

Chapter 1: Introduction, Scope and Objectives

1.1. Project overview:

Soils are the largest reservoir of terrestrial carbon (C), containing globally about 1500 Pg of organic C in the top one meter, roughly twice the amount of C found in the atmosphere as carbon dioxide (CO₂) and about three times the amount of C in vegetation (Batjes 1996; Lal 2004; Smith 2004; IPCC 2007). The main factors controlling the size of the soil C pool are land use, climate, soil, management practice and technology (Guo and Gifford 2002; Lal 2004; Smith 2005; Smith *et al.* 2005, 2008). Understanding the response of the soil C reserve to change in these factors is of critical importance, as a small change in the amount of C stored in soils would have significant effect on atmospheric CO₂ concentration (Baldock *et al.* 2012). Soil organic carbon (SOC) turnover models are able to simulate SOC dynamics under various land uses (forest, grassland, cropland etc.), management practices (crop rotation, ploughing, fertilizer application, irrigation, stubble management, soil amelioration etc.), technological improvement (varietal improvement, better machinery, improved agronomic knowledge etc.) and climatic conditions (Smith *et al.* 1997; Ludwig *et al.* 2007; Falloon and Smith 2009; Liu *et al.* 2009). They could help in improving our understanding of SOC turnover processes and the underlying C stabilization mechanisms (Balesdent 1996; Smith 2002; Ludwig *et al.* 2003, 2005). These models could also help in projection of SOC dynamics under different future scenarios of climate change, improvement in technology and change in land uses and management practices (Smith *et al.* 2005, 2006, 2007). The Rothamsted soil carbon model (RothC) (Coleman and Jenkinson 1996) is such a SOC turnover model, which was initially developed to model the turnover of organic C in arable soils in UK, but has been used successfully in a range of other environments and conditions across the world under different land use systems (Smith *et al.* 1997; Skjemstad *et al.* 2004; Smith *et al.* 2006; Cerri *et al.* 2007; Kintché *et al.* 2010). However, research on modelling SOC dynamics under different land use and crop management practices is scarce in Australia.

The major limitations in fractionation of SOC and modelling SOC dynamics are partitioning SOC into meaningful fractions and relating these measured SOC fractions with the model conceptual pools (Falloon and Smith 2000; Smith *et al.* 2002). The wet chemical

fractionation methods consider the chemical nature of SOC as the only factor to influence SOC stabilization, but ignore the influence of spatial arrangement of SOC in soil matrix (primary and secondary organo-mineral complexes) (Christensen 1996; Elliot *et al.* 1996). Physical fractionations of SOC capture the effect of spatial arrangement of primary and secondary organo-mineral particles on SOC dynamics, but they do not consider chemical nature on SOC stabilization or biochemical stabilization (Six *et al.* 2002; Oik and Gregorich 2006). Therefore, various approaches in SOC fractionation schemes have recently combined physical fractionation methods together with chemical methods to capture both the effect of spatial arrangement of primary and secondary organo-mineral complexes and chemical nature of SOC on SOC dynamics (Trumbore and Zheng 1996; Six *et al.* 2002; Plante *et al.* 2004; Skjemstad *et al.* 2004). While these different SOC fractionation approaches have been successful in showing differences in SOC fraction sizes for different soils, there has been less work in defining functionally consistent turnover times of these SOC fractions.

Zimmermann *et al.* (2007) proposed a combined physical and chemical SOC fractionation method which relates the measured SOC fractions to pools in the RothC, but only a few studies have been conducted elsewhere to test the fractionation method (Dondini *et al.* 2009; Leifeld *et al.* 2009; Xu *et al.* 2011). Its applicability to RothC pools needs to be tested further.

Model initialization with measured SOC pools is believed to reflect the real site specific conditions under which SOC has accumulated, and thus, model performance is claimed to be improved by initializing with measured pools compared to using model default equilibrium pools (Zimmermann *et al.* 2007; Leifeld *et al.* 2009; Xu *et al.* 2011). However, model improvement in RothC by initializing the model with measured pools has not been extensively assessed.

Before application, a model needs to be evaluated (Smith and Smith 2007). SOC models are generally evaluated using long-term field experimental data sets (Smith *et al.* 1997). A difficulty in evaluating the performance of SOC models is the scarcity of long-term chronosequence data sets particularly involving land use change (LUC). In the absence of long-term field experimental data, paired-site data sets can potentially be used for the

evaluation of SOC models. However, evaluation of SOC models, such as RothC, using paired-site data under conditions of LUC is rare.

A large research gap exists in the evaluation of SOC models (such as RothC) across different soil types, climate, cropping systems and management practices in Australia. There are few Australian studies evaluating RothC performance, particularly under cereal based cropping systems using long-term field experimental data sets (Smith *et al.* 1997; Skjemstad *et al.* 2004; Liu *et al.* 2009). In addition, the model has yet to be evaluated under cotton based cropping system in irrigated Vertisols with different management practices using long-term field experiment data sets in Australia.

Model initialization is the most crucial part of simulation as it can influence model prediction (Falloon and Smith 2000; Carvalhais *et al.* 2008; Yeluripati *et al.* 2009). Incorrect or flawed initialization potentially leads to fallacious trends in output as the state variables drift back towards the model ideal (Yeluripati *et al.* 2009). Researchers world-wide have proposed different methods of model initialization (Parton *et al.* 1993; Paustian 1994; Smith *et al.* 2005; Zimmermann *et al.* 2007; Yeluripati *et al.* 2009; Carvalhais *et al.* 2010; Hashimoto *et al.* 2011). The sensitivity of SOC models such as RothC to the method of model initialization in projection of grassland SOC under climate change has not been assessed yet.

About 85.4% of the Australian continent is grassland, which represent the largest share (12.5%) of total global grassland among all countries (White *et al.* 2000). In this century, increases in temperature and reductions in rainfall over most of mainland Australia are expected in both summer and winter (CSIRO and Bureau of Meteorology 2007). Although studies have examined the impact of climate change on grassland SOC elsewhere (Smith *et al.* 2005; Xu *et al.* 2011), the potential response of grassland SOC to climate change in Australia has not yet been assessed.

1.2. Objectives of this study

The main objectives of this study were to evaluate the performance of the Rothamsted Carbon model (RothC) in simulation of SOC dynamics with both presence and absence of

long-term data sets, and to explore different aspects of modelling SOC dynamics under different land use and crop management practices using RothC. The specific objectives were:

- (1) to determine turnover times of SOC fractions, separated by a combination of physical and chemical methods, in contrasting land use systems by natural ^{14}C abundance,
- (2) to examine whether the SOC partitioning method as proposed by Zimmermann *et al.* (2007) has the potential to quantify different SOC pools, as required by RothC,
- (3) to evaluate the performance of RothC in simulating the effect of LUC on SOC dynamics, particularly following a proposed LUC from native vegetation to cropping, using paired-site data sets,
- (4) to examine whether initializing RothC with measured SOC pools rather than using default model equilibrium pools improves RothC performance in prediction of LUC effects on SOC dynamics,
- (5) to evaluate RothC performance in simulation of SOC dynamics under a cotton based cropping system on an irrigated Vertosol using long-term field experiment data,
- (6) to explore different scenarios of SOC dynamics under different cotton based cropping systems in irrigated Vertosol,
- (7) to test whether RothC projections of grassland SOC under climate change were sensitive to the model initialisation method, and
- (8) to project climate change impacts on grassland SOC with three different global climate model forced with four different climate scenarios for the time period 2008-2100, using RothC in the northern slopes and plains of New South Wales (NSW), Australia

1.3. References

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Chapter 2: Review of Literature

This literature review provides a general overview of different aspects of soil organic carbon (SOC) modelling. Since the experimental chapters are written in journal article formats, parts of the review of literature might be repeated in the introduction sections of the individual experimental chapters.

2.1. Soil organic carbon – the global context

Five principal pools regulating carbon (C) cycle on earth are oceanic pool [$\sim 38,000$ Pg ($1 \text{ Pg} = 10^{12} \text{ kg} = 10^{15} \text{ g} = 1 \text{ Gt}$)], followed by the geologic ($\sim 5,000$ Pg), pedologic/soil [$\sim 2,500$ Pg to one meter depth (organic and inorganic)], atmospheric (~ 760 pg) and biotic pool (~ 560 Pg) (Houghton 1995; Batjes 1996; Lal 2004). Soils contain about 1500 Pg of organic carbon globally in top one meter, roughly twice the amount of C than that in the atmosphere as carbon dioxide (CO_2) and about three times the amount of C in vegetation (Batjes 1996; Lal 2004; Smith 2004; Powlson 2005; IPCC 2007). Although the soil organic carbon (SOC) pool is small compared with that of the oceans, potentially it is much more labile in the short term (Batjes 1996). Using respective estimates of 1500 and 720 Pg of C in soil and the atmosphere, and an atmospheric concentration of 390 ppm for CO_2 , a 1% change in the amount of carbon stored in soils would equate approximately to an 8 ppm change in atmospheric CO_2 concentration, provided all other components of the C cycle remained constant (Baldock *et al.* 2012). Thus, small change in flow of C into or out of soil C pool could have dramatic impact on a global scale (Powlson 2005; Smith *et al.* 2008a).

2.2. Factor Affecting change in soil organic carbon

2.2.1. Land use change

Each soil has a certain level of C carrying capacity *i.e.* equilibrium C content which is determined by many factors including land use, vegetation type, climate (temperature, moisture regimes etc.), edaphic factors (soil parent material, clay content, cation exchange capacity etc.) (Gupta and Rao 1994; Dawson and Smith 2007). The equilibrium C stock is the

result of a balance between net inflow and net loss of C from the soil (Fearnside and Imbrozio Barbosa 1998; Smith *et al.* 2008a). Soil C inputs are largely determined by the land use, with forest and grassland systems generally have largest inputs, and the smallest input is often found under croplands (Guo and Gifford 2002; Smith *et al.* 2008a). Removal of crop biomass in harvest products and removal of crop stubble are the main reasons behind the smaller net C input to soil under cropping (Dawson and Smith 2007). The amount of C input to the soil also depends on the vegetation productivity, which varies with climate, land cover, species composition, soil type etc. (Falge *et al.* 2002). Plant C input enters into the soil as litter input, plant leachates, root exudates or dissolved organic C, where it undergoes decomposition by soil microbes (fungi, bacteria, soil fauna etc.). Decomposition in soil is a complex process involving diverse physical, chemical and biological mechanisms that continuously transfer incoming organic matter (OM) as well as soil OM to a range of different compounds, and finally release C as CO₂ and methane (CH₄) through heterotrophic soil respiration (Berg and McClaugherty 2008). Most of the OM entering the soil decomposes rapidly, but a portion of decomposing OM forms chemically recalcitrant compounds or is stabilised by other mechanisms (Krull *et al.* 2003). This slowly decomposing portion represents majority of SOC. The processes like harvest, fire, insect damage, erosion etc. also could contribute to the loss of C from soil (Lal 2004; Smith *et al.* 2008a).

However, the equilibrium balance between C inflows and outflows is often disturbed by land use change and this disturbed soil may act as C sink or source depending upon the ratio of inflows and outflows, until a new equilibrium is reached (Guo and Gifford 2002). The magnitude of change in SOC stock, due to change in land use, depends on several factors, such as rainfall, temperature, initial C content, soil sampling depth and management practices. Guo and Gifford (2002) highlighted the influence of land use change on soil C stocks. Meta-analysis of 74 publications indicated that land use change from pasture to plantation (-10%), native forest to plantation (-13%), native forest to crop (-42%) and pasture to crop (-59%) decreased total SOC stocks, whereas land use change from native forest to pasture (+8%), crop to pasture (+19%), crop to plantation (+18%) and crop to secondary forest (+53%) increased SOC.

