THE INFLUENCE OF LAND USE ON HUMIC SUBSTANCES IN THREE SEMI-ARID AGRO-ECOSYSTEMS IN THE FREE STATE

by

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A dissertation submitted in accordance with the requirements
for the Magister Scientiae degree
in the
Department of Soil, Crop and Climate Sciences
Faculty of Natural and Agricultural Sciences
University of the Free State
Bloemfontein

May 2009

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DECLARATION

I declare that this dissertation hereby submitted by me for the Master of Science degree at the University of the Free State is my own independent work and has not previously been submitted by me at another university/faculty. I furthermore cede copyright of the dissertation in favour of the University of the Free State.

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ABSTRACT

This study was initiated to complement earlier investigations into soil organic matter degradation and restoration on account of agricultural land use in the Free State Province of South Africa. In these studies no attention was given to the response of humic substances which represent the most active fraction of organic matter. The aim with this study was therefore to quantify the influence of agricultural land use on humic substances in soils of semi-arid regions.

Topsoil (0-200 mm) samples from distinctive agro-ecosystems at Harrismith (Mean annual rainfall, MAR = 624 mm and Mean annual temperature, Ta = 13.8°C), Tweespruit (MAR = 544 mm and Ta = 14.8°C) and Kroonstad (MAR = 566 mm and Ta = 16.6°C) were selected for use in this study. An agro-ecosystem implies a region where the three environmental factors affecting yield, namely climate, slope and soil are for practical purposes homogeneous. The selected samples represent a virgin (grassland soil never cultivated before), cultivated (formerly grassland soil cultivated for at least 20 years) and restored (formerly cultivated soil converted to perennial pasture for at least 15 years) Plinthustalfs (10.6 to 13.5% clay) at every agro-ecosystem. Parameters quantified comprise crude soil, extractable soil, humic acid and fulvic acid C contents, N contents and C/N ratios. Concerning these parameters, cultivated soil was compared with virgin soil and restored soil with cultivated soil.

The crude soil C content of the virgin soils varied from 7.3 g C kg^{-1} soil in the warmer, drier Kroonstad agro-ecosystem to 21.6 g C kg^{-1} soil in the cooler, wetter Harrismith agro-ecosystem. Across agro-ecosystems the contribution of extractable to crude soil C was almost constant, namely 47.1 to 48.4%. The contribution of humic acid C to extractable soil C decreased and that of fulvic acid C to extractable soil C increased from the Kroonstad to Harrismith agro-ecosystem.

Cultivation reduced crude soil C in the three agro-ecosystems with 50.2 to 51.8%. This is equivalent to absolute losses of 3.8, 8.2 and 10.8 g C kg^{-1} soil at Kroonstad, Tweespruit and Harrismith agro-ecosystems respectively. Loss of extractable soil C was more variable ranging from 36.7% or 1.3 g C kg^{-1} soil in the warmer, drier Kroonstad agro-ecosystem to 48.2% or 5.1 g C kg^{-1} soil in the cooler, wetter Harrismith agro-ecosystem. Trends of this nature were non-existent for either humic or fulvic acid C losses.

Gains of crude soil C ranged from 5.4 g C kg^{-1} soil in the warmer, drier Kroonstad agro-ecosystem to 8.0 g C kg^{-1} soil in the cooler, wetter Harrismith agro-ecosystem. This trend manifested also in extractable soil C gains which were lowest at Kroonstad (1.5 g C kg^{-1} soil) and highest at Harrismith (2.8 g C kg^{-1} soil). Neither humic acid C nor fulvic acid C showed trends of this nature.

The N contents although more variable than the C contents are to a large extent supportive concerning organic matter in the virgin, cultivated and restored soils of the three agro-ecosystems. Further elaboration on the N contents is therefore not justified here.

Based on both C and N indices, it can be stated that humic substances did not show explicit trends on account of land use as was the case with organic matter *per se*. This phenomenon warrants further investigation since humic substances are regarded as the most reactive fraction of organic matter.

