

# CHAPTER 1

## INTRODUCTION

Cotton growing in Australia started with the arrival of the first fleet of European settlers in 1788, although the modern cotton industry began in the early 1960s. Since then, the cotton industry in Australia has evolved into an intensive production system that is now Australia's fifth-largest rural export earner after wool, meat, wheat and sugar. Production grew rapidly from 19.8 Mt in 1972 to 484 Mt in 1992 when Australia became the world's third-largest cotton exporter (Pepper, 1995). Most Australian cotton (*Gossypium hirsutum* L.) is grown on cracking clay soils in New South Wales (NSW) and Queensland (Qld) between latitudes 23°S and 32°S (Figure 1.1). These areas have a widely varying climate with summer crop season rainfall ranging from 100 to 600 mm, and average maximum and minimum temperatures ranging between 33/19°C and 17/4°C for mid-summer and mid-winter, respectively (Constable *et al.*, 1988). Cotton growing operations range in size from a few hectares on mixed dryland farms to large commercial farms of up to 45,000 hectares in north-west New South Wales.

Cultivation practices vary from one region to the other. Despite these variations, Constable *et al.* (1992) summarised a common standard system of growing cotton in Australia as follows: "Soil is cultivated with offset discs to a depth of 0.2 m, followed by chisel ploughing to a depth of 0.2 m, then the soil is formed into hills (1 m spacing, 0.2 m high); usually N is applied as anhydrous ammonia under each crop row at the same time. Deep ripping is now only recommended on dry soil if it is compacted. Herbicides are used for weed control both pre- and post-sowing; inter-row cultivation is also done during early crop growth. The crop is sown in early spring (October) to establish ten plants per metre; it is furrow irrigated on about five occasions; insect-pest-control sprays and defoliants are applied by aircraft. Mechanical harvest is in autumn (March - June), following which the stubble is slashed to within 5 cm of the soil surface. Rotations vary from continuous cotton (up to 15 years) to alternating cotton and wheat, where there is a 9-month fallow period between harvest and cotton sowing."

In recent years, Australian cotton growers have achieved average yields that are among the highest in the world (McKenzie *et al.*, 1995). However, cotton production is more demanding of the soil than most other forms of cropping as many potentially soil degrading operations are involved. As a result of the long growing season of cotton (September - April), under continuous cotton production very little time exists between the harvest of one crop and land preparation for the next crop. Soil condition is important if the full benefits of improved cotton varieties and biotechnology are to be

realised. Therefore, maintaining the long-term physical and chemical health of the soils used for cotton production must be a key goal for sustainable cotton production.

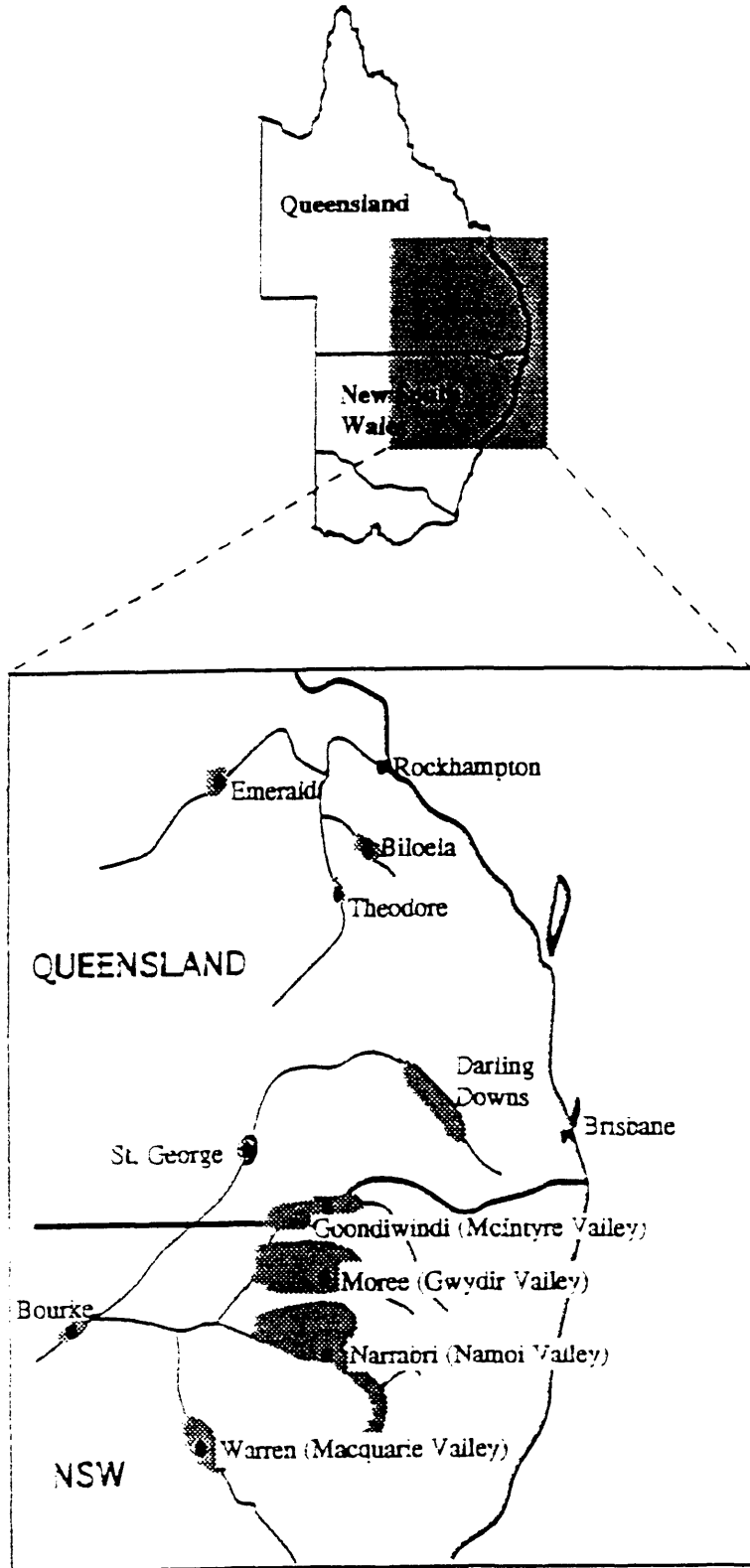


Figure 1.1: Map of Eastern Australia showing major cotton growing regions of New South Wales and Queensland

Most Australian cotton growers now realise that they have to achieve both financial and ecological sustainability when managing their soils. To achieve these goals, soil quality must be maintained at a level which ensures that none of the following soil related factors are allowed to restrict cotton growth and function; aeration, water supply, nutrition, temperature, and hardness. However, the cracking clay soils on which cotton is typically grown are prone to compaction. This can lead to a reduction in soil aeration, reduced infiltration of water, increased denitrification, and a condition where roots are unable to penetrate the dense layer of soil. This in turn reduces yields and farm income. In the longer term, a reduction in soil quality reduces the land value, and this, combined with shorter term reductions in yields and income, provides growers with strong incentives to avoid or reverse adverse soil conditions.

All of the soil problems outlined above can be alleviated through efficient management of the organic matter concentrations in the soil. The soil organic matter concentration of a soil is a key indicator of a sustainable cropping system because of its influence on the physical, chemical and biological health of a soil. Soil organic matter adds structure, stability and permeability to soils high in clay (Wallace, 1994). For all soils, it is a source of nutrients through its decomposition or through its contribution to the soil's cation exchange capacity (Schnitzer, 1991). Soil compaction and many other soil problems are mainly due to soil organic matter losses. Severe slaking of cracking clay soils have been reported when the soil is wetted if there is low organic matter (McKenzie *et al.*, 1995). Soil organic matter protects against heavy metal and salt toxicities (Wallace, 1994), it detoxifies pesticides and prevents their leaching down the soil profile (Arthur, 1989). In acid soils, organic matter has been reported to be a potential factor in improving the efficiency of soil and fertiliser phosphorus utilisation by reducing phosphorus fixation (Syers and Crasswell, 1995). With growing concern about atmospheric CO<sub>2</sub> levels, soil organic matter is a significant source and sink for atmospheric CO<sub>2</sub> (Powlson *et al.*, 1996). Therefore, the variations in organic matter concentration of a soil induced by a cropping system is a significant indicator of the sustainability of that cropping system.

A very useful example of how soil organic matter is of utmost importance to sustainable cotton production can be obtained from the experience of the Texas Blacklands, which was summarised by Wallace (1994) from the Texas Research Foundation report as follows: "The Blacklands of Texas occupy 26 million acres of land. Until about 1900, practically all of the agriculture of Texas was found in these prairies, and a long list of towns and cities grew up in this area. The soils of the Blacklands region have lost much of their fertility in the course of 50 to 100 years of continuous cultivation to cotton, and the entire area is now producing about half as much total harvested crop as was produced in the 1920s. The efficiency of agriculture in the Blacklands has fallen steadily in the last 30 years in spite of all efforts to breed better cotton, to control insects and diseases, and to adopt certain farming practices that are good in other regions. The evidence at

hand indicates that the soils have lost a major portion of the original soil humus; the soil structure has deteriorated as the soil is low in capacity to absorb and retain moisture." Wallace (1994) also quoted results from an earlier study in central Missouri and concluded that the loss of organic matter resulted in soil compaction, which hampers the circulation of air and water and hinders tillage operations at the same time, to the extent that the function of the soil in plant nutrition is disturbed. These reports, and several other reports, emphasise the need for soil organic matter management in attaining sustainable cotton production.

Management of soil organic matter under cotton production can be done through the retention of all stubble produced during the growing season or through the incorporation of a rotation crop in the cropping system. However, the success of any organic matter management strategy will have to depend to a large extent on methods that can detect and monitor short-term changes in soil organic matter quantity and quality. Since soil organic matter exists in a wide diversity of forms with considerable variability in decomposition rates, the loss of the labile fraction due to cropping is often greater than that assessed from the loss of the total soil organic matter.

The issue of what constitutes labile carbon in soil is unresolved. Approaches recommended for the estimation of the labile fraction of soil organic matter have ranged from water-extractable organic carbon (Leinweber *et al.*, 1995), carbon sorbed on carbonaceous resin capsules (Johns and Skogley, 1994), water-soluble carbohydrates (Baldock *et al.*, 1987), microbial biomass carbon (Degens and Sparling, 1996), light fraction organic carbon (Gregorich and Janzen, 1996), to permanganate-oxidisable carbon (Blair *et al.*, 1995b). Although the use of microbial biomass carbon in characterising the labile organic carbon has gained considerable interest, the question of reliable methodology remains unresolved (Martens, 1995). The light fraction carbon appears to have had the greatest consideration (Gregorich and Janzen, 1996). However,  $^{13}\text{C}$  NMR analyses have shown that the light fraction has a chemical composition similar to that of litter and plant material (Skjemstad *et al.*, 1986) and may contain charcoal (Skjemstad *et al.*, 1990), which has been identified as resistant carbon (Skjemstad *et al.*, 1996).

The primary concern of the work described in this thesis was to examine the potential value of a simple measurement of labile and non-labile carbon fractions to provide a sensitive monitoring indicator of organic matter changes under cotton cropping systems. Since sustainability is a systems issue, the study commenced with a general survey of the fertility status of soils used for cotton production (Chapter 3). The specific objectives of the survey were to examine the soil test values in the main soils used for cotton production and compare these values between cropped and uncropped reference sites. In Chapter 4, the changes in soil organic matter due to cotton production are examined using the carbon fractionation procedure based on ease of oxidation. The relationships between the carbon fractions obtained by ease of oxidation and other common measurements of soil

# CHAPTER 2

## LITERATURE REVIEW

### 2.1. INTRODUCTION

The work reported in this thesis examines the potential value of soil carbon fractions determined by ease of oxidation as indicators of sustainability. Thus, it is necessary to examine the concept of sustainability and previous attempts at developing indicators of sustainability. This literature review therefore starts by developing a framework of what constitutes a sustainable cropping system. This was followed by an examination of soil organic matter as an attribute of sustainable cropping systems and methodologies employed in assessing the dynamics of organic matter in soil.