2.2.2. Change in management practices and technology

Change in forest, grazing land and cropland management practices might increase or decrease SOC (Smith 2005). Extensive tillage associated with crop production increases the loss of SOC by breaking soil aggregates, to expose protected organic C to weathering and microbial decomposing (Besnard *et al.* 1996; Baldock and Skjemstad 2000; Dawson and Smith 2007), and also by changing temperature and moisture regimes of soil (Balesdent *et al.* 2000; Smith *et al.* 2008a). Management changes such as soil amelioration, fertilizer application, introduction of improved species, incorporation of nitrogen-fixing species, irrigation, introduction of rotation in grazing, avoiding overstocking, changing grazing intensity, introducing conservation tillage, incorporation of plant/crop residues in soil, adoption of leguminous cover crops etc. could change C return in soil, and thereby SOC stock (Smith *et al.* 2008b). Technological improvements could increase harvestable yield as well as the return of C to the soil. Such improvements include, for example, improvement in breeding (varietal improvement towards stress resistant and yield potential), better machinery, improved agronomic knowledge among the farmers and land managers etc. (Smith *et al.* 2005).

2.2.3. Climate change

Climate effects, particularly increased temperature, could speed decomposition and cause soil C stocks to decrease, whereas increased C input, resulting from CO₂ fertilization and nitrogen deposition, could slow down the loss (Smith 2005; Smith *et al.* 2005). Increased atmospheric CO₂ concentration leads to increased vegetation production directly by stimulating higher rates of photosynthesis and light-use efficiency, and indirectly *via* reduced stomatal conductance and transpiration, and improved water and nutrient use efficiencies (Drake *et al.* 1997). Increased temperature might lengthen the growing season and increase biomass production and hence increases C input to soil (Smith 2005). On the other hand, decreased rainfall and increased climatic extreme events (drought, flood, storms, fire etc.) could reduce plant productivity (Holden and Brereton 2002; Smith 2005). Thus, climate change could change SOC indirectly through soil C input by affecting ecosystem productivity. Future climate changes could directly affect SOC by affecting soil temperature and moisture regime (Lal 2004). Decomposition/mineralisation of SOC might increase under

a warmer future climate until soil moisture will allow decomposition. The balance between future increased temperature and reduced effective rainfall (precipitation-evaporation) ultimately will determine whether a soil will be a source or sink of CO₂ (Smith 2005).

2.3. Soil organic carbon fractionation

Soil organic matter (SOM) is a heterogeneous mixture consisting of plant, animal, and microbial materials in all stages of decay and stabilization degree combined with a variety of decomposition products of different age and levels of complexity intimately associated with the inorganic soil matrix (Waksman 1938; Christensen 1996; Baldock and Skjemstad 1999; Six and Jastrow 2002; Rodeghiero *et al.* 2009). The properties, qualities, availabilities and stability mechanisms of its different heterogeneous components vary widely (Krull *et al.* 2003; Von Lützow *et al.* 2008). Current models divide SOM conceptually into a series of functional pools ranging from very active (labile) to stable (non-labile) on the basis of their size and turnover rates (Falloon and Smith 2000). It is essential to identify, isolate and characterise different functional pools of SOM to understand its dynamics and different stabilisation mechanisms without altering any of their properties that might be relevant to their function in the ecosystem. This can be accomplished by partitioning SOM into different meaningful fractions which are defined by specific stabilization mechanisms (thus represents functional pools) and homogeneous in terms of compositions, accessible to plants or to the soil microbial population and their turnover times (Von Lützow *et al.* 2007).

SOM consist of C, H, O, N, P and S and it is difficult to actually measure or fractionate the SOM. Due to difficulties in direct measurement of SOM, it is substituted by the measurement or fractionation of SOC (Krull *et al.* 2004). There is no consensus on fractionation of SOC, instead a range of fractionation methods available viz. physical, chemical, biological and a combination of different methods.

2.3.1. Physical fractionation

Microorganisms must need physical access of SOC in order to use it that is inaccessibility is a prerequisite for decomposition (Von Lützow *et al.* 2007). If they have no access, the chemical composition of SOC is inconsequential because it will not be

decomposed. Chemical composition is paramount in SOC dynamics only when the structure of a system does not control the accessibility of SOC to microbes, for e.g. forest litter layer (Elliot *et al.* 1996). Physical protection is thought to hinder the access of enzymes and microbes and thus lowering the turnover rates (Evans *et al.* 2001). Physical fractionation methods are based on the premise that the association of soil particles and their spatial arrangement play a key role in SOC dynamics. This fractionation involves size and density separation of primary and secondary organo-mineral complexes.

2.3.1. Aggregate fractionation

The basic concept is that soil aggregates provide physical protection to SOC and thus influence SOC turnover rate through formation of secondary organo-mineral complexes (Tisdall and Oades 1982; Six *et al.* 2002). Aggregate fractionation is generally obtained by dry or wet sieving and slaking. Stability of SOC in different aggregates increases with decreasing the aggregate size. Occlusion of SOC within microaggregates results in comparative physical inaccessibility of SOC to the decomposers. Consequently, SOC in microaggregates (<250 μm) is usually older with longer turnover time compared to SOC in macroaggregates (>250 μm) (Six *et al.* 2002; von Lützow *et al.* 2007). However, longer different turnover times of occluded SOC could also be in addition due to their chemical recalcitrance (McLauchlan and Hobbie, 2004). SOC in different aggregate fractionations might formed by different, simultaneously acting stabilization mechanisms and thus could be defined as SOC pools (Smith *et al.*, 2002), but aggregate fractionation might still be useful as a pre-treatment to obtain more homogeneous SOC fractions (Six *et al.* 2002).

2.3.2. Particle size fractionation

Particle size fractionation divides SOC into different size classes of soil primary particles after soil dispersion (mechanical or chemical) followed by sieving. The basic principle is that SOC associated with different sized soil particles are different in composition, structure and stabilization mechanisms (von Lützow *et al.* 2007). SOC in sand size fraction (particulate organic carbon, POC) exhibits only weak bonding affinities and represents an active SOC pool; whereas SOC in clay size particle has stronger bond (adsorption, ligand exchange, polyvalent cation bridge etc) and represents an intermediate and passive pool of

SOC (Sposito *et al.* 1999; von Lützow *et al.* 2007). This is an good physical method for a rough differentiation between active and intermediate/passive SOC fractions.

2.3.3. Density fractionation

Density fraction is based on the concept that during the humification process, SOC becomes intimately associated with soil minerals; and thus more humified portion of SOC (heavy fraction, HF) is thought to be associated with soil mineral (organo-mineral complexes) and light portion (light fraction, LF) with density less than soil mineral ($<1.6-2.0 \text{ g cm}^{-3}$) is assumed to be mineral free (Barrios *et al.* 1996). Light fraction is separated from heavy fraction by centrifugation followed by decantation using organic liquid (tetrabromoethane, tetrachloromethene, bromoform etc.) or aqueous solutions of inorganic salts (sodium iodide, sodium polytungstate etc.) with a density ranging from 1.6 to 2.0 g cm^{-3} . LF could be free (free LF) or occluded in aggregates (occluded LF) (Christensen 1992). LF consists mainly of decomposing plant and animal tissues (Janzen *et al.* 1992, Christensen, 1992). LF has a faster turnover rate than HF and generally represents an active/labile pool of SOC (Janzen *et al.* 1992; Gregorich *et al.* 1995). Due to the soil physical protection of the occluded LF, the fraction has a slower turnover rate compared to free LF (Poirier *et al.* 2005). LF might contain char materials and thus, measurement of active pool by density fractionation could be overestimated and measurement of HF could be underestimated in a soil with frequent fire/burning history (Skjemstad *et al.* 1990).

2.3.2. Chemical fractionation

The chemical fractionation is based on the chemical nature/composition of SOC which inturns govern the turnover rates of different fractions (Christensen 1996; Elliot *et al.* 1996). Chemical fractionation are done by i) extraction in aquous solution or organic solvent, ii) hydrolysis with water or acid, iii) oxidation and iv) destruction of mineral phase.

2.3.2.1 Extraction of SOC

SOC is fractionated on the basis of its solubility in aquous solution, with or without electrolytes, or in organic solvent. Most popular extractable SOC fraction is dissolved soil organic carbon (DOC). DOC is defined as SOC $<0.45 \text{ }\mu\text{m}$ in solution and considered as

readily bioavailable. Different extractants are used to separate DOC from cold water to aqueous solution of different ionic strength. DOC is not homogeneous, it contains C from both new and old SOC origin viz. plant litter, soil humus, microbial biomass, root exudates etc. and only 10-40% C in this fraction is readily degradable (Kalbitz *et al.* 2000, 2003; Haynes 2005). Details reviews of fractionation and characterization methods of DOC are reviewed by Herbert and Bertsch (1995). Another most important extractable SOC is the microbial biomass carbon (MBC). There are many methods to measure MBC (Ocio and Brookes 1990), but the only direct extraction method is the chloroform-fumigation-extraction method (Jenkinson 1976; Vance *et al.* 1987). MBC, which is kinetically/functionally homogeneous SOC, is a major part of labile/active SOC (McGill 1996; Smith *et al.* 2002). The classical concept of separating humic material (fulvic acid, humic acid and humin) is based on solubility/extractability of the SOC with acid and base. Fulvic acid is soluble in alkali (e.g. 0.1M NaOH+0.1M Na₄P₂O₇) and soluble in acid (e.g. HCl). The humic acid fraction is soluble in alkali and insoluble in acid. The humin fraction is insoluble in alkali (Stevenson 1994). Different organic solvents are also used to separate humic substances, for examples n-hexane, chloroform, methanol, dichloromethane etc. A details review of this fractionation method could be found in the study done by von Lützow *et al.* (2007). However, extraction of SOC by different methods affect SOC stabilized by different mechanisms and thus could not be considered as separate functional SOC pools (smith *et al.* 2002).

2.3.2.2 Hydrolysis of SOC

In this method generally hot water and cold or hot acids (HCl and H₂SO₄) are used to fractionate SOC. Hot water extractable SOC is largely composed of carbohydrate and amino/amide N of microbial origin (Haynes 2005). It contains C which is thought to be originated from soil solution, weakly sorbed to mineral surface or humic molecules (Leinweber *et al.* 1995), and thus is not homogeneous (Gregorich *et al.* 2003). But, still this SOC fraction is believed to be a good parameter in estimating labile pool of SOC (Henriksen and Breland 1999). Acid hydrolysis, which is reflux SOC with HCl or stepwise chemical digestion with H₂SO₄ remove effectively carbohydrate and protein material by breaking hydrolic bond and leaving behind more recalcitrant alkyl and aryl material (Trumbore *et al.*, 1989; Martel and Paul 1974; Leavitt *et al.*, 1996). About 30-87% SOC is hydrolysable with

hot 6 N HCl and 5-45% with H₂SO₄ (Stevenson 1994; Paul *et al.* 1997). From a radio C study, Paul *et al.* (1997) and Leavitt *et al.* (1996) conclude that non-hydrolysable SOC fraction is a good measure of old passive SOC pool. However, Balesdent (1996) was failed to separate old and new SOC by sequential acid hydrolysis of the bulk soil with H₂SO₄. Due to the unspecified reactivity, acid hydrolysis extract SOC stabilized by different mechanisms, for examples complexed SOC, SOC sorbed through polyvalent cation bridge, occluded SOC etc. Thus, acid hydrolysis is not able to isolate a separate functional SOC pool if applied to bulk soil, as in case of a Balesdent (1996), but acid hydrolysis could help in further characterization of SOC fractions which are thought to be relevant to the SOC functions, for examples as proposed by Trumbore *et al.* (1989) and Trumbore and Zheng (1996).

