

Long-term stabilization of crop residues and soil organic carbon affected by residue quality and initial soil pH

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Abstract

Residues differing in quality and carbon (C) chemistry are presumed to contribute differently to soil pH change and long-term soil organic carbon (SOC) pools. This study examined the liming effect of different crop residues (canola, chickpea and wheat) down the soil profile (0-30 cm) in two sandy soils differing in initial pH as well as the long-term stability of SOC at the amended layer (0-10 cm) using mid-infrared (MIR) and solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. A field column experiment was conducted for 48 months. Chickpea- and canola-residue amendments increased soil pH at 0-10 cm in the Podzol by up to 0.47 and 0.36 units, and in the Cambisol by 0.31 and 0.18 units, respectively, at 48 months when compared with the non-residue-amended control. The decomposition of crop residues was greatly retarded in the Podzol with lower initial soil pH during the first 9 months. The MIR-predicted particulate organic C (POC) acted as the major C sink for residue-derived C in the Podzol. In contrast, depletion of POC and recovery of residue C in MIR-predicted humic organic C (HOC) were detected in the Cambisol within 3 months. Residue types showed little impact on total SOC and its chemical composition in the Cambisol at 48 months, in contrast to the Podzol. The final HOC and resistant organic C (ROC) pools in the Podzol amended with canola and chickpea residues were about 25% lower than the control. This apparent priming effect might be related to the greater liming effect of these two residues in the Podzol.

Key words: carbon composition, liming effect, MIR-predicted C fraction, NMR, residue types

1. Introduction

Retention of crop residue has been increasingly recognized as an essential strategy to enhance soil organic carbon (SOC) storage and compensate for SOC losses due to decomposition (Wang et al., 2016; Whitbread et al., 2003). In the context of elevated atmospheric CO_2 and global warming, the potential of soil to sequester the residue-derived carbon (C) has received intensive attention (Blair et al., 2005; Gentile et al., 2011). Increases in SOC content through increased C input from crop residue retention have been demonstrated (Dolan et al., 2006; Whitbread et al., 2000). Given that about 55% to 70% of residue C could have been mineralized and released as CO_2 within one year after addition (Johnson et al., 2007; Zech et al., 1997), residue-derived C contributes significantly (~50%) to the total CO_2 emitted from terrestrial systems (Schlesinger and Andrews, 2000). Residue management practices should aim to enhance long-term SOC sequestration and minimize the adverse impact on global climate change.

The rate of residue decomposition is influenced by residue quality as defined by C/N ratio, lignin and polyphenol concentrations. Generally, plant residues with higher C/N ratios, such as cereal crop residues, decompose more slowly than residues with lower C/N ratios such as those derived from legumes (Butterly et al. 2013; Hirobe et al., 2004; Teklay and Malmer 2004). Significant correlations have been detected between residue N content and loss of residue biomass (Heal et al., 1997; Trinsoutrot et al., 2000). Residues with high contents of lignin and other polyphenol compounds that are considered resistant to microbial degradation can persist in the soil for years (Heal et al., 1997; Marschner et al., 2008). As decomposition proceeds, the quality of the remaining residue declines due to the accumulation of these refractory C (Baldock et al., 1992; Baldock et al., 1997). Early studies suggest that it is N content and then the amount of lignin and polyphenol that controls the early and late stages of decomposition, respectively (Taylor et al., 1989; Tian et al., 1992).

While the effect of residue quality on its decomposition has been extensively studied, little is known about the nature of the residue C stabilized in the soil. Lignin and other polyphenol compounds are believed to be major precursors of stable SOC (Stevenson, 1994). Nevertheless, other studies have revealed that labile C compounds such as polysaccharides and N-containing compounds can be long-preserved due to physical protection through either aggregation (Blanco-Canqui and Lal, 2004; Six et al., 1999) or adsorption by clay minerals (Christensen, 2001; Hassink, 1997). The intrinsic property of residue shows little correlation to the decomposition rates of organic C associated with clay particles, suggesting that physical protection or the interaction with soil minerals determines the SOC stability over long periods of time (Heim and Schmidt, 2007; Schmidt et al., 2011). The major SOC stabilization mechanisms could vary among soils with different texture, however, the long-term fate of different crop residues in sandy soils with little physical protection remains largely unknown.

Apart from soil texture, the decomposition of crop residue may also be affected by other soil properties such as pH. It has been well recognized that soil pH can impact on the decomposition of SOC by directly affecting its solubility or indirectly by influencing microbial growth, activity and community structure (Pietri and Brookes, 2009; Wang et al., 2016). Microbial growth and activity are sensitive to change in soil pH, especially in the pH range of 4.3 to 5.3 (Kemmitt et al., 2006; Pietri and Brookes, 2008). Additionally, the incorporation of crop residues *per se* can affect soil pH, which in turn may affect their decomposition. The increase in soil pH upon the addition of crop residues (liming effect) is mainly attributed to the decomposition of organic anions within the residues (Butterly et al., 2013; Tang and Yu, 1999). So far, the interaction between soil pH and decomposition of different residues on soil C dynamics has been seldom studied.

This study aimed to examine the effect of initial soil pH and residue type on the decomposition and stability of three different crop residues in two sandy soils. Changes in different SOC pools and chemical composition of residue-amended soils with time were quantified by mid-infrared (MIR) and solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, respectively. We hypothesised that 1) the decomposition rate of crop residues would be slower in soil with lower initial soil pH, and 2) long-term stabilization of organic C could be affected by the quality of residues.

