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Turnover of organic carbon and nitrogen in soil assessed from δ^{13} C and δ^{15} N changes under pasture and cropping practices and estimates of greenhouse gas emissions

Ram C. Dalal ^{a, c,*}, Craig M. Thornton ^b, Bruce A. Cowie ^b

^a Department of Science, Information Technology, Innovation and the Arts, Dutton Park, Qld 4102, Australia

^b Department of Natural Resources and Mines, Rockhampton, Qld 4700, Australia

^c School of Agriculture and Food Sciences, University of Queensland, Brisbane, Qld 4072, Australia

HIGHLIGHTS

- Soil carbon declines under cropping but it is maintained under perennial pasture after land use change from native vegetation.
- Soil nitrogen declines both under cropping perennial pasture after land use change from native vegetation.
- Total greenhouse gas emissions from land use change for cropping includes CO2 and N2O.
- Total greenhouse gas emissions from land use change for pasture includes CO2, N2O and CH4.
- Long-term sustainability of the system requires consideration for both C and N management.

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ABSTRACT

The continuing clearance of native vegetation for pasture, and especially cropping, is a concern due to declines in soil organic C (SOC) and N, deteriorating soil health, and adverse environment impact such as increased emissions of major greenhouse gases (CO2, N2O and CH4). There is a need to quantify the rates of SOC and N budget changes, and the impact on greenhouse gas emissions from land use change in semi-arid subtropical regions where such data are scarce, so as to assist in developing appropriate management practices. We quantified the turnover rate of SOC from changes in δ^{13} C following the conversion of C₃ native vegetation to C₄ perennial pasture and mixed C₃/C₄ cereal cropping (wheat/sorghum), as well as δ^{15} N changes following the conversion of legume native vegetation to non-legume systems over 23 years. Perennial pasture (Cenchrus ciliaris cv. Biloela) maintained SOC but lost total N by more than 20% in the top 0–0.3 m depth of soil, resulting in reduced animal productivity from the grazed pasture. Annual cropping depleted both SOC and total soil N by 34% and 38%, respectively, and resulted in decreasing cereal crop yields. Most of these losses of SOC and total N occurred from the $>250 \,\mu\text{m}$ fraction of soil. Moreover, this fraction had almost a magnitude higher turnover rates than the 250–53 μ m and <53 μ m fractions. Loss of SOC during the cropping period contributed two-orders of magnitude more CO_2 -e to the atmosphere than the pasture system. Even then, the pasture system is not considered as a benchmark of agricultural sustainability because of its decreasing productivity in this semi-arid subtropical environment. Introduction of legumes (for N₂ fixation) into perennial pastures may arrest the productivity decline of this system. Restoration of SOC in the cropped system will require land use change to perennial ecosystems such as legume-grass pastures or native vegetation.

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1. Introduction

Organic C and N are integral components of soil organic matter, which is essential for agricultural sustainability and environmental stability, and provides a long-term terrestrial C sink. Although land use change from native vegetation to introduced pasture has been shown to increase, decrease or produce no change on soil organic C (SOC) stocks (Murty et al., 2002), that from native vegetation to cropping has consistently shown a decrease in soil organic C and N, frequently exceeding 50% of SOC and soil N levels (Haas et al., 1957; Dalal and Mayer, 1986a, 1986b, 1986c; Guo and Gifford, 2002; Dalal et al., 2005a, 2005b). A global average of 25–30% SOC loss is considered a conservative estimate when soil under native vegetation or permanent pasture is brought under cultivation for cropping (Houghton, 2010).

^{*} Corresponding author at: Department of Science, Information Technology, Innovation and the Arts, Dutton Park, Qld 4102, Australia. Tel.: +61 7 3170 5766; fax: +61 7 3870 5801.

E-mail address: Ram.Dalal@qld.gov.au (R.C. Dalal).

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Harms et al. (2005) studied the effect of land use change from native vegetation to pasture at 32 paired-sites in southern and central Queensland, Australia. Although SOC stocks declined by approximately 7% across all sites (0–0.3 m depth), significant losses in SOC stocks were found in coarse-textured soils such as Lixisols, but not in medium-fine textured soils such as Luvisols and Vertisols. These observations were confirmed for other Lixisols by Dalal et al. (2005a). In these soils, for the 0-0.3 m depth, SOC decreased by 10% and 19% under perennial pasture and cropping after 20-years. In Luvisols-Vertisols mixed soil type, Radford et al. (2007) observed no change in SOC from land use change under native vegetation to that developed for buffel (Cenchrus ciliaris cv. Biloela) pasture, even after 21 years, thus corroborating the observations of Harms et al. (2005). Under cropping, however, SOC declined by 38% and total soil N by 56% at 0-0.1 m depth over the 21-year period. Even at 0-0.3 m depth SOC declined substantially under cropping, by 33% or 21.1 Mg C ha $^{-1}$ during this period.

It is not known whether changes in SOC under pasture and cropping occurred from the SOC originating from native brigalow (Acacia harpophylla) vegetation (C_3-C) or new C inputs from either perennial buffel pasture (C_4) or crops such as sorghum (C_4) after the land use change. The source and turnover rates of SOC can be assessed since δ^{13} C values of C₃ and C₄ vegetation are distinctly different. For example, C₃ plants have δ^{13} C values of -25% to -28%whereas C₄ plants have δ^{13} C values of -11% to -14% (Balesdent et al., 1987; Skjemstad et al., 1994; Dalal et al., 2005a). Furthermore, it is possible to estimate the amount and turnover rates of C from different SOC fractions, such as labile C or particulate organic C, and that in different particle-size fractions (Martin et al., 1990; Balesdent et al., 1998; Lobe et al., 2005). This provides information on turnover rates of SOC and N in different fractions such as $>250 \,\mu\text{m}$, 250–53 μm and <53 µm (Cambardella and Illiott, 1992), which play distinctly different roles in soil aggregation (Tisdall and Oades, 1982) and C sequestration (Six et al., 2002). These fractions or components of SOC can be used in SOC modelling, for example in the RothC (Skjemstad et al., 2004) and APSIM models (Huth et al., 2010).

Loss of SOC under cropping following land use change not only reduces productivity (Radford et al., 2007) but also contributes to greenhouse gas emissions, especially CO₂ to the atmosphere. It is estimated that land use change has contributed from 108 to 188 Pg C since 1850 AD (Pongratz et al., 2009; Houghton, 2010), with a median value of 156 Pg C (1850-2005), of which at least 25% was contributed by SOC loss from agricultural soils (Houghton, 2010). Therefore, SOC loss from an agro-ecosystem also needs to be considered to assess overall impact on greenhouse gas emissions to the atmosphere. Furthermore, since the SOC loss under cropping also leads to soil N loss (Dalal and Mayer, 1986c; Radford et al., 2007), this N loss may contribute to N₂O emissions during organic N mineralisation and from denitrification processes (Dalal et al., 2003). Even a small amount of N₂O emission can make a significant contribution to greenhouse gas emissions to the atmosphere because of its large global warming potential of 298 relative to CO₂ over 100-year time horizon (IPCC, 2007). In addition, land use change from un-grazed native vegetation to pasture contributes to greenhouse gas emissions from grazing livestock as CH₄ emissions, with a global warming potential of 25 relative to CO₂ over 100-year time horizon (IPCC, 2007).

The objectives of this study were to: (i) quantify SOC and total soil N stock changes following land use change from native vegetation to either perennial pasture or annual cropping; (ii) assess the changes in the amounts of different SOC and total N fractions to evaluate the relative lability of these fractions under pasture and cropping; (iii) utilise the changes in ¹³C natural abundance of SOC following the land use change from C₃ (native vegetation) to C₄ (perennial buffel pasture, sorghum) and that of δ^{15} N to estimate the turnover rates of SOC and N in the whole soil and soil fractions; and (iv) estimate partial C and N budget and relative contribution of greenhouse gases from pasture and cropping systems in the context of agricultural

and environmental sustainability. Thus, the outcome of this study will provide the basis for the management practices which will lead to the economic and productive sustainability of the farming systems examined while minimising adverse environmental impacts, including greenhouse gas emissions.

2. Materials and methods

2.1. Sampling site

The study site is located at 24.81°S, 149.80°E at an altitude of 151 m above sea level. Mean annual rainfall is 720 mm and annual potential evaporation is 2100 mm. The mean maximum temperature is 33.1 °C in January and the minimum temperature is 6.5 °C in July (Cowie et al., 2007).

The main soil types at the site are Endosodic Calcic Vertisol and Albic Vertic Luvisol (IUSS Working Group WRB, 2006). Clay contents vary from 21 to 33%, and pH 6.6–6.9 at 0–0.1 m depths across the site (Radford et al., 2007). The dominant native vegetation at the site is brigalow (*A. harpophylla*), and belah (*Casuarina cristata*) and black butt (*Eucalyptus cambageana*) are the co-dominant species. Detailed description of the site is available from Cowie et al. (2007).

