Changes in Particulate and Mineral Associated Organic Carbon with Land Use in Contrasting Soils

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Abstract

Soil organic carbon (OC) is the largest terrestrial C stock and soils’ capacity to preserve OC varies with many factors including land use, soil type and depth. We investigated the effect of land use change on particulate organic matter (POM) and mineral-associated organic matter (MOM) in soils. Surface (0-10 cm) and sub-surface (60-70 cm) soil samples were collected from paired-sites (native and cropped lands) of four contrasting soils. Bulk soils were isolated into POM and MOM fractions, which were analysed for mineralogy, OC and nitrogen, isotopic signatures and $^{14}$C content. POMs of surface soils were relatively unaffected by land use change, possibly because of continuous input of crop residues, while corresponding POM in sub-surface lost more OC. In surface soils, oxides-dominated MOM lost more OC than phyllosilicates- and quartz-dominated MOM, which is attributed to diverse OM input and the extent of OC saturation limit of soils. In contrast, oxides-associated fractions were less affected in the sub-surface soils than the other two MOM fractions, possibly due to OC protection via organo–mineral associations. Changed isotopic signature (linked with vegetation) across the fractions suggested that fresh crop residues constituted the bulk of OM in surface soils (supported by greater $^{14}$C). Increased isotopic signatures and lower $^{14}$C in sub-surface MOM fractions suggested the association of more microbially processed, aged OC in oxides-rich fractions than other MOMs. Results reveal that quantity and quality of OC after land use change was influenced by the nature of C input in surface soils and by mineral-organic association in sub-surface soils.
Keywords: Soil organic matter, organo-mineral association, organic carbon saturation, microbial decomposition, land use change

1 Introduction

Globally, organic carbon (OC) content in the top 0 − 100 cm soil has been estimated to be between 3,500 and 4,800 Pg C (Lehmann and Kleber, 2015) and nearly a quarter of this amount is present in the top 20 cm of soil (Guo and Gifford, 2002; Jobbagy and Jackson, 2000). The soil OC pool is much greater than other terrestrial pools, i.e., vegetation (420-620 Pg C) and the atmosphere (829 Pg C) (Lehmann and Kleber, 2015). Thus, soils are viewed as a major reservoir and a potential C sink; which could sequester significant quantities of atmospheric CO$_2$. However, whether the soils will act as a sink or source of CO$_2$ is highly dependent on the land use, soil properties (Feller and Beare, 1997) — especially clay minerals, and biophysical factors, including climate (Jobbagy and Jackson, 2000). According to Six et al. (2002) land use and management are among the most important determinants of soil OC stocks. Land use changes, especially conversion of native grassland and forest to crop land, typically lead to decline in soil OC (Guo and Gifford, 2002), due to a reduction in C input in the soil. Several studies have shown 20 to 50% decline in soil OC when native forest or grassland was converted to cropping (Birch-Thomsen et al., 2007; Bruun et al., 2015; Guo and Gifford, 2002; Luo et al., 2010; McDonagh et al., 2001). The response of soil OC of a native ecosystem to land use conversion depends heavily on the specific vegetation type extent in the native land system and in the system to which the land has been converted (Bruun et al., 2009).
Soil organic matter (OM) is composed of diverse mixtures of OC compounds with differing in physiochemical properties, degree of stabilisation and turnover rate. So, different OM pools may show different susceptibility to land use and management. Thus, it appears that the extent to which land use change influences soil OM dynamics can be best evaluated by separating OM into fractions (Chenu and Plante, 2006; Jones and Singh, 2014; Sollins et al. 2006, 2009). Separation of OM pools can be done by different physical fractionation (e.g., particle size, aggregate, density separation) methods which are effective for separating specific C pools responsive to land use and management (Collins et al., 1996; Tan et al., 2007). Sequential density fractionation is able to separate soil OM into labile (light) and stable (heavy) OC pools differing in structure and function (Sollins et al., 1999; Wander and Traina, 1996) based on their specific densities (Sollins et al., 2006; von Lu’tzow et al., 2007). Moreover, this fractionation method is affirmed to focus the organo-mineral associations in MOM pools properly which has a prime importance in C turnover dynamics in soils (Basile-Doelsch et al., 2007).

Generally, labile (particulate) OM (POM) is rapidly decomposable (Zimmermann et al., 2007), hence has a relatively shorter turnover time; and it is often considered more sensitive to land use conversion than mineral associated OM (MOM) (Gregorich and Janzen, 1996; Leifeld and Kögel-Knabner, 2005; Six et al., 1998). The organo–mineral association usually results in a reduced biodegradation of OM, due to chemical interactions of OM on reactive mineral surfaces (Chenu and Plante, 2006). Thus, the MOM pool has a relatively longer turnover time (Kögel-Knabner et al., 2008) and is presumably less sensitive to land use change. Several studies have reported a decrease in POM pool as a result of land use change (Conant et al., 2004;
Franzluebbers and Stuedemann, 2002; Six et al., 1998), while others did not find any significant change in POM resulting from changed land use (Conant et al., 2003; Jastrow, 1996; Leifeld and Kögel-Knabner, 2005). Moreover, despite the longer turnover time of MOM pool compared to POM, the former pool may also respond quickly to land use changes (Chenu et al., 2001; Leifeld and Kögel-Knabner, 2005; Shang and Tissen, 2000). For example, Shang and Tissen (2000) reported a loss of 19-59% OM from MOM (silt- and clay- sized OM) pool in an Oxisol (Ferralsol in WRB) due to the land use change from forest to cereal cropping.

There are several characterization methods used for obtaining insights about soil OM pools. Among them, stable isotope (δ\textsuperscript{13}C and δ\textsuperscript{15}N) analysis is a powerful tool to assess the source and/or the degree of microbial transformation of OM in soil (Hobbie and Ouimette, 2009; Sollins et al., 2009) as well as the dynamics of different soil OM pools with land use change (Hobley et al., 2017; Leifeld and Kögel-Knabner, 2005; Rabbi et al., 2014). Radioactive isotope of C (\textsuperscript{14}C) can provide the information of mean age of C in soils which can indicate the stability of soil OM (Trumbore, 2009) pools in relation to land use conversion (Schrumpf et al., 2013) and soil types (Eusterhues et al., 2007).

Although, land use effect on soil OM has been studied extensively, study on the control of soil types, particularly soil mineralogy in relation to the impact of land use on OC pools is still rare. Moreover, majority of the studies evaluating the land use change effects on soil OC are limited to surface (~30 cm) soil (Bruun et al., 2009; Lorenz and Lal, 2005; Rabbi et al., 2014), as OC concentration and turnover are usually greater in surface soil (Conant et al., 2001). There is a growing body of evidence that land use change can also affect the OC dynamics in sub-surface
soil (Don et al., 2011; Poeplau et al., 2011; Wright et al., 2007). Thus, our study was conducted to evaluate the effects of land use change, from native vegetation to cropping, on the POM and MOM pools of both surface and sub-surface soils with contrasting mineralogies. This will aid to identify the sensitivity of the OC pools towards land use conversion varied with depth and soil types, which ultimately could provide the idea of the best land use practice for the specific soil to maintain or restore soil health by preserving OC and mitigate global warming.