2. Materials and methods

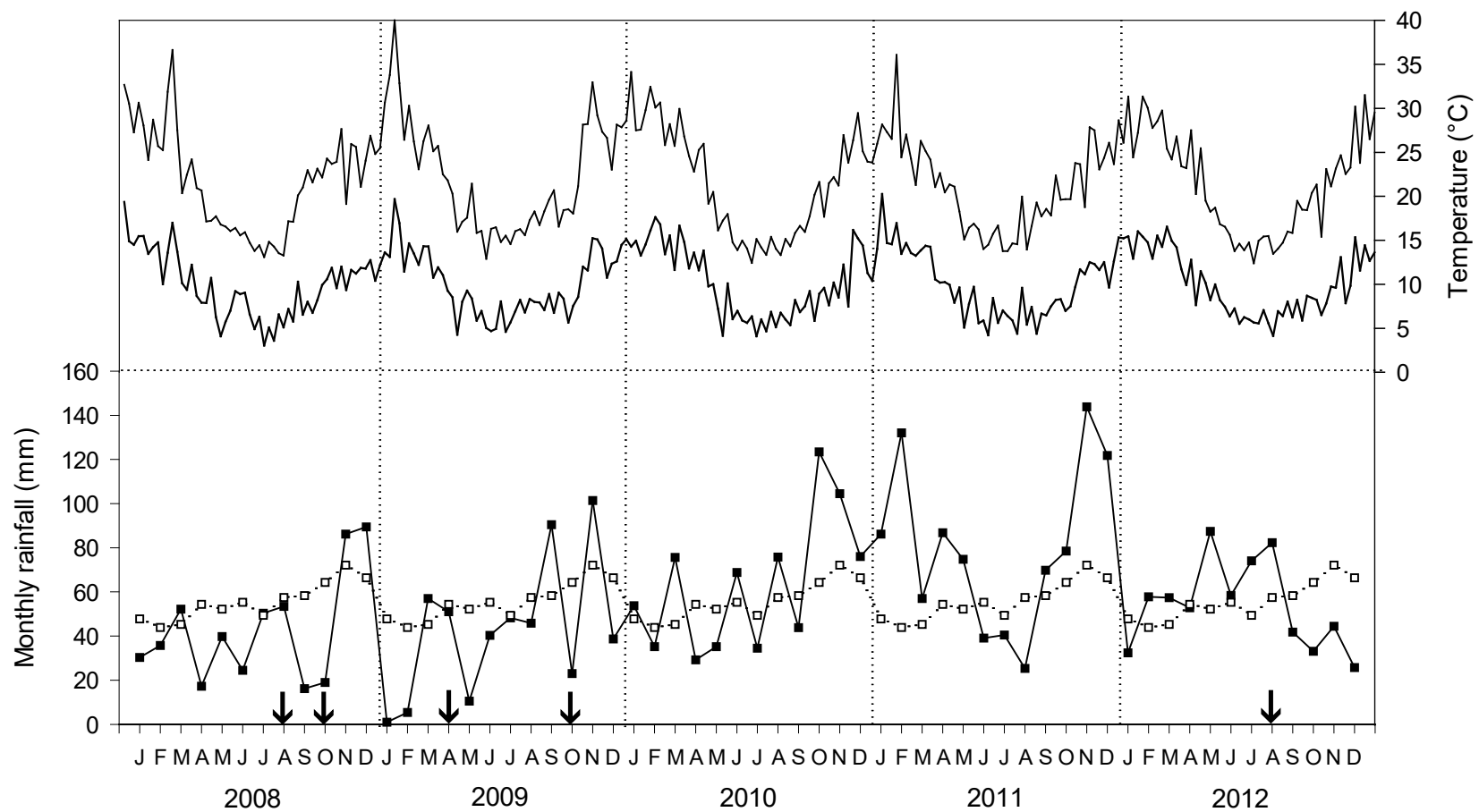
2.1. Field column experiment

A column experiment was conducted under field conditions. It consisted of two soils and four residue treatments with three replicates for each destructive harvest. The two soils were a Podosol and a Tenosol (Isbell, 1996) or Orsteinic Podzol and Chromic Eutric Cambisol (WRB, 2014) collected at a depth of 0-20 cm from Frankston (38°14'S, 145°22'E) and Sepparton (36°28'S, 145°36'E), Victoria, Australia, respectively. They had a similar texture (>80% sand) and low SOC content (<3.0 mg g⁻¹), but different initial soil pH (4.5 and 6.1, for the Podzol and Cambisol, respectively). The four residue treatments included mature residues of canola (*Brassica napus* L.), chickpea (*Cicer arietinum* L.) and wheat (*Triticum aestivum* L.), and a control without residue amendment. The C:N ratio of the residue was 41, 36.3 and 76 for canola, chickpea and wheat, respectively. The extractable organic C was 46 g kg⁻¹ for wheat residue, 37 mg kg⁻¹ for chickpea and 30 mg kg⁻¹ for canola (Butterly et al., 2013). The crop residues were dried at 70 °C, finely ground (<2 mm) and mixed into the 0-10 cm layer at a rate of 10 g kg⁻¹ soil (equivalent to 13 t ha⁻¹ on a

surface-area basis). Briefly, PVC columns (diameter 10 cm, height 30 cm, longitudinally sectioned) were constructed by adding soil without residues to create a 10-30 cm depth layer within the PVC columns and then adding soil mixed with different crop residues to create a surface 0-10 cm depth layer. The bulk density at 10-30 cm was 1.45 g cm^{-3} for the Podosol and 1.24 g cm^{-3} for the Tenosol. Nylon mesh was fitted to the bottom of PVC columns to allow free drainage during the whole experiment. After being watered to 60% field capacity, all columns were randomly arranged within trenches in the field, with the soil surface of the columns being at the same level as that of the field paddock, from August 2008 to October 2012 on the University farm ($37^{\circ}72'S$, $145^{\circ}05'E$) (Fig. 1). The water content of soil column fluctuated with rain and evaporation, and reflected field conditions. More details of the experiment can be found in Butterly et al. (2013).

