Chapter 1

Introduction

1.1. General background

Soil organic matter contains about two-thirds of the total terrestrial carbon (C) pool (e.g. Trumbore et al., 1996). Total global soil organic carbon (SOC) pool has been estimated in the order of 1500 Gt in the top one metre (Adams et al., 1990; Eswaran et al., 1993; Batjes, 1996). The most unified political approach of greenhouse gas emissions and consequent global warming has focused on the importance of the mechanisms that control the storage and release of C from soils.

The amount of soil C storage is controlled primarily by two fundamental factors: input by net primary production (its quantity and quality) and its decomposition rate. However, the biological stability of SOC is influenced by the physical and chemical environment of the soil (e.g. moisture, temperature, pH, aeration), the chemical structure of SOC (i.e. its susceptibility to decay), and the physical accessibility of the organic matter to microbes and enzymes, i.e. mechanisms of protection offered by soil minerals through adsorption and aggregation (Sollins et.al., 1996; Jastrow and Miller, 1997; Baldock and Skjemstad, 2000; Gleixner et.al., 2001). Together with the ratio of inputs and losses, these parameters determine the rate of C turnover in the soil and subsequently the SOC levels.

Organic C accumulation in soils has been observed in some long-term experiments to be linearly related to C input levels at steady state (Paustian et al., 1997; Huggins et al., 1998; Kong et al., 2005). However, C saturation behaviour has been observed in other experiments where SOC

level did not increase with increasing multiple C input (Soon, 1998; Huggins et al., 1998; Reicosky et al., 2002). Hassink (1997) observed same amount of C in silt + clay particles of Dutch arable and the corresponding grassland soils, though total organic carbon (TOC) content was higher in grassland soils. From this observation, Hassink (1997) concluded that these fine soil particles might have reached to a maximum to their capacity to store C. Hassink (1997) proposed protective capacity model depending on the relationship between % silt + clay particles and C associated with these particles. Six et al. (2002) ran regression between silt + clay particles and C associated with these particles across the land uses (forest, grassland and cultivated systems) and observed significant difference in slope and intercept among the protective capacity curve, and attributed these difference to C input and disturbance under different land uses. Influence of land use on SOC storage has been observed in many studies (Ellert and Gregorich, 1996; Guo and Gifford, 2002; Degryze et al., 2004). In all the studies lower SOC content was observed in cultivated soil compared to forest or woodland. Since land use influence SOC content, determination of soil C saturation level would give an estimation of potentiality of those soils to store C up to maximum capacity. Carbon saturation deficit was calculated from the difference between actual C content on silt + clay particles and maximum amount of C that could be associated with these particles (Hassink, 1996). Using Hassink,s protective capacity model, Angers et al. (2011) estimated C saturation deficit of French soils and observed some soils oversaturated with C. Though oversaturation might be observed because of some uncertainty around the theoretical saturation curve (Angers et al. 2011) there might have been other reasons for this oversaturation. Soil properties like presence of multivalent cations (Baldock and skjemstad, 2000), poorly crystalline Fe and Al content influence organic C content in soils (Powers and Schlesinger, 2002; Kleber et al., 2005;

Wiseman and Puttmann, 2005). Thus soil properties, other than silt + clay particles that also influence on SOC storage, might be responsible for oversaturation in some soils.

The concept of C saturation implies that SOC will be more protected in soils where protective capacity is not saturated. In soils where protective capacity is saturated, excess C will be remained as biologically available form and mineralized by decomposer organisms compared to that where protective capacity are less saturated (Baldock and Skjemstad, 2000). In addition to these, the higher the C saturation deficit in soils, the greater will be the SOC storage potential and the greater will be the efficiency to sequester added carbon (Hassink and Whitmore, 1997) either from fresh residue or dissolved organic C (DOC).

Though organic C could be stored in soils by adsorption on soil particles as well as through formation of aggregates, the present study was conducted to determine C storage capacity of soils controlled by silt + clay particles. Study on C storage in soil aggregates is also important for determining C sequestration potential of whole soil, though in some recent studies no significant difference in C content, chemical nature of C and mean residence of C has been observed between micro (53-250 μm) and macroaggregates (250-2000 μm) (Rabbi et al., 2013, 2014a, 2014b).

1.2. Hypothesis and objectives of the study

The overarching hypothesis of the research was that land use and soil properties influence C saturation of protective capacity, which will further determine the loss of existing soil C (through microbial decomposition or chemical dissolution) and potentiality of soils to sequester added C (either from fresh residue or DOC).

The specific hypothesis of the study were: (i) land use and soil properties influence soil C saturation level (ii) mineralization of SOC will be higher from soils

having lower silt + clay and lower C saturation deficit (iii) mean residence time (MRT) of soil C pool will be higher in soils having higher silt + clay and higher saturation deficit (iv) stabilization of added residue C will be higher in soils having higher saturation deficit. (v) higher C saturation of silt + clay particles will increase desorption of indigenous soil C and decrease the adsorption of added DOC.

The specific objectives of the research work were to (i) determine the protective capacity and C saturation deficit of soils using a relevant model (ii) determine the influence of C saturation on microbial decomposition of SOC (iii) find the relationship of C saturation level on the MRT of soil C pool (iv) determine the influence of C saturation level on the stabilization of added residue C (v) determine the chemical desorption of organic C from soils of different saturation level (vi) determine the adsorption of DOC on silt + clay particles of different C saturation level.

1.3. Thesis structure

An introduction and literature review covering the aspects of protective capacity and C saturation of that capacity has been presented in Chapter 1.

Chapter 2 contains calculated protective capacity and C saturation deficit of Australian Ferrosol and Dermosol using an exponential model proposed by Sparrow et al. (2006). Influence of land use (pasture, cropping and woodland) and soil properties (texture and mineralogy) on the C saturation level has also been determined to test the hypothesis that land use and soil properties influence on soil C saturation. The findings of this part of the research have been discussed in this chapter.

Chapter 3 explains the influence of C saturation levels on SOC mineralization and MRT of SOC pool. A five months incubation experiment was conducted to calculate

cumulative C mineralization (C_{min}) and percent of SOC mineralized (SOC_{min}) from Australian Ferrosol having different C saturation level. The constrained two pool SOC model was used to calculate MRT of SOC pool. The findings of the experiment have been presented in this chapter.

Chapter 4 explains the influence of C saturation level on the stabilization of added residue derived C. An eight month incubation experiment was conducted in the laboratory to determine the stabilization of residue (grass residue) derived C in 12 samples of Australian Ferrosol. Available nutrients were applied on residue in one set of samples to observe the influence of nutrients on decomposition of residues and subsequent stabilization of C in soils. The findings of the experiment have been discussed in this chapter.

Chapter 5 explains the influence of soil C saturation level on the chemical desorption of SOC and adsorption of added dissolved organic carbon (DOC). An adsorption experiment was conducted by adding solutions containing six concentrations of DOC (from 0-300 mg L^{-1}). Results were analysed by applying initial mass isotherm (IMI) approach (Nodvin et al., 1986). The findings of this experiment have been presented in this chapter.

Chapter 6 contains a summary and synthesis of all the outcomes of the above mentioned chapters, and discussed with future research implications.

1.4. Storage and protection mechanisms of SOC

The prerequisite of storage of organic carbon (OC) in soil is the protection and stabilization. Stabilization means decrease in the potential for SOC loss by respiration,

erosion or leaching. This is not the result of any single factor. Sollins et al. (1996) defined stability as the integrated effect of recalcitrance, interactions, and accessibility. Recalcitrance of organic substances arises from the characteristics of those substances due to elemental composition, presence of functional groups and molecular conformation. The term interaction refers to the molecular linkage between organics and either inorganic or organic substances. Accessibility means access of microbes and extracellular enzymes to decompose OC. The mechanism of soil organic matter (SOM) stabilization can be divided into physical, chemical or physico-chemical and biological or biochemical protection (Von Lutzow et al., 2006). However, classification of stabilization mechanism involves more confusion (Theng et al., 1989). The formation of organo-mineral complexes are considered to be physical protection by some authors, while other use the chemical or biochemical protection for the same mechanism (Von Lutzow et al., 2006).

1.4.1. Chemical stabilization

Chemical stabilization of SOM is understood to be the result of the chemical or physicochemical binding between SOM and soil minerals (i.e. clay and silt particles). Indeed, many studies have reported a relationship between stabilization of organic C and N in soils and clay or silt + clay content (Feller and Beare, 1997; Hassink, 1997; Ladd et al., 1985; Merckx et al., 1985; Sorensen, 1972). In addition to the clay content, clay type (i.e. 2:1 versus 1:1 versus allophonic clay minerals) influences the stabilization of organic C and N (Feller and Beare, 1997; Ladd et al., 1992; Sorensen, 1972; Torn et al., 1997).

Clay sized particles such as layer silicates (< 2 µm), sesquioxides (crystals 5-100 nm), short range ordered Fe-oxides (3-10 nm) and amorphous Al-oxides (< 3 nm) provide the most significant surface area on to which organic matter (OM) can be adsorbed. The stabilization of OM bound to mineral surfaces was evident from recognizing OM in silt +

clay fractions to be older (Anderson and Paul, 1984; Scharpenseel and Becker-Heidmann, 1990; Quideau et al., 2001; Eusterhues et al., 2003) or longer turnover time (Balesdent et al., 1987; Balesdent, 1996; Ludwig et al., 2003) than OM in other soil OM fractions (Chenu and Stotzky, 2002).

Kalbitz et al. (2005) showed that sorption of soluble OM to subsoil material (Bw horizon) reduced OM mineralization to 20-30% compared with mineralization in soil solution. A detailed mechanistic understanding of why sorption to soil minerals reduces decomposition rates is lacking and is complicated by artefacts in the experiments. Chenu and Stotzky (2002) suggest that small molecules sorbed to mineral surfaces cannot be utilized by microorganisms unless they are desorbed so that they can be transported into the cell (Chenu and Stotzky, 2002). It is difficult to demonstrate the unavailability of adsorbed molecules because desorption can occur through microbial secretions during the experiments (Chenu and Stotzky, 2002). The adsorption of macromolecules is considered non-reversible (Chenu and Stotzky, 2002) and associated with conformational changes that render macromolecules unavailable to the action of extracellular enzymes (Theng, 1979; Khanna et al., 1998). Degradation can also be hindered by adsorption of the relevant enzyme to clay minerals rather than by adsorption of the substrate (Demaneche et al., 2001). Various mechanisms are considered for interactions of OM with mineral surfaces, i.e. ligand exchange, polyvalent cation bridges and weak interactions, such as hydrophobic interactions including van der Waals forces and H-bonding (Theng, 1979; Oades, 1989; Vermeer and Koopal, 1998; Vermeer et al., 1998).

1.4.1.1. Ligand exchange

Anion exchange between simple coordinated OH groups on mineral surfaces, carboxyl groups and phenolic OH groups of the OM (a strongly exothermic reaction) is

one important mechanism for the formation of strong organo-mineral associations, e.g. Fe-O-C bonds (Gu et al., 1994). Complexation of OM on mineral surfaces via ligand exchange increases with decreasing pH, with maximal sorption between pH 4.3 and 4.7, corresponding to pKa values of the most abundant carboxylic acids in soils (Gu et al., 1994). Therefore, ligand exchange between reactive inorganic hydroxyls (OH groups of Fe, Al and Mn-oxides and edge sites of phyllosilicates) and organic carboxyl and phenolic OH groups is restricted to acid soils rich in minerals with protonated hydroxyl groups (Shen,1999). Kaiser and Guggenberger (2003) found that dissolved organic matter (DOM) rich in carboxyl-and aromatic-C forms strong complexes with Al and Fe oxides via ligand exchange in acid subsoils where the sorption of N-containing OM is also favoured by acidic functional groups (carboxyl, enol, phenolic OH group) and not by amino groups (Kaiser and Zech, 2000).

Exchange between cations on the surfaces of layer silicates (permanent charge) and organic cations (amino, amide and imino groups) usually occurs between pH from 5 to 6 at the iso-electric point of most amino acids (Oades, 1989; Jones and Hodge, 1999).

1.4.1.2. Polyvalent cation bridges

Organic anions are normally repelled from negatively charged surfaces in soils, but binding occurs when polyvalent cations are present on the exchange complex. Unlike Na^+ and K^+, polyvalent cations are able to maintain neutrality at the surface by neutralizing both the charge on the negatively charged surface (e.g. in clay minerals) and the acidic functional group of the OM (e.g. COO^-) and thus act as a bridge between two charged sites. The major polyvalent cations present in soil are Ca^{2+} and Mg^{2+} in neutral and alkaline soils and hydroxypolycations of Fe^{3+} and Al^{3+} in acid soils. The Ca^{2+} ions do not form strong coordination complexes with organic molecules, in contrast to Fe^{3+} and

Al^{3+}. For a long chain organic molecule, several sites of attachment to the clay particle (segment-surface contact) on permanent charge sites of expandable layer silicates are possible. Microbially secreted polysaccharides frequently carry a negative charge due to the presence of uronic acids that adsorb strongly to negatively charged clay surfaces through polyvalent cation bridging (Chenu, 1995). The bonding efficiency of OM on phyllosilicates by cation bridges is weaker compared with ligand exchange on Al and Fe hydroxides (Benke et al., 1999; Kaiser and Zech, 2000).

1.4.1.3. Weak interactions

Hydrophobic interactions are driven by the exclusion of non-polar residues (e.g. aromatic or alkyl C) from water (entropy-related interactions) to force the non-polar groups together. Van der Waals forces (electroststic forces) can operate between atoms or non-polar molecules caused by a temporarily fluctuating dipole moment arising from a brief shift of orbital electrons to one side of one atom or molecule, creating a similar shift in adjacent atoms or molecules. In the case of hydrogen bonds, a hydrogen atom with a positive partial charge interacts with partially negatively charged O or N atoms.

Non-expandable layer silicates (e.g. 1:1 layer silicates such as kaolinite) or quartz particles without layer charge and without interlayer spaces exhibit only weak bonding affinities. The negative charge on the siloxane surface of other clay minerals depends on the type and localization of the excess negative charge created by isomorphic substitution. In the absence of a layer charge a siloxane surface may be considered hydrophobic (Sposito et al., 1999). Uncharged polysaccharides and extracellular enzymes or other proteins can form linkages via hydrogen bonding or van der Waals forces because of the presence of hydroxyl and other polar groups in the molecule (Quiquampoix et al., 1995). Their typically high molecular weight offers a large number of potential surface-segment contacts and thus strong binding between uncharged polysaccharides and clays can be

established (Theng, 1979). Hydrophobic interactions become more favourable at low pH when hydroxyl and carboxyl groups of OM are protonated and the ionisation of carboxyl groups is suppressed.

1.4.2. Physical protection

Organic matter is physically protected from decomposition due to inaccessibility of microbes. The reduction in accessibility mainly results from the occlusion of soil organic matter in microaggregates. The diameter of microaggregates is smaller than 250 µm and the most stable one is 2-20 µm (Krull et al., 2003). The dimension of bacterial cell ranges from 0.2-2.0 µm (Bergey and Holt, 1994). Small microaggregates are rich in pores < 0.2 µm in diameter which is considered to be limiting size for access to bacteria.

Another mechanism of reduction of accessibility of microbes is the intercalation or interlayer complex formation of 2:1 type clay minerals with organic molecules (Righi et al., 1995; Theng, 1979). The interlayer porosity of clay minerals varies from 0.5-50 nm (Sing et al., 1985). Organic macromolecules such as enzymes, proteins, fatty acids or organic acids can intercalate into the interlayer spaces of 2:1 type expandable phyllosilicate clays at a pH < 5 (Violante and Gianfreda, 2000). Most of these fractions are transformed into microbially resistant humic substances (Flaig et al., 1975). According to Wattel-Koekkoek et al. (2001) 2:1 clay lattice minerals preserve more chemically resistant organic compounds than 1:1 clay minerals.

1.4.3. Biochemical stabilization

Biochemical recalcitrance or refractory is viewed as one of the most promising explanations of organic matter (OM) stabilization in soil. Such recalcitrance or refractory

nature of biomacromolecule is attributed to its biochemical structure. The decomposition rate of biomacromolecules depends mainly on nature of bonding of the macromolecule. The presence of hydrolytic i.e. ester, glycoside, ether, peptide, C-N bonds makes the organic molecule susceptible to decomposition. Hydrolytic enzymes such as cellulose, protease, chitinase etc. are abundant in soil. The natural polymers such as lignin is resistant to decomposition because it contains aromatic structures and has arylglycerol-β-arylether (β-O-4) linakges (Derenne and Largeau, 2001; Kogel-Knabner, 2002). The aromatic structure of waxes, cutin and suberin give these molecules resistance to decomposition (Derenne and Largeau, 2001). Moreover, hydrophobicity of organic molecules like lipids may be responsible for its slower decomposition rate (von Lutzow, 2006). With the advent of modern nuclear magnetic resonance (NMR) techniques it becomes possible to relate the decomposition rate with the functional groups present in decomposing microorganisms. Baldock et al. (1997) summarized that the rate of microbial decomposition of OM is a function of ratio between alkyl-C to O-alkyl-C ratio and it tends to increase during decomposition. In contrary to selective preservation of lignin, it was revealed that during decomposition the aromatic C content may increase, decrease or remain unchanged. Thus, relative rate of decomposition can be predicted by using presence or absence of functional groups in OM.

1.5. Capacity of mineral soils to protect OM

By all the mechanisms involved in the protection of OM against biological attack in soil, only a finite amount of OM can be protected. Thus the capacity of soil to protect OM against biological attack is not unlimited but there has a limit. Since fine soil particles especially silt + clay plays important role in protecting organic C, more physical protection has been observed in fine-textured soils compared to that in coarse-textured

soils (Jenkinson, 1988; Van Veen and Kuikman, 1990). As a consequence fine-textured soils have higher organic C contents than coarse textured soils when supplied with similar input of material (Jenkinson, 1988; Hassink, 1994). The importance of silt + clay in storing C has been observed in many experiments where SOC content were positively correlated with silt + clay contents of the soils (Hassink, 1997; Six et al., 2002; Sparrow, 2006; Barthes et al., 2008).Thus observing the importance of silt + clay particles in protecting organic C, Hassink (1996, 1997) defined protective capacity as the maximum amount of C that can be associated with silt + clay particles in the soils. Depending on this relationship, Hassink (1997) developed a model to determine the protective capacity (the capacity of a soil to physically preserve organic C by its association with clay + silt particles) of soils.

$$\text{Protective capacity (g C kg}^{-1}\text{ soil)} = 4.09 + 0.37 \text{ (\% of silt and clay particles).}$$

In the model Hassink used some published results on uncultivated soils and corresponding soils of cultivated arable land. The relationship between silt + clay content and C associated on that particles were observed from soils of Netherland, Middle and South America and Africa and were included in the model. Some published data of Australian soils (Dalal and Mayer, 1986; Turchenek and Oades, 1979) did not follow the relationship and were not included in the model. Compared to the soils of other continents, Australian soils contained lower C and N in < 20 µm particles. Since Australian soils were not different from the other soils with respect to dominant clay type, the combination of lower rainfall and higher temperature in Australian sites were considered to be responsible for not showing any relationship. In developing the model Hassink (1997) also observed that the amount of C and N in the > 20 µm particles was not correlated with content of those particles. This finding strengthens the importance of < 20 µm particles (clay and fine silt) in protecting organic C from decomposition.

Six et al. (2002) expanded the analysis of Hassink (1997) for the protection of C within primary organo-mineral complexes (silt + clay particles). They performed the regressions between the C associated with silt + clay particles and the content of silt + clay particles across ecosystems (forest, grassland and cultivated systems), clay types (1:1 versus 2:1), and size ranges for silt + clay (0-20 µm and 0-50 µm). All regressions were significant, but significant difference in slope and intercept of the curves under different ecosystems was observed. Significant difference in intercept and slope was observed in grassland and forest than cultivated soils for the 0-50 µm particles. The difference was not significant for 0-20 µm particles. However, the intercept for the 0-50 µm silt and clay particles was observed to be significantly higher than for the 0-20 µm particles. The higher intercept for 0-50 µm particles was concluded to be due to additional C that binds primary particles into silt-sized aggregates. In contrast to Hassink (1997), Six et al. (2002) observed significantly different relationships for 1:1 clays versus 2:1 clays for both 0-20 µm and 0-50 µm particles. They concluded that the lower stabilization of carbon in 1:1 type clay might be due to lower CEC and specific surface (Greenland, 1965) for adsorption of organic materials. The effect of climate was also considered another reason for lower stabilization of C in 1:1 type clays since most 1:1 clay dominated soils were located in subtropical regions, where higher temperature and moisture regimes induce faster decomposition of organic matter. The contrasting effect of Fe and Al oxides in organic C stabilization was also explained by Six et al. (2002). By being strong flocculants, Fe and Al oxides induce available surface for adsorption of SOM in one hand. The strong flocculating oxides might reduce available surface and conversely might also co-flocculate and stabilize SOM.

Another protective capacity model was proposed by Carter et al. (2003) as a simple linear regression (y = 9.04 + 0.27 % silt + clay particles) based on the data of

Elustondo et al. (1990) on maize crop and grassland soils in Canada. The model was similar to that of Hassink (1997) but the intercept was greater. At the Hassink (1997) model < 20 µm (medium sized silt) was considered as the upper limit of silt, while Elustondo et al. (1990) used 50 µm as the upper limit, following the Canada Soil Survey Committee (1977).

Sparrow et al. (2006) found significant exponential relationship between silt + clay content and the C associated with these particles using Australian Ferrosol and Sodosol under pasture and cropping in Tasmania. At this model < 53 µm was considered as the upper limit for silt + clay particles.

$$\text{Sparrow's model; } y = 6.67\, e^{0.0216x} \ (r^2 = 0.61,\ p < 0.001).$$

1.6. Soil C saturation

The concept of protective capacity arisen the concept of C saturation in soil which means, if the capacity of soil to physically protect organic C is limited, there must have a limit of C that could be adsorbed and stored in soil. Soil C saturation occurs when its level in soil cannot be increased regardless of change in land use and management practices (Fig. 1.1).

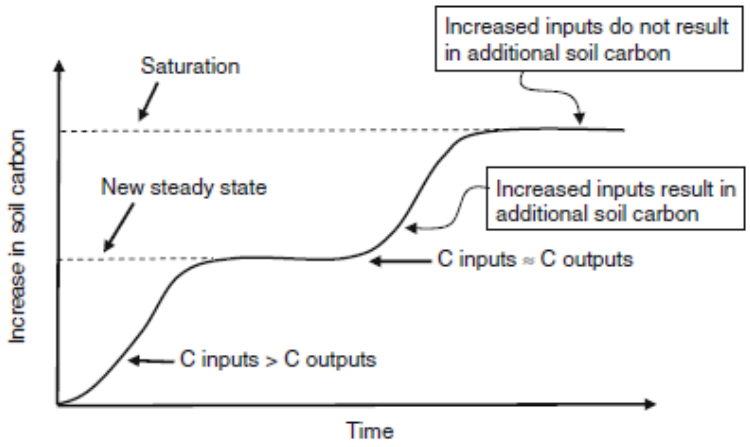

Fig. 1. 1. Dynamics of soil C following changes in management intended to sequester C. A new steady state in soil C is reached following a change in land use. If soil is C saturated, no accumulation in soil C will occur following a change in land use intended to sequester C. If soil is not C saturated, several new steady states may be reached prior to soil C saturation, following several successive changes in management (West and Six, 2007).

Soil C content at a new or any steady state represent the maximum C level at that condition (climatic regime, productivity and management practice), but not represent the actual saturation level until changed due to change in land use.

1.7. Evidence of carbon saturation

Though many long-term field experiments showed a proportional relationship between C inputs and soil C content across treatments (Paustian et al., 1997; Kong et al.. 2005), in some long-term experiments addition of varying amounts of C levels did not increase the equilibrium C content, even at higher C addition level (Campbell et al.. 1991; Solberg et al., 1997; Paustian et al., 1997; Huggins et al., 1998; Reicosky et al., 2002)

which indicated C saturation in soils. In addition, by relating C inputs with C content for 48 agricultural systems across 11 sites Paul et al. (1997) and Six et al. (2002) observed an asymptotic relationship explained slightly more of the observed variability than a linear relationship. Carbon saturation of silt + clay particles of Dutch arable and corresponding grassland soils was observed by Hassink (1997). Although the Dutch arable soils contained less C and N than the corresponding grassland soils, the amounts of C and N associated with silt + clay particles was the same, and indicated C saturation of these particles (Hassink, 1997).

1.8. Carbon saturation deficit of soil

Hassink (1997) observed C saturation in silt + clay (< 20 µm) particles. Thus using the protective capacity model Hassink (1996) calculated the C saturation deficit of the soils (the difference between the actual amount of C in the particle-size fraction <20 µm and the maximum amount that can be associated with this particle-size fraction). Many authors have used Hassink's model to calculate protective capacity and C saturation deficit of soils (Stewart et al., 2008 and 2009; Zhao, 2006; Angers et al., 2011). Higher C saturation deficit had been observed in cropping soils (Matus et al., 2008; Angers et al., 2011), and in fine-textured soils compared to coarse-textured soils (Angers et al., 2011).

1.9. Concept of specific surface area and silt + clay protective capacity of mineral soil

The stabilization of OM produced from microbial decomposition of plant residues are controlled by the specific surface area (SSA) provided by clay minerals (< 2 µm) (Saggar et al., 1996). Besides layer silicates (< 2 µm), sesquioxides (crystals 5-100 nm), short range ordered Fe-oxides (3-10 nm) and amorphous Al-oxides (< 3 nm) provide

surface area for OM adsorption. The total surface area of nonexpanding 1:1 clay mineral ranges from 10×10^3 m^2 kg^{-1} to 20×10^3 m^2 kg^{-1}, whereas the surface area of expanding 2:1 type montmorillonite can be 800×10^3 m^2 kg^{-1} (Bohn et al., 2002). The specific surface area of oxide and hydroxide minerals such as ferrihydrite, goethite, hematite, gibbsite and amorphous aluminium oxide can vary from 19×10^3 m^2 kg^{-1} to 285×10^3 m^2 kg^{-1} (Kaiser and Guggenberger, 2003). The specific surface area (SSA) of soil mineral particles increases in progressing from large to small particles. However, the surface area of minerals could not be the only predictor for extent of OM stabilization for discontinuous coverage (Kogel-Knabner et al., 2008). Mayer (1994) and Keil et al. (1994) proposed that organic C are associated with mineral surface as a single layer spread evenly over the entire surface. Ransom et al. (1997) showed the evidence of OM in patches either associated with or encapsulated by mineral surfaces. The singly coordinated, reactive OH groups on Fe and Al oxides and at edge sites of phyllosilicates, which are able to form strong bonds by ligand exchange, are a measure of the amount of OM stabilized in soils in organo-mineral associations (Kleber et al., 2004). Kaiser and Guggenberger (2003) demonstrated that sorption occurs preferentially at reactive sites such as edges, rough surfaces or micropores (e.g. edges of illite particles where amphoteric Al-OH groups are exposed, crystal surfaces of Fe-oxyhydroxides with singly coordinated OH^- groups). Thus the mineralogy, surface charge characteristics, and precipitation of amorphous Fe and Al oxides on clay mineral surfaces are involved in the protection of OM in soils. However, not only clay, but the importance of silt + clay particles in the physical protection of OM has been indicated in many studies (Theng, 1979). Hassink (1997) observed the similar organic C content in silt + clay particles (< 20 µm) of grassland and adjacent arable land in spite of higher C content in > 20 µm particles of grassland soils. Moreover Hassink (1997) observed significant positive relationship between silt + clay

content and carbon and nitrogen associated on these particles of soils from different continents and thus proposed the model of protective capacity of soils to store organic C. Six et al. (2002) used < 50 µm particles as the upper limit for silt + clay particles and observed significant positive relationship between content of these particles and associated carbon. However, higher C content in < 50 µm particles than < 20 µm was also observed (Six et al., 2002). Thus protection of organic C with silt + clay particles, and saturation of these particles with C is more explainable than specific surface area of mineral because of the complexity in the protection mechanism.

1.10. Influence of land use on the protective capacity and C saturation in soils

Land use and land management influence on both storage and mineralization of organic C from soil. The effect of land use is due to difference in input and level of disturbance. Lower organic C content in cropping soils is due to lower input and higher disturbance compared to forest and grassland. Thus the reduction in C stock upto 42% has been observed due to conversion of native forest to cropland (Guo and Gifford, 2002). The rate of loss of soil C is more in the tropics than in temperate regions, in coarse-textured soils than in fine-textured soils (Lal, 2008). The protective capacity model proposed by Hassink (1997) was based on the data of temperate and tropical regions, from cultivated and uncultivated soils. Thus this model gives an average idea of capacity of soils to protect organic C. Six et al. (2002) observed different regression line for three different ecosystems (forest, cropping and grassland). Though in the previous study, no relationship was observed between silt + clay content and C associated on these particles in Australian soils, Sparrow et al. (2006) observed an exponential relationship between these two parameter using Tasmanian Ferrosol and Sodosol under pasture and cropping.

Sparrow et al. (2006) commented that Tasmanian soils were different from soils of other regions in Australia. Plotting the data on Hassink (1997) line Sparrow et al. (2006) observed that though most of the cropping soils followed the Hassink's line, many data of Ferrosol showed positive departure from Hassink's line that had > 60 % silt + clay. The departure was higher in pasture than cropped Ferrosol. These findings indicated the influence of land use and soil type on C saturation level. Angers et al. (2011) observed saturated soils in forest and grassland and in soils containing lower clay and fine silt, by using Hassink's model. Highly unsaturated soils were also observed in cultivated lands.

1.11. Effect of carbon saturation deficit on the accumulation of added organic C in soil

Carbon saturation deficit has been observed to influence the accumulation of added residue in whole soils (Six et al., 2002; Stewart et al., 2007) as well as in individual soil C pools (Hassink, 1997; Stewart et al., 2008). Hassink (1996) observed significant positive relationship between saturation deficit and preservation of applied residue ^{14}C in silt + clay particles (< 20 µm) after 53 days of incubation. After 2.5 years of incubation experiment, conducted by Stewart et al. (2008) it was observed that both C saturation deficit and C input level influenced the stabilization of residue derived C. They used seven long-term agricultural research sites with several soil types and a range of characteristics (e.g., texture, mineralogy, and climate). To obtain differences in saturation deficit within each site, they obtained low and high OM soils by sampling the A-and C-genetic horizons. The A- and C- horizons of soils were similar in most major physical and chemical properties (e.g., clay content, pH, CEC) except for SOC content. Different amounts (i.e., 1× and 5× average annual C addition under field conditions) of ^{13}C-labeled wheat straw were added to both the A-and C-horizons. After the incubation it was

observed that samples from six of seven sites stabilized a greater proportion of added ^{13}C in the C-horizon compared to the A-horizon. The higher stabilization efficiency of C-horizon is due to larger saturation deficit compared to A-horizon.

1.12. Conclusion

The determination of protective capacity of soils depending on silt and clay particles and associated C on these particles is an indicator of C storage capacity under existing condition (climate, land use and land management). The use of any proposed model for evaluation of saturation level in soils might not indicate the actual capacity under that condition. However, influence of other factors (poorly crystalline minerals, multivalent cations) that also have capacity to store C in soil, might cause some overestimation of silt + clay protective capacity. Since all the proposed protective capacity model were based on the positive relationship between % silt + clay particles and C associated with these particles, the calculation of saturation deficit using any protective capacity model should give the similar trend of saturation level. Thus estimation of C saturation deficit using any model could be used as important parameter to determine the behaviour of C for microbial decomposition, chemical desorption, or to store DOC and stabilize added residue derived carbon.

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Chapter 2

Land use and mineralogical control of carbon saturation in Ferrosol and Dermosol of Northern New South Wales

Abstract

The concept of carbon (C) saturation implies that soils have a finite capacity to store C in the stable form, depending on their silt + clay content. Due to importance of silt + clay particles in storing C in more stable form, the protective capacity (the capacity of a soil to physically preserve organic C by its association with clay and silt particles) are calculated from the relationship between % silt + clay and C associated on these particles. The present study was conducted to calculate the protective capacity and saturation deficit of Australian Ferrosol and Dermosol using an exponential model ((y = 6.67 $e^{0.0216x}$ (r^2 = 0.61, p < 0.001)) proposed by Sparrow et al. (2006). The soils were collected from pasture, cropping and woodland areas and two soil types with different texture and mineralogy were chosen to test the hypothesis that both land use and soil properties influence soil C saturation. Land use significantly (p < 0.01) influenced C content and saturation level in Ferrosol as woodland had significantly higher C saturation (99 to 188%) compared to pasture (55 to 93%) and cropping (63 to 78%). Dermosol woodland soils had higher C content (30 to 61 g kg^{-1}) compared to pasture (19 to 49 g kg^{-1}) and cropping (23 to 31 g kg^{-1}) but the difference was only marginally significant (p < 0.06). However, higher C content caused significantly higher C saturation (p < 0.05) in woodland soils (81 to 107%) of Dermosol. Carbon saturation deficit had been observed in all the pasture and cropping soils of Ferrosol and Dermosol. Whereas two of the

woodland Ferrosols (North Dorrigo and Dorrigo 1) had C content near to saturation and two (Dorrigo 2 and Dorrigo 3) had stored 28% and 88% more C than their theoretical saturation level. Among four woodland soils in Dermosol, three samples (Clarkes, Powalgarh and Black mountain) had C content near to their saturation level and one sample (Kirby) had stored 7% more C than theoretical protective capacity of soils. Oversaturation may have been due to interaction with crystalline and poorly crystalline Fe and Al content, and presence of multivalent cations, because of their influence in soils in storing C. In Ferrosol total organic carbon (TOC) and silt + clay associated C was positively correlated with poorly crystalline Al content ($p < 0.01$). The saturation deficit in Ferrosol was also negatively correlated with poorly crystalline Al ($p < 0.01$). Thus the poorly crystalline Al might be responsible for storing C that exceeds the silt + clay protective capacity in Ferrosol. TOC was observed to be positively correlated with cation exchange capacity (CEC) in both Ferrosol ($p < 0.01$) and Dermosol ($p < 0.01$). In both soils CEC was mainly dominated by Ca^{++} ions, which might have stored C through polyvalent cation bridge. CEC was also positively correlated with clay content in Dermosol ($p < 0.01$). X-ray diffraction analysis showed that Dermosol was mainly dominated by smectite minerals that have higher specific surface area and are capable of storing C through cation-organic linkage. In contrast to Dermosol, CEC was not correlated with clay content in Ferrosol which was dominated by kaolinite, Fe and Al oxides. Thus OM itself might be the source of cations in Ferrosol that contributed to CEC, rather than influence of CEC on SOC storage.