### 2.2. THE CONCEPT OF SUSTAINABILITY

To be able to develop sustainable cropping systems, there is a need to understand what constitutes sustainable cropping systems and how sustainability can be measured. This section gives a general overview of the concept of sustainability and proposed indicators of sustainability.

#### 2.2.1. General Overview of Sustainability

The nature of scientific research is such that in order to determine whether efforts to design sustainable farming systems are successful, there has to be a conceptual framework of what sustainability is and how it can be quantified. There have been nearly as many definitions of sustainability as there have been people writing about it. Some of the definitions of sustainability are summarised in Table 2.1. Although much confusion still remains, some progress has been made in identifying the environmental, economic, and social dimensions of the concept. In the review of Keeney (1990), it was pointed out that sustainability differs widely depending on the viewpoints of the individuals and organisations involved. Zinck and Farshad (1995) mentioned that sustainability resembles a kaleidoscope with many facets which mirror variations in the concept. Each scientific discipline contributes to the definition of sustainability, and each user group adds a different dimension to the concept.

Sustainability is a systems issue. Spencer and Swift (1992) mentioned that although it is possible to talk, for example, about 'sustainable land management', sustainability is influenced as much by the interactions of soil processes with those of crop and weed growth, pest and disease

development, tillage and other labour activities as it is by each of these factors individually. Thus, in the broadest context, the concept of sustainability must address the human, cultural and ecological dimensions and include the wise management of natural resources and restoration of ecological systems.

**Table 2.1: Some Definitions of Sustainability**

Conway, 1985	Sustainability is the ability of a system to maintain productivity in spite of larger disturbances such as repeated stress or a major perturbation.
WCED, 1987	Sustainability is the ability of the present generation to meet their needs and aspirations without compromising the ability of the future generations to meet their own needs.
FAO, 1989	Sustainability is the use of agricultural systems which successfully manage resources to satisfy human need, while maintaining or enhancing the quality of the environment and conserving natural resources.
Keeney, 1989	Sustainability is the use of agricultural systems that are environmentally sound, profitable, productive and maintain the social fabric of the rural community.
Okigbo, 1991	A sustainable agricultural system is one which maintains an acceptable and increasing level of productivity, that satisfies prevailing needs and is continuously adapted to meet the future needs for increasing the carrying capacity of the resource base and other worthwhile human needs.
AIAS, 1995	Sustainable agriculture is the use of farming systems and practices which maintain or enhance the economic viability of agricultural production, the natural resource base, and other ecosystems which are influenced by agricultural activities.

Sustainability has both spatial and temporal variability (Spencer and Swift, 1992; Zinck and Farshad, 1995). Based on geographic variations in natural and human resources, the concept of sustainability has different meanings in different spatial levels. Whereas in arid areas sustainable land management is controlled by the efficient harvesting and application of water, in humid tropical areas this is achieved by nutrient conservation and cycling (Zinck and Farshad, 1995). Thus, what can be described as sustainable in one region will be different in another region. Therefore any efforts in determining sustainability of an agricultural system must take into account the spatial variability of the natural and human conditions controlling sustainability. Further questions on sustainability arise when temporal variability is considered. The issue of a time scale must also be addressed, that is, sustainable for how long? There is a need to answer questions such as the length of time a system can last without being disturbed and the length of time a disturbed system needs in order to recover. A crucial question is how to evaluate the time component of a land system under specific management practices. In their report on the sustainability of different agricultural production systems for a rainforest zone of southern Nigeria, Lal *et al.* (1990) suggested that a period of 5 - 10 years will be appropriate for agronomic productivity.

Sustainability has also been given different interpretations in different schools of thought. There are scholars who have looked at sustainability as an ideology. In this school of thought, Neher (1992) considered sustainability as an approach or a philosophy that integrates land stewardship with agriculture, where land stewardship is the philosophy that land is managed with respect for use by future generations. Francis and Youngberg (1990) also pointed out that sustainability is a philosophy based on human goals and on understanding the long-term impact of our activities on the environment and on other species. Use of this philosophy guides our application of prior experience and the latest scientific advances to create integrated, resource conserving and equitable farming systems.

There are also scholars who have looked at sustainability as a set of strategies. For instance, Carter (1989) stated that farming systems are sustainable if they minimise the use of external inputs and maximise the use of internal inputs already existing on the farm. Francis *et al.* (1987) considered sustainability as a management strategy which helps the producer to choose hybrids and varieties, a soil fertility package, pest management approach, a tillage system, and a crop rotation to reduce costs of purchased inputs, minimise the impact of the system on the immediate and the off-farm environment, and provide a sustained level of production and profit from farming. Ruttan (1988) saw sustainability as the development of technology and practices that maintain and/or enhance the quality of land and water resources.

Another school of thought has looked at sustainability as the ability to fulfil a set of goals. In this school of thought, Harwood (1990) stated that sustainable agriculture is agriculture that can evolve indefinitely toward greater human utility, greater efficiency of resource use, and a balance with the environment that is favourable both to humans and to most other species. The American Society of Agronomy (1989) concluded that a sustainable agriculture is one that, over the long-term, enhances environmental quality and the resource base on which agriculture depends, provide for basic human food and fibre needs, is economically viable, and enhances the quality of life for farmers and society as a whole.

More recently, Hansen (1996) examined conceptual and methodological barriers in using sustainability as a criterion for guiding change in agriculture and concluded that in order for sustainability to be a useful criterion for guiding change in agriculture, its characterisation should be literal, system-oriented, quantitative, predictive, stochastic and diagnostic (Table 2.2). From the available literature so far, measures to meet this characterisation are yet elusive.

**Table 2.2: Elements of a useful approach to characterising sustainability of agricultural systems**

Element	Explanation
Literal	Defines sustainability as an ability to continue through time, consistent with English usage.
System-Oriented	Identifies sustainability as an objective property of a particular agricultural system whose components, boundaries and context in hierarchy are clearly specified.
Quantitative	Treats sustainability as a continuous quality, permitting comparisons of alternative systems of approaches.
Predictive	Deals with the future rather than the past.
Stochastic	Treats variability as a determinant of sustainability and a component of predictions.
Diagnostic	Uses an integrated measure of sustainability to identify and prioritize constraints.

Adapted from Hansen (1996)

### 2.2.2. Indicators of Sustainability

Evaluation of the sustainability of cropping systems requires that there be an adequate methodology by which reliable and objective assessments can be made. From the review in Section 2.2.1., it is clear that a direct measurement of sustainability is difficult, indirect surrogates often being easier to establish. This is a result of the fact that sustainability determination entails future predictions of a situation where current assumptions may not be valid. As a result, most attempts to devise a method of measuring sustainability have concentrated on the development of indicators which are most often partial indices which estimate some aspect of the broader concept. It is highly unlikely that the use of a single indicator can provide a reliable assessment of sustainability although the likelihood of a reliable estimate will increase if a range of indicators covering all potentially unstable aspects of the system are included (Smyth and Dumanski, 1993).

In an international workshop organised in 1991 by the International Board for Soil Research and Management (IBSRAM) held in Thailand, an International Working Group (IWG) was established to develop a framework for evaluating sustainable land management (Smyth and Dumanski, 1995). The IWG came up with a Framework for Evaluating Sustainable Land Management (FESLM), details of which have been reported by Smyth and Dumanski (1995). Among the stages recommended for sustainability evaluation is the development of indicators and thresholds which serve as measures beyond which the system can be judged to be unsustainable.

In a generic sense, indicators have been defined as “variables” whose purpose is to measure change in a given phenomenon or process (Kumar, 1989; as cited by Syers *et al.*, 1995). Kumar (1989, as cited by Syers *et al.*, 1995) also mentioned that indicators should be objectively verifiable



and be replicable. Syers *et al.* (1995) stated that although direct measurements of indicators are preferred, they need not be quantitative; they may take on a surrogate or proxy form. What is clear, however, is that a change in a given indicator can only be measured with respect to time and it is in this regard that indicators of sustainability potentially find their most use. Smyth and Dumanski (1993) defined Indicators as attributes that measure or reflect environmental status or conditions of sustainability. Ideal indicators should be unbiased, sensitive to changes, predictive, referenced to threshold values, data transformable, integrative and easy to collect and communicate (Liverman *et al.*, 1985: as cited by Zinck and Farshad, 1995). Smyth and Dumanski (1995) mentioned that valuable indicator attributes are those that simultaneously reflect environmental changes important to the continuing success of specific systems of land use; show steady, reasonably predictable response to change without significant fluctuations over short periods or short distances; are a clear measure of a cause having a well understood effect; and can be measured and expressed in numerical terms. Because social and economic goals differ from one region to another, definitions as to what constitutes sustainable systems and thus the indicators that are useful for evaluating sustainability vary accordingly (Syers *et al.* 1995).

Swift and Woomer (1993) suggested that a way out of this dilemma is to adopt a step-wise approach, determine a set of attributes that constitute components of a sustainable system, develop measurement techniques for these indices and find some satisfactory way of combining them to give a broad-based, multi-factor assessment of sustainability that emphasises its holistic nature. This approach has been reported by Spencer and Swift (1992) in the use of a Total Factor Productivity index which expresses the total value of all output produced by the system during one cycle divided by the total value of all inputs used by the system in the same cycle.

Other criteria and indicators of sustainability are based on soil physical and chemical attributes. Thus, Larson and Pierce (1991) advocated the conservation and enhancement of soil quality as a means of developing sustainable cropping systems. Soil quality was defined as the capacity of a soil to function within its ecosystem boundaries and interact positively with the environment external to that ecosystem (Larson and Pierce, 1991). Other workers have been more specific in proposing soil-based indicators of sustainability. Thus, Sparling (1991) proposed the use of microbial biomass carbon, total carbon, and the ratio of microbial biomass carbon to total organic carbon as sensitive indicators of sustainable land management. Yakovchenko *et al.* (1996) proposed the use of the ratio of crop N uptake to mineralised N determined by microbial respiration plus net mineralised N found over a growing season as a useful indicator of sustainability. Dumanski *et al.* (1988) proposed an index called 'potential land flexibility index' based on the ratio of current yields and cultivated area compared to potential yields and extent of suited land. Pierce *et al.* (1983) proposed a soil erosion vulnerability index.

Because of the large number of proposed indicators of sustainable cropping systems, a complete review of all proposed indicators of sustainability is beyond the scope of this presentation. Useful reviews can be found in Dumanski *et al* (1991), Spencer and Swift (1992), Swift and Woormer (1993) and Yakovchenko *et al* (1996).

## **2.3. SOIL ORGANIC MATTER AS AN ATTRIBUTE OF SUSTAINABLE CROPPING SYSTEMS**

### **2.3.1. Role of Organic Matter in Soils**

The importance of organic matter to soil fertility and sustainable crop production is now well recognised and there have been extensive reviews covering the role of organic matter in soils (Kononova, 1966; Allison, 1973; Johnston, 1993; Wallace, 1994; Syers and Craswell, 1995). The particular significance of soil organic matter for soil fertility lies on its influence on so many soil properties. Although the total organic matter in agricultural soils rarely exceeds 5% by soil weight, it is a key component of any ecosystem, and variations in its abundance and nature have profound effects on many of the processes that occur in the system.

Soil organic matter contributes to the physical condition of a soil by holding moisture and improving soil structure (Allison, 1973). It is a direct source of plant nutrients, the release of which depends on microbial activity, and, by affecting cation exchange capacity, organic matter is directly involved in the availability of nutrients to plants (Theng *et al.*, 1989). Soil organic matter also provides carbon as energy source to micro-organisms, enhances plant growth, root initiation, crop yield, nutrient uptake, chlorophyll synthesis, and seed germination (Schnitzer, 1991). In sandy soils, organic matter adds water-holding capacity and CEC. It adds structure, stability and permeability in clay soils. Compaction and many other soil problems are due primarily to loss of soil organic carbon. Wallace (1994) mentioned that decreasing percent soil organic carbon is a better indication of soil degradation than was tons of soil loss. It was also mentioned (Wallace, 1994) that generally, the more clay in a soil, the greater the need for soil organic matter. Thus, the variation in the organic matter content of a soil induced by a cropping system is a significant indicator of the sustainability of that cropping system.