2 Materials and Methods

2.1 Site description

We sampled paired sites, i.e. native and cropped, to study the effects of land use conversion on soil OC dynamics. Four sites were selected in New South Wales, Australia, with each site representing a different soil type – Ferralsol, Luvisol, Vertisol and Solonetz. The paired sites at each location represented similar landscape, position, climatic conditions and major soil characteristics. The native lands were composed of open woodland and cropped sites had been used for cereal cultivation for over 15 years in all the soil types. Open woodlands had very few scattered low trees, mainly dominated by Eucalyptus species in association with grass understorey, and never been grazed. The cultivated cereal was maize, wheat + barley and sorghum for Ferralsol, Luvisol and Vertisol, respectively. The Solonetz cropped site had been covered with maize and lucerne. Detailed geological and climatic descriptions for the sites are given in supplementary information (S) Table S1.
2.1 Soil sampling and general characterisation of bulk soils

Random bulk soil samples were collected from several spots for the two depths: surface (0–10 cm) and sub-surface (60–70 cm) of each of the paired sites. The sub-surface samples were taken to represent the absolute mineral soils. The random samples from the corresponding depth were mixed thoroughly to make one composite sample for each of the individual sites based on the protocol used in many earlier relevant studies (Kaiser et al., 2010, 2012; Lehmann et al., 2007; Sleutel et al., 2011; Sollins et al., 2006, 2009). Admittedly, that a sampling strategy with separate two or three field replications instead of compositing replications at each site would have been advantageous to find out the spatial variability, but we still believe this sampling protocol would not limit the capacity of this study to assess land use effects in contrasting soils.

The samples were air dried, ground and passed through a 2 mm sieve. Soil pH and electrical conductivity (EC) were measured in water using 1:5 soil-to-water ratio. Cation exchange capacity (CEC) and exchangeable cations were determined by the silver thiourea method (Chhabra et al., 1975). Particle size analysis was conducted by the pipette method (Gee and Bauder, 1986). The total Fe and Al concentrations (also Mn and Si) of crystalline pedogenic oxides were estimated by the dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson, 1958). Poorly crystalline Fe and Al were quantified by acid ammonium oxalate (pH 3.0) extraction in the dark (Schwertmann, 1964); and organically complexed Fe and Al were extracted using Na-pyrophosphate (pH 10.0) (McKeague, 1967). All extracted cations were analysed using an atomic emission spectrometer (Varian 720-ES). All soil analyses were performed in triplicate except the particle size analysis where only one replicate was analysed.
2.2 Sequential density fractionation

Bulk soil samples from both land use sites and depths were separated into four density fractions (<1.8 (POM), 1.8–2.2 (1.8DF), 2.2–2.6 (2.2DF) and >2.6 (>2.6DF) g cm$^{-3}$) using the method adopted from Jones and Singh (2014) and Sollins et al. (2006, 2009) as described in Yeasmin et al. (2017a, 2017b). The densities were selected with the aim of isolating POM (<1.8 g cm$^{-3}$) and MOM (>1.8 g cm$^{-3}$) fractions in the studied soils. Briefly, 30 g of air dried soil was weighed into a 250 ml centrifuge bottle; 125 mL of sodium polytungstate (SPT) solution with a density of 1.8 g cm$^{-3}$ was added. The contents were shaken for 3 h on a horizontal shaker (300 rpm) and the suspension was centrifuged for 30 min at 970 g. The material floating on the top of SPT was extracted under suction and SPT was recovered by filtering the supernatant liquid using 0.7 μm glass fiber filter and returned to the same centrifuge tube. The tube was shaken again for 1 h on a horizontal shaker, centrifuged as described earlier and the floating material aspirated for second time. The two batches aspirated floating materials (POM: <1.8 g cm$^{-3}$) were combined and rinsed multiple times with deionised water on a 0.7 μm glass fiber filter to remove residual SPT until the water EC dropped below 50 μS cm$^{-1}$. The remaining sediment in the centrifuge bottle from the above fraction step was mixed with 125 mL SPT solution of 2.2 g cm$^{-3}$ and the whole process was repeated to obtain the 1.8DF (1.8–2.2 g cm$^{-3}$). Similarly, the next two density fractions (2.2DF and >2.6DF) were obtained using 2.6 g cm$^{-3}$ SPT solution (2.2DF: supernatant; 2.2–2.6 g cm$^{-3}$ and >2.6DF: Sediment; >2.6 g cm$^{-3}$). The whole fractionation process replicated twice. After rinsing, all recovered fractions were oven dried at 40°C, hand ground to a fine powder and stored in glass vial for further analyses.
2.3 Mineralogical analysis

Mineralogical composition of the bulk soils and density fractions was determined by X-ray diffraction (XRD) analysis using a monochromatic CuKα radiation (GBC MMA diffractometer, Diffraction Technology Pty Ltd, Australia) as described in Yeasmin et al. (2017a). Briefly, the clay fractions (<2 μm) were isolated from bulk soils by the sedimentation method and analysed for both random powder and basally oriented specimen. Density fractions were also analysed as random powder to determine their mineralogical composition. The relative proportion of each mineral in the density fractions expressed semi-quantitatively by integrating mineral peak area using TracesV6 software program (version 6.7.13, GBC Scientific Equipment Pty Ltd, Australia).

2.4 Soil organic carbon, nitrogen and stable isotopic ratio analyses

Total C, total N, δ¹³C and δ¹⁵N of the bulk and density fractions were determined by isotopic mass spectroscopy (Thermo Finnigan Delta V). Delta values are expressed in parts per mil (‰) on the Vee Pee Dee Belemnite (VPDB) scale. Duplicate samples were analysed and the precisions for total C, total N, δ¹³C and δ¹⁵N were 0.06–0.5%, 0.01–0.12%, 0.01–0.09‰ and 0.05–0.09‰, respectively. As there were no carbonates in the soil samples, total C values were considered as the OC concentration in the samples.