2.1. Introduction

Soil is a larger C pool that can hold 3.3 times as much C as the atmospheric pool and 4.5 times as much as the biotic pool (Lal et al., 2004). Soil organic matter (SOM) comprises a major portion of this pool and represents a dynamic balance between C input and output. Any change in this balance could lead to change in size of this pool and cause disruption of equilibrium with other C pools. Conversion of natural (forest, woodland, and grassland) to managed (cropland, pasture) land leads to a reduction in size of soil organic carbon (SOC) pool and causes a concomitant increase in atmospheric CO_2 level. The reduction of C stock up to 42% has been observed due to conversion of native forest to cropland (Guo and Gifford, 2002). The rate of loss is more in the tropics than in temperate regions, and in coarse-textured soils than in fine-textured soils (Lal, 2008). Fine soil particles play an important role in storing C through surface adsorption (due to high surface area of smaller particle) and formation of silt-sized smaller microaggregates (20-50 μm) (Tisdall and Oades, 1982). Organic C binds primary organo-mineral complexes into smaller aggregates (Tisdall and Oades, 1982) and protects them from decomposition. The importance of silt and clay in storing C has been observed in many experiments where soil C positively correlated with silt + clay content of the soils (Hassink, 1997; Six et al., 2002; Sparrow et al., 2006; Barthes et al., 2008). Using this relationship, Hassink (1997) developed a model to determine the protective capacity (the capacity of a soil to physically preserve organic carbon by its association with clay and silt particles) of soils.

Protective capacity (g C kg^{-1} soil) = 4.09 + 0.37 (% of silt and clay particles).

In the model Hassink (1997) used published results on uncultivated soils and corresponding soils of cultivated arable land. The relationship between silt + clay content

and C associated on those particles were observed from soils of Netherland, Middle and South America and Africa, and thus were included in the model. Due to having no relationship between the parameters, Australian soils were not included in Hassink's model. Since Australian soils were not different from the other soils with respect to dominant clay type, the combination of lower rainfall and higher temperature in Australian sites which exerted lower C storage, were considered to be responsible for not showing any relationship.

Another model of protective capacity was described by Carter et al. (2003) as a simple linear regression (y = 9.04 + 0.27% clay and silt particles) based on the data of Elustondo et al. (1990) on maize crop and grassland soils in Canada.

Sparrow et al. (2006) found significant exponential relationship between silt + clay content and the C associated with these particles using Australian Ferrosol and Sodosol under pasture and cropping in Tasmania.

$$\text{Sparrow's model: } y = 6.67\, e^{0.0216x} \; (r^2 = 0.61,\ p < 0.001).$$

The concept of protective capacity arisen the concept of C saturation in soil. Carbon saturation means, if the capacity of soil to physically protect organic C is limited, there must have a limit of C storage in soil, beyond which C will be remained as unprotected. Soil C saturation occurs when its level in soil cannot be increased regardless of change in land use and management practices. Hassink (1997) observed the same amount of C and nitrogen (N) in silt + clay particles (< 20 µm fractions) in both arable and grassland soils and concluded that silt + clay fractions of the soils were saturated with their maximum amount of C and N. Though many long-term field experiments showed a proportional relationship between C inputs and soil C content across treatments (Paustian et al., 1997; Kong et al., 2005), in some long-term experiments addition of C did not

increase the equilibrium soil C level even at higher C addition level (Campbell et al., 1991; Solberg et al., 1997; Paustian et al., 1997; Huggins et al., 1998; Reicosky et al., 2002) which indicated C saturation in soils.

Using the protective capacity model Hassink (1996) calculated the C saturation deficit of the soils (the difference between the actual amount of C in the particle-size fraction < 20 µm and the maximum amount that can be associated with this particle-size fraction). Many authors have used Hassink's model to calculate protective capacity and C saturation deficit of soils in different countries (Stewart et al., 2008 and 2009; Zhao, 2006; Angers et al., 2011). Using Hassink's model Angers et al. (2011) observed some oversaturated soils in French arable land and indicated two possible reasons for such overestimation. One reason was the uncertainty around the theoretical C saturation curve, estimated by Hassink (1997). Another reason was the error of estimation of silt + clay associated C by subtraction of unbound part of TOC (15 ± 2.5% of TOC was assumed) from TOC in soils. However, saturated soils were observed in some forest soils and soils containing lower silt + clay particles (Angers et al., 2011). Baldock and Skjemstad (2000) proposed that the chemical nature of the mineral fraction, the presence of multivalent cations and architecture of the soil matrix influence the storage and stabilization of organic C in soil. Higher organic C content in soils containing high $CaCO_3$ or amorphous Al and Fe have been observed in many studies (Spain et al., 1983; Oades, 1988; Sombroek et al., 1993). Considering all these factors, the hypothesis of this study were both land use and soil properties influence the C saturation level of soils.

To test the hypothesis the objectives of the study were:

(i) to determine the protective capacity and C saturation deficit of a range of soils using a suitable and relevant model.

(ii) to determine the influence of land uses and soil properties (mineralogical properties) on soil C content and saturation deficit of soils.

2.2. Materials and Methods

2.2.1. Site information and soil sampling

The Red Ferrosols (Isbell, 1996) (equivalent to Oxisols in US Soil Taxonomy) were collected from the Dorrigo (elevation 746 m) region of the Northern Tablelands, NSW. Soil samples were collected from the surface (0-10 cm) with three contrasting land uses from four sites namely North Dorrigo, Dorrigo-1, Dorrigo-2 and Dorrigo-3. Mean annual temperature ranges from 9.9-19.8^{o}C, annual rainfall 2074 mm (Bureau of Meteorology, 2011). Ferrosols have >5% free iron oxide content in B horizon and are concentrated mainly in rainforest areas of Australia. The land uses studied were improved pasture, cropping and woodland. During the time of sampling improved pasture species found were rye grass (*Lolium perenne*), white clover (*Trifolium repens*) and winter forages. Cropping paddocks had been prepared for potato (*Solanum tuberosum*) cultivation and were under improved pastures for the preceding four years. The woodland paddocks were remnant cool rainforests and were in close proximity to Dorrigo world heritage rainforest. Brief descriptions of the sites are listed in Table 2.1. Parent material of soils was basalt. Soil samples were collected from each land use by selecting 3 separate blocks (50 × 50) along the slope of each paddock. In each block 10 random samples were collected and then composited into one.

Dermosols (Isbell, 1996) (equivalent to Alfisols in US Soil Taxonomy) were collected from Armidale and Guyra (elevation: 980-1275 m). In Armidale mean annual temperature ranges from 7.1-20.3^{o}C, annual rainfall 791.2 mm (Bureau of Meteorology, 2011). In Guyra, mean annual temperature ranges from 5.3-17.9^{o}C, annual rainfall 880.6

mm (Bureau of Meteorology, 2011). Soil samples were collected from surface (0-10 cm) with three contrasting land uses (i) native pasture (ii) crop-pasture rotation and (iii) woodland. The sites of soil sampling were Kirby, Clarkes, Powalgarh and Black Mountain. Among the sites Kirby and Clarkes were experimental farms of University of New England, Armidale. Powalgarh and Black Mountain sites were privately owned farms located near the township of Guyra. Parent material of soils at the 4 sites was Tertiary basalt. Native pasture sites were composed of solely native perennial grasses including Red Grass (*Bothriochloa macra*), Wire Grass (*Aristida ramose*) and Wallaby Grass (*Austrodanthonia spp*.). The recently sown crops at Kirby, Clarks, Powalgarh and Black Mountain sites were fescue (*Festuca arundinace*), ryegrass (*Lolium perenne*), triticale (*Triticale hexaploide*) and millets, respectively. The woodlands at all sites consisted of Eucalyptus spp. dominated by Blakely's red Gum (*Eucalyptus blakelyi*) and Yellow Box (*Eucalyptus melliodora*). Brief descriptions of sites are listed in Table 2.2. Soil samples were collected from each land use by selecting 3 separate blocks (50 × 50) along the slope of each paddock. In each block 10 random samples were collected and then composited into one.

2.2.2. Soil sample preparation

Bulk soil samples were dried at 40°C to constant moisture content. Larger roots and other plant parts and stubbles were discarded by hand. Soil samples were crushed by applying vertical force with a manual soil crusher and sieved through 2 mm sieve. Soil samples were stored in plastic container into cool room for analysis.

2.2.3. Fractionation of silt and clay particles

One of the prerequisite in particle-size fractionation is the complete dispersion of soil samples. In this respect sonication gives maximum dispersion. However, there is a possibility of breaking down particulate organic C (POC) and redistribution of organic C with long time sonication (Baldock and Skjmestad, 2000). So ultrasonication is not recommended for bulk soil samples (0-2 mm), but it is more accurate to apply to the 0-50 µm soil-water suspension, (dispersed and separated from bulk soil) (Feller and Beare, 1997). Under these conditions, the complete dispersion of > 50 µm aggregates can be obtained by shaking the soil with water and glass beads or, by use of chemical dispersants such as sodium hexametaphosphate or sodic resin (Feller et al., 1991; Gavinelli et al., 1995). So considering all these effects the dispersion procedure had been slightly modified applying both chemical dispersant and sonication. In the procedure 10 g air-dried soil was taken in a 100 ml plastic bottle and 50 ml sodium hexametaphosphate solution (5 g L^{-1}) was added. The suspension was shaken overnight using a tumbler. After shaking, the suspensions were left 5 minutes to allow the particles to settle. Most of the POC floated on the suspension and suspension was carefully sieved through 53µm sieve. Thus POC was discarded from the settled soil particles. Excess water was added with the remaining settled material and sonicated at 40 W for 5 minutes. After sonication, the soil suspension was sieved through 53 µm sieve. All the particles that passed through 53 µm sieve as suspension were dried at 40°C to constant moisture content. Clay particles were also separated by decantation of particles using Stoke's law (Jackson, 2005), after separation of silt + clay particles as described above.

2.2.4. Particle size analysis of soils

Particle size analysis was done using pipette method. Soils were dispersed using $5gL^{-1}$ Na-hexametaphosphate solution, and then 5 minutes sonication, as was done for fractionation of particles, to overcome methodological variation.

2.2.5. Determination of organic C

The dried fraction was then homogenized by grinding with mortar and pestle and passed back through a 500 µm sieve to determine C content using LECO CNS analyser. Total organic carbon (TOC) of the whole soils was also analysed. Carbon not associated with silt + clay was calculated from the difference between TOC and silt + clay associated C. The concentration of both silt + clay-associated and silt + clay non-associated C was expressed on whole soil basis (g C kg^{-1} soil).

Table 2. 1. Site description of studied Ferrosol

Site	Land use	Geo-reference	History
North Dorrigo	Improved Pasture	30°18 11.28"S 152°41 38.88"E	Rye grass, white clover, oats and winter forages. Potato was grown > 4 years ago, un-grazed during sampling.
	Cropping	30°18 14.52"S 152°41 38.76"E	Currently under potato cultivation, fertilizer application, soil disturbance by heavy tillage machinery, irrigated, stubble removed.
	Woodland	30°18 8.4"S 152°41'32.4"E	Rainforest tree species and herbaceous layer.
Dorrigo-1	Improved pasture	30°17 15.6"S 152o37 01.9"E	Rye grass, white clover, potato was grown < 4 years ago, un-grazed during sampling
	Cropping	30°17 03.8"S 152°37 16.0"E	Currently under potato cultivation, fertilizer application, soil disturbance by heavy tillage machinery, irrigated, stubble removed.
	Woodland	30°17 16.0"S 152°37 01.6"E	Rainforest tree species and herbaceous layer.
Dorrigo-2	Improved Pasture	30°21 05.4"S 152°43 20.5"E	Red Clover, Plantain, Ryegrass, was grown < 4 years ago, un-grazed during sampling
	Cropping	30°21 02.9"S 152°43 22"E	Currently under potato cultivation fertilizer application, soil disturbance by heavy tillage machinery, irrigated, stubble removed.
	Woodland	30°21 12.6"S 152°43 32.2"E	Remnant shrub vegetation
Dorrigo-3	Improved Pasture	30°16.759′S 152°40.458′E	Ryegrass, white clover, Kikuyu grass; was grown < 4 years ago, un-grazed during sampling
	Cropping	30°31.635′S 151°56.077′E	Currently under potato cultivation, fertilizer application, soil disturbance by heavy tillage machinery, irrigated, stubble removed.
	Woodland	30°16.691′S 151°39.886′E	Rainforest tree species and herbaceous layer

Table 2. 2. Site description of studied Dermosol

Site	Land use	Geo-reference	History
Kirby	Native pasture	30°26'02"S 151°38'01"E	Native grass, lightly grazed, > 20 years under current management
	Crop-pasture rotation	30°26'03"S 151°38'02"E	Crop-pasture rotation, sporadic fertilizer application and > 20 years under current management
	Woodland	30°26'02"S 151°38'04"E	Eucalypt woodland, grass cover lightly grazed, > 20 years under current management
Clarkes	Native pasture	30°28'49"S 151°38'25"E	Native grass, lightly grazed, > 20 years under current management
	Crop-pasture rotation	30°28'50"S 151°38'28"E	Crop-pasture rotation, regular fertilizer application and > 20 years under current management
	Woodland	30°28'52"S 151°38'25"E	Eucalypt woodland, grass cover lightly grazed, > 20 years under current management
Powalgarh	Native pasture	30°09'49"S 151°36'14"E	Native grass, lightly grazed, > 20 years under current management
	Crop-pasture rotation	30°09'47"S 151°36'00"E	Crop-pasture rotation, regular fertilizer application and > 10 years under current management
	Woodland	30°09'47"S 151°36'03"E	Eucalypt woodland, grass cover lightly grazed, > 20 years under current management
Black Mountain	Native pasture	30°18'49"S 151°39'45"E	Native grass, lightly grazed, > 20 years under current management
	Crop-pasture rotation	30°18'48"S 151°39'45"E	Currently sown to millet, fertilizer application, >10 years under current management
	Woodland	30°19'34"S 151°39'43"E	Eucalypt woodland, > 20 years under current management

2.2.6. Soil pH measurement

Soil pH was measured using 1:5 soil: water ratio at 25°C (Rayment and Lyons, 2011). This is the most widely used method in Australia.

2.2.7. Determination of CEC and mineral content in soils

CEC was determined using 1M NH_4Cl solution adjusted to pH 7 (Rayment and Lyons, 2011). This method gives good estimates of exchangeable bases for acidic and neutral non-saline soils. Since the pH of all soils were from slightly acidic to near neutral and EC were <0.3 dS/m, this method was appropriate to measure exchangeable bases. CEC was calculated by sum of exchangeable bases (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}).

Poorly crystalline Fe and Al was determined using 0.2M acid-oxalate reagent (Rayment and Lyons, 2011). Crystalline and amorphous Fe and Al were determined by using 22% sodium citrate and 1 g sodium dithionite (Rayment and Lyons, 2011). Crystalline Fe and Al were calculated by subtraction of oxalate-extractable Fe and Al concentration from dithionite-extractable Fe and Al concentration.

2.2.8. Protective capacity calculation

The protective capacity of soils (maximum amount of C associated with silt and clay particles) was determined using the equation of Sparrow et al. (2006): $y = 6.67e^{0.0216x}$ ($r^2 = 0.61$, $p < 0.001$). Where y is the protective capacity of soil (g C kg^{-1} soil) and x is the % of silt + clay particles.

2.2.9. C saturation deficit and degree of saturation calculation

Saturation deficit was calculated from difference between the actual amount of C in the particle-size fraction < 53 µm and the maximum amount that can be associated with this particle-size fraction (Hassink, 1996). C saturation deficit was also expressed on whole soil basis (g C kg^{-1} soil).

The degree of C saturation of protective capacity was calculated as (Carter et al., 2003):

$$\frac{SOC\ concentration\ in\ silt + clay\ particles}{Protective\ capacity} \times 100$$

2.2.10. Statistical analysis

The exponential and linear relationships between percent silt + clay and SOC content of silt + clay particles were plotted using SigmaPlot® (version 7.0). Data were statistically analysed using R version 2.7.0 (R Development Core Team, 2008). Robust linear regression analysis was performed using ROBUST package in R to minimize the effect of influential and leverage data points. The diagnostics of the regression model was checked and data transformation was carried out where data were not normally distributed. Two-way ANOVA (sites × land uses) was used to determine the difference in TOC and silt + clay associated C under different land uses at 4 different sites. Two-sample t-test was carried out to test the statistical difference between protective capacities estimated by different exponential equations.

2.3. Result

2.3.1. Protective capacity of Ferrosol and Dermosol using relevant model

Particle size fractions and organic C associated on these particles in Ferrosols and Dermosols are listed in Table 2.3 and Table 2.5. In Ferrosols 68% to 86% of TOC was associated with silt + clay particles, whereas it was only 63% to 78% of TOC in Dermosols.

The silt + clay content in Ferrosols ranged from 86-97% and in Dermosol the range was from 43-92%. There was an exponential relationship ($p < 0.01$) between % silt + clay content and the C associated on these particles for combined data of both soils under different land uses (Fig. 2.1). By plotting the data on Hassink's (1997) and

Elustondo et al. (1990) linear model, positive departure was observed in C content in soils having > 80% silt + clay particles (Fig. 2.2). The calculated protective capacity using Sparrow's exponential model ranged from 42.8-54.0 g kg^{-1} soil in Ferrosol and from 17.0-49.9 g kg^{-1} in Dermosol (Table 2.4 and 2.6). However, the calculated capacity ranged from 35.9-44.9 g kg^{-1} in Ferrosol and from 14.8-41.6 g kg^{-1} in Dermosol using regression equation of the studied soil ($y = 6.0465^{e0.0207x}$). These values were significantly lower ($p < 0.01$) than calculated capacity using Sparrow's model.

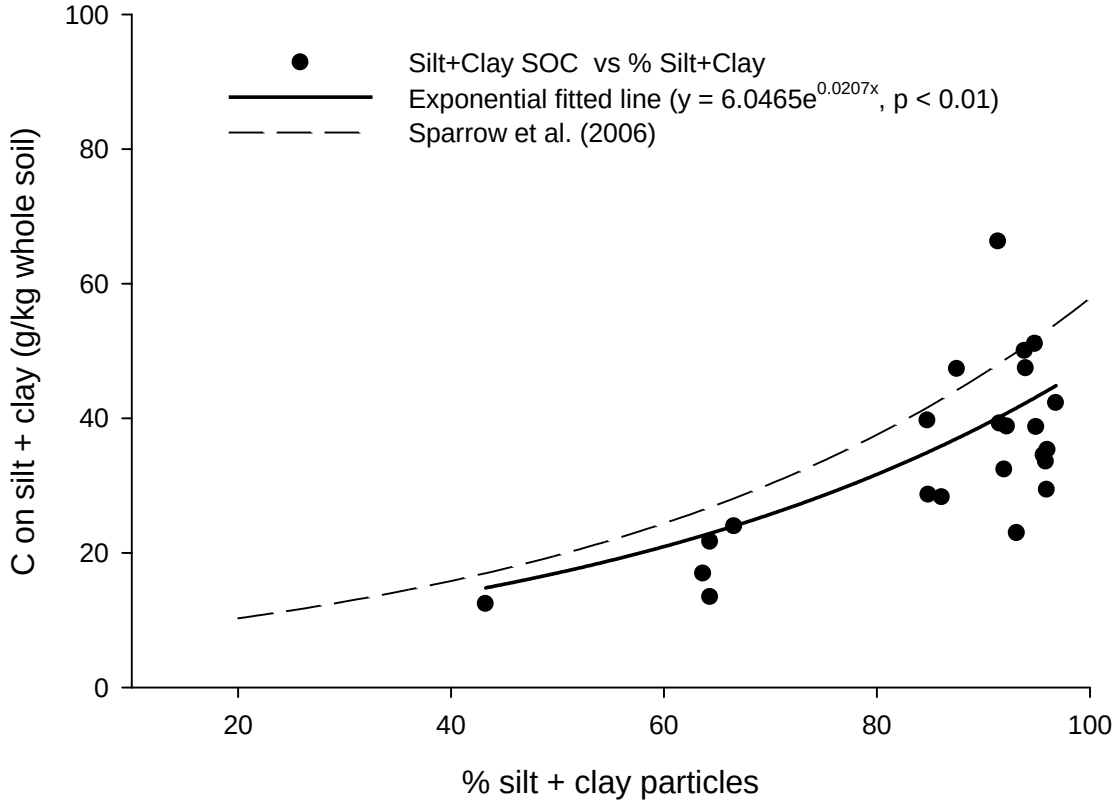

Fig. 2. 1. Relationship between carbon in the silt + clay and percentage of these particles of Ferrosol and Dermosols (under pasture, cropping and woodland soils) in NSW. The line of best fit for all data is $y = 6.05^{e0.0207x}$ ($r^2 = 0.30$, $p < 0.01$).The dashed line is the relationship of Sparrow et al. (2006) for particles <53 µm of Tasmanian pasture and

cropping soils (y=6.67 $e^{0.0216x}$) (r^2 =0.61, p < 0.001). The equation proposed by Sparrow et al. (2006) will not work on soils having silt + clay content lower than 20%, as soils containing lower silt + clay was not included in the model.

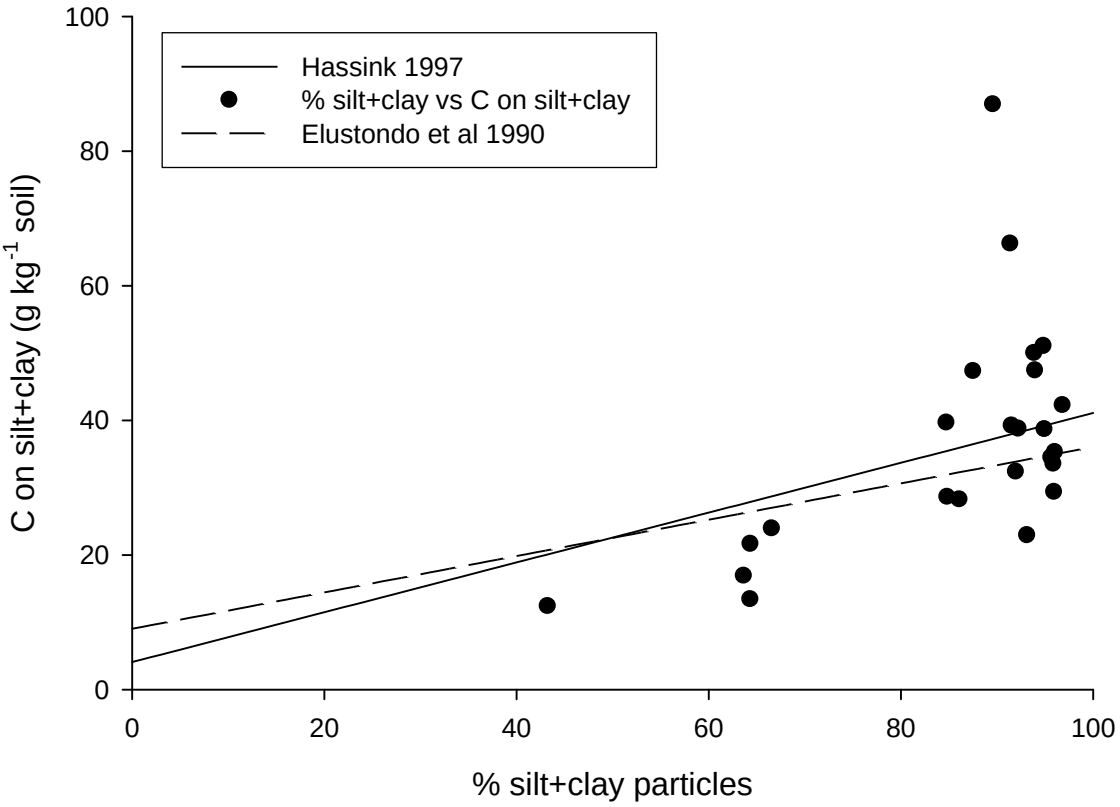

Fig. 2. 2. Relationship between carbon in the silt + clay and percentage of particles in those fractions of Ferrosol and Dermosols (under pasture, cropping and woodland soils) in NSW

The solid line is the relationship of Hassink (1997) for particles <20 µm. The dashed line is the relationship of Elustondo et al. (1990) for particles <53 µm.

2.3.2. Land use effect on SOC and degree of saturation of the soils

In the present study TOC in Ferrosol ranged from 34.3-60.1 g kg^{-1} in pasture, 36.9-53.0 g kg^{-1} in cropping and from 73.8-110.3 g kg^{-1} in woodland soils (Table 2.3). The silt + clay associated C in Ferrosol ranged from 29.4-47.4 g kg^{-1} in pasture, 28.2-42.2 g kg^{-1} in cropping and from 50-86.9 g kg^{-1} in woodland soil respectively (Table 2.3). Land use affected both TOC and silt + clay associated C in Ferrosol in which woodland soils had significantly higher C (p <0.01) than both pasture and cropping soils. In Dermosol, TOC ranged from 30.7-61.6 g kg^{-1} in woodland soils, from19.2-49.4 g kg^{-1} in pasture and from 23.7-43.3 g kg^{-1} in cropping (Table 2.5). Carbon associated with silt + clay in Dermosol was from 23.9-47.3 g kg^{-1} in woodland, from 12.4-38.8 g kg^{-1} in pasture and from16.8-32.4 g kg^{-1} in cropping (Table 2.5). TOC and silt + clay associated C in Dermosol was higher in woodland, compared to pasture and cropping but the difference was only marginally significant (p < 0.06). Cropping soils had 44% and 38% less C in their silt + clay fractions compared to woodland soils, in Ferrosol and in Dermosol respectively. In pasture soils the reduction was 42% in Ferrosol and 38% in Dermosol, compared to woodland soils. However, no significant difference in C content observed between pasture and cropping in both Ferrosol and Dermosol.

Carbon saturation deficit (calculated using Sparrow's protective capacity model) was observed in all the pasture (from -3.4 to -23.6 g kg^{-1} soil) and cropped Ferrosols (from-11.8 to -19.4 g kg^{-1} soil) (Table 2.4). Two of the woodland Ferrosol (North Dorrigo and Dorrigo 1) had C content close to their saturation level (99% of their protective capacity), and two soils (Dorrigo 2 and Dorrigo 3) had stored 28% and 88% more C (128 to 188% of their protective capacity) than their theoretical saturation level (Table 2.4). Thus the C saturation level in woodland soils was significantly higher (p < 0.01) compared to pasture and cropping soils. Carbon saturation deficit was also observed in

pasture (from -4.6 to -13.3 g kg^{-1} soil) and cropped Dermosol (from -5.1 to -26.9 g kg^{-1} soil) (Table 2.6). Among the four soil samples under woodland, three samples (Clarkes, Powalgarh and Black mountain) had C content near to their saturation level (81%, 85% and 95% respectively), while one soil (Kirby) stored 7% more C (107% of protective capacity) than the theoretical saturation level in Dermosol (Table2.6). Thus significantly higher ($p < 0.05$) level of C saturation was observed in woodland soils compared to pasture and cropping.

Table 2. 3. Selected characteristics of Ferrosols (0-10 cm)

Site	Land use	pH_w (1:5)	Fe_{OX}	Fe cd-ox	Al_{OX}	Al cd-ox	CEC (cmol kg^{-1})	Particle-size distribution (%)				C on particle (g kg^{-1} soil)			TOC (g kg^{-1} soil)
			(g kg^{-1} soil)					<2 µm	<20 µm	<53 µm	53-2000 µm	<2 µm	<53 µm	53-2000 µm	
North Dorrigo	Improved Pasture	6.1	9.62	113.82	6.91	8.7	15.26	60	85	94	6	31.3	47.4	12.7	60.1
Dorrigo1		5.7	4.68	31.31	5.89	0.6	8.56	57	90	96	4	22.6	35.3	10.8	46.0
Dorrigo 2		5.8	8.05	118.43	5.42	11.5	7.29	58	85	96	4	23.4	34.5	9.00	43.5
Dorrigo 3		5.7	7.62	105.22	5.37	4.3	6.51	62	86	96	4	20.0	29.4	5.0	34.3
North Dorrigo	Cropping	5.6	9.17	115.24	7.57	9.0	13.89	54	84	97	3	23.7	42.2	10.8	53.0
Dorrigo1		5.8	5.21	27.21	3.07	2.8	7.96	39	56	86	14	15.6	28.2	8.6	36.9
Dorrigo 2		5.7	10.11	128.89	5.11	13.1	7.61	56	85	95	5	27.1	38.7	11.7	50.4
Dorrigo 3		5.4	7.74	105.16	5.58	5.3	6.23	66	87	96	4	23.8	33.5	7.0	40.5
North Dorrigo	Woodland	5.2	7.38	92.87	6.07	6.0	5.94	64	91	94	6	31.3	50	23.9	73.8
Dorrigo1		5.3	4.25	22.52	5.67	1.8	6.7	54	90	95	5	33.9	51.1	22.8	73.8
Dorrigo 2		5.2	14.34	115.14	8.82	15.9	5.47	55	84	91	9	42.2	66.2	18.4	84.6
Dorrigo 3		6.0	8.69	65.80	13.36	0.0	34.68	56	84	90	10	49.8	86.9	23.4	110.3

Table 2. 4. Calculated protective capacity and saturation deficit in Ferrosol using proposed model (Sparrow et al., 2006)

Site	Land use	Protective capacity ($g\ kg^{-1}$ soil)	Saturation deficit ($g\ kg^{-1}$ soil)	Degree of saturation (%)
North Dorrigo	Improved pasture	50.8	-3.4 ±0.07	93.38
Dorrigo1		53.1	-17.8 ±0.09	66.43
Dorrigo 2		52.7	-18.2 ±0.23	65.47
Dorrigo 3		53.0	-23.6 ±0.06	55.40
North Dorrigo	Cropping	54.0	-11.8 ±0.05	78.23
Dorrigo1		42.8	-14.6 ±0.05	65.92
Dorrigo 2		51.9	-13.2 ±0.03	74.58
Dorrigo 3		52.9	-19.4 ±0.17	63.37
North Dorrigo	Woodland	50.7	-0.7 ±0.07	98.64
Dorrigo1		51.8	-0.7 ±0.17	98.66
Dorrigo 2		51.9	14.4 ±0.23	127.74
Dorrigo 3		46.2	40.7 ±0.29	188.23

Table 2. 5. Selected characteristics of Dermosols (0-10 cm)

Site	Land use	pH_w (1:5)	Fe_{OX} (g/kg soil)	Fe cd-ox (g/kg soil)	Al_{OX} (g/kg soil)	Al cd-ox (g/kg soil)	CEC (cmol kg^{-1})	Particle-size distribution (%)				C on particle (g kg^{-1} soil)			TOC (g kg^{-1} soil)
								<2 µm	<20 µm	<53 µm	53-2000 µm	<2 µm	<53 µm	53-2000 µm	
Kirby	Native pasture	5.84	8.72	3.52	2.2	0.3	51.95	55	81	92	8	22.7	38.8	10.6	49.4
Clarkes		5.70	8.03	6.29	2.0	1.5	20.01	46	64	85	15	18.7	28.6	9.4	38.0
Powalgarh		5.94	7.77	9.53	1.2	4.8	3.99	20	47	64	36	9.5	13.4	5.7	19.2
Black Mountain		5.93	13.55	4.67	3.8	10.6	11.88	23	39	43	57	6.9	12.4	7.4	19.8
Kirby	Crop-pasture rotation	6.09	7.26	1.96	2.6	0.1	65.69	69	88	93	7	14.9	22.9	8.3	31.2
Clarkes		6.17	8.44	6.78	2.5	1.0	31.81	61	82	92	8	23.2	32.4	10.9	43.3
Powalgarh		5.72	15.83	0.17	2.1	0.8	21.02	29	59	64	36	15.2	21.6	7.0	28.6
Black Mountain		5.84	24.62	1.60	4.1	1.6	26.98	32	59	64	36	11.3	16.8	6.8	23.7
Kirby	Woodland	6.04	8.52	0.93	2.1	0.2	52.37	68	86	88	12	37.8	47.3	14.3	61.6
Clarkes		5.41	10.36	4.29	2.7	0.9	42.72	65	84	92	8	24.8	39.2	14.0	43.3
Powalgarh		5.83	15.26	1.58	2.8	4.0	13.72	31	56	67	33	15.3	23.9	6.8	30.7
Black Mountain		5.91	13.86	2.36	3.1	0.5	43.13	33	72	85	15	27.2	39.7	14.5	54.2

Table 2. 6. Calculated protective capacity and saturation deficit in Dermosol using model (Sparrow et al., 2006)

Site	Land use	Protective capacity (g kg^{-1} soil)	Saturation deficit (g kg^{-1} soil)	Degree of saturation (%)
Kirby	Native pasture	48.9	-10.1 ±0.06	79.27
Clarkes		41.7	-13.1 ±0.21	68.66
Powalgarh		26.8	-13.3 ±0.06	50.15
Black mountain		17.0	-4.6 ±0.03	73.04
Kirby	Crop-pasture rotation	49.9	-26.9 ±0.06	46.00
Clarkes		48.6	-16.3 ±0.22	66.56
Powalgarh		26.8	-5.1 ±0.12	80.80
Black mountain		26.4	-9.5 ±0.06	64.03
Kirby	Woodland	44.2	3.1 ±0.19	107.09
Clarkes		48.2	-9.0 ±0.03	81.40
Powalgarh		28.1	-4.2 ±0.63	85.21
Black mountain		41.6	-2.0 ±0.19	95.32

2.3.3. Soil organic carbon content and degree of saturation influenced by specific soil properties (Texture and mineralogy)

The soils used in the study (Ferrosol and Dermosol) varied in texture and mineralogy. Higher silt + clay content was observed in Ferrosol (86 to 97%) compared to Dermosol (43 to 95%). Both oxalate-extractable and citrate-dithionite extractable Fe and Al content were higher in Ferrosol compared to Dermosol (Table 2.3 and 2.5). Because of these contrasting properties (texture and mineralogy) in Ferrosol and Dermosol, regression was performed between silt + clay content and the C associated on these particles for Ferrosol and Dermosol separately. Significant positive exponential relationship ($p < 0.01$) between these two parameters was observed in Dermosol (Fig. 2.3). In Ferrosol linear negative ($p < 0.001$) relationship between these two parameters was observed (Fig. 2.4a). Regression was also performed between TOC and both oxalate-extractable and dithionite-extractable Fe and Al content in Ferrosol and Dermosol. Significant positive relationship ($p < 0.01$) was observed between TOC and oxalate-extractable Al in Ferrosol (Fig. 2.4c). Saturation deficit in Ferrosol was also negatively correlated ($p < 0.01$) with oxalate-extractable Al content in soil (Fig 2.4d). Higher saturation deficit was observed in soil with higher silt + clay content in Ferrosol (Fig. 2.4b).

