Soil Carbon Pools in Adjacent Natural and Plantation Forests of Subtropical Australia

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ABSTRACT

Soil C dynamics are not only important to both productivity and sustainability of terrestrial ecosystems, but also contribute significantly to global C cycling. Adjacent natural forest (NF), and first (1R) and second rotation (2R) hoop pine (*Araucaria cunninghamii* Aiton ex A. Cunn.) plantations in southeast Queensland, Australia, were selected to investigate the effects of conversion of NF to hoop pine plantations and forest management (harvesting and site preparation of plantation) on the size and the nature of C pools in surface (0–10 cm) soils using chemical extraction, laboratory incubation and ^{13}C cross-polarization with magic-angle-spinning nuclear magnetic resonance spectroscopy (^{13}C CPMAS NMR). Conversion from NF to hoop pine plantations not only led to the reduction of soil total C (by 19.8%), water-soluble organic C (WSOC) (by 17.7%), $CaCl_2$–extractable organic C (by 38.8%), and hot water-extractable organic C (HWEOC) (by 30.9%) and bioavailability of soil C (as determined by CO_2 evolved in the incubation), but also to a change in chemical composition of soil C with lower O-alkyl C and higher alkyl C under the 1R plantation compared with NF. Harvesting and site preparation did not significantly affect total soil C and most labile C pools (except for a decrease in WSOC), but led to a lower signal intensity in the alkyl C spectral region and a decreased alkyl C/O-alkyl C (A/O-A) ratio in the soil under the 2R compared with the 1R plantation. The shifts in the amount and nature of soil C following forest conversion may be attributed to changes in litter inputs, microbial diversity and activity, and the disturbance of soil during harvesting and site preparation.

L AND-USE CHANGES or shifts in cultivation can affect soil organic matter (Howard et al., 1998; Chen et al., 2000; Mao et al., 2002; Schroth et al., 2002). Davis and Condron (2002) reviewed a series of paired-site studies in New Zealand and suggested that conversion from grassland to plantation forest decreased organic C by 9.5% in the upper layer (mainly the 0- to 10-cm soil) in the short term (<20 yr), but that accumulation of organic C in the forest floor exceeded the loss of C in the mineral soils. Smith et al. (2002) reported that, in Brazil, conversion from native Amazonian forest to plantation forests also altered the quantity of soil C, with an increase in surface soil C under *Euxylophora paraensis* Hub. plantation and decreases under *Pinus caribaea* var. *honduensis* Barrett and Golfari, and *Carapa guianensis* Aubl. plantations. Howard et al. (1998), Quideau et al. (2000), and Paul et al. (2002) also suggested that tree species had different impacts on soil C pools and dynamics. Furthermore, land-use change can also alter the chemical nature of soil organic C (Golchin

et al., 1997; Howard et al., 1998; Quideau et al., 2000). For example, Golchin et al. (1997) found that the soil organic matter developed under the grass *Miscanthus sinensis* in the Andosol was more aromatic in nature than that under adjacent forest, and invasion of grassland by forest resulted in a decrease in C aromaticity and an increase in alkyl C content of soil. More recently, a direct link between tree species and the composition of soil organic matter has been revealed (Quideau et al., 2001). However, Beets et al. (2002) reported that the impacts of management practices (e.g., forest harvesting) on soil C was unclear, while Johnson and Curtis (2001) reported that tree harvesting had little or no effects on soil C content.

Numerous methods, including chemical extraction, isotopic techniques, and various spectroscopic analyses, have been used to characterize soil C pools and dynamics (Kögel-Knabner, 2000; Chodak et al., 2002; Magid et al., 2002; Mathers et al., 2000; Zaccheo et al., 2002). Water and dilute salt solution (e.g., $CaCl_2$ and K_2SO_4) extract soil organic C representing relatively labile organic C pools in soil (e.g., Nishiyama et al., 2001). The high turnover rate of soil labile C pools indicates their significance in C and nutrient cycling in terrestrial ecosystems (Hu et al., 1997). In recent years, nondestructive spectroscopic methods, such as ^{13}C solid-state CPMAS NMR spectroscopy and pyrolysis-field ionization mass spectrometry (Py-FIMS) techniques, have been increasingly used to characterize the chemical composition of soil C without extraction and fractionation (Preston, 1996; Schnitzer, 2001). The application of CPMAS and high power decoupling techniques in solid-state ^{13}C NMR increases the ^{13}C signal and the signal/noise ratio and decreases line broadening (Wilson, 1987; Mathers et al., 2000; Quideau et al., 2001). The pretreatment of forest soil samples with 2% HF (v/v) has been found to remove interfering paramagnetic materials (e.g., Fe and Mn) and also improve the quality of ^{13}C CPMAS NMR spectra by reducing the signal/noise ratio (Mathers et al., 2002).

Hoop pine is a native rainforest species of southeast Queensland (SEQ), Australia. The majority of the current hoop pine plantations (approximately 50 000 ha) in SEQ was established on the previous natural forestland. Little information is available on the impacts of conversion from NF to hoop pine plantations on soil organic C and associated nutrients. For this study, it was hypothesized that conversion of NF to hoop pine plantations and management practice (e.g., harvesting and site prep-

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aration) can alter the size and the chemical and biological nature of soil C pools. Adjacent NF and 1R and 2R hoop pine plantations were selected and a combination of chemical, biological, and NMR methods was applied to test this hypothesis.