Keywords: fulvic acid, humic acid, organic carbon, organic nitrogen, soil organic matter

UITTREKSEL

Die studie is geïnisieer om vorige ondersoeke oor die degradasie en restourasie van organiese materiaal weens landboukundige landgebruik in die Vrystaat Provinsie van Suid-Afrika te komplementeer. In hierdie studies is geen aandag aan die reaksie van humiese stowwe, wat die mees reaktiewe fraksie van organiese materiaal verteenwoordig, gegee nie. Die doel met hierdie studie was dus om die invloed van landboukundige landgebruik op humiese stowwe in gronde van halfdroë gebiede te kwantifiseer.

Bogrondmonsters (0-200 mm) vanaf onderskeibare agro-ekosisteme by Harrismith (Gemiddelde jaarlikse reënval, GJR = 624 mm en Gemiddelde jaarlikse temperatuur, Tj = 13.8°C), Tweespruit (GJR = 544 mm en Tj = 14.8°C) en Kroonstad (GJR = 566 mm en Tj = 16.6°C) is vir die studie geselekteer. ‘n Agro-ekosisteem impliseer ‘n gebied waar die drie omgewingsfaktore wat opbrengs beïnvloed, naamlik klimaat, helling en grond vir alle praktiese doeleindes homogeen is. Die geselekteerde monsters verteenwoordig ‘n onversteurde (graslandgrond wat nooit voorheen bewerk is), bewerkte (vroeër graslandgrond wat vir ten minste 20 jaar bewerk is) en gerestoureerde (vroeër bewerkte grond wat vir ten minste 15 jaar na aangeplante weiding omgeskakel is) Plinthustalfs (10.6 tot 13.5% klei) by elke agro-ekosisteem. Parameters wat gekwantifiseer is sluit in rugrond, ekstraheerbare grond, humiensuur en fulviensuur C-inhoude, N-inhoude en C/N-verhoudings.

Die rugrond C-inhoud van die onversteurde gronde varieer van 7.3 g C kg^{-1} grond in die warmer, droër Kroonstad agro-ekosisteem tot 21.6 g C kg^{-1} grond in die koeler, natter Harrismith agro-ekosisteem. Oor agro-ekosisteme was die bydrae van ekstraheerbare tot rugrond C bykans konstant, naamlik 47.1 tot 48.4%. Die bydrae van humiensuur C tot ekstraheerbare grond C het afgeneem en die van fulviensuur C tot ekstraheerbare grond C het toegeneem van die Kroonstad tot Harrismith agro-ekosisteem.

Bewerking het die rugrond C in die drie agro-ekosisteme met 50.2 tot 51.8% verlaag. Die is ekwivalent aan absolute verliese van 3.8, 8.2 en 10.8 g C kg^{-1} grond by Kroonstad, Tweespruit en Harrismith agro-ekosisteme respektiewelik. Verlies van ekstraheerbare grond C was meer varieerbaar en varieer van 36.7% of 1.3 g C kg^{-1} grond in die warmer, droër Kroonstad agro-ekosisteem tot 48.2% of 5.1 g C kg^{-1} grond in die koeler, natter Harrismith agro-ekosisteem. Neigings van die aard bestaan nie vir humien- of fulviensuur C verliese nie.

Winste van rugrond C varieer van 5.4 g C kg^{-1} grond in die warmer, droër Kroonstad agro-ekosisteem to 8.0 g C kg^{-1} grond in die koeler, natter Harrismith agro-ekosisteem. Die neiging het ook in die ekstraheerbare grond C gemanifesteer waar winste die laagste by Kroonstad (1.5 g C kg^{-1} grond) en hoogste by Harrismith (2.8 g C kg^{-1} grond) was. Beide humiensuur C en fulviensuur C het geen neigings van die aard getoon nie.