2.2. Soil sampling

The soil columns were destructively sampled at 0, 3, 9, 15 and 48 months. The time zero represented samples collected 18 h after the columns were constructed. At each sampling time, soils columns were sectioned into depths of 0-5, 5-10, 10-12, 12-15, 15-20 and 20-30 cm. All soils were air-dried and stored until analysis. The effects of crop residue on soil pH profiles at 0-26 months were reported in Butterly et al. (2013). This paper reports the soil pH profiles at 48 months, and detailed C fractions and composition of soils in the 0-10 cm layer at 0-48 months. Total SOC below the amended layer (0-10 cm) was low and less affected by the surface residue amendments.



2 **Figure 1.** Minimum and maximum weekly mean temperatures, monthly rainfall (■) during 2008-2012 and the 34-year monthly mean
 4 rainfall (□) at Bundoora, Victoria. Arrows indicate sampling times.

2.3. Physicochemical analysis

Soil pH was measured in 0.01 M CaCl₂ (1:5 soil solution ratio, 1 h end-over-end shaking, centrifuging at 700 × g for 10 min). For determination of SOC content, MIR-predicted C fractions and the chemical composition of SOC, subsamples collected from the 0-5 cm and 5-10 cm layers were thoroughly mixed, and then ball-milled (MM400, Retsch GmbH, Haan, Germany). Total SOC was determined by dry combustion using a CHNS Analyzer (PerkinElmer EA2400, Shelton, USA). MIR spectroscopic analyses were carried out on a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific Inc., MA, USA) equipped with a PIKE AutoDiff-automated diffuse reflectance accessory (Pike Technologies, WI, USA). Concentrations of particulate organic C (POC), humic organic C (HOC) and resistant organic C (ROC) were predicted from the acquired MIR spectra using the MIR/PLSR algorithms developed by Baldock et al. (2013). This model was based on empirical measurements of POC, HOC and ROC for 312 soils covering a wide range of soil types including Podzol and Cambisol (??) and was robust for the accurate prediction of different C fractions for unknown samples ($R^2 > 0.84$). The lower inlier R value (< 1) suggests that all predicted data were within the calibration range. The regression model can be written as:

$$y = \beta_0 + \beta_1 x_1 + \dots + \beta_k x_k + \varepsilon$$

Where the square-root transformed response values (y) (e.g. POC, HOC and ROC) are approximated by a linear combination of the values of the spectral intensities (x), coefficients (β) and an error term (ε). The POC represented SOC associated with 50–2000- μ m particles excluding poly-aromatic C. The HOC represented SOC associated with particles ≤ 50 μ m excluding poly-aromatic C. The ROC represented the poly-aromatic C associated with particles ≤ 2000 μ m.

Soils for the solid-state ¹³C NMR analysis were prepared by forming single composite samples for each treatment at 0-10 cm. Sand particles were removed from the composite samples prior to NMR analysis to enhance the quality of the acquired ¹³C NMR spectra. Briefly, composite soils were dispersed in 50 g L⁻¹ sodium hexametaphosphate (soil solution ratio of 1:4), shaken for 16 h on a flatbed orbital shaker and passed through a 50- μ m sieve (Baldock et al., 2013). The coarse particulate organic materials retained on the 50- μ m sieve, but excluding particles of sand, were combined with the < 50 μ m suspension, and then freeze-dried. The dried composite samples were ground and treated with 2% hydrofluoric acid (HF) to further concentrate SOC and remove paramagnetic materials (Skjemstad et al., 1994). Solid-state ¹³C NMR analyses were completed on a Bruker 200 Avance spectrometer equipped with a 4.7-T wide-bore superconducting magnet operating at a resonance frequency of 50.33 MHz. The observability of C was more than 80% for the Cambisol and close to 100% for the Podzol. Detailed information regarding MIR and NMR set up can be found in Wang et al. (2016).

2.4. Statistical analysis

A one-way ANOVA was carried out to look at the effect of residue type on soil pH at different depth and for each soil. A two-way ANOVA was conducted to assess the effects of soil and residue type on MIR-predicted POC, HOC and ROC at each sampling time using Genstat (v. 11; VSN International, Hemel Hempstead, UK). The data were checked for normal distribution and homogeneous variances. Significant ($P=0.05$) differences between means were identified using Tukey's HSD test. For NMR analysis, duplicates were performed for one treatment of each soil type to assess the experimental error.

3. Results

3.1. Soil pH

Soil pH in the 0-10 cm depth layer of the Podzol increased by 0.36 and 0.47 units ($P < 0.01$) following canola- and chickpea-residue amendments, respectively (Fig. 2a), compared with the non-residue control. Incorporation of canola and chickpea residues also increased soil pH of the Cambisol by 0.18 and 0.31 units, respectively, at 48 months ($P < 0.05$) (Fig. 2b). The pH increase was also evident in the 10-20 cm layers ($P < 0.05$). The addition of wheat residue had little impact on soil pH, relative to non-amended soils. However, when compared with the initial soil pH (6.1), the pH decreased in all treatments of the Cambisol (Fig. 2b), indicating that the soil was acidified over the 48 months. The presence of an unidentified *Bryophyte* on the surface of the column possibly caused this acidification across all treatments (Butterly et al., 2013)