MATERIALS AND METHODS

Site Description and Soil Sampling

The site is located within the Yarraman State Forest, SEQ, Australia (26°52' S, 151°51' E), lying in the upper catchment of the Brisbane River. The soil is a Typic Durustalf (Soil Survey Staff, 1999). Altitude at the site is 428 m above sea level. Annual rainfall varies from 433 to 1110 mm, with an average of 791 mm. Winter temperatures range from 4 to 20°C, and summer temperatures from 17 to 29°C. The NF and 1R, and 2R hoop pine plantation sites are adjacent to each other on the same position of the slope of approximately 2 to 3°. The NF site is classified as a mixed rainforest/scrub and dominated by bunya pine (*Araucaria bidwilli* Hook.), yellowwood (*Terminalia oblongata* F. Muell. subsp. *oblongata*), crows ash (*Pentaceras australis* R.B.), and lignum-vitae (*Premna lignum-vitae*), with emergent hoop pine (*Araucaria cunninghamii* Aiton ex A. Cunn.). Before plantation of 1R hoop pine, larger trees of natural forests were logged using bullock teams and a small dozer, and the understory scrub and the residues were brushed off to a height no >15 cm to be scattered evenly across the site, and were burnt when dry. It should be noted that a certain extent of disturbance might occur during site preparation for 1R hoop pine plantation. The 1R hoop pine plantation was established in 1949 at approximately 1540 stems ha^{-1} by hand planting and then thinned to a final stocking of 430 stems ha^{-1}. The 2R hoop pine site was planted in November 2000 after the clearcut harvest of part of the 1R hoop pine plantation using Timco harvester in September 1999. For the site preparation, a D5M dozer (Catapillar Inc., Peoria, IL) was used for pushing row lines through the clearfall residues at 6 m intervals, the row lines were then cultivated prior to planting. The stocking density at the 2R hoop pine site was approximately 620 stems ha^{-1} when the soil was sampled. The 1R hoop pine was approximately 51 yr old and the 2R hoop pine 2 yr old when soil was sampled.

Each (about 30 by 100 m) of the research areas under adjacent NF, and 1R and 2R hoop pine plantations was divided into five subplots for soil sampling. A total of 25 soil cores (0–10 cm) were randomly collected with an auger of approximately 7.5 cm in diameter from each subplot and bulked (well mixed) in October 2001. In the 2R hoop pine plantation, the soil was sampled from areas between the windrows of postharvest residues. Field-moist soil samples were sieved (<2 mm) and stored at 4°C (approximately 2 wk) until analysis of WSOC and its fulvic and humic acid C fractions, and chloroform-released C. A subsample of each soil was air-dried for chemical analysis and incubation.

Chemical Analysis of Soil Labile Carbon

Water-soluble organic C was extracted by shaking 50 g (oven-dried equivalent) of moist soil at a soil/water ratio of 1:3 on an end-to-end shaker at 4°C for 16 h. The mixture was then spun at 6500 × g for 1 h and filtered through a Whatman GF/F filter (combusted at 450°C, 4 h) (Boyer and Groffman, 1996). The C in the extracts was determined by a SHIMADZU TOC-VCPH analyzer (Shimadzu, Kyoto, Japan) using high temperature (680°C). To fractionate WSOC, 20 mL of each

extract was acidified to pH 2 with three drops of 10% HCl (v/v); the humic acid fraction (WSOC-HAC) was precipitated at 4°C overnight and centrifuged at 750 × g for 10 min. The supernatant (acid-soluble fraction) was removed for analysis of dissolved organic C (fulvic acid C, WSOC-FAC). This C fraction contains fulvic acid, some carbohydrates, and amino acids (Boyer and Groffman, 1996). The WSOC-HAC in the water extract was estimated by calculating the difference between WSOC and WSOC-FAC.

Hot water-extractable organic C was measured by the method described by Sparling et al. (1998). In brief, 4.0 g (oven-dry equivalent) of air-dried soil was incubated with 20 mL of water in a capped test-tube at 70°C for 18 h, and test-tubes were then shaken on an end-to-end shaker for 5 min, and filtered through a Whatman 42 paper (Whatman Ltd., Maidstone, UK), followed by a 0.45-μm filter membrane. The organic C concentration in the filtrate was determined using a SHIMADZU TOC-VCPH analyzer.

Calcium chloride extractable organic C was measured by extracting 10 g (oven-dried equivalent) air-dried soil with 25 mL of 10 mM CaCl$_2$ on an end-to-end shaker for 30 min and the organic C extracted was determined using a SHIMADZU TOC-VCPH analyzer.

Biologically Available Soil Carbon—Incubation Method

Biologically available soil organic C (bioavail-C) was determined using the incubation method as described by Chen et al. (2000). In brief, 15 g of air-dried soil was adjusted to 60% of the field capacity and incubated aerobically in a 1-L sealed glass jar at 22°C, and CO$_2$ evolved from soil was trapped in 0.1 M NaOH and measured by acid titration (0.1 M HCl) after 1, 3, 7, 14, 21, 28, and 35 d. The bioavail-C was estimated by calculating the cumulative production of CO$_2$ from soil during the 35-d incubation.

Chloroform-Released Carbon

Chloroform-released organic C (CHCl$_3$-released C) was measured by the fumigation-extraction method (Vance et al., 1987). Chloroform-released C was calculated as the difference in organic C between the fumigated and the unfumigated samples. Microbial biomass C was not calculated due to the uncertainty in the conversion factor, Ec (Ross and Sparling, 1993). Chloroform-released C fraction was used to represent the microbial component of soil organic C.

Hydrofluoric Acid Pretreatment of Soil Samples and Carbon-13 Solid State NMR Spectroscopy

Pretreatment of soil samples with HF before solid-state ^{13}C CPMAS NMR analysis removes a substantial amount of Fe^{3+} and Mn^{2+} in soil and concentrates the organic matter of a whole soil sample, improving the signal/noise ratio (Mathers et al., 2002; Schmidt et al., 1997; Skjemstad et al., 1994). Consequently, after HF pretreatment, fewer scans are required for better resolution of spectra and solid-state ^{13}C CPMAS NMR analysis times can be reduced without a reduction in spectral quality. In this study, all soil samples for NMR analysis were pretreated with 2% HF according to the method described by Skjemstad et al. (1994) and modified by Mathers et al. (2002).