However, to observe the influence of silt + clay particles in storing C without the interference of land use effect, we performed regressions (Fig. 2.5) between C content in silt + clay particles and the percent of silt + clay particles in soils under three different land uses (both Ferrosol and Dermosol). The exponential relationship was significant under pasture ($p < 0.01$) and cropping ($p < 0.05$) but not under woodland soils ($p < 0.1$). Robust linear regression was also performed to see the influence of poorly crystalline Al

on storage of C without the influence of land use (Fig. 2.6). The positive linear relationship was significant only under woodland soils ($p < 0.01$).

Cation exchange capacity (CEC) of the studied soils ranged from 5.47-34.68 cmol kg^{-1} in Ferrosol and from 3.99-65.69 cmol kg^{-1} in Dermosol (Table 2.3 and 2.5). CEC of soils was positively correlated with TOC in both Ferrosol ($p < 0.01$) and in Dermosol ($p < 0.01$) (Fig. 2.7). In Dermosol, positive relationship (i.e. CEC = 0.86 × clay (%) – 6) of CEC was observed with clay content ($p < 0.01$).

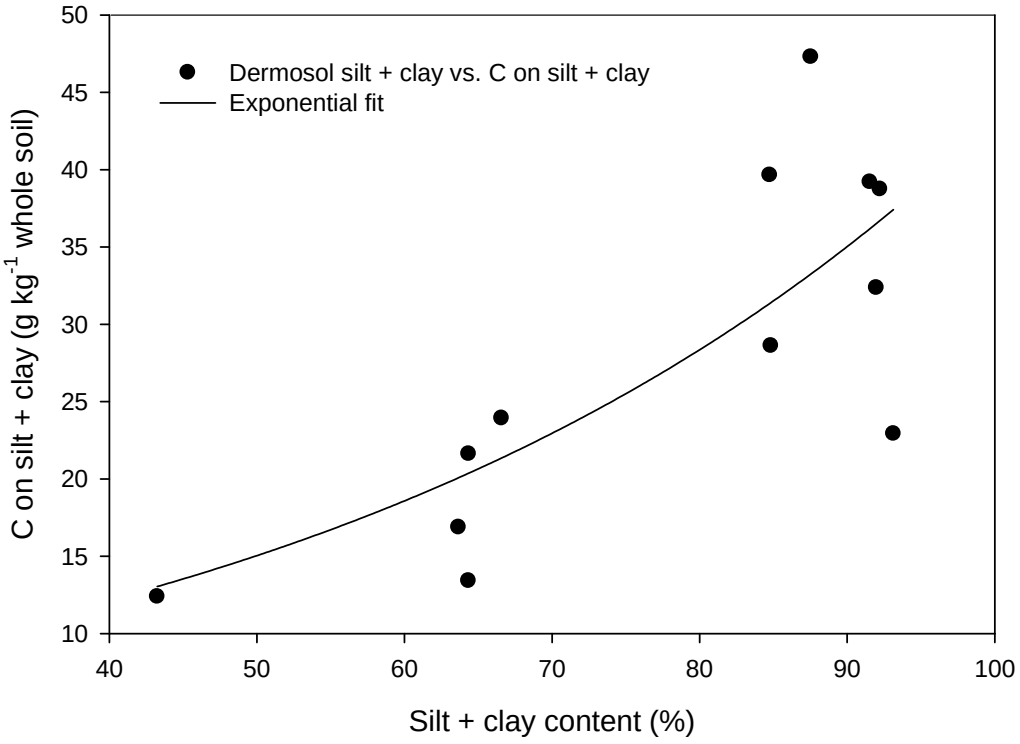

Fig. 2. 3. The relationship between silt + clay content (%) and C associated on silt + clay (g kg^{-1} whole soil) of Dermosol (y = 1.02x + 5.22) (R^2 = 0.59; P = < 0.01)

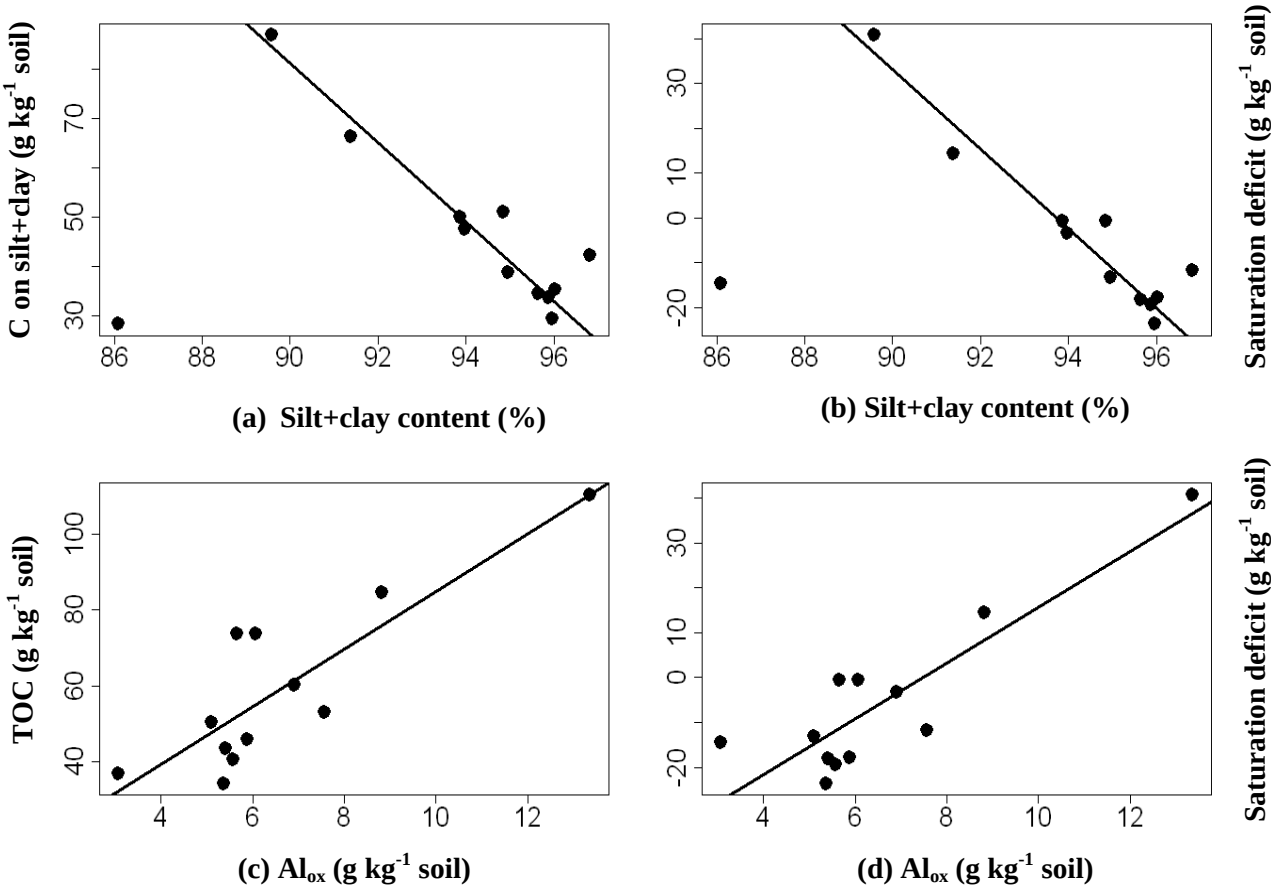

Fig. 2. 4. Relationships of TOC and saturation deficit with silt+clay content (%) and oxalate extractable Al. Relationship between silt + clay content (%) and C on these particles ($y = - 4.67x + 434.62$) ($R^2 = 0.49$; $P = < 0.001$) (a); silt + clay content (%) and saturation deficit (sd) (g kg^{-1} whole soil) ($y = - 8.1x + 761.07$) ($R^2 = 0.44$; $P = < 0.001$) (b); oxalate extractable Al (g kg^{-1} soil) and TOC (g kg^{-1} soil) ($y = 7.56x + 9.22$) ($R^2 = 0.72$; $P = < 0.001$) (c); oxalate extractable Al (g kg^{-1} soil) and saturation deficit (g kg^{-1} soil) ($y = 7.65x + 9.20$) ($R^2 = 0.77$; $P = < 0.001$) (d) in Ferrosol.

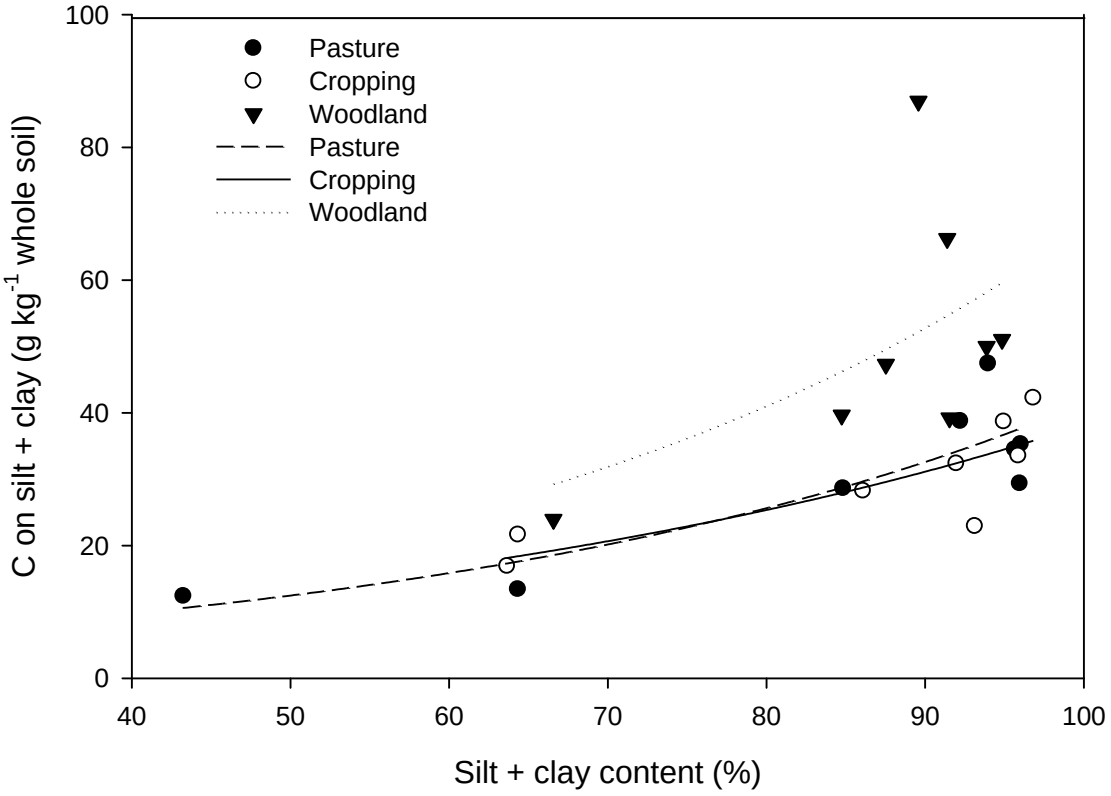

Fig. 2. 5. The relationship between silt + clay content (%) and C associated on silt + clay (g kg^{-1} whole soil) for pasture (y = 0.0240x + 3.77) (R^2 = 0.74; P = < 0.01) cropping (y = 0.02x + 4.91) (R^2 = 0.66; P = < 0.05) and woodland (y = 0.0252x + 5.47) (R^2 = 0.28; P = 0.2) soils (including Ferrosol and Dermosol)

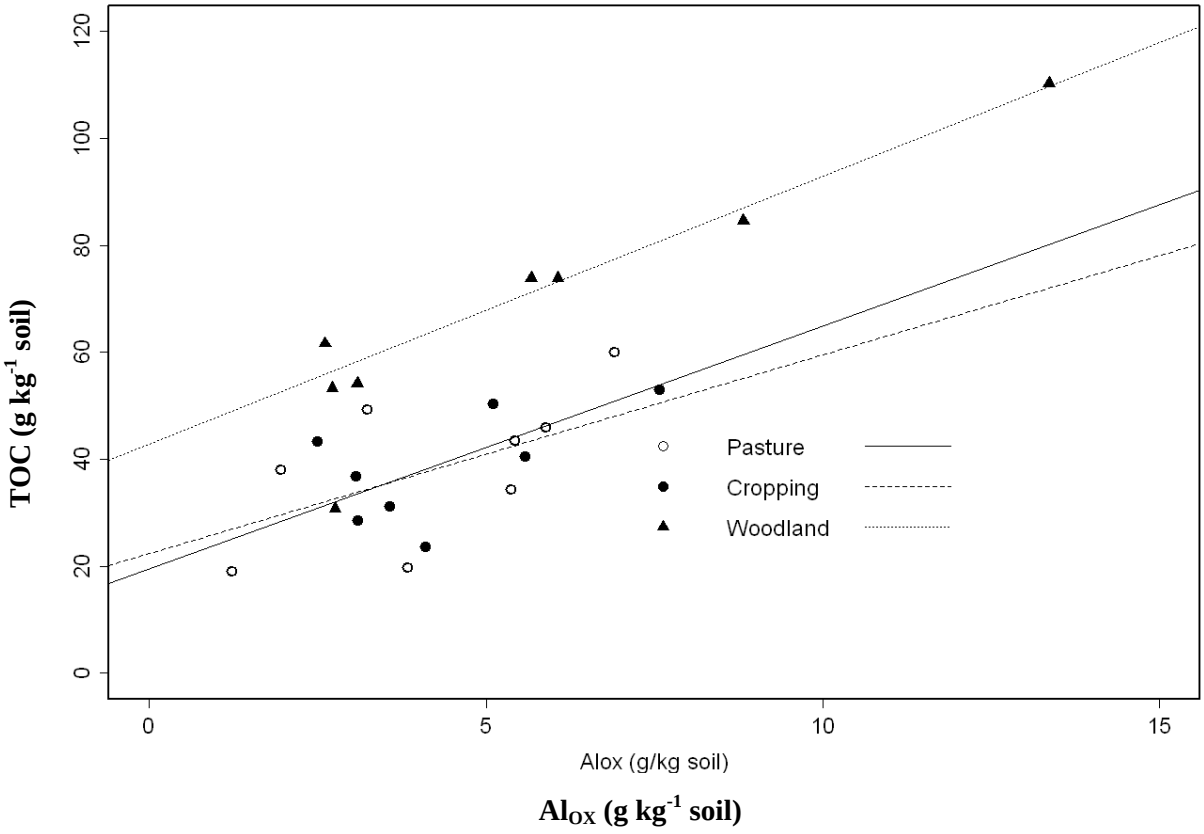

Fig. 2. 6. Relationship between poorly crystalline Al (Alox) and total organic carbon (g kg^{-1} soil) in pasture (y = 4.54x + 19.578) (R^2 = 0.40; P = 0.09), cropping (y = 3.71x + 22.407) (R^2 = 0.36; P = 0.12) and woodland (y = 5.0x + 40.28) (R^2 = 0.73; P = <0.001) soils (including Ferrosol and Dermosol).

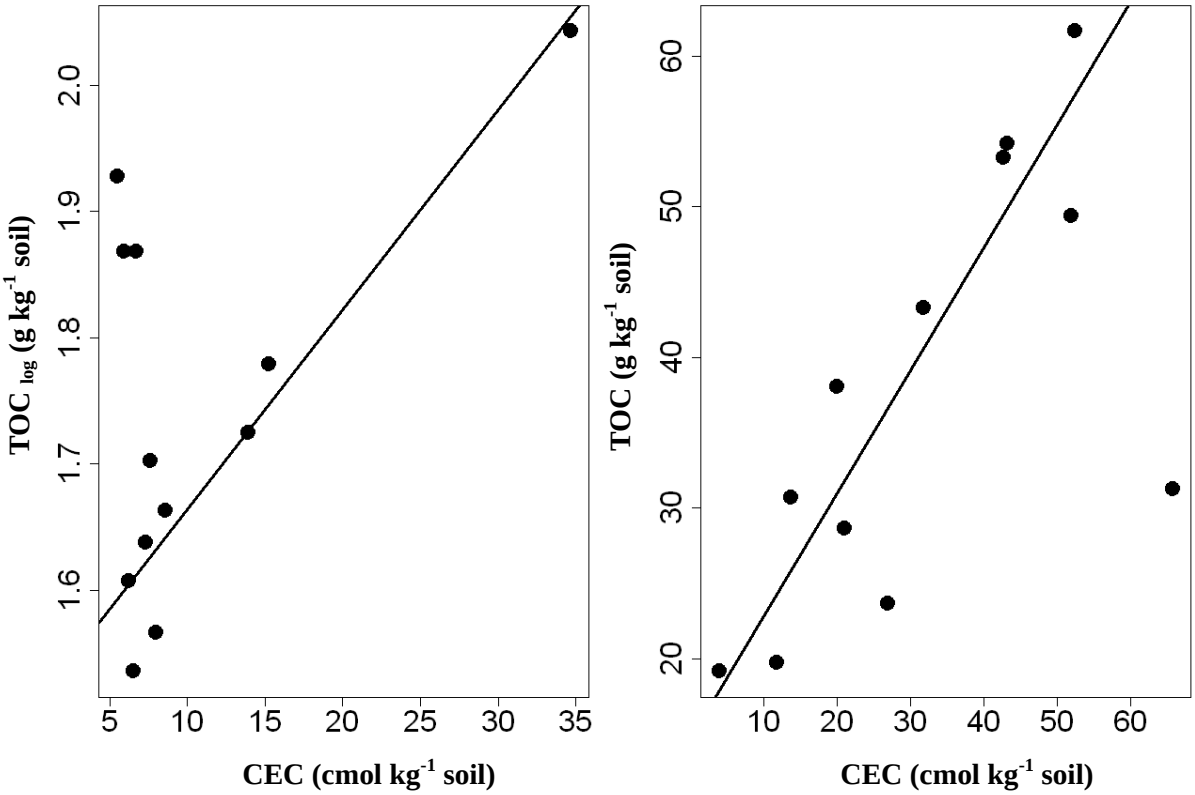

Fig. 2. 7. Relationship between CEC (cmol kg-1 soil) and TOC (g kg^{-1} soil) in (a) Ferrosol (y = 0.0132x + 1.57) (R^2 = 0.30; P = < 0.01) and (b) Dermosol (y = 0.6459x + 18.3895) (R^2 = 0.44; P = < 0.01). Data were log transformed as were not normally distributed.

2.4. Discussion

2.4.1. Protective capacity of Ferrosol and Dermosol using relevant model

The first objective of the present study was to determine protective capacity and C saturation deficit using the relationship between percent silt + clay particles and C concentration associated with these particles. In this study the silt + clay content ranged

from 86-97% in Ferrosol (Table 2.3) and from 43-92% in Dermosol (Table 2.5). The C associated with silt + clay particles ranged from 28.2-86.9 g kg^{-1} in Ferrosol (Table 2.3) and from 12.4-47.3 g kg^{-1} in Dermosol (Table 2.5). A significant positive exponential relationship between silt + clay content and the C associated on these particles ($r^2 = 0.30$, $p < 0.01$, n= 24) was observed in Ferrosol and Dermosol in this study (Fig. 2.1). The significant relationship ($p < 0.01$) between silt + clay content and C associated on these particles indicated the importance of these fine soil particles (silt and clay) in storing C. The relationship between silt + clay and C associated on these particles has also been observed in other studies (Hassink, 1997; Six et al., 2002; Sparrow et al., 2006; Barthes et al., 2008). In the present study the silt + clay associated C accounted for 68-86% of SOC in Ferrosol, and from 63-78% in Dermosol (Table 2.3 and 2.5). This higher proportion of silt + clay associated C irrespective of soil types also supported the influence of these particles in C storage in overall soil types. Zhao et al. (2006) reported that silt + clay stored 60-90% of SOC in Mollisols under cropping in China. However, 86-89% silt + clay associated C has also been reported by Gregorich et al. (2006) in their world literature review by compiling 434 particle-size analysis data. Because of the significant role of silt + clay in C storage in soils, determination of the protective capacity depending on the relationship between silt + clay content and C associated on these particles will give a clear idea of maximum soil C storage capacity.

The protective capacity of the soils in the present study was determined using the exponential model ($y = 6.67e^{0.0216x}$) proposed by Sparrow et al. (2006). Though many authors (Zhao, 2006; Angers et al., 2011) have used the linear model ($y = 4.09 + 0.37x$) proposed by Hassink (1997), this model was not used in the present study. The reason for not using this model was that: (1) By plotting the data of the studied soils on Hassink's linear curve, positive departure was observed in soils with > 80% silt + clay particles

(Fig.2.2). Significant positive departure from Hassink's relationship was also observed in Australian Ferrosol with > 60 % silt + clay (Sparrow et al., 2006). Higher C content of these higher silt + clay containing soils was responsible for this positive departure. Moreover none of the soil with > 80% silt + clay was included in Hassink's model. Thus the prediction of protective capacity of soils with > 80% silt + clay will not be appropriate using this model. Since most of the studied soils had > 80% silt + clay (with the exception of five Dermosol samples) content, C saturation level of these soils could not be assessed by using this model. Because of the same reason, the linear model of Elustondo et al. (1990) (y = 9.04 + 0.27x) was not used in the present study to calculate the protective capacity of soils. (2) In the present study < 53µm was used as the upper limit for silt + clay particles instead of the < 20 µm used by Hassink (1997). The < 53 µm particles was used in this study because of the higher capacity to store C within larger silt-sized aggregates (20-53 µm) in the 0-53 µm than in the 0-20 µm silt and clay particles (Six et al., 2002). Thus the capacity of < 53 µm silt + clay particles in this study could not be determined using Hassink's model. Thus considering all the limitations of previously proposed models for application in this study, Sparrow's exponential model was selected as being relevant for determination of protective capacity and C saturation level in studied soils. The reason for using the model was: (1) Sparrow et al. (2006) used Australian Ferrosol with > 80% silt + clay content in the model. Thus determination of the protective capacity of studied soils (Ferrosol and Dermosol) with > 80% silt + clay content would be more accurate and practical. (2) The size limit for silt + clay particles in Sparrow's model was < 53 µm, which also supported the use of this model to calculate protective capacity of the studied soil. Thus using this model the capacity of < 53 µm sized silt + clay particles could easily be determined.

The calculated protective capacity using Sparrow's exponential model ranged from 42.8-54.0 gC kg^{-1} soil in Ferrosol and from 17.0- 49.9 gC kg^{-1} soil in Dermosol (Table 2.4 and 2.6). However, the calculated capacity ranged from 35.9-44.9 gC kg^{-1} soil in Ferrosol and from 14.8-41.6 gC kg^{-1} soil in Dermosol using regression equation of the studied soil ($y = 6.05^{e0.0207x}$). These values were significantly lower ($p < 0.01$) than calculated capacity using Sparrow's model. The significantly lower protective capacity using equation ($y = 6.05^{e0.0207x}$), indicated that the overall capacity of the studied soils under existing climate and land uses were lower than under cool-temperate conditions in Tasmania. Influence of climate was also observed on lower C content (15-20 gC kg^{-1} soil)) in Ferrosol in Queensland (Bell et al., 1995), though no protective capacity model was proposed using such data. Moreover the equation ($y = 6.05^{e0.0207x}$) was not used to calculate protective capacity in the present study since the data points (24) were not sufficient to propose any protective capacity model. In fact, the climatic condition (cool-temperate) of Tasmania is more conducive to store C in soil, specifically under perennial pasture with high C input that was studied by Sparrow et al. (2006) and included in the model. Soils under this condition might store C close to their maximum capacity level. Although Sparrow's model will overestimate protective capacity relative to the data presented here because of the differential climate, determination of the protective capacity of soils in the present studies (under warmer climatic condition) using this model, will give an estimation of maximum capacity of that soil to store C under favourable climatic condition (cool-temperate climate in Tasmania) with higher input. Beside this, the determination of existing SOC content and comparison of these values with maximum capacity (calculated using Sparrow's model) will give an estimation of C saturation level of the studied soils under existing climatic condition and land uses. The saturation deficit calculated from the difference between actual C content in silt + clay and the calculated

protective capacity will also give an idea of potentiality of soils to store maximum amount of C under favourable climatic condition.

2.4.2. Effect of land use on SOC and degree of saturation of soils

The second objective of this research was to determine the influence of land use on the SOC content and C saturation level of soils. In the present study, significant positive influence of land use was observed on both TOC and silt + clay associated C in Ferrosol ($p < 0.01$) and to a lesser extent Dermosol ($p < 0.06$). In both soils woodland stored significantly higher C compared to pasture and cropping soils (Table 2.3 and 2.5). The difference in C input and soil management might be the reason for difference in C content under different land uses. In this study upto 44% less C in the silt + clay fractions was observed in cropping soils compared to woodland soils in Ferrosol. In Dermosol, the reduction in C was 38% in cropping soils than woodland soils. While in pasture soils, the reduction was 42% in Ferrosol and 38% in Dermosol, compared to woodland soils. Loss of C due to cultivation or conversion of forest to agricultural land has also been observed in other studies. Ellert and Gregorich (1996) estimated 30-35% loss of C from A and B horizons of native temperate forest soils after 30 or more years of cultivation. Degryze et al. (2004) also observed 60% reduction in surface soil (0-7 cm) C due to cultivation compared with forest soils. Thus in most cases soil C content decreased due to change from natural (forest, woodland) to managed land (cropland). Loss of C due to cultivation might be the result of tillage (Russell and Williams 1982; Dalal and Mayer, 1986), which results in fracturing, pulverisation of soil and concomitant increase in microbial activities (Rovira and Greacen, 1957) and thus consequent reduction of SOC content in soils (Roberts and Chan, 1990).

Though woodland soils stored significantly higher C compared to pasture and cropping in Ferrosol there was no significant difference in C content between pasture and cropping soils. Similar result was also observed in the studied Dermosol in which there was no significant difference in C content between pasture and cropping. In contrast to this finding Sparrow et al. (2006) observed 39% less C in Ferrosol under cropping compared to pasture. Higher C content in pasture soils compared to cropping resulted from higher input provided by pasture species (Sparrow et al., 2006). In this study, Ferrosol under pasture were mainly improved pasture that had been cropped < 4 years ago (Table 2.1). Thus the soils had not attained a new steady state within the very short period. Soil's C capacity could be defined as reaching a new steady state, following a change in land use, when soil C inputs approximate soil C outputs (West and Six. 2007). In the context of C sequestration, cropping soils attain a new steady state after 26 years for change in rotation intensity and after 21 years for tillage cessation (West and Six, 2007). However, sequestration strategies for grasslands require longer time (33 years) to reach a new steady state (West and Six, 2007). In this respect 4 years pasture management was not enough time to increase the C level and attain steady state with new land use (pasture) of the previously cropped land. In contrast, Dermosol under cropping were subjected to crop-pasture rotation (Table 2.2). In crop-pasture rotation crops were grown in rotation with a pasture species with frequent application of chemical fertilizer. Unlike conventional cropping, soils were not tilled in crop pasture rotation which might favour stable aggregate formation and C storage. Moreover, it has been reported in literature that inclusion of a pasture phase in a cropping system helps to store soil C in Australian situation (Greenland, 1971). Thus the C content in soils under native pasture and crop-pasture rotation was not significantly different in Dermosol.

Carbon saturation deficit of the studied soils was calculated after determining protective capacity using Sparrow's exponential model. The saturation deficit was calculated from the difference between the actual amount of C in the particle-size fraction < 53 μm and the maximum amount that can be associated with this particle-size fraction (Hassink, 1996). Carbon saturation deficit was observed in all the pasture (from -3.4 to -23.6 g kg^{-1} soil) and cropped Ferrosols (from-11.8 to -19.4 g kg^{-1} soil) (Table 2.4). Two of the woodland Ferrosol (North Dorrigo and Dorrigo 1) had C content close to their saturation level (98.64 to 98.66% of their protective capacity), and two (Dorrigo 2 and Dorrigo 3) had stored 28% and 88% more C (127.74 to 188.23% of their protective capacity) than their theoretical saturation level (Table 2.4). Consequently the C saturation level in woodland soils was significantly higher ($p < 0.01$) than pasture and cropping soils. Carbon saturation deficit was also observed in pasture (from -4.6 to -13.3 g kg^{-1} soil) and cropped Dermosol (from -5.1 to -26.9 g kg^{-1} soil) (Table 2.6). Among the four soil samples under woodland, three samples (Clarkes, Powalgarh and Black mountain) had C content near to their saturation level (81.4%, 85.21% and 95.32% respectively), while one soil (Kirby) stored 7% more C (107.09% of protective capacity) than the theoretical saturation level in Dermosol (Table 2.6). Saturation level in woodland soils in Dermosol was also significantly higher ($p < 0.05$) compared to pasture and cropping. The higher C saturation level in woodland soils compared to pasture and cropping might be related with higher C input from woodland trees and above-ground plants. Carbon saturation level in woodland and cropping soils were consistent with literature (Matus et al., 2008; Angers et al., 2011). Using Elustondo's protective capacity model, Matus et al. (2008) observed 56% more C content than the theoretical protective capacity in silt + clay particles of forest soils, whereas saturation deficit was observed in cropping soils in which only 32-60% of the soils capacity was saturated with SOC. Using Hassink's model

Angers et al. (2011) also observed some forest soils in France that had C content close to saturation, while some intensively cultivated land had saturation deficit.

In the present study significantly higher C content and saturation level in woodland soils compared to pasture and cropping Ferrosol and Dermosol proved the part of the hypothesis that land use influence on C saturation level in soils. Though the C content in woodland soils in Dermosol were marginally significantly higher ($p < 0.06$) compared to pasture and cropping, this was a clear indication of influence of land use on C storage in soils. However, in both Ferrosol and Dermosol, significantly lower C content and higher saturation deficit in pasture and cropping provides an indicator to the overall C sequestration potential of these soils (Ellert and Gregorich, 1996).