With increasing concern over ground and surface water pollution, soil organic matter has also been shown to be directly or indirectly involved in the movement of phosphorus downwards through the profile of agricultural soils (Johnston, 1993). In acid soils, organic matter has been reported to be a potential factor in improving the efficiency of soil and fertiliser phosphorus utilisation by reducing phosphorus fixation (Syers and Craswell, 1995). Also, in acid soils where P-fixation capacity can be

high, the incorporation of P into organic forms followed by slow release can be a favourable factor for plant roots in their competition against P-fixation (Tiessen *et al.*, 1992).

The significance of organic matter in soils is not only restricted to its role in maintaining soil quality but has also been a subject of concern in relation to global emission of greenhouse gasses. Since soils can act as both a source and sink for atmospheric CO<sub>2</sub>, soil and crop management can affect the global balance of this greenhouse gas (Varvel, 1994). For example, a recent study by the US Environmental Protection Agency (USEPA, 1991) indicated that the amount of CO<sub>2</sub> released from decomposition of organic matter in the USA alone closely approximates  $8 \times 10^6$  t/yr.

### 2.3.2. Constituents of Soil Organic Matter

An understanding of the various constituents of soil organic matter is essential for effective management of organic matter in soils. According to Schnitzer (1991), soil organic matter consists of a mixture of plant and animal residues in various stages of decomposition, and substances synthesised microbiologically and/or chemically from their breakdown products, and of the bodies of live and dead micro-organisms and small animals and their decomposing remains. Soil organic matter includes a wide spectrum of organic compounds, such as fresh vascular plant materials and microbial biomass, to refractory components which accumulate slowly over thousands of years (Trumbore, 1993). As a result of its complex nature, earlier attempts have been made to subdivide soil organic matter into groups which have similar morphological and/or chemical characteristics. Thus, organic matter in soils has been widely classified into two broad groups, Humic and Non-humic substances, although no clear line of demarcation exists between these two classes (Allison, 1973).

#### (a) Humic Substances

These are the dark coloured, amorphous macromolecules synthesised within the soil system as a result of biological and abiotic chemical and physical processes. They normally constitute the bulk of organic matter in soils (50 to 80 %) and are known to range in molecular weight from a few hundreds to several thousands (Schnitzer and Khan, 1972). Humic substances are widely considered to represent the most stable fraction of soil organic matter, a property that has been attributed to their chemical structures, their entrapment within soil aggregates, and their interactions with metal cations and soil minerals (Theng *et al.*, 1989). Based on their solubility in acid and alkali, humic substances are usually classified into the following three fractions: (i) Humic acid, which is soluble in dilute alkali but is coagulated by acidification of the alkaline extract, (ii) Fulvic acid, which is that humic fraction that remains in solution after the alkaline extract is acidified, and (iii) Humin, which is that humic fraction which cannot be extracted from the soil by acid or alkali. From data published by Schnitzer (1991), the analytical characteristics of humic and fulvic acids indicate variations in the elemental and functional group content of humic and fulvic acid (Table 2.3). Very little data had been published on

the humin constituents because of extraction difficulties. From the available literature however, it appears that the analytical characteristics of humins are similar to those of humic acids (Preston *et al.*, 1989; Schnitzer, 1991).

### (b) Non-humic Substances

These usually include well characterised chemical compounds such as carbohydrates, proteins, peptides, amino acids, fatty acids, waxes, pigments, and other low molecular weight organic substances. These can be synthesised by micro-organisms or can arise directly from, or from modifications of similar compounds in the original debris. Schnitzer (1991) reported that non-humic substances are relatively easily degraded in soils and have a short life span.

**Table 2.3: Analytical characteristics of humic and fulvic acids**

Element	Humic Acid	Fulvic Acid
	%	
C	56.4	50.9
H	5.5	3.3
N	4.1	0.7
S	1.1	0.3
O	33.9	44.8
Functional Group	meq/g	
Total acidity	6.6	12.4
-COOH	4.5	9.1
phenolic -CH	2.1	3.3
Alcoholic -OH	2.8	3.6
Quinonoid C=O	2.5	0.6
Ketonic C=O	1.9	2.5
OCH <sub>3</sub>	0.3	0.1
E4/E6	4.3	7.1

Source: Schnitzer (1991)

**(i) Carbohydrates:** Carbohydrates represent a significant pool in soil organic carbon usually ranging between 5 to 20 % of the total organic carbon in soil (Gregorich *et al.*, 1994). They occur mainly as polysaccharides (Cheshire, 1979) although small amounts of sugar alcohols have also been identified. Soil carbohydrates originate from plants, animals, and micro-organisms, their composition varying accordingly. Apart from the trace amounts of sugar, which are soluble in water, the carbohydrates in soil organic matter are not readily isolated because of their intimate association with non-carbohydrate components (Theng *et al.*, 1989).

More than 90 % of the total hydrolysable carbohydrates in soil is made up of five monosaccharides in the following order of decreasing dominance; glucose, galactose, mannose, arabinose, and xylose. Galactose and mannose are believed to be produced mainly by microbes,

whereas arabinose and xylose originate mostly from plants (Cheshire, 1977, as cited by Gregorich *et al.*, 1994). Of all soil organic matter constituents, polysaccharides are reported to be the most readily available to micro-organisms as sources of food and energy (Schnitzer, 1991). In soils, polysaccharides appear to enhance the aggregation and structural stability of soil particles, increase water-holding and exchange capacities, and contribute to metal complexing (Cheshire, 1979).

**(ii) Soil Enzymes:** Soil enzymes are proteins that are synthesised by plants and soil organisms during metabolism and are found in living organisms (biotic enzymes), or in dead cells of microbial and plant tissues (abiotic enzymes), or complexed with organic and mineral colloids (Dick, 1994). The decomposition of soil organic matter and human-added amendments is controlled by a system of heterogeneous soil enzymes operating in a cascade manner (Gregorich *et al.*, 1994). Plant residue components must be depolymerised and transformed before becoming the backbone of soil humus. Mineralisation of soil organic-N to ammonium is accomplished by a series of enzymatic reactions involving proteases, deaminases, amidases, and ureases. The dynamics of S and P in terrestrial ecosystems is controlled by arylsulfatase and phosphomonoesterase. The activity of enzymes in soil is a critical indicator of the quality of soil organic matter since the release of nutrients for plant and microbial growth, and gaseous exchange between soils and the atmosphere are controlled by enzymes. The importance of enzymes in soil organic matter has already been emphasised by Dick (1994) who suggested the use of enzyme activity as biological indicators of soil quality.

**(iii) Light Fraction and Macro-organic Matter:** The light fraction and macro-organic matter are mainly partially decomposed plant residues although residues derived from animals and micro-organisms may also be present in various stages of decomposition (Gregorich *et al.*, 1994). Because they serve as a readily decomposable substrate for soil micro-organisms and as a short-term reservoir of plant nutrients, these pools are significant to soil organic matter turnover in agricultural soils. Useful information on the extent to which plant residues have been processed by the decomposer community in soils is provided by the light fraction and macro-organic matter.

In spite of their generally wide C/N ratio, the light fraction and macro-organic matter have been shown to decompose quickly compared with organic matter in whole soil because they are generally free of mineral particles and therefore lack the protection offered by such particles (Sollins *et al.*, 1984; Christensen, 1987). As a non-humified fraction of organic matter, the size of the light fraction is a balance between residue inputs and persistence, and decomposition as determined by the soil environment (Gregorich *et al.*, 1994). This pool is responsive to management practices and may provide an earlier indication of the effects of soil management and cropping systems than the total amount of organic matter in soils.

**(iv) Microbial Biomass:** The microbial biomass is considered to be the living portion of the soil organic matter with the exclusion of plant roots and soil organisms larger than about  $5 \times 10^{-3} \mu^3$  in size (Jenkinson and Ladd, 1981). Many workers have reported that the soil microbial biomass consists of a large number of bacterial and fungal species, together with other soil organisms such as algae and protozoa (Afzal Hossain, 1990). The soil microbial biomass usually accounts for 1 to 5 % of the total soil organic carbon. Although small in size compared to other soil organic matter fractions, the soil microbial biomass is a critical indicator of the soil's ability to store and recycle nutrients and energy.

As a result of its dynamic nature, microbial biomass responds quickly to changes in soil management and soil perturbations. The turnover time of the soil microbial biomass varies markedly depending upon its degree of protection by soil colloids (Van Veen *et al.*, 1984), but as a whole, turnover has been estimated to range from less than 1 to about 3 years (Jenkinson and Ladd, 1981). The microbial biomass plays a dual role in the soil: as an agent of decomposition thus determining the release of organically-bound nutrients, and as a labile reserve of plant available nutrients (Afzal Hossain, 1990). As pointed out by Sparling (1985), the soil microbial biomass also affects root physiology and soil structure.

**(v) Nitrogenous Compounds:** Nearly all of the nitrogen found in most agricultural soils is associated with soil organic matter (Schnitzer, 1991). The main N-forms present in soil organic matter are in proteins and protein hydrolysates such as amino sugars, purines, pyrimidines, and nitrogen in heterocyclic compounds, many of which still remain to be identified (Schnitzer, 1991). Although infrared studies have shown the presence of peptide chains in soil organic matter (Jenkinson, 1988), the preponderance of evidence is that free peptides, as such, have only transient existence in soil before being hydrolysed to amino acids. As well as amino sugars and amino acids, protein hydrolysates contain unidentified acid-soluble organic nitrogen usually accounting for 10 - 20 % of soil nitrogen (Stevenson, 1982). Some 20 to 35 % of the nitrogen in soil hydrolysates is ammonium, much of which is thought to be formed during hydrolysis of certain amino acids, amides and amino sugars. Jenkinson (1988) reported that although a cultivated soil normally contains much less organic nitrogen than the corresponding native soil from which it was derived, there is relatively little change in the distribution of nitrogen between the hydrolysis products, so that cultivated and native soils contain much the same proportions of amino acids, amino sugars, and ammonium released on hydrolysis.

**(vi) Fats, Waxes, and Resins:** A diverse group of lipids ranging from fatty acids to sterols, terpenes, chlorophyll, waxes, and resins have been reported by Stevenson (1982) to be present in soils. In soil organic matter extracted from several soils by Schnitzer and Schulten (1989), using a sequential extraction with n-hexane followed by chloroform and supercritical n-pentane, <sup>13</sup>C-NMR

spectra of soil extracts showed the presence of long chain fatty acids. Most of the compounds identified appear to be indicative of the presence of waxes in the soil organic matter. Because of their hydrophobic properties, these compounds resist biodegradation and have long residence times in soils. Jambu *et al.* (1978, as cited by Schnitzer, 1991) suggested that some of the paraffins, especially the more polar ones, exert positive effects on the structural stability of soils by forming continuous films over the surface of soil aggregates.

**(vii) Organic Phosphorus compounds:** Phosphorus in soil organic matter exists mainly as complex organic compounds containing phosphate-ester linkages in which the phosphorus is bonded to carbon via oxygen, such as in nucleotides and nucleic acids (Stevenson, 1982; Tate, 1985). Although Newman and Tate (1980) have indicated that orthophosphates and their monoesters are the major forms of phosphorus identified in  $^{31}\text{P}$  NMR spectra of soils, Schnitzer (1991) reported that a substantial proportion of organic phosphorus in soils still remains to be identified. Phospholipids have also been isolated, but these comprise less than 1% of the total organic phosphorus in soils (Dormaar, 1979).

