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#### The role of active fractions of soil organic matter in physical and chemical fertility of Ferrosols

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#### Abstract

The relationships between fractions of soil organic carbon (C) oxidised by varying strengths of potassium permanganate (KMnO<sub>4</sub>) and important soil physical and chemical properties were investigated for Queensland Ferrosols. These soils spanned a wide range of clay contents (31–83%), pH values ( $4 \cdot 4$ –7 $\cdot 9$ ; 1:5 water), and total C contents ( $12 \cdot 1$ –111 g/kg). Carbon fractions were derived by oxidation with 33 mM (C1), 167 mM (C2), and 333 mM (C3) KMnO<sub>4</sub>, while organic C and total C were determined by Heanes wet oxidation and combustion, respectively.

Aggregate stability was determined by wet sieving soil from the surface crust after 30 min of high intensity (100 mm/h), simulated rainfall on disturbed samples in the laboratory. The proportion of aggregates <0.125 mm (P125) was used as the stability indicator because of the high correlation between this size class and the final rainfall infiltration rate ( $r^2 = 0.86$ , n = 42). The soil organic C fraction most closely correlated with P125 was C1 ( $r^2 = 0.79$ , n = 42). This fraction was also highly correlated with final, steady-state infiltration rates in field situations where there were no subsurface constraints to infiltration ( $r^2 = 0.74$ , n = 30).

Multiple linear regression techniques were used to identify the soil properties determining effective cation exchange capacity (ECEC, n = 89). Most variation in ECEC ( $R^2 = 0.72$ ) was accounted for by a combination of C1 (P < 0.0001) and pH (P < 0.0001).

These results confirm the very important role played by the most labile (easily oxidised) fraction of soil organic matter (C1) in key components of the chemical and physical fertility of Ferrosols. Management practices which maintain adequate C1 concentrations are essential for sustainable cropping on these soils.

Additional keywords: oxisols, organic carbon, permanganate fractions, aggregate stability, infiltration, cation exchange capacity.

#### Introduction

Red Ferrosols of the inland Burnett region in south-east Queensland and the Atherton Tableland–Lakeland Downs region in north Queensland support predominantly rainfed cropping systems producing summer grain legume and cereal grain crops. The traditional land management practices of these systems (conventional tillage, crop residue removal as hay, or low levels of residue production due to seasonal water deficits and, with the exception of phosphorus, low levels

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of fertiliser inputs) have led to a decline in the physical and chemical fertility of these soils (Bridge and Bell 1994; Moody 1994). This decline, combined with the poor seasonal conditions experienced in recent years, has seriously threatened the continued viability of these cropping systems.

Perhaps the most significant change in soil properties on cropped Ferrosols has been the decline in the concentration of soil organic matter within the top 25–30 cm of the soil profile, the zone of tillage influence (Moody 1994; Bell *et al.* 1995, 1998). Associated with this decline in organic carbon (C) has been an increasing tendency for the soil to surface-seal under high intensity rainfall, along with a marked decline in effective cation exchange capacity (the ability to retain fertiliser nutrients). Both of these soil properties are influenced by soil organic matter, particularly in acidic, non-swell/shrink soils with variable charge characteristics like the Ferrosols (Moody 1994; Oades 1995*a*). Adoption of minimum tillage systems, use of pasture leys and green manure cropping, and organic fertiliser sources (e.g. feedlot manures) are currently being investigated as ways of reversing these fertility trends through organic matter management (Bell *et al.* 1997).

The well-established simulation models of C turnover in soils (the Rothamsted model, Jenkinson and Rayner 1977; and the Century model, Parton *et al.* 1989) identify various conceptual pools of soil C with varying 'lability' (i.e. reactivity) and turnover times. However, these conceptual pools are not able to be validated due to a lack of suitable measurement techniques (Oades 1995*b*). The commonly accepted measures of organic C (Walkley and Black 1934; Heanes 1984) do not discriminate between labile and non-labile organic C and it has been shown that a sizeable proportion of the total soil organic C in agricultural systems may be in the form of inert charcoal (Skjemstad *et al.* 1996). It is likely that the more labile fraction of soil organic C (with short turnover times) determines the various soil properties of concern for sustainable agriculture, but the measurement of this fraction is problematic.

