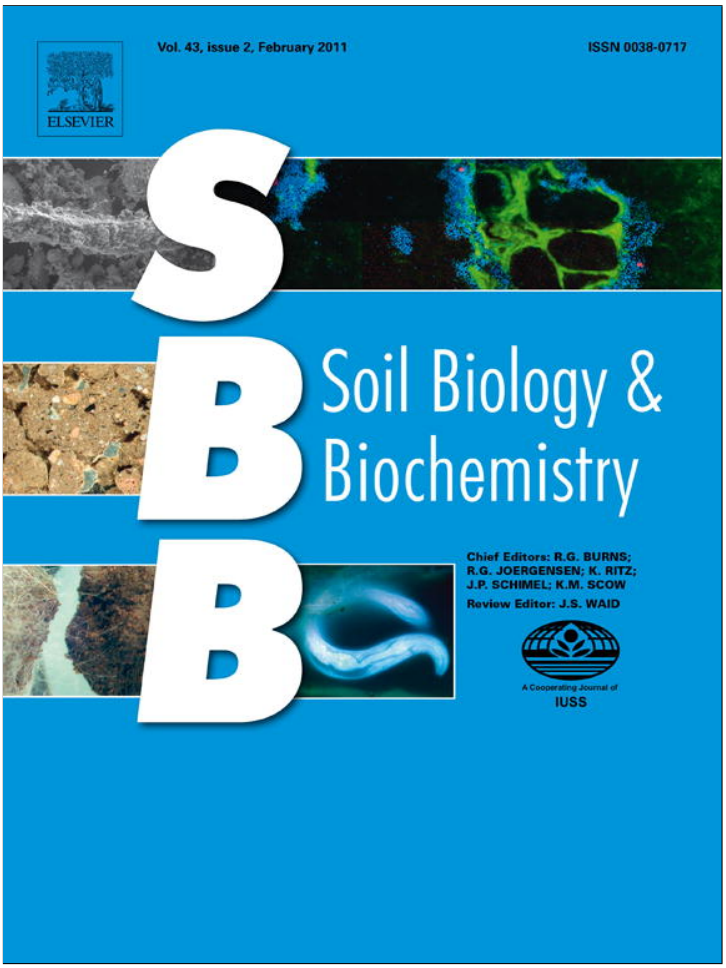

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# Post-harvest residue management effects on recalcitrant carbon pools and plant biomarkers within the soil heavy fraction in *Pinus radiata* plantations

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ABSTRACT

Forest soils contain about 30% of terrestrial carbon (C) and so knowledge of the influence of forest management on stability of soil C pools is important for understanding the global C cycle. Here we present the changes of soil C pools in the 0–5 cm layer in two second-rotation *Pinus radiata* (D.Don) plantations which were subjected to three contrasting harvest residue management treatments in New Zealand. These treatments included whole-tree harvest plus forest floor removal (defined as forest floor removal hereafter), whole-tree, and stem-only harvest. Soil samples were collected 5, 10 and 15 years after tree planting at Kinleith Forest (on sandy loam soils) and 4, 12 and 20 years after tree planting at Woodhill Forest (on sandy soils). These soils were then physically divided into light (labile) and heavy (stable) pools based on density fractionation (1.70 g $cm^{-3}$). At Woodhill, soil C mass in the heavy fraction was significantly greater in the whole-tree and stem-only harvest plots than the forest floor removal plots in all sampling years. At Kinleith, the soil C mass in the heavy fraction was also greater in the stem-only harvest plots than the forest floor removal plots at year 15. The larger stable soil C pools with increased residue return was supported by analyses of the chemical composition and plant biomarkers in the soil organic matter (SOM) heavy fractions using NMR and GC/MS. At Woodhill, alkyl C, cutin-, suberin- and lignin-derived C contents in the SOM heavy fraction were significantly greater in the whole-tree and stem-only harvest plots than in the forest floor removal plots in all sampling years. At Kinleith, alkyl C (year 15), cutin-derived C (year 5 and 15) and lignin-derived C (Year 5 and 10) contents in the SOM heavy fraction were significantly greater in stem-only harvest plots than in plots where the forest floor was removed. The analyses of plant C biomarkers and soil $\delta^{13}C$ in the light and heavy fractions of SOM indicate that the increased stable soil C in the heavy fraction with increased residue return might be derived from a greater input of recalcitrant C in the residue substrate.



## 1. Introduction

Forest soils are globally important for storage of carbon (C) (about 30% terrestrial C) that, if managed properly, can be sinks of atmospheric carbon dioxide ($CO_2$) (Lal, 2005). The C stocks and rates of $CO_2$ sequestration in managed forest soils depend on soil properties, tree species, and management (Lorenz et al., 2007). In second-rotation forest plantations, residues from tree harvest are important components of litter which is the primary source of soil organic matter (SOM). A small relative alteration in the quality and quantity of litter inputs in forest plantation systems may change the net accumulation or loss of soil C (Crow et al., 2009). The impacts of harvest residue management in forest plantations on the storage of soil C continue to receive attention (Chen and Xu, 2005; Huang et al., 2008; Huntington and Ryan, 1990), but reports on changes in the storage of soil C due to various residue management treatments often lead to divergent conclusions. For instance, Johnson and Curtis (2001) found that stem-only harvest caused increases in the C stock of surface soil, compared to whole-tree harvest and residue removal. However, Mendham et al. (2003) examined the dynamics of soil C annually for 7 years under contrasting harvest residue management in south-western Australia and noted that organic C was not significantly affected by residue management. In part, these varied results may occur because soils are highly complex media with varying soil texture (especially clay content), which is a key factor that controls soil C retention (Davidson, 1995; Meersmans et al., 2009). In addition, most studies of soil C change after contrasting residue management have involved comparison of single point in time sampling and the long-term pattern of change in soil C over time is still poorly understood (Jones et al., 2008; Olsson et al., 1996).

In a review of the effect of forest management on soil C, Jandl et al. (2007) emphasized the necessity of distinguishing between

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labile and stable pools of soil C in regard to the effects of residue management. Indeed, micro-organisms involved in decomposition of organic material in soil favor fresh, easily decomposable C compounds (Karhu et al., 2010). Long-term C sequestration is critically dependent on the quantity of stable SOM fraction (Lorenz et al., 2007; Neff et al., 2002). Density fractionation is a laboratory procedure that physically fractionates soil into light and heavy fractions. The light fraction mainly consists of plant-like and labile SOM and is reported to be sensitive to changes in forest management, including contrasting residue management (Bremer et al., 1994; McFarlane et al., 2010). The heavy fraction is more stable and consists of recalcitrant C associated with soil minerals, with turnover times of several decades to centuries (McLauchlana and Hobbie, 2004). The responses of heavy fraction of SOM and soil recalcitrant alkyl C components to contrasting harvest residue management practices in forest plantations are less clear than light fraction SOM and labile soil C components. It is also important to know if increased harvest residue return will lead to elevated recalcitrant plant components in the heavy fraction of SOM. Among these recalcitrant compounds, the variation in the amount of alkyl plant biomarkers (e.g. lignin, wax, cutin and suberin) in soil is thought to be able to reflect the input from plant litter (Crow et al., 2009; Simpson et al., 2008).