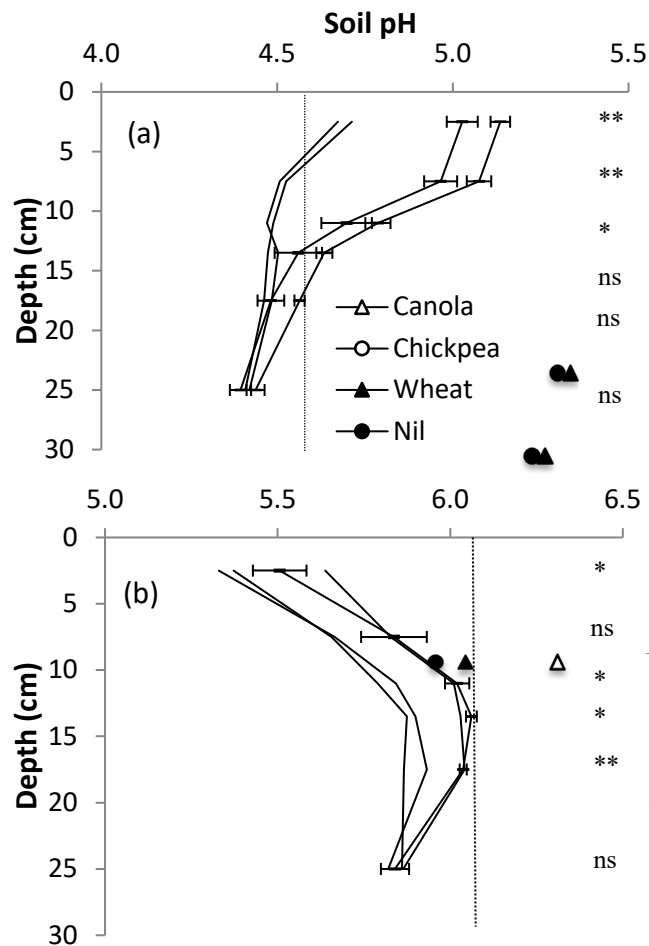


Figure 2. Soil pH in the Podzol (a) and the Cambisol (b) at 48 months either amended (0-10 cm) with canola, chickpea and wheat residues or non-amended control (Nil). Horizontal bars indicated standard error of three replicates. The dashed lines represent the initial soil pH. ns, not significant; *, $P < 0.05$; **, $P < 0.01$.

3.2. Total SOC

Changes in the concentration of total SOC with time following incorporation of the different residues differed between the Podzol and Cambisol (Fig. 3). In the Podzol, the rates of SOC loss over 9 months were gradual (~25%) for all three residues (Fig. 3a), particularly for the Podzol

receiving wheat residue during the initial 3 months. However, in the Cambisol, total SOC decreased by more than 50% after 9 months, but stabilized thereafter regardless of residue type (Fig. 3b). For both soils, SOC decreased more rapidly in soils amended with chickpea residue (within 18 hours) than with canola and wheat residues. At 48 months, little difference in SOC was detected among residue treatments in the Cambisol. The final concentration of SOC in the Cambisol at 48 months was higher in all residue-amended soils than the control soil ($P<0.05$). For the Podzol, SOC was 29% higher in the wheat residue-amended soil, but was the same as the control in the chickpea and canola residue-amended soils.

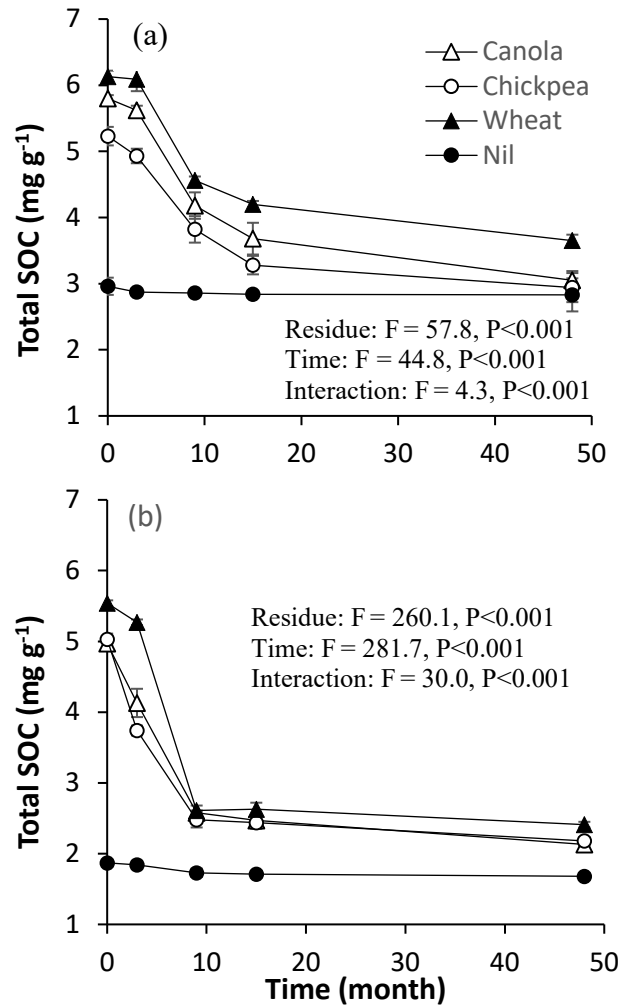


Figure 3. Total soil organic carbon (SOC) content in the top 0-10 cm layer of the Podzol (a) and the Cambisol (b) at 0 (18 hours), 3, 9, 15 and 48 months after amendment with canola, chickpea or wheat residues or non-amended control (Nil). Vertical bars indicated standard error of three replicates.

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90

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Table 1. MIR-predicted particulate organic C, humic organic C, resistant organic C for the Podzol and Cambisol at 3, 15 and 48 months either amended (0-10 cm) with canola, chickpea and wheat residues or non-amended control (nil). ns, $P>0.05$; *, $P<0.05$; **, $P<0.01$; ***, $P\leq 0.001$. Different letters indicate significant differences among treatments at each sampling time (Tukey's test, $P<0.05$).