There are a number of established physical and chemical methods of fractionating soil organic matter, along with more recent spectroscopic methods such as nuclear magnetic resonance, infrared, and mass spectroscopy (Oades 1995b). Of particular interest, because of its simplicity, is the chemical fractionation method that involves separation of soil organic matter of varying degrees of lability using oxidation with varying concentrations of KMnO<sub>4</sub> (Loginow *et al.* 1987). A simplification of the original technique was developed by Lefroy *et al.* (1993) and used by Blair *et al.* (1995) to develop a carbon management index (CMI), which described the changes in labile and total C under particular management systems relative to that in an adjoining reference site. Recently, Moody *et al.* (1997) found that the various KMnO<sub>4</sub> C fractions were well correlated with a range of soil chemical properties in a collection of acidic soils from Queensland, including Ferrosols. The development of critical values of particular labile C fractions to achieve desired levels of chemical values for physical fertility has yet to be achieved for various soil types.

This paper investigates in detail the relationship between the various  $KMnO_4$  C fractions in Queensland Ferrosols and the stability of soil aggregates (and resulting rainfall infiltration rates) under high intensity, simulated rain in both field and controlled conditions. In addition, the correlation between the  $KMnO_4$  C fractions and effective cation exchange capacity is examined.

#### Methods

#### Experimental sites

Ferrosol soils from the inland Burnett region of south-east Queensland and the Atherton Tableland and Lakeland Downs regions of north Queensland were used in this study. Sites represented a range of management histories, from virgin rainforest and savannah woodland ('virgin' subset) to grazed and ungrazed grass pastures and continuously cropped soil under conventional and no-till management systems ('agricultural' subset).

#### Rainfall infiltration and aggregate stability

Field rainfall infiltration parameters were measured at most locations using a portable rainfall simulator (Grierson and Oades 1977) with a plot area of  $1.6 \text{ m}^2$ . Two replicate measurements of infiltration were made at each site. Rainfall intensity was 140-175 mm/h(high energy rainfall;  $29 \text{ J/m}^2 \cdot \text{mm}$ ) depending on sampling occasion, with all vegetative cover carefully clipped and removed from the plot areas so that there was maximum opportunity for rain-induced crusts to form. At the north Queensland locations and some of those in the inland Burnett, the replicate infiltration measurements were made in pairs, with treatments consisting of either bared and undisturbed soil, or soil that had the surface completely protected from raindrop impact using crop residues or grass cuttings. Infiltration parameters calculated were (i) time to commencement of runoff, (ii) cumulative infiltration over 1 h, and (iii) final steady-state infiltration rate.

Laboratory rainfall simulations were conducted only on soils from the south Queensland locations, due to the relatively large amounts of soil required (approx. 50 kg/site). In these simulations, bulked samples of surface soil (0–10 cm depth) were air-dried, crumbled by hand, and loosely packed into each of 3 replicate trays 30 cm by 30 cm by 20 cm deep for each site. The trays were wetted by simulated, high intensity rain applied at a rate of 100 mm/h for 30 min, with the rainfall energy as applied to the unprotected soil surface equivalent to  $29 \text{ J/m}^2 \cdot \text{mm}$ . The infiltration rate during the final 5 min of the rainfall period was recorded for each tray. In addition, 2 samples were collected from the surface 5 mm of each tray after rain and analysed for aggregate size distribution using a modified Yoder wet-sieving apparatus (Loch 1994). Aggregate sizes ranging from >2 mm diameter to <0.125 mm diameter were collected and weighed (Loch 1995).

#### Soil chemical properties, total C, and C fractionation

Samples for chemical analyses were oven-dried  $(40^{\circ}\text{C})$  and ground to <0.125 mm for C analysis or <2 mm for other chemical analyses. Total C was determined by combustion in a Leco furnace and organic C was determined using the Heanes (1984) method with measurement of the optical density of the oxidised solution. The various C fractions were determined on duplicate samples as the amounts of C oxidised by 33, 167, and 333 mM KMnO<sub>4</sub>, as described in Blair *et al.* (1995). The C oxidised by 33 mM KMnO<sub>4</sub> was termed C1, the amount of C oxidised by 167 mM KMnO<sub>4</sub> was termed C2, and the amount of C oxidised by 333 mM KMnO<sub>4</sub> was termed C3. The difference between C3 and total C was termed C4 (recalcitrant C).

Other soil chemical analyses were undertaken using methods described by Rayment and Higginson (1992). Briefly, soil pH was determined in a 1:5 soil–water suspension, exchangeable cations were extracted with unbuffered  $1 \text{ M NH}_4\text{Cl}$ , and effective cation exchange capacity (ECEC) was determined from the sum of exchangeable cations and 1 M KCl extractable acidity.