Solid-state ^{13}C CPMAS NMR spectra of the HF-treated soils were obtained at a frequency of 100.6 MHz on a Varian Unity Inova400 spectrometer (Varian Inc., Palo Alto, CA). Samples were packed in a silicon nitride rotor (optical density = 7 mm) and spun at 5 kHz at the magic angle. Single contact times of 2 ms were applied, with an acquisition time of 14 ms, and a recycle delay of 1.5 s. Approximately 6000

Table 1. Basic chemical and physical properties in soils (0–10 cm) under adjacent natural forest (NF) and hoop pine plantations (first rotation, 1R, and second rotation, 2R).†

Vegetation type	pH	Total C	Total N	C/N ratio	Soil moisture	Bulk density	Sand	Silt	Clay
		g kg⁻¹			g kg⁻¹	Mg m⁻³		g kg⁻¹	
NF	4.7b	79.6a	6.70a	11.9b	250b	0.688a	327a	189c	484a
1R	6.0a	63.8b	4.86c	13.1a	262b	0.726a	334a	306a	360a
2R	5.6a	64.0b	5.36b	11.9b	361a	0.736a	280a	271b	449a

† Data in a column are means ($n = 5$). Means within a column followed by the same letter are not different at the 5% level of significance.

transients were collected for all samples and a Lorentzian line broadening function of 150 Hz was applied to all spectra. Chemical shift values were referenced externally to hexamethylbenzene at 132.1 ppm, which is equivalent to tetramethylsilane at 0 ppm.

The solid-state ¹³C CPMAS NMR spectra were divided into the four common chemical shift regions: alkyl C (0–50 ppm), O-alkyl C (50–110 ppm), aromatic and olefinic C (110–160 ppm) and carboxyl C (160–210 ppm), and the relative intensity for each region was determined by integration using the Varian NMR software package (Version 6.1c, Varian Inc., Palo Alto, CA). In some instances it was necessary to further divide some chemical shift regions, these were: O-alkyl C into methoxyl C (50–60 ppm), carbohydrate C (60–95 ppm), and di-O-alkyl C (95–110 ppm); aromatic C into aryl C (110–145 ppm) and phenolic C (145–160 ppm); and carboxyl C into carboxylic/amide/ester C (160–190 ppm) and ketone/aldehyde C (190–210 ppm). No attempt was made to remove spinning sidebands (SSB) during acquisition. However, the carboxyl and aromatic C spectral regions produce SSB, which appear at approximately 223 and 183 ppm, respectively. Because SSB of equal intensity are produced on either side of the originating center band, the visible carboxylic/amide/ester and ketone/aldehyde SSB in the carboxyl region were integrated, and the aromatic and carboxyl C spectral regions were corrected for the presence of these SSB. Spinning sidebands originating from the aryl signal at 133 ppm would appear at 183 and 83 ppm, but both are within other chemical shift regions, making it difficult to correct for these SSB. The aryl C region will also contain SSB originating from the carboxyl C peak (174 ppm) at 124 ppm that can be corrected for, but that would make the intensity of the aryl C peak at 133 ppm appear greater than it actually is. This would have implications for the SSB from the aryl peak (at 183 and 83 ppm) as they should not be larger in intensity than the centered band peak (133 ppm) itself.

The A/O-A ratio, the ratio of alkyl C region intensity (0–50 ppm) to O-alkyl C region intensity (50–110 ppm), which has been used as an index of the extent of decomposition (Baldock and Preston, 1995; Baldock et al., 1992) or of substrate quality for microbes (Webster et al., 2000), was also calculated in this study as an indicator of the quality of soil organic C.

Statistical Analysis

One-way ANOVA was carried out for all data on soil properties in Statistix for Window version 2.2 (Analytical Software, Tallahassee, FL). The normality of all data were checked and met before ANOVA, while we acknowledge that the limitation of this experimental study, as many other paired-site studies, was pseudo-replication. Least significant difference (LSD, $P < 0.05$) was used to separate the means when differences were significant. Pearson linear correlations between C pools were also conducted in Statistix for Windows version 2.2.

RESULTS

Table 1 shows some soil basic properties under the adjacent NF and 1R and 2R hoop pine plantations. Soil total C ranged from 72.3 to 82.9 g kg⁻¹ under NF, being significantly higher than under the 1R (56.4–67.0 g kg⁻¹) and the 2R (57.8–71.4 g kg⁻¹) plantations. Soil total N was also higher under NF compared with the 1R and 2R plantations, but soil pH was lower under NF than under 1R and 2R plantations. However, there were no significant differences in soil pH and total C between 1R and 2R plantations. Total N was significantly higher in soil under the 2R plantation than under the 1R plantation. Soil C/N ratio was lower under NF and the 2R plantation than under the 1R plantation (Table 1). Soil moisture content was significantly higher under the 2R plantation than under NF or the 1R plantation. There were no significant differences in bulk density, sand, or clay contents among three sites, but silt contents in soil under the 1R plantation were higher than under NF or the 2R plantation.

Chemical Extractable Soil Organic Carbon

Water-soluble organic C ranged from 24.1 to 53.7 mg kg⁻¹ among soils under NF and 1R and 2R plantations. Levels of WSOC under NF were highest among three sites and significantly higher in the soil under the 1R than the 2R plantation (Table 2). The WSOC only comprised 0.039 to 0.074% of total C among three sites while the ratios of WSOC/TC were greater under NF and 1R plantation than under the 2R plantation (Table 2). The WSOC-FAC in WSOC was dominant (47.2–84.6% of WSOC), compared with WSOC-HAC (15.4–52.8%) (Table 2). Levels of WSOC-FAC fractions were

Table 2. Water-soluble organic C (WSOC) and fulvic acid C (WSOC-FAC) and humic acid C factions (WSOC-HAC) in adjacent soils (0–10 cm) under natural forest (NF) and hoop pine plantations (first rotation, 1R, and second rotation, 2R).†

Vegetation type	WSOC	WSOC-FAC	WSOC-HAC	WSOC/TC‡
	mg kg⁻¹			%
NF	48.6 (5.6)a	37.7 (5.5)a	10.9 (3.1)a	0.061 (0.005)a
1R	40.0 (7.1)b	27.3 (2.3)b	12.6 (1.2)a	0.063 (0.009)a
2R	31.7 (4.9)c	20.5 (6.1)b	11.2 (2.0)a	0.050 (0.008)b