Soil type	Residue	Particulate organic C (mg g ⁻¹)			Humic organic C (mg g ⁻¹)			Resistant organic C (mg g ⁻¹)		
		3 m	15 m	48 m	3 m	15 m	48 m	3 m	15 m	48 m
Podzol	Canola	1.42 e	0.88 d	0.76 d	3.49 d	3.23 d	2.32 c	2.37 a	1.75 ab	1.67 a
	Chickpea	1.15 d	0.72 c	0.61 c	3.26 d	2.44 c	2.23 c	2.47 a	1.72 a	1.69 a
	Wheat	1.48 e	1.10 e	0.80 d	3.28 d	3.26 d	3.20 d	2.26 a	2.16 c	2.34 b
	Nil	0.48 c	0.49 b	0.46 b	3.04 d	3.00 d	3.03 d	2.24 a	2.21 c	2.23 b
Cambisol	Canola	0.24 b	0.02 a	0.02 a	1.10 ab	0.95 b	0.79 b	2.29 a	1.84 b	1.80 a
	Chickpea	0.26 b	0.03 a	0.02 a	1.24 bc	0.97 b	0.87 b	2.36 a	1.83 ab	1.80 a
	Wheat	0.33 c	0.07 a	0.05 a	1.33 c	0.90 b	0.79 b	2.42 a	1.93 b	1.81 a
	Nil	0.04 a	0.03 a	0.02 a	0.93 a	0.62 a	0.61 a	2.30 a	1.89 b	1.80 a
Two-way ANOVA										
Soil type		***	***	***	**	***	***	ns	***	***
Residue		***	***	*	***	***	***	ns	**	***
Residue × soil type		*	***	*	*	**	**	ns	*	***

3.3. MIR-predicted SOC fractions

For the Podzol, only the POC pool acted as the major sink during residue decomposition. Following residue addition, POC was the highest with wheat-residue and the lowest with chickpea-residue during the whole incubation period. The predicted concentrations of HOC and ROC in the canola- and chickpea-residue treatments was about 25% lower than the control or wheat-residue-amended soil at 48 months (Table 1).