2.5 ¹⁴C analysis

Due to the budget and time limitations, ¹⁴C content was determined using the bulk soils and the 2.2DF MOM fraction of the surface and sub-surface samples from cropped land only. The
selection of the density fraction was based on the result from our previous study (Yeasmin et al. 2017b), where we found this 2.2DF as the most potential for organo-mineral associations in the similar soils. For these analyses, samples were pre-treated with 2M HCl at 40°C for at least 24 h until dry to remove possible carbonate contaminants. The treated samples were combusted for 9 h at 900°C and the resultant CO$_2$ was then reduced to graphite using the Fe/H$_2$ method (Hua et al., 2001). The graphite was then loaded into an aluminium cathode for accelerator mass spectrometry (AMS) analysis using the STAR accelerator (Fink et al. 2004). A small portion of the graphite target was analysed for $\delta^{13}$C using an elemental analyser/isotope ratio mass spectrometer (Vario microcube EA, Elementar, Germany and IsoPrime Isotope Ratio Mass Spectrometer (IRMS), GV Instruments, UK). The $^{14}$C content was corrected for isotope fractionation using measured $\delta^{13}$C, and is reported as percent modern C (pMC) (Stuiver and Polach, 1977).

2.6 Statistical analyses

Pearson’s correlation coefficient ($r$) was calculated to observe the relationships of MOM associated OC (MOM-OC) with extractable Fe + Al, MOM-OC loss due to land use change with extractable Fe + Al in soils and aromatic: aliphatic ratio with OC in density fractions using the software package IBM SPSS 21.0.
3 Results

3.1 General soil characteristics

Soils from paired sites (native and cropped land) at both depths were non saline (EC 0.09–0.75 dS m\(^{-1}\)) and acidic in reaction (pH ≤ 6.8), except for the sub-surface soils of the Vertisol, which were slightly alkaline (pH 7.7–7.8) (Table 1). The CEC of each soil did not vary under different land uses but increased with depth for the Luvisol, Vertisol (native) and Solonetz soils and decreased slightly with depth in the Ferralsol. In general, the Vertisol had the highest CEC (200–231 mmol kg\(^{-1}\)), followed by the Luvisol (182–222 mmol kg\(^{-1}\)), the Ferralsol (69–96 mmol kg\(^{-1}\)) and the Solonetz (36–50 mmol kg\(^{-1}\)).

The textures of the studied soils were different; the surface soil of the Vertisol had the highest clay content (61%), followed by the Ferralsol (34%), Luvisol (31%), and the Solonetz had the lowest content (5%) regardless of land use. The clay content almost doubled in the sub-surface samples of the Ferralsol and Luvisol, but there was no noticeable change in the Vertisol (Table 1). In the Solonetz, the clay content increased about six-fold and ten-fold in the sub-surface soil of the native and cropped sites, respectively.

The extractable Fe and Al values were substantially different for the soils at corresponding depth and land use (Table S2). The highest amount of total (DCB-extracted) Fe and Al was found in the Ferralsol, followed by the Luvisol, Vertisol and Solonetz in regardless of the land use and depth. Poorly crystalline Fe (Fe\(\text{ox}\)) and Al (Al\(\text{ox}\)) concentrations were also highest in the Ferralsol (except for Fe in the native surface Vertisol) followed by the Vertisol, Luvisol and Soloentz. The Fe\(\text{ox}\):Fe\(\text{DCB}\) ratio expresses the fraction of poorly crystalline Fe of the total Fe
Vertisol had the highest Fe$_{\text{ox}}$:Fe$_{\text{DCB}}$ ratio, ranging from 0.27–0.53, followed by the Solonet (0.04–0.31) and Luvisol (0.09–0.19). The Ferralsol had the lowest Fe$_{\text{ox}}$:Fe$_{\text{DCB}}$ ratio (0.03–0.09), suggesting the presence of greater proportions of crystalline Fe (e.g., goethite and hematite) in this soil (Table S2). A slight decrease in the Fe$_{\text{ox}}$:Fe$_{\text{DCB}}$ ratio in the sub-surface depth was noticed in all soils. This was due to the relatively faster crystallisation of amorphous Fe in the sub-surface soils compared to that in surface soils, because of their lower OM contents (Schwertmann and Cornell 1991). Pyrophosphate extractable Fe (Fe$_{\text{Na-py}}$) and Al (Al$_{\text{Na-py}}$) ranged from 0.05–9.0 and 0.04–3.7 g kg$^{-1}$, respectively, and the order of the abundance was: Ferralsol > Luvisol > Solonet > Vertisol. Organically complexed (Na-py extractable) Fe and Al concentrations decreased noticeably in sub-surface soils, compared with surface soils, for both types of land use. There was no clear effect of land use change on pyrophosphate extractable Fe and Al.

### 3.2 Mineralogy of density fractions

The oriented and random powder of the clay fractions of the bulk soils showed contrasting mineralogy for the studied soils (Figs. S1, S2, S3i and S4i). The Ferralsol clay fraction showed the dominant presence of goethite, hematite and gibbsite. Kaolinite and illite were dominant in the clay fraction of the Luvisol, and present in moderate amounts in the Solonet. The Vertisol was dominated by smectite, with kaolinite present in moderate amount. Feldspars and quartz were also identified in the clay fraction of Luvisol, Vertisol and Solonet. The mineralogy of the paired soils was similar (Figs. S1, S2, S3i and S4i), but the overall mineral presence became slightly prominent in the XRD patterns of the sub-surface soils (Figs. S2 and S4i).
The POM fraction of all the surface soils was dominated by OM, as demonstrated by the presence of the broad hump in the ~3.55 to 4.45° (d-spacing) region of the XRD patterns (Fig. S3ii). Trace to small amounts of kaolinite, hematite and gibbsite were present in the Ferralsol, kaolinite and illite in the Luvisol and Solonetz, and kaolinite and smectite in the Vertisol (Table 2). The proportion of these minerals then increased with increasing density. Greater proportion of hematite, goethite and gibbsite was observed in the three MOM fractions (1.8DF, 2.2DF and >2.6DF) of the Ferralsol. A trace to moderate presence of kaolinite was also observed in these Ferralsol fractions. On the other hand, 1.8DF and 2.2DF of the other soils were dominated by phyllosilicates; kaolinite and illite in the Luvisol, kaolinite and smectite in the Vertisol and kaolinite only in the Solonetz. These fractions also showed the presence of feldspars and quartz, and the proportion of these minerals increased in the heaviest fraction (>2.6DF) while the phyllosilicate proportion decreased. Similar to the bulk soils, the mineralogy of the density fractions of the soils did not vary with land uses, but did show some minor differences between the surface and sub-surface soils (Table 2). For example, there was a slight increase in the proportion of kaolinite, hematite and anatase in the Ferralsol fractions, an increase in the proportion of phyllosilicates in the other three soils, and an increase in some oxide minerals in the Vertisol (hematite and anatase) and Solonetz (goethite and anatase).