Part of the site was cleared in March 1982 and split into a pasture paddock and a cropping paddock. The pasture paddock was sown to buffel pasture (*C. ciliaris* cv. Biloela) in November 1982. Grazing of the pasture commenced a year later and animal stocking rate was adjusted to maintain ground cover > 85% during the experimental period (1983–2005) (Radford et al., 2007). In the cropping paddock, the first cereal crop, sorghum (*Sorghum bicolor* L.) was sown in September 1984. Wheat (*Triticum aestivum* L.) was then sown for the next 10 years and sorghum for the last 9 sorghum seasons. During the fallow period, weeds were controlled by tillage although in later years, minimum tillage practices were introduced for wheat, barley or sorghum crops, depending on plant available water (opportunity cropping). Detailed description on pasture and crop management practices is given by Radford et al. (2007).

2.2. Soil sampling and soil organic matter fractionation

The soil samples were taken in November 2005 at three monitoring sites at three locations, each on native vegetation, pasture and cropped paddocks. Each monitoring site was divided into 5 equal blocks. 5 samples were taken down to 0.4 m depths by a hydraulic-driven corer (0.05 m dia.) and divided into 0-0.1 m, 0.1-0.2 m, 0.2-0.3 m and 0.3–0.4 m depths and bulked for respective depths, producing 3 composite samples at each depth for each land use (3 land uses \times 3 replicates). Since the profile development is weak on the Vertisols, the sampling depths based on different soil horizons were not considered but followed the standard soil depths used in soil sampling earlier at this site (Radford et al., 2007). Moreover, IPCC (2006) guidelines were followed since SOC stocks can be calculated for the top 0.3 m depths. Soil samples were dried at 40 °C and ground to pass <2 mm sieve for soil pH, particle size analysis and carbon fractionation. Intact soil cores from each depth were also taken for bulk density measurements. These samples were dried at 105 °C to a constant weight and bulk density was calculated from the oven dry mass of soil and internal core volume.

The fractionation procedure for particulate organic matter was essentially that of Cambardella and Elliott (1992), modified to separate SOC into >250 μ m, 250–53 μ m and <53 μ m fractions. Briefly, 10 g soil sample (<2 mm size) was dispersed in 30 mL of 5 g/L of sodium hexametaphosphate solution by shaking for 15 h on a reciprocal shaker. The suspension was passed through a stacked set of 250 μ m and 53 μ m sieves, rinsed with deionised water several times, and the materials retained on the sieves were collected (>250 μ m and 250–53 μ m fractions). The collected material was dried at 60 °C for 3 days, weighed and ground to <0.1 mm size for carbon and δ^{13} C,

(3)

nitrogen and δ^{15} N measurements by isotope ratio mass spectrometry. Since water soluble C generally contains <1% of total SOC and not all of that necessarily labile (Cook and Allan, 1992) it was not measured and may have been included in the <53 µm fraction. This fraction may also contain char-C (Skjemstad et al., 2004) and organo-mineral complexes.

2.3. Soil analysis for organic carbon and N, and $\delta^{13}C$ and $\delta^{15}N$

Total soil organic C (SOC), different particle-size organic C, and ¹³C natural abundance of soil, soil fraction samples were determined using an Isoprime isotope ratio mass spectrometer (IRMS) coupled to a Eurovector elemental analyser (Isoprime-EuroEA 3000, Milan, Italy) with 10% replication. Finely-ground samples containing inorganic carbonates were pretreated with HCl before analysis. The isotope ratios were expressed using the 'delta' notation (δ), with units of per mil or parts per thousand ($%_{\circ}$), relative to the marine limestone fossil Pee Dee Belemnite standard (Craig, 1953) for δ^{13} C, using the relationship in Eq. 1 below:

$$\delta^{13} C (\%) = \left(R_{\text{sample}} / R_{\text{standard}} - 1 \right) \times 1000 \tag{1}$$

where *R* is the molar ratio of ${}^{13}C/{}^{12}C$ of the sample or standard (Ehleringer et al., 2000).

The proportion of organic C in soil derived from C₄ vegetation was estimated by using δ^{13} C values and a mixing model (Boutton, 1996; Bekele and Hudnall, 2003; Dalal et al., 2005a; Dalal et al., 2011), as in Eq. 2 below:

$$\begin{aligned} \text{Soil} C_4 &- \text{derived} C_{\text{pasture}} \end{aligned} \tag{2} \\ &= \left(\delta^{13} C_{\text{soil under pasture}} - \delta^{13} C_{\text{C}_3 \text{ soil under native vegetation}} \right) / \\ &\left(\delta^{13} C_{\text{C}_4 \text{ buffel grass roots}} - \delta^{13} C_{\text{C}_3 \text{ soil under native vegetation}} \right) \end{aligned}$$

Soil C₄-derived C_{cropping}

$$= \left(\delta^{13} C_{\text{soil under cropping}} - \delta^{13} C_{\text{soil under native vegetation}} \right) /$$
$$\left(\delta^{13} C_{C_4 \text{sorghum roots}} - \delta^{13} C_{\text{soil under native vegetation}} \right)$$

where $\delta^{13}C_{soil under pasture}$ is the $\delta^{13}C$ value of soil organic C under pasture, $\delta^{13}C_{c4}$ is the average value of $\delta^{13}C$ value of C_4 buffel roots (-11.86‰; Dalal et al., 2005a) and $\delta^{13}C_{c_3}$ soil under native vegetation is the $\delta^{13}C$ value of C_3 soil C under C_3 native vegetation. The proportion of previous vegetation C_3 -derived C in the soil under pasture is the difference between the total SOC stock under pasture and the amount of C_4 -derived C in the pasture soil. Similar calculations were made for the C_4 -derived C in the pasture soil at individual depths and in different fractions, using the corresponding $\delta^{13}C$ values. Thus, no corrections were required for Rayleigh fractionation of enrichment of $\delta^{13}C$ values with soil depth. Also, a similar procedure was followed for the cropped site (sorghum roots, -12.5%) following Diels et al. (2004) and Derrien and Amelung (2011) although only indicative estimates of SOC-C₄ were made due to mixed wheat-sorghum C₃/C₄ cropping systems over the 23-year period.

The mean values of δ^{13} C-SOC measured consisted of C₃ native vegetation and C₄ buffel grass pasture or C₃ + C₄ crops as follows:

$$\begin{split} \delta^{13} \mathsf{C}_{\text{total }(23\text{yr})} &= \left(\delta^{13} \mathsf{C}_{\text{native}} \times \mathsf{C}_{\text{native}} + \delta^{13} \mathsf{C}_{\text{new }(23\text{yr})} \times \mathsf{C}_{\text{new }(23\text{yr})} \right) / \quad (4) \\ & \left(\mathsf{C}_{\text{native}} + \mathsf{C}_{\text{new }(23\text{yr})} \right) \end{split}$$

where δ^{13} C values are that of total soil organic C, under native vegetation (native), and either buffel grass pasture (new) or sorghumwheat cropping (new) and corresponding SOC stocks after 23 years (23 yr) of land use under a given practice. ^{15}N natural abundance of soil samples from the 0–0.1, 0.1–0.2, 0.2–0.3 m and 0.3–0.4 m depths was also determined using an Isoprime isotope ratio mass spectrometer coupled to a Eurovector elemental analyser (Isoprime-EuroEA 3000). Finely-ground samples containing approximately 50 μg N were weighed into 8 \times 5 mm tin (Sn) capsules and analysed against a known set of standards. The isotope ratios were expressed using the 'delta' notation (δ), with parts per thousand (‰), relative to N_{air} standards for $\delta^{15}N$ using the following relationship:

$$\delta^{15} \mathrm{N}(\%) = \left(R_{\mathrm{sample}} / R_{\mathrm{standard}} - 1 \right) \times 1000 \tag{5}$$

where *R* is the molar ratio of the heavy to light isotope (i.e. ${}^{15}N/{}^{14}N$) of the sample or standard.

2.4. Turnover of carbon in whole soil and soil fractions

The rate of loss of native vegetation C_3 -derived C in the whole soil and soil fractions after 23 years under pasture was calculated, as follows (Balesdent et al., 1998; Dalal et al., 2005a):

$$\mathbf{k} = -(\ln C_{\rm t}/C_{\rm o})/t \tag{6}$$

where C_o and C_t are the amounts of C_3 -C initially under native vegetation and at time t, 23 years under pasture after clearing of native vegetation, respectively, and k (year⁻¹) is the rate of loss of C_3 -C from soil and soil fractions. Similar calculations were also made on SOC and SOC fractions from the cropped site although data were considered tentative because of C_3 -C contributions from native vegetation and C_3 crops could not be differentiated and only general trends were shown. Single pool model was employed since SOC and its fractions under native vegetation were assumed to be at steady state after long periods (Derrien and Amelung, 2011) since C_3 vegetation has existed at this site for a long time (Johnson, 2004), over at least 1000 years.