Die N-inhoude was, alhoewel meer varieerbaar as die C-inhoud tot ‘n groot mate ondersteunend betreffende organiese materiaal in die onversteurde, bewerkte en gerestoureerde gronde van die drie agro-ekosisteme. Verdere uitbreiding oor die N-inhoude is daarom hier nie geregverdig nie.

Gebaseer op beide die C- en N-indekse kan dit gestel word dat humiese stowwe nie sulke duidelike neigings toon weens landgebruik as wat die geval met organiese materiaal was nie. Die verskynsel regverdig verdere navorsing omdat humiese stowwe as die mees reaktiewe fraksie van organiese materiaal beskou word.

Sleutelwoorde: fulviensuur, grondorganiese materiaal, humiensuur, organiese koolstof, organiese stikstof

ACKNOWLEDGEMENTS

I wish to thank the Lord the Almighty for seeing me thus far by giving me both the health and the endeavour to reach the perceived destiny. I also like to thank everyone who backed and supported me throughout the entire period. I would also wish to express my sincere gratitude to the following people who worked tediously and timelessly towards the accomplishment of this document:

Prof CC du Preez who professionally motivated, encouraged and guided me throughout the research period and the writing of the dissertation.

Elmarie Kotzé who committedly and effortlessly helped me pursue this study and encouraged me at times when all hope was lost.

The entire staff of the Department of Soil, Crop and Climate Sciences at the University of the Free State, they played a tremendous role in mentoring me and more especially Me Y Dessels who willingly offered me the technical assistance in the laboratory and finally Me G C van Heerden who always welcomed and helped me wholeheartedly to the very end.

I also wish to thank Me M.E. Du Toit, Mr T.C Birru and Mr. I Lobe for granting permission to use their collected soil samples to enhance research.

My mother who reared my son Thabang Setaka on my behalf in my absence and the rest of my family especially my siblings who were always there for me till the end.

CHAPTER 1

INTRODUCTION

1.1 Motivation

Sustainable management of the land is essential to maintain the agricultural productivity of the Free State. The following are the principles of sustainable land management (Smyth & Dumanski, 1995).

- The biological productivity must be maintained and if possible increased.
- The production risk must be lowered to ensure greater security.
- The quality of natural resources must be protected.
- The enterprise must be economically viable.
- The enterprise must be socially acceptable.

All five principles are of equal importance (Zinck & Farshad, 1995). This approach to land use reflects the concern of man regarding the degradation of the environment and the socio-economic realities in relation to future production of food and fibre.

The need for natural resources to be protected for sustainable use has caused an intense debate on soil quality among researchers worldwide during the past decade. It is currently unanimously accepted that soil quality describes its capacity to sustain biological productivity, maintain environmental quality, and promote plant, animal and human health (Doran & Parkin, 1994). This holistical definition is based on the functions of soils in any land-based ecosystem, and are described as follows by Brady and Weil (1996).

- It is the medium wherein plants grow for the production of food and fibre. Water and essential nutrients are stored in soil and supplied to plants.
- It largely determines the fate of water in the hydrological system owing to its porous nature. Polluted water is also purified when it moves through soil.
- It has the capacity to convert organic waste into beneficial humus. In this process carbon dioxide is released to the atmosphere and becomes available

for photosynthesis. Nutrients like nitrogen, phosphorus and sulphur are simultaneously released in a form that is usable by plants, animals and humans.

- It is a habitat for a vast range and number of living organisms including small mammals, reptiles, earthworms, insects, fungi, bacteria and viruses. In a teaspoon of fertile soil there are more micro-organisms than people on earth.
- It plays an important role as an engineering medium. Factories, houses, airfields and roads are built with and on soil.

According to Weil and Magdoff (2004) organic matter can be a negative factor with regard to the fitness of soil as an engineering medium but is usually a major positive factor in determining a soil's capacity to perform most of the other functions listed. Therefore it is not surprising that Allison (1973) is of the opinion that organic matter influences properties of mineral soils disproportionately to the quantities present: it is a major source of nutrients and microbial energy, holds water and nutrients in available form, usually promotes soil aggregation and root development and improves water infiltration and water-use efficiency.