**(viii) Organic Sulphur compounds:** Over 90% of the total sulphur in most non-calcareous soils is present in organic forms. Although most of the organic sulphur forms have not been identified, some progress has been made (Freney, 1986) in subdividing it into broad categories:

(a) Organic sulphur that is reduced to  $\text{H}_2\text{S}$  on treatment with hydriodic acid; this fraction includes sulphate esters in the form of phenolic sulphates, sulphated polysaccharides, choline sulphate, and sulphated lipids. These account for 30 to 70% of the organic sulphur in soils and are considered to be the most labile forms of organic sulphur;

(b) Carbon-bonded sulphur; this fraction represents the difference between the total organic sulphur and that reduced to  $\text{H}_2\text{S}$  by hydriodic acid. This fraction includes the sulphur containing amino acids, mercaptans, disulphides, sulphones, and sulphonic acids. Within this fraction are sulphur compounds that can be reduced by Raney-Ni, such as sulphur-containing amino acids (cystine and methionine), and those that are resistant to Raney-Ni.

From the foregoing review, it can be seen that the organic matter in soil exists in a wide range of substances, some of which are still to be identified.

### 2.3.3. Dynamics of Soil Organic Matter

Organic matter in soil is in a constant flux in which the net quantity at any time is a balance between the rate of addition and the rate of loss. An understanding of the factors associated with both input and loss processes is required for the development of effective soil management strategies.

The organic matter content of a soil is dependent on many factors that exert their effects both individually and collectively, and to varying degrees. A marked change in one factor may cause marked changes in the effects of the other factors (Allison, 1973), and hence in the overall net carbon accumulation. Campbell (1978) stated that marked changes in the amount and distribution of soil organic matter usually occur very slowly in virgin soil when compared to a cropped soil.

A major factor influencing the total organic matter in agricultural soils is land management. The quantity of organic matter in soil is influenced by land management in two ways; by altering the annual input from plants and animals, and by altering the rate at which these organic materials decompose (Jenkinson, 1988). Although Jenkinson (1988) reported the difficulty in separating these processes, Juma and McGill (1986) concluded that the direction of change in soil organic matter due to cultivation depends upon the previous organic matter content as well as the cropping system.

The effects of breaking a soil and cultivating it have been reported to result in large losses of organic carbon (Dalal and Henry, 1988; Oades *et al.*, 1988; Capriel *et al.*, 1991). Campbell (1978) reported that organic carbon losses during the early years after initial cultivation were more rapid than in the later years. Although it is now well understood that cultivation accelerates decomposition of soil organic matter, there is no accepted measure of organic matter quality nor is there any consensus on whether the quality of organic matter has changed. Skjemstad *et al.* (1986) used solid-state  $^{13}\text{C}$  NMR spectroscopy to study the effects of cultivation on the nature of organic matter of a vertisol. They found that although continuous cultivation resulted in a decrease in organic matter content,  $^{13}\text{C}$  NMR spectra of the cultivated soil and an adjoining native soil showed minor differences. Preston *et al.* (1987) found that the main effect of cultivation, as shown by  $^{13}\text{C}$  NMR spectroscopy, was a decrease in carbohydrate contents in the plough layer. Oades *et al.* (1988) also showed that the chemistry of organic matter in native and cropped soils was similar. It thus appears that the processes involved in the loss and gain of organic carbon in native and cropped soils are similar but occur at different rates.

The factors affecting the breakdown of organic matter in soils have been the subject of numerous reviews (eg Jenkinson, 1981, 1988; Duxbury *et al.*, 1989; Conteh, 1994; Parton *et al.*, 1994). The nature of plant material returned to the soil, moisture, temperature, aeration, and intermittent wetting and drying are major factors determining the rate at which organic matter is lost from the soil (Jenkinson, 1981; Ross, 1989).

The diversity in sources of plant-derived organic matter inputs, as well as the complexity of these substrates, results in extreme heterogeneity in the microbial reactions involved in their



decomposition (Ross, 1989). The exact molecular composition of these materials depends not only on the species and part of the plant, but also on season and age (Ross, 1989). Many microbial decomposers are limited in their ability to attack certain organic molecules because they lack the required enzymes. Attempts to predict the rate and pattern of decomposition of organic substances from a range of organic matter have utilised, among other organic matter parameters, properties such as lignin content, fibre content, or nitrogen content (usually expressed as C/N ratio). Van Cleve (1974) found a negative correlation between lignin content of tundra litter and rate of decomposition, while Latter and Howson (1977) found decomposer bacteria numbers to be negatively correlated with crude fibre content and positively correlated with nitrogen content of organic substrates. Amato *et al.* (1987) found that legume tops decompose more rapidly than wheat straw, especially soon after incorporation.

Moisture and oxygen levels affect decomposition processes mainly through microbial activity. Moisture affects microbial activity by limiting microbial movement and transport of nutrients in solution under drought conditions, and at the other extreme, by the build-up of oxygen deficiency with waterlogging, or indirectly by the controlling effects of moisture content on soil temperature (Jenkinson, 1981). The effects of oxygen on organic matter decomposition is mainly on the metabolic processes occurring in the soil. Most soil organisms are aerobes and thus in the absence of oxygen the rate of decomposition becomes suppressed as a result of (i) lack of electron acceptors for respiration processes, (ii) the production of end products, such as hydrogen sulfide and ethylene, which are toxic to soil microbes, and (iii) the presence of higher concentrations of fatty acids which inhibit microbial activity, particularly at low pH (Ross, 1989).

Intermittent wetting and drying of soil can significantly hasten the decomposition of organic matter in soils. Amato and Ladd (1980) and Amato *et al.* (1984) reported enhanced decomposition of plant material in intermittently dried and re-wetted soils. Moisture stress causes the death of a proportion of the microbial population. After re-wetting of soils, components of those dead micro-organisms and organic carbon from other sources, such as plant residues, are used as substrates for growth by the surviving populations (Van Gestel *et al.*, 1993). Ross (1989) reported both positive and negative effects of alternate wetting and drying cycles on organic matter decomposition:

(i) If the soil is saturated for long enough on each wetting cycle, the alternation of wetting and drying will be analogous to anaerobic and aerobic conditions, thus slowing down the net rate of decomposition,

(ii) Since wetting and re-drying of soil colloids cause expansion and contraction, the alternating wetting and drying can cause break-up of aggregates and particles and thus increasing the availability of organic matter for decomposition.

### 2.3.4. Modelling soil organic matter dynamics

The dynamic nature and complexity of the decomposition of organic matter and nutrient cycling processes in soil has led several workers to devise mathematical relationships and simulation models describing the dynamics of organic matter in soils. Most of these models have been validated against data obtained from field experiments in temperate systems (Jenkinson, 1988), and are expected to be applicable to tropical systems, given the understanding that the chemistry of organic matter does not differ between temperate and tropical agro-ecosystems (Theng *et al.*, 1989).

The progression in efforts to model plant residue decomposition and soil organic matter dynamics was described by Bouwman (1990). The earliest attempts in simulating organic matter decomposition and accumulation had utilised simple linear mathematical relationships in the form:

$$C_t = C_o - kt \dots\dots\dots(i)$$

where:  $C_t$  = amount of organic carbon at time,  $t$

$C_o$  = amount of organic carbon at the start

$t$  = time

$k$  = decomposition rate constant

This relationship implies a constant rate of change ( $k$ ) of organic matter over time and is independent of the initial organic matter content. As mentioned earlier in this section, organic carbon losses from soils have been reported to be more rapid in the initial stages than in the latter stages. Thus, for most decomposition studies, a negative exponential function analogous to the first-order kinetic decay of a radioactive substance is more applicable. This relationship implies the loss of a constant fraction of the weight of substrate remaining rather than the loss of constant increments by weights over successive intervals of time.

Thus,

$dC/dt = -kC$ , which integrates to:

$$C_t = C_o e^{-kt} \dots\dots\dots(ii)$$

This type of model is reported to be very useful in the description of rapidly decomposing leaf litter and for readily metabolisable substrates such as carbohydrates (Swift *et al.*, 1979; Ross, 1989). This mathematical approach has the advantage that the exponential decline coefficient ( $k$ ) can be compared between substrates and sites. The decomposition of many coniferous and broadleaved litter materials are well described by this function, as are individual components of the litter material (Swift *et al.*, 1979). A major constraint associated with the use of the first-order exponential decay

model is that, while the function is asymptotic, the remaining material approaches zero at the same proportional rate as does the first increment of decomposed material, not allowing for the effect of a more recalcitrant fraction as the material decomposes (Parton *et al.*, 1994). As a result, an alternative approach was described (Parton *et al.*, 1994) that allows for residue decomposition and deposition of recalcitrant organic matter, the basic equation of which is given by:

$dC/dt = hA - kC$ , whose derivative becomes:

$$C_e = hA/k(1 - e^{-kt}) \dots \dots \dots (iii)$$

where:

- $C_e$  = steady state level of organic carbon
- $k$  = decomposition constant
- $h$  = humification constant
- $A$  = initial organic addition

In this relationship,  $A$  is assumed to be a homogeneous substrate that is mineralised and transformed into a stabilised organic matter at rate  $h$ . The successful adoption of this approach relies on the empirical determination of the changes in  $k$  with time for each substrate and in every environment. The implication is that decomposition of applied organic matter in soils can only be appropriately predicted after a detailed investigation of decomposition process.

Dalal and Mayer (1986a) reported very useful results on the rate of loss of organic carbon with time on soils under different periods of cultivation ranging from < 1 to 70 years using the relationship:

$$C_t = C_o e^{-kt} + A/k(1 - e^{-kt}) \dots \dots \dots (iv)$$

where:

- $C_o$  = initial organic carbon content
- $C_t$  = organic carbon content at time  $t$
- $A$  = the rate at which organic matter is returned to the soil
- $k$  = the rate of loss of organic matter

Using this relationship, Dalal and Mayer (1986a) calculated the rate of loss of organic carbon in relation to the period of cultivation for six major soils of the cereal belt in Southern Queensland and obtained rate constants,  $k$ , varying from 0.041/year to 1.211/year. The  $k$  values were found to be

significantly correlated with the ratio of organic carbon/urease activity ( $r = 0.99^{***}$ ) and with the reciprocal of the clay content ( $r = 0.97^{***}$ ). Dalal and Mayer (1986a) however concluded that in spite of the successful description of organic carbon dynamics using the rate constants obtained from the above equation, the parameter probably encompassed a number of organic components which decline at different rates. The need therefore exists to develop models describing organic matter dynamics which incorporate organic matter components varying in their rates of decomposition.

A large number of computer simulation models describing the dynamics of organic matter in soils have been published and most of these were examined as part of the NATO Advanced Research Workshop (Powlson *et al.* 1996). Most of these models are based on mathematical relations relating the effects of various factors on the turnover of organic matter.

One of the most often cited deficiencies of current soil organic matter models is that functional, kinetically defined pools cannot be directly related to measurable variables (Elliott, *et al.*, 1996). Consequently, it is difficult to initialise models based on independent measures and therefore site-dependent calibrations based on total soil organic matter levels are necessary. The evaluation of whether soil organic matter model structure and function are appropriate have most often depended upon comparison of model output with measurement of total soil organic matter from treatments within sites (Jenkinson, *et al.*, 1987; Parton and Rasmussen, 1994) and occasionally from data obtained across a series of sites (Elliott *et al.*, 1996). Many experimental approaches have been used to breakdown the total soil organic matter into fractions. While these approaches have been successful in showing differences in soil organic matter pool sizes for different soils, there has been less work in defining functionally consistent turnover rates of these pools. If knowledge of turnover time is to be valuable, it must be determined on well-defined and meaningful fractions of soil organic matter.

## **2.4. SUSTAINABLE MANAGEMENT OF SOIL ORGANIC MATTER**

### **2.4.1. Crop Residue Management**

Management of crop residues has become a fundamental principle in the restoration and rehabilitation of soil organic matter following declines resulting from intensive cropping of agricultural lands. Crop residue management considers residues from the previous crop as a resource that needs proper management. It most often begins with the planting of a crop that will provide sufficient amounts of residues for the purpose it is being managed for, or involves planting a cover crop to meet these needs, and continues with the actions taken after harvest until the next crop is planted (Schertz and Bushnell, 1993). Crop residue management normally encompasses the total cropping year. Clearly, management of crop residues is a major determinant of the long-term sustainability of cropping systems.