2.4.3. Influence of soil properties on SOC content and degree of saturation in Ferrosol and Dermosol

The second objective of the study was to determine the influence of soil properties on C content and saturation level of soils. Fine textured soil contains more C than coarse textured soil, which is the fundamental basis of protective capacity model. In the present study an exponential relationship ($p < 0.01$) between silt + clay content and the C associated with this fraction was observed (Fig 2.1), independent of land use and soil mineralogy. The exponential relationship was also observed between silt + clay particles and C associated with these particles in Dermosol ($p < 0.01$) (Fig. 2.3) but in Ferrosol linear negative relationship was observed ($p < 0.001$) (Fig. 2.4a). Moreover significant positive relationship ($p < 0.01$) between TOC and oxalate-extractable Al was observed in Ferrosol (Fig. 2.4c). Oxalate-extractable Al is poorly crystalline Al with a larger surface area than crystalline minerals (Schwertmann et al., 1986) and is responsible for storage of organic C in the mineral fraction of soils (Powers and Schlesinger, 2002; Kleber et al.,

2005; Wiseman and Puttmann, 2005; Mikutta et al., 2006). In the present study the significantly higher ($p < 0.01$) C saturation has also been observed in Ferrosol having higher poorly crystalline Al content (Fig. 2.4d). The influence of land use in C storage and in reaching saturation level has been observed and explained in section 2.4.2 (Table 2.4). These findings proved the hypothesis that both land use and soil properties influence the C saturation level in soils. Since Ferrosol is higher silt + clay containing soil (86 to 97%) compared to Dermosol (43 to 95%), higher C input (contribution from land use) is necessary to saturate the soils containing higher silt + clay. In fact, saturation is more difficult to achieve in fine textured soils and may be observed in situations with very high C input or slow decomposition (Six et al., 2002; Carter et al., 2003; Barthes et al., 2008; Angers et al., 2011). The lack of significant relationship between organic C and poorly crystalline Al in Dermosol might be the result of lower content of these minerals compared to SOC content. The ratio of TOC to oxalate-extractable Al were significantly higher ($p < 0.01$) in Dermosol (5 to 29) compared to Ferrosol (6 to12). Because of this higher SOC content, the active sites in poorly crystalline Al might be saturated with C in Dermosol, as their capacity is limited to adsorb organic C (Kaiser et al., 2002; Guggenberger and Kaiser 2003; Kaiser and Guggenberger 2003; Kleber et al., 2005). The lack of significant relationship between organic C and poorly-crystalline mineral in Dermosol was consistent with other study due to higher OM content on the top soil layers (Richards et al., 2009).

The influence of soil properties (texture and mineralogy) on C storage in soils was observed by minimizing the influence of land use (Fig. 2.5 and 2.6). The data were grouped (Ferrosol and Dermosol) depending on land uses (pasture, cropping and woodland) to observe the influence of soil properties on SOC content. The relation between silt + clay content and C associated on these particles were significant under

pasture ($p < 0.01$) and cropping ($p < 0.05$) but not under woodland ($p < 0.1$). In contrast to these, woodland soils showed significant positive relationship ($p < 0.01$) between TOC and oxalate-extractable Al content (Fig. 2.6). All the above relationships indicated the influence of soil properties (texture and mineralogy) on storage of SOC in soils (without the influence of land use). In the previous section (2.4.2) it was stated that two of the woodland Ferrosol (Dorrigo1 and Dorrigo 2) had stored 28% and 88% more C and one of the woodland Dermosol (Kirby) had stored 7% more C than the theoretical protective capacity. Violation of this silt + clay protective capacity might be due to effect of land use (in both Ferrosol and Dermosol) or poorly crystalline Al content in soil (in Ferrosol).

Another soil property that influences soil C storage is the cation exchange capacity (CEC) of soils. CEC of the studied soils ranged from 5.5-34.7 cmol kg^{-1} in Ferrosol and from 4.0-65.7 cmol kg^{-1} in Dermosol (Table 2.3 and 2.5). CEC of soils was positively correlated with TOC in both Ferrosol ($p < 0.01$) and in Dermosol ($p < 0.01$) (Fig. 2.7). By X-ray diffraction analysis (XRD) it was found that Ferrosol of the studied soils were dominated by kaolinite, Fe and Al oxides. All these are variable charge materials and have lower CEC than permanent charge materials (smectite). So theoretically CEC of Ferrosol should be within the range of 2-20 cmol kg^{-1} soil (Moody, 1994). Most of the studied Ferrosols had CEC within the range except one soil of woodland (CEC was 34 cmol kg^{-1}) that had higher C content (110.3 g kg^{-1} TOC). Since OM is a source of variable charge, the higher CEC of the soil might be due to higher OM that retained much cations and increased CEC. Being the source of surface charge, OM could contribute as much as 70% of the CEC in the surface 10 cm of some Ferrosols (Gillman, 1976; Moody, 1994). So the positive linear relationship between CEC and TOC in Ferrosol (though the relationship was significant only for one point) may have double explanation: one is that SOC has contribution in Ferrosol to increase CEC, another explanation is that CEC in

soils (which is dominated by divalent Ca and Mg) could store more C by cation-organic linkages (Baldock and Skjemstad, 2000). In this study CEC in Ferrosol was not related to clay content, which further indicated the influence of SOC to increase CEC by retaining cations, rather than the influence of surface area of clay that store SOC through cation-organic linkage. However, CEC of the Dermosol were high (4.0-65.7 cmol kg^{-1}) due to presence of smectite minerals, that has high specific surface. CEC was also positively correlated with clay content in Dermosol ($p < 0.01$). So the positive relationship between TOC and CEC in Dermosol might be due to influence of higher specific surface of clay that stored organic molecules through polyvalent cation bridges (Section 1.4.1).

2.5. Conclusion

This study is the first attempt to determine the capacity of soil to store C for estimation of C saturation level under different land uses. Significantly higher C saturation deficit in pasture and cropping soils of both Ferrosol and Dermosol indicated the potential of these soils to store more C. However, the oversaturation of two woodland soils of Ferrosol and one Dermosol violated the silt + clay protective capacity model. Factors other than silt + clay particles that also store C in soils might be responsible for such violation. Significant positive influence of poorly crystalline Al in storing C in Ferrosol explained one reason for storing C beyond the silt + clay protective capacity.

Subsequent experiments were conducted to determine the rate of SOC mineralization and mean residence time of C in soils. Since highly significant difference in C saturation level was observed in Ferrosol ($p < 0.01$) compared to Dermosol ($p < 0.05$) depending on the land uses, the next experiment was conducted only on Ferrosol to observe the influence of C saturation deficit on SOC mineralization and MRT of SOC pool. The findings of this experiment are discussed in the next chapter.

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Chapter 3

Soil carbon mineralization: Influence of soil texture, saturation deficit and fractionation of soil particles

Abstract

Fine soil particles, especially silt and clay, play an important role in the stabilization of soil carbon (C) by surface adsorption and formation of aggregates. Hence the protective capacity (the capacity of a soil to physically preserve organic C by its association with silt + clay particles) of soil can be determined from the relationship between % silt + clay and C associated on these particles. Land use significantly influenced ($p < 0.01$) C saturation level of the protective capacity in the studied soils, in which woodland soils had higher C saturation level compared to pasture and cropping soils. Thus soils had a wide variation in their C saturation level. The study was conducted to test the following hypothesis: (1) SOC mineralization will be higher from soil having lower silt + clay and lower C saturation deficit. (2) SOC mineralization will be lower from aggregated (whole soil) sample compared to dispersed soil particles (silt + clay and clay) thus SOC will be more protected within aggregates compared to dispersed silt + clay and clay particles. (3) Mean residence time of C in SOC pool will be higher in soils having higher silt + clay and higher C saturation deficit. To test the hypotheses we collected topsoil (0-10 cm) from Australian Ferrosol under three contrasting land uses (pasture, cropping and woodland). Particle-size analysis (PSA) was done by pipette method after dispersion of soils with 0.5% Na-hexametaphosphate solution and 5 minutes sonication for complete dispersion of soils. Silt + clay particles (< 53 µm) were separated

by same dispersion method as PSA and subsequent sieving through 53 µm sieve. Protective capacity of soils was calculated using exponential model ((y = 6.67 $e^{0.0216x}$ (r^2 = 0.61, p < 0.001)) proposed by Sparrow et al. (2006). Carbon saturation deficit was calculated from the difference between actual amount of C in the silt + clay particles and the maximum amount of C that could be associated with this particle-size fraction (Hassink, 1996). Significantly higher (p < 0.01) C saturation was observed in woodland soils, compared to pasture and cropping soils. Three soil fractions (< 2000 µm, < 53 µm and < 2 µm) were incubated for five months, and CO_2 evolution was measured at different time intervals. The cumulative C mineralization (C_{min}) of the whole soil (< 2000 µm) was negatively correlated with silt + clay content (p < 0.001) and C saturation deficit (p < 0.001) of soils. Percent of SOC mineralized (SOC_{min}) of the whole soil was also negatively correlated with silt + clay content (p < 0.001) and C saturation deficit (p < 0.01) of soils. Significantly higher C_{min} was observed from dispersed silt + clay particles (2.65 g CO_2-C kg^{-1} sample) compared to whole soil (1.74 g CO_2-C kg^{-1} sample) (p < 0.01) and clay particles (2.16 g CO_2-C kg^{-1} sample) (p < 0.05). SOC_{min} was also higher in silt + clay (5.59%) than whole soil (2.86%) (p < 0.01) and clay (4.33%) (p < 0.05). Land use had no significant influence on SOC mineralization. A constrained two pool model ($C_t = C_{active} \exp(-k_a t) + C_{slow} \exp(-k_s t)$) was run to calculate the mean residence time (MRT) of active and slow C pools. The slow pool comprised 95-98% of SOC in all soil fractions with an average MRT of 20.9-53.4 years. In this experiment the slow pool consisted of slow + resistant pool, since resistant pool was not separated by acid hydrolysis. The MRT of combined slow and resistant pool (in the study it had been denoted as MRT_s) of whole soils were positively correlated with silt + clay (p < 0.05) and C saturation deficit (p < 0.05) of soils. Unlike MRT_s of whole soil C pool, MRT of active C pool (MRT_a) had no relation with either silt + clay content or C saturation level of these

particles, since MRT_a of whole was assumed to be comprised of C fractions not associated with silt + clay particles. Thus longer MRT of slow C pool indicated the higher protection of C in soils where protective capacity was not saturated with C.

3.1. Introduction

The process of carbon dioxide (CO_2) release from the soil is referred to as soil respiration, soil-CO_2 evolution, or soil-CO_2 efflux. Three principal components of soil respiration are: root respiration, surface-litter respiration, and the respiration of soil organic matter (SOM). Soil is a large C pool that can hold 3.3 times as much C as the atmospheric pool. However, about 10% of the atmospheric CO_2 passes through soils each year (Raich and Potter, 1995) which is more than 10 times the CO_2 released from fossil fuel combustion. Because of the magnitude of this soil-to-atmosphere CO_2 flux and potentially mineralizable C in soils (Bohn, 1982; Eswaran et al., 1993), any change in soil CO_2 emissions due to change in land use and land management, could potentially increase atmospheric CO_2 level (Schleser, 1982; Jenkinson et al., 1991; Raich and Schlesinger, 1992; Kirschbaum, 1995).

Rate of soil respiration varies with soil temperature and moisture (Singh and Gupta, 1977; Schlentner and Van Cleve, 1985; Carlyle and Theng, 1988), availability of substrates for microorganisms (Seto and Yanagiya, 1983), population of soil organisms (Singh and Shukla, 1977; Rai and Srivastava, 1981), activities and densities of plant roots (Ben-Asher et al., 1994) and soil physical and chemical properties (Boudot et al., 1986). Among the three components of soil respiration, respiration of SOM depends mostly on soil properties, because SOM is associated with soil minerals. Soil properties also influence the respiration of roots and surface litter indirectly, but that is considered under field condition where soil respiration includes all the three components. Under laboratory

condition, decomposition of SOM represents soil respiration in absence of litter and root respiration. Though laboratory condition does not represent real situation as under field condition, the small scale prediction could be possible from many laboratory experiment. However, under field condition, due to influence of so many factors, it is not possible to identify any single factor for any particular reason (Kirschbaum, 1995; Risk et al., 2008). Thus for laboratory incubation experiment, the term mineralization of SOM could be used instead of soil respiration as CO_2 is produced mainly from the decomposition of soil organic matter.

Among the soil properties, texture plays an important role in storing C. Influence of soil texture on SOC content had been observed in many studies, where SOC content was positively correlated with silt + clay or clay content (Spain, 1990; Feller et al., 1991; Hassink, 1997; Six et al., 2002). The decomposition and mineralization of SOC also decrease with increasing clay content of soils (Jensen et al., 1994; Coleman and Jenkinson, 1996). However, since the capacity of soil to protect organic C is limited (Hassink, 1996, 1997), mineralization of C from soil may be higher from soils where the protective capacity has reached to saturation. The theory of protective capacity was proposed by Hassink (1997) from the relationship between % silt + clay particles and C associated on these particles (g C kg^{-1} whole soil). Saturation deficit are calculated from the difference between actual amount of C in the silt + clay fractions and the maximum amount that can be associated with this particle-size fraction (Hassink, 1996). The mineralization of C from added residue (^{14}C-labeled ryegrass) was observed to be negatively correlated ($p < 0.01$) with C saturation deficit of the soils after 3 days and 53 days of incubation (Hassink, 1996). The relationship was poor between $^{14}CO_2$ production and soil texture (Hassink, 1996). However, since the turnover of SOC is related to recalcitrance, accessibility and interactions, it is very important to find out the relative

and combined influence of these three factors. The accessibility of SOC to microbes for decomposition is mainly determined by degree of aggregation whereby SOC could be protected against microbial attack. Organic C input increased stable macroaggregate formation in soils through electrostatic bindings between 2:1 clays, 1:1 clays and oxides (Denef et al., 2002). Thus in absence of aggregation, the extent of SOC protection must be lower than in well aggregated situation even in the same soil. Decomposability of SOC associated with textural fractions decreases in the order sand > clay > whole soil > silt in some soils (Christensen, 1987).

The components of SOC are complex and can be divided into three pools that decompose according to first order kinetics (Parton et al., 1987; Paustian et al., 1992). These pools consist of an active fraction (C_a), a slow fraction (C_s) and a resistant fraction (C_r). Several authors (Collins et al., 2000, Yang et al., 2007 and Paul et al., 2001) measured active and slow SOC pools from mineralization data using a curve-fitting approach and found on average slow SOC pool comprised ~50% of total SOC. Though the proportion of SOC in the active pool is very low compared to the slow pool, the lower MRT of active pool SOC is an indication of greater change in atmospheric CO_2 concentration due to increase in size of this pool (Yang et al., 2007). Thus the analysis of pool sizes and MRT is important for estimation of SOC dynamics that could be used in decision making related to global climate change. Collins et al. (2000) found longer MRT in higher clay soils. The mineralization of light fraction and sand-sized fractions (POM) were observed to be faster compared to that of the silt- and clay-size fractions (Tiessen and Stewart, 1983; Dalal and Mayer, 1986; Gregorich et al., 1995). Thus silt + clay content of soils and their degree of saturation with C is assumed to influence both mineralization of SOC and consequent MRT of SOC pool. The hypothesis of the research was: (1) SOC mineralization will be higher from soil having lower silt + clay and lower

saturation deficit. (2) SOC mineralization will be lower from aggregated (whole soil) sample compared to dispersed soil particles (silt + clay and clay) thus SOC will be more protected within aggregates compared to dispersed silt + clay and clay particles. (3) Mean residence time of C in SOC pool will be higher in soils having higher silt + clay and higher C saturation deficit. To test all these hypothesis, the objectives of the research was (i) to determine cumulative carbon mineralization (C_{min}) and percent of SOC mineralized (SOC_{min}) from whole soil (< 2000 µm), silt + clay (< 53 µm) and clay (< 2 µm) (ii) to determine the mean residence time of both active and slow SOC pool of three soil fractions by curve-fitting techniques.

3.2. Materials and Methods

3.2.1. Site information and soil sampling

The Red Ferrosols (Isbell, 1996) (equivalent to Oxisols in US Soil Taxonomy) were collected from the Dorrigo (elevation 746 m) region of the Northern Tablelands, NSW. Sample sites and methods of sampling are discussed in chapter 2 (Section 2.2.1 and Table 2.1)

3.2.2. Preparation and analysis of soil

Detail description of preparation of soil samples, fractionation of silt + clay particles, particle size analysis, determination of organic C, pH measurement, determination of CEC and mineral content (crystalline and poorly crystalline Fe and Al), are in chapter 2 (Section 2.2.2 to section 2.2.7).

3.2.3. Protective capacity and C saturation deficit calculation

The protective capacity of soils was determined using the equation of Sparrow et al. (2006): $y = 6.67e^{0.0216x}$ ($r^2 = 0.61$, $p < 0.001$). Carbon saturation deficit and degree of saturation was calculated based on this protective capacity. Calculation of saturation deficit and degree of saturation are discussed in chapter 2 (Section 2.2.8 and 2.2.9).

3.2.4. Incubation experiment

Four grams of soil samples (< 2000 µm, < 53 µm and < 2 µm) were wet to 70% moisture content of that of field capacity and placed in 250 ml jars. Inside the 250 ml jars, smaller jars of 15 ml containing 10 ml KOH were placed. Three control jars were also incubated with no soil samples. The air tight 250 ml jars were then kept at 25˚C for 5 months. The amount of CO_2-C produced during incubation was trapped in 1M KOH and the amount of CO_2-C trapped was determined by titration against 0.5 M HCl using TIM-850Titration Manager (Radiometer Analytical, UK) (SMBRG, 2011). The measurements were done on days 5, 12, 22, 35, 48, 78, 110 and 142 following the start of the incubation. After each measurement, each sample was returned to ambient CO_2 level by leaving the incubation jars open for an hour. The 250 ml incubation jars containing wet soil samples (70% of field capacity), were weighed prior to incubation. The weight decrease of incubation jars due to moisture loss from the sample during each incubation period was compensated by slow spraying of distilled water on the sample.

The cumulative CO_2-C mineralized (C_{min}) from different samples during the incubation period was calculated from respiration data. The C_{min} was expressed as percent of SOC mineralized (SOC_{min}) from soil samples. The size and decomposition rate constants of active and slow SOC pools were estimated by non-linear curve fitting the

CO_2 evolved per unit time using a constrained two pool first order model as described by Collins et al. (2000). The constrained two pool SOC model was as follows:

$$C_t = C_{active} \exp(-k_a t) + C_{slow} \exp(-k_s t)$$

Where C_t is the total SOC at time t, C_{active} and C_{slow} represent the size of the active and slow SOC pools, k_a and k_s are decomposition rate constants for the active and slow SOC pools. C_{active}, k_a and k_s were determined using nonlinear regression (PROC NLIN METHOD = MARQUARDT 1995) in SAS statistical software, 1995. C_{slow} was defined as $C_{slow} = C_{soc}-C_{active}$ where C_{soc} was the total SOC at the beginning of incubation. This non-linear curve fitting method is an iterative process and maximum iteration is performed to find the best fit line. The incubation data of CO_2-C evolution from each sample was used to run the model and SOC concentration of each of the sample sizes were used to constrain the measurements. k_a and k_s represent the decomposition rate constants of active and slow pools, respectively. The mean residence time of SOC pool, which is the average time C molecule resides in the pool at steady state (Six and Jastrow, 2002), were determined as the reciprocal of k_a and k_s (Six and Jastrow, 2002). In this study the slow SOC pool consisted of slow + resistant pool, since the resistant pool had not been separated by acid hydrolysis (Yang et al., 2007). In discussion, MRT of active SOC pool had been denoted as MRT_a and slow + resistant SOC pool had been denoted as MRT_s.

3.2.5. Statistical analysis

Data was analysed using statistical package R version 2.7.0 (R Development Core Team, 2008). Analysis of variance (ANOVA) of mixed effect model was performed considering land use and soil fractions as fixed factors and site as random factor. The diagnostics of mixed effect model were also checked for homogeneity, normality and

actual versus fitted plot. Tukey contrast analysis was carried out for multiple mean comparisons of fixed factors when ANOVA of main effect was significant without significant interactions between fixed factors using MULTICOMP package in R. Linear regression analysis was used to determine relationships between soil texture, saturation deficit and C mineralization. Robust linear regression analysis was performed using ROBUST package in R to minimize the effect of influential and leverage data points.

3.3. Results

3.3.1. Characteristics of studied soil

The particle-size distribution and C associated with these particles are presented in Table 3.1. Carbon content on silt + clay and clay fractions was expressed as g C kg^{-1} silt + clay or clay (Table 3.1). For calculation of protective capacity, C associated with silt + clay was expressed on whole soil basis (g C kg^{-1} whole soil) (Table 2.3). However, data of particle size distribution, protective capacity and saturation deficit are repeated from Table 2.3 and 2.5.

Table 3. 1. Selected characteristics of Ferrosols

Site	Land use	Particle-size distribution (%)			C on particles (g kg^{-1} sample)		TOC	Protective capacity	Saturation deficit
		< 2	< 53	53-2000	< 2	< 53			
		µm					g kg^{-1} soil		
North Dorrigo	Improved pasture	60	94	6	52.37 (0.07)	50.46 (0.08)	60.1 (0.25)	50.8	-3.4 (0.07)
Dorrigo 1	Improved pasture	57	96	4	39.80 (0.57)	36.72 (0.09)	46.0 (0.11)	53.1	-17.8 (0.09)
Dorrigo 2	Improved pasture	58	96	4	40.37 (0.13)	36.04 (0.24)	43.5 (0.08)	52.7	-18.2 (0.23)
Dorrigo 3	Improved pasture	62	96	4	32.00 (0.10)	30.60 (0.06)	34.3 (0.05)	53.0	-23.6 (0.06)
North Dorrigo	Cropping	54	97	3	43.90 (0.06)	43.36 (0.05)	53.0 (0.09)	54.0	-11.8 (0.05)
Dorrigo 1	Cropping	39	86	14	40.17 (0.07)	32.79 (0.06)	36.9 (0.08)	42.8	-14.6 (0.05)
Dorrigo 2	Cropping	56	95	5	48.40 (0.06)	40.73 (0.03)	50.4 (0.10)	51.9	-13.2 (0.03)
Dorrigo 3	Cropping	66	96	4	36.17 (0.03)	34.97 (0.18)	40.5 (0.21)	52.9	-19.4 (0.17)
North Dorrigo	Woodland	64	94	6	48.67 (0.03)	53.24 (0.07)	73.8 (0.66)	50.7	-0.7 (0.07)
Dorrigo 1	Woodland	54	95	5	62.57 (0.30)	53.83 (0.18)	73.8 (0.09)	51.8	-0.7 (0.17)
Dorrigo 2	Woodland	55	91	9	76.03 (0.19	69.77 (0.24)	84.6 (0.30)	51.9	14.4 (0.23)
Dorrigo 3	Woodland	56	90	10	89.50 (0.11)	97.03 (0.33)	110.3 (0.07)	46.2	40.7 (0.29)

* Values in the parenthesis indicates standard error

3.3.2. Influence of soil texture and saturation deficit on SOC mineralization

The cumulative C mineralization and percent of SOC mineralized that was calculated after 5 months incubation are presented in Table 3.2. The C_{min} from whole soil ranged from 0.78-3.92 g CO_2-C kg^{-1} sample, which were 2.3-4.1% of SOC content in soils (Table 3.2). The negative relationship of cumulative SOC mineralization (C_{min}) from whole soil with silt + clay content was only marginally significant ($p < 0.06$) (Fig. 3.1) But after minimizing the influence of one outlier using ROBUST linear regression, the relationship was highly significant ($p < 0.001$) (Fig. 3.1). Cumulative mineralization from whole soil was also higher from soils having lower C saturation deficit ($p < 0.001$) (C_{min}

= 0.0495 × saturation deficit + 2.02). The SOC_{min} of the whole soil was negatively correlated with silt + clay content ($p < 0.001$) (SOC_{min} = -0.1705 × silt+clay (%) + 18.84) and C saturation deficit of soils ($p < 0.06$) (Fig. 3.2). However, by minimizing the influence of outlier, the relation between SOC_{min} and saturation deficit was highly significant ($p < 0.01$) (Fig. 3.2).

Table 3. 2. Cumulative mineralization (C_{min}) and percent SOC mineralized (SOC_{min}) of whole soil (< 2000 µm), silt + clay (< 53µm) and clay (< 2 µm) particles (incubated for 5 months at 25˚C and 70% of field capacity)

Sites	Cumulative C Mineralization (C_{min}) (g CO_2-C kg^{-1} sample)				SOC mineralized (SOC_{min}) (percent of SOC concentration in samples)			
	Improved pasture	Cropping	Woodland	Mean	Improved pasture	Cropping	Woodland	Mean
Whole soil (< 2000 µm)								
North Dorrigo	1.93 (0.04)	1.28 (0.07)	2.24 (0.05)	1.74b	3.21 (0.07)	2.41 (0.13)	3.03 (0.07)	2.86c
Dorrigo-1	1.08 (0.02)	1.49 (0.05)	1.97 (0.01)		2.34 (0.05)	4.06 (0.13)	2.66 (0.02)	
Dorrigo-2	1.05 (0.04)	1.44 (0.03)	2.76 (0.04)		2.42 (0.10)	2.85 (0.07)	3.26 (0.05)	
Dorrigo-3	0.78 (0.08)	0.92 (0.01)	3.92 (0.05)		2.28 (0.24)	2.27 (0.02)	3.55 (0.04)	
Silt + clay (< 53 µm)								
North Dorrigo	3.32 (0.07)	2.47 (0.02)	3.06 (0.01)	2.65a	6.58 (0.15)	5.71 (0.04)	5.74 (0.03)	5.59a
Dorrigo-1	1.89 (0.03)	2.16 (0.01)	2.74 (0.01)		5.14 (0.1)	6.63 (0.02)	5.10 (0.02)	
Dorrigo-2	1.93 (0.01)	2.37 (0.02)	4.19 (0.05)		5.37 (0.02)	5.91 (0.04)	6.07 (0.08)	
Dorrigo-3	1.57 (0.01)	1.86 (0.00)	4.21 (0.06)		5.11 (0.05)	5.33 (0.01)	4.34 (0.07)	
Clay (< 2 µm)								
North Dorrigo	2.40 (0.09)	2.09 (0.01)	2.55 (0.02)	2.16b	4.59 (0.30)	4.76 (0.04)	5.23 (0.05)	4.33b
Dorrigo-1	1.38 (0.01)	1.80 (0.28)	2.89 (0.01)		3.46 (0.06)	4.48 (1.80)	4.64 (0.02)	
Dorrigo-2	1.89 (0.02)	1.63 (0.00)	3.04 (0.02)		4.67 (0.09)	3.37 (0.01)	4.00 (0.05)	
Dorrigo-3	1.48 (0.01)	1.72 (0.04)	3.05 (0.00)		4.63 (0.05)	4.76 (0.15)	3.40 (0.00)	

- Values in the parenthesis indicates standard error

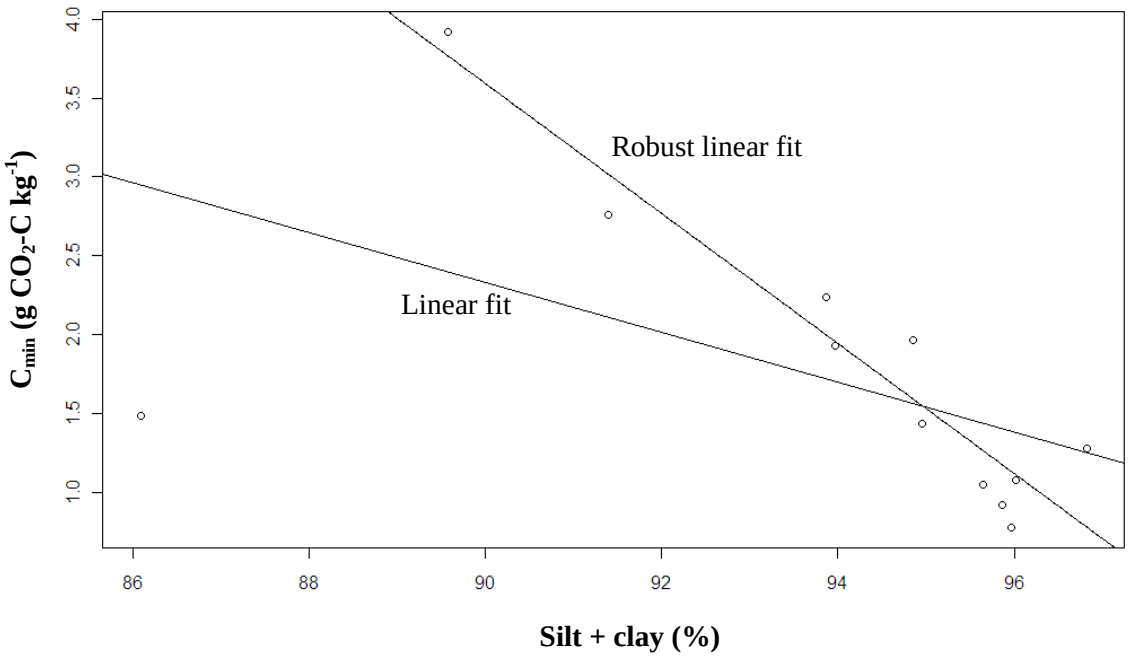

Fig. 3. 1. Relationship between cumulative mineralization of soil organic carbon (C_{min}) and silt + clay content of soils. The relation is not significant at linear fit (y = - 0.1579x + 16.54) (R^2 = 0.24; P = 0.06) and highly significant at robust fit (y = - 4.12x + 4.071) (R^2 = 0.57; P = < 0.001).

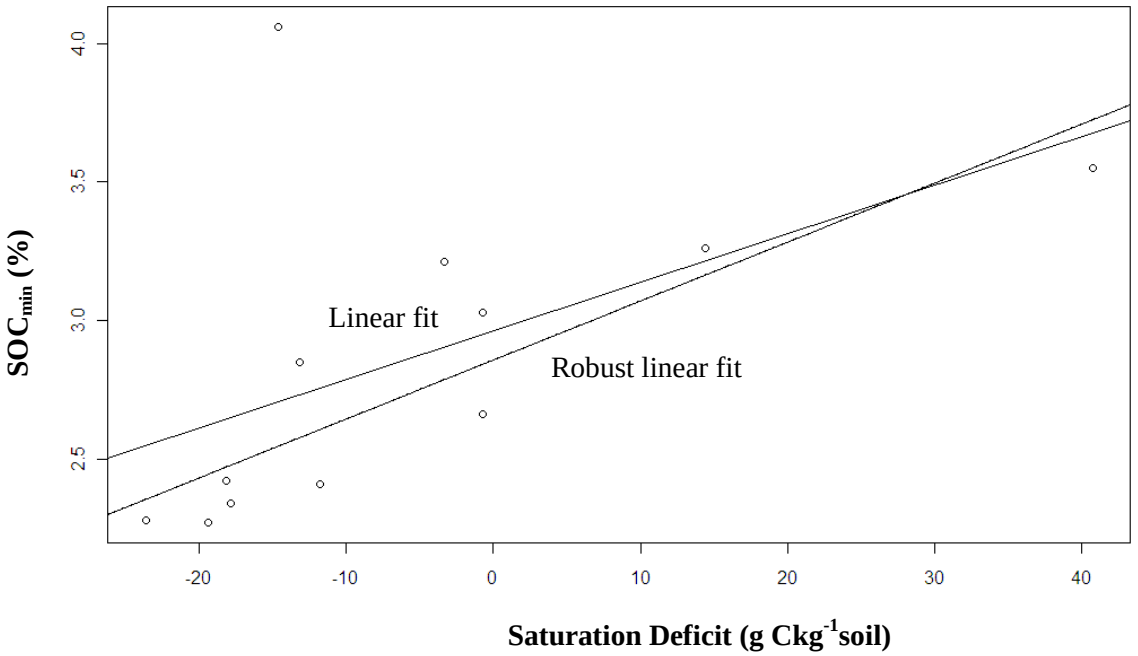

Fig. 3. 2. Relationship between percent SOC mineralized and C saturation deficit in soils. (Negative values on X-axis imply saturation deficit, positive values imply oversaturation). The relation is not significant at linear fit (y = 0.0175x + 2.96) (R^2 = 0.23; P = 0.06) and significant at robust fit (y = 0.02x + 2.85) (R^2 = 0.59; P = < 0.01).

3.3.3. Influence of soil dispersion on SOC mineralization and MRT of SOC pool

In the present study dispersion of soil increased C_{min} compared to that from whole soil (Table 3.2). Thus higher C_{min} was observed from silt + clay particles compared to whole soil ($p < 0.01$) and clay particles ($p < 0.05$). After the incubation, 5.6% SOC was mineralized from dispersed silt + clay particles, that was significantly higher ($p < 0.01$) compared to percent SOC mineralization from whole soil ($p < 0.01$) and clay particles ($p < 0.05$) (Table 3.2).Though cumulative mineralization was higher ($p < 0.01$) from woodland soils compared to pasture and cropping, percent of SOC mineralized was the same under three different land uses.

The size and MRT of SOC pool was calculated by running constrained two pool first order model (Collins et al., 2000). It was observed that less than 5% of the SOC was actively cycling at any of the sites investigated (Table 3.3). When incubating whole soil (< 2000 μm) the small proportion of active SOC pool fell by more than 50% compared with dispersed silt + clay and clay fractions (Table 3.3). However, the smaller proportion of the actively cycling part of SOC in whole soil had very shorter MRT (5.9 days) compared to dispersed silt + clay (50.3 days) and clay (69.8 days) (Table 3.4). Significantly higher ($p < 0.01$) proportion of SOC was observed not cycling actively within the incubation period in the whole soil (98.2%) compared to dispersed silt + clay (95.6%) and clay fractions (96.1%) (Table 3.3). Dispersion of soil did not influence the MRT of this non-actively cycling part or slow SOC pool, by excluding one data point (248 years) from clay fraction of improved pasture, being detected as outlier (Table 3.4). Land use had no significant influence on MRT of any of the SOC pool.