It is evident that three different mineral phases were dominant in the MOM fractions (>1.8 g cm⁻³) of the four soils regardless of the land use and depth: Fe and Al oxides in the Ferralsol fractions (1.8DF, 2.2DF and >2.6DF); phyllosilicates in the 1.8DF and >2.6DF; and feldspars and quartz (primary minerals) in >2.6DF of the Luvisol, Vertisol and Solonetz. These three
MOM fractions are referred to as oxide-OM, phyllosilicate-OM and quartz-OM, respectively, throughout the manuscript.

3.3 Organic carbon and nitrogen contents of bulk soil and density fractions

Bulk samples of the Ferralsol had the greatest OC concentration (12–63 g kg\(^{-1}\)) amongst the four soils regardless of the land use and depth (Table 3). The OC concentration in all bulk subsurface samples was much lower than their corresponding surface samples. There was a decrease in OC concentration with land use change from native vegetation to cropping in all soils. The N concentration (0.3–6 g kg\(^{-1}\)) followed a trend similar to that of OC concentration in all soils. The C:N ratio in the soils ranged from 7–14, with generally similar values for the surface soils and a slight variation among sub-surface soils.

The POM fraction of the Solonetz and Luvisol surface samples under native vegetation (remnant woodland) contributed 33–73% and 21–49% to the total OC and N, respectively (Fig. 1a1, b1). In the Ferralsol (tropical forest) and Vertisol (native grasses) surface soils, the contribution of POM to total OC was only 7–10% and thus a relatively much greater MOM contribution to total OC than in the other two soils (Fig. 1a1). The OC concentration in the POM fraction of the native surface soils ranged between 240 and 355 g kg\(^{-1}\) (Table 3), with the highest concentration in the Ferralsol compared to the other three soils. Among the MOM fractions (>1.8 g cm\(^{-3}\)), the oxide-OM (1.8DF + 2.2 DF + >2.6DF) fractions of the Ferralsol had also greater OC concentrations (245–351 g kg\(^{-1}\)) than the phyllosilicate-OM (1.8DF + 2.2 DF) fractions of the Solonetz (125–138 g kg\(^{-1}\)), Luvisol (111–124 g kg\(^{-1}\)) and Vertisol (94–101 g kg\(^{-1}\)) soils, irrespective of the type of land use (Table 3). The quartz-OM fraction (>2.6DF)
of these latter three soils had the smallest OC concentration range, at 0.4–6 g kg\(^{-1}\). The distribution of N concentration among the MOM fractions also followed the same pattern as OC in the soils: oxide-OM > phyllosilicate-OM > quartz-OM fractions. The C:N ratio varied widely in the density fractions of all soils, between 3 and 43, and showed a decreasing pattern with increasing density with few exceptions in both land uses (Table 3). Overall, the C:N ratio was greater in the oxide-OM fractions, followed by the phyllosilicate-OM and then the quartz-OM fractions.

There was a notable difference in the OC and N concentrations with land use change of each soil at corresponding depth (Table 3). After clearing the native vegetation and shifting to annual cropping, the overall POM still accounted for a major proportion (21–40%) of the total OC in the Luvisol (forage and cereal), Solonetz (improved pasture) and Vertisol (cereal) as compared to the Ferralsol OC (4%) (Fig. 1). This was also reflected in the OC concentration change (Fig. 2a1); with the former three soils lost only 5–8% of the POM-OC, whereas this loss was 20% in the Ferralsol POM fraction. The OC concentration loss with land use change increased to 50% in the oxide-OM fractions of the Ferralsol. The loss was lower in the MOM fractions of the other three soils, with a maximum of 30% loss in the phyllosilicate-OM fractions and 29% lost from the quartz-OM fraction. Nitrogen concentration was depleted most from the phyllosilicate-OM fractions of the Vertisol (54%) followed by the oxide-OM fractions of the Ferralsol (49%), Solonetz (31%) and Luvisol (24%) phyllosilicate-OM fractions (Fig. 2b1). Surprisingly, the quartz-OM fractions either lost very little N (1%) or N concentration was increased (28%) with the land use change to cropping. This resulted in a decreased C:N ratio in the quartz-OM fraction of the Luvisol, Vertisol and Solonetz (Fig. 2c1). The C:N ratios changed
less or increased in the POM and phyllosilicate-OM fractions of these three soils. The Ferralsol fractions depleted relatively more in C:N ratio, except in the >2.6DF fraction.

Considering the land uses and soil depths, variation was observed in fraction recovery (Fig. 1), particularly in the Luvisol and Solonetz samples (82-100%), which might cause overall increased proportion in the fractions where recovery was higher. Considering this fact, major contribution of the MOM fractions to the total OC was still evident (Fig. 1a2), mostly in all sub-surface soils under both land uses, compared with surface soils (Fig. 1a1). The proportion of N to the total N in fractions also followed a similar pattern to that for OC (Fig. 1b2), with a noticeably greater contribution of the phyllosilicate-OM to the total N compared to the oxide-OM and quartz-OM fractions. Overall, OC (1–409 g kg\(^{-1}\)) and N (0.1–15 g kg\(^{-1}\)) concentrations decreased remarkably with depth in all soils and showed similar trends in the density fractions (POM > oxide-OM > phyllosilicate-OM > quartz-OM) with those of the surface soils (Table 3). However, an increase in OC concentration in the POM fraction of the Ferralsol and Luvisol was noticed in sub-surface under both type of land uses. The C:N ratio became wider (3–90) and the increasing trend of the ratio in the density fractions of all soils was more prominent in the sub-surface soils than in the surface samples (Table 3).

With land use change, OC concentration reduced by 7–27% in the POM fraction of all sub-surface soils, in the order: Solonetz > Vertisol > Ferralsol > Luvisol (Fig. 2a2). In sub-surface MOM fractions, the OC concentration decreased the least in the oxide-OM (7–18%) of the Ferralsol, compared to 7–48% loss in the phyllosilicate-OM fractions (Solonetz > Luvisol > Vertisol) and 5–25% loss in the quartz-OM fraction. The N concentration (Fig. 2b2) reduced
most from both the POM fractions of all sub-surface soils and the oxide-OM of the Ferralsol. The C:N ratio decreased (3–23%) in the POM fractions of all soils in sub-surface depth (Fig. 2c2). The oxide-OM fractions ratio showed less depletion/increase (-3 to 42%). The ratio mostly decreased in phyllosilicate-OM fractions (-57 to 3%) in the order Solonet > Luvisol > Vertisol, and this reduction continued in the quartz-OM fractions (-13 to -57%) of sub-surface samples.

### 3.4 Stable isotopic signatures of bulk soil and density fractions

The Ferralsol bulk soils had lower δ^{13}C (-25.9 to -22.3‰) and higher δ^{15}N (6.2–9.7‰) values, as compared with the other three soils, irrespective of land use and depth (Table 3).