Crop residues are important to the accumulation or loss of soil carbon even in high organic matter soils (Hunt *et al.*, 1996). Results from the southeastern Coastal Plain soils of the USA have shown that crop residues constitute a significant portion of soil carbon content (Hunt *et al.*, 1996). In pastures, residue additions from legumes and grasses can greatly increase soil carbon content. The strong association between crop residue management and tillage systems has shown that addition of row crop residues to conventionally tilled (ploughed or disked) soil does not increase soil carbon content (Hunt *et al.*, 1996). In fact, Bruce *et al.* (1995) found that crop residues alone did not maintain carbon to levels obtained in no-till once the soil had been placed into cultivation with conventional tillage. Therefore, most studies on crop residue management have been carried out jointly with tillage systems.

Management of crop residues in any cropping system will not only be influenced principally by the nature and quantity of residues available and the immediate and future land use but also by many other constraints (Strong and Lefroy, 1995). The need to protect the soil surface to conserve soil water, the nature of crop and/or pasture rotation, the availability of labour and resources, and the alternative uses for the crop residues within the farming system are among such constraints. Because crop residues contain considerable quantities of carbon and nutrients, their management can markedly affect the input-output balance of plant nutrients and soil carbon.

Crop residue management has different effects on different nutrients as a result of the differential translocation of nutrients to the harvested grain and fibre. This is exemplified by the report of Lefroy *et al.* (1988) for a maize cropping system in Thailand where it was shown that the sulfur and phosphorus balance during the same period vary considerably for the same residue management system (Table 2.4).

**Table 2.4: S and P balance sheet in a maize cropping system over three years**

Input (kg/ha)	S Balance*				P Balance*			
Fertiliser	0	16	32	96	0	16	32	96
Rainfall	12	12	12	12	7.2	7.2	7.2	7.2
Total	12	28	44	108	7.2	23.2	39.2	103.9
Uptake (kg/ha)								
Grain	21.0	17.1	23.1	26.6	36.1	41.2	51.4	67.4
Residue	19.0	18.2	23.9	19.6	6.2	9.8	9.7	12.4
Balance (kg/ha)								
Residue returned	-9.0	10.9	20.9	81.4	-28.9	-18.0	-12.2	35.8
Residue removed	-28.0	-7.3	-3.0	61.8	-35.1	-27.8	-21.9	23.4

Adapted from Lefroy *et al.* (1988). \* Balance = Output - input

Blair (1994) estimated the quantities and values of nutrients accumulated in seed, lint and trash of cotton and found that in a 1.5 t/ha crop, the amounts of nutrients ranged from 35 kg/ha for Mg up to 242 kg/ha for N with the amounts increasing in the order Mg<P<S<Ca<K<N (Table 2.5). In cotton cropping systems, a considerable amount of all nutrients are returned to the soil in the leaf fall during defoliation. This source of carbon and nutrients is readily decomposable by soil micro- and macro-organisms and represents a flush of nutrients into the system at a time when crop demand is low (Blair *et al.*, 1995a). The fate of these nutrients released is an important determinant of the short- and long-term fertility of the system since little can be done to alter their fate except for the selection of tougher leaf cuticles which would slow down decay rates. A significant amount of the carbon and nutrients taken up by the cotton plant can be found in the stalks and capsules (Table 2.6) and these are the components that can be managed on the farm.

**Table 2.5: Fate of nutrients (kg/ha) in 1.5 t/ha cotton crop**

Fate	N	P	K	Ca	Mg	S
Removed in product	110	18	38	8	13	26
Returned at defoliation	48	7	22	47	9	2
Stalk + Capsules	73	12	87	51	10	10
Roots	12	3	14	6	4	2
Total	242	40	158	112	35	42
% Removed	45	45	24	7	37	62

Adapted from Blair (1994)

**Table 2.6: Nutrient ratios in returned cotton residues**

Plant part	C:N	N:S	P:S
Leaves	16.7	4.4	0.7
Stalks	38.5	8.7	1.3
Capsules	41.7	8.0	1.3
Roots	50.1	6.7	1.3

From Blair *et al.* (1995a)

From the estimates in Table 2.6, it can be seen that there is an adequate amount of N in the leaves for microbial decomposition whereas decomposition of stalks and capsules would result in short-term immobilisation of soil N. Since the stalks and capsules represent that portion of the crop residues that can be managed in the field, maintenance of these residues is essential for the long-term sustainability of cotton cropping systems.

As mentioned earlier in this section, residue management systems are closely linked with tillage systems and thus will be addressed jointly except in studies that have isolated the effects of tillage from that of crop residue management. For instance, Dalal (1989) studied the long-term (13 years) effects of no-tillage, crop residues, and nitrogen application on selected properties of a vertisol in Queensland, Australia, and found that the highest concentration of organic carbon and total nitrogen was in the surface soil (0 - 10 cm) in the combination of no-tillage, crop residue retained, and fertiliser N (Table 2.7). Mineralisable N was found to follow a similar trend. It was concluded that tillage and crop residue management substantially improve soil organic matter and microbial activity in the surface layers, and water relations and salt movements to at least 1.2 m depth. These results were very similar to those obtained by Dalal *et al* (1991) on the effects of 20 years of tillage practice, crop residue management and fertiliser N on soil organic carbon and microbial biomass.

**Table 2.7: Effects of tillage, crop residue and fertiliser N on organic carbon and total N of the surface soil (0 - 10 cm)**

Tillage practice	Crop residue	Organic C			Total N		
		0**	23	69	0	23	69
Tilled	Burned	16.6	16.8	17.6	1.46	1.40	1.49
	Returned	17.1	17.4	17.9	1.53	1.51	1.62
No-till	Burned	17.0	16.0	16.7	1.46	1.45	1.51
	Returned	17.2	19.2	19.4	1.60	1.75	1.78
LSD (0.05)	Tillage (T)		NS			0.06	
	Residue (R)		0.5			0.06	
	N		0.6			0.08	
	T x R		0.7			NS	
	R x N		0.8			NS	
	T x R X N		1.2			NS	

Source: Dalal (1989) ; \*\* Fertiliser applied at 0, 23, and 69 kg N/ha; NS = not significant

There have been numerous conflicting reports on the effects of burning or returning residues on soil organic matter. For instance, Rasmussen and Collins (1991) reported the results of a comparative study of residue-burnt (RB) and residue-incorporated (RI) and showed that although the RI treatments gave rise to higher organic matter levels, the effects of burning crop residues on the soil organic matter content after 45 years of cropping was not significant. While Pikul and Allmaras (1986) generally found less organic carbon in soils where residue was incorporated, Moss and Cotterill (1986) found greater soil organic carbon in the surface soil after burning crop residues. Biederbeck *et al* (1980) found that after 20 years of residue burning in the Canadian Prairies, soil organic carbon was reduced by 15 to 20% compared to a chopped straw treatment. These conflicting

results were interpreted by Prasad and Power (1991) who attributed the discrepancies to the degree to which residues were burnt, time of burning, depth of sampling, and tillage employed.

Although Rasmussen and Collins (1991) indicated that the effects of crop residues on soil organic matter content is highly related to the amount and chemical composition of the residue applied, an earlier study by Larson *et al* (1972) found that residues of lucerne, cornstalks, oat straw, sawdust and broomgrass produced similar increases in organic matter in a Hapludoll in Iowa. Sauerbeck (1982) in Germany also concluded that different types of crop residues had similar effects on soil organic matter. In reduced tillage systems, crop residues are reported to breakdown slowly as a result of inadequate mixing with the soil required for complete microbial decomposition (Dick, 1983). It was also pointed out that residue management practices have different effects on cultivated and native soils. For example, Dick (1983) found that after 18 years of continuous corn with no-till, minimum tillage, and conventional tillage, soil organic carbon values were 11%, 23% and 25% respectively less than the native grassland. In an extensive review of work done on crop residue management, Prasad and Power (1991) concluded that tillage of all kinds leads to a decrease in soil organic carbon as compared to native sod; incorporation of crop residues as compared to their removal usually increases soil organic matter content; leaving crop residue cover on the soil surface leads to an accumulation of organic matter and total N on the soil surface; burning of crop residues often produces a variable effect on soil organic matter content depending on soil depth, tillage practices, degree of burning, time of sampling, and other factors.

#### **2.4.2. Crop Rotations and Sustainable Organic Matter Management**

According to Cady (1991), crop rotation is a management system of growing one or more crops in sequence on the same piece of land, the sequence being repeated again and again. Every repetition of the pre-assigned order constitutes a "cycle". This practice of rotating crops in a piece of land as a soil management system has its roots in ancient times (Battese and Fuller, 1972). There is a notion that a suitably chosen rotation should give a degree of control over certain factors, such as weeds, pest and diseases, and general deterioration of soil condition, whose effects can be cumulative under continuous cropping with the same or similar crops to such an extent that virtual crop failure results.

According to Patterson (1964), crop rotation experiments fall in two broad categories:

- (i) those comparing the effects of treatments on the crops grown in a single rotation, and
- (ii) those in which different rotations are compared.



Most earlier rotations fall in the first category. Perhaps the experiments described by Crowther and Cochran (1942, as cited by Patterson, 1964) carried out in the Sudan Gezira were probably the first rotation experiments in the second class.

A well-planned crop rotation can play an important role in ensuring optimum crop productivity. The benefits of suitable rotations include improved resistance to soil erosion and degradation (Grant and Lafond, 1994), improved soil fertility and soil tilth, enhanced aggregate stability, and increased availability of soil moisture, as well as agronomic and economic benefits to the producer. According to Campbell *et al.* (1991a), rotations which include summer fallow tend to lead to lower organic matter levels than continuously cropped rotations although some studies have failed to record any effect of summer fallow (Campbell *et al.*, 1991b). Wood *et al.* (1990) found increased potential C and N mineralisation rates under a wheat-corn-millet-fallow rotation, compared with a wheat-fallow rotation, after only 3.5 years. Grant and Lafond (1994) found no effect of fallow on total C. This contrast was explained by differences in environmental conditions. Campbell *et al.* (1991a) observed higher organic matter content in rotations with lower fallow frequencies on a thin Black Chernozem after 29 years. The fallow rotation in the study of Grant and Lafond (1994) only included fallow in one year out of four, so the contrast among rotations may not have been sufficient to produce measurable differences in total carbon content over a four-year period. Also, in the study of Grant and Lafond (1994), total carbon was measured, rather than organic carbon, which could have reduced the likelihood of measuring small changes in organic carbon. Carbon:Nitrogen ratios were not affected by tillage or cropping sequence in any soil depth.

The quality of organic matter present in soil is affected by the type and quality of residues added, the cropping sequence, the climate and the soil type (Wani *et al.* (1994). Some increases in soil organic matter content of Gray Luvisols and Black soils in western Canada have been attributed to perennial forages grown in rotations with cereal. Crop rotations that include legumes increase the amount of total soil nitrogen (Campbell *et al.*, 1991) and often increase the yield of cereals subsequently grown on the same soil. It therefore appears that sustainable cropping systems can be achieved through the inclusion of legumes and other deep rooted crops in rotations so that subsoil nutrients can be brought to the surface for utilisation by subsequent crops (Wani *et al.*, 1994).

The inclusion of manure in a crop rotation either reduces the rate of loss of organic matter or increase the total amount present (Ridley and Hedlin, 1968). The outcome depends upon the initial quantity of soil organic matter, its specific decay rate, and rate of organic matter addition (McGill *et al.*, 1986). Several other studies have shown that crop rotations usually increase soil organic matter content when compared with monocultures. In a recent study (Varvel, 1994) comparing seven cropping systems (three monocultures, two 2-year, and two 4-year rotations), an analysis of soil samples at the beginning of the experiment showed no difference in soil carbon and nitrogen

concentrations of all cropping systems at all depths. After eight years, total carbon and nitrogen values were significantly higher in the four-year rotations than in the two-year rotations. Generally, total carbon and nitrogen were found to decrease in the continuous cropping while rotations increase the total carbon and nitrogen concentrations in the surface layer.