2.3.2.3 Oxidation of SOC

To isolate a passive or recalcitrant SOC and determine a labile/active SOC fraction by its difference from total SOC, SOC is often oxidized with different oxidative agents. Potassium permanganate (KMNO₄) is often suggested as a mild oxidizer to mimic enzymatic oxidation to oxidize labile SOC (Blair *et al.* 1995; Conteh *et al.* 1997). However, usefulness of KMNO₄ to separate active and passive SOC is questionable as aromatic and humic substances also react with KMNO₄. Skjemstad *et al.* (1993) proposed a high energy ultraviolet (UV) photo-oxidation method on the surface of aggregates to separate a passive from active SOC. UV oxidation-resistant residues consists of char materials along with other compound that are also exist in bulk soil. C-14 analyses supports the claim that UV oxidation-resistant residues is older and more stable than bulk SOC, and thus at least partly represent passive/inert SOC pool of the (Skjemstad *et al.* 1993). However, the method does not differentiate between SOC stabilized due to occlusion within microaggregates and due to its recalcitrance. Some strong chemical oxidizing agents, such as hydrogen peroxide (H₂O₂), sodium peroxodisulfate (Na₂S₂O₈) and sodium hypochlorite (NaOCl), are also used for preferentially remove young labile SOC leaving behind old, stable residues (Theng *et al.* 1992; Eusterhues *et al.* 2003, 2005; Mikutta 2005; Simpson and Hatcher 2004). As, fresh aliphatic plant materials are also resistant to H₂O₂ oxidation, separation of particular soil organic C is recommended before H₂O₂ oxidation. Use of these chemical oxidizing agents seems to have potential to isolate passive/recalcitrant SOC pool. However, isolated oxidation-

resistant residues represent a stable/passive pool whether due to selective removal of young and labile SOC or due to interaction of SOC to the mineral phase is needed to be further investigation von Lützow *et al.* (2007).

2.3.2.4 Destruction of mineral phase

Hydrofluoric acid (HF) is believed to dissolved mineral associated SOC (primary organo-mineral complex) through dissolution of hydrated silicate minerals and could be used to separate mineral-associated from non-mineral-associated SOC (Stevenson 1994; Eusterhues *et al.* 2003). However, SOC could be effected (10-30% loss in total SOC) due to the HF treatment and separation of mineral associated SOC is not always completed as its magnitude depends on soil types and soil depth (Rumpel *et al.* 2006; Eusterhues *et al.* 2007).

2.3.4. A combination of physical and chemical fractionation method

The physical SOC fractionation methods elucidate spatial arrangement of primary and secondary organo–mineral complexes on SOC stabilization (e.g. SOC stabilized within occluded aggregates vs. free SOC, SOC stabilized by different primary soil minerals etc.), but unable to give importance also to chemical nature/composition of SOC on its stabilization. Similarly, chemical fractionation technique, when applied to bulk soil, consider only the chemical nature/composition of SOC on its turnover, but ignore SOC stabilization mechanisms through spatial arrangement of primary and secondary organo–mineral complexes (Six *et al.* 2002; Oik and Gregorich 2006). Physical fractionations are suitable to partitioned SOC first into different size/density class according the hierarchy of soil structure and then chemical fractionation methods are suitable for advanced chemical characterization to elucidate molecular-level interactions between SOC and soil mineral particles and within SOC (Oik and Gregorich 2006). Therefore, to capture all the SOC stabilization mechanisms together, various approaches in SOC fractionation schemes have combined physical and chemical methods together subsequently. One common approach is density or size fractionation prior to chemical analysis. By removing LF (by density fractionation), or the sand fraction (by particle size fractionation), which contains mainly fresh plant materials, rest of the fractions are then further characterized chemically by acid hydrolysis or base extraction (Martel and Paul 1974; Trumbore *et al.* 1989; Theng *et al.* 1992; Trumbore and

Zheng 1996; Six *et al.* 2002; Wattel-Koekkoek *et al.* 2003; Wattel-Koekkoek and Buurman 2004) or oxidation with H_2O_2 /NaOCl/ $Na_2S_2O_8$ (Leifeld and Kögel-Knabner 2001; Plante *et al.* 2005; Plante *et al.* 2004). These combined methods still produce a range of heterogeneous SOC fractions which are composite and not unique as defined by Smith *et al.* (2002), and hence might not be define as SOC pools. But, there are some physico-chemical methods which have shown good promise to relate measured SOC fractions with SOC pools, for example Baldock and Skjemstad (1999) and Krull *et al.* (2004) have proposed a physico-chemical methods where they suggested to divide SOC into POC (particle size fractionation), dissolved organic carbon (DOC), charcoal carbon (photo-oxidation) and humus (by difference from the total SOC); Skjemstead *et al.* 2004 also proposed almost the same fractionation method, but excluding DOC (Fig 2.1), whereas Zimmermann *et al.* (2007) suggested a separate physico-chemical fractionation method (Fig. 2.2) to partion SOC into free LF (size fraction by wet sieving followed by density fractionation), DOC (water extraction), stable aggregate and sand associated C, silt and clay associated C, and inert organic carbon (NaOCl oxidation of silt + clay associated C).

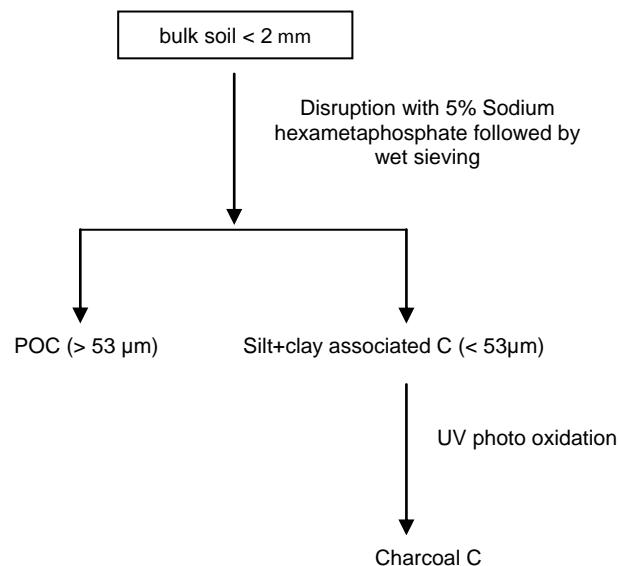


Fig 2.1. Physico-chemical SOC fractionation method after Skjemstead *et al.* (2004). POC: particulate organic carbon.

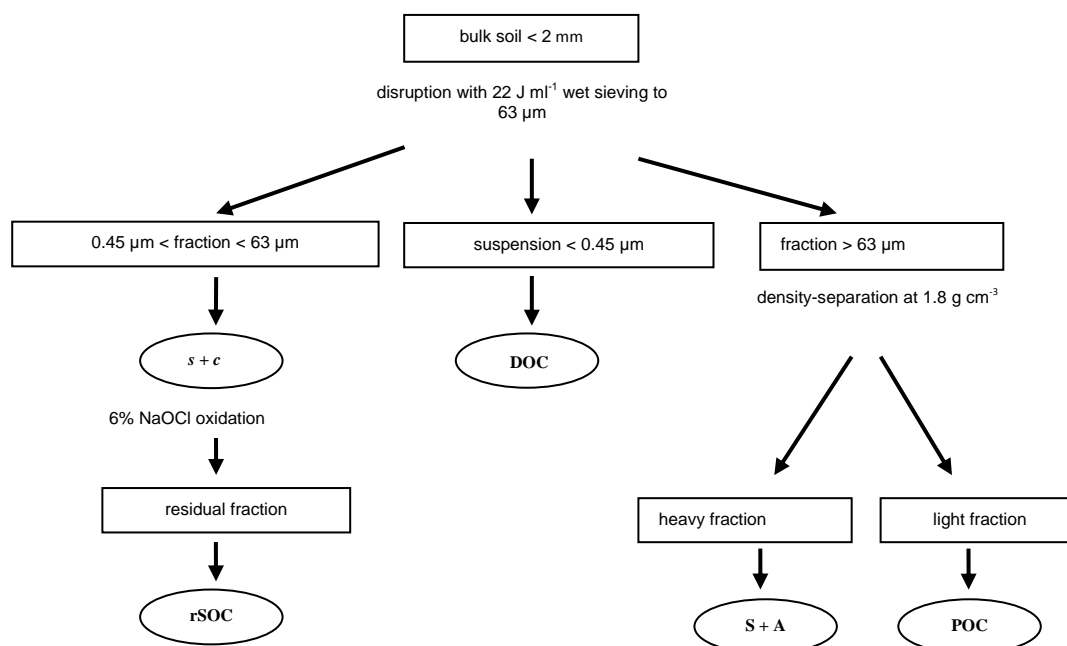


Fig. 2.2. Physico-chemical SOC fractionation method after Zimmermann *et al.* (2007). POC: particulate organic carbon, DOC: dissolved soil organic carbon, S + A: soil organic carbon in sand and stable aggregate, s + c – rSOC: soil organic carbon in silt and clay fraction excluding inert organic carbon, rSOC: chemically resistant soil organic carbon/inert organic carbon.

2.3.3. Black carbon

Black carbon is an inorganic carbon compound produced from the incomplete combustion of organic material having a graphitic microstructure (Novakov 1984; Braadbaart and Poole 2008). In the literature, several terms are used synonymously with black carbon, such as charcoal, soot, elemental carbon, or pyrogenic carbon. These materials are generally finely divided ($<53 \mu\text{m}$) and highly aromatic in nature, but unlike lignins and tannins, contain relatively low levels of O-aryl carbon (Skjemstad *et al.* 1998). Black carbon is resistant to oxidation and microbial activity and so is persistent on a geological timescale (Herring 1985). Due to this recalcitrant nature, black carbon is assumed to represent part of the inert organic carbon pool. This pools are expected in higher proportion of total SOC in fire prone region. Historically, black carbon in soils has been calculated by digesting away organic matter using nitric acid and heat, and then sorting char particles by hand or under microscope (Swain 1973; Zackrisson *et al.* 1996). New analytical methods to estimating char materials in mineral

soils include using benzenepolycarboxylic acids (BPDA) during nitric acid digestions as markers for black C (Glaser *et al.* 1998), chemical digestion (Kurth *et al.* 2006) and using a combination of high energy ultraviolet photo-oxidation and nuclear magnetic resonance spectroscopy (Skjemstad *et al.* 1993) or a combination of chemical oxidation followed by solid-state ^{13}C nuclear magnetic resonance spectroscopy (Simpson and Hatcher 2004). However, there is no consensus among these different methods. Schmidt *et al.* (2001) tested several forms of thermal oxidation, chemical oxidation by photooxidation, and a chemical oxidation/molecular marker method on eight Australian soil samples. The resulting black carbon values for individual samples varied over two orders of magnitude indicating great disparity between individual methods. Due to being light in weight and smaller in size, black carbon often interferes with the density and particle size fractionation methods.

2.4. Measurement of turnover rate of soil organic carbon

Soil organic carbon is a dynamic entity, and even in a state of equilibrium, SOC is in a continual state of dynamics through incoming new C inputs into the SOC pool and outgoing fluxes of C (CO_2 and C) from the pool (Six and Jastrow 2002). Primary production and soil microbial decomposition together govern the incoming and outgoing C fluxes from the SOC pool. The turnover of SOC does not only include decomposition/mineralization, but also loss of C from the pool due to lateral and vertical loss, and in reality is termed as ‘mean residence time’ (MRT) (Krull *et al.* 2003). MRT of organic C present in a pool is defined as the average time it resides in the pool at steady state or the average time required to completely renew the content of the pool at steady state (Six and Jastrow 2002). Several factors in combination control the turnover rate of SOC, for example climate (temperature, precipitation etc.), vegetation types (distribution of above and below ground biomass, C/N ratio, lignin content etc.), parent materials (soil type, mineralogy, texture, structure, aeration, water and nutrient supply capacity, pH, habitat for soil microbes etc.), management practice, soil disturbance etc. An understanding and measurement of SOC turnover is important for quantifying SOC and associated other nutrient cycles, and determining temporal responses of SOC and nutrient budgets (Six and Jastrow 2002; Smith *et al.* 2008a).