† Data in a column are means ($n = 5$); data in parentheses are standard errors of the means. Means within a column followed by the same letter are not different at the 5% level of significance.
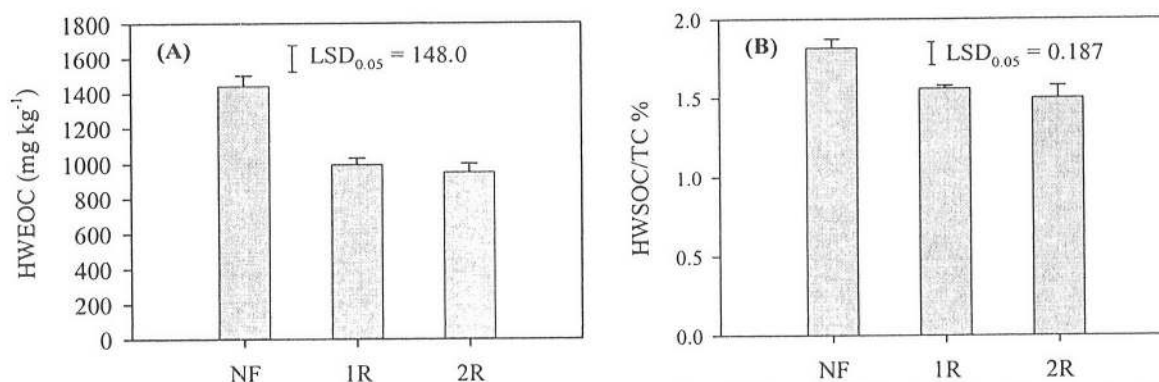‡ The ratio of WSOC to total C in soil.

Fig. 1. (A) Hot water-extractable organic C (HWEOC) and (B) as percentage of total C in soils (0–10 cm) under adjacent natural forest (NF) and first (1R) and second (2R) rotation hoop pine plantations at Yarraman State Forest, southeast Queensland.

significantly greater under NF than under either 1R or 2R plantations (Table 2), but there were no significant differences in soil WSOC-HAC fractions amongst the three sites.

Hot water-extractable organic C ranged from 1265 to 1600 mg kg^{-1} in soil under NF. This was significantly higher than under the 1R (871–1072 mg kg^{-1}) and the 2R (808–1113 mg kg^{-1}) plantations (Fig. 1). The HWEOC comprised 1.7 to 2.1% of total C in soil under NF, which was significantly greater than under the 1R (1.5 to 1.7%) and the 2R (1.3 to 1.7%) plantations (Fig. 1). There were no significant differences in soil HWEOC between the 1R and 2R plantations (Fig. 1). The $CaCl_2$ extractable organic C ranged from 174 to 218 mg kg^{-1} in soil under NF. This was significantly greater than under the 1R (69–163 mg kg^{-1}) and the 2R (72–182 mg kg^{-1}) plantations (Fig. 2). There were no significant differences in $CaCl_2$ extractable organic C between the 1R and 2R plantations.

Chloroform-released Carbon and Bioavailable Soil Organic Carbon

Chloroform-released C appears to be greater in soils under NF (247–458 mg kg^{-1}) and the 2R plantation (310–405 mg kg^{-1}) compared with the 1R plantation (152–412 mg kg^{-1}), although the differences among NF, 1R, and 2R hoop pine plantations were not statistically

significant (Fig. 3). The bioavail-C was significantly and consistently greater in soil under NF (1149–1362 mg kg^{-1}) than under the 1R (718–829 mg kg^{-1}) and 2R (613–746 mg kg^{-1}) plantations (Fig. 4). However, there were no significant differences in bioavail-C between soils under the 1R and 2R plantations (Fig. 4).

Carbon-13 CPMAS NMR Spectra

It has been suggested that the information obtained from ^{13}C CPMAS NMR spectroscopy is semi-quantitative due to some technical reasons (e.g., different efficiency of the cross-polarization for different C forms, SSB and so on) (Preston, 1996, 2001; Mathers et al., 2000). However, ^{13}C CPMAS NMR spectra can be compared for soil samples of similar origin run under identical conditions (Preston, 1996; Quideau et al., 2001). More recently, Conte et al. (2002) revealed that C measured by ^{13}C CPMAS NMR spectroscopy provided a quantitative representation of the whole C content in humic substance. The relative intensities of C functional groups in the HF-treated soils under adjacent NF and 1R and 2R hoop pine plantations are shown in Table 3. Representative ^{13}C NMR spectra are shown in Fig. 5. Across all soil samples among three sites, the intensity in the alkyl C spectral region was highest (32.3–42.9% of total intensity), followed by O-alkyl C (24.0–31.0%) and carboxyl C (the sum of carboxylic/amide/ester C
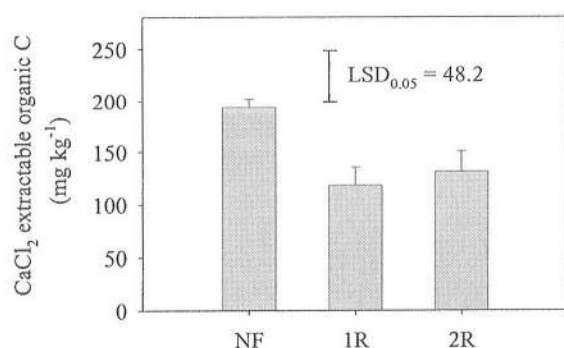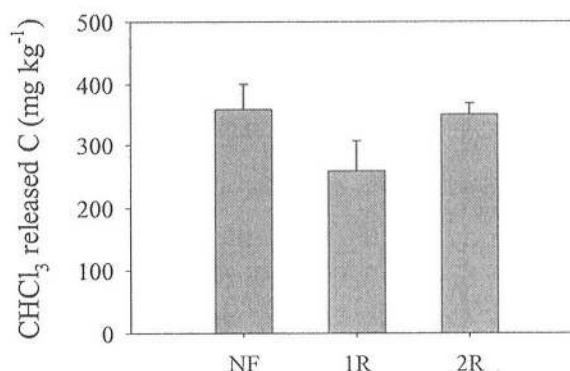

Fig. 2. The $CaCl_2$-extractable organic C in soils (0–10 cm) under adjacent natural forest (NF) and first (1R) and second (2R) rotation hoop pine plantations at Yarraman State Forest, southeast Queensland.