Here, we describe the impact of harvest residue management on mineral soil C at 0–5 cm depth in the 20 years following planting second rotations *Pinus radiata* in New Zealand. The objectives of this study were to: (1) determine the changes in stocks of C in the whole soil and its light and heavy fractions subject to different harvest residue management in two soil types; (2) examine the chemical composition in the heavy fractions of SOM and the changes in plant biomarkers; and (3) assess the reasons for the changes of stable C pools in the heavy fraction of SOM.

## 2. Materials and methods

### 2.1. Study sites and experimental designs

The study sites are part of the Long-term Site Productivity Trials Series I located within Kinleith and Woodhill Forest, in second-rotation *P. radiata* (D.Don) plantations in the North Island of New Zealand. The long-term trials were fully described by Smith et al. (2000). Briefly, the Kinleith trial (38°14′S, 175°58′E) was established in 1992 on an Immature Orthic Pumice sandy loam soil derived from pumiceous tephra. The Woodhill trial (36°43′S, 174°24′E) was installed in 1986 on a Typic Sandy Recent Soil, derived from coastal sand dunes along the Tasman Sea. The soil properties in the 0–10 cm layer several months before the planting of second plantations are listed in Table 1.

First rotation plantations were clearfell harvested at Kinleith and Woodhill in 1991 and 1986 respectively using chainsaws. Three common harvest residue management practices, including whole-tree harvest plus forest floor carefully removed (defined as forest floor removal hereafter), whole-tree, and stem-only harvest, were established after the clearfell harvest (Smith et al., 2000). A split-plot randomized block design was used at both sites. At Kinleith, the three residue management treatments were replicated four times and applied to twelve 80 m × 40 m plots. Each plot was split and either fertilized or not fertilized. At Woodhill, there were three replicates for each residue management treatment and each plot was 60 m × 30 m in size. Again, half of each plot was fertilized and the other half left unfertilized. A 5-m buffer was used within the fertilized sub-plots at both sites.

**Table 1**
Soil properties (0–10 cm layer) before the planting of second-rotation plantations at Kinleith and Woodhill.

| | pH | TC (%) | TN (%) | Clay (%) | Sand (%) | Silt (%) | CEC (cmol $kg^{-1}$) |
|---|---|---|---|---|---|---|---|
| Kinleith | 4.9 | 13.9 | 0.32 | 13 | 49 | 38 | 21.2 |
| Woodhill | 5.6 | 1.3 | 0.03 | 7 | 90 | 3 | 3.0 |

### 2.2. Soil sampling

Within each unfertilized sub-plot, a total of 20 hoffer cores were randomly collected from 0 to 5 cm soil depth at 4, 12 and 20 years after tree planting at Woodhill to give one bulked sample per sub-plot. Forest floor materials (needle litter and fermented materials) were carefully removed before the soil cores were collected. The same sampling method was applied at 5, 10 and 15 years after tree planting at Kinleith. Bulk density was determined several months before tree planting and we assumed that there was no change in bulk density over the sampling period. Soils were air-dried and sieved through a 2 mm mesh to remove roots, fragments of wood and bark. A subsample of the mineral soil from each sub-plot was archived.

### 2.3. Density fractionation

Soil was physically divided into two pools based on density fractionation. The soil light fraction was collected by a modified method of Carter and Gregorich (2008). Briefly, 10 g air-dried soil were placed in a centrifuge tube with 50 mL NaI (Fisher Chemical, UK) with a density of 1.70 g $cm^{-3}$. The tubes were shaken by hand for 3 min, then centrifuged at 1000 rpm for 15 min. The floating material was aspirated from the surface of tubes (about the top 20 mL) and then placed into a filter unit (in a funnel containing Whatman GF A/E filter paper). The shaking–centrifugation–aspiration process was repeated at least four times, until no floating material remained. The samples on the filter paper were rinsed thoroughly with deionised water, collected and designated as light fraction. The material (heavy fraction) remaining at the bottom of the centrifuge tube was quantitatively washed onto a separate funnel and then rinsed repeatedly with deionised water (about 300 mL). Both the light and heavy fractions were dried at 60 °C for 48 h and then ground in a mortar and pestle for analysis.

### 2.4. Total C and $\delta^{13}C$

Total C in the whole soil was determined on finely ground (<0.20 mm) bulked soil samples using a LECO EPS-2000 CNS thermal combustion furnace (LECO Corp., St Jose, MI). The $\delta^{13}C$ of SOM in the light and heavy fractions as well as the C contents in the light fraction samples were measured using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Isotope results are reported in the conventional δ notation as per mil deviation relative to the $\delta^{13}C$ of the PDB standard. Soil C mass in the whole soil and light fraction were calculated conventionally as the product of concentration, bulk density and soil thickness (Davis et al., 2007). The C mass in the heavy fraction was the difference between the C mass in the whole soil and light fraction.

### 2.5. Solid-state CPMAS $^{13}C$ NMR analysis of heavy fraction materials

Soil sub-samples of the replicates in the heavy fractions from the same harvest residue management treatment, sampling year and site were bulked for solid-state $^{13}C$ CPMAS NMR analyses. The composite samples were pre-treated with 10% hydrofluoric acid using the modified method of Skjemstad et al. (1994). The pre-

treatment can remove a large amount of $Fe^{3+}$ and $Mn^{2+}$ in soil, concentrate the SOM of samples and improve the signal/noise ratio. After pre-treatment, times for NMR analysis can be decreased without a reduction in spectral quality (Mathers et al., 2002).

The NMR spectra were obtained at a frequency of 100.59 MHz on a Varian Unity Inova400 spectrometer (Varian Inc., Palo Alto, CA), as described by Huang et al. (2008), and divided into seven regions representing different chemical environments of a $^{13}C$ nucleus. These regions were alkyl C (0–45 ppm), N-alkyl C (45–60 ppm), O-alkyl C (60–90 ppm), acetal C (90–110 ppm), aromatic and C (110–145 ppm), phenolic C (145–165 ppm) and carboxyl C (165–210 ppm). The relative intensity of each functional group was measured by integration using the Varian NMR software package.

The NMR spectra can be considered to be reasonably representative of the soil C groups in the heavy fraction because of C-to-Fe ratios $\gg 1$ (Arshad et al., 1988). The proportions of spectral areas allocated to different functional classes were converted to mass by multiplication with soil C mass in the heavy fraction as suggested by Sjögersten et al. (2003).