3.3.5. Influence of soil texture and saturation deficit on the Mean residence time of SOC pool

Mean residence time of slow SOC pool was observed to be positively correlated ($p < 0.05$) with silt + clay content in whole soil (MRT = 1.132 × silt+clay (%) – 85.20). Soil C saturation deficit in whole soil was observed to be positively correlated with MRT_s ($p < 0.05$) (MRT = 0.18 × saturation deficit + 19.96). However, the MRT of active pool was not correlated with silt + clay content or C saturation level of the protective capacity.

Table 3. 3. The sizes of active and slow SOC pools of whole soil (< 2000 µm), silt + clay (< 53 µm) and clay (< 2 µm) fractions under improved pasture, cropping and woodland of Ferrosol

Sites	Active pool				Slow pool			
	Percent of SOC concentration in soil particles							
	Improved pasture	Cropping	Woodland	Mean	Improved pasture	Cropping	Woodland	Mean
Whole soil (< 2000 µm)								
North Dorrigo	2.2 (0.03)	1.93 (0.06)	1.55 (0.02)	1.85b	97.80 (0.03)	98.07 (0.06)	98.45 (0.02)	98.15a
Dorrigo-1	1.78 (0.09)	3.02 (0.07)	1.63 (0.02)		98.22 (0.09)	96.98 (0.07)	98.37 (0.02)	
Dorrigo-2	1.95 (0.05)	2.18 (0.06)	1.89 (0.04)		98.05 (0.05)	97.82 (0.06)	98.11 (0.04)	
Dorrigo-3	1.13 (0.06)	1.13 (0.01)	1.82 (0.03)		98.87 (0.06)	98.87 (0.01)	98.18 (0.03)	
Silt + clay (< 53 µm)								
North Dorrigo	3.70 (0.14)	2.88 (0.11)	4.92 (0.24)	4.45a	96.30 (0.14	97.12 (0.11)	95.08 (0.24)	95.55b
Dorrigo-1	5.51 (0.50)	4.22 (0.19)	4.87 (0.39)		94.49 (0.50)	95.78 (0.19)	95.13 (0.39)	
Dorrigo-2	4.93 (0.17)	3.68 (0.10)	5.42 (0.16)		95.07 (0.17)	96.32 (0.10)	94.58 (0.16)	
Dorrigo-3	4.16 (0.33)	4.72 (0.11)	4.44 (0.32)		95.84 (0.33)	95.28 (0.11)	95.56 (0.32)	
Clay (< 2 µm)								
North Dorrigo	4.84 (0.46)	4.53 (0.50)	4.11 (0.09)	3.94a	95.16 (0.46)	95.47 (0.50)	95.89 (0.09)	96.06b
Dorrigo-1	4.16 (1.06)	4.66 (0.65)	2.82 (0.19)		95.84 (1.06)	95.34 (0.65)	97.18 (0.19)	
Dorrigo-2	4.84 (0.04)	2.53 (0.04)	2.77 (0.10)		95.16 (0.04)	97.47 (0.04)	97.23 (0.10)	
Dorrigo-3	3.72 (0.10)	5.11 (0.38)	3.16 (0.09)		96.28 (0.10)	94.89 (0.38)	96.84 (0.09)	

* Values in the parenthesis indicates standard error

Table 3. 4. Mean residence time of active (MRTa) and slow (MRTs) pools of whole soil (< 2000 µm), silt + clay (< 53 µm) and clay (< 2 µm) particles under improved pasture, cropping and woodland of Ferrosol

Sites	Mean residence time of active pool (MRT_a) (day)				Mean residence time of slow pool (MRT_s) (year)			
	Improved pasture	Cropping	Woodland	Mean	Improved pasture	Cropping	Woodland	Mean
Whole soil (< 2000 µm)								
North Dorrigo	8.37 (0.71)	8.13 (0.26)	9.37 (0.64)	5.94c	18.9 (1.12	30.9 (2.68)	18.1 (0.42)	20.96
Dorrigo-1	4.37 (0.70)	6.64 (0.11)	5.16 (0.53)		30.3 (2.74)	17.6 (1.31)	22.3 (0.63)	
Dorrigo-2	4.83 (0.59)	4.88 (0.14)	6.23 (0.23)		24.7 (1.14)	19.7 (0.57)	15.9 (0.22)	
Dorrigo-3	3.15 (0.44)	5.67 (0.29)	4.45 (0.13)		19.4 (2.04)	21.2 (0.10)	12.8 (0.15)	
Silt + clay (< 53 µm)								
North Dorrigo	31.45 (2.27)	31.94 (1.62)	36.29 (2.83)	50.31b	10.2 (0.48)	11.1 (0.29)	21.1 (2.28)	22.70
Dorrigo-1	71.35 (7.17)	41.41 (1.82)	64.98 (6.58)		58.5 (6.53)	14.9 (0.62)	28.9 (5.85)	
Dorrigo-2	72.33 (3.84)	29.55 (1.54)	39.53 (0.46)		16.0 (7.99)	12.6 (0.54)	21.5 (0.69)	
Dorrigo-3	47.27 (3.26)	58.37 (1.22)	79.26 (4.46)		21.3 (2.73)	21.9 (1.05)	34.2 (5.20)	
Clay (< 2 µm)								
North Dorrigo	45.24 (2.07)	75.75 (5.98)	44.44 (0.73	69.77a	58.4 (6.5)	29.5 (7.76)	18.9 (0.88)	53.39
Dorrigo-1	121.04 (3.01)	112.64 (2.00)	73.91 (4.81)		248.00* (8.5)	52.8 (13.63)	14.7 (0.58)	
Dorrigo-2	61.38 (0.80)	43.11 (0.71)	54.71 (2.93)		40.8 (2.49)	27.1 (0.47)	20.8 (0.64)	
Dorrigo-3	46.35 (1.41)	71.14 (2.81)	87.52 (1.53)		22.8 (0.74)	73.9 (3.62)	32.9 (1.65)	

* Values in the parenthesis indicates standard error

3.4. Discussions

3.4.1 Influence of soil texture and saturation deficit on SOC mineralization

The first objective of this research was to determine cumulative C mineralization (C_{min}) and percent of SOC mineralized (SOC_{min}) from soils to test the hypothesis that SOC mineralization will be higher from soil having lower silt + clay and lower C

saturation deficit. A 5 months incubation experiment was conducted to calculate the cumulative C mineralization and percent of SOC mineralized from soils with different C saturation level. In the present study the negative relation ($p < 0.001$) of C_{min} (Fig. 3.1) and SOC_{min} with silt + clay particles indicated the influence of silt + clay particles in protecting C from microbial decomposition. Lower decomposition rate of organic residue was observed in fine textured soils compared to coarse textured soils (Jenkinson, 1988; Ladd et al., 1985). The influence of soil texture in C storage has been observed in a range of studies in which SOC was positively correlated with silt + clay content of soils (Hassink, 1997; Six et al., 2002; Sparrow et al., 2006; Barthes et al., 2008). The stabilizing effect had been ascribed to adsorption of organic C onto clay surfaces (Oades, 1989), encapsulation between clay particles (Tisdall and Oades, 1982) or entrapment in small pores in silt-sized aggregates due to inaccessible to microbes (Elliott and Coleman, 1988). However, in the present study silt + clay content of Ferrosol was negatively correlated with both TOC and C associated with silt + clay particles ($p < 0.001$) (Section 2.3.3). Difference in C input under different land uses influenced on C saturation level of soils (Section 2.4.2). Because of the influence of land use on C storage, silt + clay particles were not saturated to a similar degree. Thus in this study though the influence of silt + clay content was observed on both C_{min} and SOC_{min}, it would be more logical to find the relationship of C saturation level with C_{min} and SOC_{min}. Significant negative relationship of C_{min} ($p < 0.001$) and SOC_{min} ($p < 0.01$) (Fig. 3.2) from whole soil with C saturation deficit explained the importance of both silt + clay content (as silt + clay associated C was determined for calculation of protective capacity) and degree of saturation of the protective capacity on SOC mineralization. Since the binding capacity of soil particles is limited (Hassink, 1997), excess C will remain in a biologically available form (Baldock and Skjemstad, 2000) and be more susceptible to microbial

decomposition. Thus in the present study the significantly higher SOC mineralization from soils with higher level of C saturation supported the silt + clay protective capacity model for protection of C in soils and proved the first hypothesis that SOC mineralization will be higher from soils having lower silt + clay content and lower saturation deficit.

3.4.2 Influence of soil dispersion on SOC mineralization and MRT of SOC pool

The study was also conducted to calculate the C_{min} and SOC_{min} from whole soil (< 2000 µm), silt + clay (< 53 µm) and from clay (< 2 µm) to prove the hypothesis that SOC mineralization will be lower from aggregated (whole soil) sample compared to dispersed soil particles (silt + clay and clay). Dispersion of soils increased SOC mineralization compared to whole soils (Table 3.2). The significantly higher ($p < 0.01$) C_{min} and SOC_{min} from silt + clay particles compared to whole soil might be due to break down of aggregates during dispersion of whole soil which released silt sized POC (particulate organic carbon) in the < 53 µm sized particle. Because of less protection in absence of aggregation, these POC mineralized faster than those inside aggregates of the whole soils. The significantly higher ($p < 0.01$) SOC_{min} from clay particles compared to whole soil could also be the consequence of the release of clay sized POC in clay particles. Christensen (1987) observed higher decomposition of SOC associated with clay than the whole soil. In the present study the significant difference in SOC_{min} from silt + clay and clay particles might be the result of sequential separation procedure that was followed for separation of silt + clay and clay particles (Section 3.2.3). In this study the clay particles were separated from the previously dispersed silt + clay, by decantation of particles applying Stoke's law. Thus the larger silt sized POC that was released after dispersion of whole soil, was not separated with clay particles. Because of the presence of larger silt

sized POC in silt + clay compared to clay the SOC_{min} was significantly higher ($p < 0.05$) from silt + clay particles. In the present study significantly higher C_{min} and SOC_{min} from dispersed silt + clay particles compared to whole soil proved the hypothesis that SOC mineralization will be lower from aggregated soils (whole soil) compared to dispersed soil particles (silt + clay and clay). Whole soils contained both silt + clay associated C (C associated with < 53 µm particles) and silt + clay non-associated C (> 53 µm C fractions). Light fraction C (mineral non associated C) was observed to be significant contributor of SOC mineralization from whole soil (Janzen et al., 1992; Alvarez et al., 2000). Though silt + clay fractions were separated from larger particles (> 53 µm particles and associated C), the SOC_{min} was higher from silt + clay associated C compared to whole soil, because of more access of microbes to decompose C associated with dispersed silt + clay particles. Loss of C from heavy fraction (mineral associated C) was observed in six cultivated soils (Dalal and Mayer, 1986). Loss of C due to cultivation might be the result of tillage (Russell and Williams, 1982; Dalal and Mayer, 1986), which results in fracturing, pulverisation of soil and concomitant increase in microbial activities (Rovira and greacen, 1957). In the present study higher loss of silt + clay and clay associated C after dispersion or breakdown of aggregates might be an explanation of significantly lower C in silt + clay particles of cropping and pasture soils compared to woodland soils.

Influence of aggregation in the protection of C was also observed from subsequent part of analysis, where MRT of SOC pool was analysed by constrained two pool model (Collins et al., 2000). Though the MRT of active pool in whole soil (5.9 days) was shorter ($p < 0.01$) compared to dispersed silt + clay (50.3 days) and clay particles (69.8 days), this actively cycling pool comprised of only 1.9% of SOC in whole soil (Table 3.3 and 3.4). Dispersion significantly ($p < 0.01$) increased the proportion of active

SOC pool. Since whole soil consisted of silt + clay associated C (< 53 µm fractions) as well as silt + clay non-associated C (> 53 µm fractions), the active pool might be comprised of silt + clay non-associated C which mineralized faster compared to silt + clay associated C. Higher mineralization of light fraction and silt + clay non-associated fractions of C than the silt- and clay-size fractions was observed in many studies (Tiessen and Stewart, 1983; Dalal and Mayer, 1986; Gregorich et al., 1995). Though larger C fractions (> 53 µm) were not included in silt + clay and clay particles (particles were separated by sieving), the size of the active pool was significantly larger compared to whole soil which further indicated the higher mineralization of C from dispersed soil particles. Significantly higher proportion ($p < 0.01$) of slow SOC pool in whole soil compared to dispersed soil particles also indicated the higher protection of C and proved the hypothesis that SOC will be more protected within aggregates compared to dispersed silt + clay and clay particles. .

3.4.4 Influence of soil texture and saturation deficit on the Mean residence time of SOC pool

In the present study, the MRT of active and slow SOC pool was calculated to prove the hypothesis that MRT of SOC pool will be higher in soils having higher silt + clay content and higher C saturation deficit. MRT of slow SOC pool was observed to be positively correlated ($p < 0.05$) with silt + clay content and C saturation deficit in whole soil.

The significant negative relationship of SOC_{min} with silt + clay content ($p < 0.001$) and saturation deficit ($p < 0.01$) was observed and explained in section 3.4.1. The protection of SOC in soil containing higher silt + clay might be the reason for lower SOC_{min} and consequent longer MRT_s in whole soil. The longer MRT in soils with higher

clay content was observed by Collins et al. (2000). The influence of silt + clay particles in storing C was observed in many studies in which SOC was positively correlated with silt + clay content of soils (Hassink, 1997; Six et al., 2002; Barthes et al., 2008). In contrast to this, SOC content in the studied Ferrosol was negatively correlated ($p < 0.001$) with silt + clay content of soils (Section 2.3.3; Fig. 2.4a). Higher C saturation deficit was also observed in soils with higher silt + clay ($p < 0.01$) (Section 2.3.3; Fig. 2.4b). In spite of higher capacity (indicated by higher silt + clay), the soils were remained unsaturated with C because of lower C input depending on land uses (Section 2.4.2). Since the protective capacity of higher silt + clay containing soils were not saturated, the existing C was highly protected compared to the soils where the capacity was more saturated, because of their availability for microbial decomposition (Baldock and Skjemstad, 2000). Thus higher MRT of slow SOC pool in soils with higher silt + clay and higher C saturation deficit indicated higher protection of C in these soils. .

3.5. Conclusion

Silt + clay particles in soils plays important role in storing C. However, SOC will be highly protected in soils where the capacity of these particles are less saturated with C. Higher SOC mineralization from soils with lower silt + clay content and lower C saturation deficit was observed in this study which supported the positive effect of both texture and C saturation level on SOC protection. Because of this higher protection, MRT_s of SOC was higher in soil with higher silt + clay and higher saturation deficit. The mechanism of SOC protection by silt + clay is the adsorption and subsequent aggregate formation that protects SOC from microbial decomposition. Thus dispersion of soil particles increased SOC mineralization, compared to non dispersed sample (whole soil).

Similar reason could be attributed for higher C loss from cropping soil or soil under disturbance compared to undisturbed woodland soils even having similar silt and clay percent.

Since lower mineralization and higher protection of C in soils with higher C saturation deficit was observed in this study, subsequent experiment was conducted to determine the stabilization of added residue C in the same soils having different level of C saturation. The findings of the study have been discussed on the next chapter.

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Chapter 4

Organic carbon stabilization in soil: Influence of saturation deficit, freshly added residue and available nutrients

Abstract

An incubation experiment was conducted for eight months to observe the influence of saturation deficit on the stabilization of carbon (C) from added grass residue, kikuya (spp. *Pennisetum clandestinum* Chiov). 12 samples of Ferrosol with different level of C saturation were incubated with grass residue with and without available nutrients. A control experiment was also conducted with soils where no residue was added. Whole experiment was conducted with three replications. Total organic carbon (TOC) and silt + clay associated C decreased in soils where no residue was added after eight months of incubation. The decrease in silt + clay associated C was smaller compared to TOC, suggesting loss of C from silt + clay non-associated fractions was greater. Though residue addition increased both TOC and silt + clay associated C in some soils, it decreased in soils with oversaturated or near saturation of C due to positive priming effect. Even though nutrient addition increased the decomposition of residue, it did not increase C content due to the priming effect. Stabilization of residue derived C was higher ($p < 0.01$) in silt + clay fractions of soils having higher C saturation deficit, which indicated the higher potentiality to stabilize added C of these soils.

4.1. Introduction

Soil organic carbon (SOC) content represents a dynamic equilibrium between input and output which determines the existing C capacity and the potential of soils to store more C. Several environmental variables which include regional climate, soil physical and chemical properties and land management influence the soil C stock and capacity of soil to store C. Any change in these factors could break the equilibrium and consequently could increase or decrease the soil C content. Conservation management practices that decrease soil disturbance and increase the addition of organic residue generally increase SOC stock (Stewart et al., 2009). However, no increase in equilibrium SOC stock was observed in some long-term agroecosystems having treatments with varying C addition levels (Paustian et al., 1997; Huggins et al., 1998; Reicosky et al., 2002). These findings indicated the saturation of soil C at equilibrium (Six et al., 2002; Stewart et al., 2007). Other long-term agroecosystem experiments showed reduced stabilization efficiency of SOC in high C compared to low C soils under the same treatments (Campbell et al., 1991; Nyborg et al., 1995) suggesting the limit to the stabilization of added C in soil (Six et al., 2002; Stewart et al., 2007). Carbon associated with silt and clay particles is more stable compared to whole soil C and thus the capacity of soil to store C is calculated from the relationship between silt + clay content and C associated on these particles (Hassink, 1997). The degree of saturation of the protective capacity of soils is an important factor affecting preservation of added residues to soils (Hassink, 1996). Higher preservation of applied residue C in soils having higher saturation deficit (difference between existing C on silt + clay particles and maximum amount of C that could be adsorbed on that particles) has been observed (Stewart et al., 2008; 2009). After 53 days of incubation Hassink (1996) also found a significant positive relation between C saturation deficit and percentage of applied ^{14}C recovered in silt and

clay fractions. These experiments were conducted to quantify preservation of added residue to soil particles but not to determine the change in C content in soils under new equilibrium condition. Generally soils in the field remain in an equilibrium condition under long-term management practice until disturbed by change in management system. Undisturbed SOC content therefore represents the maximum C storage capacity. Conservation management practice which added residue with minimum disturbance might increase the C content or there might have no change in C depending on the saturation level of the soils. When soil samples are collected to conduct experiment in the laboratory, the equilibrium condition is disturbed and time is required to create a new equilibrium condition. Under this condition preservation of applied residue might not be higher or equal to the mineralization of SOC, since mineralization of SOC increase due to disturbance. In that case the stabilization of added residue might not replenish the C loss due to SOC mineralization.

The stabilization of added residues to soils requires decomposition, which is related to mineralization and humification. Rapid mineralization of labile components is the dominant process during the first phase of decomposition. Mineralization still occurs in the second phase but is slowed down due to the accumulation of refractory molecules (Zech et al., 1997). Decomposition of residues is affected by their nutrient content. Presence of available nutrients accelerates microbial growth and thus decomposition of residue.

The hypothesis of the research was: (1) Nutrient addition will increase decomposition and preservation of applied residue C in soils. (2) Stabilization of applied residue will not replenish the initial C loss but will add some additional C to soils depending on saturation deficit of soils.

The objective of the research was to: (1) Estimate the increase or decrease in SOC content due to application of grass residue with or without nutrients. (2) Test the influence of C saturation deficit on stabilization of residue derived C in soils.

4.2. Materials and Methods

4.2.1. Site information and soil sampling

The Red Ferrosols (Isbell, 1996) (equivalent to Oxisols in US Soil Taxonomy) were collected from the Dorrigo (elevation 746 m) region of the Northern Tablelands, NSW. Sample sites and methods of sampling are discussed in chapter 2 (Section 2.2.1 and Table 2.1)

4.2.2. Preparation and analysis of soil

Detail description of preparation of soil samples, fractionation of silt + clay particles, particle size analysis, determination of organic C are in chapter 2 (Section 2.2.2 to section 2.2.5).

4.2.3. Protective capacity and C saturation deficit calculation

The protective capacity of soils was determined using the equation of Sparrow et al. (2006): $y = 6.67e^{0.0216x}$ ($r^2 = 0.61$, $p < 0.001$). Carbon saturation deficit and degree of saturation was calculated based on this protective capacity. Calculation of saturation deficit and degree of saturation are discussed in chapter 2 (Section 2.2.8 and 2.2.9).

4.2.4. Incubation experiment

An incubation experiment was conducted to observe the influence of added grass residue with and without available nutrients on the stabilization of C in soils. Grass residue was selected in the experiment, because grass was common to all land uses. Ten grams of soil were used for both treated and untreated soil and 1.6 g of partially senescent grass residue (8-mm sized) was incorporated. Nutrient solution was spread on residue and added to soils to determine the influence of available nutrient on decomposition of residue. Thus three treatments were used in the experiment (with 3 replications) including untreated soils where no residue was added. The nutrient solution was prepared using NH_4NO_3, K_2SO_4 and K_2HPO_4 as the source of available N, S and P in a concentration that contained 2% N, 0.15% S and 0.2% P, required for maximum decomposition of residue (Hartenstein, 1981). Soils were wetted to 70% moisture content of that of field capacity and placed in 500 ml jars. Inside the 500 ml jars, smaller jars of 15 ml containing 10 ml KOH were placed. Three control jars were also incubated with no soil samples. The air tight 500 ml jars were then kept at 25˚C for eight months. The amount of CO_2-C produced during incubation was trapped in 1M KOH and the amount of CO_2-C trapped was determined by titration against 0.5 M HCl using TIM-850Titration Manager (Radiometer Analytical, UK) (SMBRG, 2011). Trapped CO_2 was measured in every one week for the first two months and then once in every month. After each measurement each sample was returned to ambient CO_2 level by leaving the incubation jars open for an hour. The 500 ml incubation jars containing wetted soil samples (70% of field capacity), were weighed prior to start incubation. The weight decrease of incubation jars due to moisture loss from the sample during each incubation period was compensated by slow spraying of distilled water on the sample.

At the end of the incubation, soil samples were dried at 40˚C, sieved through 2 mm sieve to separate residue not included as soil organic matter (SOM). Silt + clay of the soils were separated from a portion of soil sample using Na-hexametaphosphate solution (5g L^{-1}). Total organic carbon and silt + clay associated C was determined using LECO CNS analyser. Carbon content on silt + clay was converted to g C kg^{-1} whole soil. Carbon not associated with silt + clay for each treatment was calculated by subtracting silt + clay associated C from TOC of that treatment. The change in TOC and silt + clay associated C due to addition of grass residue with and without nutrient was calculated by subtracting these values from control soils (without adding residue) after incubation.

4.2.9. Statistical analysis

The linear relationships between saturation deficit and change in organic C content after incubation were plotted using SigmaPlot (version 7.0).

4.3 Results

4.3.1 Characteristics of studied soil

Some important properties of studied soils were listed in Table 4.1. Data are repeated from Table 2.3 and 2.4. The protective capacity of soils was calculated using equation: $y = 6.67e^{0.0216x}$ ($r^2 = 0.61$, $p < 0.001$) (Sparrow et al., 2006). Carbon saturation deficit was calculated from the difference between actual C content on silt + clay particles and the calculated protective capacity (Hassink, 1996). Carbon saturation deficit was observed in all soils with the exception of two woodland soils (Dorrigo 2 and Dorrigo 3) that had stored 28% and 88% more C than their theoretical saturation level.

Table 4. 1. Selected characteristics of Ferrosols

Site	Land use	Particle-size distribution (%)			C content (g kg^{-1} soil)			Protective capacity (g C kg^{-1} soil)	Saturation deficit (g C kg^{-1} soil)
		< 2	< 53	53-2000	TOC	Silt + clay (<53 µm)	53-2000 µm		
		µm							
North Dorrigo	Improved Pasture	60	94	6	60.1 (0.25)*	47.4 (0.08)	12.7	50.8	-3.4 (0.07)
Dorrigo 1	Improved Pasture	57	96	4	46 (0.11)	35.3 (0.09)	10.8	53.1	-17.8 (0.09)
Dorrigo 2	Improved Pasture	58	96	4	43.5 (0.08)	34.5 (0.24)	9.0	52.7	-18.2 (0.23)
Dorrigo 3	Improved Pasture	62	96	4	34.3 (0.05)	29.4 (0.06)	5.0	53.0	-23.6 (0.06)
North Dorrigo	Cropping	54	97	3	53.0 (0.09)	42.2 (0.05)	10.8	54.0	-11.8 (0.05)
Dorrigo 1	Cropping	39	86	14	36.9 (0.08)	28.2 (0.06)	8.6	42.8	-14.6 (0.05)
Dorrigo 2	Cropping	56	95	5	50.4 (0.10)	38.7 (0.03)	11.7	51.9	-13.2 (0.03)
Dorrigo 3	Cropping	66	96	4	40.5 (0.21)	33.5 (0.18)	7.0	52.9	-19.4 (0.17)
North Dorrigo	Woodland	64	94	6	73.8 (0.66)	50.0 (0.07)	23.9	50.7	-0.7 (0.07)
Dorrigo 1	Woodland	54	95	5	73.8 (0.09)	51.1 (0.18)	22.8	51.8	-0.7 (0.17)
Dorrigo 2	Woodland	55	91	9	84.6 (0.30)	66.2 (0.24)	18.4	51.9	14.4 (0.23)
Dorrigo 3	Woodland	56	90	10	110.3 (0.07)	86.9 (0.33)	23.4	46.2	40.7 (0.29)

* Values in the parenthesis indicates standard error

4.3.2. Change in soil C content after incubation

After 8 months of incubation, it was observed that TOC decreased by ~2-19 g kg^{-1} soil of their initial C content when no residue was added (Table 4.1 and 4.2). Unlike TOC, decrease in silt + clay associated C from their initial C content was very small in nine soil samples (~0.4-10 g kg^{-1} soil) and increased (~0.05-2 g kg^{-1} soil) in three soils (pasture in Dorrigo 2 and Dorrigo 3, and cropping in Dorrigo 3) when no residue was added (Table 4.1 and 4.2). The silt + clay associated C content increased in three soils (Pasture soils in Dorrigo 2 and 3, cropping soil in Dorrigo 3) having higher saturation deficit (-18.2 g kg^{-1} soil, -23.6 g kg^{-1} soil and -19.4 g kg^{-1} soil respectively).

Mineralization of SOC increased 20 times when only residue was added, and 21 times when residue with nutrients was added to soils. Residue addition both with and without nutrients increased TOC and silt + clay associated C in most soils but did not compensate for the loss of initial C (Table 4.3). Mineralization of C from soils without residue, soil + residue and soil + residue + nutrients is shown in Fig. 4.1. Mineralization from other soils is not presented as the trend was the same. After doing mass balance (TOC + residue C = TOC after incubation + SOC respiration) it was observed that around 24% C was unaccounted.

Table 4. 2. Mean carbon content in soil fractions determined after eight months of incubation

Site	Land use	C content without adding residue (g kg^{-1} soil)			C content after adding residue (g kg^{-1} soil)			C after adding residue with nutrients (g kg^{-1} soil)		
		TOC	Silt + clay associated	Silt + clay non-associated	TOC	Silt + clay associated	Silt + clay non-associated	TOC	Silt + clay associated	Silt + clay non-associated
North Dorrigo	Improved Pasture	55.69 (0.3)*	46.25 (0.02)	9.44	60.32 (0.45)	47.32 (0.02)	13.00	55.64 (1.32)	47.36 (0.01)	8.28
Dorrigo 1	Improved Pasture	41.72 (0.94)	34.84 (0.01)	6.88	42.84 (0.66)	36.60 (0.01)	6.23	41.75 (0.19)	33.98 (0.15)	7.77
Dorrigo 2	Improved Pasture	37.30 (0.52)	34.52 (0.02)	2.79	39.75 (0.36)	36.74 (0.04)	3.02	40.34 (2.16)	36.94 (0.05)	3.4
Dorrigo 3	Improved Pasture	32.02 (0.12)	31.51 (0.02)	0.50	34.90 (1.47)	31.88 (0.02)	3.02	33.55 (0.54)	31.94 (0.04)	1.61
North Dorrigo	Cropping	48.27 (0.25)	41.61 (0.02)	6.65	48.58 (0.83)	44.06 (0.02)	4.52	48.14 (0.54)	42.95 (0.03)	5.19
Dorrigo 1	Cropping	33.56 (0.15)	27.64 (0.04)	5.92	34.66 (0.54)	28.40 (0.02)	6.26	33.98 (0.52)	29.42 (0.02)	4.56
Dorrigo 2	Cropping	45.08 (0.52)	37.92 (0.03)	7.16	47.05 (0.68)	39.50 (0.03)	7.55	44.49 (1.10)	39.63 (0.03)	4.86
Dorrigo 3	Cropping	36.87 (0.31)	34.84 (0.02)	2.03	42.18 (1.52)	34.55 (0.02)	7.63	38.37 (0.93)	34.23 (0.03)	4.14
North Dorrigo	Woodland	68.62 (0.91)	46.31 (0.01)	22.32	67.74 (0.77)	47.10 (0.03)	20.63	68.11 (1.22)	47.21 (0.04)	20.90
Dorrigo 1	Woodland	55.16 (2.45)	40.75 (0.01)	14.41	59.21 (1.00)	43.97 (0.03)	15.24	58.21 (2.5)	42.98 (0.05)	15.23
Dorrigo 2	Woodland	79.06 (1.45	61.65 (0.04)	17.40	78.61 (2.91)	60.94 (0.08)	17.68	75.71 (0.71)	61.58 (0.09)	14.13
Dorrigo 3	Woodland	105.01 (1.45)	83.21 (0.11)	21.80	105.79 (2.36)	77.86 (0.09)	27.94	105.55 (0.22)	78.22 (0.21)	27.34

*Values in the parenthesis indicates standard error

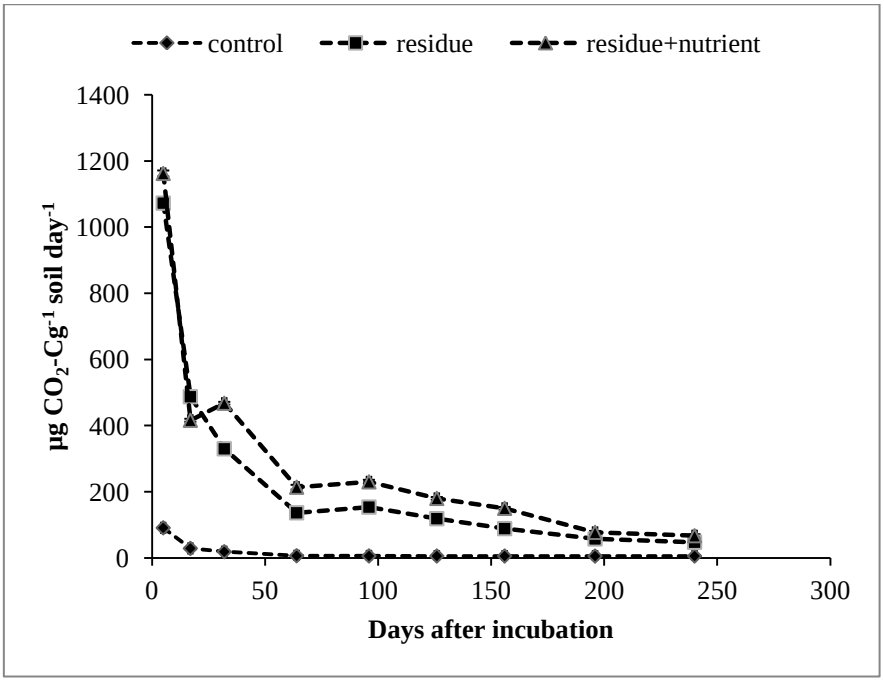

Fig. 4. 1. Soil and residue carbon mineralization during eight months of incubation (Improved pasture from North Dorrigo)

Table 4. 3. Increase/decrease in TOC and silt + clay associated carbon after incubation

Site	Land use	Increase in soil carbon content due to addition of residue (g C kg^{-1} soil)		Increase in soil carbon content due to addition of residue with nutrient (g C kg^{-1} soil)	
		TOC	Silt + clay associated	TOC	Silt + clay associated
North Dorrigo	Improved Pasture	4.6 (0.7)	1.06 (0.4)	-0.1 (1.11)	1.11 (0.6)
Dorrigo 1	Improved Pasture	1.1 (0.35)	1.76 (0.2)	0.00 (0.86)	-0.86 (0.22)
Dorrigo 2	Improved Pasture	2.4 (0.74)	2.22 (0.3)	3.0 (2.53)	2.43 (0.5)
Dorrigo 3	Improved Pasture	2.9 (1.57)	0.37 (0.5)	1.5 (0.65)	0.42 (0.5)
North Dorrigo	Cropping	0.3 (1.06)	2.45 (0.6)	-0.1 (0.57)	1.34 (0.6)
Dorrigo 1	Cropping	1.1 (0.63)	0.77 (0.4)	0.4 (0.39)	1.78 (0.4)
Dorrigo 2	Cropping	2.0 (1.00)	1.58 (0.6)	-0.6 (1.6)	1.71 (0.22)
Dorrigo 3	Cropping	5.3 (1.27)	-0.29 (0.4)	1.5 (0.24)	-0.61 (0.45)
North Dorrigo	Woodland	-0.9 (1.18)	0.80 (0.6)	-0.5 (0.54)	0.91 (0.36)
Dorrigo 1	Woodland	4.1 (2.45)	3.22 (0.7)	3.1 (2.96)	2.23 (0.8)
Dorrigo 2	Woodland	-0.4 (2.2)	-0.71 (0.3)	-3.3 (1.19)	-0.07 (0.42)
Dorrigo 3	Woodland	0.8 (1.99)	-5.36 (0.4)	0.5 (1.67)	-5.00 (0.44)

* Values in the parenthesis indicates standard error

4.3.3. Influence of saturation deficit on the accumulation of added C

Carbon saturation deficit had no influence on accumulation of C in whole soil. But there was significant positive relationship ($p < 0.01$) between saturation deficit and increase in silt + clay associated C due to addition of grass residue with and without nutrients (Fig. 4.2).