Fig. 3. The $CHCl_3$-released organic C in soils (0–10 cm) under adjacent natural forest (NF) and first (1R) and second (2R) rotation hoop pine plantations at Yarraman State Forest, southeast Queensland (spinning side band, ssb).
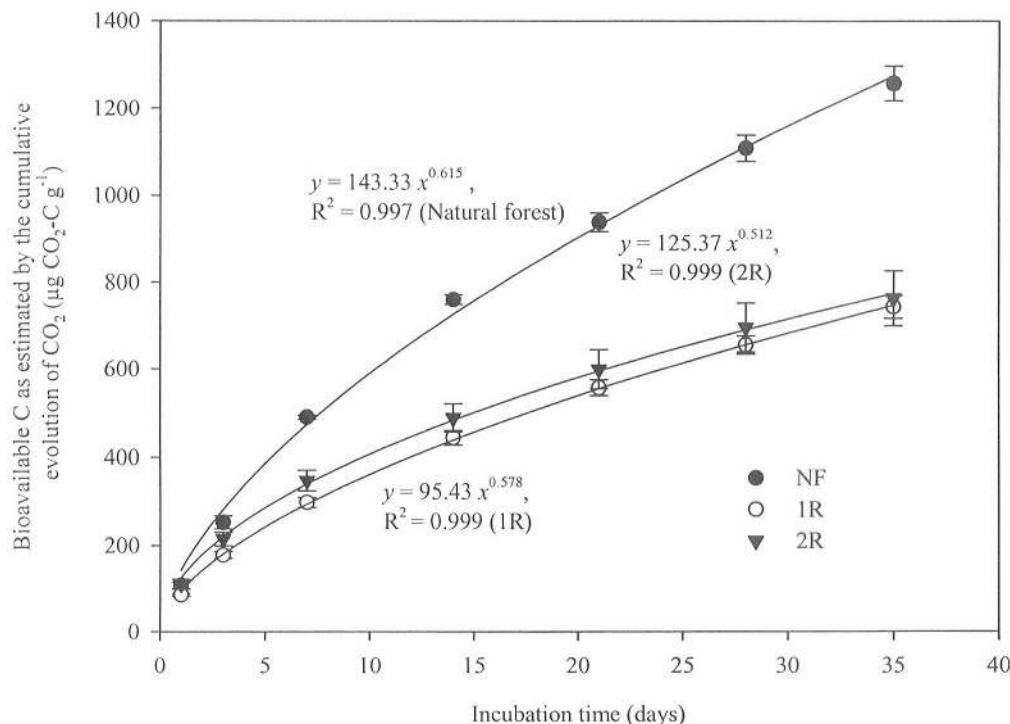
Fig. 4. Bioavailable organic C in soils (0–10 cm) under adjacent natural forest (NF) and first (1R) and second (2R) rotation hoop pine plantations at Yarraman State Forest, southeast Queensland.

and ketone/aldehyde C, 25.5–36.6%), and the lowest intensity was found in the aromatic region (the sum of aryl C and phenolic C, 3.2–7.6%). The signal intensity in the alkyl C spectral region (0–50 ppm) was significantly higher in soil under the 1R hoop pine plantation than under NF or the 2R plantation, while there were no significant differences observed in this spectral region between the NF and the 2R plantation (Table 3 and Fig. 5). There was a significantly higher intensity in the O-alkyl C spectral region (50–110 ppm) in soil under the NF than under the 1R plantation; there was no significant difference in the intensity of O-alkyl C spectral region between NF and the 2R plantation nor between the 1R and 2R plantations. When the O-alkyl C region was divided into methoxyl (50–60 ppm), carbohydrate (60–95 ppm) and di-O-alkyl C (90–110 ppm), the trend in intensity of the carbohydrate C region was the same as that of O-alkyl C region. There were no significant differences in the methoxyl and di-O-alkyl C spectral regions also among three sites. There was no significant difference in the aromatic C region (including both aryl C and phenolic C) among the soils under the NF and 1R and 2R hoop pine plantations. The intensity

of the carboxyl C region was greater in soil under the 2R plantation than under NF or the 1R plantation. There were no significant differences in ketone/aldehyde C region among three sites. However, the A/O-A ratio was higher in soil under the 1R plantation compared with NF and the 2R plantation.

Relationships between the Soil Carbon Pools

Pearson correlation analysis showed that O-alkyl C was significantly correlated with $CaCl_2$ organic-extractable C ($r = 0.681$, $P < 0.01$). The $CHCl_3$–released C was positively correlated with $CaCl_2$ extractable organic C ($r = 0.672$, $P < 0.01$) and with O-alkyl C ($r = 0.626$, $P < 0.05$) but negatively correlated with alkyl C ($r = -0.634$, $P < 0.05$) (Fig. 6A). As expected, the $CHCl_3$–released C was negatively correlated with the A/O-A ratio (Fig. 6B). Bioavailable soil organic C was positively correlated with total C ($r = 0.830$, $P < 0.01$), $CaCl_2$–extractable organic C ($r = 0.631$, $P < 0.05$), WSOC ($r = 0.730$, $P < 0.01$), and WSOC-FAC ($r = 0.810$, $P < 0.01$). Bioavailable soil organic C was also highly correlated with HWEOC ($r = 0.974$, $P < 0.01$) (Fig. 7A). In addi-

Table 3. Composition of C functional groups (%) in HF-treated soils (0–10 cm) under adjacent natural forest (NF) and hoop pine plantations (first rotation, 1R, and second rotation, 2R) as characterized by ^{13}C cross-polarization magic-angle-spinning nuclear magnetic resonance (CP MAS NMR) spectroscopy.†

Soils	Alkyl C	Methoxyl C	Carbohydrate C	Di-O-alkyl C	O-Alkyl C	Aryl C	Phenolic C	Carboxyl C	Ketone/ aldehyde C	Alkyl C/O-alkyl C ratio
NF	36.6 (1.1)b	6.0 (0.4)a	21.1 (0.2)a	2.3 (0.4)a	29.4 (0.5)a	5.4 (0.6)a	0.6 (0.3)a	22.7 (0.5)b	5.3 (0.6)a	1.3 (0.1)b
1R	41.1 (1.1)a	6.7 (1.3)a	17.3 (1.9)b	2.0 (0.4)a	26.1 (1.0)b	4.5 (0.9)a	1.0 (0.8)a	22.2 (0.6)b	5.1 (0.7)a	1.6 (0.1)a
2R	36.0 (0.8)b	5.8 (0.4)a	20.1 (0.6)ab	1.6 (0.4)a	27.5 (0.9)ab	3.8 (0.7)a	0.3 (0.5)a	26.0 (1.6)a	6.4 (0.8)a	1.3 (0.1)b