### 2.6. Quantification of plant biomarkers in the heavy fraction of SOM

Owing to the labor-intensive nature of these analyses, single measurements of composite samples from four or three treatment replicates were conducted for soil C biomarker analyses. Air-dried heavy fraction samples (1.0 g for sandy loam soil at Kinleith and 5.0 g for sandy soil at Woodhill) were subjected to sequential chemical extractions (Solvent extraction, base hydrolysis and alkaline CuO oxidation) to isolate cutin- and suberin-derived compounds and lignin-derived phenols (Bull et al., 2000; Naafs and van Bergen, 2002; Otto et al., 2005). The heavy fraction of soils were extracted with organic solvents as follows: samples were sonicated for 15 min with 30 mL methanol, then dichloromethane:methanol (1:1; v/v), followed by dichloromethane. The combined solvent extracts were filtered through glass fiber filters (Whatman GF/F), concentrated by rotary evaporation, and then dried under $N_2$ in 2 mL glass vials. The residue from solvent extraction was air-dried, weighed and then refluxed for 3 h with 50 mL of 1 N methanolic KOH. Perdeuterated tetracosane ($C_{24}D_{50}$) was added as an internal standard after cooling. The suspension was centrifuged for 30 min at 2500 rpm with the supernatant kept in the refrigerator. The extracts were acidified to pH 1 with addition of 6 M HCl. Hydrolysable lipids were recovered by liquid–liquid extraction in a separation funnel with diethyl ether, concentrated by rotary evaporation and dried under $N_2$ in 2 mL glass vials. The base hydrolysis residues were air-dried and weighed for alkaline CuO oxidation to isolate lignin-derived phenols. The residues were extracted with 1 g CuO (pre-extracted with dichloromethane), 100 mg ammonium iron (II) sulfate hexahydrate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$] and 10 mL of 2 M NaOH in 15 mL Teflon-lined vessels under $N_2$ for 3 h at 170 °C. The vessels were then cooled with internal standard (Ethylvanillin) added. The extracts were acidified to pH 1 using 6 M HCl and left in the dark to avoid reactions of cinnamic acids for 1 h. After centrifugation (30 min at 2500 rpm), the supernatant was subject to liquid–liquid extraction with diethyl ether. The ether extracts were concentrated by rotary evaporation, transferred to 2 mL glass vials and dried under $N_2$.

Dried extracts were redissolved in 500 μL dichloromethane:methanol (1:1; v/v). After drying in a stream of $N_2$, aliquots of the extracts (100 μL) were converted to trimethylsilyl (TMS) derivatives by reaction with 90 μL *N,O*-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) and 10 μL pyridine for 1 h at 70 °C. Excess reagent was then removed under gentle $N_2$ flow and redissolved in 200 mL dichloromethane for analysis. Plant biomarkers (lipids and lignin-derived phenols) were analyzed using GC/MS, an Agilent model 6890N GC coupled to an Agilent model 5973N quadrupole mass selective detector (MSD).

Individual compounds were identified by comparison of mass spectra with literature and Wiley MS library data, and interpretation of mass spectrometric fragmentation patterns. Quantification of lipids and lignin phenols was based on an internal standard in the total ion current. The concentration of individual compounds was normalized to sample organic C content in the heavy fraction. In this study, the contribution of cutin and suberin to the heavy fraction of SOM was estimated by quantification of the major hydroxyalkanoic and alkanedioic acids (Otto and Simpson, 2006). Cutin-derived compounds were the sum of mid-chain hydroxyalkanoic $C_{14}$, $C_{15}$, $C_{17}$ acids, $C_{16}$ mono- and dihydroxy acids. Suberin-derived compounds included hydroxyalkanoic and alkanedioic acids in the range of $C_{20}$–$C_{26}$, 9, 10-epoxy-α, ω-$C_{18}$ dioic acid. The ω-$C_{16}/\sum C_{16}$ and ω-$C_{18}/\sum C_{18}$ ratios were determined as measures of the cutin and suberin degradation, where $\sum C_{16}$ consisted of ω-hydroxyl $C_{16}$ acid, α, ω-dioic $C_{16}$ acid and mid-chain-substituted acids with 16C and $\sum C_{18}$ included the same types of acids with 18C.

The weight sum (mg) of eight lignin phenols (three vanillyl phenols: vanillin, acetovanillone, vanillic acid; three syringyl phenols: syringaldehyde, acetosyringone, syringic acid; and two cinnamyl phenols: p-coumaric acid and ferulic acid) was also calculated. The ratios of vanillic acid/vanillin (Ad/Al)v and syringic acid/syringaldehyde (Ad/Al)s were determined as measures of lignin decomposition (Crow et al., 2009; Otto and Simpson, 2006). The contents (kg $ha^{-1}$) of plant biomarkers in the heavy fraction of SOM in the 0–5 cm layer were calculated by multiplication of relative abundance (mg $g^{-1}$ C) with soil C mass of the heavy fraction.

### 2.7. Data and statistical analyses

All data and statistical analyses were performed using SPSS 11.5 for Windows (SPSS 2003) or Microsoft Excel 2003. Effects of harvest residue management and the variation of sampling time at each site were assessed using two-factor analysis of variance (ANOVA) with replication (e.g. C mass and $\delta^{13}C$) or without replication (e.g. proportions of functional C classes and relative abundance of biomarkers) and Tukey's-b post hoc tests. The significance of differences between means among three residue management treatments for each sampling year was determined using the *t*-test and a *P* value $<0.05$ was used to indicate a significant difference.

## 3. Results

### 3.1. Soil C mass

Analysis of variance showed that harvest residue management had significant effects ($P < 0.01$) on C mass of the whole soil and its light and heavy fractions at Kinleith. Forest floor removal significantly reduced the C mass ($P < 0.05$) of the whole soil and its light fraction in all sampling years (Fig. 1A–C). In the stem-only harvest plots, the C mass in the heavy fraction was greater than that in the forest floor removal plots, but the difference was only significant for the year 15 samples (Fig. 1C). There were no significant differences in the C mass in either the whole soil or the light and heavy fractions between the whole-tree and stem-only harvest plots throughout the three sampling years. The soil C mass in the whole soil and its heavy fraction showed no significant change among the sampling years, but a trend of increasing soil C in the light fraction with increasing age of the plantation was evident in both the forest floor removal and whole-tree harvest plots ($P < 0.05$) (Fig. 1A–C).