2.5. Partial N budget and estimation of greenhouse gas emissions

A partial N budget was constructed from the changes in total soil N stocks, cumulative N removed in the produce either removed in grain or animal produce (Radford et al., 2007; unpublished data, C M Thornton, personal communication) and estimates from Radford et al. (2007). Residue and root N were estimated from perennial pasture data on a similar Vertisol soil in this region used for pasture containing 2.5 Mg ha⁻¹ DM litter, 0.8% N, and 10 Mg ha⁻¹ DM roots containing 0.8% N (Robertson et al., 1993). N contained in the crop residue was estimated as 2 Mg ha⁻¹ DM using harvest index of 0.4 from average grain yield of 1.4 Mg ha⁻¹ over the 23-year period (from unpublished data, Thornton, personal communication) and crop residue containing v N (values similar to Robertson et al., 1993, for sorghum in this region).

Estimations of greenhouse gas emissions following land use change over the 23-year period were made from SOC changes, estimated N₂O emissions and animal CH₄ emissions, expressed in CO₂-equivalents (CO₂-e). N₂O emissions were estimated from N removed in animal produce and cereal grain, assuming 50% N use efficiency of mineralised N as nitrate-N, and using the emission factor of 1.0% for mineralised N (IPCC, 2006). Conversion from N to N₂O was 1.57 and global warming potential of N₂O relative to CO₂ over 100-year time horizon, 298 (IPCC, 2007) were used. Average stocking rate over 23-year period was taken as 0.5 animals ha⁻¹ (Radford et al., 2007), and emission factor of 60 kg CH₄ annually from each animal, and global warming potential of CH₄ relative to CO₂, 25 (IPCC, 2006, 2007) were used.

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0.0-0.1

2.6. Statistical analysis

The results are presented as mean values of SOC and soil total N stocks. Analysis of variance (ANOVA) was performed to test the differences in SOC and SOC fractions between native vegetation, pasture and cropped soils using land use change as the main treatment plots and depths as the sub-plots in a split-plot design. Fisher's protected least significant difference (LSD) was used to determine significant differences in SOC, total N, δ^{13} C and δ^{15} N, and different size fractions in soil under different land uses at *P* < 0.05.

3. Results

3.1. Soil bulk density

Soil bulk density was higher in both the pasture $(1.30 \pm 0.01 \text{ Mg m}^{-3})$ and cropped $(1.26 \pm 0.03 \text{ Mg m}^{-3})$ soils compared to the native $(1.19 \pm 0.02 \text{ Mg m}^{-3})$ soil at 0–0.1 m depths (Table 1). In the cropped soil, bulk density was also higher at 0.1–0.2 m depths than the native soil, although bulk density for the pasture soil was not significantly different from either the cropped or the native soil. Below these depths bulk densities of soil under all three land uses were essentially similar. The cumulative amounts of SOC and total N for 0–0.1 m, 0–0.2 m, 0–0.3 m, and 0–0.4 m depths were, therefore, corrected for the equivalent soil mass under native vegetation, using the polynomial relationship ($r^2 > 0.99$) between the amount of soil carbon and soil mass (soil depth × bulk density) (Dalal et al., 2005a). Soil depths reported here, therefore, refer to those of native vegetation.

3.2. Soil organic carbon and carbon distribution in different soil fractions

Organic C stocks in the top 0–0.1 m depths were highest in soil under native vegetation and lowest in that under cropping (Fig. 1). The pasture soil tended to have lower SOC stocks than the native vegetation soil but these values were not significantly different from either the cropping or the native vegetation soil. Similar trends in SOC stocks were observed at 0.1–0.2 m, 0.2–0.3 m, as well as 0.3–0.4 m depths under all three land uses. The SOC stocks under cropping were lower by 32–34% as compared to that under native vegetation at all depths studied.

Cumulative SOC stocks varied from 20.5 ± 2.8 Mg C ha⁻¹ at 0–0.1 m depth in the cropped soil to 84.0 ± 4.8 Mg C ha⁻¹ at 0–0.4 m depth in the native vegetation soil (Table 2). The SOC stocks in the pasture soil were between cropped and native vegetation soil although these values were not significantly different from either land use. For the 0–0.3 m and 0–0.4 m depths, SOC stocks decreased, respectively, by 22.8 and 24.1 Mg C ha⁻¹ over 23 years of cropping. Thus, on average, about 1 Mg C ha⁻¹ year⁻¹ was lost under cropping.

Amounts of organic C in $> 250 \ \mu m$ fractions differed significantly among different land uses and varied from 13.4 Mg C ha⁻¹ in soil under native vegetation to 3.1 Mg C ha⁻¹ under pasture and only 0.9 Mg C ha⁻¹ under cropping at 0–0.1 m depth (Table 3). Therefore, the loss of organic C from the $> 250 \ \mu m$ fraction at 0–0.1 m depth was

Table 1

Bulk density of soil under native vegetation, and after 23 years of land use for cereal cropping and perennial pasture.

| Soil depth (m) | Soil bulk density (Mg m ⁻³) | | | | Level of |
|----------------|--|------|------|------|---------------------------|
| | Native Pasture Cropped LSD _{0.05} | | | | significance ⁴ |
| 0.0-0.1 | 1.19 | 1.30 | 1.26 | 0.06 | * |
| 0.1-0.2 | 1.35 | 1.43 | 1.5 | 0.14 | * |
| 0.2-0.3 | 1.52 | 1.54 | 1.65 | 0.15 | ns |
| 0.3-0.4 | 1.56 | 1.59 | 1.67 | 0.13 | ns |

^a Significant (*) at P<0.05; ns, not significant.

Fig. 1. Distribution of soil organic C at different depths in native, pasture and cropped soils. The line height on top of the bar shows one standard error (n = 9). Values from Dalal et al. (2011) for native vegetation and pasture soil. At all depths, the cropped soil contained significantly lower SOC stocks than the native vegetation soil. SOC stocks of the pasture soil at all depths did not differ significantly from either the native vegetation or the cropped soil.

Soil depth (m)

0.2-0.3

0.3-0.4

0.1-0.2

77% and 93% from pasture and cropped soils, respectively, compared to that in the native vegetation soil. As proportions of total SOC, organic C in the >250 μ m fraction in the native vegetation soil and after 23 years of pasture and cropping was 43%, 12% and 5%, respectively. At 0.1–0.2 m depth, organic C in the >250 μ m fraction was significantly lower in the cropped soil (0.5 Mg C ha⁻¹) than that in the native vegetation soil (3.1 Mg C ha⁻¹) although in the pasture soil it was similar to that of the native vegetation soil. No significant differences in organic C in the >250 μ m fraction were observed at 0.2–0.3 m and 0.3–0.4 m depths among the land uses.

Organic C in the 250–53 μ m fractions did not differ significantly among the land uses at any depth (Table 3). However, organic C in the <53 μ m fraction was significantly higher in both pasture and cropped soils at 0–0.1 m depth, compared to that in the native vegetation soil (Table 3). As a proportion of total SOC, organic C in the <53 μ m fraction under the native vegetation and after 23 years of pasture and cropping was 41%, 70% and 82%, respectively. While, in the native vegetation soil, organic C was almost equally distributed between the >250 μ m fraction and the <53 μ m fraction, in the pasture as well as the cropped soils, much greater proportion of the organic C was in the <53 μ m fraction. In fact, at 0–0.1 m depth, the <53 μ m fraction contained 4.3 and 5.1 Mg C ha⁻¹ more under cropping and pasture, respectively, than under native vegetation.

3.3. $\delta^{13}C$ values and C_4 -C in soil organic carbon and different soil fractions

SOC δ^{13} C values of pasture (-20.1 ± 0.5‰) and cropped (-21.4 ± 0.7‰) soils were significantly higher (less negative) than the native vegetation (-25.5 ± 0.1‰) soil at 0–0.1 m depth. That is, there was C₄ vegetation–C contribution to SOC in both pasture (from C₄ buffel grass) and cropping (from C₄ sorghum crops) during

Table 2

Organic C stocks in soil under native vegetation, and after 23 years of cereal cropping and perennial pasture land use (corrected for equivalent soil mass).

| Soil depth (m) | Soil organ | | Level of | | |
|----------------|--|------|----------|------|---------------------------|
| | Native ^b Pasture ^b Cropped LSD _{0.05} | | | | significance ^a |
| 0-0.1 | 31.0 | 25.1 | 20.5 | 10.3 | * |
| 0-0.2 | 52.4 | 44.0 | 34.7 | 15.6 | * |
| 0-0.3 | 67.7 | 58.3 | 44.9 | 16.8 | * |
| 0-0.4 | 84.0 | 71.6 | 55.9 | 16.0 | * |
| | | | | | |

^a Significant (*) at P<0.05.

^b Values from Dalal et al. (2011).