Colins *et al* (1992) reported the effects of three rotations, wheat-fallow, wheat-wheat, and wheat-pea, on the soil carbon and microbial dynamics. They showed that total soil carbon and microbial biomass C and N contents were significantly greater in annual-crop than wheat-fallow rotations, except where manure was applied. The microbial biomass C in the annual-crop and wheat-fallow rotations averaged 50% and 25% respectively, of that in grass pasture. Residue management specifically affected the level of microbial biomass carbon; for example, burning residues reduced microbial biomass to 57% of that in plots receiving barnyard manure. In their study on the effects of crop rotations and fertilisation on soil organic matter, Campbell and Zetner (1993) monitored the soil organic matter content at various depths of a 24-year crop rotation experiment conducted on a medium-textured Aridic Haploboroll. Prior to the study, the land had been in a hard red spring wheat-fallow rotation for approximately fifty years. Significant differences were found only in the 0 - 15 cm depth. Changes in organic matter were directly related to the amount of crop residues produced by these systems. Soil organic matter was found to be inversely related to apparent N deficit (i.e., N exported in grains minus N applied as fertiliser). It was thus concluded that the amount of organic matter in the top 15 cm depth of soil will vary depending on the amount and N content of the crop residues returned to the soil.

More recently, Chang and Juma (1996) studied the impact of continuous barley and a four-year rotation consisting of faba beans, barley intercropped with field peas, and barley after the intercrop on the soil biological properties of a Gray Luvisol. They found that the average size of microbial N over the growing season was 20% greater when barley followed faba bean or intercropping than in the faba bean and intercropped plots. Microbial N was 14.9% greater when barley followed faba bean or intercropping than in the continuous barley plots. Generally, it was found that microbial N was significantly higher in the barley of rotation plots than in the continuous barley plots, an indication that rotation systems with annual legumes improved soil biological properties.

Earlier, Edwards *et al.* (1992) examined the effects of ten years of conservation tillage and crop rotation on soil fertility. Their tillage systems included no-till (NT) and conventional-till (CT); crop rotations were continuous corn-wheat cover (CW), continuous soybean-wheat (SW), and corn-wheat-soybean-wheat (CWSW). It was observed that tillage systems do not affect soil pH due to the application of N fertilisers. The crop rotations that returned residues with high C/N ratio (CW or CWSW) were shown to be more important in increasing soil organic matter. The magnitude of

difference in organic matter between crop rotations was found to be less than between tillage systems in organic matter management. Generally, these studies show that the more dynamic soil characteristics, such as carbon mineralisation, respond more rapidly and strongly to crop management changes than do characteristics such as total organic matter.

## 2.5. METHODS USED IN ASSESSING THE DYNAMICS OF ORGANIC MATTER IN SOILS

A wide range of approaches has been adopted for the determination of organic matter in soils and some earlier reviews can be found in Hesse (1972), Nelson and Sommers (1982), and Stevenson and Elliott (1989). Some of the most common methods used for organic matter analysis are described in this section.

### 2.5.1. Loss-on-ignition

This was one of the earliest methods of determining the organic matter content of soils. The procedures involved in this method are essentially gravimetric in which the organic matter content of a pre-weighed soil is supposedly destroyed by ignition and the loss in weight used as a measure of the organic matter content. Hesse (1972) indicated that ignition can be carried out either at low temperatures (350 - 400°C) or at high temperatures (800 - 900°C). Inadequacies of this approach have been ascribed (Nelson and Sommers, 1982) to the lack of discrimination between loss of organic matter and loss of mineral matter such as carbon dioxide from carbonates and water and hydroxyl groups from clay.

Proponents of this method such as Ball (1964), Davies (1974), Spain *et al.* (1982), and Donkin (1991) have argued that ignition carried out at temperatures below 450°C can give estimates of organic matter that are sufficiently accurate for most purposes. Ball (1964) examined the loss-on-ignition procedure for over one hundred soils having a wide range of organic matter content and obtained significant correlations with the dichromate method of Tinsley (1950). Davies (1974) found that the presence of carbonates in soil does not affect its loss-on-ignition value at 430°C and concluded that the gravimetric estimation of soil organic matter is generally applicable to both calcareous and non-calcareous soils provided that the furnace temperature is controlled between 375 and 450°C. Davies (1974) mentioned an exception in soils having gibbsite in their clay fraction because of previous reports that gibbsite loses substantial amounts (approximately 35 %) of water at around 300°C. Ben-Dor and Banin (1989) also obtained significant linear correlations ( $r = 0.97$ ) between organic matter determined by the loss-on-ignition procedure and organic carbon determined by the method of Walkley and Black (1934) in soils from the arid region of Israel. Spain *et al.* (1982) compared the organic matter values determined by the Walkley-Black procedure and the loss-on-

ignition for 766 surface soil samples representing 21 soil groups in Australia and found a close relationship between the two measurements. They found that the Walkley-Black values range from 0.1 to 14 % and the loss-on-ignition from 0.8 to 36 %. Generally, most studies utilising the loss-on-ignition method in estimating organic matter content reported satisfactory results. It is however, still unclear as to what extent this method is applicable to soils from a wide range of ecosystems.

### 2.5.2. Dry Combustion Techniques

In dry combustion techniques, a sample is combusted in a furnace at elevated temperatures to convert all carbon-containing compounds to carbon dioxide (CO<sub>2</sub>) which is subsequently measured to give an indication of organic carbon content. The evolved CO<sub>2</sub> can be measured by a wide range of procedures which include gravimetric, titrimetric, volumetric, spectrophotometric and gas chromatographic techniques (Navarro *et al.*, 1993). This method has a limitation that samples containing significant quantities of carbon in the form of carbonates and elemental carbon will give an overestimate of organic carbon contents (Nelson and Sommers, 1982). This limitation can be minimised by treating the samples with dilute acid before combustion to remove all carbon existing in the form of carbonates. Alternatively, inorganic carbon can be measured separately and subtracted from the total carbon measurements to give an estimate of soil organic carbon content (Neal and Younglove, 1993). A detailed description of various dry combustion procedures can be found in Nelson and Sommers (1982).

In recent times, there has been an increase in the number of studies that determine organic carbon status using continuous-flow analysers (Grewal *et al.*, 1991; Lefroy *et al.*, 1993; Blair *et al.*, 1995b; Skjemstad *et al.*, 1996). One of the best known continuous-flow analysers is the Automatic Carbon and Nitrogen Analyser by Mass Spectrometry or ANCA-MS (Barrie, 1991). This instrument is usually used for the automated analysis of <sup>15</sup>N and <sup>13</sup>C in plant and soil samples but can also determine %N and %C on weighed samples. Samples containing up to 5 mg C are placed in tin capsules and dropped into a heated silica combustion tube (>1000°C) containing Cr<sub>2</sub>O<sub>3</sub> granules as oxidation catalyst. A pulse of pure oxygen is introduced into the He gas stream which flows continuously through the combustion tube. The timing of the O<sub>2</sub> pulse and the tin capsule introduction is so arranged that flash combustion of the sample occurs (Figure 2.1). The combustion products are then swept through a heated (~600°C) reduction furnace containing copper wire in which NO is reduced to N<sub>2</sub>. Water vapour is then removed by passage through a moisture trap containing magnesium perchlorate, after which the remaining combustion products, N<sub>2</sub> and CO<sub>2</sub>, are separated on a chromatographic column. Percentage C is determined as CO<sub>2</sub> using a thermal conductivity detector placed between the moisture trap and the mass spectrometer. Although modern dry combustion instruments are capable of handling large numbers of samples with minimal variability due to operator error, they are often very costly and cannot be afforded by most analytical laboratories.

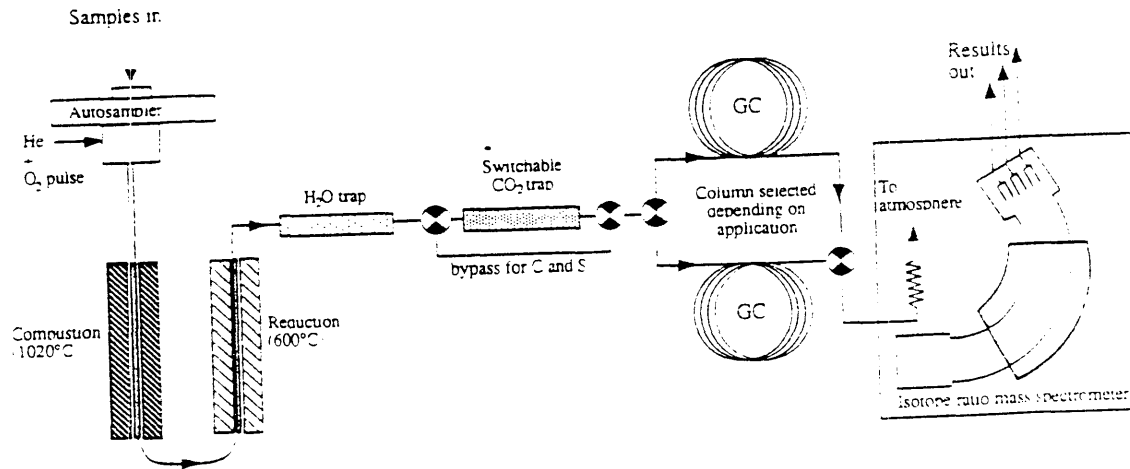
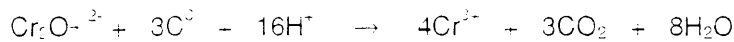


Figure 1.1: Schematic of an ANCA-MS system.

Source: Barrie and Prosser (1996)

### 2.5.3. Wet Oxidation Techniques

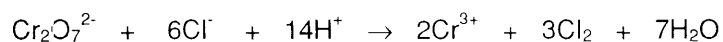
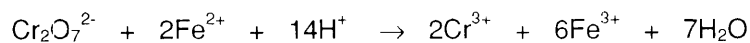
Several oxidising agents have been employed for the determination of organic carbon in soil, the most common of which has been the dichromate oxidation proposed by Schollenberger (1927) and modified by Walkley and Black (1934). The fundamental principle of the method is that all organic carbon is oxidised by the dichromate under acid conditions, and the amount of dichromate consumed, or  $\text{Cr}^{3+}$  released, or  $\text{CO}_2$  evolved, gives an indication of the organic carbon content (Hesse, 1972; Nelson and Sommers, 1982):



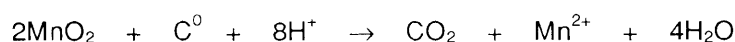
This method has been employed in so many studies that a complete review of its applications is beyond the scope of this review. The procedure has been the basis of routine organic carbon determination in most soil laboratories. The various modifications of this method that have been proposed abound in the literature (eg. Heanes, 1984; Gillman *et al.*, 1986; Vickery *et al.*, 1995).

In spite of its wide usage, dichromate procedures are subject to certain limitations. Several studies have shown that recovery of organic carbon is rarely complete and varies considerably between soils (Nelson and Sommers, 1982). In addition to the incomplete recovery of organic carbon, several substances present in soil can interfere with the determination of oxidisable carbon, notably chlorides, iron (II) and higher oxides of manganese leading to incorrect values for organic

carbon because of the participation of these ions in redox reactions involving chromic acid mixtures. For example,



Therefore, the presence of these ions in soils in significant amounts can result in higher values of organic carbon. The presence of higher oxides of manganese ( $\text{MnO}_2$ ) can result in underestimation of organic carbon values because of competition with the dichromate for oxidisable substances. For example,



In addition to the aforementioned limitations, the assumption that all organic carbon in soil exists in a valence state of zero may not be appropriate. There has been no study to evaluate this assumptions.