At Woodhill, both harvest residue management ($P < 0.05$) and sampling year ($P < 0.01$) significantly affected the C mass in the whole soil and its light and heavy fractions. The forest floor removal

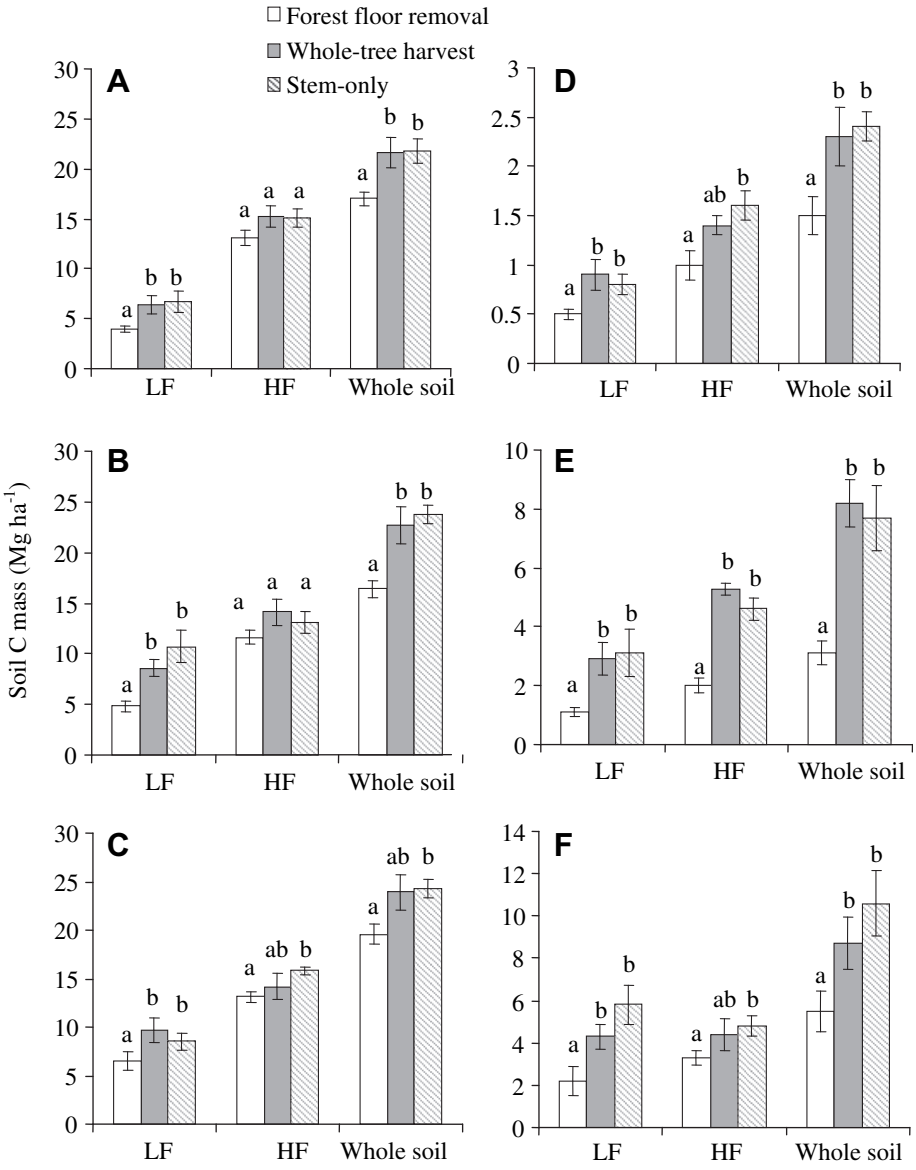


**Fig. 1.** The C mass (Mg ha$^{-1}$) in the whole soil, and its light (LF) and heavy (HF) fractions of 0–5 cm soil layer in forest floor removal, whole-tree, and stem-only harvest plots. Means and standard deviations are shown for Kinleith (A, year 5; B, year 10; and C, year 15) ($n = 4$) and Woodhill (A, year 4; B, year 12; and C, year 20)($n = 3$). For the same soil fraction, the same letters above the bars are not significantly different from each other by $t$-test ($P > 0.05$).

plots had significantly lower C mass in the whole soil and its light and heavy fractions ($P < 0.05$), compared to the stem-only harvest plots. Whole-tree harvest plots had more C mass in the whole soil and its light and heavy (year 20 only) fractions than forest floor removal plots. The C mass in the whole soil and its light and heavy fractions remained unchanged between the whole-tree and stem-only harvest plots. On the other hand, the C mass in the whole soil and its light and heavy fractions markedly increased with increasing age of the plantation in the forest floor removal and stem-only harvest plots ($P < 0.05$) (Fig. 1D–F).

### 3.2. $^{13}$C CPMAS NMR spectra analysis

The proportion of functional C classes was not significantly affected by harvest residue management in either forest as revealed by ANOVA without replication. However, at Kinleith, the O-alkyl C mass of the heavy fraction of SOM was significantly greater ($P < 0.05$) in year 5 in the whole-tree and stem-only harvest plots than in the forest floor removal plots. At year 10, there was a larger mass of aromatic C in the whole-tree harvest plots ($P < 0.05$) than in the forest floor removal plots. At year 15, a significantly larger alkyl C mass ($P < 0.05$) was observed in the stem-only harvest plots than in the whole-tree harvest and forest floor removal plots (Table 2). At Woodhill, the stem-only harvest plots had significantly larger contents of both alkyl and O-alkyl C in all three sampling years than the forest floor removal plots ($P < 0.05$). The whole-tree harvest plots had significantly larger ($P < 0.05$) alkyl C and O-alkyl C mass than the forest floor removal plots at year 12 (Table 3).

### 3.3. Biomarker analysis

The ANOVA without replication showed both harvest residue management ($P < 0.05$) and sampling year ($P < 0.01$ and $P < 0.05$ at Kinleith and Woodhill, respectively) induced significant changes in the relative abundance of cutin-derived compounds at both sites. The stem-only harvest plots had a significantly higher relative

**Table 2**
Functional C classes (Mg ha$^{-1}$) in the heavy fractions of SOM in 0–5 cm mineral soils under three harvest treatments at Kinleith, New Zealand.

| Years after planting | Treatment | Alkyl C (0–45 ppm) | N-alky C (45–60 ppm) | O-alkyl C (60–90 ppm) | Acetal C (90–110 ppm) | Aromatic C (110–145 ppm) | Phenolic C (145–165 ppm) | Carboxyl C (165–210 ppm) |
|---|---|---|---|---|---|---|---|---|
| 5 | Forest floor removal | 2.78(21.2)a* | 1.09(8.3)a | 3.96(30.2)a | 1.59(12.1)a | 1.94(14.8)a | 0.8(6.1)a | 0.97(7.4)a |
| | Whole tree | 3.15(20.7)a | 1.26(8.3)a | 4.64(30.5)b | 1.78(11.7)a | 2.31(15.2)a | 0.93(6.1)a | 1.14(7.5)a |
| | Stem only | 3.07(20.3)a | 1.22(8.1)a | 4.68(31)b | 1.81(12)a | 2.22(14.7)a | 0.95(6.3)a | 1.15(7.6)a |
| 10 | Forest floor removal | 2.78(24.0)a | 1.17(10.1)a | 3.43(29.6)a | 1.24(10.7)a | 1.64(14.1)a | 0.63(5.4)a | 0.72(6.2)a |
| | Whole tree | 3.21(22.8)a | 1.38(9.8)a | 4.13(29.3)a | 1.51(10.7)a | 2.03(14.4)b | 0.85(6.0)a | 1.02(7.2)b |
| | Stem only | 3.08(23.4)a | 1.18(9.0)a | 3.93(30.0)a | 1.40(10.7)a | 1.85(14.1)ab | 0.74(5.6)a | 0.96(7.3)b |
| 15 | Forest floor removal | 2.63(20.1)a | 1.21(9.2)a | 3.90(29.8)a | 1.47(11.2)a | 2.07(15.8)a | 0.81(6.2)a | 1.02(7.7)a |
| | Whole tree | 2.77(19.5)a | 1.27(9.0)a | 4.25(29.9)ab | 1.66(11.7)a | 2.22(15.6)a | 0.92(6.5)a | 1.11(7.8)a |
| | Stem only | 3.46(21.9)b | 1.44(9.1)a | 4.68(29.6)b | 1.77(11.2)a | 2.40(15.2)a | 0.92(5.8)a | 1.15(7.3)a |