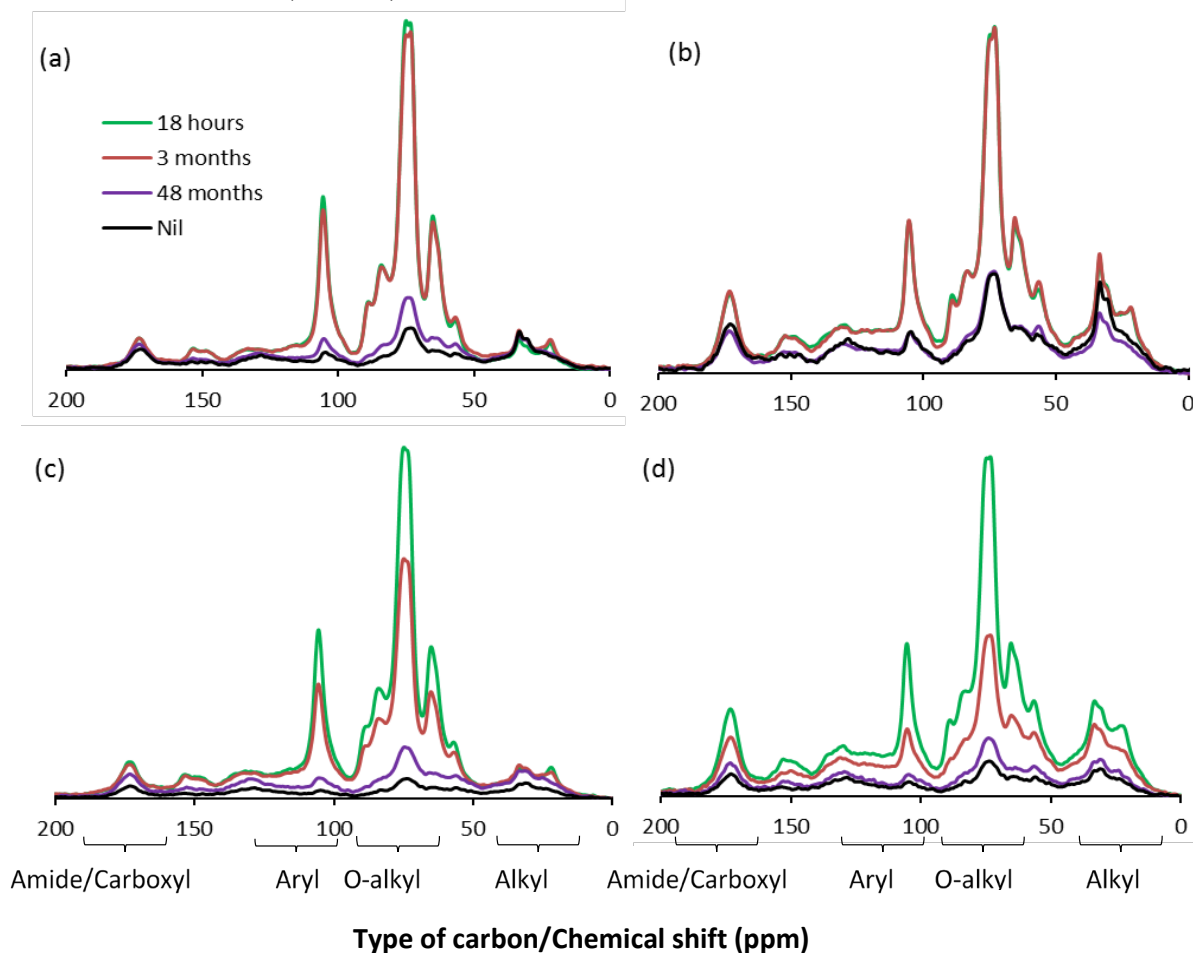


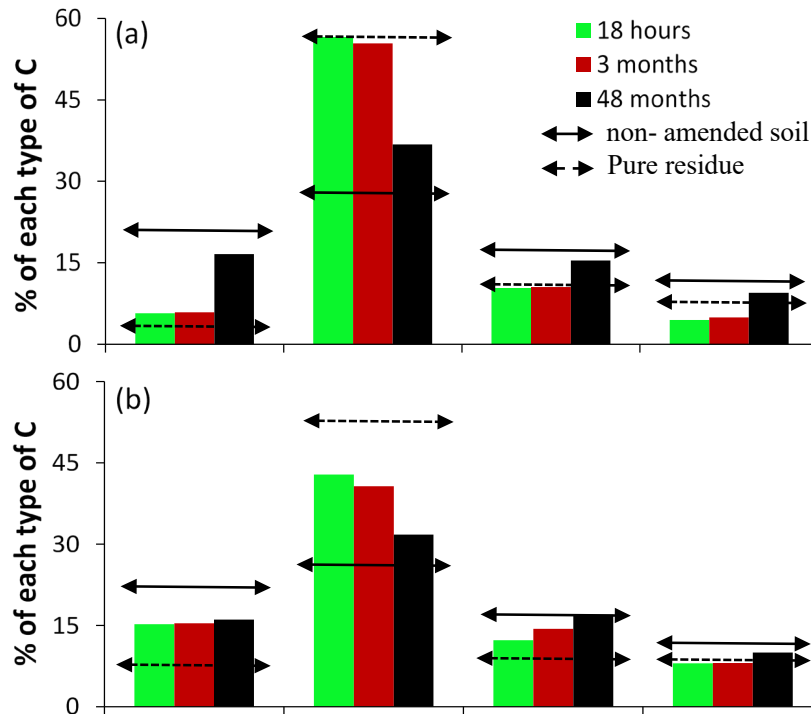
Figure 4. Solid-state ^{13}C CP/MAS NMR spectra acquired from the HF-treated Podzol amended with wheat (a) and chickpea (b) residue and the Cambisol amended with wheat (c) and chickpea (d) and non-amended control (nil) after 18 hours, 3 and 48 months.

Incorporation of crop residue into the Cambisol led to a significant increase in MIR-predicted POC and HOC, but not ROC (Table 1). The increase in POC at 3 months accounted for 45% of the increase in SOC. The MIR-predicted POC was higher in the Cambisol receiving wheat than chickpea and canola residue at 3 months, but the difference between residue treatments decreased with time and the effect of residue on POC diminished after 15 months. A similar trend was also detected for the HOC pool except that the concentration of HOC at 48 months remained higher in the residue-amended soils than the control.

3.4. Chemical composition of SOC

All pure crop residues were dominated by O-alkyl C which accounted for more than 50% of total signal intensity (Fig. 4). The aromatic C and alkyl C were low and varied between 4 and 10%. Chickpea residue contained more alkyl C (8%) than did wheat residue (4%). During residue decomposition, C loss was mainly from O-alkyl C, followed by aryl C, and alkyl C in chickpea-amended soils only (Fig. 4). Consequently, the proportion of O-alkyl C decreased with time, in contrast to increase in the proportion of alkyl C (Fig. 5). Changes in each C type were minimal between 18 hours and 3 months in the Podzol (Fig. 4), but apparent loss of all type of C, especially O-alkyl C, was detected in Cambisol (Fig. 5a, b). The final distribution of each type of C in the Cambisol was similar between residue-amended and non-amended soils (Fig. 5c, d). However, the proportion of O-alkyl C was 25 and 13% higher in wheat- and chickpea-residue-amended Podzol than the control, respectively, in contrast to 28-30% decrease in alkyl C (Fig. 5a, b). Noticeably, loss of alkyl C was only detected in chickpea-amended Podzol after 3 months (Fig. 4).

The alkyl-to-O-alkyl C ratio was higher in chickpea than in wheat residue, and in Podzol than Cambisol without residue amendment (Fig. 6). The alkyl/O-alkyl C ratio significantly increased within 18 hours in chickpea-residue-amended compared to wheat-residue-amended soils. Regardless of residue type, this ratio showed no change in the Podzol between 18 hours and 3 months, but increased by 40% in the Cambisol over the same period (Fig. 6).



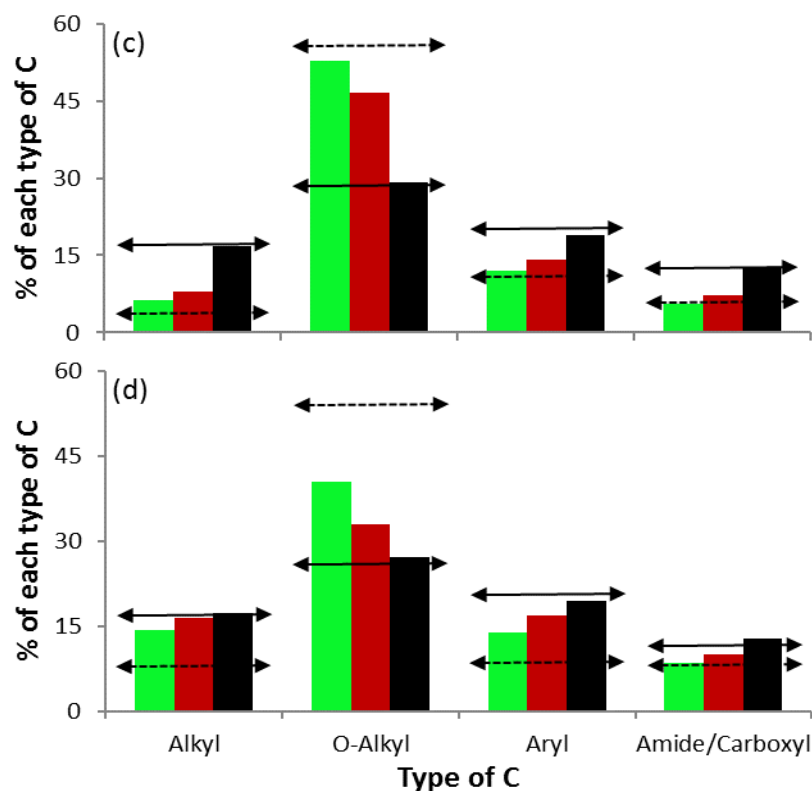


Figure 5. Distribution of each type of C in the HF-treated Podzol amended with wheat (a) and chickpea (b) residue and the Cambisol amended with wheat (c) and chickpea (d) residue after 0, 3 and 48 months.