† Data in a column are means ($n = 5$); data in parentheses are standard errors of the means. Means within a column followed by the same letter are not different at the 5% level of significance.
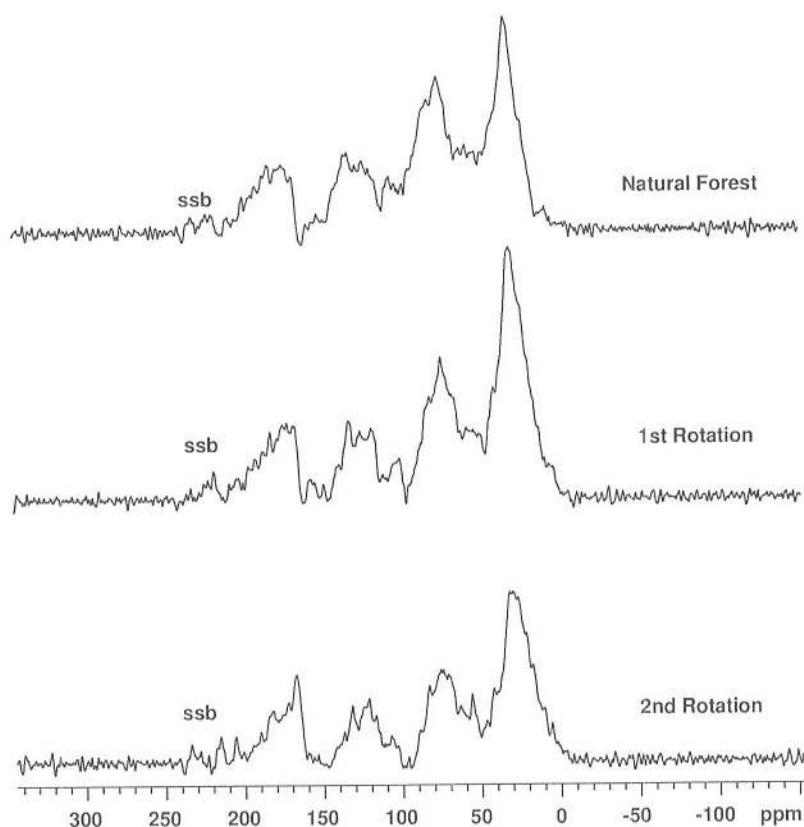
Fig. 5. Carbon-13 CPMAS NMR spectra of HF-treated soils (0–10 cm) under adjacent natural forest (NF) and first (1R) and second (2R) rotation hoop pine plantations at Yarraman State Forest, southeast Queensland.

tion, bioavail-C was correlated with O-alkyl C (r = 0.533, $P < 0.05$) (Fig. 7B).

DISCUSSION

The assumption that adjacent soils under different vegetation types were originally similar has been the basis for many paired-site studies (Chen et al., 2000, 2001; Beets et al., 2002; Priha and Smolander, 1999; Smith et al., 2002; Smolander et al., 2001). In the present study, three sites were on the same position of the slope and adjacent to each other and had similar vegetative cover (i.e., NF) prior to the establishment of the 1R

hoop pine plantation. Moreover, the underlying soils were developed from the same basaltic parent material. Thus we assume that differences in the quantity and quality of soil C among three sites were mainly due to the conversion from NF to hoop pine plantations and the impacts of forest management practices (i.e., harvesting and site preparation). The differences in soil C between NF and the 1R plantation may reflect the effects of land-use change, including different tree species and disturbance during NF logging and site preparation and following forest management (e.g., thinning), while the difference between the 1R and 2R hoop pine plantations may reflect the effects of harvesting and site prepara-
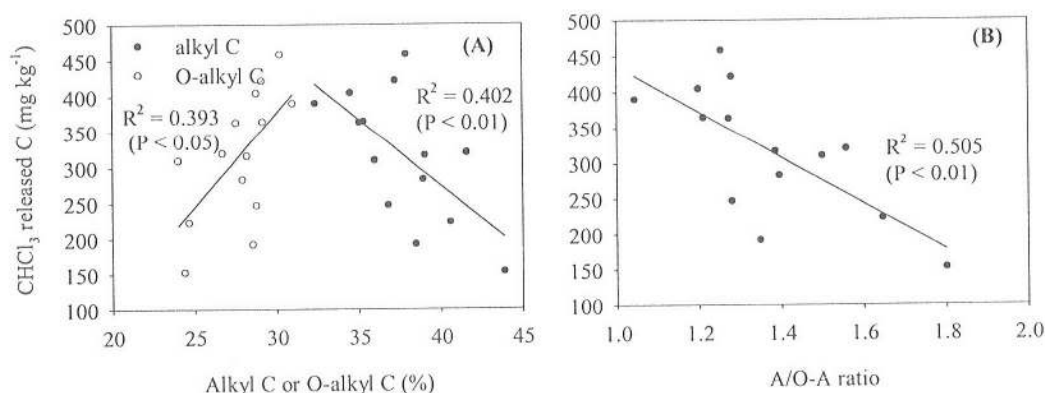

