.

CHAPTER SIX

Long-term Impacts of Harvest Residue Management on Nutrition, Growth and Productivity of an Exotic Pine Plantation of Subtropical Australia

6.1 Introduction

Increased demand for plantation timber and a reduction in the land available for plantation expansion increases the importance of the adoption of sustainable production forestry practices. Retaining residues on-site following clear-cut harvesting of timber plantations is an important strategy for sustaining the productivity of subsequent rotations (Smethurst and Nambiar, 1990a). Harvest residues are a source of soil organic matter (SOM) and nutrients in forest plantations (Blumfield and Xu, 2003; Mathers and Xu, 2003; Goncalves et al., 2004a). Although the effect of harvest residues is not always observed (Olsson et al., 1996; Knoepp and Swank, 1997), studies on pines (Proe and Dutch, 1994; Smith et al., 2000; Simpson et al., 2003; Tiarks et al., 2003) and eucalypts (Jones et al., 1999; Nzila et al., 2002; Mendham et al., 2003b) have shown significant growth responses as a result of residue retention. A number of these studies have clearly demonstrated the direct linkage of tree growth to the nutrition effect of harvest residues (Proe et al., 1999; Nzila et al., 2002; Mendham et al., 2003b; Blumfield et al., 2004b).

Residue impacts on tree growth, however, may change over time (Smith et al., 2000; Simpson et al., 2003) and therefore, the extent to which residues impact on productivity needs to be determined so that alternative management practices are integrated with residue management to sustain plantation productivity. Long-term experiments are,

therefore, necessary to understand the variation in tree growth over time in response to different site preparation and management regimes. While a number of studies have assessed the long-term impacts of harvest residues (Proe and Dutch, 1994; Simpson et al., 2003; Tiarks et al., 2003), most of these studies were conducted in temperate regions where soil processes and tree growth rates are slower. Long-term studies of this nature under tropical or sub-tropical conditions, where tree growth is faster and therefore growth demand for nutrients is greater, are limited.

In sub-tropical Queensland, Australia, clear-cut harvesting of slash pine plantations generates between 30 and 46 tha^{-1} of residues (Simpson et al., 2003). An experiment established to assess the benefits of the residues on soil properties and plantation productivity, showed positive impacts of residue retention on soil total carbon (C), total nitrogen (N), SOM quality parameters, and tree growth in the first six years compared to residue removal (Mathers and Xu, 2003; Simpson et al., 2003; Chen and Xu, 2005). Foliar nutrients, however, showed no significant difference across the treatments and were all above critical concentrations.

In this study, we were interested in assessing the long-term (over 10 years) nutrition and productivity of slash pine plantations, which have an expected rotation length of 25 years. Initial studies by Simpson et al. (2003) indicated that the residue effects might be rather limited. However, other studies suggest that the nutrition effect of harvest residues may be demonstrated in the longer term (Proe and Dutch, 1994; Olsson et al., 2000; Mendham et al., 2003b), probably due to the late release of nutrients from slowly decomposing residues (Smith et al., 2000; Pu et al., 2001; 2002). We therefore, hypothesised that the nutritional effect could become significant in the long term as more nutrients were released from the residues over the 10 years. We also hypothesised

that C input through residue retention would result in more C fixed through foliar production and litter recycling when nutrients important for maximising photosynthesis or leaf area index are released from the decaying harvest residues. Litterfall is an important source of C and nutrient fluxes to the forest floor (Pedersen and Bille-Hansen, 1999) and contributes to the overall ecosystem C balance. A long-term study by Tiarks et al. (2003) showed significantly higher total litter biomass in treatments where harvest residues were retained. Thus, the benefits of retaining harvest residues could extend to subsequent rotations in the form of litter biomass C and nutrients.

Therefore, the main objective of this study was to assess the long-term impact of residue retention on foliar nutrition, tree growth and C and nutrient cycling as represented by litterfall. Unlike other studies, we determined both the total growth and the periodic growth rates to assess the extent to which residue retention would impact on tree growth.

6.2 Materials and Methods

6.2.1 Site description and experimental design

This study was carried out at experiment 321GYM, Toolara State Forest (26° 00'S, 152° 49'E), southeast Queensland. The details of this site, including soil physical and chemical properties are described in Chapter 2 and in past publications of the experiment (Mathers and Xu, 2003; Simpson et al., 2003; Chen and Xu, 2005). As described in Chapter 2, the experiment is a randomised complete block design with six treatments and four blocks. This study focused on the three harvest residue retention regimes, which are: (1) no residues retained, RR₀; (2) single quantity of harvest residues retained (operational quantity), RR₁; and (3) the double quantities of harvest residues retained, RR₂. The three treatments were each applied with 50 kg ha⁻¹ of P as superphosphate during the establishment of the trial. The plots were planted with the F1

hybrid between slash pine (*Pinus elliottii* var. *elliotti*) and Caribbean pine (*Pinus caribaea* var. *hondurensis*), with the measurement plots planted with stock from 6 different families of the hybrid.

6.2.2 Tree measurements and foliar and litter production sampling

In July 2006, 10 years after establishment, diameter at breast height (DBH) (measured at 1.3 m above ground), basal area (BA) and tree height (HT) were determined from all trees within the net plots of each treatment. Growth data were obtained from past samplings for the years 1998, 2000, 2002 and 2004. Foliage was sampled from the northward facing side of the tree canopy, the side having the longest exposure to sunlight during the day (Xu et al., 1995b; Xu et al., 2000; Simpson et al., 2003). Fifty fascicles of the most recent, fully expanded needles (approximately 1 year old) were collected from four average trees within a treatment plot and bulked as one sample (Simpson et al., 2003). These same four trees had been sampled in the previous years, unless a tree lost its 'average tree' status. As in the previous samplings, foliar sampling was carried out in mid to late winter when tree growth was minimal and foliar nutrient concentrations were at maximum (Xu et al., 1995b; Piatek and Allen, 2000).

Litterfall was measured quarterly over 15 months from July 2005 to October 2006 from five 1.0 m² litter traps, systematically positioned in each plot by dividing each measurement plot into quarters and placing 4 quadrats in each quarter away from the centre of the plot, and the fifth quadrat in the centre of the plot. Litter from the five quadrats were bulked into one sample per plot. We also sampled two distinct layers (L and F horizons) of forest floor litter, which represented different timeframes, to determine if earlier litter N and P concentrations would show the treatment effects. The L horizon comprised of the current year, fresh, brightly brownish in colour litter

needles, while the F Horizon comprised of the fermenting or decomposing litter layer. These horizons were sampled from five quadrats (1.0 m^2) systematically positioned in each plot. The litter horizons were sampled in only three out of the four replicates for each treatment. Assuming the lifespan of fully expanded needles is about two years (Wienand and Stock, 1995; Piatek and Allen, 2000), the 2005-2006 litter needles of the L horizon represented foliar production of the 2003-2004 period, while the litter in the F horizons, which appeared to be at least 1-2 years older than the L horizons, were likely to be from foliar production of year 2002 or earlier. Thus, F horizon chemical parameters were related to the growth data of 2000-2002 periods.

All foliage and litter samples were oven dried at 60°C for at least 5 days, sorted into fruiting bodies and needles before dry weight was determined. Since litter needles comprised more than 95% of the litter biomass, they were presented here as the total litter biomass. Sub-samples of the litter samples were ground to powder in a puck and ring mill before chemical analyses.

6.2.3 Chemical analyses

Foliar and litter total C and N were determined by a Eurovector 3000 elemental analyser (Milan, Italy) coupled to a GVI Isoprime mass spectrometer (Manchester, UK). Foliar and litter total P, and foliar Ca, Mg and K concentrations, were analysed following nitric/perchloric ($\text{HNO}_3/\text{HClO}_4$) acids digestion of samples (Kalra, 1998; Olsson et al., 2000a). Total P was determined by the ascorbic acid method (Murphy and Riley, 1962), while foliar Ca, Mg and K concentrations were determined by flame atomic absorption spectrophotometer (FAAS) (Avanti, GBC Sigma). Foliar samples from 1998, 2000 and 2002 were also analysed along with those of 2006 for total N, P and K concentrations to determine changes in long-term nutrition. Samples of all years were digested and

analysed as one batch so that they were subjected to the same analytical conditions and therefore allow valid comparisons across the years.

6.2.4 Periodic annual increment (PAI)

In order to follow the growth process over the 10 years, the periodic annual increments (PAI) of tree growth indices were calculated over an interval of 2 years as follows:

PAI = difference in total growth of two consecutive years / time (2 years)

While calculations showed that DBH, BA and HT all showed similar trends, peaking at age 4 years and declining thereafter, only the PAI of DBH (PAID) and BA (PAIB) were presented in the results to represent the growth process and to correlate with the other parameters.

6.2.5 Total litter N and P content

Litter N and P contents for each sampling were obtained by multiplying N and P concentrations of litters with the total litter biomass for each collection. The N and P content from each sampling over the year were added together to estimate the annual N and P recycled or transferred to the forest floor as litter biomass (Piatek and Allen, 2000).

6.2.6 Statistical analysis

Analysis of variance (ANOVA) was carried out on tree growth data, litter production, nutrient turnover and chemical parameters of each treatment at each age. For comparisons of data at ages 2 – 10 years an ANOVA with repeated measures was carried out on parameters of interest. Least significant difference (LSD) analysis at $p < 0.05$ was carried out to determine significant differences between treatments. Linear

regression and Pearson's correlation analyses were carried out to determine relationships between the growth indices and chemical parameters. All statistical analysis was carried out using Statistix (Version 8.0).

6.3. Results

6.3.1 Tree growth

Measurements of DBH and BA at age 10 years showed that the cumulative growth was greater in both the RR₁ and RR₂ treatments than in the RR₀ treatment (Table 6.1), an observation which was consistent with the early growth (Fig. 6.1a-b). However, the gap among the treatments appeared to be narrowing at age 10 years (Fig. 6.1a-b). This observation might be related to the declining periodic PAID and PAIB after age 4 years (year 2000). Although these growth indices showed significant treatment effects during the early growth, the PAID and PAIB declined substantially ($p < 0.005$) after peaking in year 2000 (Fig. 6.1c-d). Treatment effects also disappeared after year 2000, except for PAIB. By year 2006, the PAID had dropped by 68 – 78%, and both PAID and PAIB across the treatments were in the order RR₀ > RR₁ > RR₂ after the drop in growth rate, reversing the trend prior to year 2000. This trend in growth rate showed a significant

Table 6.1. The cumulative basal area (BA), diameter at breast height (DBH) and tree height (HT) of the 10 year-old F1 hybrid exotic pine plantation with three harvest residue management regimes in sub-tropical Australia.

Treatments	BA (m ² ha ⁻¹)	DBH (cm)	HT (m)
Residue removal (RR ₀)	24.90 ^c *	21.37 ^c	15.45 ^b
Single residue retention (RR ₁)	26.53 ^b	22.00 ^b	15.73 ^{ab}
Double residue retention (RR ₂)	28.31 ^a	22.86 ^a	16.00 ^a

*Means followed by the same letter in each column are not significantly different ($p > 0.05$)

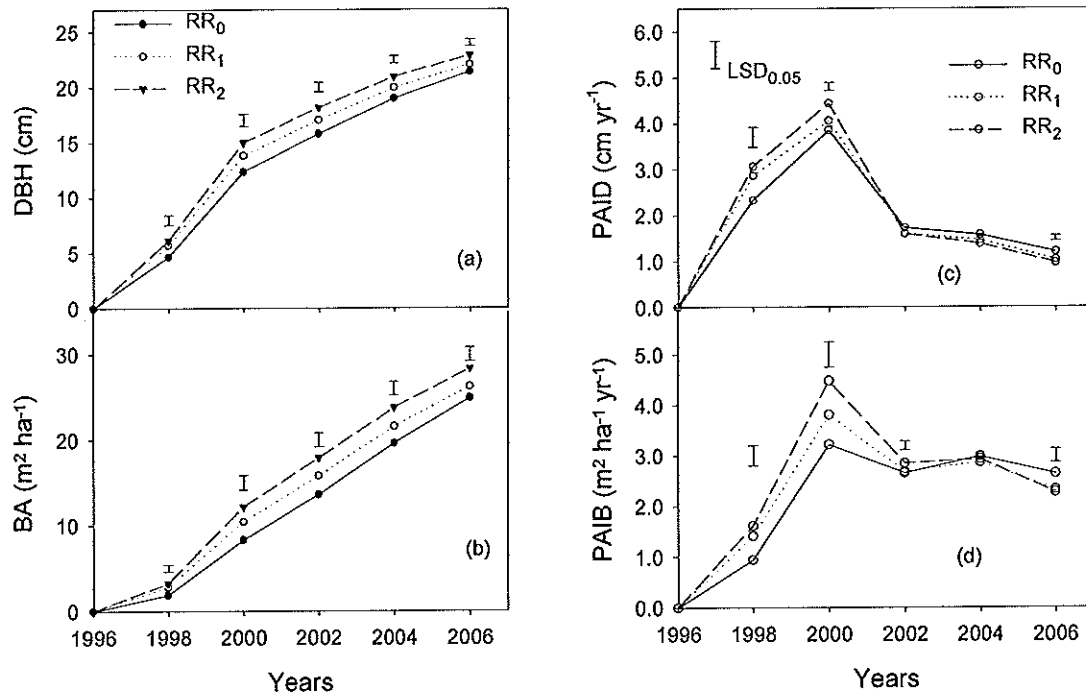


Fig. 6.1. The effect of different residue management treatments on the diameter at breast height (DBH) (a) and basal area (BA) (b), and the periodic mean annual increment of tree DBH (PAID) (c) and basal area (PAIB) (d) of the F1 hybrid exotic pine plantation over 10 years. The residue treatments are: (1) residue removal, RR₀; (2) single residue retention, RR₁; and (3) double residue retention, RR₂. The bars are least significant differences (LSD) ($p < 0.05$).

time x treatment interaction ($p < 0.005$), in contrast to the total growth measurements (Fig. 6.1a-b), which showed no such interactions (ANOVA table not shown). Nonetheless, the relatively higher growth rates in the RR₀ at age 10 years were not large enough to offset the growth gains of the RR₁ and RR₂ treatments at this stage.

6.3.2 Foliar nutrient concentrations and tree growth

Foliar analyses revealed that foliar nutrient concentrations of the major nutrients ranged from 0.79 – 0.94% N, 0.058 – 0.082 % P, 0.12 – 0.26 % Ca, 0.11 – 0.19 % Mg and 0.30

– 0.52% K (Table 6.2). Except for K, these concentrations were not significantly different across the treatments. The nutrient ratios showed that the P:N ratio was higher in the RR₁ treatment. Nonetheless, these observations together with the Ca:N and Mg:N ratios could not explain the differences in the growth indices (Table 6.1) or be related to the residue management regimes. Both foliar N and P concentrations (Table 6.2) were either marginal or below critical levels (N = 0.90%; P= 0.093-0.11%). Foliar K concentration and K: N ratios (Table 6.2) were significantly greater in both the RR₁ and RR₂ treatments compared to the RR₀ treatment. This observation occurred consistently over the past 10 years (Fig. 6.2a). In addition, a highly significant correlation between foliar K concentration and growth indices was also observed from year 2000 (age 4 years) (Table 6.3). This strong relationship became negative with PAID and PAIB after 2002. In addition, there was no significant relationship between foliar K concentration and tree growth in 1998 (Fig. 6.2), even though significant variations in tree growth occurred along with increasing residue-loading rates (Simpson et al., 2003).