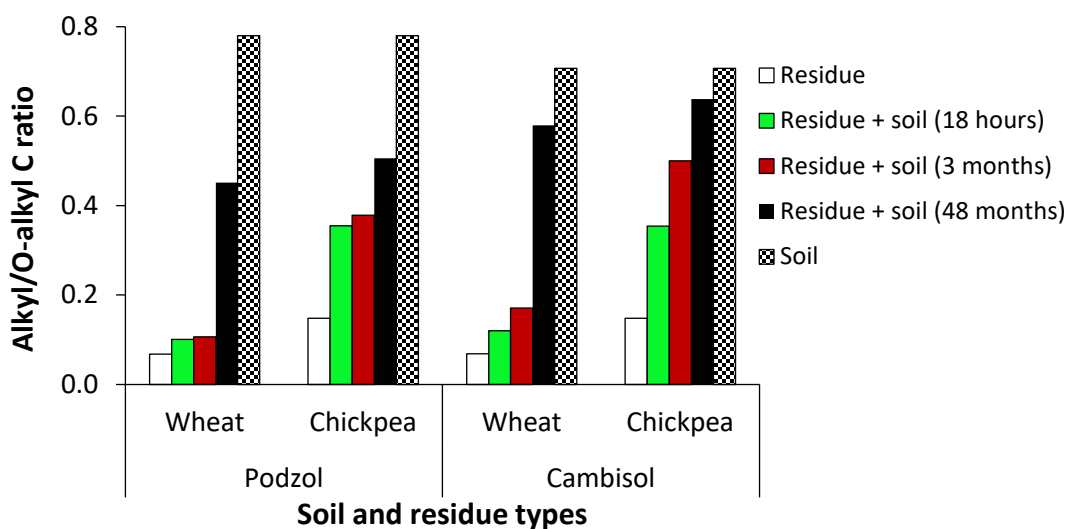


Figure 6. Alkyl/O-alkyl C ratios in residues and the Podzol and Cambisol with and without wheat and chickpea residue amendments after 18 hours, 3 and 48 months.

4. Discussion

4.1. Effect of residue amendment on change in soil pH

Chickpea and canola residues were more effective in ameliorating topsoil acidity compared to wheat residues, and this effect persisted for at least 48 months. This was attributed to the relatively high alkalinity generated from the decomposition of chickpea and canola residues during the first 3 months, as reported by Butterly et al. (2013). The relationship between ash alkalinity content in residues and their liming potential had been well established (Butterly et al., 2011; Noble et al., 1996; Tang et al., 1999). Biological reactions such as decarboxylation of organic anions or ammonification of organic N compounds were believed to be the main mechanisms of residue-induced increase in soil pH (Butterly et al., 2011; Rukshana et al., 2012; Tang and Yu, 1999). Particularly, chemical association of H^+ with organic anions might have contributed greatly to raising the soil pH of the Podzol because its initial pH (4.5) was likely lower than the pK_a values of most of organic acid groups (Butterly et al., 2011; Rukshana et al., 2012). Also, an increase in soil pH due to abiotic reactions could have subsequently facilitated biological reactions which might have been initially suppressed by low pH of the Podzol.

Initial soil pH appeared to be critical in determining the net effect of residue amendment on the change in soil pH after 48 months. For instance, the liming effect of chickpea and canola residues persisted 48 months after addition but the extent of liming effect (pH increase) was less in the Cambisol than in the Podzol, provided that the two soils had similar pH buffer capacities (Butterly et al., 2013). In addition, the soil pH in all residue treatments was lower than the initial pH in the Cambisol but not in the Podzol (Fig. 1). Nitrification and subsequent nitrate leaching were mainly responsible for the decrease in soil pH over time (Marschner and Noble, 2000; Tang and Yu, 1999; Xu et al., 2006; Xu and Coventry, 2003). Ample evidence has indicated that biological reactions such as nitrification were more sensitive to low pH than ammonification, and that nitrification rates increased linearly with increasing soil pH over the pH range of 4 to 6.5 (Fu et al., 1987; Hayatsu, 1993; Reid and Waring, 1979). In this study, nitrification was greatly inhibited in the Podzol but favored in the Cambisol with a higher initial pH (Butterly et al., 2013), which could account for re-acidification of the residue-amended Cambisol at 48 months. Tang and Yu (1999) and Tang et al. (1999) also found that the liming effect of residue amendments was greater in soils with lower initial pH due to reduced nitrification.

4.2. Effect of initial soil pH and residue quality on total SOC and C fractions

This study demonstrated that the decomposition of crop residues was retarded in the Podzol with lower initial soil pH relative to the Cambisol during the first 9 months. Specifically, the decrease in total SOC in the Podzol due to residue decomposition was less apparent (25%) than that in the Cambisol (55%). Moreover, POC acted as the major C sink for residue-derived C in the Podzol, in contrast to the depletion of POC and recovery of residue C in HOC within 3 months in the Cambisol. Restricted microbial activity at the lower initial soil pH might account for the decreased decomposition rate of residues in the Podzol, given the negative relationship between microbial activity and soil pH in the range of 4.3 to 5.3 (Kemmitt et al., 2006; Motavalli et al., 1995; Pietri and Brookes, 2008). Contrarily, the rapid build-up of HOC in the Cambisol following residue amendments within 3 months could be attributed to enhanced decomposition and humification of residues at its higher initial pH. Many studies have found that efficient microbial process favored by certain soil conditions often resulted in more C stabilized in humic fraction (Cotrufo et al., 2013; Martins et al., 2012; Prescott, 2010).