Turnover rate of SOC is estimated by four different methods viz. i) simple first-order modeling, ii) ^{13}C natural abundance, iii) ^{14}C dating and iv) “bomb” ^{14}C technique. The common first order model for determining turnover rate assumes constant zero-order input with constant proportional mass loss per unit time, and the estimate of annual soil C inputs (I) is required ($\delta S/\delta t = I - kS$, where S is SOC stock, t is time, I is C input and k is the turnover rate). (Olson 1963; Jenny 1980). The natural ^{13}C technique relies on the assumption that the ^{13}C natural abundance signature of SOC is identical to that of plants from which it is derived and need vegetations with different photosynthetic pathways [Calvin cycle (C3 plants) vs. Hatch–Slack cycle (C4 plants)]. Thus, where a change in vegetation type has occurred at some known point of time, the rate of loss of the C derived from the original vegetation and the incorporation of C derived from the new vegetation can be derived from the resulting change in the ^{13}C natural abundance signature of the soil. The turnover of C derived from the original vegetation is then calculated by using the first-order decay model. In conventional ^{14}C dating technique, the presence of ^{14}C with a half-life of 5570 yr in plants and the transformation of this ^{14}C into SOC with little isotopic discrimination allows the SOC to be dated and provides an estimate of the age of SOC (Goh 1991). Conventional ^{14}C dating technique assumes that the C in the different SOC fractions is of the same age. The assumption is questionable as C in SOC fractions has entered the soil continuously over different long period, thus the method could be used for specific situation only, for example layer of peat soil (Bruun *et al.* 2005). Thermonuclear bomb testings in the 50s and 60s sharply increased the atmospheric ^{14}C content, which then falled down drastically when the tests were halted. This sequence of events created an in situ tracer experiment through incorporation of bomb-produced ^{14}C into SOC. After the tests stopped, incorporated radiocarbon allows estimates of the turnover of SOC. Many ^{14}C bomb models have been developed to estimate the turnover rate of SOC by using the peak of bomb ^{14}C (Balesdent 1987; Harkness *et al.* 1991; Cherkinsky and Brovkin 1993; Hsieh 1993; Trumbore *et al.* 1996). All the models are same in basic structure and use the same basic assumptions viz. i) soil has reached equilibrium between decomposition and inputs. ii) inputs are constant and that the ^{14}C content of the inputs are known, iii) SOC fractions decay by first-order kinetics and iv) no isotopic fractionation occurs during the decay of organic matter (Bruun *et al.* 2005). The first assumption is indicating that the bomb ^{14}C models can be used for only those soils

which are fairly close to equilibrium. Second assumption suggests that variation in inputs as well as ^{14}C content of the inputs might influence the estimated turnover rates. Third assumption is pointing out that SOC fractions should be unique and non-composite in nature to describe their turnover rate by first-order kinetics. The fourth assumption is of concern as because SOC is gradually becomes enriched with the stable ^{13}C isotope. However, instead of these limitations, the bomb ^{14}C techniques could be used fairly for estimating both short-term turnover of active SOC fractions by taking the advantage of the recent appearance of the bomb peak and long-term turnover of more resistant fractions of SOC by taking advantage of the natural decay of ^{14}C (Bruun *et al.* 2005). The MRT estimated by different methods has wide differences, for example, MRTs estimated by simple first-order modeling and ^{13}C natural abundance are generally smaller by an order of magnitude than MRTs estimated by radiocarbon dating due to the different time scales that the two methods measure (Six and Jastrow 2002). The ^{13}C method is generally used in medium-term observations or experiments (5–50 yr) and thus this method gives an estimate of turnover dominated by relatively recent inputs and C pools that cycle within the time frame of the experiment. In contrast, the oldest and most recalcitrant C pools dominate estimates by radiocarbon dating because of the long-term time frame (200–40,000 yr) that this method measures (Goh 1991).

2.5. Modelling soil organic carbon

A model is a simplified representation of reality, designed to meet specific objectives (Smith and Smith 2007). A model may be a physical miniature of real entity, such as a clay sculpture, a hypothetical description of a complex entity or process, or a schematic/mathematical representation of a real-world system, theory, phenomenon or situation. SOC turnover/dynamics models represent turnover or decomposition of SOC as well as its transformation in soil-plant-atmosphere system. Models of SOC change have been published at least since 1940s and one of the earliest SOC model was proposed by Jenny (1941) to describe C accumulation or loss from soil:

$$\frac{dX}{dt} = -kX + A$$

Where, dX = change in state variable (e.g. soil C)

k = first order rate constant,

A = addition rate (mass t⁻¹) which is independent of loss and amount present

Since then many SOC models have been developed to meet different specific objectives.

2.5.1. Classification of soil organic carbon models

SOC turnover models can be broadly classified into three groups: 1) process-oriented models, 2) organism-oriented/food-web models, and 3) cohort models (Paustian 1994; McGill 1996; Smith 2002; Falloon and Smith 2009). These models are described below.

2.5.1.1. Process-oriented models

Process-oriented models focus on the processes controlling the movement and transformations of matter or energy (Paustian 1994). Process-based models can be divided into 1) single compartmental models: early SOC models considered SOC as one homogeneous compartment/pool (Jenny 1941); 2) two-compartmental models: later, SOC was considered as two compartments (Jenkinson 1977) and 3) multi-compartmental models: with the accessibility to computers, multi-compartmental models were developed (McGill 1996; Molina and Smith 1997). Models in types 1 and 2 are mostly static (*i.e.* where the environmental variables remain constant), whereas the models in type 3 are mostly dynamic (*i.e.* where environmental variables vary with time). Most current SOC models are process-based, dynamic and multi-compartmental, describing SOC as a finite number of pools, each of which is homogeneous, well mixed and characterized by its own position in the model's structure and decay rate (Falloon and Smith 2000; Smith 2002). Decay rates are usually expressed by first-order kinetics with respect to the concentration (C_p) of the pool as:

$$dC_p/dt = -kC_p$$

where, t is the time, and k is the rate constant. The pool's half-life [$h = (\ln 2)/k$], is the time required to reduce the concentration by half when there is no input. The turnover time ($1/k$) is also sometimes used instead of k to characterize a pool's dynamics. Lower the decay rate constant, the higher the half-life, the turnover time, and the stability of the C pool. The compartments interact by exchanging materials themselves, and by exchanges with the environment (Parshotam 1996). The flows of C within most models represent a sequence of C going from plant and animal debris to the microbial biomass, and then to soil organic pools

of increasing stability. Some models also use feedback loops to account for catabolic and anabolic processes and microbial successions. The output flow from an organic C pool is usually split into a microbial biomass pool, another C pool and atmospheric loss of CO₂. This split simulates the simultaneous anabolic and catabolic activities and growth of a microbial population feeding on one substrate. Two parameters quantify the split flow *viz.* microbial efficiency (utilization) and stabilization factor (humification), which control the flow of decayed C to the biomass and humus pools, respectively. The sum of the efficiency and humification factors must be inferior to one to account for the release of CO₂ (Smith 2002).

2.5.1.2. Organism-oriented/food-web models

Organism-oriented models focus on flow of energy and matter (C and N) through food-webs of soil organisms (Paustian 1994; Smith *et al.* 1998). Such models are dynamic models and explicitly account for different trophic levels or functional groups of biota in the soil. Food-web models require a detailed knowledge of the biology of the system to be simulated and are usually parameterized for application at specific sites.

2.5.1.3. Cohort models

This type of model considers each fresh addition of plant debris as a separate cohort, which decays in a continuous way *i.e.* model describe decomposition as a continuum (McGill 1996; Smith 2002). Most of such models are dynamic models and account SOC as one pool which decays with a feedback loop into itself. The SOC pool is divided into an infinite number of components, characterized by its ‘quality’ with respect to degradability as well as impact on the physiology of the decomposers. One of the examples of this type of model is Q-SOIL (Bosatta and ÅGren 1995). The model is represented by a single rate equation, which represents the dynamics of each SOC component of quality *q*, and is quality dependent. Exact solutions to the rate equations are obtained analytically (Bosatta and Ågren 1994).

Processed-based multi-compartmental models are most popular due to their advantage in ease of use and transferability; different compartments actually simplify very complex physical, biological and chemical characteristics of SOC, and thus help to understand and depict the underlying turnover process (Smith *et al.* 2002).

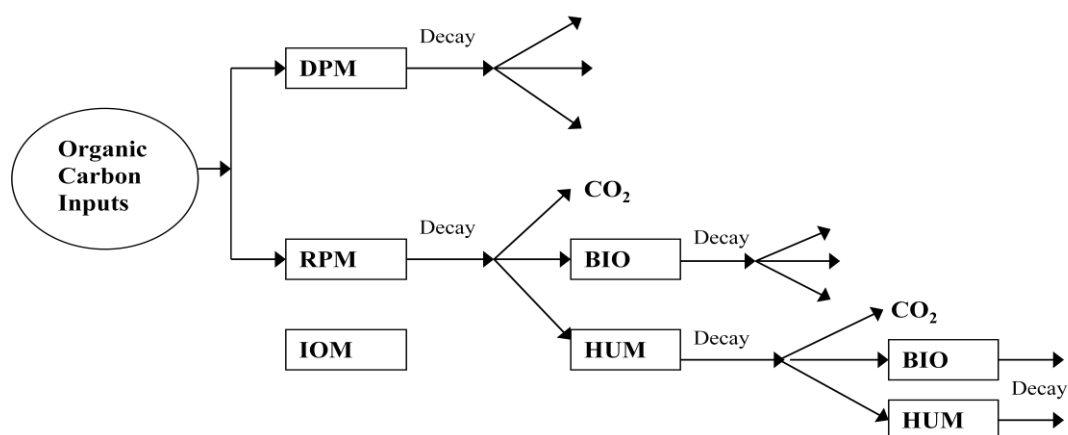
2.5.2. Factors affecting turnover of soil organic carbon in models

Decomposition rate constants (k) of different compartments or SOC pools following first-order kinetics are constant for a given set of biotic and abiotic conditions. For non-optimum environmental circumstances, the maximum value of k is modified by multiplication with a reduction factor μ , values ranging from 0 to 1. Environmental factors considered by SOC models for the modification of k include soil temperature, water, oxygen, pH, nitrogen, clay content, cation exchange capacity, salinity, and type of vegetation, plant cover and tillage (Smith 2002; Carvalho Leite *et al.* 2004; Falloon and Smith 2009; Setia *et al.* 2011).

2.5.3. Rothamsted carbon model

RothC (Coleman and Jenkinson 1996) is a process-based multi-compartmental dynamic SOC turnover model for non-waterlogged top-soils that allows evaluation of the effects of soil type, temperature, moisture content, land use and management effect on the SOC turnover process. RothC was originally developed and parameterized to model the turnover of organic C in arable soils from the Rothamsted long term field experiments in the UK - hence the name. Later, it has been extended to simulate turnover of C under different land uses in different soils and climates throughout the world (Smith *et al.* 1997; Skjemstad *et al.* 2004; Smith *et al.* 2006; Cerri *et al.* 2007; Kintché *et al.* 2010).

In the model, soil organic C is split into four active compartments or SOC pools *viz.* decomposable plant material (DPM), resistant plant material (RPM), microbial biomass (BIO) and humified organic matter (HUM), and an inert organic matter pool (IOM). The structure of RothC is as below (Fig. 2.2):



DPM: Decomposable Plant Material

RPM: Resistant Plant Material

BIO: Microbial Biomass

HUM: Humified Organic Matter

IOM: Inert Organic Matter

Fig. 2.3. Structure of the Rothamsted Carbon Model

Each compartment decomposes by a first-order process with its own characteristic rate constant. The IOM compartment is resistant to decomposition and does not enter in decomposition process. The model uses a monthly time step to calculate SOC decomposition on years to centuries time scale. If an active compartment contains $Y \text{ t C ha}^{-1}$, it declines to $Y e^{-abckt} \text{ t C ha}^{-1}$ at the end of a given month. Thus, the amount of material in an active compartment which decomposes in that particular month is

$$Y (1 - e^{-abckt}) \text{ t C ha}^{-1}$$

Where, a, b and c are the rate modifying factor for temperature, moisture and soil cover, k is the decomposition rate constant for that compartment and t is time *i.e.* 1/12, since k is based on a monthly decomposition rate. The values of decomposition rate constants, k, in years⁻¹ for different compartments have been set at 10.0, 0.3, 0.66 and 0.02 for DPM, RPM, BIO and HUM, respectively. These values were originally set by tuning the model to data from some of the long-term field experiments at Rothamsted (Jenkinson *et al.* 1987, 1992) and are not normally altered when using the model.