In general, both isotopic values were lowest in the POM fraction of all surface soils under both land uses, with δ^{13}C values ranging from -27.1 to -21.1‰ and δ^{15}N ranging from 1.7 to 8.1‰ (Table 3). The δ^{13}C and δ^{15}N values then increased (-27.2 to -20.4‰ for δ^{13}C; 1.7-10.8 ‰ for δ^{15}N) with the density in all surface soils for both land uses. The increment continued throughout all MOM fractions of the Ferralsol, but increased up to 2.2DF for the Luvisol, Vertisol and Solonetz and then decreased in the >2.6DF. Oxide-OM fractions had overall lower δ^{13}C and δ^{15}N values, compared with the phyllosilicate-OM and quartz-OM fractions. After land use change, δ^{13}C value change (Δδ^{13}C) across the density fractions showed an enrichment of 13C by 0.4–4.8‰, with a pattern increasing with density in the Ferralsol, which was different to other three soils (Fig. 3a1). The Vertisol fractions had enrichment of 13C but to a smaller extent (0.9–1.6‰), while the Luvisol fractions showed an overall depletion of 13C (up to -1.5‰). The POM fraction had a large 13C enrichment (4.6‰) in the Solonetz fractions but the
enrichment then decreased with density (up to 1.5‰). The δ¹⁵N value change (Δδ¹⁵N) showed a depletion of ¹⁵N in all fractions of the Ferralsol (up to -3.8‰), Luvisol (up to -2‰) and Solonetz (up to -0.6‰, except the >2.6DF), whereas there was an enrichment of ¹⁵N (up to 2.3‰) in the Vertisol fractions (Fig. 3b1).

The δ¹³C and δ¹⁵N values in the density fractions of sub-surface soils followed trends similar to surface soils; i.e., increased with increasing density and lower values in the Ferralsol fractions than in the other soils (Table 3). However, both isotopic values increased (-25.9 to -11.7 ‰ δ¹³C, 3.4–14.4 ‰ δ¹⁵N) in the density fractions of all soils with depth under both land uses. Prominent enrichment of isotopic values in sub-surface density fractions also exhibited with land use change (Fig. 3a2). In general, δ¹³C value enrichment was lower in the POM fractions (up to 2.2‰); it then increased (up to 3.8‰) in the MOM fractions of all soils in the order: oxide-OM > phyllosilicate-OM (Vertisol > Luvisol > Solonetz) > quartz-OM (Fig. 3a2). The δ¹⁵N change showed an overall consistent enrichment (up to 4.5 ‰) with increasing density in all soils after land use conversion (Fig. 3b2).

3.5 ¹⁴C content

The ¹⁴C content value in all the surface bulk soils from cropped site and their 2.2DF fractions was >100 pMC (101.4-108.1), except in the Vertisol bulk soils (99.7 pMC), indicating the presence of modern OC (Table 3). Modern OC means the OC bears a signature of post-bomb (post-1950) ¹⁴C content (higher than 100 pMC) (Hua et al., 2013). In the sub-surface cropped soils, ¹⁴C content ranged from 60.2 - 81.3 pMC in the bulk soils and 62.7 - 107.8 pMC in the 2.2DF fractions, suggesting relatively older OC (¹⁴C content was lower than 100 pMC).
compared to their corresponding surface soils. The $^{14}$C content of the sub-surface bulk soils was in the order of: Ferralsol < Vertisol < Solonetz < Luvisol and it was in the order: Vertisol < Ferralsol < Luvisol < Solonetz in the 2.2DF fractions (Table 3). The $^{14}$C content of 2.2DF fractions of cropped soils was negatively correlated with the corresponding $\delta^{13}$C ($R^2 = -0.41$) and $\delta^{15}$N ($R^2 = -0.24$) (Fig. 4).

4 Discussion

4.1 General trends of organic carbon throughout the density fractions of surface and sub-surface soils under native and cropped land use

Narrower C:N ratio and larger $\delta^{13}$C and $\delta^{15}$N values in the MOM fractions, compared to the POM fractions, in all the soils (Table 3) suggest a more advanced stage of decomposition of OM in the MOM fractions (Baldock et al., 1992; John et al., 2005). Generally, the C:N ratio in soils decreases with depth (Rumpel and Kögel-Knabner, 2011), which is ascribed to more microbially processed OC (Boström et al., 2007). The C:N ratio in the MOM fractions of the sub-surface soils of this study also showed an overall decrease (or slight increase); however, an increase in the C:N ratio in the POM fractions of all soils was observed (Table 3). This trend was more evident in the Ferralsol. The increased C:N ratio in the sub-surface POM fractions could be due to the lack of microbial processing (Schrumpf et al., 2013). However, the increased stable isotopic values ($\delta^{13}$C and $\delta^{15}$N) do not support this assertion (Table 3). Increased C:N ratios in the POM fractions could be related to the composition of the below-ground OM source. It has been reported that fine roots in sub-surface soils have lower N contents than the surface soil, which can result in a large C:N ratio (Ugawa et al., 2010). The increased C:N could also
be due to the presence of charred organic material (Rumpel and Kögel-Knabner, 2011), however we did not specifically measured the charcoal C concentration in the samples.

4.2 Effect of land use change on surface soil organic carbon: influence of vegetation type

The POM fractions of surface mineral soils are known to be more sensitive to land use change than the MOM fractions, due to their relatively fast turnover rates and close link to litter input (Bird et al., 2007; Ellerbrock and Gerke, 2013; Golchin et al., 1995; Haynes, 2005). The changes in the proportion (Fig. 1a1) and concentration of OC (Fig. 2a1) in the surface soil fractions in this study contradict with these previously reported results. In our study, the MOM fractions of the surface soils lost relatively more OC with land use change than the POM fractions. Input of organic residues from annual crops probably compensated the decomposed POM, which resulted in a small loss of POM-OC after converting native land to cropping land. Ontl et al. (2015) reported an increase in unprotected POM-OC pool after monitoring OM in soil with different cropping systems; i.e., grass and cereals for three years. They attributed the gain of this pool to the least decomposed and most recent deposited OM from crop residues.

The pattern of OC concentration in the MOM fractions (Table 3) of the four soils (oxide-OM > phyllosilicates-OM > quartz-OM) indicates the role of minerals, especially the surface reactivity of mineral phases, in OC stabilisation (Kögel-Knabner and Kleber, 2011). It has been extensively reported that soil with Fe (hydro)oxides and poorly crystalline Al silicates have a greater potential to protect more OC than the soils dominated by phyllosilicates and primary
minerals (Eusterhues et al., 2005; Kögel-Knabner et al., 2008; Kögel-Knabner and Kleber, 2011). Significant positive correlations of MOM-OC to total (DCB) and poorly crystalline (oxalate) Fe and Al oxides support this hypothesis (Fig. S5). With larger specific surface area (SSA) and hydroxyl surface groups, these minerals are able to form stronger bonds via ligand exchange to associate with OC, as compared to the weaker cation bridge on phyllosilicates (Gu et al., 1995; Kaiser and Zech, 2000; Yeasmin et al., 2014). Consequently, OC adsorbed to oxide mineral surfaces is expected to be more protected from decomposition than the OC associated with permanent charged phyllosilicates (Yeasmin et al., 2014).