*Values in parenthesis are the proportions (%) of functional C classes in the heavy fraction of soil and single measurements of bulked samples from four replicates, each of 20 cores. Within each column for each sampling year, the means of functional C mass followed by the same letter are not significantly different from each other by *t*-test ($P > 0.05$).

abundance of cutin-derived compounds than the forest floor removal plots. The relative abundance of cutin-derived compounds increased with the increasing age of plantations in the two forests (Tables 4 and 5).

At Kinleith, there were larger amounts of cutin-derived compounds in the heavy fraction of SOM in the stem-only harvest plots than in the forest floor removal plots at years 5 and 15 (Table 4). At Woodhill, the stem-only and whole-tree harvest plots had significantly larger amounts of cutin-derived compounds in the heavy fraction of SOM compared to the forest floor removal plots in the three sampling years (Table 5).

No compounds with a chain length more than $C_{26}$ were detected in any significant amount in either forest. The relative abundance of suberin-derived compounds was impacted significantly ($P < 0.05$) by harvest residue management at Woodhill whereas the relative abundance did not change at Kinleith across the harvest residue management treatments. Forest floor removal caused markedly lower relative abundance and mass of suberin-derived compounds at Woodhill compared to the whole-tree and stem-only harvest treatments ($P < 0.05$) (Table 5). Sampling year had significant effects on the relative abundance of suberin-derived compounds in both forests (Tables 4 and 5).

Harvest residue management significantly affected the relative abundance of total lignin-derived phenols in both forests. The stem-only and whole-tree harvest plots had significantly higher relative abundances of total lignin-derived phenols in the SOM heavy fraction than the forest floor removal plots, which led to significantly larger contents of lignin-derived phenols in all three sampling years (Tables 4 and 5).

Neither $\omega$-$C_{16}/\sum C_{16}$ nor $\omega$-$C_{18}/\sum C_{18}$ were significantly affected by harvest residue management in either forest, whereas sampling year did markedly influence the two ratios based on the ANOVA without replication (Table 6). There was no significant variation in (Ad/Al)s and (Ad/Al)v in the three harvest residue management treatments or among sampling years in either forest (Table 7).

### 3.4. Soil $\delta^{13}C$ analysis

The $\delta^{13}C$ in the heavy fractions of SOM was significantly ($P < 0.05$) affected by harvest residue management and varied between years since harvest at Kinleith. Trends of declining $\delta^{13}C$ with increasing level of residue return (i.e. forest floor removal > whole-tree harvest > stem-only harvest) were evident in the heavy fraction of SOM and the differences were significant at $P < 0.05$ between the forest floor removal and the stem-only or whole-tree harvest plots. The increasing age of plantation also led to declining $\delta^{13}C$ values in both the light and heavy fractions of SOM (Fig. 2A).

At Woodhill, both harvest residue management and sampling year significantly affected the $\delta^{13}C$ values in the light fraction of SOM in the 0–5 cm soil layer. A trend of increasing $\delta^{13}C$ with increasing level of residue return (i.e. stem-only harvest > whole-tree harvest > forest floor removal) was found in the light fraction of SOM (Fig. 2B). There was no significant difference in the $\delta^{13}C$ values of SOM in the heavy fraction among three harvest residue management treatments.

## 4. Discussion

The significantly lower total C mass in the forest floor removal plots compared to stem-only and whole-tree harvest plots shown in this study is consistent with the findings of Jones et al. (2008), Powers et al. (2005) and Smaill et al. (2008), who found lower

**Table 3**
Functional C classes (kg ha$^{-1}$) in the heavy fractions of SOM in 0–5 cm mineral soils under three harvest treatments at Woodhill, New Zealand.

| Years after planting | Treatment | Alkyl C (0–45 ppm) | N-alkyl C (45–60 ppm) | O-alkyl C (60–90 ppm) | Acetal C (90–110 ppm) | Aromatic C (110–145 ppm) | Phenolic C (145–165 ppm) | Carboxyl C (165–210 ppm) |
|---|---|---|---|---|---|---|---|---|
| 4 | Forest floor removal | 291(29.1)a* | 81(8.1)a | 245(24.5)a | 57(5.7)a | 119(11.9)a | 72(7.2)a | 135(13.5)a |
| | Whole tree | 396(28.3)ab | 116(8.3)ab | 386(27.6)ab | 85(6.1)ab | 151(10.8)a | 116(8.3)ab | 148(10.6)a |
| | Stem only | 446(27.9)b | 150(9.4)b | 450(29.1)b | 101(5.3)b | 160(10.0)a | 136(8.5)b | 157(9.8)a |
| 12 | Forest floor removal | 564(28.2)a | 154(7.7)a | 502(25.1)a | 126(6.3)a | 218(10.9)a | 156(7.8)a | 280(14.0)a |
| | Whole tree | 1426(26.9)b | 466(8.8)b | 1309(24.7)b | 376(7.1)b | 588(11.1)b | 435(8.2)b | 700(13.2)b |
| | Stem only | 1242(27.0)b | 382(8.3)b | 1141(24.8)b | 336(7.3)b | 538(11.7)b | 396(8.6)b | 566(12.3)b |
| 20 | Forest floor removal | 914(27.7)a | 261(7.9)a | 855(25.9)a | 228(6.9)a | 323(9.8)a | 264(8.0)a | 455(13.8)a |
| | Whole tree | 1166(26.5)ab | 374(8.5)ab | 1140(25.9)ab | 330(7.5)ab | 445(10.1)ab | 365(8.3)ab | 581(13.2)a |
| | Stem only | 1310(27.3)b | 413(8.6)b | 1181(24.6)b | 350(7.3)b | 504(10.5)b | 389(8.1)b | 653(13.6)b |

*Values in parenthesis are the proportion (%) of functional C classes in the heavy fraction of soil and single measurements of bulked samples from three replicates, each of 20 cores. Within each column for each sampling year, the means of functional C mass followed by the same letter are not significantly different from each other by *t*-test ($P > 0.05$).