Unlike foliar K concentration, foliar N and P concentrations over the 10 years (Fig. 6.2) were not significantly different among the treatments. However, both nutrients declined significantly ($p < 0.005$) after age 4 years (year 2000), with foliar P concentration about 12 – 39 % lower in the subsequent years (Fig. 6.2b). Similarly, foliar N concentration declined after year 2000 and was about 22-29 % lower in 2002 but increased again in 2006, although still less than those in 2000 (Fig. 6.2c). Both foliar P and N concentrations were either marginal or below critical values at this stage, and regression analyses showed that the decreases in PAID and PAIB were significantly related to foliar P and N concentrations (Fig. 6.3a-d), and together they accounted for 62 % of the variations of PAI ($p < 0.05$) over the 10 years.

Table 6.2. Foliar nutrient concentrations of the 10-year-old F1 hybrid exotic pine plantation under three harvest residue management regimes.

Treatments	N (%)	P (%)	Ca (%)	Mg (%)	K (%)	P:N (%)	Ca:N (%)	Mg:N (%)	K:N (%)
Residue removal (RR ₀)	0.91 ^a	0.068 ^a	0.16 ^a	0.15 ^a	0.34 ^b	7.2 ^b	17.6 ^a	16.0 ^a	36.6 ^c
Single residue retention (RR ₁)	0.89 ^a	0.073 ^a	0.21 ^a	0.17 ^a	0.45 ^a	8.5 ^a	23.6 ^a	19.2 ^a	48.4 ^b
Double residue retention (RR ₂)	0.90 ^a	0.067 ^a	0.16 ^a	0.15 ^a	0.50 ^a	7.6 ^b	17.9 ^a	17.1 ^a	58.5 ^a

^aMeans followed by the same letter in each column are not significantly different (p>0.05).

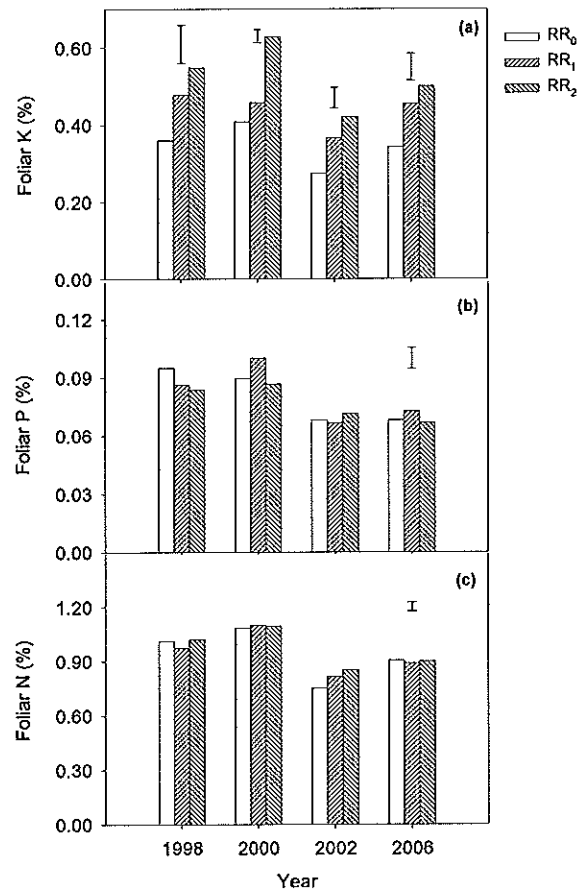


Fig. 6.2. Changes in foliar N, P and K concentrations during the 10 years in the F1 hybrid exotic pine plantation under the (1) residue removal, RR₀; (2) single residue retention, RR₁; and (3) double residue retention, RR₂, treatments. The bars in (a) are the least significant differences (LSD_{0.05}) across the treatments while the single bar in (b) or (c) represent the time effect LSD_{0.05}.

Table 6.3. Pearson's correlation of foliar K concentration with the basal area (BA), diameter at breast height (DBH), height (HT), and mean annual increments of DBH (PAID), BA (PAIB) and HT (PAIH) of the F1 hybrid exotic pine plantation.

Year	DBH	BA	HT	PAID ^a	PAIB	PAIH
<u>1998</u>						
Foliar K	0.54 ^{ns}	0.54 ^{ns}	0.51 ^{ns}	0.54 ^{ns}	0.54 ^{ns}	0.51 ^{ns}
Foliar K:N ratio	0.62 ^{*b}	0.63 [*]	0.61 [*]	0.62 [*]	0.63 [*]	0.61 ^{ns}
<u>2000</u>						
Foliar K	0.82 ^{***}	0.82 ^{***}	0.63 [*]	0.88 ^{***}	0.85 ^{***}	0.30 ^{ns}
Foliar K:N ratio	0.76 ^{**}	0.76 ^{**}	0.56 ^{ns}	0.81 ^{**}	0.78 ^{**}	0.24 ^{ns}
<u>2002</u>						
Foliar K	0.90 ^{***}	0.89 ^{***}	0.79 ^{**}	-0.62 [*]	0.60 [*]	-0.52 ^{ns}
Foliar K:N ratio	0.70 [*]	0.69 [*]	0.59 [*]	-0.40 ^{ns}	0.60 [*]	-0.36 ^{ns}
<u>2006</u>						
Foliar K	0.74 ^{**}	0.76 ^{**}	0.28 ^{ns}	-0.81 ^{**}	-0.73 ^{**}	-0.69 [*]
Foliar K:N ratio	0.78 ^{**}	0.79 ^{**}	0.42 ^{ns}	-0.85 ^{***}	-0.79 ^{**}	-0.68 [*]

^aPAID and PAIB are mean periodic annual increments calculated over 2 year intervals.

^bAsterisks *, **, and *** indicate significance at $p < 0.05$, 0.01, and 0.001, and ns = not significant ($p > 0.05$).

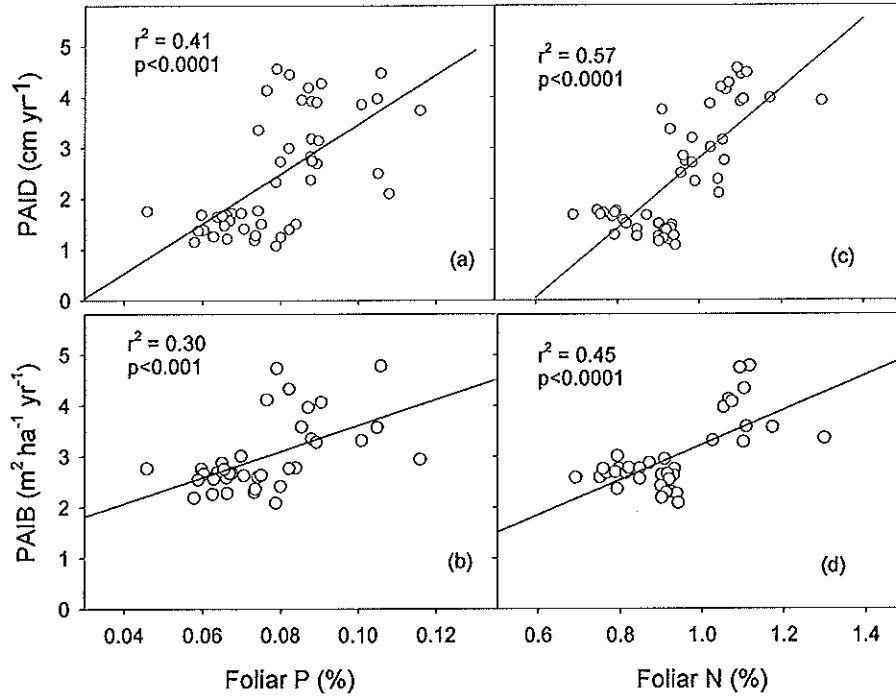


Fig. 6.3. The relationships between foliar P concentration and the mean annual increment of diameter at breast height (PAID) (a) and the mean annual increment of basal area (PAIB) (b), and between foliar N concentration and PAID (c) or PAIB (d) as measured after age 4 years (year 2000).

6.3.3 Litter production and C, N and P turnover

Fig. 6.4 shows the seasonal dynamics of litter production and indicates that the highest litter production occurred in the summer to autumn season. The annual litter production ranged from 1750–2500 kg ha⁻¹ yr⁻¹. Table 6.4 shows that mean litter production was highest in the RR₂ treatment compared to the RR₁ treatment but not significantly different from the RR₀ treatment. Similar trends were observed for total C turnover through the litter biomass (Table 6.4). Total N and P turnovers were also not significantly different among the treatments.

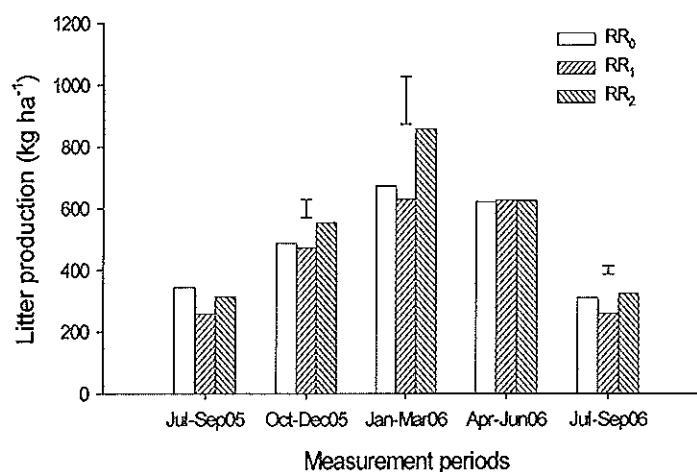


Fig. 6.4. Litter needle biomass production over 15 months of the F1 hybrid exotic pine in the (1) residue removal, RR₀; (2) single residue retention, RR₁; and (3) double residue retention, RR₂ treatments at age 10 years. The bars are least significant differences (LSD) ($p < 0.05$).

Table 6.4. Annual (Jul '05 to Jun '06) litter production and total C, N and P turnover of the 10 year-old F1 hybrid exotic pine plantation under the (1) residue removal, RR₀; (2) single residue retention, RR₁; and (3) double residue retention, RR₂, treatments.

Treatments	Total biomass (kg ha ⁻¹ yr ⁻¹)	C (kg ha ⁻¹ yr ⁻¹)	N (kg ha ⁻¹ yr ⁻¹)	P (kg ha ⁻¹ yr ⁻¹)
RR ₀	2124 ^{ab} ¹	1068 ^{ab}	6.14 ^a	0.27 ^a
RR ₁	1984 ^b	1006 ^b	6.00 ^a	0.35 ^a
RR ₂	2348 ^a	1177 ^a	7.16 ^a	0.29 ^a

¹Means followed by the same letter in each column are not significantly different ($p > 0.05$).

Analysis of the forest floor litter horizons showed no differences in the N and P concentrations of the L horizon (Table 6.5). In contrast, the fermenting needles showed

significantly higher N and P concentrations, and lower C:N ratios, in the RR₁ and RR₂ treatments compared to the RR₀ (Table 6.5). Although the total litter biomass and C

Table 6.5. Litter N and P concentrations in the L (fresh new litter approx. 1 year old) and F (fermenting litter) horizons of the 10-year-old F1 hybrid exotic pine plantation under the three harvest residue management regimes (RR₀, RR₁ and RR₂).

Treatments	N (%)	P (%)	C/N ratio
<i><u>L horizon</u></i>			
Residue removal (RR ₀)	0.37 ^a ^l	0.026 ^a	139 ^a
Single residue retention (RR ₁)	0.41 ^a	0.033 ^a	125 ^a
Double residue retention (RR ₂)	0.38 ^a	0.027 ^a	133 ^a
<i><u>F horizon</u></i>			
Residue removal (RR ₀)	0.46 ^c	0.028 ^b	108 ^a
Single residue retention (RR ₁)	0.56 ^b	0.037 ^a	90 ^b
Double residue retention (RR ₂)	0.61 ^a	0.037 ^a	82 ^c

^lMeans in each column and horizon followed by the same letter are not significantly different ($p > 0.05$).

content were not significantly different among the treatments, total N and P turnovers were significantly higher in the RR₁ and RR₂ treatments compared to the RR₀ treatment (Table 6.6). Since we estimated the F horizon to be the result of foliar production in year 2002 or earlier, we correlated litter N or P concentrations with the DBH, BA and PAIB of year 2002 (Table 6.7). The correlations showed significant relationships

between F horizon litter N and P concentrations and the DBH. The F horizon litter C:N ratio also showed a significant relationship with the DBH and BA.

Table 6.6. Total litter biomass and total C, N and P contents of the F horizon of the F1 hybrid exotic pine plantation under three harvest residue management regimes.

Treatments	Biomass (kg ha ⁻¹)	C (kg ha ⁻¹)	N (kg ha ⁻¹)	P (kg ha ⁻¹)
Residue removal (RR ₀)	3443 ^a	1720 ^a	15.90 ^b	0.72 ^b
Single residue retention (RR ₁)	3098 ^a	1554 ^a	17.40 ^b	0.85 ^{ab}
Double residue retention (RR ₂)	3963 ^a	1977 ^a	24.37 ^a	1.10 ^a

¹Means followed by the same letter in each column are not significantly different (p>0.05).

Table 6.7. Correlations between F horizon litter chemical parameters and tree diameter at breast height (DBH), basal area (BA) and mean annual increment of BA (PAIB) of 2002 (age 6 years) in the F1 hybrid exotic pine plantation.

Variables	DBH	BA	PAIB
Nitrogen (N)	0.68 ^{*a}	0.64 ^{ns}	0.56 ^{ns}
Phosphorus (P)	0.67 [*]	0.65 ^{ns}	0.43 ^{ns}
P x N interaction	0.71 [*]	0.68 [*]	0.55 ^{ns}
C:N ratio	-0.69 [*]	-0.66 [*]	-0.54 ^{ns}

^aAsterisk * indicates significance at p<0.05, and ns = not significant (p>0.05).

6.4 Discussion

6.4.1 Tree growth

The impact of harvest residues on plantation productivity has generated great interest globally as reflected in the numerous publications on this subject. However, the long-term impacts of the residues on soil fertility and plantation productivity have not been explored extensively, probably due to the expensive task of maintaining such experiments (Corbeels et al., 2005). The present study, therefore, provided some insights into the long-term impacts of residue retention on tree growth, particularly in a subtropical environment. Results of this study agree with other limited long-term impact studies of harvest residues (Proe and Dutch, 1994; Smith et al., 2000; Tiarks et al., 2003) in demonstrating that total growth was increased by residue retention and this impact of residues on tree growth could still be observed in the long term. The residues gave the growing trees a head start, even though growth rates declined after 4 years. The declining PAID and PAIB trends indicated that the influence of residues on tree growth might be rather limited after age 4 years (Fig. 6.1c-d), and that the current total growth observed at age 10 years mostly accumulated during the early growth phase when PAID and PAIB were significantly higher in the RR₁ and RR₂ treatments compared to the RR₀ treatment. The significant variations of PAID and PAIB at age 10 years indicated that growth decline was more severe in the RR₁ and RR₂ treatments compared to the RR₀ treatment. Jokela and Martin (2000) reported a similar observation with the control treatments, suggesting nutrient depletion as a result of faster growth rates under alternative treatments as the main cause. However, foliar nutrient analyses at age 10 years (Table 6.2) did not support this view. The significant differences in growth rates, however, contributed to the narrowing of the variations of DBH and BA among the treatments at age 10 years (Fig. 6.1a-b), perhaps due to factors raised later in the discussion.