Fig. 6. Relationships between CHCl₃-released organic C and (A) alkyl C or O-alkyl C and (B) A/O-A ratio in soils (0–10 cm) under adjacent natural forest (NF) and first (1R) and second (2R) rotation hoop pine plantations at Yarraman State Forest, southeast Queensland.
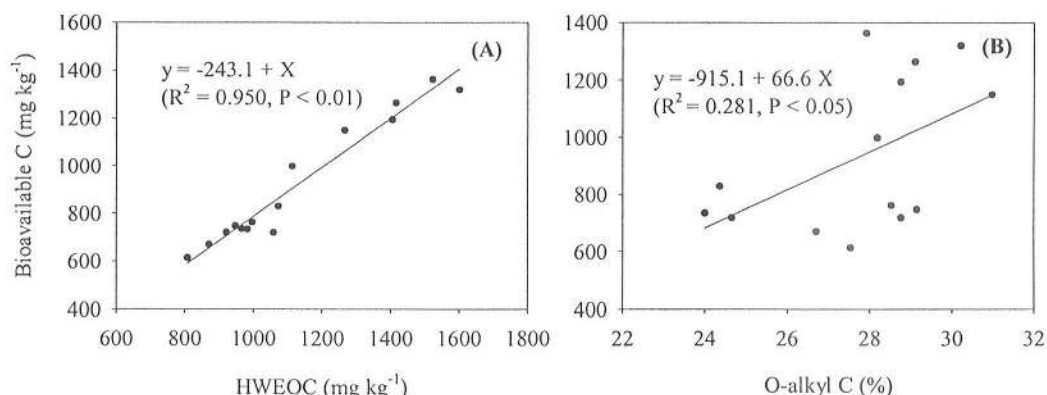
Fig. 7. Relationships between bioavailable organic C and (A) hot water-soluble organic C (HWSOC) and (B) O-alkyl C in soils (0–10 cm) under adjacent natural forest (NF) and first (1R) and second (2R) hoop pine plantations at Yarraman State Forest, southeast Queensland.

tion. It is acknowledged that limitation of pseudo-replication in this study and thus the results from this study may represent a case study.

Effects of Conversion of Natural Forest to Hoop Pine Plantation on Soil Organic Carbon

Trees can alter soil properties through root-microbe interaction, root exudation, root turnover, and aboveground organic inputs. Smith et al. (2002) found that the effects of land-use change from native Amazonian forest to plantation forests in Brazil on soil C content were tree species-dependent. A number of studies have also indicated that tree species can have different impacts on soil C content (Howard et al., 1998; Paul et al., 2002; Pinzari et al., 1999). However, Shiels et al. (2001) found that there was no significant difference in soil C under adjacent krummholz tree species (*Picea engelmannii* krummholz and *Pinus aristata* krummholz Engelm.). In the present study, soil C content under the NF was significantly higher than under the 1R and 2R plantations (Table 1). This may be partly attributed to differences in the amount, chemical composition, and transformation rate of organic materials derived from leaf and root litter between the two forest types. Tree species have been shown to be different in the quantity and quality of litterfall and root inputs in various studies (Vogt et al., 1991; Attiwill and Adams, 1993; Vesterdal et al., 2002). Leaf litterfall and root inputs were not measured in this study, but it was found that the C/N ratios for leaf litter materials under NF were lower (23.5) than those under the 1R hoop pine plantation (42.5) (S. Ward, personal communication, 2003), which indicated better quality of leaf litter materials under NF. Lower soil pH under NF than under the 1R and 2R plantations may also contribute to the higher content of soil C observed under the NF. Beets et al. (2002) reported significant negative relationships between soil C and soil pH, indicating that lower soil pH lead to the increased formation of Al/humic acid complexes and, thus, enhanced the accumulation of soil C. It has been suggested that low soil pH can decrease microbial biomass and activity (Blagodatskaya and Anderson, 1998) and might also lead to the accumulation of soil C (Beets et al., 2002). However, in this study, the soil under NF

had the lowest pH, but the highest microbial biomass C (Fig. 3) and microbial activity as measured by CO_2 respiration (data not shown). Also, using DNA techniques, it has been found that soil under NF has a higher microbial diversity than those under the plantations (J. He, personal communication, 2003). This indicates that there may be more diverse microbial communities and/ or specific microbial functional groups in soil under NF and their activities may contribute to the greater accumulation of soil C. In addition, the disturbance during harvesting and site preparation might also decrease physical protection of soil organic matter for microbial attack (Lessa et al., 1996) and led to the lower levels of soil C under 1R and 2R hoop pine plantation compared with those under NF. But the nature and detail of such disturbance occurring approximately 50 yr ago are not available for appropriate comparisons.

The size and dynamics of soil labile C can vary with tree species (Hu et al., 1997; Menyailo et al., 2002) and land-use type (Boyer and Groffman, 1996). Smolander and Kitunen (2002) compared adjacent soils under silver birch (*Betula pendula* Roth), Norway spruce (*Picea abies* (L.) Karst), and Scots pine (*Pinus sylvestris* L.) and found that concentrations of water dissolved organic C were higher in the birch and spruce soils than in the pine soil. Results from the present study showed that conversion from NF to hoop pine plantations led to decreased labile C pools extracted using cold water, $CaCl_2$, or hot water (Table 2; Fig. 1 and 2), and bioavail-C (Fig. 4). These labile C pools were generally correlated with soil total C ($r = 0.656$–0.879, $P < 0.05$). It has been suggested that labile C (e.g., WSOC) may be mainly of microbial origin and could be derived from the leaching of forest floor materials (Gregorich et al., 2000; McGill et al., 1986; Qualls and Haines, 1991). The higher labile C pools in soil under the NF compared with the 1R plantation may be associated with the greater content of soil C and higher microbial activity under NF.

Significant correlations ($r = 0.605$–0.786, $P < 0.05$) determined between the labile C pools extracted with various solutions of different chemical and physical strengths (cold water, $CaCl_2$ and hot water) indicated that they partly represented similar C pools in soil. However, the magnitude was very different among these

pools. For example, the concentration of HWEOC was 20 to 30 times greater than that of WSOC (Table 2, Fig. 1). Hot water may not only extract soluble organic C in soil, but also part of the soil microbial components (Sparling et al., 1998). The highly significant linear relationship determined between HWEOC and bioavail-C in this study showed that HWEOC could be a good indicator of biologically labile organic C in soil (Fig. 7A), while the size of bioavail-C was smaller than that of HWEOC by 243 mg kg^{-1} and approximately 9.2 to 32.1% of HWEOC was not biologically available. Some other researchers found a strong correlation between organic C extracted by hot water and mineralizable C and but also suggested some parts of soluble organic C were slowly decomposable (Davidson et al., 1987; Gregorich et al., 2003). In addition, it should be noted that the fulvic acid fraction of water-soluble organic C (WSOC-FA) was more sensitive to forest conversion compared with the humic acid fraction (WSOC-HA) (Table 2). However, the biological implication of this finding is not well understood.