#### Statistical analyses

Least-squares linear regressions were fitted to the relationships between the concentrations of the various C fractions and the steady-state infiltration rate in field rainfall simulator plots or the percentage of aggregates <0.125 mm in the surface crust after the laboratory rainfall runs. Similar regression techniques were used to quantify the relationship between the percentage of aggregates <0.125 mm and the infiltration rate during the final 5 min of the laboratory simulations.

Multiple linear regression models were used to determine the relative contributions of pH, clay content, and the various fractions of total C to ECEC in soils from all locations. In addition to C1, C3, and C4, another fraction (C3 - C1) was included in the analyses. When regression data are presented, standard errors of regression coefficients are shown in parentheses.

Table 1. Means, ranges, and medians of selected chemical properties of 89 Ferrosols (0-10 cm)

Attribute	Mean	Range	Median
pH (1:5 water)	$6 \cdot 2$	$4 \cdot 4 - 7 \cdot 9$	$6 \cdot 3$
Total C (g/kg)	$25 \cdot 4$	$12 \cdot 1 - 111$	19.7
Organic C (g/kg)	$23 \cdot 0$	$9 \cdot 88 - 99 \cdot 1$	$18 \cdot 3$
C1 (33 mM permanganate) (g/kg)	$2 \cdot 14$	$0 \cdot 89 - 10 \cdot 5$	1.57
C2 (167 mM permanganate) (g/kg)	$6 \cdot 43$	$2 \cdot 63 - 24 \cdot 2$	$5 \cdot 22$
C3 (333 mM permanganate) (g/kg)	$6 \cdot 46$	$2 \cdot 88 - 32 \cdot 8$	$4 \cdot 94$
C4 (total C – C3) (g/kg)	$18 \cdot 9$	$9 \cdot 22 - 78 \cdot 0$	$15 \cdot 1$
ECEC $(\text{cmol}(+)/\text{kg})$	12.5	$4 \cdot 4 - 31 \cdot 8$	$11 \cdot 8$
Clay (%)	63	31 - 83	65

#### Results

#### Total C and C fractions

There was a wide range in total C and the various C fractions in soil from the 89 sites sampled in north and south-east Queensland (Table 1). As neither the soil pH nor the soil types would suggest that any CaCO<sub>3</sub> was present, Leco C was assumed to represent total organic C. While total C varied by a factor of  $9 \cdot 2$ , C1 and C3 varied by factors of  $11 \cdot 9$  and  $11 \cdot 4$ , respectively. Heanes organic C (y) was related to total C (x) by the following equation:

$$y = 0.9375(\pm 0.012)x - 0.74(\pm 0.38) \qquad (r^2 = 0.987) \tag{1}$$

indicating that, on average, 94% of the total oxidisable C in these soils was measured by the Heanes wet oxidation method.

 
 Table 2. Correlation matrix representing the relationships between the additional amounts of soil C oxidised by increasing KMnO<sub>4</sub> concentrations

	Data are shown for soils within the agricultural subset $(n = 78)$			
	(C1)	(C2 - C1)	$(C3 - \dot{C}2)$	Leco $C - C3$
C1	1			
C2 - C1	$0.63^{**}$	1		
C3 - C2	-0.02 n.s.	$-0.73^{**}$	1	
Leco $C - C3$	$0.79^{**}$	$0.57^{**}$	$-0\!\cdot\!006$ n.s.	1

\*\* P < 0.01, n.s. not significant.

The correlations between the additional amounts of C oxidised by increasing concentrations of  $KMnO_4$  for soils in the agricultural subset are shown in Table 2. Results show a degree of significant correlation between some C components but not others, with these correlations either positive or negative. These results suggest no consistent relationship between the strength of the  $KMnO_4$  oxidant

and the proportion of additional total C oxidised. For simplicity and practicality, subsequent analyses of the relationship between fractions of soil organic C and soil physical and chemical properties were based on the total amounts of C oxidised by each concentration of KMnO<sub>4</sub>.

The C2 fraction was highly linearly correlated with C3  $(r^2 = 0.902)$  and comprised, on average, 97% of C3. This is a considerably higher proportion of C3 than that recorded by Lefroy *et al.* (1993) for 3 red brown earths, and suggests that similar information would be gained from consideration of C2 or C3 in Ferrosols. The carbon management index of Blair *et al.* (1995) currently uses C3 as a measure of labile C (Blair and Daniel 1996; Conteh *et al.* 1997).