The PAID and PAIB patterns exhibited over the 10 years by the plantation were similar to those of other studies (Forrest and Ovington, 1970; Jokela and Martin, 2000). However, the peak growth increments reached at age 4 years or less in the present study, in contrast to age 8 years for slash and loblolly pines in Florida, southern USA (Jokela and Martin, 2000) and ages 5-7 years for radiata pine in south-eastern Australia (Forrest and Ovington, 1970), suggest that peak leaf area development, and therefore growth of the F1 hybrid exotic pine plantation may have occurred comparatively earlier. Declining tree growth following peak stand development has been associated with a number of factors, including nutrient limitation, hydraulic conductance limitation, increased maintenance respiration costs and biomass accumulation to the belowground growth (Gower et al., 1996; Ryan and Yoder, 1997; Jokela and Martin, 2000). The nutrient limitation hypothesis appeared to be consistent with the declining growth in the present study, irrespective of the residue management regime. This conclusion was supported by the significant positive relationship between declining PAID or PAIB and decreasing foliar N and P concentrations at ages 4 – 10 years (2000 – 2006) (Fig. 6.3). Available soil N and P and their foliar concentrations have been linearly correlated with the leaf area index, which increases the light use efficiency and C assimilation capacity of trees (Nambiar, 1990; Nambiar and Sands, 1993; Samuelson et al., 2004).

6.4.2 *Foliar nutrition*

In contrast to past studies in temperate northern hemisphere (Proe and Dutch, 1994; Olsson et al., 2000), long-term residue impacts on tree nutrition could not be observed in this study, except for foliar K concentration, at age 10 years (Fig. 6.2b and 6.2c). Except for P and N concentrations, foliar nutrient concentrations were above critical levels (K = 0.30 %; Mg = 0.07 %; and Ca = 0.12 %) reported for the slash and Caribbean pines, the parent taxa of the F1 hybrid (Simpson and Osborne 1993; Xu et

al., 1995c). The element to N ratios (Table 6.2) were also above suggested critical levels for most tree species: K:N = 29 – 35 %; Ca:N = 2.5 % and Mg:N = 4 % (Proe et al., 1999; Olsson et al., 2000; Moilanen et al., 2005). The foliar P concentrations in all treatments at age 10 years, however, were below the critical concentration of 0.093 – 0.11% suggested for slash pine (Xu et al., 1995a). The P:N ratio was also below the recommended ratio of 10% or more for most tree species (Proe et al., 1999). Foliar N concentration was marginal when compared to the recommended critical concentration of 0.90% for slash pine (Xu et al., 1995a). This is puzzling when soil labile N pools reported in chapter 5 appeared to be similar or greater than those reported previously by Chen and Xu (2005) when the plantation was 6 years old. Further work is required to ascertain if these low levels of foliar N and P at age 10 years were due to nutrient immobilisation from the residues or lack of soil moisture. Nutrient competition from the current stocking density of 694 trees per hectare might also contribute to the apparent low N and P supply. A fertiliser response trial to examine the role of residues in nutrient availability is therefore necessary to confirm these possibilities. Perhaps integrating fertiliser programs with residue retention (Smith et al., 2000b) might be useful in sustaining the long-term benefits of harvest residues on plantation productivity.

The significant decline in foliar P and N concentrations to the deficient or marginal levels from ages 6 – 10 years in the present study was consistent with the concomitant decline in PAI discussed earlier. Phosphorus is the major limiting nutrient in the coastal areas of southeast Queensland (Xu et al., 1995c). However, the fact that foliar N concentration was better than foliar P concentration in explaining the variations in declining PAIs in this study (Fig. 6.3c-d) further supports the conclusion that N might be as important as P in these coastal sandy soils for the fast growing F1 hybrid taxon. However, unlike its parent taxa, the F1 hybrid's specific nutrient requirements have not

been determined, and the current N and P application rates are based on those of the parent taxa. Potassium has been reported to influence various processes associated with C fixation (Huber, 1984). However, the non-limiting foliar K concentrations in all the treatments over the past 10 years (Fig. 6.2), and the weak relationship between foliar K concentrations and growth indices in 1998 (Table 6.3), when significant variations in both foliar K concentration and tree growth occurred along with increasing residue loading rates, did not support the involvement of K in increasing photosynthetic capacity as the cause of the variation in tree growth. On the other hand, the higher foliar K concentrations maintained in the RR₁ and RR₂ treatments, even though the tree growth rates decreased after year 2000, were possibly due to ‘luxury’ uptake of K, which was previously reported to be of greater concentration in the soil under the residue retention treatments (Simpson et al., 2003). The higher foliar K concentration could also be a response to water stress (Xu et al., 2000; Fernandez et al., 2006), due to the drier conditions in the last 10 years at this site and the apparent demands of larger trees in the RR₁ and RR₂ treatments. Studies on other plant species showed that the maintenance of leaf pressure potential as a result of increased K during drought conditions did not always prevent the reduction in growth when other factors have more over-riding effects (Ashraf et al., 2001). This could be the case in the variations of foliar K concentrations in relation to tree growth in this study.

6.4.3 Litter production, C and nutrient turnovers

The lack of significant differences in the litter biomass and C turnover between the RR₀ and RR₂ treatments at age 10 (Table 6.4) and in the F horizon (Table 6.6) did not support our hypothesis that residue retention could lead to greater foliar production and therefore the amount of C recycled as litter. This finding is in contrast to the results of a 10-year-old *Pinus taeda* plantation (Tiarks et al., 2003). The lower litter production in

the RR₁ treatment relative to the RR₀ and RR₂ treatments suggest that the variations in litter biomass and total C recycled across the treatments appeared to be unrelated to residue loading rates. Other factors, such as soil moisture stress, could lead to shedding of foliage (Högberg et al., 1993; Pedersen and Bille-Hansen, 1999).

The negative relationship between the F horizon litter C:N ratio and DBH or BA of 2002 (Table 6.7) was consistent with the study of Smith et al. (2000) showing a significant negative relationship between forest floor C:N ratio and the DBH of *Pinus radiata*. This observation together with the significant correlations of F horizon litter N and P concentrations with the BA and DBH of 2002 (Table 6.7) indicates that harvest residues did affect tree N and P nutrition during the early growth of this plantation. Although the relationship between re-translocation rates in senescing needles and litter nutrient concentrations is fraught with inconsistencies (Aerts, 1996), the above evidence supports the proposition that litter nutrient concentrations are reflective of tree foliar nutrient status to some extent, consistent with studies that showed a linear relationship between litter and foliar nutrient concentrations (Nambiar and Fife, 1991; Kavvadias et al., 2001). We speculate that the lack of variations in foliar N and P concentrations during early growth (Fig. 6.2) might be related to nutrient dilutions (Xu et al., 1995b) in the faster growing, larger biomass trees of the RR₁ and RR₂ treatments, as well as internal nutrient re-translocation to the new foliar needles from the lower canopy or older, not necessarily senescing needles (Nambiar and Fife, 1991).

6.5 Conclusion

Harvest residue retention increased tree total growth and this could still be observed after 10 years following the establishment of the F1 hybrid exotic pine plantation. Most of this growth was accumulated in the first 4 years, after which tree growth declined

significantly, most likely as a result of declining foliar N and P concentrations. Foliar N and P concentrations at age 10 years showed no treatment effects and were either marginal or deficient. On the other hand, litter N and P concentration variations suggest nutritional impact of residues during the early growth, and could be a useful indicator of tree nutritional status. The influence of residues on litter production and biomass C recycling at age 10 years is not clear at present. These findings support the conclusion that harvest residues did have a positive impact on tree growth; however, its impact appeared to be reduced at age 10 years as indicated by the periodic growth rates and the closing gap among the treatments. Whether total tree growth in the RR_0 treatment will draw level with those in the RR_1 and RR_2 treatments is not certain at this stage. Perhaps integrating alternative management strategies such as later age fertilisation with residue retention strategies may be necessary to ensure the benefits of residue retention are sustained to the end of the rotation.

CHAPTER SEVEN

Foliar and Litter Needle Carbon and Oxygen Isotope Compositions Reveal the Influence of Nutrients and Water in an Exotic Pine Plantation under Different Residue Management Regimes of Subtropical Australia

7.1 Introduction

Plant organic matter carbon (C) and oxygen (O) isotopic ratios ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively) are widely used to determine the influence of genetic and environmental factors on plant growth (Xu et al., 2000; Warren et al., 2001; Barbour et al., 2002; Prasolova et al., 2005; Keitel et al., 2006). They are regarded as integrative measures of eco-physiological processes over the period in which the constituents of the plant material are formed, indicating past environmental factors and therefore can better account for tree growth than instantaneous measurements of stomatal conductance, water use efficiencies and net photosynthesis (Zhang and Cregg, 1996; Prasolova et al., 2003; Xu et al., 2003; Barbour, 2007).

The theory behind varying plant $\delta^{13}\text{C}$ composition as a result of varying moisture conditions is well established (Farquhar et al., 1982; Farquhar and Richards, 1984; Barbour et al., 2000; Warren et al., 2001). During photosynthesis, the C fixing enzyme, ribulose biphosphate carboxylase/oxygenase (Rubisco), discriminates against the heavier $^{13}\text{CO}_2$. This discrimination, however, diminishes as the leaf internal CO_2 concentration (C_i) decreases (Farquhar et al., 1982), such as when stomatal conductance (g_s) is decreasing in response to low soil moisture. Thus, a significant correlation

between plant $\delta^{13}\text{C}$ and soil moisture availability can be established (Farquhar and Richards, 1984; Xu et al., 2000; Warren et al., 2001).

The C_i , however, can also be influenced by the photosynthetic capacity, therefore confounding the relationship between g_s and $\delta^{13}\text{C}$ of plant tissues. This limitation, however, can be overcome by the combined determination of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, to separate the effects of g_s and photosynthesis on $\delta^{13}\text{C}$ variation, since the $\delta^{18}\text{O}$ signature is not dependent on Rubisco activity (Scheidegger et al., 2000; Xu et al., 2000; Keitel et al., 2003; Barbour, 2007). The ^{18}O fractionation theory had been discussed extensively in Barbour et al. (2000; 2007). In brief, it suggests, in general, that plant $\delta^{18}\text{O}$ composition is negatively related to g_s , and that a positive relationship between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ indicates that $\delta^{13}\text{C}$ enrichment is largely driven by g_s (Saurer et al., 1997; Farquhar et al., 1998; Barbour et al., 2000; Keitel et al., 2003).

A number of studies have indicated that tree growth and bulk stem wood or tree ring ring cellulose $\delta^{13}\text{C}$ are related (Dupouey et al., 1993; McNulty and Swank, 1995; Livingstone and Spittlehouse, 1996; Garcia-G et al., 2004; Fernandez et al., 2006). Furthermore, studies of conifer plantation species showed that whole leaf or foliar $\delta^{13}\text{C}$ could be related to cumulative tree growth (Högberg et al., 1993; Xu et al., 2000). Limited studies, however, have successfully related either whole stem wood or leaf $\delta^{18}\text{O}$ to tree growth (Xu et al., 2000). The study by Xu et al. (2000), however, has indicated that the foliage sampled be reflective of the period that growth occurred as illustrated by the better correlation of 1 year-old foliar $\delta^{13}\text{C}$ to the middle and top (relatively new growth) rather than the bottom merchantable stem volumes. Thus, there is a need to explore the relationships between foliar $\delta^{13}\text{C}$ and actual growth rate that coincide over the life of the foliage material, as total growth may not be truly reflective of current

foliar $\delta^{13}\text{C}$. Furthermore, the use of leaf litter $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, which are likely to be representative of longer eco-physiological history, has been largely unexplored. The use of litter needles could allow routine sampling and measurements of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variations, without having to climb or shoot down foliar needles of tall trees for such investigations.

A study at age 0 – 6 years (Simpson et al., 2003), and a recent study at age 10 years of the same plantation (Chapter 6), on the impact of residue management on tree nutrition and growth showed significant variations among treatments of the cumulative tree growth and periodic mean annual increment (PAI) prior to the peaking of growth (Fig. 6.1). This variation of tree growth could not be related to foliar nutrient concentrations, other than foliar potassium (K) concentration, the only nutrient that showed significant residue treatment effects in both the soil and the foliage (Chapter 6). Therefore, the role of K on increasing the photosynthetic capacity (A_{max}) of trees is of great interest, especially during early growth. Results in Chapter 6, however, indicated the likely influence of tree water stress on the foliar K concentration, where larger or faster trees in the residue treatments were much more water stressed than those in the no residue treatments. This was consistent with studies showing growth-induced water stress due to the high demand of faster growing trees for soil water when N or P supply are non-limiting (Högberg et al., 1993). On the other hand, the foliar K concentrations could merely be due to a luxury uptake of K.

Studies that have clearly separated the mulching or nutritional effects of logging harvest residues through their influence on g_s and/or photosynthetic capacity (A_{max}) and therefore foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and their relationships to tree growth, are limited. Therefore, this study aimed to better understand the impact of harvest residues, in

relation to the soil moisture or nutrition hypotheses and tree growth, through a retrospective analysis of foliar and litter needle $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. The main objectives of this study were to: (1) determine the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of archived and current year foliar samples and relate these to periodic mean annual increments of diameter at breast height (PAID) and basal areas (PAIB) of the above exotic pine plantation; (2) establish relationships between the $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and foliar K concentrations or tree growth rates to assess whether soil moisture through g_s , or nutrition through A_{max} or WUE, could explain the variation in tree growth under different residue management regimes; and (3) explore the potential of using litter needle $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ as a tool for understanding the influence of environmental factors on tree growth in the exotic pine plantation.

7.2 Materials and Methods

7.2.1 Site description and experimental design

This study was carried out in experiment 321GYM, Toolara State Forest (26°00'S, 152°49'E), southeast Queensland, Australia, which has been described in detail in Chapters 2 and 6. In brief, it is generally flat, with a deep sandy soil classified as gleyic acrisols (FAO, 1974). The climate is humid sub-tropical with a mean annual rainfall of 1354 mm, with 56% falling in December to March (Simpson et al., 2003). The July to September period is relatively dry, which may extend to November (Xu et al., 2000). The summers are hot and moist with a mid-summer mean daily temperature of 24.9 °C and a relative humidity of 70%, while the winters are mild, with a mid-winter mean daily temperature of 14.0 °C and a mean relative humidity of 64 %. Exotic pine plantation trees in this region often experience both well-watered and water-limited conditions in the same year, even in a wet summer season (Xu et al., 2000; Prasolova et al., 2005). In addition, annual rainfall has been below average for the last 10 years.

As stated in Chapter 6, this study focussed on the three harvest residue treatments: (1) residue removal, RR_0 ; (2) single residue retention, RR_1 ; and (3) double residue retention, RR_2 . The plots were planted in mid 1996 with the F1 hybrid between slash pine (*Pinus elliottii* var. *elliottii*) and Caribbean pine (*Pinus caribaea* var. *hondurensis*) seedling stocks from 6 different families.