Results from the ^{13}C CPMAS NMR spectroscopy showed that the relative intensities of different C functional groups in soils under different vegetation types were within the normal ranges reported (Mahieu et al., 1999), with the intensity of the alkyl C spectral region in soils at all three sites being the highest (Table 3, Fig. 5). This was consistent with the findings of Oades et al. (1988), in which the alkyl C region was predominant in three Australian soils studied. The significant relationship found between the O-alkyl C region and the bioavail-C (Fig. 7B) showed that at least part of the O-alkyl C was biologically available, which was consistent with other studies (Novak et al., 1992; Guinto et al., 1999; Webster et al., 2000).

The conversion from NF to hoop pine plantations led to a change in the chemical composition of soil C with a higher intensity in the O-alkyl C spectral region and lower intensity in the alkyl C spectral region in soil under NF than under the 1R plantation (Table 3, Fig. 5). Among the chemical components of the O-alkyl C region, the higher intensity observed in carbohydrate C spectral region in soil under NF compared with the 1R plantation indicated that carbohydrate C was sensitive to the land-use change from natural forest to hoop pine plantation (Table 3, Fig. 5). The A/O-A ratio has been used to indicate the extent of decomposition of organic matter (Baldock and Preston, 1995). The lower A/O-A ratio in soil under NF than under the 1R plantation indicated that less accumulation of relative recalcitrant C components had occurred in the soil and the quality of soil organic C was better under NF. This result may also show that litter materials from the hoop pine plantations may contain more recalcitrant components than those from NF. A number of studies have suggested that the nature of soil C is closely associated with vegetation type (Baldock and Preston, 1995; Condron and Newman, 1998; Golchin et al., 1997; Quideau et al., 2001). For example, Quideau et al. (2001) found that soil carbonyl C was dominant under oak, soil O-alkyl C under, and soil alkyl C under conifers. These effects

have been attributed to different chemical composition of litter materials, soil environmental factors, soil organic C-mineral interactions, and the composition of microbial community and associated decomposition and humification processes under different vegetation types (Baldock et al., 1992; Beyer, 1995; Oades et al., 1988; Quideau et al., 2001; Schmidt et al., 2000; Trofymow et al., 1995; Webster et al., 2000).

There were significant negative relationships between CHCl$_3$-released C and alkyl C (Fig. 6A) and between CHCl$_3$-released C and the A/O-A ratio (Fig. 6B), which were consistent with other studies (Beyer, 1995; Webster et al., 2000). These results also showed that microbial degradation of alkyl C might be retarded in soil under the 1R plantation. Quideau et al. (2001) found that the prevalence of alkyl C in the fine silt fractions under coniferous species might be associated with low microbial activity and arise from the selective preservation of recalcitrant litter moieties (e.g., cutin, waxes etc.). The positive relationship determined between CHCl$_3$-released C and O-alkyl C (Fig. 6A) showed that higher microbial biomass (and activity) in soil under NF favored the production and/or accumulation of O-alkyl C. It was believed that in this study more diverse microbial communities and wider associated synthetic pathways under NF played a key role in the differences observed in the chemical structure of soil C between NF and the 1R plantation. Yanagi et al. (2002) also revealed that the resistance of soil humic acids to microbial degradation was related to differences in their chemical structure and was also microbial species dependent. The NF in this study was a mixture of different tree and shrub species with broad leaves and needles, and the quality of associated leaf litters (C/N ratio, see above) was assumed to be better compared with the hoop pine plantations. Therefore, differences in chemical composition of soil C observed between NF and the 1R plantation may be accounted for by a combination of factors including chemical composition of litter materials, microbial community structure, and organomineral interaction.

Effects of Plantation Harvesting and Site Preparation on Soil Organic Carbon

No significant differences in soil total C were observed between the 1R and 2R plantations, indicating that harvesting and site preparation of the hoop pine stands did not have significant impacts on soil total C, at least in the short term (2 yr after harvesting). Johnson and Curtis (2001) also found that tree harvesting had little or no effects on soil total C content 15 yr after harvesting. In addition, there were no significant differences in labile soil organic C pools, except in WSOC between the 1R and 2R plantations (Table 2, Fig. 1, 2, and 4). The WSOC was the most labile C pool but least in magnitude compared with CaCl$_2$ and HWEOC (Table 2, Fig. 1 and 2). The increased aggregate disruption and decreased physical protection of soil C by disturbance caused by harvesting and site preparation in soil under the 2R plantation may account for the lower

WSOC compared with the 1R hoop pine plantation (Dai et al., 2001; Zinn et al., 2002). Results from the solid-state ^{13}C CPMAS NMR analysis showed that harvesting and site preparation significantly reduced signal intensity in the alkyl C spectral region (Table 3), leading to a decreased A/O-A ratio (Table 3, Fig. 5). This is presumed to be due to less physical protection of soil organic C under the 2R plantation because of the disturbance and the higher soil microbial biomass and activity under the 2R than the 1R plantation (Fig. 3), which favored the degradation of soil alkyl C under 2R plantation. In addition, the signal intensity in the carboxyl C spectral region was higher in soil under the 2R plantation compared with the 1R plantation and NF (Table 3). This indicated that carboxyl C was sensitive to the disturbance caused by harvesting and site preparation (Lessa et al., 1996).

CONCLUSIONS

The conversion from NF to hoop pine plantations led to a reduction in soil total C, labile C pools and the bioavailability of soil C, and to the change in chemical composition of soil C with higher O-alkyl C and lower alkyl C under NF compared with the 1R plantation. These differences in the quantity and quality of soil C between the NF and the 1R plantation may be attributed to a combination of factors including more diverse microbial communities, higher microbial activity and better quality of litter materials under the NF than the 1R plantation and site disturbance during the establishment of 1R plantation. Tree harvesting and site preparation in the 2R hoop pine plantation did not significantly affect soil total C and labile C pools (except the decrease in WSOC), but led to lower signal intensity in the alkyl C spectral region, which decreased the A/O-A ratio in soil under the 2R plantation than under the 1R plantation. The decrease in WSOC and the increase in signal intensity of the alkyl C spectral region in soil under the 2R plantation than the 1R plantation may be partly attributed to the decreased physical protection of soil C caused by harvesting and site preparation and higher microbial biomass and activity under the 2R plantation. It is worthwhile to note that this is a case study and future studies are needed to further support these findings.

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