#### 2.5.4. Physical Fractionation

The use of physical fractions in organic matter studies has received considerable attention and has been the basis of several studies on soil organic matter turnover (eg Janzen *et al.*, 1992; Camberdella and Elliott, 1993, 1994; Golchin *et al.*, 1994; Guggenberger *et al.*, 1995a, 1995b). Physical fractionation of soil organic matter is considered by several workers to be less destructive, and the results obtained from physical soil fractions are believed to relate more directly to the structure and function of soil organic matter *in situ* (Golchin *et al.*, 1994). Two basic methods of physical fractionation of soil have been reported; particle-size fractionation and particle density fractionation.

Physical fractionation of soil according to particle size has been used extensively to study soil organic matter (Turchenek and Oades, 1979; Tiessen and Stewart, 1983; Christensen, 1986, 1987; Camberdella and Elliott, 1993) and the methods have proven to be useful in revealing differences in the structural and dynamic properties of organic matter from different soils. Methods used for particle-size fractionation have extended from dry sieving, which may retain macro-aggregates in the mm size range, to crushing of soil in mills and the use of chemical extractants to achieve complete dispersion (Ladd *et al.*, 1993). The most common method used to obtain a high degree of disruption of the soil structure prior to physical fractionation is ultrasonication (Christensen, 1987). The use of sonication prior to physical fractionation has the potential problem of creating redistribution of organic matter among the various size fractions (Camberdella and Elliott, 1993). Although differences observed in the distribution of organic matter and particle-size fractions have been used to reveal differences in organic matter turnover under various management practices, such differences may also arise as a result of differences in methodology (Christensen, 1987).

Physical fractionation of soil organic matter has also been carried out on the basis of particle density (Skjemstad *et al.*, 1990; Barrios *et al.* 1996; Magid *et al.*, 1996). Such fractionation allows the physical separation of organic matter found within a specific size class from the heavier density mineral particles. Separations based on density have been used for two main purposes in soil organic matter studies; to separate the 'light fraction' (free or non-complexed soil organic matter) consisting largely of undecomposed residue and their partial decomposition products, and to separate organo-mineral associations, usually in aggregates (Golchin *et al.*, 1994). Fractions separated on the basis of particle density have yielded useful information on the extent of association of organic and inorganic materials in soils, as well as some mineralogical characterisation of the fraction components (Turchenek and Oades, 1979). Generally, soil samples ground no finer than 0.2 mm are suspended in solutions of known density and centrifuged to separate the materials with greater and lower density than the solution. The light fraction obtained by the use of solutions with densities less than  $1.6 \text{ Mg/m}^3$  consists largely of unaltered or partially degraded plant materials and charcoal (Skjemstad and Dalal, 1987; Skjemstad *et al.*, 1990; 1996). It has also been shown (Dalal and Mayer, 1986b; Skjemstad and Dalal, 1987) that the rate of loss of carbon from a number of fractions separated from vertisols decreased with increasing density and time of cultivation.

### 2.5.5. Fractionation of humic substances

The fractionation scheme proposed by Oden (1919, as cited by Hayes and Swift, 1978) appears to have been the earliest and most widely used fractionation of soil organic matter. This fractionation scheme is based on differences in solubilities of organic constituents in acid and alkali. The technique involves extraction with an alkaline reagent, separation of the alkaline extract from the residue, and then acidification of the extract. This procedure gives rise to three gross fractions, Humic acid (HA), Fulvic acid (FA) and Humin. These fractions have been discussed under humic substances (Section 2.3.2.). This has been a common technique used to separate and examine soil organic matter and has been the basis of many studies (eg Anderson *et al.*, 1974; Schnitzer, 1978; Schnitzer *et al.*, 1981; Schnitzer and Schuppli, 1989). The chemical properties of HA and FA have been studied extensively. HA is believed to be the most biologically resistant fraction of soil organic matter (Anderson and Schoenau, 1993), with a core of strongly condensed aromatic structures surrounded by aliphatic side-chain components. FA appears to be composed mainly of microbial metabolites and younger material not highly associated with the mineral fraction, although all material, young and old, can be part of the FA (McGill *et al.*, 1975).

This fractionation scheme has provided useful guide in interpretation of organic matter dynamics. For example, the C:N:P ratios of HA and FA fractions have been used to assess the origin and turnover of nutrients in soil organic matter from different depths and zones (Schoenau and Bettany, 1987). The HA:FA ratios have also been used as indicators of the degree of humification in

a soil. Higher HA:FA ratios found in surface soils of most environments are believed to reflect more intense humification as a result of greater biological activity (Anderson and Coleman, 1985). The ratio of the optical densities or absorbances of dilute aqueous solutions of HA and FA at 465 and 665 nm (E4/E6 ratio) has been used to indicate the degree of condensation of the aromatic carbon network, with a low ratio indicative of relatively high degree of condensation of aromatic humic constituents (Chen *et al.*, 1977). Conversely, a high E4/E6 ratio reflects a low degree of aromatic condensation and infers the presence of relatively large proportions of aliphatic structures.

The major problem with this fractionation scheme has been the choice of a suitable solvent for extracting organic matter from soils. This difficulty arises from the varying properties of the many organic compounds present in soils and the ability of these compounds to be bound, in varying degrees, to each other and complexed with inorganic components (Pierce and Felbeck, 1972). The ideal extractant should remove practically all organic matter from soil without altering its physical and chemical properties. The use of dilute aqueous solutions of NaOH as SOM extractant has been proposed by Archard (1786, as cited by Schnitzer and Schuppli, 1989), and has gained considerable applications. The major concerns with the use of NaOH are the creation of artefacts in the extracted organic matter due to hydrolysis and auto-oxidation (Stevenson, 1982) and the arbitrary nature of the separation into HA and FA fractions. Other reagents that have been widely used for the extraction of organic matter in soil include dilute solutions of neutral salts such as  $\text{Na}_4\text{P}_2\text{O}_7$  (Anderson *et al.*, 1974). Little is known as to whether and to what extent soil organic matter extracted by dilute NaOH solution differs from that removed by dilute  $\text{Na}_4\text{P}_2\text{O}_7$  solution (Schnitzer and Schuppli, 1989). Problems with hydrolysis and auto-oxidation appear to be at least partly overcome by extracting under an atmosphere of  $\text{N}_2$  (Anderson and Schoenau, 1993) although Tan *et al.* (1991) found no difference between organic matter extracted under air and under  $\text{N}_2$ .

In spite of the popularity of this fractionation scheme, the fractions obtained are not conceptual pools but procedurally defined fractions with limited utility in studies of SOM dynamics (Stevenson and Elliott, 1989).

### 2.5.6. Isotopic Techniques

Soil organic matter has also been studied extensively using both stable and radioactive isotopes of carbon. The type of isotopic measurements performed usually depends on the type of information required and the objectives of the study. The use of isotopes is reported to provide precise quantification of changes in SOM during decomposition (Carter and Gregorich, 1996). The most common isotopic techniques used are  $^{14}\text{C}$ -labelling and  $^{13}\text{C}$  natural abundance. Generally,  $^{14}\text{C}$ -labelling is used to study short-term dynamics of SOM, and the  $^{13}\text{C}$  natural abundance is used to characterise the long-term status.



**(a)  $^{14}\text{C}$ -labelling**

The application of  $^{14}\text{C}$  in studies of SOM seems to have been first brought to the attention of soil chemists by Bingerman *et al.* (1953) and Hallam and Bertholomew (1953). Since then  $^{14}\text{C}$  has been used in so many aspects of SOM research that a complete review of its applications is beyond the scope of this presentation. The use of  $^{14}\text{C}$  as a label has been made possible because of its radioactive nature; a  $\beta$ -emitter with a half-life of 5730 years. The use of  $^{14}\text{C}$ -labelled substrates has been found necessary to trace the fate of added organic matter in various soil constituents. Substrates labelled with  $^{14}\text{C}$  have ranged from simple compounds, such as glucose and amino acids, to complex compounds, such as proteins and cellulose (Chesire and Mundie, 1981), to plant leaves and roots (Jenkinson, 1971, 1977; Nelson *et al.*, 1996). With the addition of  $^{14}\text{C}$ -labelled substrates to the soil, information has been obtained on the amount and rate of mineralisation of the substrate. This approach has been used by Chesire and Mundie (1981) to examine the distribution of labelled carbohydrates among size fractions from soils incubated with  $^{14}\text{C}$ -labelled glucose (28 days), rye-grass (1 year) and straw (4 years).

Despite the popularity of  $^{14}\text{C}$ -labelling techniques in SOM studies, erroneous conclusions may be drawn if the decay rates of the  $^{14}\text{C}$ -labelled components of plant materials differ from those of the unlabelled components (Voroney *et al.*, 1991). Also, producing artificially and uniformly labelled plant material remains difficult and requires sophisticated equipment.

**(b)  $^{13}\text{C}$  Natural abundance**

Carbon has two stable naturally occurring isotopes,  $^{12}\text{C}$  and  $^{13}\text{C}$ . The isotope  $^{12}\text{C}$  makes up approximately 98% of the carbon in nature while  $^{13}\text{C}$  makes up approximately 1%. The ratio of these two stable isotopes ( $^{13}\text{C}/^{12}\text{C}$ ) is affected by differences in photosynthetic pathways in plants (Park and Epstein, 1960). As a result plants have been classified into C3, C4 and CAM based on photosynthetic pathway. The  $^{13}\text{C}/^{12}\text{C}$  ratio is often measured relative to a standard and expressed as  $\delta^{13}\text{C}$ . Plants with a C4 pathway have a higher  $^{13}\text{C}/^{12}\text{C}$  ratios ( $\delta^{13}\text{C}$  of approximately -12 to -21‰) than C3 plants ( $\delta^{13}\text{C} < -21‰$ ). Detailed reviews on the mechanistic causes of variations in the carbon isotope ratios in plant materials are given by Smith and Epstein (1971) and Boutton (1991, 1996). The use of  $^{13}\text{C}$  natural abundance as a tracer in SOM studies is based on the fact that the  $^{13}\text{C}$  content of SOM corresponds closely to the  $^{13}\text{C}$  content of the plant material from which it is derived, and that there is negligible fractionation of  $^{13}\text{C}$  during the decomposition of plant material in soil (Carter and Gregorich, 1996). Therefore, the incorporation of C3 plant material into a soil that previously carried C4 vegetation will lead to a corresponding change in the  $\delta^{13}\text{C}$  value of the soil. This approach has been used to study SOM dynamics and plant residue carbon in particle-size fractions in temperate (Balesdent *et al.*, 1988) and tropical soils (Desjardins *et al.*, 1994). Using this method, Lefroy *et al.* (1993) studied the changes in SOM as a result of cropping, Bonde *et al.* (1992) studied the dynamics of SOM in particle-size fractions of forested and cultivated oxisols, and Balesdent and Balabane

(1992) used it to quantify maize root-derived soil organic carbon. Some extensive reviews on the use of  $^{13}\text{C}$  natural abundance in SOM studies have been presented by Boutton (1996) and Balesdent and Mariotti (1996). A major source of error in the use of this technique is the changes in the isotopic composition of SOM during decomposition which in turn may be due to differences in  $\delta^{13}\text{C}$  between degradable and recalcitrant SOM (Balesdent and Mariotti, 1996).

### 2.5.7. Spectroscopic Techniques

A wide range of spectroscopic techniques have been employed in understanding the nature and dynamics of organic matter in soils. The use of such techniques has made it possible to identify different compounds present in soil organic matter based on functional groups. Such techniques are known to be non-abrasive and therefore can provide detailed information on the nature of soil organic materials *in situ*. The most common spectroscopic techniques employed in studies of SOM are solid-state  $^{13}\text{C}$  NMR (Nuclear Magnetic Resonance) spectroscopy and pyrolysis-mass spectrometry, and these will be covered in this review. Other spectroscopic techniques include Infrared spectroscopy and electron spin resonance spectroscopy.