**Table 4**
The mass (kg ha$^{-1}$) and relative abundance (values in parenthesis, mg g$^{-1}$) of plant biomarkers in the heavy fraction of SOM in 0–5 cm layer under three harvest treatments at Kinleith, New Zealand.

| Years | Treatments | Cutin-derived | Suberin-derived | Lignin-derived phenols | | | |
|---|---|---|---|---|---|---|---|
| | | | | Vanillyls | Cinnamyls | Syringyls | Sum |
| 5 | Forest floor removal | 18.3 ± 3.7 a(1.4)* | 38.0 ± 5.6 a(2.9) | 7.9 ± 2.2(0.6) | 1.7 ± 0.3(0.13) | 4.7 ± 0.6(0.36) | 14.3 ± 3.1 a(1.09) |
| | Whole tree | 22.8 ± 4.0 ab(1.5) | 38.0 ± 6.9 a(2.5) | 10.3 ± 1.5(0.68) | 2.7 ± 0.5(0.18) | 7.1 ± 0.9(0.47) | 20.1 ± 4.5 b(1.33) |
| | Stem only | 24.2 ± 4.8 b(1.6) | 40.8 ± 9.5 a(2.7) | 11.3 ± 2.7(0.75) | 3.0 ± 0.6(0.20) | 10.4 ± 1.0(0.69) | 24.7 ± 4.9 b(1.64) |
| 10 | Forest floor removal | 19.7 ± 7.0 a(1.7) | 42.9 ± 7.7 a(3.7) | 6.8 ± 1.9(0.59) | 2.0 ± 0.2(0.17) | 4.6 ± 0.5(0.40) | 13.4 ± 3.5 a(1.16) |
| | Whole tree | 26.8 ± 4.5 a(1.9) | 43.8 ± 8.0 a(3.1) | 10.4 ± 2.0(0.74) | 3.1 ± 0.2(0.22) | 5.4 ± 0.4(0.38) | 18.9 ± 4.6 b(1.34) |
| | Stem only | 26.2 ± 3.6 a(2.0) | 43.2 ± 6.9 a(3.3) | 10.1 ± 2.3(0.77) | 3.0 ± 0.4(0.23) | 7.3 ± 0.8(0.56) | 20.4 ± 2.7 b(1.56) |
| 15 | Forest floor removal | 24.9 ± 5.4 a(1.9) | 41.9 ± 9.8 a(3.2) | 9.3 ± 1.6(0.71) | 1.6 ± 0.3(0.12) | 6.4 ± 0.8(0.49) | 17.3 ± 2.0 a(1.32) |
| | Whole tree | 29.8 ± 6.1 ab(2.1) | 46.9 ± 3.9 a(3.3) | 12.4 ± 2.8(0.87) | 3.1 ± 0.4(0.22) | 7.7 ± 1.1(0.54) | 23.2 ± 5.1 b (1.63) |
| | Stem only | 39.5 ± 7.2 b(2.5) | 52.1 ± 5.6 a(3.3) | 10.9 ± 2.1(0.69) | 3.0 ± 0.5(0.19) | 8.4 ± 1.5(0.53) | 22.3 ± 6.3 ab(1.41) |

*Within each column for each sampling year, the mass means ± standard errors followed by the same letter are not significantly different from each other by *t*-test ($P > 0.05$) ($n = 4$).

C content in mineral soil to a depth of 20, 10 and 2.5 cm in forest floor removal plots, respectively. The responses of C mass in the whole soil to harvest residue management in the two forest soils were similar despite the differences in soil types and textures, however, we found that the C mass in the whole soil increased with increasing age of forest at Woodhill. This supports the argument that soil C buildup in sandy soils is possible under a system where continuous input of organic materials is provided and soil disturbance is minimized (Vityakon et al., 2000).

At Woodhill, both the stem-only and whole-tree (year 12) harvest plots had significantly larger C contents in the heavy fraction of SOM than the forest floor removal plots. At Kinleith, the significant difference in C mass in the heavy fraction of SOM was only found between the stem-only harvest and forest floor removal plots in year 15. Percival et al. (2000) suggested that for New Zealand soils, the concentrations of pyrophosphate-extractable Al, rather than clay and silt, were associated with long-term SOM stabilization. The pumice soils contained more Al than the sandy recent soils (Percival et al., 2000), which might explain the less variation of soil organic C at Kinleith than at Woodhill. The NMR analysis of the SOM heavy fraction revealed that the proportions of the functional soil C classes in the three harvest residue management plots were similar. The only apparent difference was a higher proportion of O-alkyl C in the stem-only harvest plots (29.1%) than in the forest floor removal plots (24.5%) in the soil samples collected in year 4 at Woodhill, which is consistent with the findings of Mathers and Xu (2003). Zech et al. (1997) suggested that the larger soil O-alkyl C under harvest residues at the early stage of forest growth might be attributed to rapid mineralization of labile components in residues which is a dominant process during the first phase of litter decomposition. In the present study harvest residue management had a variable and quantitatively unimportant impact on the proportion of alkyl C in the heavy fraction of SOM. However, the alkyl C mass in the heavy fraction, converted by multiplication of the proportion of functional C classes with soil C mass in the heavy fraction, was significantly larger in the stem-only harvest plots than the forest floor removal plots in year 15 at Kinleith and in all three sampling years at Woodhill. Alkyl C is an polymethylenic compound consisting of long-chain aliphates, fatty acids, wax, cutin and suberin and is among the biologically most stable forms of soil organic C (Lorenz et al., 2007; Mathers et al., 2007). The larger soil alkyl C mass, especially in the heavy fraction of SOM, due to the increasing level of harvest residue return was thus beneficial to the long-term C sequestration and stability of organic C in soil as noted by Zhang et al. (2009).

The larger stable (alkyl) C mass in the heavy fraction of SOM in the stem-only or whole-tree harvest plots compared to the forest floor removal plots are also supported by our analyses of plant biomarkers using GC/MS (Tables 4 and 5). The biomarkers of SOM, such as cutin- and suberin-derived compounds and lignin-derived phenols, are thought to be recalcitrant (Gleixner et al., 1999, 2001) and can provide information regarding their specific organic sources and the stage and rate of SOM degradation (Simpson et al., 2008). The relative abundance of cutin-derived compounds in the heavy fraction of SOM varied between 1.4 and 2.7 mg g$^{-1}$ C and are within the range reported in other studies (Feng et al., 2008, 2010; Otto and Simpson, 2006). Cutin-derived compounds, which originate from the waxy coating of leaves, contain special compounds in different botanic classes (Goñi and Hedgesa, 1990; Otto and Simpson, 2006). The cutin monomers observed in this study

**Table 5**
The mass (kg ha$^{-1}$) and relative abundance (values in parenthesis, mg g$^{-1}$) of plant biomarkers in the heavy fraction of SOM in 0–5 cm mineral soils under three harvest treatments at Woodhill, New Zealand.