Organic C loading based on the specific surface area of minerals is also important; as this can control the stability of the organo–mineral associations (Kaiser and Guggenberger, 2003). The capacity of soils to stabilise OC can be restricted by their OC saturation limit (Hassink, 1997). When a soil approaches its OC saturation, OC stability declines, probably to the changes in type and strength of OC–mineral interactions with increasing OC loading (Kleber et al., 2007; Sollins et al., 2009). As surface loading increases beyond a certain threshold, the new OC might not form direct bonds to mineral surfaces but may instead form organic multilayers through hydrophobic interactions or polyvalent cation bridge between organic ligands of already sorbed and new organic molecules (Kaiser and Guggenberger, 2003). In the zonal model for OM stabilisation, Kleber et al. (2007) proposed the occurrence of greater abundant weaker organic–organic interactions than stronger organo–mineral interactions in soils with increasing OC loadings. Therefore, the weakly sorbed OC may be relatively more sensitive to land use change being more readily available for microbial decomposition than the directly bonded and strongly sorbed OC (Krull et al., 2003). The greater loss of OC and N from MOM fractions of the studied
soils (Fig. 2a1,b1) is consistent with the OC saturation concept. The soils in the study, particularly Ferralsol, possibly received large organic residue input when under native vegetation, which subsequently added more OC to the soil (Table 3). Therefore, the MOM fractions may have already attained their OC saturation point and a significant proportion of OC was associated by forming weak organic–organic multilayers under native vegetation land use (Kleber et al., 2007). Although we did not measure the saturation point of our soil, however, if we compare the data of our soils with the OC saturation curve derived by Fujisaki et al. (2018), it showed that the soil had already reached the saturation point. Since the soil had OC greater than its saturation point, the land use change to agricultural cropping resulted in the microbial mineralisation of the OC that was retained by weak association with soil minerals.

The change in OC and N concentrations in the density fractions of the surface soils was more influenced by the vegetation type rather than the soil mineralogy. The significant negative correlations ($r = -0.97$) of MOM-OC depletion with total and poorly crystalline Fe and Al oxide concentrations (Fig. 5a) in the cropped surface soils indicate a weaker control of soil minerals on OC loss due to the effect of land use change. This perception is also supported by the change in $\delta^{13}$C and $\delta^{15}$N values. Generally, changes in stable C isotopic composition ($^{13}$C/$^{12}$C) of soil occur for two reasons (Werth and Kuzyakov, 2010): (i) preferential stabilisation of substrates with $^{12}$C (e.g., lipids, phenols, lignin) or $^{13}$C (e.g., cellulose, amino acids, hemicellulose) and/or (ii) stabilisation of microbial products that are enriched in $^{13}$C after one or more microbial utilisation cycles (because of release of CO$_2$ with $^{12}$C) (Guina and Kuzyakov, 2014; Sollins et al., 2006; von Lützow et al., 2006). The second mechanism (microbial utilisation) causes greater $^{13}$C enrichment than the first mechanism (Guina and Kuzyakov, 2014); this $^{13}$C
increment also shows an increased pattern with the density. However, the trend of $\delta^{13}C$ change (either decrease or increase) among the POM and MOM fractions were marginal and/ inconsistent in all soils except the Ferralsol (Fig. 3a1). The might suggests accumulation of less decomposed OC under high OC input in surface soils (Margenot et al., 2015). The overall high $^{14}C$ content in the bulk soils and MOM (2.2DF) fraction also supports the presence of young C in surface soils (Table 3). Therefore, we hypothesise that the change in stable isotopic values reflects the change in the isotopic signature of the OM source; i.e., the vegetation type rather than the preferential stabilisation or microbial utilisation of OC. Although we did not estimate the share of different types of vegetation C in OC pool after land use change, we could relate the isotopic signature variations with the information of the existing vegetation types (C3 or C4) in the paired sites. It is known that C3 plant species have a lower $\delta^{13}C$ value (~ -23 to -40‰) than C4 plant species (~ -9 to -19‰). The Ferralsol native open woodland site was perhaps covered by both C3 and C4 plants. When the land use shifted to a C4 maize crop, the $\delta^{13}C$ value increased because of the dominance of the input of OM from C4 plants. Mixed plant species (C3 and C4) supposedly also existed on the Luvisol and Vertisol native sites (woodland), and after clearing and growing C3 cereals, such as wheat and barley, might cause an overall decrease in $\delta^{13}C$ of all the fractions of these soils.

4.3 Effect of land uses on sub-surface soil organic carbon: influence of soil mineralogy

A greater potential of sub-surface soil for OC preservation has been explicitly proven by isolating older C in the separated OM pools of sub-soils than its bulk OM (Helfrich et al., 2007;
Paul et al., 2001; Rumpel et al., 2008) and surface soil OM (Bruun et al., 2008; Hobley et al., 2017). Prolonged protection of OC in the sub-surface soil has been attributed to stronger organo–mineral interactions with smaller OM loading (Kögel-Knabner et al., 2008; Schrumpf et al., 2013). However, Fontaine et al. (2007) reported reduced input of OM; i.e., energy limitation for microbes in the sub-surface soil, as the reason for slow decomposition of OM, rather than strong organo–mineral association. They showed that supplying of fresh plant-derived C stimulated the decomposition of old OM in the sub-surface soil (60–80 cm). Linking these two theories, we speculate that there might be a threshold point of OC input/energy supply at which the microbial activity becomes minimum, and that could also be variable among soils, land uses and climatic conditions. This assumption is in line with the trend of OC loss from both POM and MOM fractions in the sub-surface soils of this study (Fig. 2a2). Overall POM-OC losses were similar in all soils, while the loss of MOM-OC was greater in the Luvisol, Vertisol and Solonetz than in the Ferralsol (Fig. 2a2). Reduced OM input (compared to the surface layer) was perhaps still greater than the previously mentioned threshold point that led to continued microbial activity in the sub-surface soils. Under low OC input conditions, microbes probably first utilised the most easily available POM fractions and then mineralised relatively weakly bound OC to mineral surfaces in the MOM fractions. Greater reduction in the POM-OC of the sub-surface soils than the surface soils (Fig. 2a1,a2), and subsequent variable MOM-OC losses among the soils, i.e. greater losses in the phyllosilicate-OM and quartz-OM fractions of the Luvisol, Vertisol and Solonetz than in the oxide-OM of the Ferralsol (Fig. 2A2), support our hypothesis. Desorption of the relatively weakly bound OC from phyllosilicates and
quartz was probably enhanced by mechanical disturbance during tillage in cropped lands, which caused greater OC loss with the change in land use.