Residue type affected the SOC content in the Cambisol initially (after 0 and 3 months of incubation), but showed no impact after 9 months. Chickpea residue, with a low C/N ratio, decomposed faster than the wheat residue with a higher C/N ratio during the first 9 months. This is consistent with other findings where microbial activity was enhanced by the addition of plant residues with higher N contents (Bayala et al., 2005; Hirobe et al., 2004; Teklay and Malmer, 2004; Trinsoutrot et al., 2000). Nevertheless, SOC content in the residue-amended soils was not affected by residue type at 48 months, contradicting the long-held belief that residues varying in quality, as assessed by N, phenol and lignin contents, would contribute differently to SOC content (Fließbach et al., 2007; Puttaso et al., 2011). Other field studies also found that residue quality did not affect SOC stabilization on time scales of 1.5-3 years (Gentile et al., 2010; Gentile et al., 2011; Helfrich et al., 2008). Possibly, as the C/N ratios of the decomposing substrates reduced with the extent of decomposition, the limiting factors affecting the microbial growth shifted from N to C availability. Recent studies highlighted that physical protection mechanisms rather than intrinsic biochemical recalcitrance of C played a more important role in regulating long-term SOC stabilization (Rabbi et al., 2013; Rabbi et al., 2014). In this study, all residue C could have been equally decomposed at the later stages if physical protection from soil minerals were similar or less significant in both soils low in clay content.

The apparent priming effect of chickpea and canola residues on SOC decomposition in the Podzol but not Cambisol might be related to their liming effect. In contrast to the Cambisol where HOC and ROC fractions showed gradual decline with time, these pools were relatively stable in the Podzol with no residue addition. Given that physical protection of HOC and ROC fractions from soil minerals was likely negligible in the Podzol (clay content less than 2%), chemical constraints such as low soil pH would have accounted for their higher stability. Thus, increase in soil pH following the addition of chickpea or canola residue could promote SOC decomposition in the Podzol, possibly via enhanced microbial growth and activity, or increased solubility of SOC (Andersson and Nilsson, 2001; Garbuio et al., 2011). The delayed priming effect of canola residue on the HOC fraction, compared with chickpea residue, was consistent with its delayed liming effect reported by Butterly et al. (2013). Also, wheat residue, showing the least liming effect in the Podzol, was less decomposed and had the least impact on SOC decomposition. It can be assumed that soluble organic anions, once released from chickpea or canola residue, favored microbial C decomposition of native SOC via enhanced energy sources as well as soil alkalization.

4.3. Effect of residue quality and initial soil pH on the chemical composition of total SOC

The residue C chemistry showed little impact on the chemical composition of total SOC in both soils at 48 months. In this study, changes in the proportion of alkyl and O-alkyl C in both soils with time followed the general trend of an increase in the ratio of alkyl/O-alkyl with the extent of residue decomposition reported by other studies (Baldock et al., 1997; Carvalho et al., 2009; Nierop et al., 2001). Loss of C occurred predominantly from O-alkyl C, resulting in an increase in the proportion of both alkyl C and aryl C. The increase in alkyl/O-alkyl C ratio was attributed to the selective degradation of more biological labile C and accumulation of more recalcitrant aliphatic material such as lipids and biopolyesters (Almendros et al., 2000; Baldock et al., 1997). This was also aligned with the fact that aliphatic compounds make up a significant portion of soil humic fractions (Almendros et al., 1998; Augris et al., 1998). The intrinsic biochemical recalcitrance of alkyl C might indicate that chickpea residues with high alkyl C content would

contribute more to the final SOC content at 48 months, however, the chemical composition of total SOC did not differ between two residues.

The chemical composition of total SOC at 48 months was more affected by the initial soil pH than the quality of residues. The ratio of alkyl/O-alkyl C acted as an indicator of the change in the extent of residue decomposition as affected by either soil pH and residue types. The reduced decomposition of residues at low pH was supported by the invariably lower alkyl/O-alkyl C ratios in the residue-amended Podzol than Cambisol. Also, the accumulation of O-alkyl C in the Podzol at 48 months, compared with the control, was in line with the build-up in POC following residue amendments. The apparent increase in alkyl/O-alkyl C ratio within 18 hours in chickpea-amended soil, relative to wheat-amended soil, was consistent with the highest liming effect and decomposition rate of chickpea residue in the Podzol. On the other hand, loss of alkyl C from chickpea-amended Podzol between 3 and 48 months, relative to the control, coincided with increase in soil pH and decrease in HOC and ROC pools, indicating an enhanced decomposition of alkyl C following chickpea-induced increase in soil pH. Many studies found that alkyl C could be selectively preserved in acidic soils, but was vulnerable to decomposition under high-pH conditions (Nierop et al., 2003, 2005; Wang et al., 2016).

5. Conclusions

The decomposition of crop residues and their priming effects largely depended on residue type, initial soil pH and their interactions. Microbial decomposition of crop residue at the initial stage (9 months) was greatly retarded by poor residue quality (high C:N ratio) and lower initial soil pH. Long-term SOC sequestration in the Cambisol was less affected by residue quality. Efforts to increase total SOC content in soils with higher initial pH should rely on increases in total C input. The residue-induced change in soil pH was possibly an important mechanism in regulating long-term SOC stabilization in the Podzol with low initial soil pH. Amelioration of acidity for acid sandy soils by incorporation of crop residue should also consider the loss of SOC via the liming effect of different residues. More than one addition might be required for different residues to produce significant difference in SOC composition over 48 months.

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