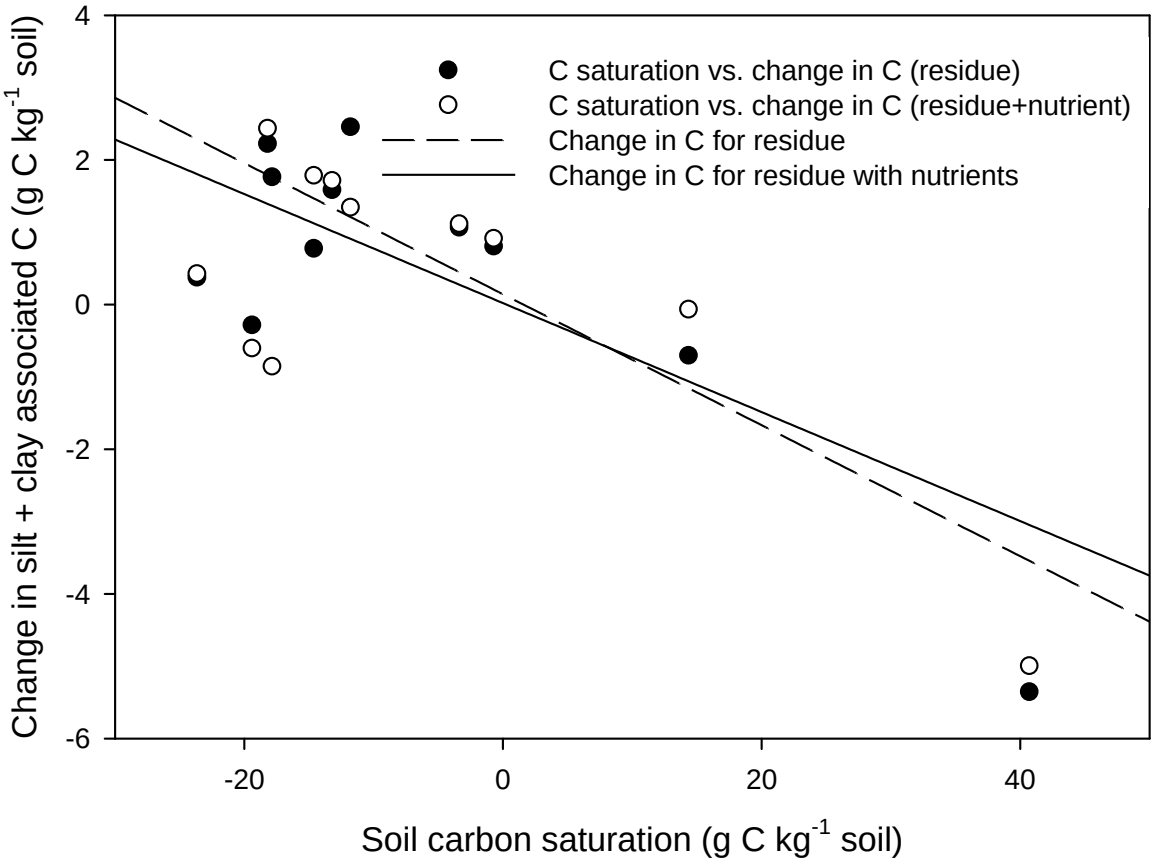

Fig. 4. 2. Relationship between saturation deficit and increase in silt + clay associated carbon due to addition of grass residue. Negative values on X-axis imply saturation deficit, positive values imply oversaturation

The dashed line is the relationship (*y = -0.09x + 0.14*) between soil carbon saturation and change in silt + clay associated carbon when residue was added ($R^2 = 0.55$; P = < 0.01).

Solid line is the relationship (*y = -0.07x + 0.02*) of these when nutrients was added with residue (R^2 = 0.45; P = < 0.05).

4.4. Discussions

4.4.1. Change in soil C content after incubation

The first objective of the research was to estimate the increase or decrease in SOC content due to addition of residue, with and without nutrients after 8 months of incubation. After 8 months of incubation TOC decreased from ~2-19 g C kg^{-1}soil from their initial C content without adding residue. In contrast, the decrease in silt + clay associated C from their initial C content was very small (~0.4-10 g kg^{-1} soil), and decrease in C was observed in 75% of samples. Carbon content in silt + clay increased (~0.05-2 g kg^{-1} soil) in three soil samples (pasture in Dorrigo 2 and Dorrigo 3, and cropping in Dorrigo 3). The smaller decrease in silt + clay associated C indicated that the loss of SOC was mainly due to mineralization of C not associated with silt + clay particles. In the previous study, mean residence time (MRT_a) of active pool of whole soil was observed to be significantly shorter (5.94 days) compared to silt + clay (50.31 days). Since whole soil comprised of silt + clay associated C and silt + clay non- associated C, it was assumed that the active pool of whole soil consisted of silt + clay non associated C, due to faster turnover rate compared to silt + clay associated C. That assumption was supported in the present study by direct measurement of TOC and silt + clay associated C after 8 months of incubation. Light fraction C (mineral non associated C) was observed to be significant contributor of SOC mineralization from whole soil (Janzen et al., 1992; Alvarez et al., 2000). In the present study, higher decrease (3 times) in TOC compared to silt + clay associated C was consistent with literature (Janzen et al., 1992; Alvarez et al., 2000). However, the increase in silt + clay associated C was observed in three soils having higher C saturation deficit (-18.2 g kg^{-1} soil, -23.6 g kg^{-1} soil and -19.4 g kg^{-1} soil

respectively). The increase in silt + clay associated C in these soils might be the result of humification (product of decomposition) of C not associated with silt + clay. The stabilization of humification product was observed in soils having higher saturation deficit (-18.2 g kg^{-1} soil, -23.6 g kg^{-1} soil and -19.4 g kg^{-1} soil respectively) because of the higher potentiality of these soils to sequester more C on silt + clay particles.

In the present study, residue addition increased SOC mineralization by 20 times than the soils where no residue was added. It was also observed that residue addition increased TOC in most soils compared to soils where no residue were added, but did not compensate for the loss of initial C (C content before incubation) (Table 4.3). Moreover, TOC decreased (0.4 and 0.9 g kg^{-1} soil) in two of the woodland soils (North Dorrigo and Dorrigo 2) even after addition of residue (Table 4.3). Like TOC, residue addition increased silt + clay associated C in most soils, compared to that where no residue was added, with the exception of two woodland (Dorrigo 2 and Dorrigo 3) and one cropping soil (Dorrigo 3) (Table 4.3). Though higher mineralization (21 times higher than soils without residue) was observed in all soils where nutrients were added with residue (e.g., Fig. 4.1), surprisingly TOC and silt + clay associated C decreased in some soils, compared to those where no residue was added (Table 4.3). The decrease in SOC content due to addition of fresh residue and nutrients was mainly the result of priming effect, which is the acceleration or retardation of mineralization of soil organic matter (SOM) by the addition of organic substances to soil (Kuzyakov et al., 2000). Priming effects were observed in many studies following addition of plant residues, decaying microorganisms, high-molecular and low-molecular substances or mineral N. The intensification of SOC mineralization due to incorporation of fresh organic matter such as green manure or straw in soils has been observed in studies (Broadbent, 1947; Broadbent and Bartholomew, 1948; Sorensen, 1974; Wu et al., 1993). In absence of fresh residue, the lower

mineralization of SOC is the result of lower quality of soil organic matter (SOM) that limits the amount of available energy for soil microorganisms, and in turn the rate of SOM mineralization. Incorporation of fresh residue cause an increase in overall microbial activity due to the availability of energy and nutrients released from fresh organic matter (Lohnis, 1926; Broadbent, 1947; Bingeman et al., 1953; Sorensen, 1974). In this study positive priming effect was observed due to addition of fresh residue as available energy source for microorganisms for decomposition of SOC. Nutrient addition increased SOC mineralization 1.1 times higher compared to that when only residue was added to soils (Fig. 4.1). The source of mineralized C could not be detected as the residue was not labelled. However, 1.4 times lower stabilization of C in silt + clay fraction due to addition of residue + nutrient compared to only residue addition indicated the higher mineralization of SOC, due to available nutrients (Table 4.3). Nutrient content of the substrate is an important factor for decomposition, since decomposer organisms has high nutrient requirement (Goldman et al., 1987). Higher nitrogen and phosphorus content increase the decomposition of substrate due to fast growth of microbial population (Goldman et al., 1987). Thus in the present study, nutrient addition increased the decomposition of applied residue, but at the same time decreased stable C (SOC), compared to that when only residue was added because of positive priming effect and rejected the hypothesis that nutrient addition will increase decomposition and preservation of added residue C.

However, the lower priming effect in TOC compared to silt + clay associated C might be the result of compensation from decomposition product of added residue that was not associated with silt + clay. After incubation, the residue larger than 2 mm was separated by sieving through 2 mm sieve and the fraction of residue smaller than 2 mm was incorporated in soils and quantified as TOC. The reason for missing C (30 g kg^{-1} soil)

which was 24% of total C input was the result of separation of residue greater than 2 mm that was not quantified and included in the mass.

4.4.2. Influence of saturation deficit on the stabilization of residue derived carbon

The second objective of the present research was to test the influence of C saturation deficit on the stabilization of residue derived C. In this study, significant positive relationship was observed between C saturation deficit and increase or decrease in silt + clay associated C due to addition of residue with and without nutrients ($p < 0.01$) (Fig. 4.2) and proved the second hypothesis that C saturation deficit will influence the stabilization of residue derived C in soils. This finding indicated the higher potentiality of soils to stabilize more C having higher C saturation deficit. However, no significant influence of C saturation was observed on increase or decrease in TOC content after incubation. This result was consistent with Stewart et al. (2008 and 2009) who observed C saturation behaviour in chemically and biochemically protected pools but not in non-protected pool. After addition of ^{13}C-labeled wheat straw to both the A and the C horizons of mineral soils, greater stabilization of residue-derived C was observed in C (having higher C saturation deficit) compared to A (having lower C saturation deficit) horizon (Stewart et al., 2008, 2009). Significant positive relationship between C saturation deficit and percentage of residue derived ^{14}C recovered in the silt and clay fraction was observed by Hassink (1996). In the present study, stabilization of C was observed in almost all soils that had C saturation deficit (Fig. 4.2). Higher loss of silt + clay associated C after residue addition was observed in soils that was initially oversaturated or close to C saturation (Fig. 4.2). The reason for higher loss of C may be explained in two ways. First, these oversaturated soils also contained more C than the other soils potentially increasing the magnitude of the priming effect following addition of fresh residue (Hart et al., 1986). Second, as these soils were initially oversaturated with C, all the C molecules were not

strongly adsorbed and protected by silt + clay particles, because of the limited capacity of silt + clay particles. Thus C not bound with silt + clay particles was more susceptible to decomposition when microbial communities were activated due to addition of available substrates for energy source.

4.5. Conclusions

Silt + clay and saturation of these particles with C are important for both stabilization of existing C in soils and accumulation of added residue C. More C will be lost from soils where protective capacity has already been saturated or oversaturated with C. Stabilization of added residue derived C will also be higher in soils having higher C saturation deficit. Because of the positive priming effect, residue addition will accelerate decomposition of SOC depending on their saturation level. Soil C loss due to saturation could be the main reason in some long-term experiments where addition of residue did not increase SOC content of soils.

Decomposition of fresh residue and subsequent incorporation of stable C in soil, require more time as this is a slow process. Thus in the laboratory the batch experiment could be a good approach to get quick response of addition of DOC in soils having different C saturation level. The experiment that was conducted to get the quick response of C saturation behaviour upon addition of DOC are discussed in the next chapter.

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Chapter 5

Sorption of dissolved organic carbon (DOC) on soil particles: Influence of soil properties and concentration of DOC added.

Abstract

Sorption of dissolved organic carbon (DOC) on silt + clay particles (< 53 µm) of 12 soil samples was conducted in laboratory at 4°C to observe the influence of soil properties (initial C content, C saturation deficit, poorly crystalline minerals) on the desorption of indigenous C and adsorption of added dissolved organic carbon (DOC). The protective capacity of soils was calculated using proposed model: $y = 6.67e^{0.0216x}$ (r^2 = 0.61, p < 0.001) by Sparrow et al. (2006). Carbon saturation deficit of soils was calculated from the difference between actual C content on silt + clay particles and maximum amount of C that could be adsorbed on these particles (Hassink, 1996). The soils (Ferrosol) were collected from four different sites in Dorrigo, under three different land uses (pasture, cropping and woodland). Dissolved organic carbon was extracted from partially senescent grass, Kikuya (spp. *Pennisetum clandestinum* Chiov) with deionised water. The initial concentration of DOC was 300 mg L^{-1}. Adsorption was conducted by preparing 6 initial solutions with different DOC concentration (from 0 to 300 mg L^{-1}). The results were analysed using the initial mass isotherm (IMI) (Nodvin et al., 1986) due to desorption of indigenous soil C. The intercept *b* of the initial mass isotherm was positively correlated with initial C content of the silt + clay particles (p < 0.01) and negatively correlated with C saturation deficit of soils (p <0.01). Unlike *b*, the slope *m* of the regression had no influence on either desorption or sorption of DOC on soil particles because of multiple factors influencing it (e.g. the origin, molecular

weight, polarity and molecular configuration of both soil C and added DOC). However, though initial C content of the soils was positively correlated with poorly crystalline Al, desorption of soil C was higher in soils having higher content of this mineral. Saturation of this mineral with organic C might be the reason for this higher desorption.

5.1. Introduction

Dissolved organic matter (DOM) is an easily degradable fraction of organic matter in soils compared with the solid fraction (Burford and Bremner, 1975). But this biodegradable form of organic matter could be a significant part of organic C in mineral subsoil. The source of this DOC is the decomposition of surface litter passing through the soil profile. The flux of DOC from the forest floor into the mineral subsoil has been estimated at 115-500 kg C ha^{-1} $year^{-1}$ (Guggenberger and Zech, 1993; Currie et al., 1996; Michalzik and Matzner, 1999; Solinger et al., 2001; Kaiser et al., 2001). Compared to this flux, the concentration and export of DOC from mineral subsoil horizons is small (Guggenberger and Zech, 1993; Michalzik and Matzner, 1999; Solinger et al., 2001), typically 40-370 kg DOC ha^{-1} $year^{-1}$ are retained in the mineral subsoil (Currie et al., 1996; Guggenberger and Kaiser, 2003). Adsorption on the mineral surface might be the main process for such retention (Kaiser and Guggenberger, 2000). Laboratory studies showed that sorption of DOC depends on soil properties, such as organic C content, Al and Fe oxides/hydroxides, and the content and mineralogy of clay fractions (McDowell and Wood, 1984; Jardine et al., 1989; Donald et al., 1993; Kaiser and Guggenberger, 2000; Kalbitz et al., 2000). Sorption of DOC is higher in soils with higher clay content (Nelson et al., 1992; Shen, 1999) and lower initial C content (Jardine et al., 1989; Kaiser and Zech, 2000; Shen, 1999). Positive relationships have also been observed between the specific surface area (SSA, BET-N_2 method) of soils and sorption of DOC (Nelson et al.,

1992; Kaiser et al., 1996). A close relations between organic C and BET surface area in coastal sediments (Mayer, 1994; Keil et al., 1994) and subsoil horizons (Mayer, 1994) represented the " monolayer equivalent" (ME) theory for mineral surface loadings with OM (Mayer, 1994). The surface area of soils increases by removal of organic C due to coverage of mineral surface with organic matter (Christensen, 1996; Theng et al., 1999). This phenomenon suggests that the lower the C content in soil, the more the surface will be exposed for further DOC sorption. Similarly Hassink (1997) proposed the concept of protective capacity for maximum C storage in soils. Protective capacity of soils is calculated from relationship between silt + clay content and C associated on these particles. The degree of saturation of the protective capacity is important for preservation of applied residue C in soils (Hassink, 1996). Much of the added C was preserved in soils having higher saturation deficit (Hassink, 1996; Stewart et al., 2008). Saturation deficit means how far the soils are from their maximum saturation level. The difference between existing C level on silt + clay and their theoretical protective capacity will represent saturation deficit on soils (Hassink, 1996). Since adsorption is a dominant process for preservation of C in soils, it was hypothesized that: (1) Desorption of indigenous soil C will be lower from soils having higher saturation deficit. (2) Higher saturation deficit will increase the sorption of applied DOC. The objectives of the research were (1) to describe the sorption of DOC to silt + clay particles of soils (2) to develop a general description of the relationships between soil properties and DOC sorption.

5.2. Materials and Methods

5.2.1. Site information and soil sampling

The Red Ferrosols (Isbell, 1996) (equivalent to Oxisols in US Soil Taxonomy) were collected from the Dorrigo (elevation 746 m) region of the Northern Tablelands, NSW. Sample sites and methods of sampling are discussed in chapter 2 (Section 2.2.1 and Table 2.1)

3.2.2. Preparation and analysis of soil

Detail description of preparation of soil samples, fractionation of silt + clay particles, particle size analysis, determination of organic C, pH measurement, determination of mineral content (crystalline and poorly crystalline Fe and Al), are in chapter 2 (Section 2.2.2 to section 2.2.7).

3.2.3. Protective capacity and C saturation deficit calculation

The protective capacity of soils was determined using the equation of Sparrow et al. (2006): $y = 6.67e^{0.0216x}$ ($r^2 = 0.61$, $p < 0.001$). Carbon saturation deficit and degree of saturation was calculated based on this protective capacity. Calculation of saturation deficit and degree of saturation are discussed in chapter 2 (Section 2.2.8 and 2.2.9).

5.2.4. Extraction of Dissolved Organic Carbon (DOC)

Water soluble organic C was extracted from partially senescent grass Kikuya, (spp. *Pennisetum clandestinum* Chiov) grown in pasture land. Grass sample was selected for DOC extraction as the studied soils were collected from three different land uses

(pasture, cropping and woodland), where grass was the common plant population. For extraction of DOC, 2 litres of deionized water was added to 500 g of the grass sample. After 15 minutes stirring with a glass rod, the suspension was allowed to stand for 18 hours at room temperature (Kaiser and Guggenberger, 2007) then passed through a 0.45-µm nylon filter (Kahle et al., 2003). The concentration of DOC in the extract was 300 mg litre^{-1} determined by TOC analyser (InnoVox, GE, Germany). We prepared 6 initial solutions ranging from 0 to 300 mg DOC litre^{-1} for the sorption experiment by diluting the extract with a solution of similar inorganic composition and the same pH. The pH of the extract was 5.5 and electrical conductivity 606 µs cm^{-1}. The major cations were K^+ (90 mg L^{-1}), Ca^{2+} (21 mg L^{-1}), Mg^{2+} (16 mg L^{-1}), and the major anions were SO_4^{2-} (22 mg L^{-1}) and PO_4^{2-} (14 mg L^{-1}).

5.2.5. Sorption experiments

For the sorption experiment, DOC solution of each concentration was added to silt + clay at the 100:1 ratio (Kahle et al., 2003). Briefly, 40 ml solution was added to 0.4 g silt + clay. The suspensions were tumbled for 18 hours in the dark at 4˚C to inhibit microbial decomposition of DOC in solution (Zhou and Wong, 2000). The suspensions were then centrifuged for 20 minutes at 3000 rpm and filtered through 0.45 µm nylon filter. The amount of DOC sorbed was calculated from the difference between DOC concentrations in the initial and equilibrated solutions.

Due to release of indigenous DOC from soil particle surface, the results could not be analysed by Freundlich or Langmuir isotherms. Thus the initial mass isotherm (Nodvin et al., 1986) was applied. This approach has been shown to describe the sorption of DOC to soils in many studies (Vance and David, 1989; Guggenberger and Zech, 1992; Donald et al., 1993; Kaiser et al., 1996). In the initial mass approach, the concentration of

substance adsorbed or released (normalized to soil mass, *RE*) is plotted against the initial concentration of the substance (normalized to soil mass, X*i*):

$$RE = m \cdot Xi - b$$

Where *m* is the slope of the partition regression, which is similar to the partition coefficient. The coefficient *m* is a measure of the affinity of the substance to the sorbent. The intercept of the regression (*b*) indicates the amount of substance released from the soil when a solution with a zero sorbate concentration is added.

The null-point concentration (Mendoza and Barrow 1987) of DOC (DOCnp, mg L^{-1}), at which there is no net removal or release of DOC from the solution, was taken as the intercept of the sorption isotherm (i,e., when RE or net sorption = 0).

The intercept (*b*) and the slope (*m*) of the linear relationship were used to calculate the reactive soil pool (RSP) (Nodvin et al., 1986):

$$RSP = b/(1-m)$$

The RSP can be defined as the amount of a substance present in the soil that can readily exchange with substance in solution under the conditions of the experiment (Nodvin et al., 1986). Thus intercept *b*, represents the amount of RSP not retained (or released) by the soil when $Xi = 0$, and therefore it will always be zero or negative. If the intercept is equal to zero, the RSP does not exist, and the total reactive solute in the system is equal to the amount added in the solution.

The solution with zero DOC concentration was also added to whole soil (< 2000 µm), to determine desorption of indigenous DOC from soil. The soil to solution ratio (100:1) and time for tumbling was same as it was for dispersed silt + clay particles. Since only one solution concentration was added, the result was not analysed using IMI (Initial mass isotherm). This additional work was done to compare desorption of DOC from dispersed silt + clay particles with that from whole soil.

5.2.6. Statistical analysis

Sorption of DOC was analysed by use of the initial mass (IM) relationship (Nodvin et al., 1986). In the IM approach, the quantity of C adsorbed or released (normalized to soil mass, RE) was plotted against the initial quantity of the added DOC (normalized to soil maxx, Xi) using SigmaPlot (version 7.0).The linear relationships between soil properties and IMI parameters were plotted using SigmaPlot (version 7.0).

5.3. Results

5.3.1. Characteristics of studied soil

Some important characters of Ferrosol are listed in Table 5.1. All data are repeated from Table 2.3 and 2.4, with the exception of C content in silt + clay particles. Carbon associated with silt + clay was expressed on whole soil basis (g C kg^{-1} soil) for calculation of protective capacity and thus presented in Table 2.3. But in this chapter, C content in silt + clay particles are expressed in g C kg^{-1} silt + clay particles and presented in Table 5.1, as adsorption was conducted on dispersed silt + clay particles. Initially the protective capacity of soils was calculated using equation: $y = 6.67e^{0.0216x}$ ($r^2 = 0.61$, $p < 0.001$) (Sparrow et al., 2006). Carbon saturation deficit was calculated from difference between actual C content in silt + clay particles and the theoretical protective capacity (Hassink, 1996). Total and silt + clay associated C was positively correlated with oxalate extractable Al ($p < 0.001$) in soils. The saturation deficit was also positively correlated with oxalate extractable Al content in soils ($p < 0.001$). The pH values of silt + clay were very similar and ranged from 5.6-6.3 (Table 5.1) which was very close to pH of the whole soil (Table 2.3). No relation of pH with organic C was observed

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Table 5. 1. Selected characteristics of Ferrosols

Site	Land uses	TOC (g kg^{-1} soil)	Silt + clay particles (%) (< 53 µm)	C on silt + clay particles (g kg^{-1} silt + clay)	pH of silt + clay particles	Protective capacity	Saturation deficit	Fe_{ox}	Fe_{cd-ox}	Al_{ox}	Al_{cd-ox}
						g kg^{-1} soil					
North Dorrigo	Improved Pasture	60.1 (0.25)*	94	50.46 (0.08)	6.2	50.8	-3.4 (0.07)	9.62	113.82	6.91	8.7
Dorrigo 1	Improved Pasture	46 (0.11)	96	36.72 (0.09)	6.1	53.1	-17.8 (0.09)	4.68	31.31	5.89	0.6
Dorrigo 2	Improved Pasture	43.5 (0.08)	96	36.04 (0.24)	6.2	52.7	-18.2 (0.23)	8.05	118.43	5.42	11.5
Dorrigo 3	Improved Pasture	34.3 (0.05)	96	30.60 (0.06)	6.0	53.0	-23.6 (0.06)	7.62	105.22	5.37	4.3
North Dorrigo	Cropping	53.0 (0.09)	97	43.36 (0.05)	6.2	54.0	-11.8 (0.05)	9.17	115.24	7.57	9.0
Dorrigo 1	Cropping	36.9 (0.08)	86	32.79 (0.06)	6.0	42.8	-14.6 (0.05)	5.21	27.21	3.07	2.8
Dorrigo 2	Cropping	50.4 (0.10)	95	40.73 (0.03)	6.3	51.9	-13.2 (0.03)	10.11	128.89	5.11	13.1
Dorrigo 3	Cropping	40.5 (0.21)	96	34.97 (0.18)	6.3	52.9	-19.4 (0.17)	7.74	105.16	5.58	5.3
North Dorrigo	Woodland	73.8 (0.66)	94	53.24 (0.07)	6.0	50.7	-0.7 (0.07)	7.38	92.87	6.07	6.0
Dorrigo 1	Woodland	73.8 (0.09)	95	53.83 (0.18)	5.7	51.8	-0.7 (0.17)	4.25	22.52	5.67	1.8
Dorrigo 2	Woodland	84.6 (0.30)	91	69.77 (0.24)	6.0	51.9	14.4 (0.23)	14.34	115.14	8.82	15.9
Dorrigo 3	Woodland	110.3 (0.07)	90	97.03 (0.33)	6.0	46.2	40.7 (0.29)	8.69	65.80	13.36	0.0

*Values in the parenthesis indicates standard error

5.3.2. DOC sorption to silt and clay particles of mineral soil

Adsorption isotherms for silt + clay of 12 soil samples under different land uses with DOC extracted from grass residue are illustrated in Fig. 5.1, 5.2 and 5.3. The amount of DOC released or retained was a linear function of the added DOC for all the soil samples. The coefficient of determination (r^2) of the linear regression between the initial DOC addition and the amount of total DOC released or retained ranged from 0.90 to 0.98. All regressions were significant at the $p < 0.01$ to $p < 0.001$ level.

The intercept *b* of the initial mass isotherm ranged from 5.8 to 14.2 g kg^{-1} (Table 5.2). The reactive soil pool (RSP) ranged from 12.6 to 64.00 g kg^{-1} of soil particles (Table 5.2). DOC_{np} concentrations, calculated from the regression when RE (or net sorption) = 0, ranged from 106.9-200.1 mg L^{-1} which was equivalent to 10.7-20 g C kg^{-1} of soil particles (Table 5.2). The partition coefficient *m* for DOC ranged from 0.54 to 0.84 (Table 5.2).

Desorption of DOC from whole soil ranged from 0.8 to 1.4 g C kg^{-1} soil. However, desorption from dispersed silt + clay was 5 to 11 times greater than that from whole soil, when solution with zero DOC concentration was added to soils.

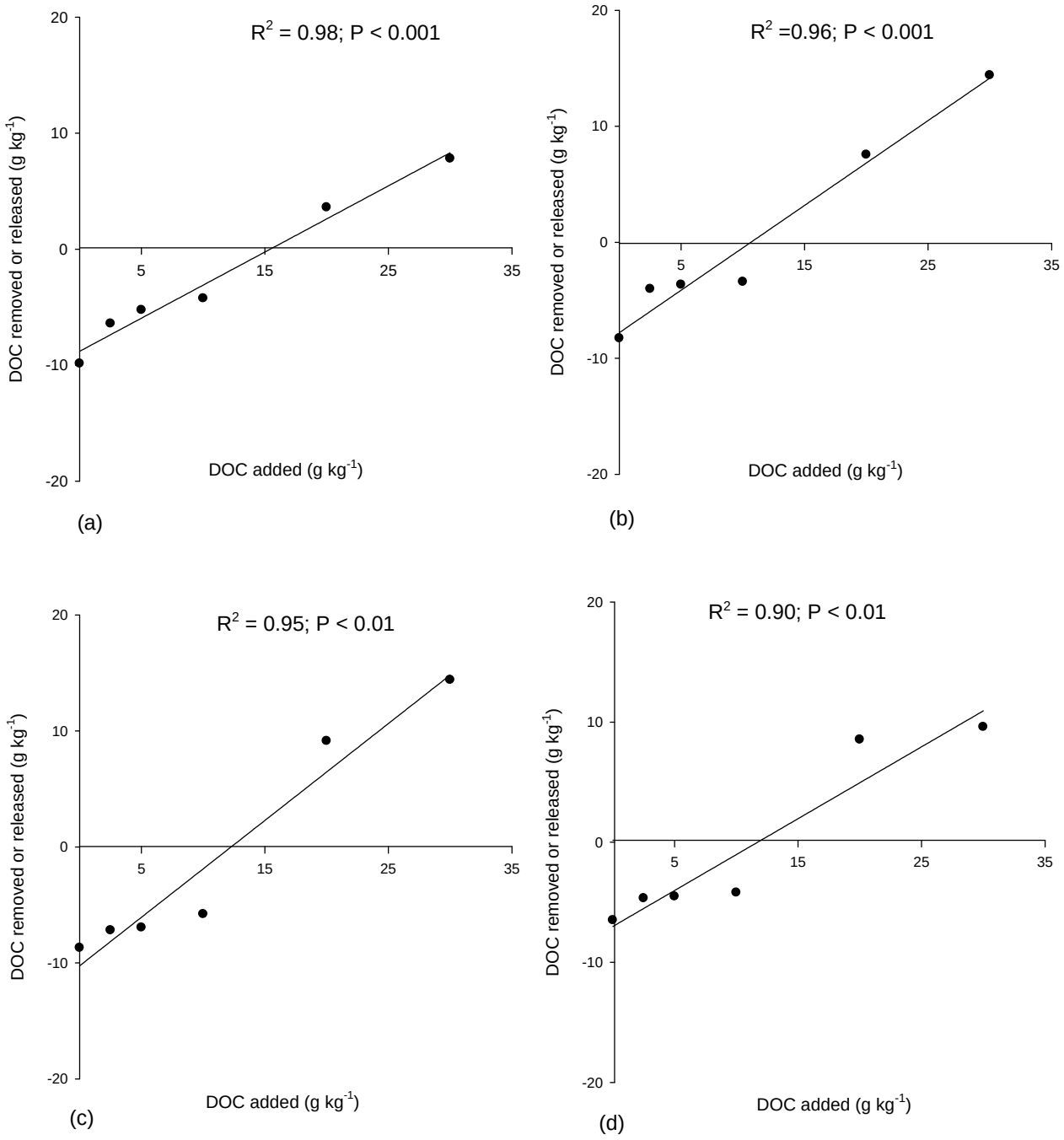

Fig. 5. 1. DOC sorption isotherm of pasture soils (a) North Dorrigo; (b) Dorrigo-1; (c) Dorrigo-2; (d) Dorrigo-3

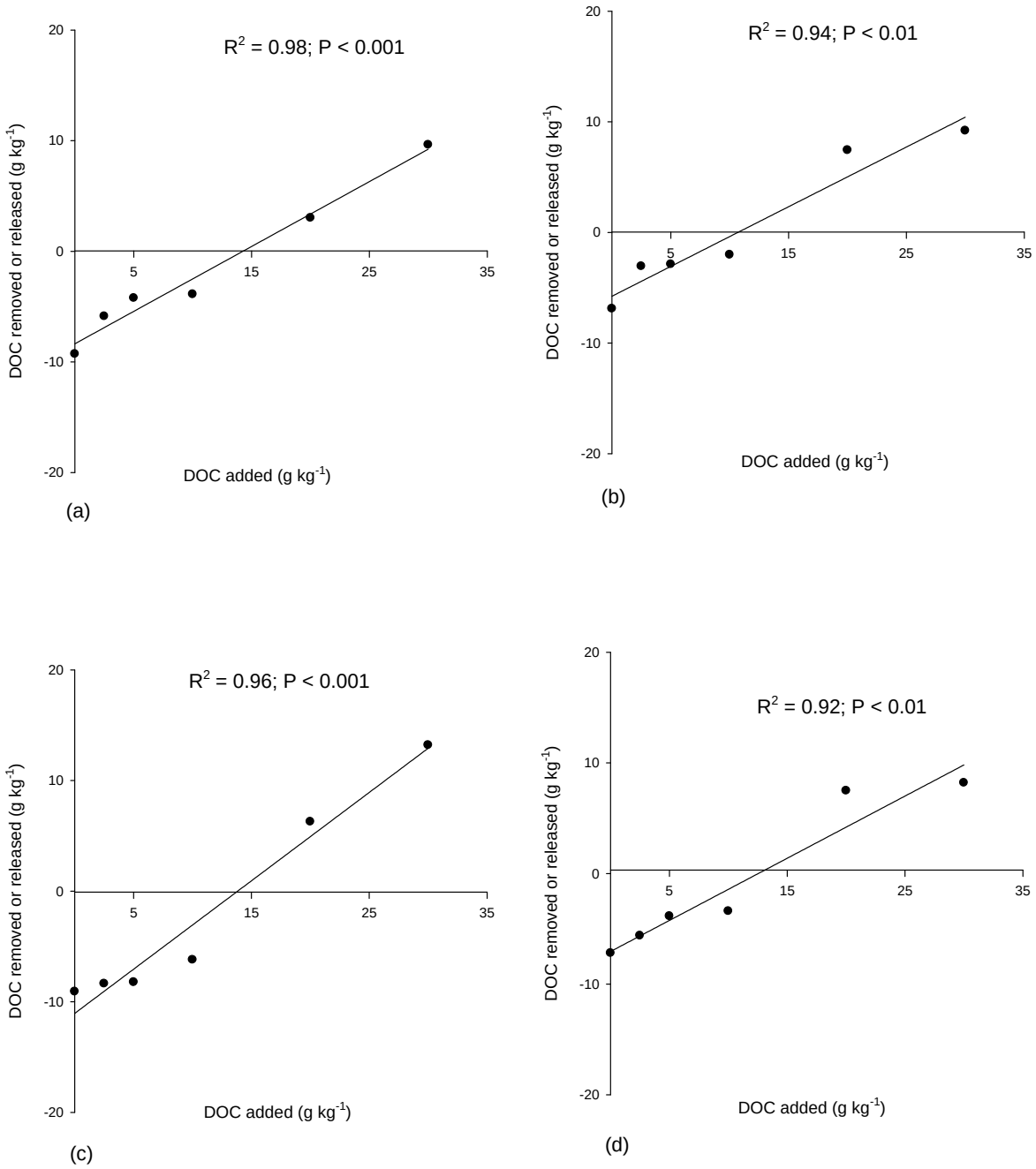

Fig. 5. 2. DOC sorption isotherm of cropping soils (a) North Dorrigo; (b) Dorrigo-1; (c) Dorrigo-2; (d) Dorrigo-3