7.2.2 *Measurement of growth and foliar and litter sampling*

Detailed tree growth measurements and foliar and litter sampling methods were as described in Chapters 2 and 6. The growth indices, diameter at breast height (DBH), basal area (BA) and tree height (HT) presented in this study were those measured for the years 2000 and 2006 reported in Chapter 6. In addition, periodic mean annual increments (PAI) over a two year period of DBH (PAID), BA (PAIB) and HT (PAIH) presented in this study were those determined at ages 2, 4, 6, 8 and 10 years in Chapter 6. Foliar samples at age 10 years and archived samples at ages 2, 4 and 6 years (1998, 2000 and 2002, respectively; no foliar sampling in 2004) were all collected from the northward facing (sunny) side of the tree canopy (Xu et al., 2000; Prasolova et al., 2005), and sampling was conducted on the same trees over the 10 years. Fifty fascicles of the most recent, fully expanded needles (approximately 1 year old) were collected from 4 trees within a plot and bulked as one sample (Simpson et al., 2003). Litter needles used here were those collected quarterly from July 2005 to June 2006 in Chapter 6. All plant materials were oven dried at 60 °C for 5 days before being ground to powder in a Rocklab puck and ring mill.

7.2.3 *Chemical analyses*

Foliar and litter C isotope compositions ($\delta^{13}\text{C}$) were determined by a Eurovector 3000 elemental analyser (Milan, Italy) coupled to a GVI Isoprime mass spectrometer

(Manchester, UK). The O isotope compositions ($\delta^{18}\text{O}$) were determined by a VARIO EL III elemental analyser (Hanau, Germany) coupled to a Sercon Hydra 20-20 mass spectrometer (Crewe, UK). Foliar N, P and K concentrations in this study were obtained from foliar nutrient analyses determined in Chapter 6. The foliar and litter $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were calculated relative to the PDB and IAEA VSMOW standards, respectively (Chapter 2, section 2.5.3) (Barbour et al., 2000; Xu et al., 2000; Prasolova et al., 2001).

7.2.4 *Precipitation measurements*

Rainfall data were obtained from the weather station at Toolara State Forest, where this experiment was established. The rainfall data presented (Table 7.1) were the effective rainfalls, which occurred within 18, 12, 6, 4 and 2 months prior to the date of foliar sampling. Total rainfall of the growing season preceding each foliar sampling date was also obtained.

7.2.5 *Statistical analyses*

An analysis of variance (ANOVA) was carried out on $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and K concentrations of foliage and litter samples to detect differences between the treatments at $p < 0.05$. The least significant difference (LSD) test at $p < 0.05$ was carried out to determine the degree of the variations between the treatments. Pearson's correlation and linear regression analyses were carried out to determine relationships among tree growth indices and foliar $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, N, P and K concentrations. Correlations between PAID and PAIB and the interacting terms were carried out by multiplying the numerical values of the interacting parameters (for each replicate) and the sum of these were correlated with the PAID and PAIB values. Litter $\delta^{13}\text{C}$ sampled from July 2005 to July 2006 were regressed with foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ sampled in July 2006 and PAID (2004 – 2006). The Statistix (Version 8.0) software was used for all the statistical analyses.

7.3 Results

7.3.1 Precipitation measurements

Effective rainfall data are presented in Table 7.1. The rainfalls were below the annual mean, and in general decreased over time, with the lowest 12 months rainfall in 2002. Although year 2000 had the highest rainfall, the last 2-6 months prior to sampling were relatively drier compared to the other years. In contrast, rainfall was more evenly distributed throughout the 12 months before sampling in 1998, therefore remaining relatively high within 2-6 months prior to sampling. Growing season total rainfall was lowest in 2006.

Table 7.1. Total effective rainfall that occurred within 2, 4, 6, 12 and 18 months, and the total growing season (September to March) rainfall, prior to each foliar sampling in the F1 hybrid exotic pine plantation in sub-tropical Australia.

Year	Total effective rainfall (mm)					
	18 months	12 months	6 months	4 months	2 months	Growing season
1998 ^a	1590	1019	601	395	108	687
2000	2099	1180	455	300	58	785
2002	1326	929	499	325	46	667
2006	1620	935	395	342	156	657

^aFoliar samplings were carried out in mid to late winter (July-August) of each year, except for 2000, which was in September.

7.3.2 Foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and growth of the exotic pine plantation

Significant treatment effects on foliar $\delta^{13}\text{C}$ occurred in 2000 and 2006 only (Table 7.2), where $\delta^{13}\text{C}$ was lower in the RR₀ treatment compared to the RR₁ and RR₂ treatments in both years. The largest differences in $\delta^{13}\text{C}$ variations between the treatments were 0.90

‰ and 0.87 ‰ in 2000 and 2006, respectively. The $\delta^{18}\text{O}$, however, only showed significant treatment effects in 2000 when $\delta^{18}\text{O}$ was lowest in the RR_0 treatment ($p < 0.05$) compared to the RR_1 and RR_2 treatments (Table 7.2). These two years represented the periods of peak growth (2000) and declining growth (2006) according to the PAIB and PAID trends reported in Chapter 6.

Table 7.2. Foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of current year (2006) and archived foliar samples of an F1 hybrid exotic pine plantation under three harvest residue management regimes (RR_0 , RR_1 and RR_2), measured in 1998 - 2006. No foliar sampling was conducted in 2004.

Treatments	Year			
	1998	2000	2002	2006
<i>Foliar $\delta^{13}\text{C}$ (‰)</i>				
Residue removal (RR_0)	-30.70 ^a	-30.63 ^b	-27.88 ^a	-29.25 ^b
Single residue retention (RR_1)	-30.80 ^a	-30.30 ^a	-28.00 ^a	-29.00 ^{ab}
Double residue retention (RR_2)	-30.73 ^a	-30.25 ^a	-27.75 ^a	-28.85 ^a
<i>Foliar $\delta^{18}\text{O}$ (‰)</i>				
Residue removal (RR_0)	25.70 ^a	26.33 ^b	28.98 ^a	30.93 ^a
Single residue retention (RR_1)	26.53 ^a	30.48 ^a	27.63 ^a	27.20 ^a
Double residue retention (RR_2)	24.80 ^a	29.85 ^a	27.55 ^a	29.35 ^a

^aMeans with the same letter are not significantly different ($p > 0.05$).

Correlations of tree growth indices of the 2000 data with foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Table 7.3) showed that both isotopic ratios were positively related to almost all growth indices. Foliar K concentration, however, displayed a stronger relationship with most tree growth indices than did either $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ (Table 3). Regression analyses of actual growth gains (PAID) with foliar K concentration showed that it could explain almost 80% of the variation in PAID compared to both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, which could only

Table 7.3. Pearson's correlation coefficients of tree growth indices with foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and potassium (K) concentrations at ages 4 and 10 years of the F1 hybrid exotic pine plantation under three harvest residue management regimes (RR₀, RR₁ and RR₂).

Growth indices	Variables		
	Foliar $\delta^{13}\text{C}$	Foliar $\delta^{18}\text{O}$	Foliar K
<i>Year 2000 (age 4 years)</i>			
Diameter at breast height (DBH) ^a	0.66 ^{*d}	0.73 ^{**}	0.85 ^{***}
Basal area (BA)	0.64 [*]	0.73 ^{**}	0.85 ^{***}
Height (HT)	0.63 [*]	0.61 [*]	0.69 [*]
Volume index (VI) ^b	0.64 [*]	0.69 [*]	0.84 ^{***}
Periodic annual increment of DBH (PAID) ^c	0.59 [*]	0.56 [*]	0.88 ^{***}
Periodic annual increment of BA (PAIB)	0.62 [*]	0.69 [*]	0.87 ^{**}
Periodic annual increment of HT (PAIH)	ns	ns	ns
Foliar $\delta^{18}\text{O}$	0.76 ^{**}	-	0.60 [*]
Foliar $\delta^{13}\text{C}$	-	0.76 ^{**}	0.70 ^{**}
K x $\delta^{18}\text{O}$	0.76 ^{**}	-	-
K x $\delta^{13}\text{C}$	-	-0.56 [*]	-
<i>Year 2006 (age 10 years)</i>			
Diameter at breast height (DBH)	0.78 ^{**}	ns	0.74 ^{**}
Basal area (BA)	0.80 ^{***}	ns	0.76 ^{**}
Height (HT)	ns	ns	ns
Volume index (VI)	0.70 ^{**}	ns	0.66 [*]
Periodic annual increment of DBH (PAID)	-0.81 ^{**}	ns	-0.81 ^{***}
Periodic annual increment of BA (PAIB)	-0.68 [*]	ns	-0.73 ^{**}
Periodic annual increment of HT (PAIH)	ns	ns	ns
Foliar $\delta^{13}\text{C}$	-	ns	0.87 ^{**}

^a Measured at 1.3 m above ground level.

^b Calculated according to Xu et al (2000), where $VI = \pi DBH^2 H / 12$.

^c Mean of periodic growth calculated from growth over 2 years.

^d Asterisks *, **, and *** indicate significance at $p < 0.05$, 0.01 and 0.001, respectively, and ns = not significant ($p > 0.05$).

explain about 35% and 33%, respectively, of the variations of PAID (Fig. 7.1a and 7.1c). Both foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, however, better explained the variations of PAIB than the PAID (Fig. 7.1a-d). The relationship between foliar K concentration and growth indices in 1998 was weaker than 2000 ($p < 0.07$) even though there were significant foliar K concentration variations across the treatments.

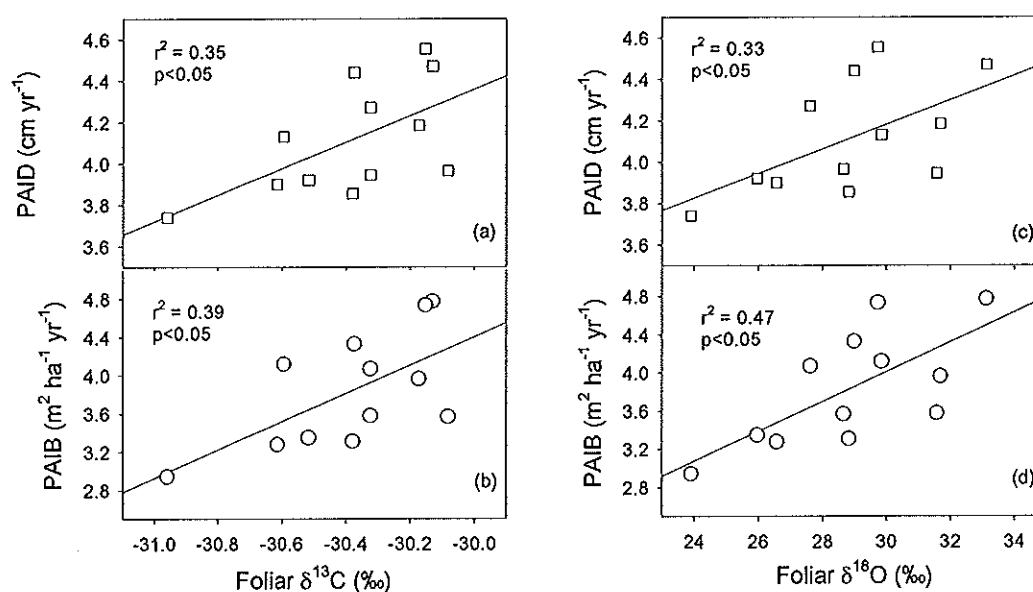


Fig. 7.1. Relationships between foliar $\delta^{13}\text{C}$ and mean periodic annual increments of tree diameter at breast height (PAID) (a) or basal area (PAIB) (b), and between foliar $\delta^{18}\text{O}$ and (PAID) (c) or basal area (PAIB) (d) for the 1998 –2000 period (ages 2 – 4) of the F1 hybrid exotic pine plantation. The plantation was under three harvest residue management regimes: (1) residue removal, RR_0 ; (2) single residue retention, RR_1 ; and (3) double residue retention, RR_2 , following clear-cut harvesting.

This study also found that foliar $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and K concentration in 2000 were inter-related (Table 7.3). Increasing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ across the treatments coincided with the concomitant increase in foliar K concentration (Fig. 7.2a). Likewise, foliar $\delta^{13}\text{C}$ and

$\delta^{18}\text{O}$ were significantly related to each other ($r^2=0.58$; $p<0.01$), with a slope of 7.70‰ increase in $\delta^{18}\text{O}$ per 1.0‰ increase in $\delta^{13}\text{C}$ (Fig. 7.2b). In addition, both foliar K concentration and $\delta^{18}\text{O}$ together improved the regression model and were able to explain about 67 % of the variation of $\delta^{13}\text{C}$ ($p<0.01$) in comparison to the foliar $\delta^{18}\text{O}$ alone.

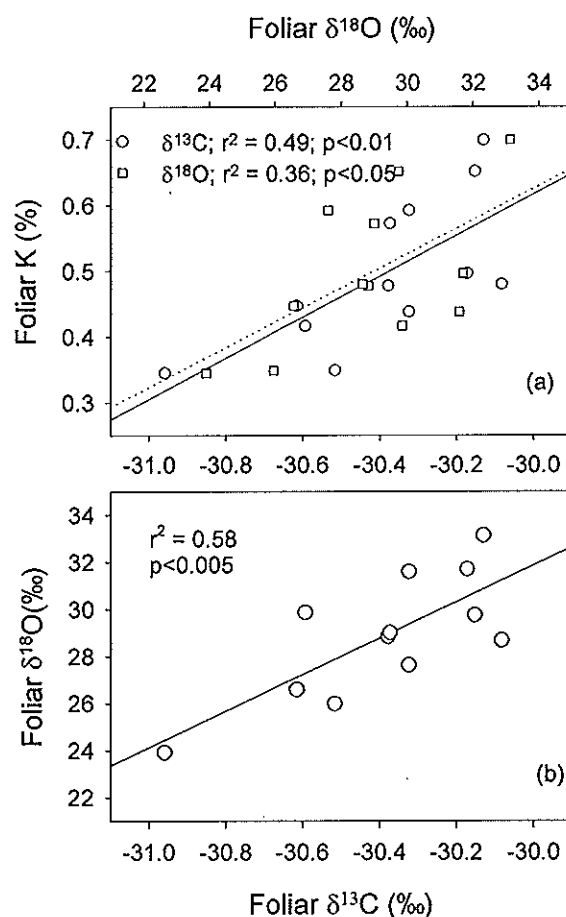


Fig. 7.2. Relationships between foliar K concentration and $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ (a), and between foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (b) of the F1 hybrid exotic pine plantation at age 4 years (year 2000). The plantation was under three harvest residue management regimes: (1) residue removal, RR_0 ; (2) single residue retention, RR_1 ; and (3) double residue retention, RR_2 , following clear-cut harvesting

In 2006, foliar $\delta^{13}\text{C}$ was negatively related to PAID and PAIB (Table 7.3 and Fig. 7.3a-b), consistent with indications of decreasing stomatal conductance, which apparently decreasing with increasing residue loading rates in the order: $\text{RR}_0 < \text{RR}_1 < \text{RR}_2$. Both

foliar $\delta^{13}\text{C}$ and K concentration were also positively related to DBH ($r = 0.78$, $p < 0.01$; and $r = 0.74$, $p < 0.01$) (Table 7.3), probably due to the long-term impact of the residues from early growth on current cumulative stem growth. Soil moisture and foliar K status in 2000 were similar to those of 2006. This was corroborated by the fact that foliar K concentration in 2000 (age 4 years) better accounted for the variation of DBH in 2006 ($r^2 = 0.74$; $p < 0.001$). No significant relationship between $\delta^{13}\text{C}$ and HT was found.