Table 3

Amount of organic C in >250 µm, 250–53 µm, and <53 µm soil particle-size fractions under native vegetation, and after 23 years of land use for cereal cropping and perennial pasture.

| Depth (m) | pth (m) $> 250 \ \mu m \ (Mg \ C \ ha^{-1})^a$ | | 250–53 μm | 250–53 μm (Mg C ha ⁻¹) ^a | | | <53 µm (Mg C ha ⁻¹) ^a | | |
|-----------|--|---------|-----------|---|---------|---------|--|---------|---------|
| | Native | Pasture | Cropped | Native | Pasture | Cropped | Native | Pasture | Cropped |
| 0.0-0.1 | 13.4a | 3.1b | 0.9b | 5.0a | 4.4a | 2.7a | 12.6a | 17.7b | 16.9b |
| 0.1-0.2 | 3.1a | 2.5a | 0.5b | 1.7a | 1.6a | 0.8a | 16.6a | 14.8a | 12.9b |
| 0.2-0.3 | 3.1a | 1.8a | 1.0a | 1.5a | 1.6a | 1.4a | 10.7a | 10.9a | 7.8a |
| 0.3-0.4 | 3.7a | 2.1a | 2.8a | 2.4a | 2.8a | 1.6a | 10.2a | 9.3a | 6.7a |

^a Row means for each soil fraction followed by letters not in common differ significantly at P < 0.05.

the 23-year period of land use change from C₃ vegetation. At 0.1–0.2 m depth, only SOC δ^{13} C values of the pasture soil were significantly higher than the native vegetation soil. Below this depth, SOC δ^{13} C values among the three land uses were not significantly different from each other.

 $\delta^{13}\text{C}$ values of organic C in the >250 μm fraction at 0–0.1 m depth in soil under pasture $(-19.4\pm0.2\%)$ were significantly higher than that under cropping $(-21.2\pm0.3\%)$ and native vegetation $(-25.5\pm0.3\%)$, and the $\delta^{13}\text{C}$ values in cropping were significantly higher than the native vegetation. Similar trends in $\delta^{13}\text{C}$ values were observed at 0.1–0.2 m, 0–2-0.3 m and 0.3–0.4 m depths although due to large variations in the $\delta^{13}\text{C}$ values significant differences among the land uses were not consistently observed.

 $δ^{13}$ C values of organic C in the 250–53 µm soil fraction followed generally similar trends to those in the >250 µm fraction down to 0.3 m depths, that is, $δ^{13}$ C values in the 250–53 µm soil fraction were higher under pasture and cropping than native vegetation at these depths, and those under pasture were also higher than cropping at 0–0.1 m and 0.1–0.2 m depths. $δ^{13}$ C values of organic C in the <53 µm fraction under pasture and cropping were higher than that under native vegetation at 0–0.1 m depth only. Below this depth, no significant differences in $δ^{13}$ C values of organic C in the >250 µm fraction were observed (data not shown).

The proportion of C_4 -C (C_4 -C/(C_4 -C + C_3 -C)) in the whole soil under buffel grass pasture varied from 39% (0–0.1 m and 0.1–0.2 m depths) to 44% at 0.2–0.3 m depths (Table 4). Distribution of C_4 -C among the various soil size fractions generally followed similar trend to that of the whole soil (Table 4). That is, after 23 years, 34–45% of organic C in this soil was replaced by the C₄-C contributed by buffel grass pasture and this new C entered into all the soil particle-size fractions.

The contribution of C₄-C by the sorghum crops to total SOC and SOC fractions under cropping was substantial. The proportion of C₄-C in the whole soil under cropping was 31% in the 0–0.1 m depth and 42% at 0.2–0.3 m depth (Table 4), thus, overall it was only slightly smaller than that from buffel pasture. Again, the distribution of C₄-C among the different soil particle-size fractions was

similar to that of the whole soil, between 30 and 40% (Table 4), showing thereby that substantial amount of C₄-C from sorghum also entered into all the soil particle size fractions.

3.4. Turnover rates of organic carbon in soil and different soil fractions

Since the land use change from native vegetation to pasture resulted in the change from C₃ derived SOC to C₄-C input to SOC for a period of 23 years, the turnover rates of C₃-SOC were calculated from the change in δ^{13} C values of organic C in soil under pasture compared to that under native vegetation using mixed model, Eqs. 2–4 and 6 (Balesdent et al., 1998; Dalal et al., 2005a; Lobe et al., 2005). The rates of SOC loss decreased from 0.031 ± 0.005 year⁻¹ at 0–0.1 m depth to 0.026 ± 0.002 year⁻¹ at 0.1–0.2 m depth; below this depth the rates of SOC loss were slightly lower than that at the 0.1–0.2 m depth (Table 5). The rates of SOC turnover from 250 to 53 µm fraction were similar to, or lower than, the whole soil while that of the <53 µm fraction were generally lower than the whole soil, especially at 0.3–0.4 m depth (Table 5). The rates of SOC turnover from the >250 µm fraction were up to 4-fold faster than the <53 µm fraction down to 0.4 m depths.

The turnover rates of SOC in the cropped soil were similar to that of the pasture soil in the 0–0.1 m and 0.1–0.2 m depths (Table 5). At 0.2–0.3 and 0.3–0.4 m depths, the turnover rates of SOC were similar to the top soil depths. The rates of SOC turnover from the >250 μ m fraction were up to 4-fold faster than the whole SOC and from 2 to 10 times faster than the <53 μ m fraction (Table 5).

3.5. Soil total N and N distribution in different soil fractions

Total N stocks in soil under pasture and cropping were significantly lower than that under native vegetation at all depths (Fig. 2). At 0–0.1 m depth, total N stocks decreased by 19% under pasture and 37% under cropping. Even at 0.3–0.4 m depth, the corresponding losses showed a similar trend, that is, 23% and 40% losses under

Table 4

Percentage of C₄-C (C₄-C/(C₃-C + C₄-C)) in the whole soil and soil particle-size fractions after 23 years of land use change from C₃ (native vegetation) to (a) C₄ (buffel grass) pasture and (b) sorghum cropping.

| Soil depth (m) | C4-C (%) | | | | |
|----------------|----------------|----------------|----------------|----------------|--|
| | Whole soil | >250 µm | 250–53 μm | <53 µm | |
| (a) Buffel | | | | | |
| 0.0-0.1 | 39.6 ± 4.0 | 44.9 ± 1.5 | 38.9 ± 1.4 | 38.2 ± 5.4 | |
| 0.1-0.2 | 38.6 ± 5.3 | 39.8 ± 8.1 | 33.9 ± 3.3 | 41.4 ± 8.0 | |
| 0.2-0.3 | 44.4 ± 5.3 | 59.9 ± 11.5 | 39.2 ± 8.6 | 43.9 ± 3.6 | |
| (b) Sorghum | | | | | |
| 0.0-0.1 | 31.1 ± 5.8 | 33.1 ± 2.2 | 32.3 ± 1.2 | 29.5 ± 6.9 | |
| 0.1-0.2 | 34.1 ± 1.1 | 36.8 ± 9.6 | 34.6 ± 1.7 | 34.0 ± 1.8 | |
| 0.2-0.3 | 41.7 ± 8.9 | 40.3 ± 12.5 | 39.4 ± 3.3 | 41.8 ± 10.1 | |

Table 5

Estimated rates of SOC-C₃ loss (k) from whole soil and soil particle-size fractions after 23 years of land use change from C_3 (native vegetation) to (a) C_4 (buffel grass) pasture and (b) sorghum cropping.

| _ | | | | | | | |
|---|----------------|--|-------------------|-------------------|-------------------|--|--|
| | Soil depth (m) | Rate of SOC-C ₃ loss (year ^{-1}) | | | | | |
| | | Whole soil | >250 µm | 250–53 μm | <53 µm | | |
| | (a) Buffel | | | | | | |
| | 0.0-0.1 | 0.031 ± 0.005 | 0.088 ± 0.011 | 0.023 ± 0.11 | 0.019 ± 0.003 | | |
| | 0.1-0.2 | 0.026 ± 0.002 | 0.048 ± 0.016 | 0.024 ± 0.013 | 0.017 ± 0.003 | | |
| | 0.2-0.3 | 0.019 ± 0.003 | 0.051 ± 0.020 | 0.013 ± 0.007 | 0.016 ± 0.003 | | |
| | 0.3-0.4 | 0.017 ± 0.005 | 0.062 ± 0.026 | 0.010 ± 0.005 | 0.010 ± 0.002 | | |
| | | | | | | | |
| | (b) Sorghum | | | | | | |
| | 0.0-0.1 | 0.035 ± 0.002 | 0.135 ± 0.010 | 0.039 ± 0.003 | 0.011 ± 0.003 | | |
| | 0.1-0.2 | 0.026 ± 0.005 | 0.096 ± 0.007 | 0.050 ± 0.017 | 0.017 ± 0.006 | | |
| | 0.2-0.3 | 0.040 ± 0.009 | 0.098 ± 0.007 | 0.026 ± 0.001 | 0.035 ± 0.008 | | |
| | 0.3-0.4 | 0.043 ± 0.026 | 0.057 ± 0.026 | 0.039 ± 0.005 | 0.022 ± 0.010 | | |



Fig. 2. Distribution of soil total N at different depths in native, pasture and cropped soils. The line height on top of the bar shows one standard error (n = 9). At all depths, soil total N stocks of both the cropped and pasture soils were significantly lower than the native vegetation soil and that of the cropped soil were significantly lower than the pasture soil at all depths.

pasture and cropping, respectively. The cumulative total N stocks at 0–0.4 m depths varied from 3414 ± 235 kg N ha⁻¹ in soil under cropping to 5564 ± 235 kg N ha⁻¹ in soil under native vegetation, thus showing a loss of 39% under cropping; under pasture, the N loss was only 22% (Table 6). Over 23-year period, the annual rates of N loss from 0 to 0.3 m and 0–0.4 m depths were estimated to be 78.8 and 93.5 kg N ha⁻¹ year⁻¹ under cropping and 44.7 and 53.1 kg N ha⁻¹ year⁻¹ under pasture.