It is generally assumed that the organic matter content of soils reaches a maximum equilibrium level under specific natural environmental conditions for which inputs equal losses (Tate, 1992). This level of equilibrium is influenced in order of importance by: climate > vegetation > topography = parent material > time (Stevenson & Cole, 1999). Human intervention disturbs this equilibrium through cultivation which results in a depletion of soil organic matter (Haas *et al.,* 1957; Campbell & Souster, 1982; Dalal & Mayer, 1986; Rasmussen & Collins, 1991). Most researchers (Adu & Oades, 1978; Sanchez *et al*., 1982; Brown *et al*., 1993) ascribe the phenomenon to the following:

- The amount of organic debris returned to the soil is reduced as the bulk of plant material is removed as a crop.
- Cultivation results in higher microbial activity in soils through better aeration and allows micro-organisms access to organic matter within aggregates through disruption which enhances decomposition of soil organic matter.

- Cultivated soil is vulnerable to erosion and without proper precaution measures, losses of organic matter results in this manner.

The organic matter content of agricultural soils is highly correlated with their potential productivity, tilth and fertility (Smith & Elliot, 1990). In a review paper Scotney and Dijkhuis (1990) claim that there exist major gaps in current knowledge of changes in the fertility status of South African soils, especially with regard to organic matter changes on account of land use. However, several studies on the effect of land use on organic matter changes in semi-arid soils have been done by postgraduate students over the past 20 years.

Prinsloo (1988) was the pioneer of these studies to investigate the long-term impact of land use on soil organic matter. He studied the effects of present and past cultivation on nitrogen fertility in some Free State soils by comparison of paired samples of cultivated or reverted soils with uncultivated soils. Cultivation caused large losses of nitrogen fertility from the topsoil. Reversion to pasture appeared to restore nitrogen fertility in the topsoil where leguminous trees were present but not in their absence.

The findings of Prinsloo (1988) motivated Du Toit (1992) to study the trend of organic C and N depletion with regard to cultivation period in five distinctive agro-ecosystems of the semi-arid highveld. The term agro-ecosystem as used by her refers to a region where the three environmental factors affecting yield, namely climate, slope and soil are for practical purposes homogenous (MacVicar *et al.,* 1974). On the same set of soil samples from the five agro-ecosystems her husband (Du Toit, 1993) studied the effect of cultivation on sulphur fractions. Van Zyl (1995) also used this set of soil samples from the five agro-ecosystems to study the effect of cultivation on phosphorus fractions. Cultivation, irrespective of the period, caused a significant decrease in soil organic matter of all five agro-ecosystems as indicated by organic C, N and S but not organic P. Loss of soil organic matter was high during the initial period of cultivation, where after it decreased until a new equilibrium was reached. However, the pattern of decline in soil organic matter differed between the agro-ecosystems.

The results from above mentioned three studies (Du Toit, 1992; Du Toit, 1993; Van Zyl, 1995) motivated Lobe (2003) to proceed with an investigation on the fate of soil organic matter in some of the agro-ecosystems. He restricted his investigation to the three agro-ecosystems in the Free State, namely Harrismith, Kroonstad and Tweespruit that have Plinthustalfs. Long-term cultivation of native grassland reduced organic matter in bulk soil by 60%, reaching equilibrium after 30 years. Losses of soil organic matter occurred from all particle size separates, with increasing rate loss constants as particle size increased. In all aggregates soil organic matter decreased, while fastest in the larger aggregates. The contribution of lignin-derived phenols to total C did not change in the bulk soil during cultivation, suggesting that there was no selective enrichment of lignin moieties as total C was lost during cultivation. Increased ratios of phenolic acids to aldehydes suggested that side chains were increasingly oxidized during cultivation. After 90 years of cultivation ^{13}C values of the bulk soil organic matter indicated that 40% of grassland-derived C was replaced by wheat-derived C, which dominated over maize-derived C. In contrast, 80% of the C in lignin was crop-derived, suggesting that the majority of remaining grassland C was recycled through microbial biomass. Amino sugar analyses suggested that during this recycling, fungal residues were better preserved than bacterial residues, while total microbial residues declined by 60%.