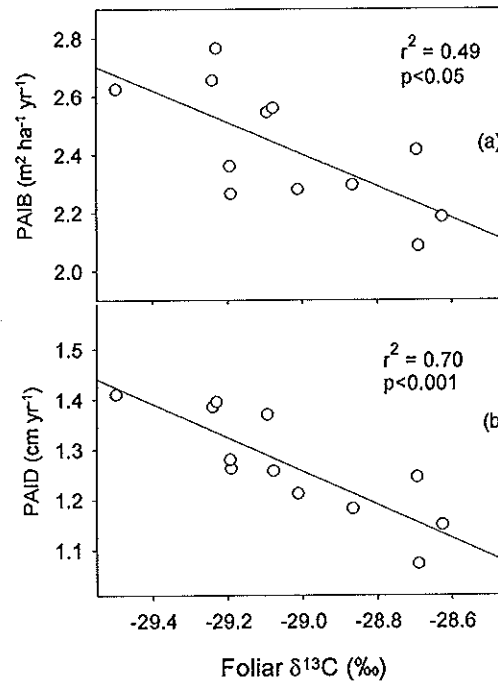


Fig. 7.3. Relationships between foliar $\delta^{13}\text{C}$ and periodic mean annual increment of the basal area (PAIB) (a) or periodic mean annual increment of diameter at breast height (PAID) (b) of the period 2004 – 2006 (ages 8 – 10 years) of an F1 hybrid exotic pine plantation under the (1) residue removal, RR_0 , (2) single residue retention, RR_1 ; and (3) double residue retention, RR_2 treatments.

Table 7.2 also shows that both foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ increased over the last 10 years ($p < 0.05$), with means ranging from -30.80‰ to -28.85‰ for $\delta^{13}\text{C}$, and from 24.80‰ to 30.93‰ for $\delta^{18}\text{O}$ from 1998 to 2006, respectively. Plotting rainfall (Table 7.1) against

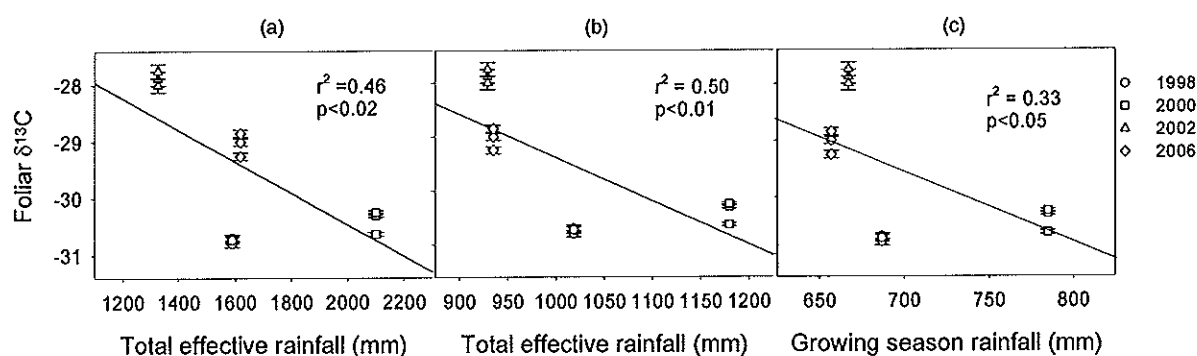


Fig. 7.4. Relationships between annual foliar $\delta^{13}\text{C}$ and total effective annual rainfall over 10 years in an F1 hybrid exotic pine plantation. The $\delta^{13}\text{C}$ were means of three residue management treatments sampled at ages 2, 4, 6 and 10 years and regressed against the total effective rainfall within 18 months (a) and 12 months (b), and the growing season (September – march) rainfall (c), preceding foliar sampling date of each year.

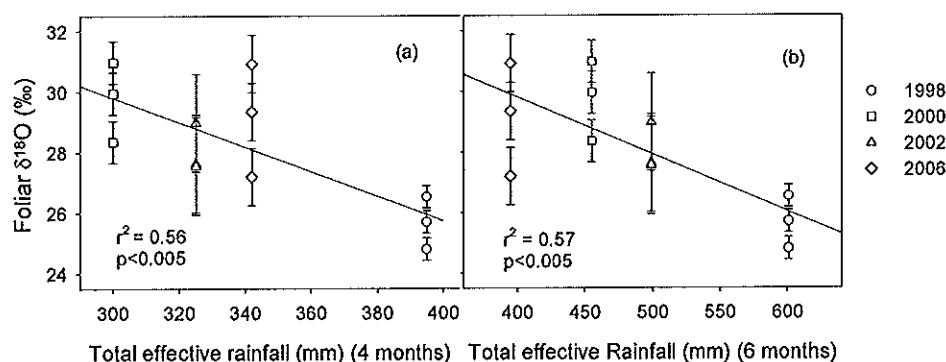


Fig. 7.5. Relationships between annual foliar $\delta^{18}\text{O}$ and total effective rainfall in each year over the 10 years in the F1 hybrid exotic pine plantation. The $\delta^{18}\text{O}$ were means of three residue management treatments sampled at ages 2, 4, 6 and 10 years, and regressed against total rainfall of 4 months (a) and 6 months (b) prior to the sampling date.

foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ showed that foliar $\delta^{13}\text{C}$ displayed a much stronger relationship with the 18 and 12 months total effective rainfall (Fig. 7.4), while a weak relationship ($r^2 = 0.12$; $p < 0.05$) existed with the six months effective rainfall, and no relationship established with the two to four months effective rainfall prior to sampling. In contrast, foliar $\delta^{18}\text{O}$ displayed a significant relationship with the total effective rainfall occurring within the four and six months prior to sampling in each year (Fig. 7.5).

The inverse relationships between effective rainfalls or growing season rainfall and the foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ closely reflected the declining PAID and PAIB. Correlation coefficients showed that growing season rainfall and foliar $\delta^{13}\text{C}$ were positively and negatively related, respectively, to the PAID and PAIB (Table 7.4). Since the declining PAID has been correlated with the declining foliar N and P concentrations (Chapter 6), I investigated if there was an interaction between rainfall and foliar N and P concentrations. This study found significant relationships among rainfall, foliar $\delta^{13}\text{C}$, N and P concentrations (Table 7.4), suggesting the probable influence of growing season rainfall or soil moisture availability on foliar N and P concentrations. This was supported by the improved coefficient of the correlation between the PAID or PAIB and the rainfall \times N \times P \times $\delta^{13}\text{C}$ interactions (Table 7.4). Correlation coefficients showed that foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were also positively related to tree height over the 10 years (Table 7.4).

7.3.3 Litter needle $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the exotic pine plantation

Litter needle $\delta^{13}\text{C}$ ranged from -29.53‰ to -29.13‰ throughout the seasons (Table 7.5). Although the variations in litter needle $\delta^{13}\text{C}$ between the treatments at each sampling were relatively small ($0.27 - 0.33\text{‰}$) compared to the foliar $\delta^{13}\text{C}$, they were significant ($p < 0.01$) in three of the four seasons assessed. In each case, $\delta^{13}\text{C}$ increased in

the following order: $RR_0 < RR_1 < RR_2$, a similar trend as shown in the foliage. Significant differences in litter needle $\delta^{18}O$ between the treatments were observed in the January – March 2006 season only, where higher $\delta^{18}O$ occurred in the RR_0 treatment compared to the RR_1 treatment (Table 7.5). This observation, however, could not be related to litter needle $\delta^{13}C$.

Table 7.4. Pearson's correlation coefficients of the relationships between long-term annual changes in foliar $\delta^{13}C$ and $\delta^{18}O$, their interactions with growing season rainfall, foliar nitrogen (N) and phosphorus (P) concentrations, and periodic mean annual increment of tree diameter at breast height (PAID) and tree basal area (PAIB), and cumulative tree height (HT) over a 10-year period in an F1 hybrid exotic pine plantation in subtropical Australia.

Variables	PAID ^a	PAIB	N	P	P x N	HT
Foliar $\delta^{18}O$	ns	ns	ns	ns	ns	0.46 **
Foliar $\delta^{13}C$	-0.70 *** ^b	-0.62 ***	-0.74 ***	-0.69 ***	-0.78 ***	0.66 ***
Rainfall (R)	0.93 ***	0.86 ***	0.75 ***	0.62 ***	0.77 ***	-
Nitrogen (N)	0.75 ***	0.67 ***	- ^d	-	-	-
Phosphorus (P)	0.63 ***	0.54 ***	-	-	-	-
N x P ^c	0.78 ***	0.70 ***	-	-	-	-
R x N x P	-0.84 ***	-0.69 ***	-	-	-	-
R x P x N x $\delta^{13}C$	-0.85 ***	-0.74 ***	-	-	-	-

^aPAID and PAIB were means of annual periodic growth calculated over 2-year intervals.

^bAsterisks *, **, and *** indicate significance at $p < 0.05$, 0.01, and 0.001, respectively, and ns = not significant ($p > 0.05$).

^cInteractions between the variables.

^dDash lines mean that correlation coefficients for these parameters were not determined.

Table 7.5. Litter needle $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the 10 year-old F1 hybrid exotic pine plantation under three harvest residue management regimes (RR_0 , RR_1 and RR_2).

Treatment	Sampling Periods			
	Jul-Sept05	Oct-Dec05	Jan-Mar06	Apr-Jun06
<u>Litter $\delta^{13}\text{C}$ (‰)</u>				
Residue removal (RR_0)	-29.46b ^a	-29.41b	-29.50b	-29.53a
Single residue retention (RR_1)	-29.35b	-29.37b	-29.51b	-29.26a
Double residue retention (RR_2)	-29.19a	-29.13a	-29.17a	-29.42a
<u>Litter $\delta^{18}\text{O}$ (‰)</u>				
Residue removal (RR_0)	21.48a	21.65a	21.88a	21.18a
Single residue retention (RR_1)	21.20a	21.65a	21.08b	20.80a
Double residue retention (RR_2)	21.05a	21.33a	21.35ab	21.15a

^a Means assigned with the same letter were not significantly different ($p > 0.05$).

This study also showed that the litter needle $\delta^{13}\text{C}$ and foliar $\delta^{13}\text{C}$ were related (Fig. 7.6a-b). However, only litter needle $\delta^{13}\text{C}$ from the July – September 2005 season was significantly related to the PAID (2004 – 2006 period) (Fig. 6c) ($r^2 = 0.47$; $p < 0.05$). Regressing PAID with litter needle $\delta^{13}\text{C}$ of all seasons that have significant $\delta^{13}\text{C}$ variations showed that litter needle $\delta^{13}\text{C}$, in general, could be related to the PAID ($r^2 = 0.26$; $p < 0.005$) (Fig. 7.6d). Furthermore, Table 7.5 shows a temporal trend in the variation of litter needle $\delta^{13}\text{C}$ between the treatments. The occurrence or absence of significant variations in litter needle $\delta^{13}\text{C}$ between treatments at each period appeared to closely follow the seasonal changes in the rainfall and temperature, where a greater variation between the treatments occurred in the periods with the lowest rainfall or highest daily temperature (Fig. 7.7).

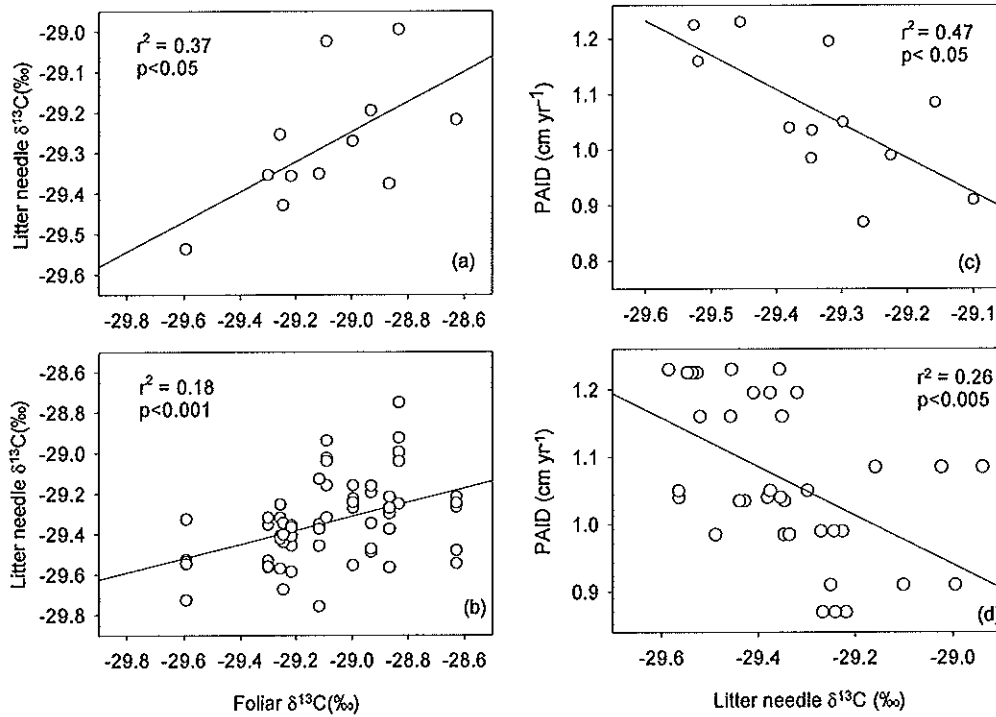


Fig. 7.6. Relationships between foliar $\delta^{13}\text{C}$ sampled in 2006 and litter needle $\delta^{13}\text{C}$ sampled from the July – September 2005 period (a) and all periods that have significant $\delta^{13}\text{C}$ variations (Table 5) (b). Litter needle $\delta^{13}\text{C}$ was also significantly related to the periodic mean annual increment of diameter at breast height (PAID) of the 2004 – 2006 period (age 8 – 10 years) as shown by the negative relationship between PAID and litter needle $\delta^{13}\text{C}$ sampled in the July – September 2005 period (c) and periods that have significant litter needle $\delta^{13}\text{C}$ variations (d).

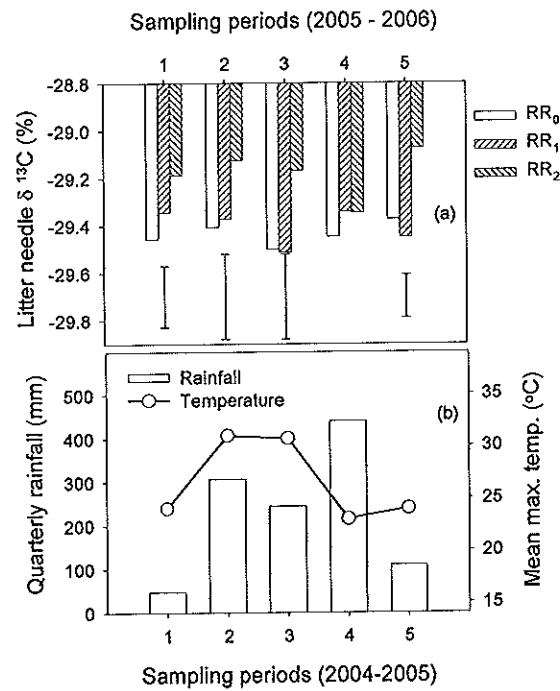


Fig. 7.7. The occurrence of litter needle $\delta^{13}\text{C}$ variation between the treatments for each season or quarter from the 2005 to 2006 litter collection period was closely related to the rainfall (a) and temperature (b) patterns of the same periods in the previous year (2004-2005). The vertical bars are least significant differences (LSD) between the treatments, and the sampling periods are: (1) Jul - Sept 2005, (2) Oct - Dec 2005, (3) Jan - Mar 2006, (4) Apr - Jun 2006, and (5) Jul - Sept 2006.