Among the different soil fractions, significant losses of N occurred primarily from the >250 μ m fraction at all depths studied (Table 7). The cropped soil lost 93%, 85%, 85% and 65% at 0–0.1 m, 0.1–0.2 m, 0.2–0.3 m and 0.3–0.4 m depths, respectively, from the >250 μ m fraction. From 50% to 55% of total N losses from the cropped soil occurred from the >250 μ m fraction (43.4 kg N ha⁻¹ year⁻¹ at 0–0.3 m depth and 46.3 kg N ha⁻¹ year⁻¹ at 0–0.4 m depth). The losses from the pasture soil were 77%, 52%, 62% and 60% at 0–0.1 m, 0.1–0.2 m, 0.2–0.3 m and 0.3–0.4 m depths, respectively. Total N loss from the >250 μ m fraction at 0–0.3 m and 0–0.4 m depths was 33.8 and 36.4 kg N ha⁻¹ year⁻¹; from 69% to 76% of the total soil N losses over 23-year period occurred from this fraction.

3.6. $\delta^{15}N$ values of total nitrogen and different soil fractions

 $δ^{15}$ N values varied between 5.5‰ and 8.2‰ for the total N, 2.2‰ and 5.3‰ for the > 250 µm fraction, 3.4‰ and 7.8‰ for the 250–53 µm fraction, and 6.0‰ and 9.8‰ for the <53 µm fractions. Thus, in general, finer soil fractions had higher $δ^{15}$ N values, reflecting the increased turnover/ transformation of N in the finer fractions than that in the coarser fractions. However, there were very few significant differences due to land use change. Only the soil under cropping (8.6‰) had a higher $δ^{15}$ N value than either the native vegetation soil (5.4‰) or the pasture

Table 6

Total N stocks in soil under native vegetation, and after 23 years of land use for cereal cropping and perennial pasture (corrected for equivalent soil mass).

| Soil depth (m) | Soil total | N (kg ha^{-1}) | | Level of | |
|----------------|------------|-------------------|---------|---------------------|--------------|
| | Native | Pasture | Cropped | LSD _{0.05} | significance |
| 0-0.1 | 2234 | 1813 | 1408 | 296 | ** |
| 0-0.2 | 3746 | 2983 | 2332 | 351 | ** |
| 0-0.3 | 4711 | 3684 | 2898 | 363 | ** |
| 0-0.4 | 5564 | 4342 | 3414 | 476 | ** |

^a Significant (**) at P<0.01.

soil (5.5%) (LSD_{0.05} = 1.8%) at 0–0.1 m depth, indicating increased turnover of soil N under cropping (data not shown).

3.7. Carbon:nitrogen ratio of soil and soil fractions

Carbon:nitrogen ratio varied from 14 to 20 for the whole soil and increased from 14 at 0–0.1 m depth, 15 at 0.1–0.2 m depth, 18 at 0.2–0.3 m depth and 20 at 0.3–0.4 m depth. However, no significant difference due to different land uses was observed. Among the soil fractions, highest carbon:nitrogen ratios were found in the >250 μ m and lowest in the <53 μ m fraction. Again, no significant differences within soil fractions due to land use change were found, although the lowest carbon:nitrogen ratios generally tended to be in soil under native vegetation (data not shown).

3.8. Partial N budget and estimates of greenhouse gas emissions

A partial N budget after 23 years of annual cropping and perennial pastures following land use change from native vegetation is produced in Table 8. We have included total soil N at 0–0.3 m depths, N removed in produce (grain N from cereal crops, and N in animal produce) (Radford et al., 2007) and estimated plant residue and root N. N retained in plant biomass in the cropping system immediately after harvest is low, but substantial amount of N occurs in pasture plant biomass, especially in the roots of the perennial pasture in this region (Robertson et al., 1993). Total N removed in the grain of cereal crops was more than 20 times that removed in animal produce (Radford et al., 2007). Unaccounted for N in both pasture and cropped systems was estimated to be essentially similar, that is, $39-42 \text{ kg N ha}^{-1} \text{ year}^{-1}$.

Estimates of a greenhouse gas budget over the 23-year period for CO_2 , N_2O and CH_4 emissions, expressed as CO_2 -e ha⁻¹, showed that SOC losses from the cropping system accounted for 97% of the total CO_2 -e emissions, the remaining being N_2O emissions (Table 9). For the pasture system, animal CH_4 emissions made up most of the greenhouse gas budget. When greenhouse gas emissions of cropping and pasture systems were compared, it was apparent that SOC losses contributed almost two-orders of magnitude more to the greenhouse gas budget of the cropping system than the pasture system.

4. Discussion

4.1. Dynamics of organic carbon in soil and soil fractions

Land use change effects on total SOC stocks between native vegetation and perennial pasture after 23 years were not significantly different at any depth (Fig. 1) or cumulatively down to 0.4 m depth (Table 2). This corroborates the observations made by Radford et al. (2007), who found no decrease in SOC over the 21-year period of pasture, although it inherently contained lower SOC concentrations throughout this period. This may possibly be as a consequence of clearing and burning of native vegetation biomass for pasture development (Cowie et al., 2007). Notwithstanding the similar total SOC stocks in soil under native vegetation and pasture, the distribution of SOC among soil fractions differed significantly. For example, the >250 μm fraction contained only 12% of SOC under pasture compared to 43% under native vegetation, that is, a loss of 70% of the > 250 μ m SOC fraction. On the other hand, the < 53 μ m fraction contained 70% of the total SOC under pasture but only 41% under native vegetation at 0-0.1 m depth, as was observed by Shang and Tiessen (2000). In spite of large differences in the changes in the total amount of SOC in different size fractions under pasture, proportions of C₄-C contribution by buffel grass was essentially similar in the whole soil and particle-size fractions, about 40-50% (Table 5). Conversely, it can be argued that up to half of C_4 -C input was sequestered in soil under pasture. That is, SOC losses from C₃-C were almost

Table 7

Amount of total N in >250 µm, 250-53 µm and <53 µm soil fractions under native vegetation, and after 23 years of land use for cereal cropping and perennial pasture.

| Depth (m) | Depth (m) $> 250 \ \mu m \ (kg \ N \ ha^{-1})^a$ | | | 250–53 μm | 250–53 μm (kg N ha ⁻¹) ^a | | | $<53 \ \mu m \ (kg \ N \ ha^{-1})^a$ | | |
|-----------|--|---------|---------|-----------|---|---------|--------|--------------------------------------|---------|--|
| | Native | Pasture | Cropped | Native | Pasture | Cropped | Native | Pasture | Cropped | |
| 0.0-0.1 | 802a | 185bc | 49b | 320a | 305a | 166a | 956a | 1279a | 1167a | |
| 0.1-0.2 | 178a | 86b | 26b | 105a | 89a | 46a | 1167a | 914b | 838b | |
| 0.2-0.3 | 110a | 42b | 16b | 85a | 64a | 56a | 679a | 534a | 438a | |
| 0.3-0.4 | 100a | 40b | 35b | 113a | 136a | 44a | 531a | 477a | 326a | |

^a Row means for each soil fraction followed by letters not in common differ significantly at P < 0.05.

balanced by C₄-C sequestration after the land use change from native vegetation to buffel grass pasture. Further work is required to elucidate the dynamics of aggregate formation and stabilisation with regard to SOC under native vegetation versus pasture in this soil.