Fig. 1. Relationship between infiltration rate after 30 min of simulated, high intensity rain in the laboratory and the percentage of aggregates <0.125 mm in the surface crust of Ferrosols.

#### Aggregate stability, C fractions, and infiltration of simulated rain

Soil samples from 42 of the 89 sites were subjected to simulated rain in the laboratory, with the percentage of aggregates <0.125 mm in the soil surface at the end of the rainfall event (P125) a good indicator of the rainfall infiltration rate for that soil (Fig. 1). Values of P125 ranged from 7.7% to 28.5%, with values for most conventionally tilled, continuously cropped soils in the range 24–28%. Data suggested that soils with P125  $\leq 12.7\%$  would result in rainfall infiltration rates >100 mm/h.

The concentration of total C and the fractions C1, C3, and C4 were all highly (P < 0.01) linearly correlated with P125 (Fig. 2). However, the concentration of the most labile C fraction (C1) was able to account for a significantly greater proportion of the variation in P125 than the other C fractions. By using the equations describing the relationship between total C or C1 and P125 in Fig. 2,



**Fig. 2.** Relationship between the percentage of aggregates <0.125 mm in the surface crust after 30 min of simulated, high intensity rain and (a) C1, (b) C2, (c) C3, (d) C4, and (e) total C.

#### Field rainfall infiltration and soil C

The relationship between infiltration of high intensity rain in the field and the total and labile C contents of soil in the top 10 cm of the profile were examined for 52 of the 89 sites in this study (Fig. 3), with 23 of these sites common to those on which laboratory rainfall simulations had been undertaken. Upon initial examination of the whole data set, the concentration of total or labile C was not a good predictor of the steady-state infiltration rate at these sites  $(r^2_{\rm TC} = 0.34; r^2_{\rm C1} = 0.48)$ , although this was not surprising given the variable roles that surface and subsurface limitations can play in limiting infiltration rate in the field.



Fig. 3. Relationship between final, steady-state infiltration rate of high intensity, simulated rain in the field and (a) total C and (b) C1. Sites are classified on the basis of surface or subsurface limitations to rainfall infiltration.

An attempt was made to classify the field sites where field infiltration measurements were undertaken on the basis of the degree of subsurface limitation to rainfall infiltration. Sites at which there was clear evidence of a subsurface limitation to infiltration (on the basis of a lack of response to surface cover, or very low estimates of saturated hydraulic conductivity derived from disc permeameter measurements at 10 cm depth) were delineated as 'subsurface limited', while the remainder were loosely classified as 'surface limited'. This division resulted in the groups of sites shown in Fig. 3, where steady-state infiltration rate was either strongly influenced by the C content (surface limited), or independent of C content (subsurface limited). Consistent with the results from the laboratory studies with aggregate stability under rain, the most labile C fraction (C1) accounted for a significantly greater proportion of the variation in steady-state infiltration rate in the field.

In order to compare results from the field and the laboratory rainfall simulations, the relationships shown in Fig. 3 were used to derive the contents of total C or C1 required to achieve a steady-state infiltration rate of 100 mm/h. These corresponded to 2.99 g/kg for C1 and 33.5 g/kg for total C, respectively. The values for both C1 and total C were approximately 15% higher than those derived from the laboratory studies (i.e. 2.58 and 29.30 g/kg, respectively).

#### C fractions, pH, and effective cation exchange capacity

A subset of the Ferrosol collection (67 samples) was used to investigate the contributions of soil pH, clay content, and the concentration of total C and the various C fractions towards effective cation exchange capacity (ECEC) using single factor and multiple regression techniques. Single factors were only able to account for a relatively small proportion of the total variation in ECEC, which ranged from  $4 \cdot 4$  to  $31 \cdot 8 \operatorname{cmol}(+)/\text{kg}$  (Table 1). The factor able to account for most variation in ECEC was C1 ( $r^2 = 0.38$ ), with C3 ( $r^2 = 0.31$ ) also a better predictor than total or Heanes C ( $r^2 = 0.24$  and 0.23, respectively). Neither soil pH ( $r^2 = 0.26$ ) nor clay content ( $r^2 = 0.06$ ) was as well correlated with ECEC as the more labile C fractions.