#### (a) Solid-state $^{13}\text{C}$ NMR Spectroscopy

The application of NMR spectroscopy to SOM studies appears to have first been carried out by Barton and Schnitzer (1963) in their studies on  $^1\text{H}$  NMR of a methylated humic acid. Many studies on the application of  $^{13}\text{C}$  NMR spectroscopy to SOM studies have been conducted. Useful reviews regarding the principles and applications of NMR spectroscopy in the study of SOM can be found elsewhere (Wilson, 1987, 1991; Bleam, 1991; Hatcher *et al.*, 1994; Kinchesh *et al.*, 1995a; Preston, 1996; Baldock *et al.*, 1997).

$^{13}\text{C}$  NMR spectroscopy is widely accepted as being one of the most powerful forms of spectroscopy for structural elucidation of complex biomolecules. It offers the possibility of quantification which should allow the relative amounts of carbon in different chemical environments to be determined (Kinchesh *et al.*, 1995a). The great strength of NMR in SOM research is its unique ability to provide information on very complex materials, such as those characterised by low solubility, irregular structures, and strong physical or chemical links to each other or to mineral matter (Preston, 1996). The information provided by NMR spectroscopy can also aid in choosing appropriate methods for conventional chemical analysis, for example, for individual lipids, sugars, or amino acids (Preston, 1996). Initially, the low sensitivity of the  $^{13}\text{C}$  nucleus meant that carbon values above 2% were generally required to obtain spectra with an acceptable signal-to noise ratio (Skjemstad *et al.*, 1986). However, the development of Fourier-transform (FT) techniques for data acquisition, and CPDAS (Cross-Polarisation Magic-Angle Spinning) methods have further improved the sensitivity of solid-state  $^{13}\text{C}$  NMR spectroscopy (Kinchesh *et al.*, 1995a). Also, Skjemstad *et al.* (1994) and Schmidt *et al.* (1997) showed that the treatment of a soil sample with a solution of 2 % and 10 % HF,

respectively, can remove mineral matter without significantly affecting the organic component, thereby improving the  $^{13}\text{C}$  NMR spectra obtained.

The technique of CPMAS  $^{13}\text{C}$  NMR has been applied to a wide range of studies in understanding the processes of SOM decomposition and has produced voluminous information (eg. Skjemsatd *et al.*, 1986; Oades *et al.*, 1987, 1988; Preston *et al.*, 1987, 1994; Baldock *et al.*, 1990, 1992; Kögel-Knabner *et al.*, 1992a, 1992b). Probably the most important discovery from  $^{13}\text{C}$  NMR spectroscopy is that soil organic matter, in general, contains significant quantities of aliphatic macromolecules which are not carbohydrates, proteins, or low molecular weight waxes. These compounds are often referred to as polymethyleneic or paraffinic structures (Hatcher *et al.*, 1994). Other important findings from the application of  $^{13}\text{C}$  NMR showed that phenolic carbon is not as dominant a structural feature of soil organic matter as previously thought, and that labile substances such as carbohydrates are only a transitory component of soil organic matter. Using this technique, it has been shown that the most noticeable change in the initial stages of decomposition is a decrease in the ratio of o-alkyl to alkyl C (Amalfitano *et al.*, 1995; Baldock and Preston, 1995). This change is often associated with the loss of the most easily metabolisable carbohydrates and an accumulation of alkyl carbon. The technique has also been used in understanding the structure and dynamics of organic matter in size and density fractions of soils (Golchin *et al.*, 1994; Guggenberger *et al.*, 1995a, 1995b; Kinchesh *et al.*, 1995b).

Although the use of  $^{13}\text{C}$  NMR has produced useful information on SOM studies, the method requires the presence of more carbon than many agricultural soils contain and the results can be obscured by the presence of paramagnetic  $\text{Fe}^{3+}$  ions (Arshad *et al.*, 1988). Also, in studies of SOM, signals in  $^{13}\text{C}$  NMR spectra tend to be broad and overlap. As such, only information on carbon types (eg aliphatic, aromatic, carbonyl etc) can be derived from these spectra (Schnitzer and Schulten, 1995). Furthermore, the high cost associated with the equipment required for such analysis makes it of remote accessibility for most soil laboratories.

### **(b) Pyrolysis-Mass Spectrometry**

The technique of pyrolysis-mass spectrometry (Py-MS), as applied to soil organic matter studies, appears to have been pioneered by Schulten (1977). In this technique, the sample is pyrolysed directly under vacuum in the ion source of a mass spectrometer during which weaker bonds in organic compounds are broken by a pulse of thermal energy and the volatile compounds are identified by mass spectrometry. Based on the identified products, the nature of the original macromolecule is inferred. The ratios of the different products obtained give an indication of the degree of humification. Extensive reviews regarding the origin, principles and applications of this technique in SOM studies have been published in recent years (Saiz-Jimenez, 1994, 1996; Schnitzer and Schulten, 1995).

Pyrolysis-Mass Spectrometry has been applied extensively in the investigation of complex biomaterials (Schulten *et al.*, 1987), humic substances (Schulten, 1987) and forest soils ranging widely in organic matter contents (Hempfling *et al.*, 1988). Further improvements in the technique, which include Curie-point Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS), Pyrolysis-Field Ionization Mass Spectrometry (Py-FIMS), and Pyrolysis-Field Desorption Mass Spectrometry (Py-FDMS) have enabled the characterisation of molecular subunits of SOM (Hempfling and Schulten, 1988, 1990). These techniques are described in detail in Schnitzer and Schulten (1995).

Despite the wealth of information provided by the technique of pyrolysis-mass spectrometry, Saiz-Jimenez (1996) cautioned that pyrolysis data of humic substances are not correctly interpreted, and misunderstandings often occur in pyrolysis papers. The technique can cause drastic modifications of the original building blocks which can lead to incorrect conclusions. The technique considers pyrolysis products as building blocks of the macromolecules from which they were derived. Other studies have failed to confirm this. For example, Saiz-Jimenez and de Leeuw (1984, 1986) found that pyrolysis of plant and soil polysaccharides results in complex pyrolysates containing a wide variety of volatile, relatively low molecular weight compounds. Pyrolysis of cellulose was found to produce carbonyl compounds, mainly aldehydes and ketones of different chain lengths, acids, furans, pyranones, benzenediol, hydroxybenzaldehyde and dihydroxyacetophenone (Pouwel *et al.*, 1989). Based on these results, there is a tendency to conclude that cellulose is a polymer made up of all those compounds identified. Cellulose, however, is known to be a polymer of glucopyranose units linked by  $\beta$ -1,4 linkages, but no such units were found in cellulose pyrolysis products. Similar observations have been made in the pyrolysis products of proteins (Chiavari and Galletti, 1992). These, and many other observations, have shown that interpretations of the chemical nature of biomacromolecules in the light of information provided by pyrolysis data is a difficult task.

### 2.5.8. Oxidation by potassium permanganate ( $\text{KMnO}_4$ )

Solutions of potassium permanganate ( $\text{KMnO}_4$ ) have been used extensively for the oxidation of organic compounds, the rates and extents of oxidation of the different substrates governed by their chemical composition (Hayes and Swift, 1978). An extensive literature dealing with the oxidation of organic compounds by permanganate is given by Stewart (1965). It was Piret *et al.* (1957, as cited by Hayes and Swift, 1978) who first brought to the attention of soil chemists the usefulness of  $\text{KMnO}_4$  solutions in oxidising soil organic matter when they showed that oxidation of peat by  $\text{KMnO}_4$  yielded 12 to 22% of aromatic polycyclic acids. More recently, extensive work in understanding the chemistry of soil organic matter had utilized the oxidising power of  $\text{KMnO}_4$  (Schnitzer and Desjardin, 1964). Most of the work, however, was concerned with identification of the oxidation products of humic and fulvic acids.

The need to investigate the products formed by the use of different concentrations of permanganate over varying conditions of time had been felt over the years. For instance, studies with less than the theoretical amounts of permanganate required for complete oxidation could reveal the quantity of readily oxidisable components. Some attempts to carry out studies in this direction had been undertaken by Savage and Stevenson (1961), Schnitzer and Desjardins (1964), and Hansen and Schnitzer (1967), which however, were based on the use of strong oxidisers for investigation into the chemical structures of humic compounds.

In relatively recent years, Loginow *et al.* (1987) developed a method of fractionating soil organic matter based on susceptibility to oxidation by  $\text{KMnO}_4$ . In its original form, the degree of oxidation with three different concentrations of  $\text{KMnO}_4$  was used, in conjunction with the total carbon concentration of the soil to obtain four fractions of soil organic carbon based on their ease of oxidation. Although the technique cannot be used to obtain the organic fractions *in substantio*, work done by Lefroy *et al.* (1993) has shown the technique to be useful for monitoring small, short-term changes in soil organic matter, characterisation of organic matter of various soils, and evaluation of qualitative changes occurring under the influence of organic and mineral fertilisation. The method is based on the supposition that the oxidative action of potassium permanganate on soil organic carbon is comparable to that of enzymes produced by soil microorganisms. The procedure involves reacting the soil organic matter with an excess of three different concentrations of  $\text{KMnO}_4$ . As some classes of organic compounds are oxidised, the permanganate is reduced and the reduced permanganate, which is equivalent to the amount of carbon oxidised, is measured by spectrophotometry. The lower the concentration of  $\text{KMnO}_4$  required for oxidation of a certain class of compounds, the more labile that organic component. Using this procedure, Loginow *et al.* (1987) obtained four fractions with 3 different concentrations of permanganate.

After detailed experimentation, Blair *et al.* (1995b) proposed the use of one concentration of  $\text{KMnO}_4$  solution, 333 mM, to determine the labile component of soil organic matter. The un-oxidised fraction, referred to as the non-labile carbon, is calculated from the total carbon concentration. By comparing the labile and non-labile carbon of a cropped soil relative to a native or reference soil, Blair *et al.* (1995b) developed a carbon management index as an indicator of organic matter status of soil. The  $\text{KMnO}_4$  oxidation procedure of Blair *et al.* (1995b) has been employed in several recent studies (eg Whitbread, 1996; Conteh *et al.*, 1997b). Shang and Tiessen (1997) showed that oxidation by  $\text{KMnO}_4$  was able to predict the proportion of labile carbon which indicated a decrease in organic matter stability after cultivation. The main focus of the study reported in this thesis is to evaluate the labile carbon obtained by  $\text{KMnO}_4$  oxidation and the carbon management index as indicators of sustainable cropping systems.

## 2.6. SUMMARY

The literature reviewed in this chapter started with an examination of the concept of sustainability and the proposed indicators of sustainability. It was seen that although it is possible to talk about, for example, sustainable soil management, sustainability is influenced as much by the interactions of soil processes with those of crop and weed growth, pest and disease development, tillage and other labour activities, as it is by each of these factors individually. Sustainability can be appropriately assessed through the use of indicators, which are partial indices that estimate some aspect of the broader concept. The selection of indicators can be achieved through a step-wise approach, by identifying a set of attributes that constitute components of a sustainable system and then develop techniques for measuring these attributes.

Soil organic matter is a key attribute of a sustainable cropping system because of its influence on the physical, chemical and biological health of the soil. Soil organic matter contributes to the physical condition of a soil by holding moisture and improving soil structure and is a direct source of plant nutrients. The quantity of organic matter in soil is influenced by land management by altering the annual input from plants and animals, and by altering the rate at which these organic materials decompose. Management of crop residues is a fundamental principle in the restoration of soil organic matter following declines resulting from intensive cropping of agricultural lands. Crop residues are important to the accumulation or loss of soil carbon even in high organic matter soils. Because of the complex nature of organic matter in soil and its association with the mineral matrix, a wide range of approaches have been employed for its estimation. The study reported in this thesis examines the potential value of a simple fractionation of soil organic matter by ease of oxidation, relate these fractions to other common measurements of soil organic matter, and then use these fractions to study organic matter changes under different crop residue management systems and crop rotation sequences in cotton cropping systems. In the following chapter (Chapter 3), the results of a survey of the chemical fertility status of soils used for cotton production in Australia is presented. This is followed by an examination of the changes in soil organic carbon due to cultivation as studied by soil carbon fractionation (Chapter 4).