| Years | Treatments | Cutin-derived | Suberin-derived | Lignin-derived phenols | | | |
|---|---|---|---|---|---|---|---|
| | | | | Vanillyls | Cinnamyls | Syringyls | Sum |
| 4 | Forest floor removal | 2.0 ± 0.5 a(1.9)* | 2.5 ± 0.6 a(2.4) | 0.8 ± 0.2(0.81) | 0.3 ± 0.1(0.23) | 0.4 ± 0.1(0.34) | 1.4 ± 0.3 a(1.38) |
| | Whole tree | 2.9 ± 0.6 b(2.1) | 4.5 ± 1.2 b(3.2) | 1.2 ± 0.2(0.85) | 0.4 ± 0.1(0.25) | 0.7 ± 0.1(0.47) | 2.2 ± 0.4 b(1.57) |
| | Stem only | 3.7 ± 0.8 b(2.3) | 4.8 ± 1.0 b(3.0) | 1.1 ± 0.3(0.70) | 0.5 ± 0.1(0.30) | 0.8 ± 0.1(0.51) | 2.4 ± 0.4 b(1.51) |
| 12 | Forest floor removal | 4.5 ± 0.9 a(2.1) | 6.9 ± 1.1 a(3.5) | 1.6 ± 0.4(0.77) | 0.6 ± 0.1(0.37) | 0.7 ± 0.2(0.33) | 2.9 ± 0.5 a(1.47) |
| | Whole tree | 11.7 ± 2.1 b(2.2) | 19.6 ± 3.9 b(3.7) | 3.5 ± 0.8(0.65) | 2.3 ± 0.5(0.43) | 2.1 ± 0.3(0.40) | 7.9 ± 1.8 b(1.48) |
| | Stem only | 12.6 ± 2.4 b(2.6) | 17.9 ± 4.1 b(3.9) | 3.2 ± 0.7(0.69) | 1.7 ± 0.4(0.36) | 2.2 ± 0.4(0.48) | 7.1 ± 2.0 b(1.53) |
| 20 | Forest floor removal | 7.6 ± 2.0 a(2.3) | 12.5 ± 3.5 a(3.3) | 2.6 ± 0.5(0.79) | 1.3 ± 0.4(0.38) | 1.6 ± 0.6(0.49) | 5.5 ± 1.2 a(1.66) |
| | Whole tree | 11.9 ± 3.2 b(2.6) | 15.8 ± 2.7 ab(3.6) | 3.8 ± 0.8(0.86) | 1.9 ± 0.5(0.43) | 2.6 ± 0.7(0.58) | 8.3 ± 1.7 b(1.87) |
| | Stem only | 12 ± 3.9 b(2.5) | 17.8 ± 4.0 b(3.7) | 4.2 ± 1.0(0.87) | 1.9 ± 0.7(0.40) | 2.7 ± 0.7(0.57) | 8.8 ± 2.0 b(1.84) |

*Within each column for each sampling year, the mass means ± standard errors followed by the same letter are not significantly different from each other by *t*-test ($P > 0.05$) ($n = 3$).

**Table 6**
The ω-$C_{16}/\sum C_{16}$[a], ω-$C_{18}/\sum C_{18}$[b], (Ad/Al)s[c] and (Ad/Al)v[c] ratios in the heavy fraction of SOM in the 0–5 cm soil layer under three harvest residue management treatments at Kinleith. No significant effects of harvest residue management on these ratios were found according to ANOVA without replication.

| Year | Treatments | ω-$C_{16}/\sum C_{16}$ | ω-$C_{18}/\sum C_{18}$ | (Ad/Al)s | (Ad/Al)v |
|---|---|---|---|---|---|
| 5 | Forest floor removal | 0.40 | 0.21 | 1.41 | 0.92 |
| | Whole tree | 0.40 | 0.18 | 1.35 | 0.84 |
| | Stem only | 0.37 | 0.19 | 1.42 | 0.81 |
| 10 | Forest floor removal | 0.37 | 0.19 | 1.35 | 0.87 |
| | Whole tree | 0.35 | 0.17 | 1.51 | 0.96 |
| | Stem only | 0.33 | 0.20 | 1.28 | 0.74 |
| 15 | Forest floor removal | 0.36 | 0.19 | 1.72 | 0.91 |
| | Whole tree | 0.35 | 0.18 | 1.39 | 0.79 |
| | Stem only | 0.34 | 0.15 | 1.36 | 0.78 |

[a] Indicators of cutin degradation. $\sum C_{16}$ consists of ω-hydroxyl $C_{16}$ acid, α, ω-dioic $C_{16}$ acid and mid-chain-substituted acids with 16C. The ratio increases with the increasing decomposition of cutin-derived compounds.
[b] Indicators of suberin degradation. $\sum C_{18}$ includes ω-hydroxyl $C_{18}$ acid, α, ω-dioic $C_{18}$ acid and mid-chain-substituted acids with 18C. The ratio increases with the increasing decomposition of suberin-derived compounds.
[c] (Ad/Al)v and (Ad/Al)s are the ratios of vanillic acid/vanillin and syringic acid/syringaldehyde, respectively. Both ratios are indicators of lignin degradation and increase with increasing degree of lignin oxidation through propyl side-chain oxidation.

**Table 7**
The ω-$C_{16}/\sum C_{16}$, ω-$C_{18}/\sum C_{18}$, (Ad/Al)s and (Ad/Al)v ratios in the heavy fraction of SOM in the 0–5 cm soil layer under three harvest residue management treatments at Woodhill. No significant effects of harvest residue management on these ratios were found according to ANOVA without replication. The explanation of these ratios can be found in Table 6.

| Year | Treatments | ω-$C_{16}/\sum C_{16}$ | ω-$C_{18}/\sum C_{18}$ | (Ad/Al)s | (Ad/Al)v |
|---|---|---|---|---|---|
| 4 | Forest floor removal | 0.45 | 0.30 | 0.77 | 1.21 |
| | Whole tree | 0.43 | 0.27 | 0.73 | 1.29 |
| | Stem only | 0.40 | 0.29 | 0.74 | 1.26 |
| 12 | Forest floor removal | 0.32 | 0.18 | 0.79 | 1.33 |
| | Whole tree | 0.29 | 0.12 | 0.81 | 1.40 |
| | Stem only | 0.30 | 0.15 | 0.85 | 1.40 |
| 20 | Forest floor removal | 0.31 | 0.12 | 0.74 | 1.19 |
| | Whole tree | 0.29 | 0.09 | 0.78 | 1.27 |
| | Stem only | 0.27 | 0.10 | 0.76 | 1.38 |

comprised α, ω-alkanedioic ($C_{14}$–$C_{17}$), ω-hydroxyalkanoic ($C_{14}$–$C_{17}$), hydroxy-α, ω-alkanedioic and polyhydroxyalkanoic acids, which mostly match the previously reported cutin constituents of pine needles (Franich and Volkman, 1982; Otto and Simpson, 2006). Suberin-derived compounds, which mainly originate from roots and bark, were affected significantly by the residue management at Woodhill but not at Kinleith Forest. Previous studies did not find any significant differences between plant groups in the suberin compounds detected in roots and bark (Goñi and Hedgesa, 1990; Otto and Simpson, 2006). Therefore, it is difficult to understand the plant sources of increased suberin contents in the heavy fraction of SOM (e.g. *P. radiata* vs understory weeds) due to increased harvest residue retention at Woodhill.