Since land use change to pasture also led to the change from C₃ vegetation to C_4 vegetation, SOC dynamics could be investigated in the whole soil and soil fractions due to the change in natural δ^{13} C abundance (Balesdent et al., 1987; Martin et al., 1990; Balesdent et al., 1998; Boutton et al., 1998; Dalal et al., 2005a,). Whole soil and soil fractions were significantly enriched in δ^{13} C (pasture soil–native vegetation soil) by as much as 6.1‰ at 0–0.1 m depths although smaller differences occurred below this depth. That is, C_4 -C from buffel grass pasture entered all soil fractions and at all depths studied (Table 4). Similar results were obtained by Desjardins et al. (2004) where grass C was found in all the soil fractions 15 years after the forest land was converted to grass pastures. Assuming the decomposition rates of SOC-C₃ and SOC-C₄ were similar (Balesdent et al., 1998), SOC turnover rates were calculated (Table 5). As expected, SOC turnover rates were highest in the top 0.1 m soil and decreased below this depth. Among the soil fractions, $>250 \,\mu m$ fraction turned over fastest although the turnover rates of the 250–53 μ m and <53 μ m fractions were similar. Since total SOC stock was not significantly different over 23-years of pasture from that under native vegetation, it was assumed that the rate of C addition to the soil was similar to that of C loss (rate of C addition = $k \times SOC$ stock). We estimated the rates of C addition to the soil by perennial pasture to be 0.80, 0.32, 0.26, and 0.21 Mg C ha⁻¹ year⁻¹ at 0-0.1 m, 0.1-0.2 m, 0.2-0.3 m, and 0.3-0.4 m depths, respectively or 1.59 Mg C ha⁻¹ year⁻¹ at 0–0.4 m depths. Assuming buffel grass pasture roots contained 40% C, almost 4 Mg root dry matter ha^{-1} year⁻¹ was added to maintain SOC stocks during the 23-year period of pasture. These values of required root dry matter additions are close to the field measured estimates of perennial pastures in this region, Robertson et al. (1993) measured the root biomass of a perennial pasture, green panic (Panicum

Table 8

Partial N budget after 23 years of land use for cereal cropping and perennial pasture. Soil N under native vegetation for 0–0.3 m depth = $4711 \text{ kg N ha}^{-1}$.

| Land use | Soil N | Removed | Removed Residue | | unted N |
|--------------------|-----------------------|-------------------------------------|-------------------------------------|-------------|----------------------------|
| | 0–0.3 m | in produce | and root N | Total | Annual |
| | kg N ha ⁻¹ | | | | kg N ha $^{-1}$ yr $^{-1}$ |
| Pasture Cropped | 3684 2898 | 40 ^a 849 ^d | 100 ^b 10 ^e | 887° 954 | 38.6 41.5 |

^a Estimated from the values given by Radford et al. (2007).

^b Estimated from perennial pasture data on a similar Vertisol soil, 2.5 Mg ha^{-1} DM litter containing 0.8% N and 10 Mg ha^{-1} DM roots containing 0.8% N (Robertson et al., 1993).

 $^{\rm c}$ Unaccounted N was calculated as follows: soil total N (0–0.3) under native vegetation (4711 kg N ha⁻¹) - (soil total N (0–0.3 m) under pasture or crop + N removed in produce + residue and root N).

^d Unpublished data (C M Thornton, personal communication) and estimated from Radford et al. (2007).

^e Crop residue estimated as 2 Mg ha⁻¹ DM using harvest index of 0.4 from average grain yield of 1.4 Mg ha⁻¹ over the 23-year period (from unpublished data, Thornton, personal communication) and crop residue containing 0.5% N (values similar to Robertson et al., 1993, for sorghum in this region).

maximum var. *trichoglume*) and found that it varied from 6 Mg dry matter ha^{-1} to 11.4 Mg dry matter ha^{-1} in the top 0.28 m depth. Dalal et al. (1995) measured root biomass of 9.7–11.0 Mg dry matter ha^{-1} in 0–1.5 m depth of purple pigeon (*Setaria incrassata* Staff.) and Rhodes grass (*Chloris gayana* Knuth.) pasture containing some legumes; more than half of the total root biomass was present in the top 0.3 m depths.

Land use change from native vegetation to cropping led to significant decrease in total SOC stocks. Decreases in SOC stocks of 33–34% at all depths (Fig. 1) and cumulatively at 0–0.4 m depths were observed (Table 2). These findings are consistent with numerous studies where land use change occurred from native vegetation (usually fertile soil) to annual cropping, resulting in up to 50% loss (Haas and Evans, 1957; Dalal and Mayer, 1986a, Marty et al., 2002; Dalal et al., 2005a; Zach et al., 2006; Radford et al., 2007). This is primarily considered to occur due to the reduced addition of organic materials and often increased soil erosion (Dalal and Mayer, 1986a, Marty et al., 2002; Lobe et al., 2005).

In addition, there may be exposure of new soil surfaces due to aggregate disruption during tillage operations. This generally results in the enhanced loss of coarse organic matter (Cambardella and Elliott, 1992), which should be evident from SOC distribution among soil fractions. We found that the >250 μ m SOC fraction under cropping decreased by more than 90% at 0–0.1 m depth and more than 80% at 0.1–0.2 m depth (Table 3). The 250–53 μ m fraction showed much smaller changes, and generally was not significantly different from either the native vegetation or the pasture soil fractions although SOC in the <53 μ m fraction was significantly higher in the pasture and cropped soils than the native vegetation soil. Dalal and Mayer (1986b) found that coarse organic matter from the sand-size fraction (20–2000 μ m) was mostly lost after about 45 years of annual cropping from a similar soil. It is, therefore, expected that losses of SOC may also occur from the 250–53 μ m fraction as the period of annual cropping increases.

Table 9

Estimates of greenhouse gas (CO₂, N₂O and CH₄) emissions following land use change from native vegetation to pasture and cropping over the 23-year period.

| Land use | SOC change ^a (kg C ha ⁻¹) | Soil N ₂ O emissions ^b (kg N ha ⁻¹) | Animal CH ₄ emissions ^c (kg CH ₄ ha ⁻¹) | Total GHG emissions |
|--------------------|---|---|--|------------------------|
| Pasture Cropped | 0 22,800 | 0.4 8.5 | 30 0 | - |
| | kg CO ₂ -e ha $^{-1}$ | | | |
| Pasture Cropped | 0 83,600 | 187 3977 | 750 0 | 937 87,577 |

 $^a\,$ Significant decrease in SOC stocks (0–0.3 m) under cropping but not under pasture. $^b\,$ N₂O emissions estimated from N removed in animal produce and grain assuming

 $^{\circ}$ N₂O emissions estimated from N removed in animal produce and grain assuming 50% N use efficiency, using the emission factor of 1.0% for mineralised N (IPCC, 2006). Conversion from N to N₂O, 1.57 and global warming potential of N₂O over 100-year time horizon, 298 (IPCC, 2007).

^c Average stocking rate, 0.5 animals ha^{-1} (Radford et al., 2007), emission factor of 60 kg CH₄ annually from each animal, and global warming potential, 25 (IPCC, 2006, 2007).

In contrast to land use change from native vegetation to pasture, the cropping system used C_3 crops (13 wheat crops and 1 barley crop, 9 wheat crops in the first 10 years of cropping period) as well as C₄ crops (9 sorghum crops, mostly during 11–23 years of cropping period) (Radford et al., 2007; Huth et al., 2010; CM Thornton, personal communication). Therefore, the enrichment of $\delta^{13}C$ of whole soil and particle-size fractions was less than that of the pasture soil and soil fractions, although C₄-sorghum C significantly increased δ^{13} C values in the whole soil and soil fractions compared to that of native vegetation at 0–0.1 m and 0.1–0.2 m depths. Although C₄-C contribution to SOC by sorghum was lower than that from the perennial buffel grass pasture it was substantial, 30–40% (Table 4). Moreover, C₄-C was distributed almost similarly (30-40%) in all the particle-size fractions and down to 0.3 m depth (Table 4). As Diels et al. (2004) and Lobe et al. (2005), from mixed C₃-C₄ cropping, found that the C inputs from recently grown crops makes significant difference in soil δ^{13} C and newly introduced C, we found that SOC was significantly enriched and contained substantial amounts of C_{4} -C in the whole soil as well as the soil fractions due to the high frequency of sorghum crops grown in the last 13 years of this study. Since turnover rates of SOC in soil under cropping were essentially similar to those under pasture, 0.035 \pm 0.002 yr^{-1} at 0–0.1 m depth and 0.026 \pm 0.005 yr^{-1} at 0.1-0.2 m depths (Table 5), we estimated that rates of C addition were 0.66, 0.24, 0.18, and 0.18 Mg C ha⁻¹ year⁻¹ at 0–0.1 m, 0.1– 0.2 m, 0.2–0.3 m, and 0.3–0.4 m depths or 1.26 Mg C ha⁻¹ year⁻¹. Considering that crop roots contain 40% C (Dalal et al., 1995), the rate of dry matter addition was estimated to be 3 Mg dry matter ha^{-1} year⁻¹, a value 50% higher than that measured (2 Mg C ha^{-1} year⁻¹) at a 60-year old cropping site on a similar soil. Robertson et al. (1993) measured the same value of root biomass of sorghum (2 Mg dry matter ha^{-1}) on a similar soil type.