7.4 Discussion

7.4.1 Foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$

Harvest residue management clearly influenced the variations in foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in 2000, and $\delta^{13}\text{C}$ in 2006 (Table 7.2), as indicated by the consistent increase in foliar $\delta^{13}\text{C}$ in the order $\text{RR}_0 < \text{RR}_1 < \text{RR}_2$ in both years. Whilst the variations in foliar $\delta^{13}\text{C}$ across the treatments were only 0.90‰ and 0.87‰ in 2000 and 2006, respectively, they were consistent with those studies having small variations of 1.0‰ or less, yet showing significant increases in both g_s , A_{max} and growth (Olbrich et al., 1993; Fischer et al., 1998; Barbour et al., 2000; Xu et al., 2000).

The absence of significant variations in foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ between the treatments in some years could be due to high water availability (Keitel et al., 2003) as reflected in the rainfall data (Table 7.1). In year 2000, the relatively drier four to six months prior to sampling was probably critical in the variations across the treatments, especially for $\delta^{18}\text{O}$, which was related to the rainfall within this timeframe (Fig. 7.6). Variations in foliar $\delta^{13}\text{C}$ would therefore occur in concurrence with the variations of $\delta^{18}\text{O}$ (Barbour et al., 2000). On the other hand, variations in foliar $\delta^{13}\text{C}$ between the treatments in 2006 were likely to be linked to the 18 and 12 months effective rainfalls (Fig. 7.5). However, total rainfall alone may not fully explain these observations. Rainfall distribution (Garcia-G et al., 2004), duration of drier conditions (Fernandez et al., 2006), N nutrition (Högberg et al., 1993), ambient temperature and vapour pressure deficit (VPD) (Korol et al., 1999; Barbour et al., 2002) have also been reported to influence tree foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

7.4.2 Foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in relation to tree growth

The significant correlation of foliar $\delta^{13}\text{C}$ of the F1 hybrid exotic pine with the growth indices was consistent with the past studies on conifer species, using foliar $\delta^{13}\text{C}$ (Högberg et al., 1993) or ^{13}C discrimination (Δ) (Xu et al., 2000) and stem or wood cellulose $\delta^{13}\text{C}$ (Dupouey et al., 1993; McNulty and Swank, 1995). The positive relationship of foliar $\delta^{18}\text{O}$ with tree growth (Fig. 7.2c-d), however, has not been reported in the past. In fact, studies on other plants showed that plant $\delta^{18}\text{O}$ was negatively related to the growth in accordance with the g_s theory (Barbour et al., 2000). This discrepancy will be discussed later.

One of the objectives of this study was to relate foliar $\delta^{13}\text{C}$ to actual growth gained (PAID or PAIB). However, at the early growth period, the correlation co-efficient and the direction of change for the periodic growth rate and cumulative or absolute growth were comparable to those of Xu et al. (2000). Nonetheless, this approach was useful when the direction of periodic growth rates diverged from cumulative growth after peak growth, allowing foliar $\delta^{13}\text{C}$ to relate to the dynamic changes in growth over time. The negative relationship of foliar $\delta^{13}\text{C}$ with PAID and PAIB as shown in 2006 (Fig. 7.4) had been reported for *Pinus greggii* using wood cellulose $\delta^{13}\text{C}$ (Garcia-G et al., 2004). Foliar $\delta^{13}\text{C}$ in this study showed a much stronger relationship with periodic annual increments of the basal area (PAIB) ($r = -0.68$ in 2006) (Table 7.3) than wood cellulose $\delta^{13}\text{C}$ ($r = -0.42$) (Garcia-G et al., 2004), suggesting the validity of foliar $\delta^{13}\text{C}$ in predicting stem growth.

7.4.3 Foliar $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, K concentration and growth variations

The negative relationship between foliar $\delta^{13}\text{C}$ and growth indices in 2006 (Fig. 7.4) was clearly due to reduced g_s . This growth response was consistent with decreasing g_s , which reduces C_i , thus photosynthetic rate and therefore growth (Farquhar et al., 1982; Fischer et al., 1998; Barbour et al., 2000; Garcia-G et al., 2004). This result suggested a decrease in g_s with increasing residue-loading rates, which was unexpected against the background of published work suggesting the conservation of moisture by residues (Proe et al., 1999b; Scott et al., 2005). However, the decreasing growth rate with increasing harvest residue loading rates and foliar $\delta^{13}\text{C}$ in 2006 was strong evidence for water limitation in the R_1 and R_2 treatments. Perhaps the thick residue layer, combined with the below-average rainfall in the last 10 years, prevented water from percolating into the soil, making water less available for the roots. Nonetheless, the growth rates in the RR_0 treatments were not large enough to offset the growth gain in the RR_1 and RR_2

treatments prior to 2000 therefore overall growth was still higher in the RR₁ and RR₂ treatments after 10 years (see Chapter 6).

The positive relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ observed in 2000 (Fig. 7.3b) was also indicative of the influence of decreasing g_s on C_i (Fischer et al., 1998; Barbour et al., 2000; Scheidegger et al., 2000). Decreasing stomatal conductance, which increases $\delta^{13}\text{C}$, results in an increase in leaf surface temperature and hence the atmosphere to intercellular vapour pressure ratio, resulting in more evaporation and therefore enrichment of the heavier H_2^{18}O molecule at the evaporating site (Fischer et al., 1998; Barbour et al., 2000). Thus, both the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ would increase. This observation was consistent with studies of tropical forest trees (Sternberg et al., 1989), tree ring cellulose (Saurer et al., 1997), whole leaf tissue of cotton (Barbour and Farquhar, 2000) and tree phloem sap (Keitel et al., 2003). The slope of the $\delta^{18}\text{O}/\delta^{13}\text{C}$ relationship (7.70 ‰ increase in $\delta^{18}\text{O}$ per 1‰ increase in $\delta^{13}\text{C}$) in this study (Fig. 7.3b), however, was very steep compared to those reported by Barbour et al. (2000) and Keitel et al. (2003), which were 2.9 ‰ and 1.11 ‰, respectively.

The positive relationships between growth indices and foliar $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ in the context of increasing residue-loading rates in 2000 (Table 7.3 and Fig. 7.2), however, were inconsistent with the g_s theory as a mechanism for growth. Higher g_s was expected to cool the leaves, and therefore the canopy, resulting in increased internal CO_2 concentration, and higher light-saturated photosynthetic rate of plants (Fischer et al., 1998). In contrast, the increase in $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ with increasing tree growth rates (Fig. 7.2), was probably the result of higher growth rates in the RR₁ and RR₂ treatments, causing periodic or sustained water stress to which foliar $\delta^{18}\text{O}$ was sensitive. Growth-induced water stress, has been suggested by some published work (Högberg et al., 1993;

Xu et al., 2000; Garcia-G et al., 2004). This effect might explain the very steep slope of the $\delta^{18}\text{O}/\delta^{13}\text{C}$ relationship mentioned above, where higher growth demands for water established a steep gradient of g_s across the treatments. I would speculate that growth demands for soil water might have, over time, increased soil water deficit (SWD) in the RR₁ and RR₂ treatments as observed in 2006.

I have considered the role of foliar K concentration in increasing A_{\max} (Peoples and Koch, 1979; Longstreth and Nobel, 1980; Huber, 1984; Pervez et al., 2004), given that foliar K concentration was significantly related to the tree growth and foliar $\delta^{13}\text{C}$. In addition, foliar K was also related to the steep positive $\delta^{18}\text{O}/\delta^{13}\text{C}$ relationship, which could also indicate increased photosynthetic rate (Scheidegger et al., 2000; Keitel et al., 2006; Barbour, 2007). However, it is difficult to extend this explanation to 1998 (age 2 years), which exhibited significant variations in both foliar K concentration and tree growth rates, yet showed no significant variations in foliar $\delta^{13}\text{C}$. If foliar K concentration played a major role in increasing A_{\max} , then variations in foliar $\delta^{13}\text{C}$ would have occurred during high soil water availability (Högberg et al., 1993), which was likely in 1998 (Table 7.1). Therefore, a more appropriate interpretation of the $\delta^{18}\text{O}/\delta^{13}\text{C}$ relationship would be in relation to the $\delta^{18}\text{O}/\text{K}$ relationship (Fig. 7.3a), which suggests the involvement of K in tree water relations (Xu et al., 2000). This conforms with studies showing increased water use efficiency (WUE) with enhanced K supply under arid conditions (Pervez et al., 2004) or decreased stomatal conductance (i.e. increased $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in this case) (Fernandez et al., 2006). Potassium possibly functions through its maintenance of leaf water and pressure potential (Ashraf et al., 2001; Pervez et al., 2004), allowing photosynthesis to proceed under dry conditions.

The WUE hypothesis is consistent with the weak relationship between foliar K concentration and growth indices in 1998 (Chapter 6) when effective rainfall was well distributed (Table 7.1). The apparent enhanced uptake of K in the RR₁ and RR₂ treatments, therefore, became less important to growth, which points to the conclusion that the primary cause of increased growth prior to year 2000, and in wetter periods, might still be improved N or P nutrition (Chapter 6). Hogberg et al. (1993) pointed out that the addition of an N source to an N-limited soil would increase foliage biomass and therefore growth rate, which in most cases led to water stress in drier sites due to growth demands. This observation was consistent with the increases in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ along with increasing growth in this study, and that the significant $\delta^{13}\text{C}/\text{K}$ relationship (Fig. 7.3a) was a response of drought-stressed trees, rather than increased photosynthesis. This observation parallels a separate study of the F1 hybrid exotic pine clones, which showed a better correlation between foliar mineral concentrations and $\delta^{13}\text{C}$ in drought stressed trees, compared to non-water stressed trees (Prasolova et al., 2005).

7.4.4 Longer-term variations of foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and declining growth

The long-term annual changes in foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ over the 10 years were also striking in this study, revealing additional information relevant to long-term tree growth. The increasing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ over time was probably due to the declining mean annual rainfall over the last 10 years (Chapter 2, Fig. 2.2) combined with the hot summer temperatures causing longer periodic water stress, which is common in this region (Xu et al., 2000). The correlation of foliar $\delta^{18}\text{O}$ with rainfalls of shorter time lengths (four to six months prior to foliar sampling) (Fig. 7.6), suggests that foliar $\delta^{18}\text{O}$ could be associated with rapid turnover C, which are C compounds rapidly transferred to other parts of the plant (Scheidegger et al., 2000). The rapid adaptation of $\delta^{18}\text{O}$ relative to $\delta^{13}\text{C}$ has also been observed in other plants (Scheidegger et al., 2000). Thus, foliar $\delta^{18}\text{O}$

may be a sensitive indicator of short-term changes in environmental conditions, particularly short-term rainfall events. On the other hand, the correlation of foliar $\delta^{13}\text{C}$ with longer-term rainfall data suggests that the foliar $\delta^{13}\text{C}$ measurements are reflecting structural C. Bulk needles have been reported to reflect $\delta^{13}\text{C}$ of either structural or rapid turnover C (Brendel, 2001).

The significant correlation between increasing $\delta^{13}\text{C}$ with declining PAID over time (Table 7.4) was consistent with reduced stomatal conductance induced by SWD (Farquhar and Richards, 1984; Barbour et al., 2000). This was supported by the strong correlation of declining rainfall with the declining PAID over time. The likely influence of rainfall was in contrast to our earlier proposition that the decline in foliar N and P concentrations was the main cause of the decline in tree growth (Chapter 6). However, the significant relationship between rainfall or $\delta^{13}\text{C}$ and foliar N and P concentrations (Table 7.4) suggests that the declining foliar N and P concentrations in Chapter 6 might be related to the effect of soil moisture limitation on nutrient mineralisation, mass movement and therefore uptake by the trees (Högberg et al., 1993). The improved correlation coefficient among interactions of rainfall, foliar N and P concentrations with PAID or PAIB (Table 7.4) is an indication of the influence of soil water availability on nutrient availability. A number of studies reported that nutrient limitation is one of the causes of declining forest growth (Gower et al., 1996; Jokela and Martin, 2000). This study suggests that nutrient limitation may be exacerbated by declining rainfall, and therefore has significant implications for climate change impacts on forest growth (Sardans and Penuelas, 2007).

A number of studies have also suggested that declining tree growth could also be due to the stomatal or hydraulic limitation theory, which proposes that increasing tree height

limits water transport and therefore, reduces the leaf-specific hydraulic conductance (Gower et al., 1996; Ryan and Yoder, 1997; McDowell et al., 2005). Evidence for this theory was suggested by the significant correlation of increasing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ with increasing HT, and the concomitant decline of PAID (Table 7.4; Fig. 7.1) as the plantation aged. However, the simultaneous decline in rainfall weakened this theory in this situation. Furthermore, a study of one and seven year old Eucalyptus plantations, of comparable age to this plantation and in a tropical setting, found that the hydraulic limitation theory could not explain the decline in tree growth, due to compensatory changes in tree architecture (Barnard and Ryan, 2003).

7.4.5 Litter $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the F1 hybrid exotic pine

The significant relationships between foliar and litter $\delta^{13}\text{C}$ across the treatments (Fig. 7.7a-b), is supportive of the suggestion above that a significant quantity of foliar $\delta^{13}\text{C}$ was part of leaf structural C, which remained with the litter after senescence. The apparent depletion in litter $\delta^{13}\text{C}$ in all seasons relative to foliar $\delta^{13}\text{C}$ in 2006, and the narrower range (0.27 – 0.33‰) across the treatments (Table 7.5), was reflective of C mobilisation or re-translocation during the senescence. Regardless of this, litter needle $\delta^{13}\text{C}$ was able to show significant variations across the treatments in at least two seasons, with the highest $\delta^{13}\text{C}$ in the RR₂ treatment, consistent with the trend of foliar $\delta^{13}\text{C}$ in 2006. This consistency was further demonstrated in the significant relationship between litter $\delta^{13}\text{C}$ and MAID in 2006 (Fig. 7.7d). The negative relationship between litter needle $\delta^{13}\text{C}$ and tree growth in 2006 supported the conclusion drawn from the foliage, where the inverse relationship between foliar $\delta^{13}\text{C}$ and PAID or PAIB suggested moisture stress, and therefore g_s (Farquhar and Richards, 1984; Zhang and Cregg, 1996; Barbour et al., 2000), as the controlling factor for the variation in tree growth in 2006. Furthermore, the occurrence or absence of litter needle $\delta^{13}\text{C}$ variations

between the treatments across the seasons clearly reflects the influence of temperature and rainfall, whereby seasons with higher mean maximum temperatures and relatively low rainfalls of the previous year resulted in the significant variations in litter $\delta^{13}\text{C}$ of those seasons in the present year (Fig. 7.8). Although the litter $\delta^{13}\text{C}$ measurements were carried out for 15 months only, these results were consistent with studies of wood cellulose $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variations, where increasing temperature and low rainfall resulted in increasing wood cellulose $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Korol et al., 1999; Barbour et al., 2002), similar to that with litter $\delta^{13}\text{C}$ of this study. Thus, litter $\delta^{13}\text{C}$ may be a potential indicator of soil moisture status, and its use could substitute for foliar sampling of taller trees.

7.5 Conclusion

This study has demonstrated that harvest residues have significant influence on the variations in foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the F1 hybrid exotic pine trees, and therefore provides a means to assess tree growth in relation to water or nutrient issues. In this case, foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variations and their relationships with periodic tree growth indices helped to reveal the mechanism for regulating tree growth. Both the mulching and nutritional effects were reflected in the foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variations. However, the nutritional effect, including K nutrition and its impact on the WUE, appeared to be the dominant influence during the early growth in the residue retention plots, inducing water stress and long-term SWD as reflected in the $\delta^{13}\text{C}$ over the 10 years. Long term foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variations have provided a valuable insight into understanding the growth declines in the current plantation. Litter needle $\delta^{13}\text{C}$ variation has potential for studying soil moisture in relation to tree growth. Nonetheless, direct measurements of g_s and A_{max} are necessary to confirm these observations in the field.