The ω-$C_{16}/\sum C_{16}$ and ω-$C_{18}/\sum C_{18}$ ratios have been reported to increase with progressing cutin degradation (Goñi and Hedgesa, 1990; Otto and Simpson, 2006). The (Ad/Al)s and (Ad/Al)v ratios also increase with increasing degree of lignin oxidation through propyl side-chain oxidation (Opsahla and Bennera, 1995). None of these indicators changed significantly in the heavy fraction of SOM across three residue management treatments at either site. Therefore, the changes in alkyl C mass in the heavy fraction of SOM among different harvest residue managements should not be attributed to the varied decomposition rates of SOM.

The observed buildup of alkyl C mass in the SOM heavy fraction in the stem-only or whole-tree harvest plots compared to forest floor removal plots therefore seems likely to be due to increased inputs from forest debris. Ganjegunte et al. (2006) measured the chemistry of aqueous extracts of Oi layer in a 20-year-old *P. radiata* plantation in New Zealand and found that 25% of organic C in the aqueous extracts could be assigned to the alkyl region. It may therefore be expected that the elevated litter mass in the Oi layer in the stem-only or whole-tree harvest plots compared to forest floor removal plots which was observed by Smaill et al. (2008) would increase the release of alkyl C into the mineral soil and its heavy fraction.

In addition, the analysis of $\delta^{13}C$ in SOM provides support for the argument that the observed buildup of alkyl C mass in the heavy fraction of SOM under greater harvest residue return can be attributed to increased inputs from the light fraction of SOM and/or

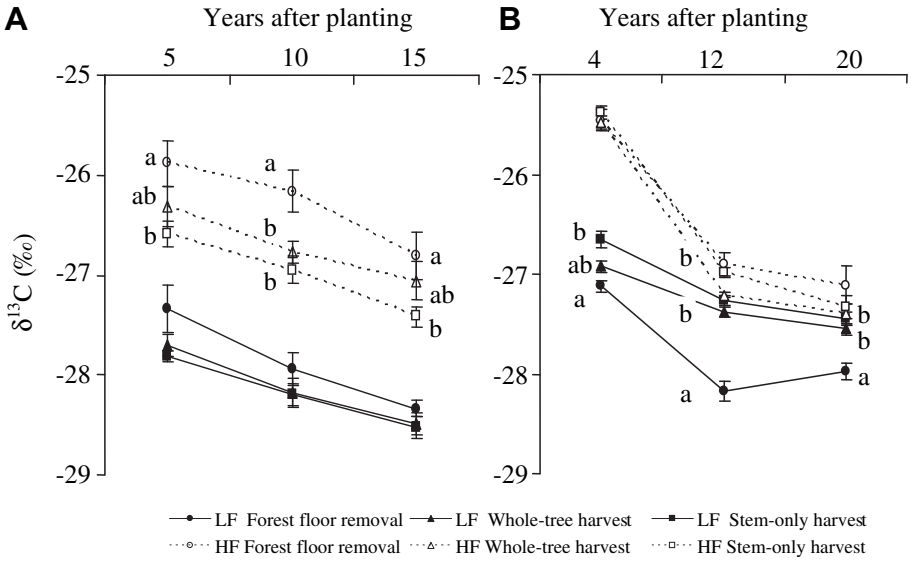


**Fig. 2.** The $\delta^{13}C$ (‰)of light (LF) and heavy (HF) fractions of SOM in the 0-5 cm soil layer in forest floor removal, whole-tree, and stem-only harvest plots. Means and standard deviations are shown for Kinleith (A) ($n = 4$) and Woodhill (B) ($n = 3$). For the same soil fraction and sampling year, means with the same letter are not significantly different from each other among three harvest residue management treatments by *t*-test ($p > 0.05$). No significant effect of harvest residue management on the $\delta^{13}C$ of the light fraction of SOM at Kinleith or of the heavy fraction of SOM at Woodhill was found according the ANOVA.

directly from forest debris. At Kinleith, there are two possible reasons for the less negative $\delta^{13}C$ in the heavy fraction of SOM in the forest floor removal plots (Ågren and Bosatta, 1996; Garten et al., 2000). Firstly, soil micro-organisms discriminate against $^{13}C$ and preferentially use $^{12}C$ compounds during decomposition, hence residual SOM should become more enriched in $^{13}C$ (Nadelhoffer and Fry, 1988). The higher decomposition rate may therefore increase the natural abundance of $\delta^{13}C$ (less negative) in SOM (Billings and Richter, 2006). However, this reasoning conflicts with our analyses of biomarker degradation indices and therefore is implausible. Secondly, C-mixing theory suggests that $\delta^{13}C$ values in SOM are influenced by the mixing of new C inputs with existing and older SOM pools (Billings and Richter, 2006). The average $\delta^{13}C$ of light fraction soil was −28‰, which is lower than that of heavy fraction soil (averaged at −26.5‰). In forests, surface litter has lower $\delta^{13}C$ relative to existing SOM in mineral soil and this may also contribute to a shift in $^{13}C$:$^{12}C$ ratios in the heavy fraction of SOM (Garten et al., 2000). There was no significant difference in $\delta^{13}C$ of the soil light fraction (Fig. 2A) or plant litter (unpublished data) among three harvest residue management treatments at Kinleith. The lower C input from the light fraction or/and surface litter to the heavy fraction therefore may lead to the less negative $\delta^{13}C$ in the heavy fraction of SOM in the forest floor removal plots compared to plots with greater harvest residue return. At Woodhill, the lack of significant differences in $\delta^{13}C$ values of the heavy fraction of SOM among the three residue management treatments may be due to the significantly different $\delta^{13}C$ values in the light fraction of SOM (Fig. 2B).

In this study, soil in the 0–5 cm layer was studied as more organic C is stored here than at greater depths. Although variation of deeper soil total C due to contrasting harvest residue managements has been observed (Jones et al., 2008; Mendham et al., 2003), additional information on the fate of alkyl C and aliphatic compounds in deeper SOM is necessary to provide a more comprehensive knowledge of the impacts from residue management. Our results clearly demonstrate that increased residue return can increase the stable C pool in the heavy fraction of the upper mineral soil through elevated input of recalcitrant compounds from the litter and/or light fraction of SOM. The molecular-level analyses provide direct evidence on the origins of recalcitrant C (i.e. plant-derived vs microbial derived C) in soil.

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