Depending on the DPM/RPM ratio, all the incoming plant material C is split and passes through the compartments of DPM and RPM only once. A DPM/RPM ratio of 1.44, 0.67 and 0.25 are used for most of the agricultural crops/improved grassland, unimproved grassland/scrub including Savanna and deciduous/tropical woodland, respectively. Both DPM and RPM decompose to form CO₂, BIO and HUM. The proportion of CO₂ to BIO+HUM is determined by the clay content of the soil according to the equation below:

$$x = 1.67 (1.85 + 1.60 \exp (-0.0786 \% \text{clay}))$$

where, x is the ratio CO₂/(BIO+HUM), then x/(x + 1) is evolved as CO₂ and lost from soil to atmosphere, and 1/(x + 1) is formed as BIO+HUM. The scaling factor 1.67 to 3.51 is used to set the CO₂/(BIO+HUM) ratio in Rothamsted soils (23.4% clay), the same scaling factor is used for all soils. The BIO+HUM is then enter into BIO and HUM in the proportions of 0.46 and 0.54, respectively. BIO and HUM both decompose again with time to form more CO₂, BIO and HUM.

RothC is one of most successful SOC turnover model in the world across different land use and management systems (Smith *et al.* 1997; Skjemstad *et al.* 2004; Smith *et al.* 2006; Cerri *et al.* 2007; Kintché *et al.* 2010). The model is most popular due to its simplicity, its few input requirements which are readily available and its satisfactory performance across the world under different land use and management systems. It needs monthly climate data *viz.* average monthly mean temperature (°C), monthly rainfall (mm) and monthly open pan evaporation (mm), an estimate of the decomposability of the incoming plant material (DPM/RPM ratio), depth of soil layer sampled (cm), clay percentage, soil cover and monthly input of plant residues (t C ha⁻¹). The major limitation of this model is that it is solely concerned with soil processes and does not contain a sub-model for plant production, and does not attempt to calculate annual returns of plant C to the soil. Thus, the model works on user defined soil C inputs; hence the model is free from any error carried from simulation of soil C input.

2.5.4. Application of soil organic carbon models

The SOC turnover models are used for many purposes in soil, agronomy and environmental science. They are one of the most important tools for improving our understanding of C turnover process in soil as well as underlying C stabilization mechanisms in soil (Balesdent 1996; Falloon and Smith 2002; Ludwig *et al.* 2003, 2005; Malamoud *et al.* 2009). These models are now even being extensively used to extrapolate our understanding of SOC dynamics both temporally (future projections) (Smith *et al.* 2005) and spatially *i.e.* from national (Lee *et al.* 1993), regional (Falloon *et al.* 1998) to global scales (Goto *et al.* 1994; Post *et al.* 1996). Another important application of SOC models is in agronomy, through its incorporation into decision support system to improve agronomic efficiency and environmental quality *e.g.* APSIM (McCown *et al.* 1996), DSSAT-CSM (Jones *et al.* 2003), SUNDIAL-FRS (Smith *et al.* 1996a) etc.

The SOC models can be used to explore and investigate SOC dynamics under different management and environmental scenarios even beyond the realm of experimental work (Smith *et al.* 2006, 2007). They can be used for interpolation and extrapolation of experimental data both on time and space, and also making projections of SOC behaviour under current and future environmental and management conditions (Smith 2002). The SOC models are now increasingly being used by the policy makers also at the national, regional and global scales, for example, in post Kyoto debate on capacity of terrestrial ecosystem to store C (IPCC 2000).

2.5.5. Measured and modelled pools

Soil organic matter represents a chemically and spatially heterogeneous mixture of organic materials that exists along a continuum of various stages of decomposition (Waksman 1938). Thus, SOC cannot be separated easily into different pools, rather it exist as one continuous pool with an almost infinite range of turnover times from minutes to millennia (Krull *et al.* 2003). To simulate SOC dynamics successfully, most of the process-based SOC models divided SOC into multiple conceptual pools defined by their sizes and turnover times governed by first order rate constants and modified by different climatic and edaphic factors (Falloon and Smith 2000; Smith *et al.* 2002). Thus, SOC turnover in models

has been described using simplified, deterministic, multi-compartmental simulations that are primarily based on empirically derived relationships (Cambardella 1998). A major limitation of processed-based multi-compartmental SOC models is that the various conceptual model compartments/pools often do not correspond to measureable fractions (Elliot *et al.* 1996; Smith *et al.* 2002; Bruun *et al.* 2003; Zimmermann *et al.* 2007). The only measured quantities are the microbial biomass C and total SOC. Thus, it is often not possible to validate the dynamics of modelled SOC pools with measured pools. Using measured pools in a model has the advantage of allowing more thorough model evaluation and more accurate specification of the initial conditions (Smith *et al.* 2002).

A pool may be defined as a compartment containing material that is chemically indistinguishable and equally accessible to plants or to the soil microbial population (Jenkinson *et al.* 1985). A measured fraction represents a pool when it is “unique” (*i.e.* it should not represent only a portion of chemically and biologically indistinguishable material) as well as “non-composite” otherwise, it may increase unnecessary propagation of errors and may not be transferred reliably to novel environment (Smith *et al.* 2002). On the other hand, other researchers have given the importance to the mechanism and process of SOC stabilization in modelling SOC dynamics (Krull *et al.* 2003).

During last few decades, different chemical methods were proposed to separate SOC into different pools (Blair *et al.* 1995; Piccolo *et al.* 1996; Chan *et al.* 2001; Rovira and Vallejo 2002). The wet chemical fractionation methods only consider the chemical nature of SOC as the only factor to influence the turnover rate of SOC pools, but ignore the ‘soil protection’ on SOC *i.e.* the influence of spatial arrangement of SOC in soil matrix (primary organo-mineral complex) and soil structure/aggregate (secondary organo-mineral complex) on stabilization/decomposition mechanism of SOC (Christensen 1996; Elliot *et al.* 1996). Microorganisms must have physical access of soil C in order to use it. If they have no access, the chemical composition of soil C is inconsequential because it will not be decomposed. In a situation where the structure of a system does not control the accessibility of soil C to microbes, for e.g. forest litter layer, then chemical composition is paramount in soil C dynamics (Elliot *et al.* 1996). Soil microbes generally consume most organic substrate fallen or deposited onto the soil, yet there is tremendous accumulation of organic C in the soil. So,

there must be some protection of incoming organic C in the way that prevents it from being completely consumed. In the last 1-2 decades, physical fractionation methods have increased in importance over chemical methods for fractionating SOC (Cambardella and Elliot 1992, 1993, 1994; Gregorich and Janzen 1996; Balesdent *et al.* 1998; Six *et al.* 1998, 2000; Christensen 2001; Sohi *et al.* 2001). Although physical fractionations capture the effect of spatial arrangement of primary and secondary organo-mineral complexes, they do not consider chemical or biochemical stabilization mechanisms (Six *et al.* 2002; Olk and Gregorich 2006). Recently, various approaches in SOC fractionation schemes have combined physical fractionation methods together with chemical fraction methods to capture both soil protections and chemical nature of SOC (Trumbore and Zheng 1996; Six *et al.* 2002; Plante *et al.* 2004; Skjemstad *et al.* 2004; Zimmermann *et al.* 2007). Two of these SOC fractionation methods which shown to have good potential to relate measured SOC fraction with SOC pools of RothC across different land use system were proposed by Skjemstad *et al.* (2004) and Zimmermann *et al.* (2007). The concept of relating SOC fractions with model pools is summarized in Fig 2.1 & 2.4 and Fig 2.3 & 2.5.

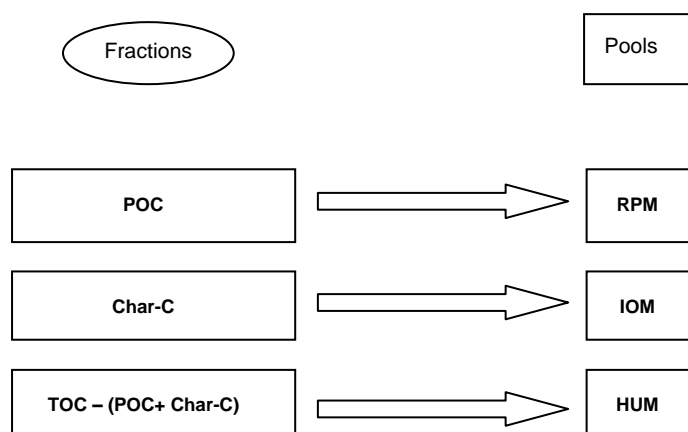


Fig. 2.4. The concept of relating measured soil organic carbon fractions to conceptual pools of RothC after Skjemstead *et al.* (2007). POC: particulate soil organic carbon, Char-C: charcoal carbon, TOC: total soil organic carbon, TOC - (POC + Char-C): soil organic carbon excluding POC and Char-C, RPM: resistant plant material, IOM: inert organic matter and HUM: humified organic matter.

Fig 2.1 and 2.4 show the partitioning SOC into different fractions and then relating SOC fraction to RothC pools after Skjemstad *et al.* (2004). POC (particle size fractionation) is the measured of the RPM, charcoal carbon is the measure of IOM and the amount of HUM pool is calculated by difference [HUM = total soil organic carbon – (POC + Charcoal carbon)].

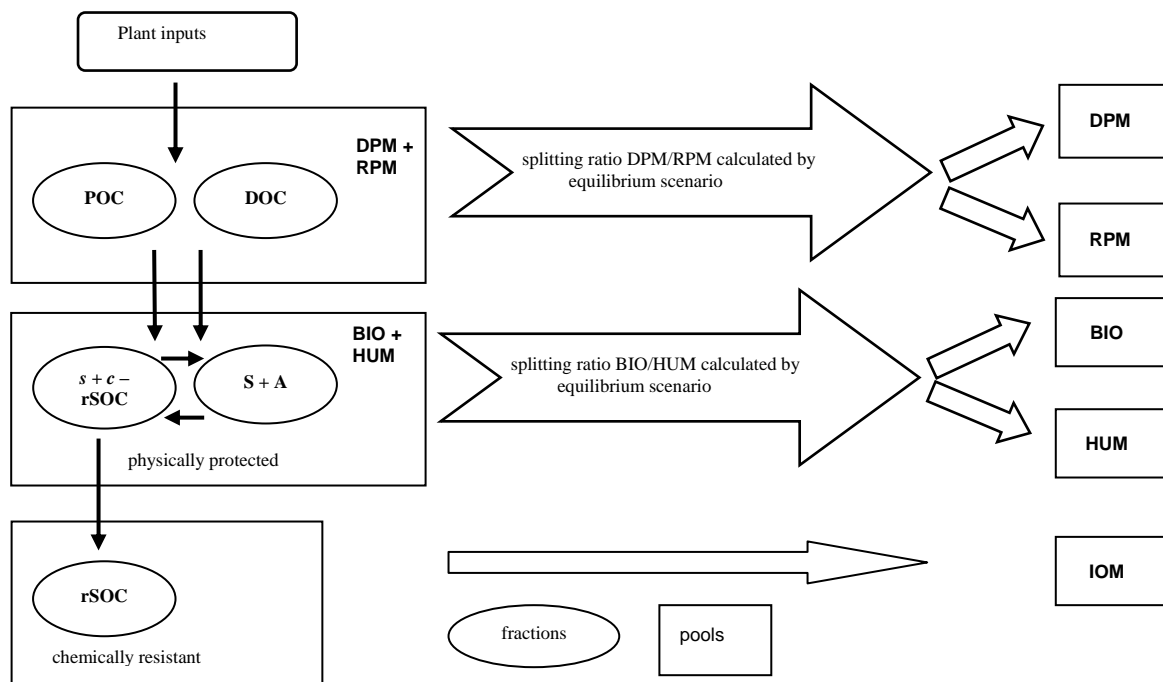


Fig. 2.5. The concept of relating measured soil organic carbon fractions to conceptual pools of RothC after Zimmermann *et al.* (2007). POC: particulate soil organic carbon, DOC: dissolved soil organic carbon, S + A: soil organic carbon in sand and stable aggregate, s + c - rSOC: soil organic carbon in silt and clay fraction excluding inert organic carbon, rSOC: chemically resistant soil organic carbon/inert organic carbon, DPM: decomposable plant material, RPM: resistant plant material, BIO: microbial biomass, HUM: humified organic matter and IOM: inert organic matter.