In general, variable losses of OC with land use conversion indicate the influence of soil mineralogy. This is supported by a significant positive correlation between change in the MOM-OC and poorly crystalline Fe and Al oxides in the cropped soils (Fig. 5b). The data indicate smaller losses of OC with increased concentration of poorly crystalline Fe and Al oxides in the sub-surface soils. Kasier and Guggenberger (2000) also emphasised the importance of Fe oxides in providing surface area for OC sorption in sub-surface soils. Kögel-Knabner et al. (2008) also suggested Fe oxides as more important sorbents than phyllosilicates, for the formation of organo-mineral associations in sub-surface soils. Parafitt et al. (1997) also reported greater OC stabilisation in Fe oxides and poorly crystalline Al silicates rich Andisol and Inceptisol, which was resistant to land use change from pasture to cropping. In this present study, relatively greater radiocarbon age of the oxides-MOM fraction of the Ferralsol compared to age (average) of the phyllosilicates-OM fractions of the other three soils establish the potential of Fe and Al oxides in long-term OC stabilisation in soil.

The distinct increasing enrichment trend of both $^{13}$C and $^{15}$N in the density fractions of all sub-surface soils (Fig. 3a2,b2) demonstrated the presence of more microbially processed OC and supports the hypothesis of OC stabilisation by association with minerals (Gunina and Kuzyakov, 2014) in sub-surface soils. However, the increased C:N ratio in the Ferralsol fractions (as opposed to the other soils) did not support the microbial processing hypothesis (Fig. 2c2). This could happen for several reasons, such as (i) C-rich OM input in the cropped
land which leached down to the sub-soil, (ii) enrichment of microbial-derived C, such as sugar (Spielvogel et al., 2008), and (iii) selective decomposition of N rich OM (Yeasmin et al., 2014).

Greater loss of N than of OC in the Ferralsol fractions supports the selective utilisation of N-rich OM in the Ferralsol hypothesis (Fig. 2a2,b2). Nitrogen depletion pattern in the MOM fractions of the studied soils, which was greater in the Ferralsol than the other soils (Fig. 2b2), might suggest a higher affinity of phyllosilicates and quartz minerals towards N-rich OC compounds (Jagadamma et al., 2010; Mikutta et al., 2009); this is consistent with the overall higher depletion of C:N ratios in the Luvisol, Vertisol and Solonetz soils (Fig. 2c2).

5 Conclusions

Our results show that the land use change impacts the OC in both surface and sub-surface soils. The MOM fractions are not necessarily resistant to land use conversion, particularly in the surface soils. Inconsistent changes in δ13C and δ15N values (close to crop residue), a decreasing trend in the OM decomposition index and a greater 14C content highlight the vegetation effect on the OC change through fresh OM supply in the surface soils. Under different OC loading conditions in surface soil, POM was less sensitive due to continuous input of agricultural crop residues. Among the MOM fractions, oxide-OM fractions of the Ferralsol lost more OC than did the phyllosilicate-OM and quartz-OM fractions of the Luvisol, Vertisol and Solonetz after land use changes. The variable OC loss in the MOM fractions can be attributed to greater OM supply in the Ferralsol and possible OC saturation on the mineral surface. In sub-surface soils with limited OC supply, the POM fraction was more sensitive to land use change than in the surface soil. In the MOM fractions of the sub-surface soils, oxides-OM fractions of the Ferralsol
preserved more OC than did the phyllosilicate-OM and quartz-OM fractions of the Luvisol, Vertisol and Solonetz, after land use changes. The OC accumulated in the MOM fractions of sub-surface soils was highly microbially processed (enriched in $\delta^{13}$C and $\delta^{15}$N) and relatively older (lower $^{14}$C content) in nature.

Organic matter concentration in both the POM and MOM fractions of the surface soils is highly sensitive to land use change. The association of OM with minerals is more relevant in preserving soil OC and controlling the impact of land use change in the sub-surface soils. Sub-surface soils can act as a potential C sink for long-term C storage, together with improved land use and vegetation management systems.

**Data availability**

All data have been included in the supporting information of this article.

**Author contribution**

Yeasmin, S. planned and conducted the experiment, performed data analysis and critical interpretation of data and wrote the manuscript. Singh, B. helped plan the experiment, supervised the laboratory work and was involved in interpretation of the results and reviewed the manuscript. Johnston, C.T. supervised DRIFT data analysis and reviewed the manuscript. Sparks, D.L. reviewed and edited the manuscript. Quan, H. performed radiocarbon analysis, $^{14}$C (pMC) calculation and helped to interpret the results and reiewed the manuscript.
Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

The corresponding author acknowledges the financial support of the International Postgraduate Research Scholarships and Postgraduate Research Support Scheme of the University of Sydney, NSW, Australia. The authors express gratitude to Australian Institute of Nuclear Science and Engineering for providing a research grant (ALNGRA15536) for AMS $^{14}$C analysis. We also thank Dr Claudia Keitel of the Centre for Carbon, Water and Food, The University of Sydney, and Dr Elizabeth Carter and Dr Joonsup Lee of the Vibrational Spectroscopy Facility at The University of Sydney, for technical and analytical supports in mass spectroscopic analysis and DRIFT analysis, respectively. All data have been included in the supporting information of this article.

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**Figure Captions**

**Fig. 1** Proportion of total OC (a) and total N (b) in the density fractions of four surface (1= 0–10 cm) and sub-surface (2= 60–70 cm) soils under native and cropped land uses. Density fractions (DF): POM = <1.8 g cm⁻¹ and MOM: 1.8DF = 1.8–2.2 g cm⁻¹, 2.2DF = 2.2–2.6 g cm⁻¹ and >2.6DF = >2.6 g cm⁻¹. The numbers on the top of the columns represent total recovery after sequential density fractionation.