CHAPTER EIGHT

General Discussion, Conclusions and Future Research

8.1 Summary

In southeast Queensland, future wood production will rely on second-rotation plantations (Simpson et al., 2003). This increases the importance of sustainable forestry management practices including harvest or logging residue retention for the maintenance of SOM, and therefore soil fertility, in forest plantations. Recent studies of soil and tree growth under different residue management regimes in exotic pine plantations of southeast Queensland provided valuable insights into the impact of harvest residue retention (Mathers and Xu, 2003; Simpson et al., 2003; Chen and Xu, 2005). However, a number of questions have been left unanswered by these past studies. These questions included the nature of the residues, their decomposition and nutrient release dynamics, and the short- and long-term impacts of the residues on soil C, N and P pools, long-term soil C sequestration, tree nutrition, growth and productivity. A greater understanding of the relationship between residue management and these factors is critical for sustainable plantation production.

This study determined the decomposition and nutrient release dynamics of harvest residues, including the chemical nature of the residue fractions (Chapter 3). Harvest residue decomposition followed the exponential decay model, with foliage showing the greatest decomposition rate followed by the twigs, branches then barks. By 2.5 years about 50 % of the foliage had decomposed and modelling has indicated that the foliage fraction would have been completely decomposed in less than 10 years. The foliage fraction not only comprised the largest proportion of residue biomass, it also contained the largest proportion of nutrients, and therefore would be an important short-term

source of C and nutrients. This study, therefore, suggested that the impact of residues on soil C and nutrients reported to occur in the first 6 years during previous investigations at experiment 321GYM (Mathers and Xu, 2003; Simpson et al., 2003; Chen and Xu, 2005) would have been largely due to the contribution of the foliage fraction, including the litter needle fraction. The branch and bark fractions showed the slowest decomposition rates, and modelling indicated a half-life of more than 10 years. This was consistent with the forest floor biomass measurements after 10 years (Chapter 5), in which the H horizons in the single residue retention (RR₁) and double residue retention (RR₂) treatments consisted of recognisable woody and bark materials greater than 2 mm. The half-life of branches (Chapter 2) confirmed that the woody remains after 10 years in the experiment 321GYM site were generally that of the branch fraction of the residues. These results demonstrate that the branch and bark residue fractions would be a long-term source of C and represent an important C sink in forest plantations.

Although the size of the residues might play a part in the variability of the decomposition rates among the residue fractions, residue quality was an influential factor. In particular, the C/N ratio and the methoxyl, aryl and O-aryl C fractions as revealed by ¹³C NMR were significantly correlated with the decomposition rate. This explained the slow decomposition of twigs, branch and bark residue fractions, which contained greater methoxyl, aryl and O-aryl C, and had higher C/N ratios, compared to the foliage fraction. These C functional groups represented phenolic and lignin compounds, which are important regulators of decomposition. Furthermore, this study showed a continuous change in the chemistry, and therefore the quality of the residues as decomposition progressed, which would have affected the decomposition and nutrient release dynamics of each residue fraction over time. In particular, the decrease in the O-alkyl C intensity, due to the depletion of the readily decomposable

carbohydrate C, and the increase in the recalcitrant alkyl C intensity over time, was consistent with the slower rates of decomposition in the later stages. The increase in the methoxyl C intensity in all residues, aryl C in foliage and O-aryl C in bark suggested an increase in the proportion of lignin compounds over time. The changes in the decomposition indicators such as alkyl/O-alkyl C (A/O-A), carbohydrate C/methoxyl C (CC/MC) and (aryl + O-aryl C)/Carbonyl C (AO/C) ratios also indicated the changing chemistry of harvest residues as decomposition progressed. The change in the decomposition indicators closely followed the decomposability of the residue fraction, with the CC/MC ratio being a more sensitive indicator, probably due to the rapid loss of the more labile carbohydrate C fraction. Nonetheless, these changes have significant implications on the long-term residue decomposition and nutrient release dynamics, when an increasing proportion of recalcitrance may become dominant. Changes in the residue ^{13}C NMR functional groups were also strongly linked to the mineralisation of C, N and P from the residues in this study.

The greater proportion of aryl and O-aryl C of the branch and bark fractions as revealed by the decomposition study may have also influenced the chemistry of forest floor biomass, other than litter needles, and SOM, especially the light fraction organic matter (LFOM), in the long term (Chapter 5). As revealed in Chapter 5 the aromaticity of SOM increased, despite the significantly lower A/O-A ratio, under the RR_1 and RR_2 treatments. This was in contrast to reports where SOM quality was indicated in terms of a relatively lower A/O-A ratio and aromaticity following residue retention. Mathers and Xu (2003) also reported relatively lower A/O-A ratio and aromaticity following residue retention at the experimental site when the plantation was 2 years old. However, these discrepancies can be understood in terms of the decomposition dynamics of the residues. As indicated in Chapter 3, the half-life of the twig fraction was about 5 years

and those of the branch and bark fractions about 10 – 11 years, thus their contribution towards the SOM pool and its chemical nature would have become dominant over a period greater than 2 years. Thus, the aromaticity of SOM may not necessarily be a product of microbial processing as has been established in the past. Rather, it may be reflective of the inherent chemical nature of the originating plant matter, demonstrating the influence of residue quality on SOM chemistry. The greater aromaticity may be a mechanism for soil C sequestration under forest plantations, increasing the proportion of non-hydrolysable or recalcitrant C pools (Chapter 5).

Harvest residue retention was responsible for an increase in SOM through residue decomposition in the exotic pine plantations. While a reduction in soil total C was evident in the first 12 months in the macro-plots (Chapter 4), soil total C levels recovered to pre-harvest levels in as little as 18 months following clear-cut harvesting under the RR₁ and RR₂ treatments. The significantly greater soil total C under residue retention (Chapter 4) was consistent with an earlier study at experiment 321GYM when the plantation was 2 years old (Mathers and Xu, 2003). Residue retention continued to show greater soil total C in both the RR₁ and RR₂ treatments after 10 years, consistent with the quantities of the forest floor biomass C in this plantation (Chapter 5). The significant variation among the treatments both in the short and long term were in contrast to other studies (Johnson et al., 2002), and might be due to the relatively rapid decomposition rate of slash pine residues in this sub-tropical environment (Chapter 3), or the low pre-harvest soil total C levels, thus accentuating the impact of residue decomposition and subsequent incorporation as SOM. Nonetheless, the lack of a significant change in total C after 10 years (Chapter 5) compared to those reported earlier (Mathers and Xu, 2003; Chen and Xu, 2005) for each treatment demonstrated

that residue management, rather than clear-cutting or time *per se*, has a large impact on soil C maintenance and storage both in the short and long term.

Residue management also had significant short- and long-term impacts on the SOM quality of the exotic pine plantations. This was suggested by the greater quantities of labile organic C, N and P pools in the RR₁ and RR₂ treatments compared to the residue removal (RR₀) treatment 18 months after clear-cut harvesting and residue retention (Chapter 4). The impact of residue retention on labile C pools in Chapter 4 was consistent with the semi-quantitative analysis of SOM quality carried out by ¹³C NMR spectroscopy at experiment 321GYM when the plantation was 2 years old, when greater O-alkyl C and lower A/O-A ratios of SOM was observed under the residues (Mathers and Xu, 2003). The impact of residue retention on SOM quality was more apparent in the longer-term study (Chapter 5), where significant variations in hot water extractable organic C (HWEOC), light fraction C (LFC), HCl hydrolysable C and heavy fraction $\delta^{13}\text{C}$ between the residue removal and operational residue retention level (RR₁) were more clearly determined than in the earlier years. This study showed that increasing total C would increase the amount of the labile C fractions consistent with the relatively greater O-alkyl C and lower A/O-A ratios observed under residue retention. This suggested that the chemistry of SOM as revealed by ¹³C NMR was influenced by the quantity of these labile C fractions. The significant variations in HWEOC, hot water extractable organic N (HWEON) and hot water extractable organic P (HWEOP) in this study (Chapters 4 and 5) demonstrated the importance of residue retention as a source of C and nutrients, while the significant correlations among these indicators demonstrated how C is closely tied up with N and P. Furthermore, residue retention not only increased the labile C fractions, it also increased the non-hydrolysable C or stabilised organic matter pool in the long term (Chapter 5). Thus, residue retention in plantation

ecosystems has significant implications for soil C sequestration, and may become a factor when assessing the role of plantation forestry in climate change mitigation schemes.

This study also demonstrated that residues contained a significant amount of nutrients, and these were released during the decomposition of the residues. Nutrient release dynamics showed varying patterns and were dependent on residue fraction decomposability and some biochemical factors. In this study, residue N concentration increased in the first 18 months (Chapter 3) due to N immobilisation from N uptake by the decomposer microbial community. This was also consistent with the apparent immobilisation of soil mineral N over time in Chapter 4. Woody residues have been reported to initiate N and P immobilisation in other studies (Carlyle et al., 1998). Nonetheless, the decreasing percentage N remaining after 18 months indicated the release of N from the residues (Chapter 3), consistent with the significantly greater soil total N and mineral N in the RR₁ and RR₂ treatments after 18 months following clear-cut harvesting (Chapter 4).

Phosphorus release dynamics closely followed the mass loss pattern (Chapter 3). The significant positive correlation between residue P and percentage mass remaining indicated that P was largely associated with labile organic compounds, which became oxidised during the decomposition process. This was supported by the significant correlation between foliage P remaining and the ¹³C NMR O-alkyl C fraction (Chapter 3), and the positive correlation between soil labile P and HWEOP (Chapter 4). The significantly greater HWEOP and hot water extractable total P (HWETP) under the residue retention treatments (Chapter 4) demonstrated that these P fractions were directly released from the residues through residue decomposition.

This study demonstrated that the greater soil N and P availability following clear-cut harvesting and residue retention resulted in significantly greater tree growth in the RR₁ and RR₂ treatments although there were no significant variations in foliar N and P concentrations among the treatments (Chapter 6). This was supported by the stable isotope study in Chapter 7, in which the increasing foliar C isotope composition ($\delta^{13}\text{C}$) and O isotope composition ($\delta^{18}\text{O}$), as well as foliar K concentration, with the increasing tree growth during the early phase, was consistent with growth-induced water stress usually linked to greater availability of nutrients, especially N and P. This would be consistent with the greater readily available N and P from the residues confirmed in Chapter 4. If the indicated water-stress were the cause of the significant variation in tree growth then the growth rate would have had a negative relationship with $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ according to theory (Saurer et al., 1997; Keitel et al., 2006; Barbour, 2007). Further evidence of the influence of residues on tree nutrition, and therefore early growth, was revealed by the significant variations in N and P concentrations of the F horizon litter needles, which were significantly correlated with tree growth rate (Chapter 6). This study proposed that the lack of significant variations in foliar nutrient concentrations during early growth could be due to nutrient re-translocation from older or lower canopy needles to the younger photosynthesising needles sampled in this study. Thus, future sampling of needles at different canopy positions or age may be an appropriate diagnostic tool for nutrient management in the exotic pine plantations.

This study, however, revealed that the impact of the residues on tree nutrition and growth was limited to the early growth phase, especially the first 4 years. The declining foliar N and P concentrations over 10 years, from an initial level above critical concentrations to levels below critical or at marginal concentrations (Chapter 6), and the concomitant decline in growth rate regardless of residue management, supported this

conclusion. The decreasing foliar N concentration was consistent with the low soil mineral N concentrations at age 10 years (Chapter 5), compared to the greater mineral N determined at age 6 years (Chen and Xu, 2005). Likewise, the low foliar P concentrations at age 10 years (Chapter 6) were consistent with the soil available P (Bray1_P and $\text{NaHCO}_3\text{-P}$) concentrations (Appendix I). These concentrations of soil available P were relatively low compared to those reported by Mathers and Xu (2003) in the same plantation at age 2 years, the age when foliar P concentrations were significantly greater than at age 10 years (Chapter 6). In addition, $\text{CaCl}_2\text{-P}$, hot water extractable P (HWE_P) and HWE_{TP} at age 10 years (Appendix I) were lower when compared to those measured at age 2 years following clear-cut harvesting in a nearby plantation (Chapter 4). However, this declining trend in available N and P were in contrast to the trend of soil total N and P over the long term, which did not change or increased slightly (Chapter 5 and Appendix 1). Even HWE_{ON} increased from that reported after 6 years (Chen and Xu, 2005) to that reported in Chapter 5 after 10 years in the same plantation. Nonetheless, the greater soil total N in the RR₁ and RR₂ treatments was not reflected in the mineral N pool in the long term (Chapter 5). Thus, changes in available nutrients in the sandy soils will be a function of SOM availability and quality. Changing residue quality, and therefore SOM quality, from the foliage and then the branches and bark contribution to SOM as decomposition progressed, may have caused greater N and P immobilisation leading to the lower soil N and P availability and therefore uptake. The low availability of N and P may also be due to greater uptake of larger trees or intense competition for these nutrients by the larger trees leading to the depletion of available N and P regardless of residue management. The supply of available N and P may also be influenced by a slower mineralisation rate induced by soil water limitation, which may have affected microbial activity. Soil water limitation was a likely factor given the declining rainfall over the last 10 years. This

factor was supported by the negative relationship between $\delta^{13}\text{C}$, or foliar K, and growth rate at age 10 years, suggesting the influence of water stress on tree growth (Chapter 7). The suggested greater water stress, and therefore slower tree growth rate, at age 10 years under residue retention treatments was probably due to the thick organic layer limiting rainwater penetration into the soil mineral layer. Greater competition intensity for soil moisture due to the current stocking rate and larger tree biomass under the RR_1 and RR_2 treatments may also have been a factor. The significant correlation between tree growth rate and the interactions among rainfall, foliar N and P concentrations and $\delta^{13}\text{C}$ (Chapter 7) indicated that long-term tree growth in this study was probably influenced by a combination of low available nutrient supply and soil water limitation. The long-term impact of residues on tree nutrition and growth, therefore, may be more clearly established through a fertiliser response trial and more direct soil moisture stress measurements, which were beyond the scope of this project.

8.2 Conclusions

This study makes the following major conclusions:

- (1) Slash pine logging residues contained significant amounts of nutrients, released at varying rates depending on the decomposability of the residue fractions and biochemical nature of the nutrients. The decomposition and nutrient release of slash pine logging residues in southeast Queensland are comparatively faster than those reported by other studies due to the sub-tropical climate. Phosphorus release was faster than N release, and that P release closely followed the mass loss dynamics. Thus, slash pine logging residues are potentially an immediate source of P following the retention of the residues. The ^{13}C NMR spectroscopy study of the harvest residues showed that harvest residues have a heterogeneous chemical nature, which influenced the varying rates of decomposition of the

residue fractions. It also showed that the C chemistry composition of the residues changes over time, with the CC/MC ratio being a sensitive decomposition indicator across a number of residue fractions in the short term. The changes in the ^{13}C NMR functional groups can be related to the mineralisation of N and P from the residues and that residue chemistry reflects the chemistry of SOM over time.