Similarly, Fig 2.2 and 2.5 show the partitioning SOC into different fractions and then relating SOC fraction to RothC pools after Zimmermann *et al.* (2007). The measured C in rSOC fraction is directly associated with the inert organic carbon pool. The sum of C in POC and DOC fractions has been split into DPM and RPM pools using the ratio of DPM: RPM

obtained by RothC under equilibrium condition. The same procedure has also been used to separate the sum of C in S + A and $s + c - r$ SOC fractions into BIO and HUM pools.

One of the most important issue in the SOC model is inert organic matter pool (IOM)/refractory SOC. Falloon and Smith (2000) discuss the issue of the IOM and its representation in models. IOM is defined in the RothC as an inert pool which does not go under decomposition, means that it is not a dynamic pool. Although, different chemical methods are able to produce an old, chemically recalcitrant and stable SOC fractions, they nevertheless are not completely inert and do not correspond to IOM as defined by RothC (Bruun *et al.* 2008; Balesdent 1996; Falloon and Smith 2000). Further model research into harmonising measured recalcitrant fractions of SOC and the IOM pool of RothC may be necessary.

There is debate on “modelling the measureable or measuring the modelable” (Elliot *et al.* 1996), however, process-oriented multi-compartmental models could be improved by modifying their different pools/compartments so that they are based on measureable SOC fractions which are unique, non-composite and in accordance with different stabilization mechanisms of SOC.

2.5.6. Initialization of SOC models

Model initialization (initial distribution of total SOC between model pools) is required in order to simulate SOC dynamics (Thornton and Rosenbloom 2005). Model initialization has been described as the most crucial part of simulation study as it can influence whether model predicted soil C will increase or decrease (Falloon and Smith 2000; Carvalhais *et al.* 2008). Incorrect or flawed initialization potentially leads to incorrect assessment of inter-annual variability, and can also produce fallacious trends in output as the state variables drift back towards the model ideal (Yeluripati *et al.* 2009). As various pools in SOC models are based on qualitative concepts and often do not correspond to measureable fractions, the partition of SOC appropriately into different pools for the purpose of model initialization introduces an initialization problem (Falloon and Smith 2000). Thus, the model output may reflect not only the effect of the modelling objectives, but also initialization procedure. The most common approach to solve the initialization problem is to achieve the initial SOC pool

distribution by a spin-up run of the model, *i.e.* a run of the model over several hundreds to thousands of years to find equilibrium/steady state SOC, assuming initial SOC and its distribution among the model pools are at equilibrium/steady state with the current land use and climatic conditions (Jenkinson 1990; Smith *et al.* 2005; Coleman and Jenkinson 2008). The observed soils, however, may not be at equilibrium due to disturbances such as fire, erosion, land use and management changes (Wutzler and Reichstein 2007). The equilibrium/steady state assumption for the ecosystem C cycle has been challenged (Cannell and Thornley 2003; Ludwig *et al.* 2010) and its limitation in modelling approaches emphasized (Pietsch and Hasenauer 2006; Wutzler and Reichstein 2007). In second method, where recent land use and management condition is known, the model is started with default or steady-state pool distribution and then run for a few decades to obtain a quasi-steady state distribution under recent conditions (Parton *et al.* 1993; Kelly *et al.* 1997; Smith *et al.* 2009). However, there is rarely enough information about the past condition for a large area to initialize model correctly. A third approach is to run most pools to steady state and then adjust the slowest pool so that the total SOC content matches the measured content (Parton and Rasmussen 1994; Wutzler and Reichstein 2007). Rapidly turnover pools reflect the current and recent state of the system, while slowly turnover pools reflect historical condition. Additionally, a fourth method is the using statistical model-data fusion technique to match pool distribution with observed C dynamics during the period of model simulation (Yeluripati *et al.* 2009; Carvalhais *et al.* 2010). Finally, the fifth method of initialization of SOC model is initializing model with measured SOC pools.

The use of measured SOC pools has the advantage over other initialization methods as field measurements are independent of the model or any assumption, and information regarding past land use and management history are not required (Zimmermann *et al.* 2007). Any process that is ignored in the model, but which could influence SOC dynamics, is also taken into account in SOC partitioning. Thus, measured fractions reflect better the real site specific conditions under which SOC is accumulated (Zimmermann *et al.* 2007; Xu *et al.* 2011). Once the SOC pools are measured by a reliable fractionation method, model initialization issues can be solved and model performance can also be improved (Leifeld *et al.* 2009).

2.5.7. Evaluation of SOC models

Model evaluation is the assessment of model performance and is a prerequisite before model application (Smith and Smith 2007). There are many benefits of model evaluation: 1) it shows how well a model can be expected to perform in a given situation i.e. it determine the accuracy of the simulation, 2) it analyses the behaviour of model, whether the model responds in the expected way to changes in the conditions of simulation, 3) it determines which components of the model are most important in influencing the results, and 4) it can help in improving the understanding of the system as well as improving the model specially where the model fails (Smith 2002; Smith and Smith 2007; Falloon and Smith 2009). A graphical analysis gives a quick approximate evaluation, whereas a quantitative analysis determines the statistical accuracy of the simulation and tells us how confident we can be in simulated results. Some statistics measure association and others measure coincidence between measured and simulated values. A sensitivity analysis evaluates the behaviour of model, whereas uncertainty analysis determines how much uncertainty is introduced in model output by each component of the model. These statistical parameters are defined in Smith *et al.* (1996b, 1997) and summarised in Smith and Smith (2007).

Model performances are generally assessed using long-term experimental data set. Models can be evaluated at different levels viz. individual process level, subset process level (*e.g.* net mineralization), or the model's overall outputs (*e.g.* changes in total SOM over time). Many forms of SOC model evaluation were presented by Molina and Smith (1997). The most comprehensive evaluation of SOC models was completed by Smith *et al.* (1997). Nine models were tested against 12 data sets, across different countries including Australia, from seven long-term experiments representing arable rotations, managed and unmanaged grassland, forest plantations, and natural woodland regeneration. Results showed out of nine SOC models, six model including RothC performed well.

2.5.8. Evaluation of SOC models under land use change

Land use change (LUC) is of global concern as it is the second largest source of human-induced greenhouse gas emission after the combustion of fossil fuels (IPCC 2007). Historically, soils have lost between 40-90 Pg C globally through cultivation and disturbance

(Schimel 1995; Houghton *et al.* 1999), and it is estimated that change in land use alone emitted 1.6 ± 0.8 Pg C yr⁻¹ to the atmosphere during 1990s (IPCC 2001; Smith 2004). Expansion of cropland is one of the major drivers of LUC emissions (Smith *et al.* 2010) and is likely to continue into the future. The magnitude of change of SOC following LUC varies widely among different sites due to different environmental conditions (such as soil type, texture, mineralogy etc.), climate, ecosystem productivity, plant species and the intensity of management (Guo and Gifford 2002; Poeplau *et al.* 2011). The prediction of change in SOC as a consequence of rapid changes in land use is a very important task for the future, and SOC dynamic models are one of the most promising tools in this respect (Barancikova *et al.* 2010). Model performances are generally evaluated using long-term field experimental data set, collected in chronosequence (Smith *et al.* 1997). Model performance in simulating change in SOC under LUC can also be assessed using chronosequence data sets (Cerri *et al.* 2007). However, there are extremely few cases where chronosequence data have been collected before and after a LUC. In this respect, paired-sites offer an opportunity to study LUC effects on SOC and can provide a basis for SOM model evaluation. Paired-site consists of two sites viz. a site where LUC already occurred several years before and an adjacent remnant, native-vegetation site, located on a common soil type, landscape position, aspect and slope angle.

2.5.9. Projection of soil organic carbon under climate change

A number of studies have examined the potential of soil C sequestration for climate mitigation options (Lal 2004; Smith 2004; Smith *et al.* 2008b); but, climate change will be a key driver of change in soil C stock during 21st Century (Smith *et al.* 2005). Increases in mean air temperature are likely to accelerate SOC decomposition and loss of SOC in future, until soil moisture is not a constraint (Smith *et al.* 2005, 2006). On the other hand, any increase in soil C input from, for example, increased ecosystem productivity through CO₂ fertilization or climate change, or technological and management improvement, could compensate the loss (Smith 2005; Smith *et al.* 2005). Increase extreme climatic events and drier climate could reduce ecosystem productivity and thus could offset any positive impacts of climate change and CO₂ fertilization on soil C inputs through ecosystem productivity. Ultimately increase in SOC decomposition and change in soil C inputs will determine the fate

of soil C reserve under future climate change. Therefore, simulation of the fate of SOC under climate change is very important.

Grassland is one of the most important and widespread terrestrial ecosystems, covering approximately 40% of the global land surface, and containing the largest share (39%) of terrestrial soil C stocks (~ 580 Gt C) (White *et al.* 2000). Any change in SOC storage in grasslands will have a significant and long-lived effect on global C cycles (Parton *et al.* 1995). Therefore, estimates of changes in grassland soil C stocks under climate change are of critical importance (Smith *et al.* 2005).

2.6. Soil carbon modelling efforts in Australia

Modelling SOC dynamics with long-term Australian datasets in different pasture and cereal cropping systems was started in late 90s, for example Smith *et al.* (1997) used two long-term data (Tamworth legume/cereal rotation and Waite permanent rotation) to evaluate nine SOC model (RothC, CENTURY, DNDC, CANDY, DAISY, SONM, NCSOIL,ITE and Verberne), with most the model perform satisfactorily. From a another simulation study with DNDC by using the same data sets, Li *et al.* (1997) reported significant loss of SOC stocks due to conversion of grassland to cropland with reaching a new SOC equilibrium within ~70 years at about 44% of the previous SOC level. After that many SOC models (APSIM, SOCRATES, CENTURY, RothC etc.) has been successfully used in Australia for simulations of SOC dynamics under different pasture and cropping systems with a ranges of different management practices (Ranatunga *et al.* 2001; Hill 2003; Skjemstad *et al.* 2004 Grace *et al.* 2006a, 2006b; Liu *et al.* 2009; Luo *et al.* 2011). The Australian Government's National Carbon Accounting System (NCAS) was developed over the past decade to report Australia's land-based greenhouse gas emissions and removals (transfers to and from the atmosphere) to the United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto Protocol (AGO 1999). The NCAS integrates a wide range of spatially referenced data and modelling that estimates carbon stock changes and greenhouse gas (GHG) emissions at fine spatial and temporal resolutions and support greenhouse gas mitigation and the sinks development agenda. Under the NCAS project, RothC was calibrated at two sites, Brigalow Catchment Study in the arid subtropics in Queensland, and Tarlee Rotation Trial in a

Mediterranean climate in South Australia. Result showed that the measured soil carbon pools fitted well with the ‘conceptual’ pools of the RothC, provided that the decomposition rate constant of the RPM pool reduced from 0.3 to 0.15 y^{-1} . (Skjemstad and Spounce 2003; Skjemstad *et al.* 2004). The performances of the calibrated model, which was further evaluated by using a total of 26 long-term rotation trials and existing paired sites (studying land use change effects on SOC) across Australia, showed good model performance (Skjemstad and Spounce 2003). This soil carbon model (RothC) has been incorporated as soil sub-model into a full carbon system model FullCAM developed by the Australian green house office (AGO) (Richard and Evans 2000). FullCAM, operates in a fully spatial context; after calibration and testing (Richards 2001), the model is being used for development of carbon and GHG inventories in Australia.