4.2. Dynamics of total N in soil and soil fractions

Land use change from native vegetation to perennial pasture significantly decreased total soil N at all depths as well as cumulative N at 0–0.4 m depths (Fig. 2, Table 6). This is in contrast to total SOC which was similar under both land uses. Dalal et al. (2005b) found that total soil N loss was higher than that of total SOC due to land use change from *Acacia aneura* to perennial buffel pasture after 20 years. In the present study, the decrease in total soil N under pasture was 1027 kg N ha⁻¹ or almost 45 kg N ha⁻¹ year⁻¹ loss at 0–0.3 m depth compared to that under native vegetation. At 0–0.4 m depths, the total soil N loss was even higher, 53 kg N ha⁻¹ year⁻¹. Similar δ^{15} N values of the whole soil between the native vegetation, predominantly brigalow (*A. harpophylla*, a legume species) and pasture indicated that the mature brigalow was not actively fixing N₂ in this soil during the study period, and presumably has reached the steady-state over more than 1000 years.

Similar to the changes in SOC stocks of the soil fractions, soil total N was primarily lost (52–77%), from the >250 µm fraction at all depths (Table 7), thus, emphasising the importance of this soil fraction for the dynamics of both the SOC and total soil N stocks in this soil. These findings also corroborate those from a Lixisol in which light fraction N (<1.6 Mg m⁻³) declined by 60–70% after 20-years of buffel pasture (Dalal et al., 2005b). Although δ^{15} N values of the soil fractions increased with increasing fine fractions, thus, confirming the increased transformation with finer size fractions (Nadelhoffer and Fry, 1988; Robinson, 2001; Lobe et al., 2005), there were no significant differences in δ^{15} N values of these fractions between native vegetation and pasture. Therefore, essentially similar N transformation processes occurred under both native vegetation and pasture system.

Total soil N decreases under cropping were much greater than those under pasture. Again total soil N decreased significantly at all depths (Fig. 2) and cumulatively at 0–0.4 m depth (Table 6). Cumulative total soil N decreases at 0–0.3 m and 0–0.4 m depths were 1813 and 2150 kg N ha⁻¹ or 79 and 93 kg N ha⁻¹ year⁻¹, respectively, over the 23-year period. These soil N losses were much larger than those observed by Dalal and Mayer (1986c), 67 kg N ha⁻¹ year⁻¹ over a 45-year period of annual cropping. Since total soil N in this soil is still decreasing (Radford et al., 2007), albeit at a reduced rate due to reduced total soil N supply, further soil N losses are expected. Similar to the pasture, δ^{15} N values were essentially similar among all three land uses except for the significantly enriched δ^{15} N values in the total soil N at 0–0.1 m depths, possibly due to preferential N transformation and greater N uptake and removal by the crop than pasture, leaving behind the soil with enriched N (Robinson, 2001).

Soil N declined mainly from the >250 μ m fraction under cropping, as compared to native vegetation, and generally soil N stocks tended to be lower than those under pasture. These findings are similar to those observed by Dalal and Mayer (1987) for the 20–2000 μ m fraction under 45–70 years of cropping, and Dalal et al. (2005b) for the light fraction (<1.6 Mg m⁻³) under annual cropping for 20 years. Thus, greater changes in N stocks in the coarse soil fraction or light fraction are again confirmed, as for that of SOC, and hence for the soil organic matter in this environment (Dalal et al., 2005a, 2005b) and elsewhere (Lobe et al., 2005). Soil N losses under cropping from the other soil fractions were generally not significant from either the native vegetation or pasture.

4.3. Partial N budget, sustainable agro-ecosystems and greenhouse gas emissions

Partial N budget after 23 years of annual cropping and perennial pastures following land use change from native vegetation showed that the unaccounted for N in both pasture and cropped systems was estimated to be essentially similar, that is, 39-42 kg N ha⁻¹ year⁻¹, possibly largely due to deep leaching of mineral N. Dalal and Mayer (1986c) found total soil N losses of 67 kg N ha⁻¹ year⁻¹ from a 45-year old cropped Vertisol, including 51 kg N ha⁻¹ year⁻¹ removed in the grain and 16 kg N ha⁻¹ year⁻¹ unaccounted for N losses, mainly due to deep leaching of mineral N. In the present study, similar magnitude of soil N losses was found, but much smaller amounts of N were removed in the grain (36 kg N ha^{-1} year⁻¹) (Radford et al., 2007; Table 8). Therefore, greater amounts of N remained unaccounted for, presumably lost due to deep leaching since in this cropping system, about 14 mm year⁻¹ was leached below 1.5 m depth (Cowie et al., 2007). Further evidence of deep leaching was provided by total soil chloride loss of 27–60% from the grazed and cropped soil below 1.5 m depth (Cowie et al., 2007). Nitrate-N losses, therefore, could be similar in magnitude to that of soil chloride at this site. Some losses via denitrification are also possible (Huth et al., 2010).

A partial N budget for the perennial buffel pasture, showing the decreasing amounts of soil total N (Radford et al., 2007) and unaccounted for soil N losses (more than 20 times of that removed in the produce), was similar to the cropping system in this semi-arid subtropical environment. For example, Glover et al. (2010) suggested that harvested perennial grasslands could provide ecological benchmarks for agricultural sustainability by conserving resources, especially soil C and N. The perennial buffel pasture system did maintain the SOC stocks similar to the native vegetation soil, but soil N declined during the pasture phase so much so that pasture productivity also declined (Radford et al., 2007). Therefore, this practice may not be considered sustainable in the long-term in this region. It can be argued that introduction of a legume component (for N₂ fixation) in the perennial buffel pasture may restore, or at least reduce, soil N decline and therefore provide long-term agricultural sustainability.

Estimates of greenhouse gas emissions were made from the losses in SOC stocks under cropping, potential N₂O emissions from both pasture and cropping systems, and CH₄ emissions from animals grazing the pasture using IPCC default emission factors (IPCC, 2006, 2007) (Table 9). It is apparent that SOC losses from the cropped soil dominated the total greenhouse gas budget from this agro-ecosystem. Greenhouse gas emissions as N₂O (cropping system) and CH₄ (pasture system) were almost two-orders of magnitude lower than CO₂ emissions from SOC loss from the cropping system. It should be added, however, the cropped system did not receive fertiliser N, and application of fertiliser N may increase N₂O emission from the cropped soil (Dalal et al., 2003; Huth et al., 2010). Land use change from either native vegetation or permanent pasture to cropping resulting in SOC losses has been responsible for a large contribution, mainly CO₂, to greenhouse gas emissions to the atmosphere. For example, Houghton (2010) estimated 156 Pg (Gt) was emitted between 1850 and 1998 due to the conversion of native vegetation to agriculture; of this, at least 25% of CO₂ emissions were contributed by SOC loss. Therefore, increasing the storage of C in SOC through enhanced root biomass, such as may occur when converting cropped land to perennial pastures, and by using appropriate management practices, including introduction of legumes, is an attractive option for the mitigation of greenhouse gases.

5. Conclusions

Land use change from native vegetation to perennial pasture has maintained SOC but reduced total N by more than 20% in the top 0.3 m depth of soil, consequently steadily reducing animal productivity from the grazed buffel grass pasture over the 23-year period. Moreover, land use change from native vegetation to annual cropping depleted both SOC and total soil N by 34% and 38%, respectively, and resulted in decreasing cereal crop yields during the experimental period. Most of these losses of SOC and total N were largely from the >250 μ m fraction of soil. However, changes in the δ^{13} C natural abundance of soil fractions showed that native vegetation SOC-C3 losses occurred from both pasture and cropping systems although the >250 µm fraction of soil had almost a magnitude higher turnover rates than the 250–53 μ m and <53 μ m fractions. Loss of SOC during the cropping period contributed more than two-orders of magnitude CO₂-e to the atmosphere than the pasture system, including CH₄ emissions from grazed animals. Even then, the pasture system is not considered as a benchmark of agricultural sustainability due to decreasing productivity in this semi-arid subtropical environment. Introduction of legumes (for N₂ fixation) into perennial pastures may arrest the productivity decline of the pasture system. For cropping system to be sustainable in terms of increasing SOC and N and reducing greenhouse gases requires a major shift in land use change from cropping to perennial pasture (including legume component) or even restoring to native vegetation although environmental sustainability needs to be balanced by food security.

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References

- Balesdent J, Mariotti A, Guillet B. Natural ¹³C abundance as a tracer for studies of soil organic matter dynamics. Soil Biol Biochem 1987;19:25–30.
- Balesdent J, Besnard E, Arrouays D, Chenu C. The dynamics of carbon in particle-size fractions of soil in a forest-cultivation sequence. Plant Soil 1998;201:49–57.
- Bekele A, Hudnall WH. Stable carbon isotope study of the prairie-forest transition soil in Louisiana. Soil Sci 2003;168:783–92.
- Boutton TW. Stable carbon isotope ratios of soil organic matter and their use as indicators of vegetation and climate change. In: Boutton TW, Yamasaki S, editors. Mass Spectrometry of Soils. New York: Marcel Dekker, Inc; 1996. p. 47–82.