**Fig. 2** Changes in OC (a) and N (b) concentrations and C:N ratio (c) in density fractions of four surface (1= 0–10 cm) and sub-surface (2= 60–70 cm) soils with land use conversion from native to cropped. Density fractions (DF): POM = <1.8 g cm⁻¹ and MOM: 1.8DF = 1.8–2.2 g cm⁻¹, 2.2DF = 2.2–2.6 g cm⁻¹ and >2.6DF = >2.6 g cm⁻¹. Error bars represent S.E. of two replicates.
Fig. 3 Change in isotopic values, i.e., Δδ^{13}C (a) and Δδ^{15}N (b) in density fraction of four surface (1= 0–10 cm) and sub-surface (2= 60–70 cm) soils with land use change. Density fractions (DF): POM = <1.8 g cm$^{-1}$ and MOM: 1.8DF = 1.8–2.2 g cm$^{-1}$, 2.2DF = 2.2–2.6 g cm$^{-1}$ and >2.6DF = >2.6 g cm$^{-1}$. Error bars represent S.E. of the two replicates. Change (Δ) = cropped – native

Fig. 4 Relation of δ^{13}C (a) and δ^{15}N (b) in the MOM fraction (2.2DF = 2.2–2.6 g cm$^{-3}$) of cropped soils (surface + sub-surface)

Fig. 5 Relation of mineral associated (MOM)-OC loss [% loss = (cropped-native) /native ×100] from 1.8DF, 2.2DF and >2.6DF] with land use conversion with oxalate (ox) and DCB extractable Fe + Al oxides of cropped soils in surface (a: 0–10 cm) and sub-surface (b: 60–70 cm). r = Pearson’s correlation coefficient and * p <0.05 of the correlations
Table 1 General characteristics of the four bulk soils (<2 mm) from two depths of paired sites (native and cropped) at four locations in NSW, Australia

<table>
<thead>
<tr>
<th>WRB soil order</th>
<th>Land uses</th>
<th>Depth (cm)</th>
<th>pH (1:5 H₂O)</th>
<th>EC (1:5 H₂O)</th>
<th>CEC (mmol c kg⁻¹)</th>
<th>Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
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All parameters representing mean value of three replicates, except particle size analysis; standard error (S.E.) for pH = 0.00-0.02, EC = <0.01, CEC = 0.1-10.
### Table 2  Semi-quantitative mineralogical composition obtained from XRD analysis of the density fractions of four soils from two depths (surface and sub-surface)

<table>
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<th>WRB soil order</th>
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<th>Feldspars</th>
<th>Phyllosilicates</th>
<th>Metal oxide</th>
<th>Feldspars</th>
<th>Quartz</th>
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Density fractions: POM = <1.8 g cm$^{-3}$ and MOM = 1.8-2.2 g cm$^{-3}$, 2.2DF = 2.2-2.6 g cm$^{-3}$ and >2.6DF = >2.6 g cm$^{-3}$. Mineral abbreviations used: Kaol = kaolinite, Ill = illite, Sm = smectite, Goe = goethite, Hem = hematite, Gib = gibbsite, Rut = rutile, Ant = anatase, Mic = microcline, Ort = orthoclase, Pla = plagioclase, Alb = albite. Estimated proportion of mineral: xxxx = dominant (>60%), xxx = large (40-60%), xx = moderate (20-40%), x = small (5-20%), tr = trace (<5%), - = non-detectable. *Yeasmin et al. (2017b)
### Table 3

Mean values (n=2) of organic carbon (OC) and nitrogen (N) concentrations, C:N ratios, δ^{13}C, δ^{15}N and \(^{14}C\) activity in the bulk and density fractions of four soils (surface and sub-surface) from native and cropped sites

<table>
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<tr>
<th>WRB soil order</th>
<th>Depth (cm)</th>
<th>Density fraction</th>
<th>OC (g kg(^{-1}))</th>
<th>N (g kg(^{-1}))</th>
<th>C:N</th>
<th>δ^{13}C (‰)</th>
<th>δ^{15}N (‰)</th>
<th>(^{14}C) (pMC)</th>
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Density fractions: POM = <1.8 g cm\(^{-3}\) and MOM: 1.8DF = 1.8-2.2 g cm\(^{-3}\), 2.2DF = 2.2-2.6 g cm\(^{-3}\) and >2.6DF = >2.6 g cm\(^{-3}\). pMC = percent modern C. S.E. of the bulk soils: OC (0.0-0.1), N (0-0.7), δ^{13}C and δ^{15}N (0-0.02); POM: OC (0.1-3.7), N (0-1.2), C (0.1-1.4), δ^{13}C (0-0.1) and δ^{15}N (0-0.01); 1.8DF: OC (0.1-1.7), N (0-0.4), C (0-0.6), δ^{13}C (0-0.04) and δ^{15}N (0-0.02); 2.2DF: OC (0.2-2.2), N (0-4), C (0-1.1), δ^{13}C (0-0.03) and δ^{15}N (0-4); >2.6DF: OC (0.0-7), N (0-0.1), C (0-1.2), δ^{13}C (0-0.1) and δ^{15}N (0-0.01). ±1σ uncertainty of pMC = 0.19-0.28.
<table>
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<th>Depth (cm)</th>
<th>Density fraction</th>
<th>OC (g kg(^{-1}))</th>
<th>N (g kg(^{-1}))</th>
<th>C:N</th>
<th>(\delta^{13}C) (‰)</th>
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<td>-22.7</td>
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</tbody>
</table>

Density fractions: POM = <1.8 g cm\(^{-3}\) and MOM: 1.8DF = 1.8-2.2 g cm\(^{-3}\), 2.2DF = 2.2-2.6 g cm\(^{-3}\) and >2.6DF = >2.6 g cm\(^{-3}\); pMC = percent modern C. S.E. of the bulk soils: OC (0.0-0.6), N (0-0.1), C (0-0.7), \(\delta^{13}C\) and \(\delta^{15}N\) (0-0.02); POM: OC (0.1-3.7), N (0-1.2), C (0-1.1-1.4), \(\delta^{13}C\) (0-0.1) and \(\delta^{15}N\) (0.01); 1.8DF: OC (0.1-1.7), N (0-0.4), C (0-0.6), \(\delta^{13}C\) (0-0.04) and \(\delta^{15}N\) (0-0.02); 2.2DF: OC (0-2.2), N (0-4), C (0-0.1), \(\delta^{13}C\) (0-0.03) and \(\delta^{15}N\) (0-4); >2.6DF: OC (0-0.7), N (0-0.1), C (0-0.1), \(\delta^{13}C\) (0-0.1) and \(\delta^{15}N\) (0-0.01). ±1σ uncertainty of pMC = 0.19-0.28.
Figure 3
Figure 4

(a) $y = 5.26x - 14.9$, $R^2 = 0.41$

(b) $y = -3.05x + 124.5$, $R^2 = 0.24$
Figure 5

(a) 0-10 cm

Oxalate and DCB extractable Fe + Al in cropped land soils (g kg⁻¹)

- (Fe+Al)ox
  - \( y = -4.3367x - 39.29 \)
  - \( R^2 = 0.94, r = -0.97^* \)
- (Fe+Al)DCB
  - \( y = -0.5055x - 48.83 \)
  - \( R^2 = 0.95, r = -0.97^* \)

(b) 60-70 cm

MoO3-OC change (%) with landuse conversion

- (Fe+Al)ox
  - \( y = 11.841x - 124.61 \)
  - \( R^2 = 0.98, r = 0.99^* \)
- (Fe+Al)DCB
  - \( y = 0.8515x - 94.29 \)
  - \( R^2 = 0.52, r = 0.72^* \)