2.7. Summary and research gap

A combination of physical fractionation methods with chemical fractionation methods have been successful in showing differences in SOC fraction sizes for different soils (Six *et al.* 2002; Zimmermann *et al.* 2007), However, there has been less work in defining functionally consistent turnover times of SOC fractions, and there remains a lack in methodologies that can fractionate SOC selectively in relation to their residence times and stabilization mechanisms (Chabbi and Rumpel 2009).

With regard to combined physical and chemical fractionation methods which relate measured SOC fraction to model pools, one such fractionation procedure has been proposed by Zimmermann *et al.* (2007). However, few studies have been conducted to test the Zimmermann *et al.* (2007) approach (Dondini *et al.* 2009; Leifeld *et al.* 2009; Xu *et al.* 2011) and its applicability to RothC pools needs to be tested further.

Evaluation of model performance is one of the most important steps in a simulation study. The performance of SOC models such as RothC have not been evaluated thoroughly across different soil types, climate, cropping systems and management practices in Australia. There are few studies which evaluated RothC performance particularly under cereal based cropping systems using long-term field experimental data sets (Smith *et al.* 1997; Skjemstad

et al. 2004; Liu *et al.* 2009). For example, RothC performance has not yet been evaluated in Australia under cotton based cropping system in irrigated Vertisols with different tillage practices using long-term field experiments.

In the absence of long-term chronosequence data sets particularly under LUC, paired-sites data sets could offer an opportunity for the evaluation of SOC models. However, evaluation of SOC models, such as RothC, using paired-site data under LUC is scarce.

Model initialization is the most crucial part of simulation. However, sensitivity of SOC model such as RothC to the method of model initialization in projection of grassland SOC dynamics under climate change has not been assessed yet.

About 85.4% of Australian continent is grassland, which represent the largest share (12.5%) of total global grassland among all countries (White *et al.* 2000). Increases in temperature and reductions in rainfall over most of mainland Australia are expected in 21st century (CSIRO and Bureau of Meteorology 2007). Although some studies have examined the potential impact of climate change on grassland SOC elsewhere (Smith *et al.* 2005; Xu *et al.* 2011), the potential response of grassland SOC to climate change in Australia has not yet been assessed.

The above mentioned research gaps have been utilised to develop the hypotheses in this thesis. The following experimental chapters (chapters 3-7) deal with evaluation of the performance of RothC in simulation of SOC dynamics with both paired site data sets and long-term data set, and exploration of different aspects of modelling SOC dynamics using RothC under different land use and crop management practices.

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Chapter 8: General conclusion and future research

In this thesis, RothC was evaluated, and aspects of modelling SOC dynamics under different land use and crop management practices were explored using the same SOC turnover model through the five experimental chapters (chapter 3-7). This final chapter summarizes the key findings, conclusions, implications of the results and provides an indication of scope for future research.

8.1. Key findings

- (1) Particulate organic carbon (POC) contained modern carbon (C) with short to medium turnover time (~10 - 360 yr), silt + clay (*s+c*) associated C was relatively older with an intermediate turnover time (~230 - 3100 yr), and the inert organic carbon fraction (IOC) contained the oldest C with a radio C age ~ modern – 2000 yr (chapter 3).
- (2) Over all the sites (16 native vegetation areas and 16 cropped areas), the measured soil organic carbon (SOC) pools of biomass (BIO), humus (HUM) and inert organic matter (IOM), as determined by a combined physical and chemical laboratory SOC fractionation method, proposed by Zimmerman *et al.* (2007), were very close to their corresponding default equilibrium SOC pools of Rothamsted carbon model (RothC), whereas modelled values of the decomposable plant material (DPM) and resistant plant material (RPM) pools were slightly larger compared to measured values, particularly in cropping land. Across all sites, measured and modelled pools were significantly correlated (chapter 4).
- (3) When RothC was evaluated using paired-site data sets, the model performed satisfactorily ($r = 0.97 \sim 0.98$, $EF = 0.93 \sim 0.96$, $RMSE = 5.89 \sim 7.82$, $E = -1.82 \sim 2.64$) in simulating the effect of land use change (LUC) on SOC dynamics, particularly following the LUC from native vegetation to cropping (chapter 4).

- (4) Initializing RothC with measured SOC pools ($r = 0.98$, $EF = 0.96$, $RMSE = 5.89$, $E = -1.82$) rather than using default model equilibrium pools ($r = 0.97$, $EF = 0.93$, $RMSE = 7.82$, $E = 2.64$) did not improve model performance in prediction of LUC effects on SOC dynamics. The absolute deviations between measured and simulated total SOC values of the two initialization methods separately were not significantly different. (chapter 4).
- (5) RothC satisfactorily simulated SOC dynamics for the period 1994 - 2008 under continuous cotton/minimum tillage (CC/MT) (LOFIT = 44-46, $RMSE = 3.1$, $E = -2.2$ and $r = 0.90$) and cotton-wheat rotation/minimum tillage (CW/MT) (LOFIT = 48-172, $RMSE = 3.2-5.9$, $E = -1.9$ to -4.8 and $r = 0.88-0.92$), but the model performance was poor under continuous cotton/conventional tillage (CC/CT) (LOFIT = 220-223, $RMSE = 7.5-7.6$, $E = -6.6$ and $r = 0.80-0.81$). A minimum of 69% reduction in soil C input could significantly simulate the SOC dynamics under CC/CT (LOFIT = 58, $RMSE = 3.9$, $E = -0.6$ and $r = 0.88$) (chapter 5).
- (6) The dynamics of SOC were simulated under present cotton-based cropping systems for the period 1994 – 2008 for evaluation of RothC (Key finding 5). These simulations were continued from 2009 onwards to explore different scenarios of SOC dynamics. In an irrigated Vertosol, existing cotton based cropping systems were predicted to lose soil C continuously from 2009 onwards until they reached equilibrium. At equilibrium, a loss in SOC of 62%, 2% and 16% of their 2008 levels were predicted under CC/CT, CC/MT and CW/MT, respectively and the losses were 70%, 18% and 34%, respectively of their initial (1994) levels. Simulated results showed that inclusion of winter vetch (*Vicia spp.*) in the fallow period with cotton monoculture and cotton–wheat system could potentially reduce the loss in SOC stocks from their initial levels to 2 - 17% and 7%, respectively within 15 years. Similarly, inclusion of a summer forage legume with the CW/MT system had the potential to reduce the loss in SOC stocks to 11%, whereas inclusion of summer grain cereals could improve SOC stock by 1 - 10% compared to initial SOC level within the same time period. These proposed simulated cotton based cropping/tillage systems could potentially elevate equilibrium SOC levels by 0.5 - 2.0 times compared to the equilibrium levels under the current cropping systems (chapter 5).

- (7) Averaged over the sites and initialization methods, maximum absolute variations as well as averaged absolute variations in projection of grassland SOC under climate change across the northern slopes and plains of New South Wales (NSW), Australia, were 2.2% and 1.6%, respectively throughout the projection period (2008 -2100). There were no significant differences in projected grassland SOC stocks under climate change after 93 years (2008-2100) of simulation with model initialization by different methods. Averaged over the sites, mean absolute variation in the projected SOC stocks was 1.6% after 93 years of simulation in 2100 across the initialisation methods (chapter 6).
- (8) When climate impacts on SOC were considered alone, averaged over the global climate models (GCMs), grassland SOC stocks across the northern slopes and plains of NSW were predicted to fall 12%, 10%, 8% and 6% on 2008 levels by 2100 under A1FI, A2, B2 and B1 climate scenarios, respectively. This represents a cumulative emission of 66-159, 66-158, 65-157 and 65-156 t carbon dioxide (CO₂) ha⁻¹ across the region under A1FI, A2, B2 and B1 climate scenarios, respectively. There was no significance difference between different GCMs forced with same climate scenarios in projected SOC stocks as well as cumulative losses of CO₂ in 2100. Projected SOC stocks in 2100 under different GCMs forced with same climate scenarios were significantly correlated. Correlations were also significant between GCMs in projected cumulative losses of CO₂ in 2100 (chapter 7).

8.2. General conclusions and implication of the results

8.2.1. Combined physical and chemical SOC fraction methods and meaningful SOC fractions

Partitioning SOC into well defined and meaningful fractions with distinct turnover rates and in accordance with SOC stabilization mechanisms is always a challenge. Although the POC fractions of the present study contains both free as well as occluded particulate organic matter and had short to medium (10 ~ 360 yr) turnover time, strong evidence of soil physical protection, as provided by secondary soil mineral complex *i.e.* soil aggregates (Six *et al.* 1999, 2002), was not found when comparing mean residence time (MRT) of this fraction

between Vertosols and Chromosols. Reasons for this may relate to interferences from charcoal material present in this fraction and lack of sample replications. This fraction was, however, comparatively younger and had distinct MRT compared to that other fractions across the soil types and land use systems. A relatively older C with an intermediate turnover time (235-3155 yr) was found in the *s+c* fraction, suggesting a comparatively longer SOC protection provided by silt and clay particles in accordance with the theory of chemical stabilization mechanism (Six *et al.* 2002). Chemical oxidation treatment of the *s+c* fraction resulted in an old C fraction that could be considered as stabilized through biochemical stabilization mechanism due to its chemical inertness (Six *et al.* 2002). The results provided confidence for the approach to capture different SOC stabilization mechanisms with a combined physical and chemical fractionation method, as compared to only using either of these two methods. Similar results were reported by other studies (Trumbore and Zheng 1996; Six *et al.* 2002; Plante *et al.* 2004). Thus, a combination of physical and chemical fractionation methods could separate SOC into meaningful SOC fractions, *i.e.* fractions with different ages and turnover times in accordance with different SOC stabilization mechanisms. A combined SOC fractionation method would be appropriate to relate different measured SOC fractions with different conceptual pools of SOC turnover models.

*8.2.2. SOC fractionation method of Zimmermann *et al.* (2007) and conceptual pools of RothC*

Measured SOC fractions often do not correspond to model pools, because model pools are conceptual and their relative proportions as well as turnover times have been derived from empirical relationships. However, results from the previous objective (8.2.1) showed that a combined physical and chemical fractionation method could help in linking measured SOC fractions with conceptual pools of SOC turnover models. A more detailed approach of a combined SOC partitioning method has been suggested by Zimmermann *et al.* (2007) to directly relate measured SOC fractions specifically with conceptual pools of RothC. Results of the present study indicated that both the fractionation method and the model RothC partitioned the total SOC into pools with equal efficiency at equilibrium under native

vegetations. However, under cropping, the agreement between measured and modelled pools of DPM and RPM was less satisfactory. The reasons for less satisfactory agreement between these measured pools in cropping land and model equilibrium pools could relate to the violation of equilibrium assumption in the cropping land which might not be under equilibrium due to recent (23 - 47 years) land use change history, and soil sampling time, which is not taken into account by the model equilibrium condition, but would be reflected in the measurements. Leifeld *et al.* (2009) too found systematic differences in the measured and modelled pools of DPM, RPM, and BIO under cropping land in a study of conventional *versus* organic farming. In a study for Irish bioenergy croplands (*Miscanthus*), Dondini *et al.* (2009) observed the best correlation between measured and modelled pools for the HUM pool only. Similar results were reported by Zimmermann *et al.* (2007) in cropping land. However, measured SOC pools reflect better the real site specific conditions under which SOC is accumulated compared to model conceptual pools, as the measurements are independent of the model or any assumptions and any process that is ignored in the model, but which could influence SOC dynamics, is also taken into account in SOC partitioning (Zimmermann *et al.* 2007; Xu *et al.* 2011). The model RothC might need modification, and subsequent recalibration for these pools (such as DPM, RPM), to simulate SOC dynamics more accurately under a land use which has recent disturbance history.