In the same three agro-ecosystems the restoration of soil organic matter by conversion of cultivated land to perennial pasture was studied by Birru (2002). His results showed a wide variation in the rate of soil organic matter restoration between sites in each of the agro-ecosystems, due mainly to differences in natural resource factors and management techniques. Most important of the latter was the application of nitrogen fertilizer. Where this was inadequate or absent very low soil organic matter restoration rates were generally measured.

From this brief review of completed research regarding the influence of land use on organic matter in soils of semi-arid South Africa it is clear that the fate of humic substances has not yet been investigated. Humic substances, which represent the most active fraction of humus, consist of a series of highly acidic, yellow to black coloured polyelectrolytes referred to by names such as fulvic and humic acids (Stevenson & Cole, 1999). These substances are formed by secondary synthesis reactions and have properties distinctively different from those of the biopolymers of living organisms, including the lignin of higher plants. Research in recent years has showed that humic substances are of utmost importance in controlling soil quality (Weil & Magdoff, 2004). Proper knowledge is therefore essential on the chemical composition of humic substances and to what extent they are vulnerable to change, on account of varying land uses under prevailing environmental conditions.

This study is complementary to those mentioned earlier, especially that of Birru (2002) and Lobe (2003) which were done in the Free State on Harrismith, Kroonstad and Tweespruit agro-ecosystems with Plinthustalfs. The focus will be on the characterization of organic matter with regard to humic substances in some of the virgin, cultivated and restored soils sampled by Du Toit (1992), Birru (2002) and Lobe (2003) for their studies. For the purpose of this study the definitions of the three forms of land uses that will be compared are as follows:

- Virgin soil – soil covered with native vegetation and therefore never cultivated before.
- Cultivated soil – soil having been ploughed for a long enough period so that the organic matter has reached a new equilibrium, usually 35 years and longer.
- Restored soil – cultivated soil converted to perennial pasture for a minimum of 14 years.

1.2 Hypothesis

The change of agricultural land use in the Free State Province on three agro-ecosystems with Plinthustalfs can influence soil organic matter quantity and quality as indicated by humic substances.

1.3 Objectives

The overall objective of this study was to investigate the influence of agricultural land use on organic matter quantity and quality as manifested in humic substances of Plinthustalfs from three agro-ecosystems in the Free State Province. The sub-objectives were therefore:

- To determine and compare organic C and N content as indices of organic matter in virgin, cultivated and restored soils within each agro-ecosystem and also between them.
- To determine and compare the organic C and N contents of fulvic and humic acids in virgin, cultivated and restored soils within each agro-ecosystem and also between them.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Soil organic matter studies have long been an important part of the discipline of soil science. Research on the role of organic carbon in determining soil quality and sustainability of land management systems is well documented. Also soil scientists generally accept that human activities such as agricultural land uses and management practices as well as the environmental factors that define an agro-ecosystem, have a profound effect on soil organic matter turnover. Considerably less however, is known on how these factors affect the reactivity of humic substance components of organic matter, especially in coarse textured Plinthstalfs of South Africa.

Firstly the nature and composition of soil organic matter, that make it an important attribute for assessing soil quality, are highlighted. Then differences between humic and non-humic substance constituents of soil organic matter are laid out so as to distinguish the two soil organic matter components. Next the humic and fulvic acid fractions of the humic substances are compared and contrasted in terms of their chemical structure (functional groups building blocks), chemical composition (elemental make-up) and the C/N ratios. Lastly advances in the characterization of soil organic matter, in order to evaluate the humic substances C and N quantities, are discussed.