- (2) Residue retention and its subsequent decomposition did contribute C and nutrients to the soil pools. Clear-cut harvesting impacts on C and N pools were limited only to the first year, while residue management had a significant impact in the second year, returning soil total C to levels similar to or greater than pre-harvesting levels under residue retention. Residue retention also increased labile C and N pools such as HWEOC and HWEON, which consistently showed residue treatment effects after 12 months. Similarly, residue retention significantly increased labile P pools in the residue-retained treatments.
- (3) Residue management has a long-term impact on the C and N stocks of a plantation ecosystem. Residue management also has a significant impact on the sizes of the labile and recalcitrant C pools, which impact on both the quality of SOM and the potential for C sequestration. The HWEOC, HWEON, heavy fraction $\delta^{13}\text{C}$, and hydrolysable C were the most sensitive indicators of long-term residue management. This study also showed that the size of labile C pools were related to the SOM chemistry as revealed by ^{13}C NMR spectroscopy analyses and that harvest residue chemical composition would influence the chemistry of SOM, which could change over time as residue quality changes during the progression of decomposition.

- (4) The impact of residue retention on total tree growth was observed over time. However, the impact of residue retention on the growth rate was limited to the early growth phase. Foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and litter N and P analyses suggested that the greater early growth rate under residue retention was due to the impact of the residues on tree nutrition, rather than the impact of the residues on soil water conservation. The subsequent decline in tree growth rates after 3-4 years was probably due to a combination of soil water limitation and N and P deficiencies at age 10 years, which occurred regardless of residue management. The significant negative relationship between growth rate and foliar $\delta^{13}\text{C}$ at age 10 years, suggested that soil moisture limitation might be the most influential factor impacting on growth rate at this stage, and this was more severe under the RR_1 and RR_2 treatments. Greater competition by larger trees might also have led to the depletion of soil water and nutrients and therefore affected growth in the long term. The influence of residues on litter production and biomass C recycling at age 10 years is not clear at present. Nonetheless, these findings support the conclusion that harvest residues did have a positive impact on tree growth; however, its impact appeared to be reduced at age 10 years as indicated by the periodic growth rates and the closing gap among the treatments. Integrating later age fertilisation and soil water management with residue retention strategies may be necessary to ensure the benefits of residue retention are sustained to the end of the rotation”

8.3 Future Research Direction

This study did provide a greater understanding of the nature and decomposition dynamics of exotic pine harvest residues, and the impact residue management has on

soil C and nutrient pools, tree nutrition and growth both in the short and long term. However, I acknowledge that this study has its own limitations and that further work is needed to fully understand residue management impacts on C and nutrient cycling and the growth of the exotic pine plantations of southeast Queensland. In particular the following areas need to be explored in the future:

- This study for the first time, to my knowledge, measured labile P pools based on hot water extractions. The sensitivity of HWETP to residue management in this study warrants further testing of hot water extractable P as it involves a simple procedure, and can be a useful indicator of management or land use practices, as well as potential for plant growth.
- The distance of the research sites and limited funding prevented the study of detailed soil processes. Future direct measurements of N mineralisation and nitrification in the exotic pine plantations in relation to residue management may be able to better predict soil nutrient availability.
- While residue management has a significant long-term impact on the microbial biomass C (MBC), the impact on the microbial diversity and community structure as a measure of sustainability is currently unknown in this region.
- Continued monitoring of soil C sequestration and tree growth until the end of the rotation will be useful to fully understand the long-term impact of residue management.
- There is a need to further explore the influence of resource competition, especially of nutrients and soil water availability, in relation to residue management through fertiliser and irrigation response trials in the long-term experiment.
- This study falls short of determining the residue management impact on the total ecosystem C balance. Thus, there is a need to determine the total tree and under-

ground biomass C to compliment the current data on the soil total C, and litter and forest floor biomass C. This would need the development of allometric equations linking key tree parameters and tree biomass C. Currently there is no such information for exotic pine plantations in southeast Queensland.

- A detailed study of nutrient re-translocation in the exotic pine plantations is necessary to prove the proposition that nutrient re-translocation camouflaged the impact of residues on tree nutrition. In addition, future assessment of residue management impacts on tree nutrition may need to sample different canopy positions in relation to nutrient re-translocation. This approach may be a useful diagnostic tool for nutrient management in exotic pine plantations.
- Data based purely on foliar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses suggested the impact of residue management on nutrition or soil water conservation. This needs to be further ascertained by combining $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ with gas exchange measurements to fully understand the impact of residue management on the key eco-physiological processes. Measurements of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in different canopy positions may also be useful.

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APPENDIX I

Residue Management Impact on Labile Phosphorus Pools in a 10-Year-Old Exotic Pine Plantation of Subtropical Australia

Introduction

Harvest residue retention has been shown to increase soil total C and N in a second rotation exotic pine plantation in southeast Queensland, Australia (Mathers and Xu, 2003; Simpson et al., 2003; Chen and Xu, 2005). However, the impact of the residues on soil P has not been clearly established in the exotic pine plantations, in spite of the fact that harvest residues have been shown to be the main source of soil solution P after clear-cut harvesting in other studies (Bekunda et al., 1990; Palviainen et al., 2004a). The difficulty with the assessment of the impact of residues on soil P has been linked to the compounding effects of residual P from past P fertiliser applications (Simpson et al., 2003). Thus, there is a need to identify suitable soil P fractions that may be useful indicators of residue management. This study, therefore, investigated the impact of residue management on soil P pools in a 10-year-old exotic pine plantation by measuring several labile P pools and therefore potential P availability for long-term tree growth.

Materials and Methods

Site description and experimental design

The experimental site is located at Toolara State Forest (26°00'S, 152° 49'E), Maryborough district, southeast Queensland, Australia. Forestry Plantations Queensland (FPQ) established the experiment in July 1996 to assess the impact of harvest residue management. Details of this site and soil properties have been reported in Chapter 2 and by Mathers and Xu (2003), Simpson et al. (2003) and Chen and Xu (2005). In brief, it

has a deep, acidic sandy soil classified as Gleyic Acrisol (FAO, 1974) comprised of 5.3 % clay, 7.3% silt, 33.8% sand and 53.9% coarse sand (Mathers and Xu, 2003).

The experiment is a randomised complete block design with six treatments and four blocks. This study focussed on the three residue-loading treatments, which are: (1) residue removal, RR_0 ; (2) single residue retention, RR_1 ; and (3) double residue retention, RR_2 (Chapter 2). The plots were planted with the F1 hybrid between slash pine (*Pinus elliottii* var. *elliottii*) and Caribbean pine (*Pinus caribaea* var. *hondurensis*).

Soil sampling and chemical analyses

Composite soil samples were collected at 0 – 10 cm depths from five soil cores (ca. 7.5 cm diameter) systematically positioned within the net plots (Simpson et al., 2003; Chen and Xu, 2005) at 10 years after clear-cut harvesting and establishment of the experiment. Soil was air-dried and sub-samples were ground to powder in a puck and ring mill (Rocklab). Soil total P was determined by the ascorbic acid method (Murphy and Riley, 1962; Lajtha et al., 1999) following nitric/perchloric ($HNO_3/HClO_4$) acid digestion of ground soil (Sparks, 1996; Chen et al., 2002). Labile P pools were determined from air-dried (<2 mm) soil. Bicarbonate extractable P ($NaHCO_3_P$) was determined in a soil to solution ratio of 1:20 (Bekunda et al., 1990) after shaking end-over –end 2.5 g soil in 50 ml of 0.5 M $NaHCO_3$ (pH 8.5) for 16 hours at 25 °C. Bray 1 P ($Bray1_P$) was determined after shaking 5 g of soil with 35 ml of 0.03 M NH_4F /0.025 M HCl solution for 60 s (Rayment and Higginson, 1992). Calcium chloride extractable P ($CaCl_2_P$) was determined in soil extracts after shaking 8 g of soil in an end-over-end shaker for 18 hours in 40 ml of 5 mM $CaCl_2$ (Rayment and Higginson, 1992).

Hot-water extractable P (HWEP) was determined following the hot water extraction method for labile C described Chen and Xu (2005). Eight grams (oven-dried equivalent) of air-dried soil was incubated at 70 °C for 18 hours in 40.0 ml of de-ionised water (Millipore purified), shaken end-over-end for 5 minutes, centrifuged then filtered through a 0.45 µm filter membrane. The HWEP was determined from the soil extracts and hot water-extractable total P (HWETP) was determined after HNO₃/HClO₄ acid digestion of 10 ml of the hot water extracts. Hot water-extractable organic P (HWEOP) was the difference between P determined in undigested and that of digested hot water soil extracts.

Light fraction organic P (LFOP) was determined following the separation of the light fraction organic matter (LFOM) from the heavy fraction organic matter (HFOM) by flotation with aqueous sodium polytungstate (SPT) adjusted to 1.75 g cm⁻³ (Sollins et al., 1999; Marriot and Wander, 2006a; Yamashita et al., 2006). Two 10 g sub-samples of air-dried soil from each replicate were added with 30 ml of SPT, shaken in an end-over-end shaker for 12 minutes at 80 rpm, allowed to settle over night, and then centrifuged at 3500 rpm for 30 minutes prior to isolation on a pre-weighed 0.45 µm nitrocellulose filter paper. The isolated LFOM and HFOM were rinsed with de-ionised water, dried at 50 °C for 24 hours and weighed. The LFOM and HFOM sub-samples were then pooled, mixed thoroughly, then sub-samples of the LFOM (0.25 g) and HFOM (0.60 g) were digested in HNO₃/HClO₄ acid before determination of light fraction organic P (LFOP) and heavy fraction P (HFP). Phosphorus concentrations in all extracts were determined colorimetrically at 880 nm using the ascorbic acid method (Murphy and Riley, 1962; Lajtha et al., 1999), and expressed per kg of air-dried soil (Rayment and Higginson, 1992).

Analyses of variance (ANOVA) were carried out for all P pools to determine residue management effects. Where there was a significant treatment effect at $p < 0.05$, the data were subjected to the least significant difference (LSD) test.

Results and discussion

This study showed no significant differences in total P among the residue treatments (Table A1). This was consistent with total P analyses in earlier studies in the same plantation (Simpson et al., 2003). However, total P in the RR_0 and RR_2 treatments of this study were slightly greater than those measured at age 2 years of the plantation, when the total P in the RR_0 and RR_2 treatments were 28.6 ± 1.7 and 41.7 ± 0.1 , respectively (Mathers and Xu, 2003). Analyses of labile P pools only showed significant variations among the treatments for $NaHCO_3_P$ and LFOP, where both P pools showed significantly greater P under the RR_1 and RR_2 treatments (Table A1). Results also showed no significant variation in HFP among the treatments, but HFP constituted 50% of total P in the RR_0 treatment compared to 33% and 26 % in the RR_1 and RR_2 treatments, respectively. This indicated that a large proportion of P in the RR_1 and RR_2 may be water soluble or associated with water soluble labile C other than the LFOM collected during density fractionation. The HFP, on the other hand, constituted both heavy fraction organic P and adsorbed inorganic P. Pearson's correlation analyses showed significant relationships between HWEP and $NaHCO_3_P$, and also between HWEP and HWETP (Table A2). There were also significant relationships between LFOP and $CaCl_2_P$ or HWEP (Table A2) and a weak relationship between LFOP and $NaHCO_3_P$ ($r = 0.65$, $p < 0.06$).

Table A1. The total P, Bray 1 extractable P (Bray1P), calcium chloride extractable P (CaCl₂P), bicarbonate extractable P (HCO₃P), hotwater extractable P (HWEOP), hotwater extractable organic P (HWEOP), hotwater extractable total P (HWEOP), light fraction P and heavy fraction P under the residue removal (RR₀), single residue retention (RR₁) and double residue retention (RR₂) treatments obtained for the 0-10 cm soil depth at age 10 years old.

Treatments	Total P mg kg ⁻¹	Bray1_P mg kg ⁻¹	CaCl ₂ _P µg kg ⁻¹	NaHCO ₃ _P mg kg ⁻¹	HWEOP mg kg ⁻¹	HWEOP ^a mg kg ⁻¹	LFP mg kg ⁻¹	HFP mg kg ⁻¹	
RR ₀	33.72a	3.77a	21a	2.33b	0.45a	0.74a	1.19a	2.55b	16.89a
RR ₁	43.61a	4.16a	34a	4.46a	0.68a	0.93a	1.27a	4.25ab	14.41a
RR ₂	48.12a	3.59a	50a	4.05a	0.64a	1.36a	2.00a	5.67a	12.43a

Table A2. Pearson's correlations between soil total P, Bray 1 extractable P (Bray1_P), calcium chloride extractable P (CaCl₂_P), bicarbonate extractable P (NaHCO₃_P), hotwater extractable P (HWEP), hotwater extractable organic P (HWEOP), hotwater extractable total P (HWETP) and light fraction organic P (LFOP) under different harvest residue management regimes in a 10 year old exotic pine plantation of southeast Queensland.

	Bray1_P	CaCl ₂ _P	NaHCO ₃ _P	HWEP	HWEOP	HWETP	LFOP
CaCl ₂ _P	-0.10 ns						
NaHCO ₃ _P	0.52 ns	0.38 ns					
HWEP	0.09 ns	0.60 ns	0.81 ** ^a				
HWEOP	-0.35 ns	0.45 ns	0.21 ns	0.27 ns			
HWETP	-0.14 ns	0.29 ns	0.44 ns	0.45 ns	0.88 **		
LFOP	0.11 ns	0.86 **	0.65 ns ^b	0.72 *	0.35 ns	0.30 ns	
TOTAL P	0.16 ns	0.12 ns	0.41 ns	0.39 ns	0.30 ns	0.38 ns	0.03 ns

^aAsterisks *, **, and *** indicate significance at $p < 0.05$, 0.01 and 0.001, respectively, and ns = not significant ($p > 0.05$).

^bLFOP vs NaHCO₃_P significant at $p < 0.06$.

Large within treatment variations in CaCl₂_P may be responsible for the lack of significant differences among the treatments. This could also be due to uneven leaching of solution P among the treatments. The significant variation in NaHCO₃_P between the RR₀ and RR₁ or RR₂ treatments was in contrast to the lack of significant differences in available P at age 2 years of the same plantation (Mathers and Xu, 2003). Bray 1_P and

NaHCO₃_P represented available P, however, these P pools appeared to be lower than the available P measured at age 2 of this plantation (Mathers and Xu, 2003). The lack of significant variations in HWEP, HWEOP and HWETP among the treatments was in contrast to the significantly greater LFOP in the RR₁ and RR₂ treatments. The hot water extractable P pools were also lower than those reported 2 years after clear-cut harvesting and residue retention in another plantation at the same location of this study (chapter 4), indicating that residue management impacts on water soluble P may be limited to the early growth phase of the trees. In addition, while the LFOP was significantly correlated with CaCl₂_P, the CaCl₂_P was significantly lower than those reported 2 years following clear-cut harvesting in a nearby plantation (Chapter 4). Organic P mineralisation is the main source of available or inorganic P (Harrison, 1982), however, the lack of a significant correlation between LFOP and HWEOP or HWETP indicated other limiting factors on the mineralisation of organic P. This was supported by the low solution P as indicated by the CaCl₂_P. Soil microbial activity or soil water availability can limit N or P mineralisation (Chen et al., 2003). Thus, this study showed that while there was an obvious long-term impact of residue management on soil organic P, its effect on the immediately available P could not be established and that available soil P might be below critical levels regardless of residue management. This conclusion was supported by foliar P concentrations of the exotic pine trees at age 10 years, which were marginal compared to those at age 2 years old when soil labile P was greater (Chapter 6).

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