Overall the partitioning method of SOC has the potential to partition SOC into pools as close as model conceptual pools in RothC. The method could be useful for determining details of the initial SOC pools structure of RothC and thus could enable model initialisation at any point in the landscape without knowing detailed management history of the site. The method also may provide a rare opportunity in thorough evaluation of RothC performance, not only for final output but also for all individual model pools. Thus, it could help in building confidence in using the SOC model, improve our understanding of SOC dynamics, and assist in model improvement.

8.2.3. Paired site data set and evaluation of RothC

Long-term chronosequence data are often used for model evaluation. But, such chronosequence data sets for SOC under the scenario of LUC are generally scarce. RothC performed satisfactorily in simulating the effect of LUC on SOC dynamics when the model was evaluated using paired site data sets. The study showed that in the absence of long-term data sets, paired site data could be useful to evaluate RothC in simulation of the effect of LUC on SOC dynamics. RothC could be used with confidence in projection of SOC stocks under LUC in the northern plains and slopes of NSW, Australia. RothC can be used to predict total SOC stock at any point in time after LUC from native vegetation to cropping in the region. However, to more widely use RothC in Australia's other agro-ecological regions, the model will first need to be evaluated with more paired-site data sets across as many different regions and soil types as possible.

8.2.4. Model initialization with measured pools vs. model equilibrium pools and performance of RothC in prediction of land use change effects on SOC dynamics

Laboratory measurements of model pools are often believed to better reflect site specific conditions as they are independent of models or any assumptions, and as they include all processes under which soil C actually accumulated. Thus, initialization of SOC models with measured pools, rather than using model spin up pools or any other mathematically calculated pools, could improve the model performance.

Leifeld *et al.* (2009) reported slight improvement in RothC performance in simulation of cropping land SOC dynamics by initializing the model with a measured SOC pool structure compared to model equilibrium pools. However, the question remained unanswered in their study whether the improvement in model performance was significant. It was also not known, whether the model performance in simulating the effect of LUC on total SOC, particularly following a proposed LUC from native vegetation to cropping, could significantly be improved by the use of measured SOC pools for model initialization instead of using model default equilibrium SOC pools.

The results of the present study showed that absolute deviations between measured and simulated total SOC stocks values with the two initialisation methods [initialization with detailed SOC pools structure as measured by the method suggested by Zimmermann *et al.* 2007 (section 8.2.2) vs. model equilibrium pools] separately were not significantly different. Thus, improvement in the model performance was not significant. Therefore, the laborious analytical effort in partitioning SOC into pools for the purpose of model initialization may not be justified in simulation of the effect of LUC on SOC dynamics, particularly LUC from native vegetation to cropping.

8.2.5. Evaluation of RothC under cotton based cropping system in irrigated Vertosols

Results from evaluation of RothC under cotton based cropping system, on an irrigated Vertosol with minimum tillage, with a long-term field experimental data set showed that the model performed satisfactorily to simulate the SOC dynamics. Kintché *et al.* (2010) too had reported satisfactory RothC performance under cotton-based cropping systems in Africa. RothC has good potential in simulation of SOC dynamics under cotton based cropping system in irrigated Vertosols in Australia, in particular for the exploration of different scenarios of SOC dynamics under different crop management systems. But, for the predictive modelling of SOC dynamics under cotton based systems with conventional tillage, the model might require further improvements. The model RothC does not take account of soil aggregation dynamics and its inclusion in the model could improve model performance under different tillage management systems (Krull *et al.* 2003; Liu *et al.* 2009).

8.2.6. Exploration of different scenario of SOC dynamics under cotton based cropping system

Simulation results indicated continuous loss of SOC under present cotton based cropping systems in irrigated Vertosols in the study region, until they reach their equilibrium. One of the options applied to reduce the loss of SOC under these cropping systems is the adoption of minimum tillage. The results of the present study were in line with reported data from different field experiment studies under cotton based cropping on irrigated Vertosols

(Constable *et al.* 1992; Hulugalle *et al.* 1997, 2005; Hulugalle and Daniells 2005; Hulugalle and Scott 2008).

Model simulation results of the present study showed that inclusion of winter vetch (*Vicia spp.*) in the winter fallow period of the cotton monoculture (summer cotton-winter fallow) has the potential to reduce the loss of SOC significantly under continuous cotton, both with conventional and minimum tillage. Similarly, inclusion of summer forage legumes or summer grain cereals, such as corn and sorghum in summer fallow, or winter and autumn vetch in winter fallow, in cotton-wheat/minimum tillage (summer cotton-winter wheat-summer fallow-winter fallow) has the potential to reduce the loss of SOC stocks under cotton based cropping system in irrigated Vertosols. Potential reduction in loss of SOC, or even improvement in SOC levels, under proposed simulated cropping/tillage systems could be explained by increased amount of total annual soil C inputs from new crop inclusions in fallow period and reduction in SOC decomposition due to extra soil cover as provided by the new crops in fallow periods (Jenkinson 1977). The benefits of inclusion of rotation crops, such as winter and autumn vetch, summer and winter legumes, and summer cereals, with the cotton-based cropping systems on SOC have been reported from different field and simulated studies (Rochester *et al.* 1998; Hulugalle and Scott 2008; Kintché *et al.* 2010, Hulugalle *et al.* 2012).

8.2.7. Projection of change in grassland SOC under climate change by RothC and sensitivity RothC to the method of model initialization

Model initialization is a crucial step for future projections, as incorrect or flawed initialization could potentially lead to incorrect assessment of inter-annual variability and produce fallacious trends in output. Investigation on the sensitivity of RothC to the different methods of model initialization in projection of grassland SOC dynamics under climate change showed that the maximum absolute variations as well as averaged absolute variations throughout the projection period of 2008-2100 were very small. Averaged over the sites, absolute variation in projection of grassland SOC due the different initialisation method was also small after 93 years of simulation in 2100. Differences in projected grassland SOC stocks

with different methods of model initialization under climate change were also non-significant in 2100. Thus, the study implied that model projections of change in grassland SOC under climate change are relatively insensitive to the methods of model initialization in relatively undisturbed land use systems such as native grassland, and simple model spin-up of SOC pools is as reliable for model initialization as more labour intensive and expensive soil fractionation methods.

8.2.8. Projection of change in grassland SOC under climate change in the northern slope and plane of NSW, Australia, 2008-2100

Simulation of the direct climate impact on SOC stocks in native grassland in the northern plains and slopes of NSW projected a fall of 6-12% in SOC stocks on the 2008 levels within a time period of 93 years, 2008-2100, with the range defined by the climate scenario. The direct climate impact projection on grassland SOC stocks of the present study (10-11% fall in a period of 93 years) was comparable to other similar studies in Europe (Smith *et al.* 2005; Xu *et al.* 2011). Smith *et al.* (2005) projected a loss of 6-10% of the mean European grassland SOC stocks within a time frame of 90 years (1990-2080) depending on the emission scenarios, whereas Xu *et al.* (2011) projected a loss of 2-6% of grassland SOC stocks in Ireland across different emission scenarios within a time period of 40 years (2021-2060).

To offset the direct climate impacts, as simulated in the present study, on grassland SOC in the northern plains and slopes of NSW, a regional average increase of 15-27% in the grassland annual soil C inputs (compared to 2008 levels) was projected to be required. On average, a regional increase of up to 6.5% in total annual soil C input in grassland is likely to be gained from ongoing technological and management improvements (such as introduction of improved grass species, incorporation of clover, grazing control, application of super-phosphate, pasture cropping, lime/gypsum application). Thus, loss of grassland SOC stock in the region under climate change seems to be unavoidable. However, a 1% increase in C input

could offset a 0.46%-0.47% loss in grassland SOC under climate change for the time period 2008-2100. Any fall in C input could exacerbate SOC loss at similar rates.

8.3. Scope for future research

Soil organic C turnover models, such as RothC, do not take detailed account of the entire process of soil aggregate formation and destruction which is essential to examine closely different types of soil management practices (such as application of crop residues, manure, irrigation, handling of farm machinery) and tillage (intensity and types of tillage implements). The dynamics of soil aggregation and aggregate breakdown alter the turnover rates of SOC; strong soil aggregation may slow down the turnover rate of different SOC pools, and aggregate disruption by continuous intensive tillage could enhance the turnover rates (Krull *et al.* 2003). Future work is needed to include aspects of soil aggregate behaviour into RothC to potentially improve model performance under different types of tillage management systems.

In this study, climate change impact was projected on grassland SOC stocks. Climate change impact on SOC stocks in cropping land deserves further detailed investigations across agro-ecological regions and cropping systems. Change in soil carbon input in cropping land through changes in crop productivity due to climate change and improvement in technology also require to be taken into account in climate impact studies on cropping land SOC dynamics. Crop production models such as APSIM (Agricultural Production Systems Simulator) offer value in future research to incorporate these changes in crop productivity by accounting for differences in soil C input. At the same time, it will be important to examine whether RothC will also remain insensitive to different initialization methods in projection of change in cropping land SOC stocks under climate change.

Soil C turnover models are being increasingly used to support policy decisions regarding change in SOC storage and CO₂ emission from soil, as influenced by future land use change, climate change and change in land management practices. In this present study

the SOC turnover model RothC was evaluated under limited conditions, using both long-term field experiment data and paired-site data sets under land use change, in the northern slopes and plains of New South Wales. Further research is required to expand the model evaluation as widely as possible across different soil types, climate, ecology and land use management practices across all of Australia's agro-ecological regions, to gain confidence for its wider application at regional and national scales.

In this study, annual soil C inputs were calculated separately to run RothC, as the model does not have any crop sub-model or any sub-module to calculate soil C inputs. Thus, the model is devoid of any response in plant productivity due to change in particular soil processes. Other models which link plant and soil modelling together such as DNDC, CENTURY, APSIM and DAISY could be used in future studies to examine a set of similar objectives as used in this study, but in multi-model mode for comparing model performance and evaluating opportunities for model improvements.

Model performances are generally assessed with respect to the model's overall outputs (*e.g.* changes in total SOC over time) and thus model evaluation at individual process level or subset process level (*e.g.* net mineralization) remains untouched. It often raises questions about robustness of its structure at different conceptual compartments. A major limitation of processed-based multi-compartmental SOC turnover models is that SOC is described by the various conceptual compartments/pools using simplified, deterministic and multi-compartmental simulations that are primarily based on empirically derived relationships which often do not correspond to measureable fractions (Cambardella 1998; Elliot *et al.* 1996; Smith *et al.* 2002; Bruun *et al.* 2003; Zimmermann *et al.* 2007). There remains a lack of methodology that can partition SOC into different pools in relation to their size, residence time and stabilization mechanisms as assumed in different multi-compartmental models. To improve confidence in using these multi-compartmental SOC turnover models, they should be further evaluated for their individual compartments. A combined physical and chemical SOC fractionation method proposed by Zimmermann *et al.* (2007) was evaluated in this study to link measured SOC fractions to conceptualized pools of RothC. However, such methods need

to be assessed across a wider range of soil types, climatic regions and land use systems using long-term experimental data sets. Evaluation of RothC performance with long-term data sets for its individual pools against measured pools could be a task of future work, potentially resulting in subsequent model recalibration for different soil types, climatic regions and land use systems. Thus, process-oriented multi-compartmental models could be improved by modifying their different compartments/pools, so that they are based on measurable SOC fractions. Further research is also needed to demonstrate that measured SOC fractions are in accordance with different SOC stabilization mechanisms, and are equivalent to model pools, *i.e.* measured fractions are unique as well as non-composite, otherwise these measured fractions will add no extra information but only enhance model complexity and propagation of errors.

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