Multiple linear regression models were used to derive the best combination of soil properties for explaining the observed variation in ECEC:

ECEC =  $1 \cdot 64(\pm 0 \cdot 18)$  C1 +  $4 \cdot 56(\pm 0 \cdot 56)$  pH -  $19 \cdot 82(\pm 3 \cdot 56)$  ( $R^2 = 0 \cdot 72$ ) (2)

Both C1 and pH made highly significant (P < 0.0001) contributions to ECEC, while the addition of clay content or other C fractions did not increase the variation accounted for.

#### Discussion

These results confirm the very important role played by the labile fractions of soil organic matter in key chemical and physical properties of Ferrosol soils. The general decline in ability to allow high intensity storm rain to infiltrate and the reduction in ECEC, which are characteristic of most of the cropped Ferrosols in both north and south Queensland (Bridge and Bell 1994; Moody 1994; Bell *et al.* 1998), have negatively affected the long-term viability of both rainfed and irrigated farming systems. Our data suggested that management practices designed to redress these problems will necessarily involve both maximisation of C inputs and maintenance of the labile C component.

Results from these studies have confirmed the usefulness of the KMnO<sub>4</sub> oxidation technique as a measure of labile C fractions of importance to Ferrosol soils, with the C1 fraction providing the best indicator of key soil physical and chemical properties (Fig. 2 and Eqn 2). This result is consistent with the findings of Moody *et al.* (1997), who concluded that the functional groups associated with C1 appeared to determine ECEC of a range of acid soils including Ferrosols. However, the suggested use of C1 as an indicator of labile C from these studies contrasts with Lefroy *et al.* (1993) and Blair *et al.* (1995), who claimed that as all the labile C fractions showed similar sensitivities to management, the fraction oxidised by 333 mm KMnO<sub>4</sub> (our C3) should provide the basis of a carbon management index. Our data (Table 1) support the fact that C1

and C3 show similar sensitivities to management, with 11-fold variation across sites compared with only 9-fold variation for total C. The significantly greater correlation between C1 and both aggregate stability and ECEC, combined with the lack of any significant improvement in these models by adding the additional fraction (C3-C1), suggests C1 is the most important indicator for Ferrosols.

In the agricultural subset, C1 averaged 7.9% of total C compared with 9.5% in the virgin soils. However, within the agricultural subset, there was a considerable range (5.7-10.0%) in the proportion of total C as C1. This suggests that it is possible to manipulate the proportion of labile C by management.

The strong relationship between P125 and the infiltration rate of simulated rain in the laboratory (Fig. 1) was consistent with the results of Loch (1989), although in our case the rainfall was over a 30-min period rather than continuing until a steady-state infiltration rate was achieved. There were strong correlations between P125 and the concentration of C1 (Fig. 2) in the laboratory and between C1 and steady-state infiltration rates in the field as long as surface sealing was the dominant factor controlling infiltration at that site (Fig. 3). This demonstrated that C1 provided a very practical indicator of potential infiltration rates and erosion risk in the field. The higher concentration of C1 required to achieve an infiltration rate of 100 mm/h in the field, as opposed to that in the laboratory, probably reflected the greater energy input and resulting aggregate breakdown under higher rainfall intensities (140–175 mm/h  $v.~100~{\rm mm/h})$  over a longer rainfall duration (1 h v. 0.5 h). Indeed, Cleary et al. (1987) and Loch et al. (1988) have shown that the proportion of fine particles in the surface seal of a particular soil increased with time, although an equilibrium value was eventually reached.

The dominant role of C1 and pH in determining ECEC across Ferrosols with a wide range in clay contents demonstrated the variable charge characteristics of these soils and the relative unimportance of the kaolin and iron and aluminium oxides (Isbell 1994; Moody 1994). It also emphasises the need to maintain soil pH and labile C levels if leaching losses of nutrient cations are to be prevented (Uehara and Gillman 1981). The importance of pH in our results (Eqn 2), compared with that of Moody *et al.* (1997), is merely a reflection of the much wider range of soil pH represented in our soils (i.e.  $4 \cdot 4 - 7 \cdot 9$ , Table 1). Analyses of subsets of samples within narrower pH ranges showed that C1 could account for much greater proportions of the variation in ECEC (e.g. 62% and 83% of the variation in ECEC for pH ranges of  $5 \cdot 5 - 6 \cdot 0$  and  $6 \cdot 5 - 7 \cdot 2$ , respectively) than in the full data set (namely 38%).

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