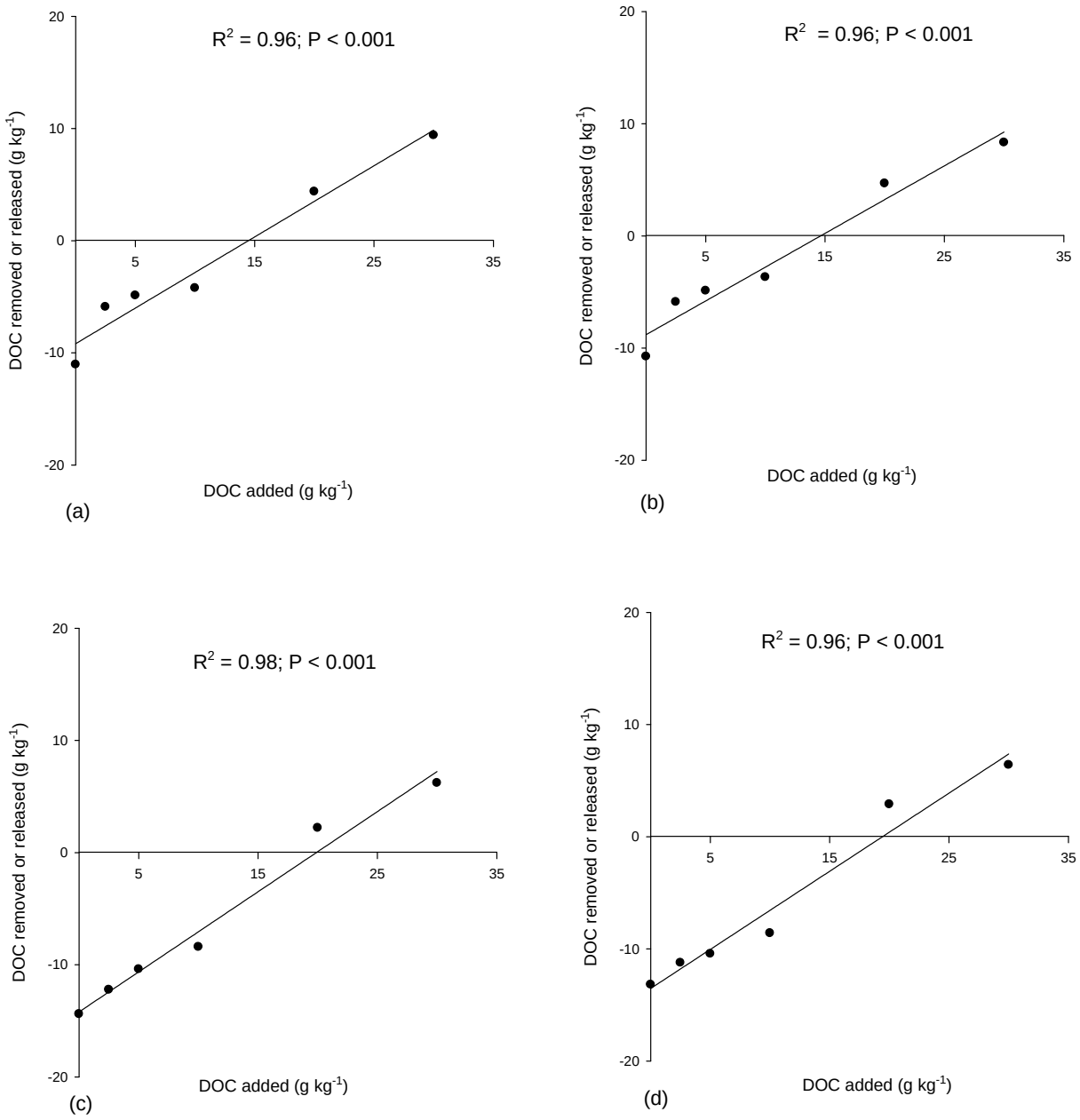

Fig. 5. 3. DOC sorption isotherm of woodland soils (a) North Dorrigo; (b) Dorrigo-1; (c) Dorrigo-2; (d) Dorrigo-3

Table 5. 2. Adsorption parameters from initial mass isotherms (IMI) using DOC solution of 0-300 mg L-1 for 12 silt and clay samples of soils under 3 different land uses

Site	Land use	m	-b ($g\ kg^{-1}$)	RSP ($g\ kg^{-1}$)	DOC_{np} ($g\ kg^{-1}$)
NorthDorrigo	Improved Pasture	0.57	8.81	20.71	15.4
Dorrigo 1	Improved Pasture	0.73	7.80	28.89	10.7
Dorrigo 2	Improved Pasture	0.84	10.24	64.00	12.2
Dorrigo 3	Improved Pasture	0.60	7.02	17.55	11.7
North Dorrigo	Cropping	0.59	8.40	20.49	14.3
Dorrigo 1	Cropping	0.54	5.80	12.56	10.8
Dorrigo 2	Cropping	0.80	11.05	55.25	13.8
Dorrigo 3	Cropping	0.56	7.06	16.05	12.6
North Dorrigo	Woodland	0.63	9.20	24.86	14.5
Dorrigo 1	Woodland	0.60	8.80	22.00	14.6
Dorrigo 2	Woodland	0.71	14.21	49.00	19.9
Dorrigo 3	Woodland	0.70	13.53	45.10	19.4

5.3.3. Relation of initial mass isotherm parameters with soil properties

The intercept of the initial mass isotherm *b* was positively correlated with initial C content of the silt + clay particles ($p < 0.01$) and negatively correlated with saturation deficit of soils ($p < 0.01$) (Fig. 5.4). The intercept was also positively correlated with oxalate-extractable Al_{ox} ($p < 0.01$) and Fe_{ox} ($p < 0.05$) (Fig. 5.5). Desorption of C from whole soil was also positively correlated with TOC content of the soils ($p < 0.001$) and negatively with C saturation deficit ($p < 0.001$) (Fig. 5.6). Desorption was also positively correlated with oxalate-extractable Al content of soils ($p < 0.01$) (Fig. 5.7).

Like intercept, DOC_{np} was positively correlated with C content of silt + clay particles ($p < 0.001$) and negatively with saturation deficit of the soils ($p < 0.001$) (Fig. 5.8).

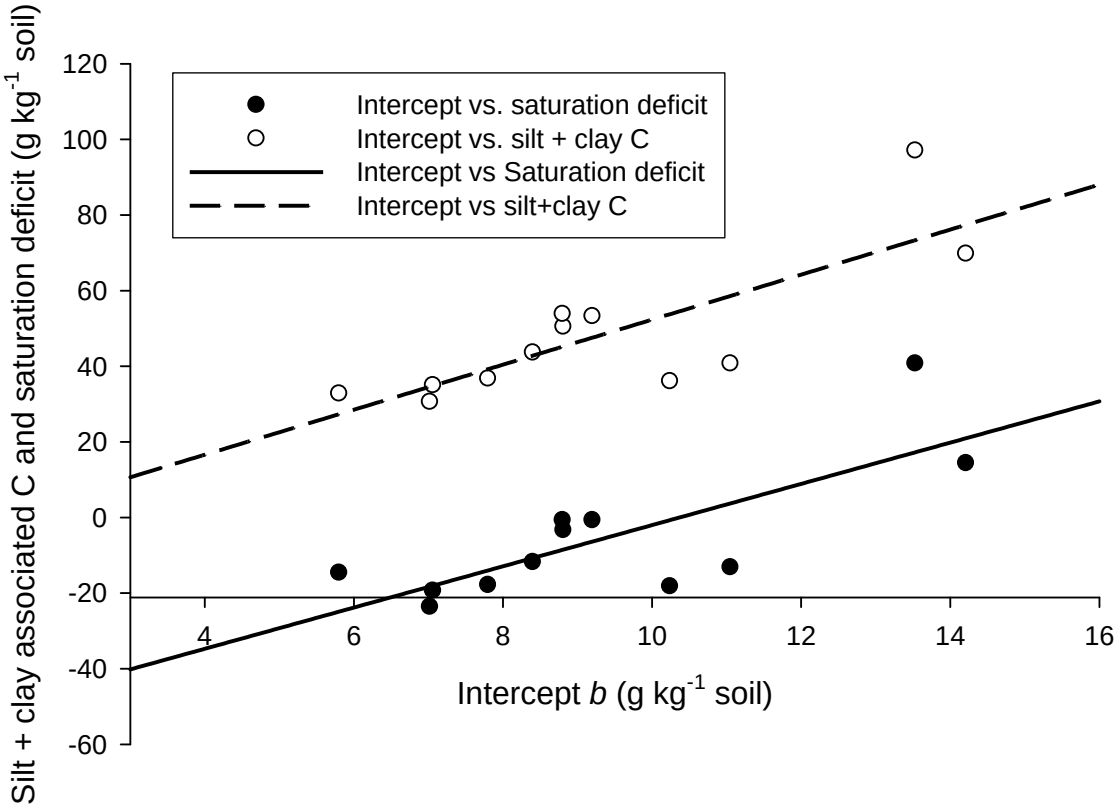

Fig. 5. 4. Relationship of intercept *b* of the initial mass isotherm, with C associated with silt + clay (y + 5.9546x – 7.2195) (R^2 = 0.639; P = <0.01), and C saturation deficit (y + 5.4524x – 56.533) (R^2 = 0.5944; P = < 0.01) of soils. Negative values on y axis imply C saturation deficit, and positive values imply oversaturation

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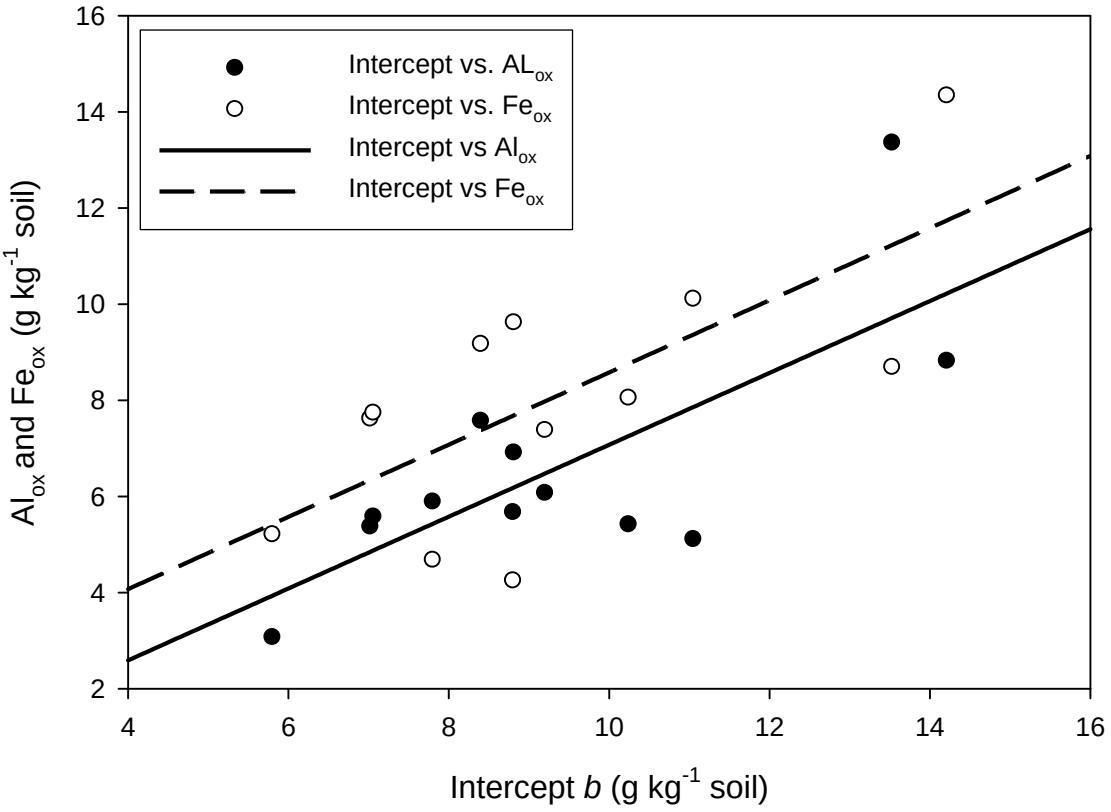

Fig. 5. 5. Relationship of intercept *b* of the initial mass isotherm, with oxalate extractable Al (y = 0.7475x – 0.4012) (R^2 = 0.558; P = < 0.01) and Fe (y = 0.7510x + 1.0669) (R^2 = 0.4918; P = < 0.05)

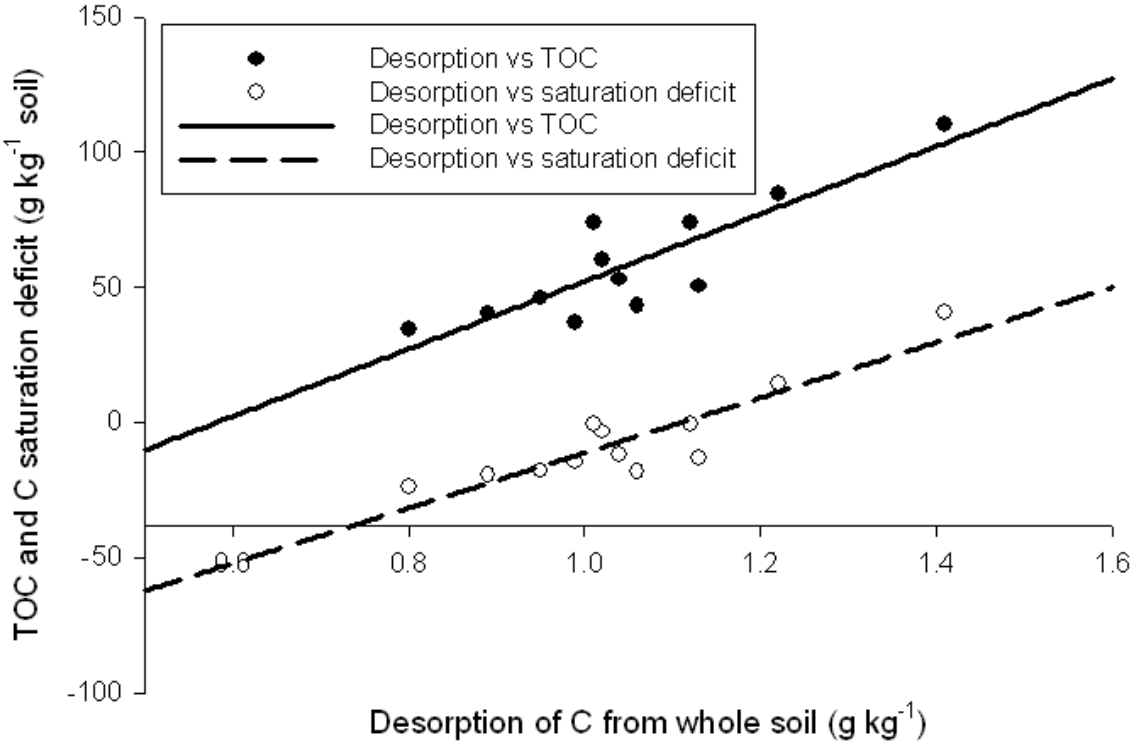

Fig. 5. 6. Relationship of desorption of C from whole soil with total organic carbon (y = 124.8415x – 72.5497) (R^2 = 0.7253; P = < 0.001) and C saturation deficit (y = 102.0502x – 113.1746) (R^2 = 0.7723; P = < 0.001) of soils. Negative values on y axis imply C saturation deficit and positive values imply oversaturation

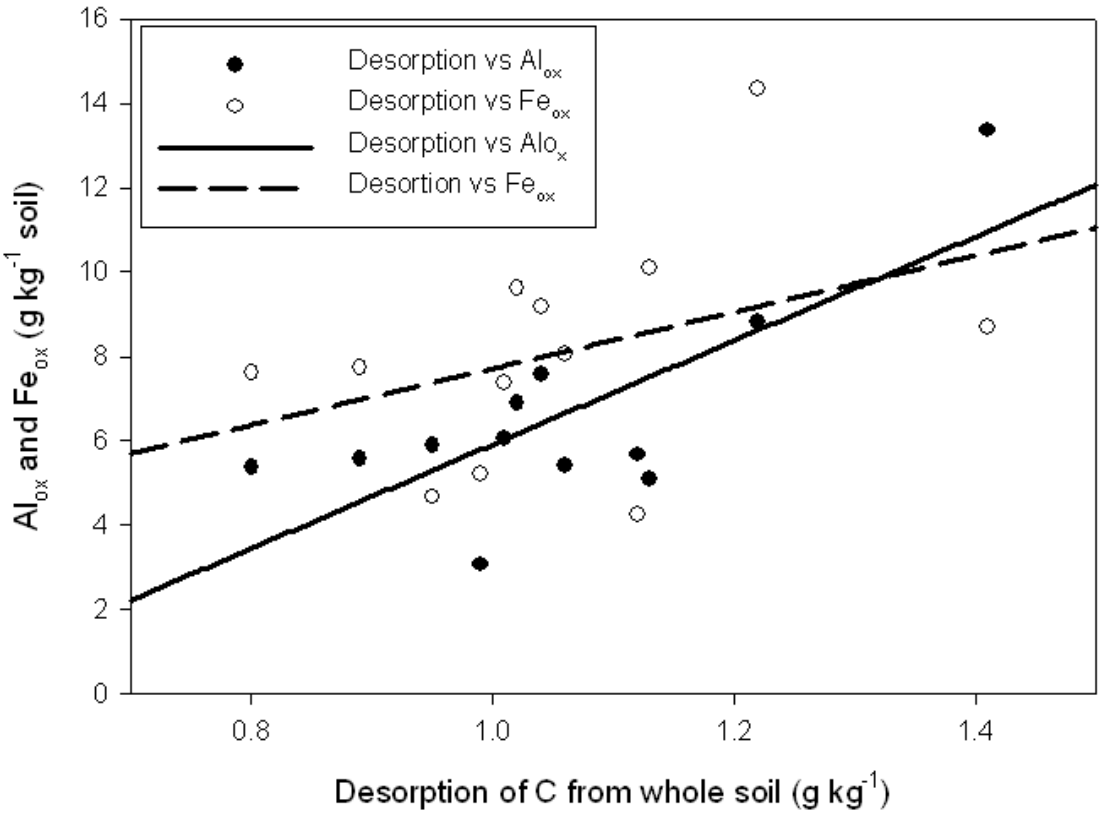

Fig. 5. 7. Relationship of desorption of C from whole soil with oxalate extractable Al (y = 12.3028x – 6.389) (R^2 = 0.5343; P = < 0.01) and Fe (y = 6.6795x + 1.0359) (R^2 = 0.0629; P = 0.21)

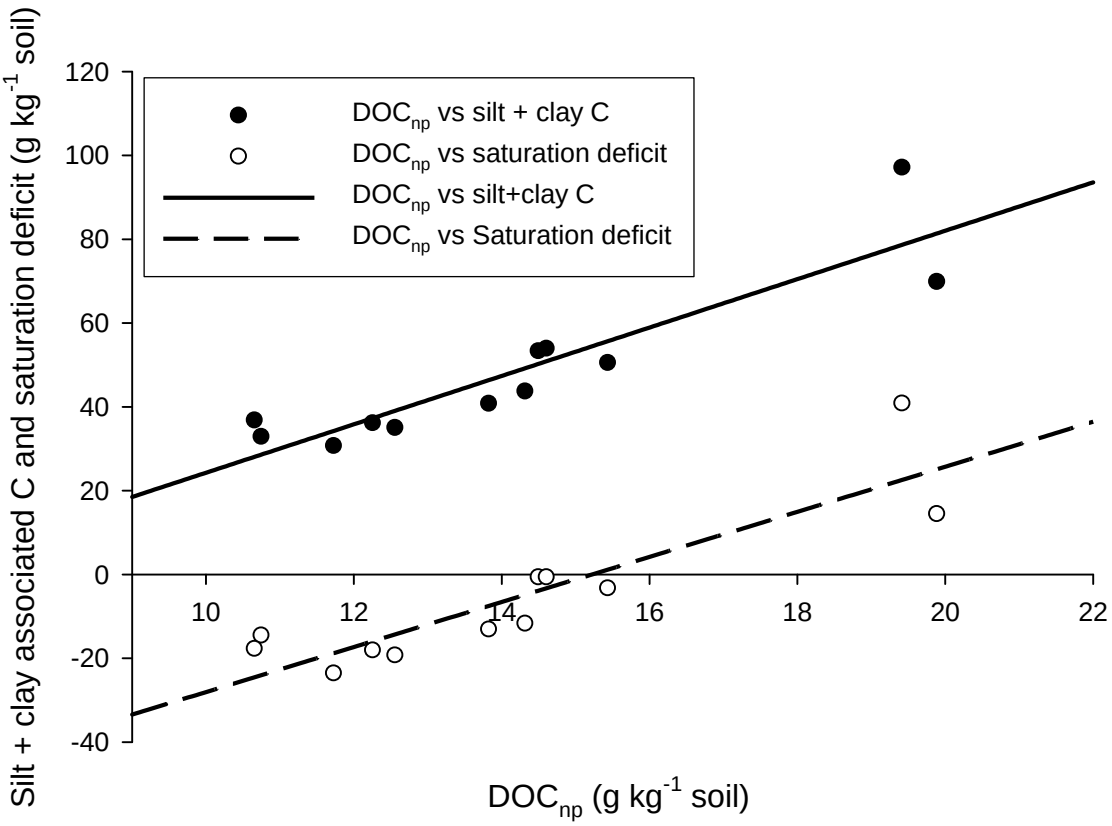

Fig. 5. 8. Relationship of null point concentration of DOC (DOC_{np}) with C associated with silt + clay (y = 5.7748x – 33.4784) (R^2 = 0.8059; P = < 0.001) and C saturation deficit (y = 5.3757x – 81.8243) (R^2 = 0.7703; P = < 0.001). Negative values on y axis imply C saturation deficit and positive values imply oversaturation

5.4. Discussion

5.4.1. DOC sorption to silt and clay particles of mineral soil

The study was conducted with 12 samples of Ferrosol collected from Dorrigo, NSW, under three different land uses (Table 2.1). The protective capacity of soils was calculated using equation: $y = 6.67e^{0.0216x}$ (r^2 = 0.61, p < 0.001) (Sparrow et al., 2006). Carbon saturation deficit was calculated from the difference between actual C content in silt + clay particles and the calculated protective capacity (Hassink, 1996). Carbon

saturation deficit was observed in all the pasture (-3.4—23.6 g C kg-1 soil) and cropping soils (-11.8—19.4 g C kg-1 soil) (Table 5.1). Among the four woodland soils two soils (North Dorrigo, Dorrigo 1) had C content close to their saturation level, and two soils (Dorrigo 2 and Dorrigo 3) stored 28% and 88% more C than their theoretical saturation level. Thus different degree of C saturation was observed in the studied soils depending on their land uses. Since the first objective of the research was to describe the sorption of DOC to silt and clay particles of soils with different degree of C saturation, an adsorption experiment was conducted in laboratory at 4°C using DOC of 6 initial concentrations (from 0-300 mg L^{-1}). Adsorption isotherms for silt + clay of 12 soil samples under different land uses with DOC extracted from grass residue were illustrated in Fig. 5.1, 5.2 and 5.3. The significant linear relationship between DOC sorption and initial DOC concentration in the added solution supported the use of initial mass approach (Nodvin et al., 1986) to describe the relationship.

The intercept *b* of the initial mass isotherm, in the present study ranged from 5.8 to 14.21 g kg^{-1} soil (Table 5.2). Lower intercept values (0.03-0.52 g kg^{-1}soil) were observed by Moore et al. (1992) from sorption experiment of < 2000 µm fraction. Since < 53 µm particles was used in the present study to observe desorption of C, an additional test was also conducted with <2000 µm soil particles, to compare desorption from dispersed soil particles with their aggregated form (< 2000 µm). However, only solution with zero DOC concentration was added to < 2000 µm soil fractions to observed desorption, instead of using 6 initial conc. of DOC that was added to silt + clay particles. Desorption of DOC from dispersed silt + clay particle was observed to be 5 to 11 times greater than that from < 2000 µm fractions (0.8-1.4 g kg^{-1} soil). Though desorption of C from < 2000 µm fractions was estimated by adding zero conc. of DOC solution instead of making adsorption isotherm, this desorption values will give an overall idea of lower

desorption from larger soil fractions compared to dispersed silt + clay fractions. Moreover, desorption from < 2000 µm fractions (0.8-1.4 g kg^{-1} soil) in the study were very close to that (0.03-0.52 g kg^{-1} soil) observed by Moore et al. (1992). In the present study, higher desorption of C from < 2000 µm soil samples compared to that of Moore et al. (1992) might be due to higher initial C content in soils (34.3-110.3 g C kg^{-1} soil) compared to soils (1-43 g C kg^{-1} soil) that were studied by Moore et al. (1992). However, the higher desorption of C from silt + clay particles (< 53 µm) in the present study might be the result of breakdown of aggregates during dispersion of < 2000 µm fractions (Section 5.2.3), which released silt-sized particulate organic carbon (POC) into silt + clay mixture. Significantly higher ($p < 0.01$) microbial mineralization of C from dispersed silt + clay particles (< 53 µm) compared to < 2000 µm fractions was observed in the same soils (Section 3.4.2). Both higher microbial mineralization and chemical dissolution (at 4^oC to inhibit microbial influence) of C from dispersed silt + clay fractions (< 53 µm) compared to < 2000 µm fractions indicated the higher protection of C in aggregated soils. In spite of this, the present experiment was conducted with dispersed silt + clay particles, to overcome the influence of desorption from larger POC present in < 2000 µm soil fractions that were not associated with silt + clay particles (as C saturation deficit was calculated based on silt + clay associated C).

The intercept (*b*) and the slope (*m*) of the linear relationship were used to calculate the reactive soil pool (RSP) (Nodvin et al., 1986). The reactive soil pool (RSP) ranged from 12.6 to 64.00 g kg^{-1} of silt + clay particles (Table 5.2). The RSP value for DOC calculated from the adsorption experiments suggested that 38.32 to 78.68% of the native organic C of the silt + clay particles of soils was reactive as DOC. However, two soils (Pasture and Cropping in Dorrigo 2) had RSP values of 64 and 55.25 g kg^{-1} which represented 178 and 136% of silt + clay associated C reactive as DOC (Table 5.2). The

reason for overestimation was not identified but this might be due not to better application of this IM approach to these two soils.Vandenbruwane et al. (2007) observed negative RSP values for deeper unsaturated soils for a wide DOC concentration range. Moreover study on C fractions (hydrophilic and hydrophobic fractions) in both soil particles (silt + clay) and added DOC might give some explanations. Kaiser et al. (1996) observed 61 to 100% release of hydrophilic DOC, of the total DOC released from soils after addition of DOC free solution. In the present study, as DOC was extracted by using deionised water, there was less possibility of having hydrophobic C fractions in DOC solution. Soil samples were collected from three different land uses (pasture, cropping and woodland). So there might have possibility of difference in C fractions in studied soils depending on land uses. Though C fractions (hydrophobic or hydrophilic) was not analysed in this study, future research should be directed on it to get more explanation.

Null point DOC concentration (DOC_{np}), calculated from the regression when RE (or net sorption) = 0, ranged from 106.85-200.14 mg L^{-1} which was equivalent to 10.7-20 g C kg^{-1} of soil particles (Table 5.2). Moore et al. (1992) observed DOC_{np} concentrations of 6.7 to 85.4 mg DOC L^{-1} which was equivalent to 0.07 to 0.85 g DOC kg^{-1} soil, for < 2000 µm soil fractions. In the present study higher DOC_{np} was observed, since addition of zero concentration of DOC caused higher desorption (5.8 to 14.21 g C kg^{-1} soil) of initial soil organic C. Thus there should be an adequate concentration of C in solution so that desorption will be minimum or zero to show the DOC concentration when net sorption will be zero.

The partition coefficient *m* for DOC ranged from 0.54 to 0.84. The slope of the initial mass isotherm, *m* or the partition coefficient represents the fraction of the total reactive substance present in the soil-water system that is retained by the soil (Nodvin et al., 1986). Moore et al. (1992) reported *m* values between 0.15 and 0.78. The *m* values for

total DOC was between 0.01 and 0.86, in which lower values were observed in topsoils, and higher values were observed in subsoils (Kaiser et al., 1996). The *m* values (0.54-0.84) in the present study represented average higher retention of DOC on overall all soils.

5.4.2. Relation of initial mass isotherm parameters with soil properties

The second objective of the research was to develop a general description of the relationships between soil properties and DOC sorption, to test the hypothesis that desorption of indigenous soil C will be lower from soils having higher saturation deficit, and adsorption of added DOC will be higher in soils having higher saturation deficit.

The intercept, *b*, of the initial mass isotherm was a measure of desorption, which indicated the amount of substance released from the soil when a solution with zero sorbet concentration was added. In this study, lower desorption of C was observed from soils having lower initial C content ($p < 0.01$), and higher C saturation deficit ($p < 0.01$) (Fig. 5.4). Significant positive relationship ($p < 0.001$) was also observed between TOC and desorption of C from < 2000 µm soil samples, when solution of zero DOC concentration was added (Fig. 5.6). Desorption of C from < 2000 µm soil samples was also negatively correlated ($p < 0.001$) with C saturation deficit (Fig. 5.6). Moore et al. (1992) and Kaiser et al. (1996) also observed positive relationship between organic C content and intercept of the linear curve. However, in the present study significant negative relationship between intercept and saturation deficit indicated that degree of saturation of the silt + clay protective capacity was important factor for protection of C from chemical dissolution. In soil where silt + clay particles were not saturated with C, the existing C would be more strongly adsorbed on soil particles compared to soils where protective capacity was already saturated with C. Thus, significantly higher desorption of C from

soil particles (silt + clay and whole soil) having lower C saturation deficit proved the first hypothesis that, desorption of indigenous soil C will be lower from soils having higher C saturation deficit.

The positive relationship of intercept *b*, with oxalate extractable Fe ($p < 0.05$) and Al ($p < 0.01$) was observed in this study (Fig. 5.5). Significant positive relation ($p < 0.01$) was also observed between oxalate-extractable Al and desorption of C from < 2000 µm soil sample, when solution of zero DOC concentration was added (Fig. 5.7). However, in this study higher initial organic C content in soils having higher concentration of oxalate-extractable Al (Section 5.3.1)) might be one reason for higher desorption of C from these soils. Since initial C content of the soils was positively correlated with oxalate extractable Al (Section 5.3.1), more C was stored in soils having higher content of these minerals and caused higher desorption. The influence of oxalate-extractable Al which was the poorly crystalline Al, in storing C was observed in other studies (Powers and Schlesinger, 2002; Kleber et al., 2005; Wiseman and Puttmann, 2005; Mikutta et al., 2006) for their large surface area compared with crystalline minerals. However, the stability of C (from chemical dissolution) that was stored in soils through adsorption on these minerals was not tested so far, especially where the minerals had different degree of C saturation. Carbon saturation deficit in silt + clay was estimated in this study using equation: $y = 6.67e^{0.0216x}$ ($r^2 = 0.61$, $p < 0.001$) (Sparrow et al., 2006). Saturation deficit in these poorly crystalline minerals was not estimated, as there was no proposed model for calculation of C saturation deficit. Since higher desorption of C was observed from soils that had lower saturation deficit (based on silt + clay saturation deficit), it could be predicted that higher level of C saturation of poorly crystalline Al caused higher desorption, because of less protection of C compared to that where the minerals were less saturated. Since the amount of SOC protected by silt + clay or poorly crystalline Al was not quantified

separately, and adsorption was conducted without separating these poorly crystalline minerals, it could not be detected the actual site of desorbed C. For clear explanation, future experiments could be conducted by removing SOC (using H_2O_2), both crystalline and non-crystalline Fe and Al content (using Na-dithionite and oxalate) from soils.