- Boutton TW, Archer SR, Midwood AJ, Zitzer SF, Bol R.
 ^{§13}C values of soil organic matter and their use in documenting vegetation change in subtropical savannah ecosystems. Geoderma 1998;82:5-41.
- Cambardella CA, Elliott ET. Particulate soil organic matter changes across a grassland cultivation sequence. Soil Sci Soc Am J 1992;56:777–83.
- Cook BD, Allan DL. Dissolved organic carbon in old field soils: total amounts as a measure of available resources for soil mineralization. Soil Biol Biochem 1992;24:585–94.
- Cowie BA, Thornton CM, Radford BJ. The brigalow catchment study: 1. Overview of a 40-year study of the effects of land clearing in the brigalow bioregion of Australia. Aust J Soil Res 2007;45:479–95.
- Craig H. The geochemistry of the stable carbon isotopes. Geochim Cosmochim Acta 1953;3:53–92.
- Dalal RC, Mayer RJ. Long-term trends in fertility of soils under continuous cultivation and cereal cropping in Southern Queensland. II Total organic carbon and its rate of loss from the soil profile. Aust J Soil Res 1986a;24:281–92.
- Dalal RC, Mayer RJ. Long-term trends in fertility of soils under continuous cultivation and cereal cropping in Southern Queensland. III Distribution and kinetics of soil organic carbon in particle-size fractions. Aust J Soil Res 1986b;24:293–300.
- Dalal RC, Mayer RJ. Long-term trends in fertility of soils under continuous cultivation and cereal cropping in Southern Queensland. V Rate of loss of total nitrogen from the soil profile and changes in carbon:nitrogen ratios. Aust J Soil Res 1986c;24: 493–504.
- Dalal RC, Mayer RJ. Long-term trends in fertility of soils under continuous cultivation and cereal cropping in Southern Queensland. VI Loss of nitrogen from different particle-size and density fractions. Aust J Soil Res 1987;25:83–93.
- Dalal RC, Strong WM, Weston EJ, Cooper JE, Lehane KJ, King AJ, et al. Sustaining productivity of a Vertisol at Warra, Queensland, with fertilisers, no-tillage, or legumes I. Organic matter status. Aust J Exp Agric 1995;35:903–13.
- Dalal RC, Wang W, Robertson GP, Parton WJ. Nitrous oxide emission from Australian agricultural lands and mitigation options: a review. Aust J Soil Res 2003;41: 165–95.
- Dalal RC, Harms B, Krull E, Wang W. Total soil organic matter and its labile pools following Mulga (*Acacia aneura*) clearing for pasture development and cropping 1. Total and labile carbon. Aust J Soil Res 2005a;43:13–20.
- Dalal RC, Harms B, Krull E, Wang W. Total soil organic matter and its labile pools following Mulga (*Acacia aneura*) clearing for pasture development and cropping 1. Total and labile nitrogen. Aust J Soil Res 2005b;43:179–87.
- Dalal RC, Cowie BA, Allen DE, Yo SA. Assessing lability of particulate organic matter from δ^{13} C changes following land-use change from C₃ native vegetation to C₄ pasture. Aust J Soil Res 2011;49:98-103.
- Derrien D, Amelung W. Computing the mean residence time of soil carbon fractions using stable isotopes: impacts of the model framework. Eur J Soil Sci 2011;62: 237–52.
- Desjardins T, Barros E, Sarrazin M, Girardin C, Mariotti A. Effects of forest conversion to pasture on soil carbon content and dynamics in Brazilian Amazonia. Agric Ecosyst Environ 2004;103:365–73.
- Diels J, Vanlauwe B, Van der Meersch MK, Sanginga N, Merckx R. Long-term soil organic carbon dynamics in a subhumid tropical climate: ¹³C data in mixed C₃/C₄ cropping and modelling with ROTHC. Soil Biol Biochem 2004;36:1739–50.
- Ehleringer JR, Buchmann N, Flanagan LB. Carbon isotope ratios in belowground carbon cycle processes. Ecol Appl 2000;10:412–22.
- Glover JD, Culman SW, Dupont ST, Broussard W, Young L, Mangan ME, et al. Harvested perennial grasslands provide ecological benchmarks for agricultural sustainability. Agric Ecosyst Environ 2010;137:3-12.
- Guo LB, Gifford RM. Soil carbon stocks and land use change: a meta analysis. Glob Chang Biol 2002;8:345–60.
- Haas HJ, Evans CE, Miles EF. Nitrogen and carbon changes in Great Plains soils as influenced by cropping and soil treatments. U.S. Dep Agric Tech Bull No. 1164, Washington, D.C; 1957.
- Harms BP, Dalal RC, Cramp AP. Changes in soil carbon and soil nitrogen after tree clearing in the semi-arid rangelands of Queensland. Aust J Bot 2005;53:639–50.
- Houghton RA. How well do we know the flux of CO₂ from land use change? Tellus 2010;62B:337–51.
- Huth N, Thorburn PJ, Radford BJ, Thornton CM. Impacts of fertilisers and legumes on N₂O and CO₂ emissions from soils in subtropical agricultural systems: a simulation study. Agric Ecosyst Environ 2010;136:351–7.
- IPCC. Guidelines for National Greenhouse Gas Inventories. , 4Kanagawa, Japan: IPCC National Greenhouse Gas Inventories Programme; 2006 [2006].
- IPCC. Climate Change 2007: The Physical Science Basis. Cambridge, UK: Cambridge University Press; 2007 [Chapter 2:212].
- IUSS Working Group WRB. World reference base for soil resources 2006. World Soil Resources Reports No. 103. Rome: FAO; 2006.
- Johnson RW. Vegetation survey of the Brigalow Research Station, Theodore, Qld. Proc Royal Soc Qld 2004;111:39–61.
- Lobe I, Bol R, Ludwig B, Du Preez CC, Amelung W. Savanna-derived organic matter remaining in arable soils of the South African Highveld long-term mixed cropping: evidence from ¹³C and ¹⁵N natural abundance. Soil Biol Biochem 2005;37: 1898–909.
- Martin A, Mariotti A, Balesdent J, Lavelle P, Vuattoux R. Estimate of organic matter turnover rate in a savanna soil by ¹³C natural abundance measurements. Soil Biol Biochem 1990;22:517–23.
- Murty D, Kirschbaum MUF, McMurtie RE, McGilvray H. Does conversion of forest to agricultural land change soil carbon and nitrogen? A review of the literature. Glob Chang Biol 2002;8:105–23.
- Nadelhoffer KJ, Fry B. Controls on natural nitrogen-15 and carbon-13 abundances in forest soil organic matter. Soil Sci Soc Am J 1988;52:1633–40.

- Pongratz J, Reick C, Raddatz T, Claussen M. Effects of anthropogenic land cover change in the carbon cycle of the last millennium. Global Biogeochem Cycles 2009;23: GB4001.
- Radford BJ, Thornton CM, Cowie BA, Stephens ML. The brigalow catchment study: III. Productivity changes on brigalow land cleared for long-term cropping and for grazing. Aust J Soil Res 2007;45:512–23.
- Robertson FA, Myers RJK, Saffigna PG. Distribution of carbon and nitrogen in a long-term cropping system and permanent pasture system. Aust J Agric Res 1993;44:1323–36.
- Robinson D. δ^{15} N as an integrator of the nitrogen cycle. Trends Ecol Evol 2001;16:153–62.
- Shang C, Tiessen H. Carbon turnover and carbon-13 natural abundance in organo-mineral fractions of a tropical dry forest soil under cultivation. Soil Sci Soc Am J 2000;64:2149–55.
- Six J, Callewaert P, Lenders S, De Gryze S, Morris SJ, Gregorich EG, et al. Measuring and understanding carbon storage in afforested soils by physical fractionation. Soil Sci Soc Am J 2002;66:1981–7.
- Skjemstad JÖ, Catchpoole VR, Le Feuvre RP. Carbon dynamics in Vertisols under several crops as assessed by natural abundance ¹³C. Aust J Soil Res 1994;32:311–21.
- Skjemstad JO, Spouncer LR, Cowie B, Swift RS. Calibration of the Rothamsted organic carbon turnover model (RothC ver. 26.3), using measurable soil organic carbon pools. Aust J Soil Res 2004;42:79–88.
- Tisdall JM, Oades JM. Organic matter and water-stable aggregates in soils. J Soil Sci 1982;33:141-63.
- Zach A, Tiessen H, Noellemeyer E. Carbon turnover and carbon-13 natural abundance under land use change in semiarid savanna soils of La Pampa, Argentina. Soil Sci Soc Am J 2006;70:1541–6.