In this study, positive relationship of DOC_{np} was observed with organic C content ($p < 0.001$) and negative relationship was observed with C saturation deficit of silt + clay particles ($p < 0.001$) (Fig. 5.8). Significant positive relation of DOC_{np} with SOC content in soils was also observed in other studies (Dalva and Moore, 1991; McDowell and Wood, 1984). Null point DOC concentration (DOC_{np}) is the concentration of initial solution at which the net sorption on soil particle will be zero. Since addition of zero concentration of DOC caused desorption of initial soil organic C, there should be an adequate concentration of C in solution so that desorption will be minimum or zero. As higher organic C content in soil caused higher desorption, more C should be present in initial solution to achieve an equilibrium with the soil C at which no desorption will occur. Thus DOC_{np} will be higher for soil with higher initial C content. In this study DOC_{np} was negatively correlated with C saturation deficit of the soils. Since significantly higher desorption of C was observed from soil particles having higher C saturation deficit ($p < 0.01$), less C would be required in initial solution to achieve an equilibrium with initial soil C, so that the net sorption would be zero. These findings were also an indication of importance of initial C content and C saturation deficit on sorption of DOC to soils, as sorption started just after increasing the C concentration in initial solution from DOC_{np} concentration.

In the present study, the partition coefficient *m* had no relation with soil properties. This result contrasted with Kaiser et al. (1996) who observed negative relation

of *m* with organic C content and positive relation with oxalate-extractable Al and Fe content of the soils. The slope of the initial mass isotherm, *m* represents the fraction of total reactive substance in a soil/water system that is retained by the soil (Nodvin et al., 1986). The result of this study indicated that soil properties had no influence on sorption or binding affinity of DOC, though sorption occurred at higher concentration of DOC in all soils. The regression curve between DOC sorbed (retained or released) and added DOC showed that at up to 100 mg L^{-1} (10 g kg^{-1}) of initial DOC concentration there was no sorption (Fig. 5.1, 5.2 and 5.3). This was consistent with the higher RSP value of most soils. The addition of higher concentration of DOC caused sorption of C and followed linear relationship (Fig. 5.1, 5.2 and 5.3). The sorption of DOC at higher concentration might not be influenced by soil properties but on the properties and composition of C initially adsorbed on soil particles (Chiou et al., 1983; Garbarini et al., 1986; Ainsworth et al., 1989). The importance of organic coatings on mineral surface in adsorbing organic compounds was also observed by other authors (Kummert et al., 1980; Morse, 1986; Murphy et al., 1990). The influence of organic matter on sorption of DOC depends on the origin (Carter et al., 1982), molecular weight (Chiou et al., 1986; Hassett and Anderson., 1979), polarity and molecular configuration (Chiou et al., 1986; Gauthier et al., 1987). Higher molecular weight hydrophobic substances (Donald et al., 1993) showed preferential adsorption on soil surface compared to hydrophilic substances (Kaiser et al., 1996; Guggenberger and Kaiser 2003). Because of the complexity of factors, the partition coefficient *m* of the sorption experiment had showed no relationship with soil properties which rejected the second hypothesis that sorption of added DOC will be higher in soils having higher C saturation deficit. Since the stability of adsorbed DOC was not tested in this study, it could not be assumed the relative protection of adsorbed C against microbial decomposition or chemical dissolution. Moreover the adsorption of OC at higher C input

might be a reason for oversaturation of capacity of silt + clay (Dorrigo 2 and Dorrigo 3). Higher adsorption of DOC beyond the capacity of soil minerals contradicts the so called monolayer-equivalent C loading of the particles (Mayer, 1994; Hedges and Oades, 1997). In the monolayer theory of SOC coverage on minerals, organic C should be stored in a single layer and the concentration and stability of C should be influenced by soil properties. (Specific surface area). In contrast to this theory several authors (Ransom et al., 1997; Salmon et al., 2000) proposed that only a fraction of the mineral surface was covered with organic matter, which occurred as patches and formed microaggregates with clay-sized particles. However, in the present study, the chemical nature of SOC might be responsible for adsorption of added DOC that was no more associated with soil particles (silt + clay) and poorly crystalline minerals. Analysis of chemical composition of SOC and DOC by solid and liquid state NMR, visual observation of C both before and after adsorption would give more clear explanation in future study.

5.5. Conclusion

Organic C storage in soils is influenced by content of fine soil particles (silt + clay) and poorly crystalline minerals, specifically poorly crystalline Al. Stability of stored C will be higher in soils where the protective capacity of soils is not saturated, since organic C is strongly adsorbed on binding sites of the mineral surface. In soils where protective capacity is saturated or close to saturation, organic C molecules are susceptible to be lost from soil system. For this reason higher desorption of organic C had been observed in soils having lower saturation deficit. Similar to this mechanism, carbon will even be lost from soil containing higher amount of poorly crystalline Al, when binding capacity of these minerals will be saturated with C. Finally, carbon will be stored in soil not only depending on the surface area or binding capacity of soil particles or minerals,

but on the properties and composition of the initial C content of the minerals and added C molecules. Hydrophobic organic molecule will be preferentially adsorbed on soil particles compared to hydrophilic molecule.

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Chapter 6
General Discussion

6.1. Overview

In this PhD thesis the protective capacity of Australian Ferrosol and Dermosol has been calculated using a model ($(y = 6.67e^{0.0216x}$ ($r^2 = 0.61$, $p < 0.001$)) proposed by Sparrow et al. (2006). The influence of land use and soil properties (texture and mineralogy) on C saturation level was determined by calculating the saturation deficit of two different soils (Ferrosol and Dermosol) under three different land uses (pasture, cropping and woodland). Land use significantly influenced C saturation level in Ferrosol ($p < 0.01$) and Dermosol ($p < 0.05$) where woodland soils had higher C saturation compared to pasture and cropping. Two of the woodland Ferrosol (Dorrigo 2 and Dorrigo 3) and one Dermosol (Kirby) were oversaturated with C that violated silt + clay protective capacity model. Since the oversaturation was 20 and 88% higher in Ferrosol compared to only 7% higher in Dermosol, subsequent experiments were conducted on Ferrosol to observe the C saturation behaviour on overall C dynamics in soils. A five months incubation experiment was conducted to determine the influence of silt + clay content and C saturation deficit on cumulative carbon mineralization (C_{min}) and percent of SOC mineralized (SOC_{min}) from whole soil (< 2000 µm). Soil organic carbon (SOC) mineralization from different size fractions, as silt + clay (< 53 µm) and clay (< 2 µm) were also determined to observe the relative influence of aggregated soil (< 2000 µm) compared to dispersed soil particles on microbial decomposition of SOC. Using the constrained two pool SOC model, the mean residence time (MRT) of active and slow SOC pool was calculated and influence of C saturation deficit on MRT of SOC pool was determined. Since higher SOC mineralization and lower MRT of SOC pool was observed

in soils that were close to C saturation or oversaturated with C, subsequent experiment was conducted to observe the influence of C saturation on the stabilization of added residue C. The influence of C saturation deficit on the stabilization of added residue C was determined by conducting an eight months incubation experiment and addition of grass residue with and without nutrients to enhance the decomposition of residue. Residue addition increased C mineralization compared to soils where no residue was added. However, more C was stabilized in silt + clay fractions of soils where protective capacity was less saturated with C. Loss of C from silt + clay particles due to addition of residue was observed that was oversaturated with C. Higher loss of C from oversaturated soils indicated the importance of silt + clay protective capacity model for protection of C. Since decomposition of residue is a slow process time is required to get more clear response of SOC in soils having different C saturation level, upon addition of residue. An adsorption experiment was conducted to observe quick response of SOC upon addition of solutions containing DOC of different concentrations. Carbon saturation level of soils influenced the chemical dissolution of SOC. Higher desorption of SOC was observed from soils that was oversaturated with C when solution with zero DOC concentration was added. Addition of higher concentration of DOC increased the adsorption of C but the adsorption was not correlated with any of the soil properties. The pathways and findings of the current research are presented in Fig. 6.1.

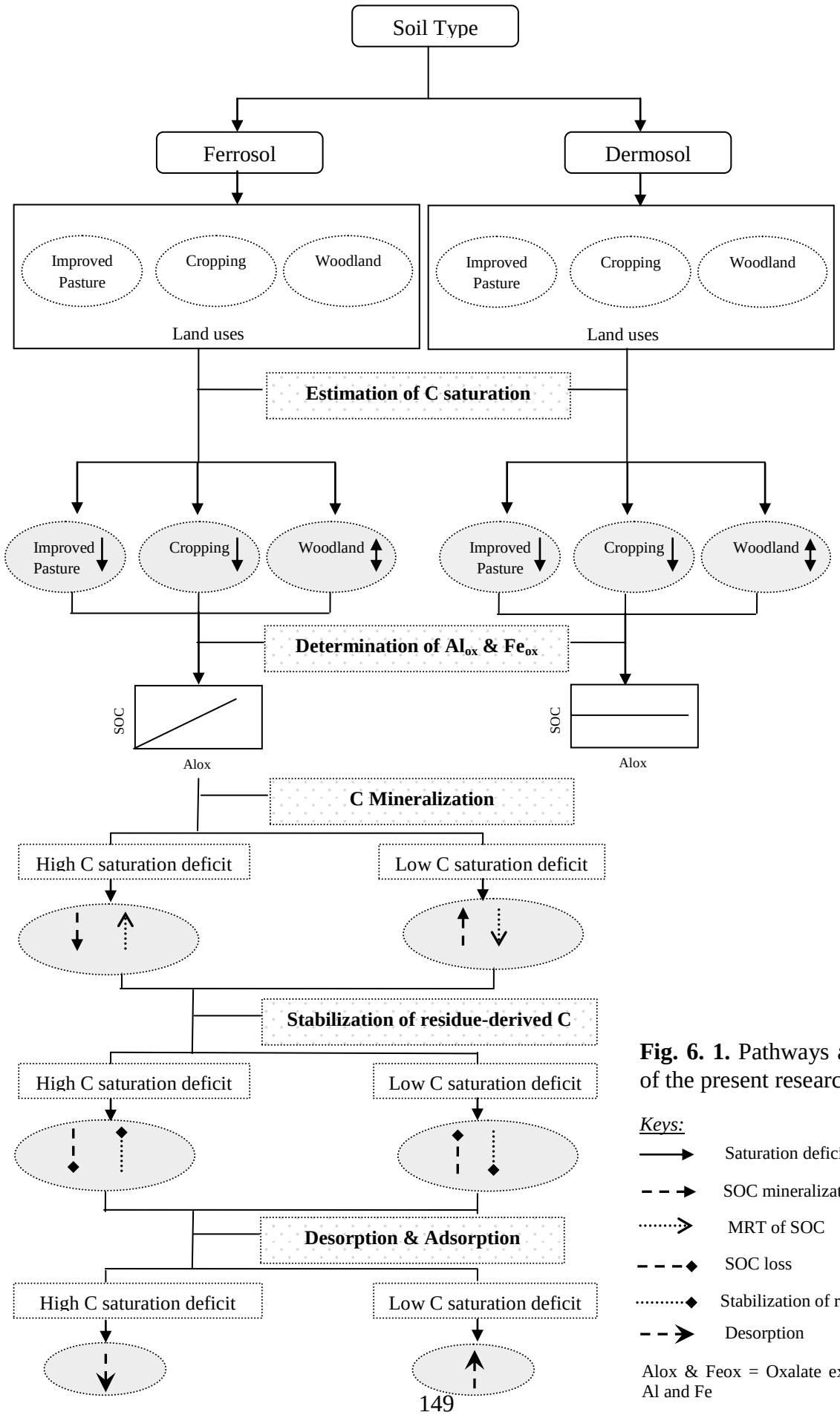

Fig. 6. 1. Pathways and findings of the present research

6.2. Key findings

6.2.1. Both land use and soil properties influence C saturation level in soils

Land use influenced C saturation level in both Ferrosol ($p < 0.01$) and Dermosol ($p < 0.05$). In both soils woodland stored significantly higher C compared to pasture and cropping. Carbon saturation deficit was observed in all the pasture and cropping soils in Ferrosol and Dermosol. Woodland soils at North Dorrigo and Dorrigo 1 sites on Ferrosol had C content close to their saturation level, while soils at Dorrigo 2 and Dorrigo 3 sites had stored 28% and 88% more C than the theoretical protective capacity. In Dermosol, woodland soil at Clarkes, Powalgarh and Black Mountain sites had C content close to their saturation level, whereas woodland soil at Kirby site had 7% more C than theoretical saturation level. Higher C input and lower disturbance in woodland soils might be a reason for significantly higher C content in both Ferrosol and Dermosol. In Ferrosol TOC was positively correlated with oxalate-extractable Al (poorly crystalline Al). However, the oversaturation in Ferrosol beyond the silt + clay protective capacity might be the result of higher content of poorly crystalline Al that has higher specific surface area to adsorb C. Influence of poorly crystalline Al in C storage was not clear in Dermosol, because of higher C/Al ratio compared to that in Ferrosol. In both Ferrosol and Dermosol, TOC was positively correlated ($p < 0.01$) with CEC. Positive relation ($p < 0.01$) of CEC with clay content in Dermosol indicated the influence of clay mineral (dominated by smectite minerals) on CEC that has influence on C storage in soil.

6.2.2. Mineralization and MRT of SOC are influenced by C saturation level of soils

After five months of incubation, the cumulative mineralization of carbon C_{min}) from whole soil (< 2000 µm) was observed to be negatively correlated with silt + clay content ($p < 0.001$) and C saturation deficit ($p < 0.001$) of soils. Percent SOC

mineralization (SOC_{min}) of the whole soil of Ferrosol had negative relation with silt + clay content ($p < 0.001$) and C saturation deficit ($p < 0.01$). Using the constrained two pool SOC model, it was observed that MRT of slow pool of whole soils was positively correlated with silt + clay content ($p < 0.05$) and saturation deficit ($p < 0.05$) of soils. Significantly lower SOC mineralization from soils with higher silt + clay indicated the protection of C by association with silt + clay particles. Because of this protection MRT of slow SOC pool was higher in soils having higher content of silt + clay. Protection of SOC was also higher where protective capacity (based on silt + clay and associated C) was less saturated with C. Thus significantly higher SOC mineralization and shorter MRT of SOC pool was observed in soils where protective capacity was saturated or oversaturated with C. All the findings supported the importance of silt + clay particles in protecting SOC and the use of silt + clay protective capacity model to estimate the C saturation level in soils. Higher protection of SOC was also observed when soil particles were aggregated (< 2000 µm) compared to dispersed silt + clay (< 53 µm). Thus significantly higher SOC mineralization was observed from dispersed silt + clay particles compared to whole soil ($p < 0.01$) and clay particles ($p < 0.05$). This finding indicated that silt + clay particles protect C not only by surface adsorption but through formation of aggregates.

6.2.3. Carbon saturation deficit determines the stabilization of residue derived C to soils

After eight months of incubation, decrease in TOC (~2-19 g C kg^{-1} soil) in all soils and silt + clay associated C (~0.4-10 g kg^{-1} soil) in 9 soils out of 12 soils, was observed, when no residue was added. This lower decrease in silt + clay associated C compared to TOC indicated the higher loss of C from silt + clay non-associated fractions. Residue addition increased both TOC and silt + clay associated C in most soils compared

to that when no residue was added but this did not compensate for the SOC loss from their initial content. Stabilization of residue derived C was higher in soils that were less saturated with C. Higher mineralization was observed from all soils when residue was added with available nutrients. Surprisingly, TOC and silt + clay associated C decreased in some soils after addition of residue (both with and without nutrient element). Decrease in SOC due to addition of residue might be the result of positive priming effect, which is the acceleration of decomposition of SOC due to supply of available energy source for microorganisms. In this study both grass residue and added nutrients increased microbial activities that accelerated the mineralization of both residue C and SOC. Loss of SOC due to priming effect was mainly observed in soils that were oversaturated with C. This finding also supported the importance of silt + clay protective capacity model, since excess C will be remained in the biologically available form.

6.2.4. Desorption of indigenous soil C and adsorption of DOC are influenced by saturation level of soils

After conducting an adsorption experiment it was observed that the amount of DOC released or retained was a linear function of the added DOC for all the soil samples (Fig. 5.1, 5.2 and 5.3). The coefficient of determination (r^2) of the linear regression between the initial DOC addition and the amount of total DOC released or retained ranged from 0.90 to 0.98. All regressions were significant at the $p < 0.01$ to $p < 0.001$ level.

The intercept *b* of the initial mass isotherm, which indicated the amount of substance released from the soil when a solution with zero sorbet concentration was added, was negatively correlated ($p < 0.01$) with C saturation deficit of soils. Lower desorption of C from soils that were less saturated with C indicated the higher protection

of SOC in these soils. Intercept *b*, was also positively correlated with oxalate-extractable Al_{ox} ($p < 0.01$) and Fe_{ox} ($p < 0.05$) content of soils. Though initial C content of soils were positively correlated with oxalate-extractable Al content of soils and indicated the importance of these poorly crystalline minerals to store C, the higher desorption of C from soils with higher content of these mineral might be the result of oversaturation of these minerals. Partition coefficient *m* (slope of the initial mass isotherm), was not influenced by any of the soil properties, because of multiple factors responsible for adsorption of DOC to soils.

6.3. Synthesis and overall discussion

Present study showed that land use had significant effects on C content in overall all soils which influenced to reach to saturation of protective capacity. Since protective capacity was calculated depending on silt + clay and associated C content, it was not unusual to contain more C than the theoretical capacity, since other soil factors (poorly crystalline minerals, multivalent cations) also influenced on SOC storage. Carbon saturation level of the protective capacity had significant implications on other mechanisms (microbial decomposition, chemical dissolution and stabilization of added C) in soils that might have ultimate effects on global C cycle. Higher loss of C either through microbial decomposition or chemical dissolution was observed from soils where protective capacity was saturated. Stabilization of added residue derived C was higher in soils having higher C saturation deficit. Since silt + clay particles protect C not only by adsorption on surface but formation of aggregates, higher loss of C was observed when soil samples were dispersed. These findings have been discussed in the following sections.

6.3.1. Both land use and soil properties influence carbon saturation level in soils

The study was conducted to evaluate C saturation level of protective capacity under different land uses. Carbon saturation deficit was observed in all the pasture and cropping soils of both Ferrosol and Dermosol. Lower C input and higher disturbance might be a reason for not reaching the soils to their saturation level. On the other hand, higher input and lower disturbance might be responsible for higher C content and reaching close to saturation level of two woodland soils of Ferrosol (North Dorrigo, Dorrigo 1) and three Dermosol (Clarkes, Powalgarh and Black Mountain). Carbon content within the saturation level clearly supports the silt + clay protective capacity model. However, oversaturation of two woodland soils in Ferrosol (Dorrigo 2 and Dorrigo 3) and one Dermosol (Kirby) violated silt + clay protective capacity model. The reason for this violation was explained by analysing other soil properties. In Ferrosol, significant positive relationship ($p < 0.01$) between TOC and poorly-crystalline Al content might be a reason for violation of the protective capacity model. Because of higher specific surface area, these poorly crystalline Al could store C in soil beyond the capacity of silt + clay particles. Since Ferrosol contained higher poorly crystalline Al, the influence on SOC storage was not unusual. The influence of poorly-crystalline Al in SOC storage was not clear in Dermosol, because of higher TOC/Al ratio. Compared to Ferrosol, poorly-crystalline Al content was lower in Dermosol. X-ray diffraction analysis showed that Dermosol was mainly dominated by smectite minerals that have higher specific surface area. Organic C might be stored in such soils either by direct surface adsorption or through polyvalent cation bridge. Significant positive relation of cation exchange capacity (CEC) with TOC in Dermosol was an indication of influence of these smectitic minerals to store SOC that dimmed the influence of poorly crystalline Al on C storage. Finally this could be stated that land use significantly influenced C saturation

level in soils, since woodland soils had higher C saturation level compared to pasture and cropping in both Ferrosol and Dermosol. However, soils properties other than silt + clay particles might have influence on C saturation level, and sometimes violated silt + clay protective capacity model depending on their relative content in soils.

6.3.2. Carbon saturation deficit determines the loss of SOC

In the present study, significant influence of C saturation level depending on silt + clay protective capacity was observed on loss of SOC. After five months of incubation it was observed that the cumulative mineralization (C_{min}) and percent of SOC mineralization (SOC_{min}) was lower in soils having higher silt + clay content and higher saturation deficit. The MRT (calculated from constrained two pool SOC model) of slow pool was also higher in soils having higher carbon saturation deficit. This lower mineralization and higher MRT of carbon in soils having higher saturation deficit indicated the importance of silt + clay to protect C more strongly where they are less saturated. Loss of C was observed not only due to microbial decomposition, but also by chemical dissolution. By conducting adsorption experiments, higher desorption of C was observed from soils having lower saturation deficit. Actually silt + clay particles protect C through surface adsorption as well as formation of microaggregates (Six et al., 2002). This mechanism is contrast to the monolayer theory of OM coverage of mineral surface (Mayer, 1994). Rather it supports the existence of organic matter in patches either associated with or encapsulated by mineral surfaces (Ransom et al., 1997). The singly coordinated, reactive OH groups on Fe and Al oxides and at edge sites of phyllosilicates, which are able to form strong bonds by ligand exchange, are a measure of the amount of OM stabilized in soils in organo-mineral associations (Kleber et al., 2004). The organic molecules adsorbed first might be strongly stabilized by multiple ligand attachment. At

larger surface loadings, sorption can take place with fewer ligand attachments involved, which leaves parts of the molecule not attached to the surface and thus renders them more susceptible to degradation (Kaiser and Guggenberger, 2003) (Fig. 6.2 and 6.3). Thus in the present study the higher mineralization of C was observed that was not attached to the mineral surface by ligand exchange (in soils having higher C saturation) but was simply attached through weak interactions.

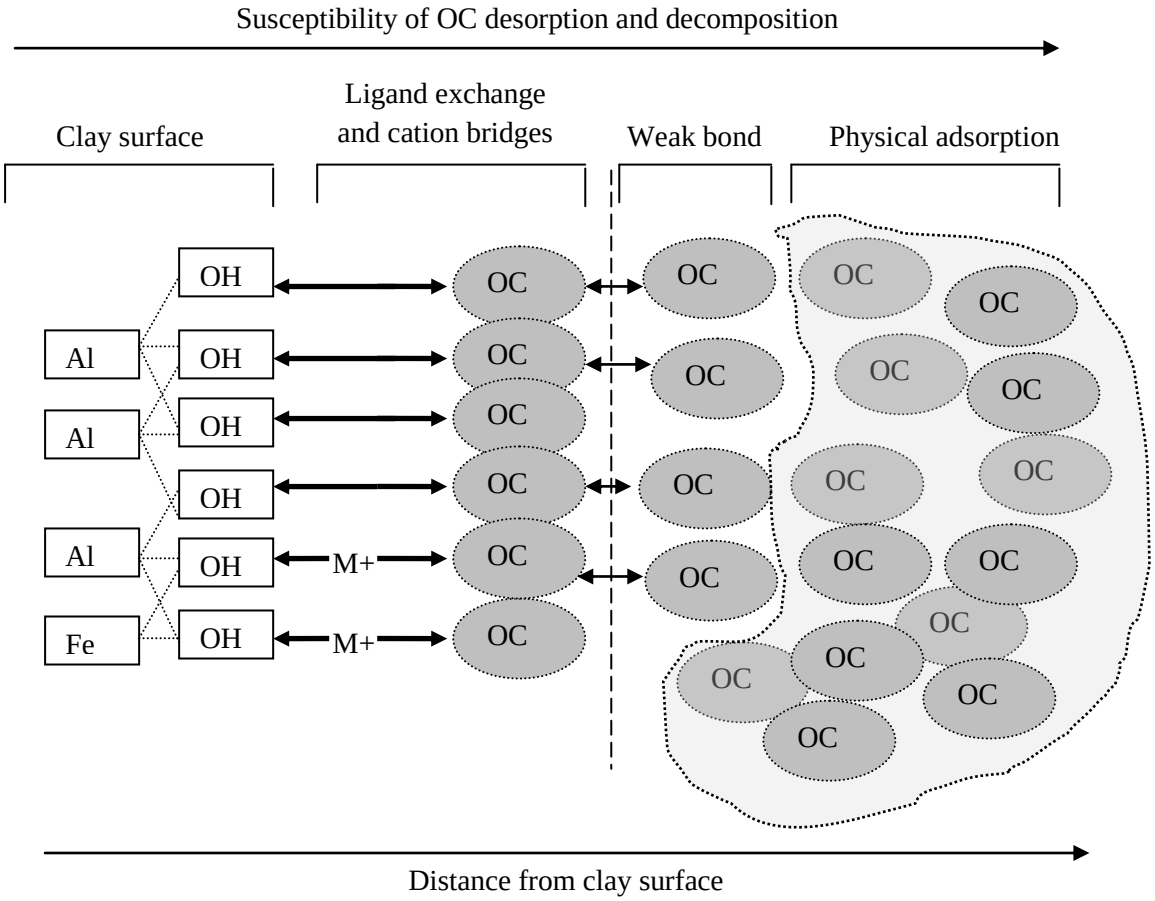

Fig. 6. 2. Schematic diagram of organic carbon (OC) adsorption on clay surface in soils with low C saturation deficit

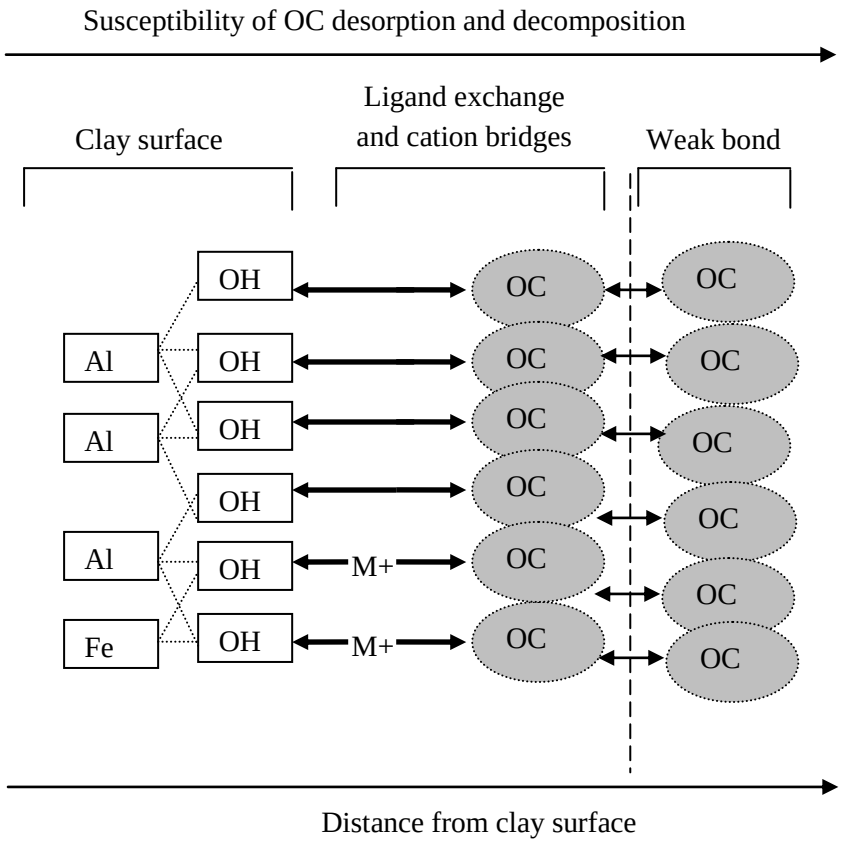

Fig. 6. 3. Schematic diagram of organic carbon (OC) adsorption on clay surface in soils with high C saturation deficit

6.3.3. Carbon saturation deficit determines the stabilization of added C to soils

In the present study, C saturation deficit was observed to influence on stabilization of added C, through microbial decomposition of fresh grass residue. After conducting an eight months incubation experiment, higher stabilization of C was observed in silt + clay particles where protective capacity was less saturated. Higher level of C saturation not only reduced stabilization of added residue C, but showed higher SOC loss even after addition of residue. Positive priming effect might be responsible for higher loss of SOC, by getting available energy source from fresh residue, for microorganisms to decompose SOC. Since C remain in biologically available form when protective capacity are

saturated (Baldock and Skjemstad, 2000), microorganisms can easily decompose them to get energy. However, in presence of available energy source (added residue) microbial population flourish and become more active to decompose SOC depending on their availability. At the same time, the decomposition products of residue tend to stabilize in silt + clay fractions when they are less saturated.

6.3.4. Soil organic C loss due to dispersion of particles explains the reason for lower C content in disturbed soils (cropping) compared to woodland soils

Significantly higher SOC mineralization was observed in this study from dispersed silt + clay particles compared to whole soils (discussed in chapter 3). Dispersion of soils broke down the larger aggregates (< 2000 µm) into smaller particles (< 53 µm) and released < 53 µm sized particulate organic carbon (POC) that was protected within aggregates before dispersion. Thus microbial decomposition of these POC was higher in dispersed silt + clay particles compared to that in whole soils. Dispersion of soils influenced not only on microbial decomposition of SOC but chemical dissolution of C (discussed in chapter 5). Thus 5 to 11 times higher desorption of C was observed from dispersed silt + clay compared to whole soils. Loss of C from silt + clay particles indicated that, though silt + clay particles store C in stable form compared to larger fractions, this stable form of C could also be lost upon disturbance. Because of this effect, significantly lower C was observed in even silt + clay fractions of cropping and pastures soils compared to woodland soils. This result was consistent with Sparrow et al. (2006) who observed 39% less C in silt + clay fractions of cropping soils compared to perennial pasture. Thus protection could not be considered as complete reduction of decomposition of organic C, but rather to a state that is more protected from decomposition relative to similar unprotected materials.

6.4. General conclusion

The present study focused on two important aspects. First the application of any protective capacity model to soils for prediction of theoretical protective capacity and estimation of C saturation level of that capacity. Second the relevance of using a model based on silt + clay protective capacity for estimation of saturation level, and how this saturation level controls other behaviour of SOC like mineralization, desorption, adsorption of added DOC and change in mineralization due to application of fresh residue. Land use could be important factor for saturation of protective capacity, as significant difference in saturation was observed among three land uses in both Ferrosols ($p < 0.01$) and Dermosol ($p < 0.05$). However, oversaturation of two woodland soils of Ferrosol and one Dermosol arise the need to find out other factors that also contribute C to soils beyond the capacity of silt + clay particles. Positive influence of poorly crystalline minerals in C storage was observed in Ferrosol and explained one reason for oversaturation. However, the relative stability (from microbial decomposition and chemical dissolution) of SOC was higher in soils where silt + clay protective capacity was not saturated. Higher loss of C from oversaturated soil due to contribution of poorly crystalline Al further raised questions about the relative stability of silt + clay protected and poorly crystalline Al protected C. Since poorly crystalline Al protected C was not separated in the research, it could not be concluded that all C fractions that imparted oversaturation of silt + clay protective capacity, was stored due to this Al. Thus oversaturation of silt + clay and poorly crystalline Al might be responsible for higher loss of C from soil. Though relative stability of C associated with silt + clay and Al was not tested in this study, future research should be directed on it.

6.4. Future implications

The experiments that was designed and conducted in this research were based on specific and limited soil samples. Since the duration of this research was constraint, it was not possible to run the experiments for long time and on large number of samples. Future work should be designed based on the limitations that were faced in the present study.

- In the present study the model (Sparrow et al., 2006) that was used to calculate protective capacity and C saturation level, was based on soils analysed in one specific climatic condition (cool-temperate climate in Tasmania). Prediction of C saturation level using this model will not be possible under different climatic condition. Model should be proposed in future study by including wide range of soils (different texture and mineralogy) under different climatic condition.
- One of the key finding in this research was the influence of poorly crystalline Al on SOC storage in soils that was conspicuous in Ferrosol but not in Dermosol. Higher ratio of C/Al in Dermosol (indication of higher saturation of these minerals) compared to Ferrosol might be a reason for not showing any relationship. To find more clear explanation, future research should be designed including soils with wide range of C/Al ratio. Analysis of soils on different depth could be another approach to get this relationship, because of higher content of these minerals in subsoil.
- In the present study, positive priming effect was observed when fresh residue was added both with and without nutrient elements. However, increase in C content was also observed depending on C saturation deficit. Specific source of this increased C could not be detected since the residue was not labelled. Future research should be designed by applying labelled residue. Mineralization of CO_2

should be determined both from labelled (residue) and non-labelled C (native SOC). After incubation, SOC content should be determined. Thus from the cumulative SOC mineralization and remaining SOC content after incubation, it will be easier to detect the source of stabilized C in soils.

- The adsorption experiment that has been discussed in chapter five was conducted on silt + clay particles having different level of C saturation. Though the findings explained the actual response of C saturation level upon addition of DOC, the relative significance of silt + clay and poorly crystalline mineral in adsorbing DOC could not be assessed. However, to get more clear explanation, several adsorption experiments could be conducted by removing SOC (using H_2O_2), both crystalline and non-crystalline Fe and Al content (using Na-dithionite) from soils.

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