2.2 Nature and composition of soil organic matter

Organic matter is of central importance in defining the characteristics of a soil, and its suitability for agriculture (Brown *et al*., 1993). Soil organic matter in this perspective refers to the sum total of all organic C containing substances in soils, consisting of non-living components which are a heterogeneous mixture composed largely of products resulting from microbial and chemical transformation of organic debris (Schnitzer, 1991). MacCarthy *et al.* (1990) further describes soil organic matter as those substances that include: unidentified high molecular weight organic materials such as polysaccharides and proteins; simpler substances such as sugars, amino acids as well as other small molecules; and humic substances all of which are synthesized by living organisms. In studies undertaken by Stevenson (1982), the term soil organic matter represents the organic constituents in the soil, excluding undecayed plant and animal tissue, their partial decomposition products and the soil biomass.

Organic matter is not the same in all soils. Climate, topography and vegetation for example have a profound influence on soil water content, aeration and temperature, that are determinants for the soil population, and all of these together with management practices affect the kind and amount of organic matter present in a soil. Soil organic matter is therefore truly a product of its environment, consisting of non-humic (±35% w/w) and humic (±65% w/w) substances (Schnitzer, 1978; MacCarthy *et al.,* 1990).

2.2.1 Non-humic substances

These are chemically well defined organic substances and consist of low molecular weight aliphatic and aromatic acids, carbohydrates, amino acids and their polymeric derivatives such as polypeptides, proteins, polysaccharides and waxes (MacCarthy *et al*., 1990; Gregorich *et al*., 1994). In general these compounds are relatively easily degraded in soils, they have rapid turnover and are used readily as substrates for soil microorganisms.

2.2.2 Humic substances

They are a mixture of naturally occurring macromolecules with varied chemical structure and chemical composition. Their structural and chemical composition is affected by differences in parental biomaterials and environmental conditions. This is because humic substances are found in soil, soil interstitial waters, streams, ground water, sea and ocean waters that are widely different from one another (Malcolm, 1990; Kang *et al*., 2003). Overall however, the structural similarities between the different humic substances of soil are more pronounced than their differences (MacCarthy *et al*., 1990). For instance, they all have an abundance of oxygen containing functional groups like carboxyl, phenol, alcohol, hydroxyl and carbonyl which dominate their chemical properties (Cresser *et al*., 1993). Also Schnitzer (1977) found that the humic substances from arctic, temperate, subtropical and tropical soils are structurally alike. Other researchers also reported that humic substances from varying climates, soil types and management practices were generally similar (Christopher, 1996).

Generally humic substances are amorphous, highly transformed, series of yellow to black polyelectrolytes (Stevenson, 1982; Stevenson & Elliot, 1989; Schnitzer, 1991; Swift, 1996; Zalba & Quiroga, 1999). Humic substances are divided into three crude fractions based on their solubility in aqueous acids and bases; these include humin, humic acids (HA) and fulvic acids (FA). Each of these three fractions, despite having a name denoting singularity, is not made of a single pure compound. Each is a heterogeneous mixture of organic substances having a wide range of molecular weights and negative charges (Haynes & Swift, 1990). Humic substances no longer exhibit specific chemical characteristics normally associated with phenolic and benzene carboxylic building blocks, instead they show a significant degree of resistance to biodegradation (Hayes & Clapp, 2001; MacCarthy, 2001; Swift, 2001).

In the same way that humic substances isolated from soils coming from different climates and environments have nearly similar structures, as portrayed by possession of similar functional groups; so is the case with elemental concentrations of humic substances. In general the elemental composition range of HA and FA from soils all over the world are remarkably consistent (Kononova, 1966; Allison, 1973). Data of elemental analyses of C and N of HA and FA formed under widely differing climatic conditions is given in Table 2.1. Schnitzer (1977) noted that in general the C content ranges for HA were narrower than those for FA, indicating a greater homogeneity for the former, also HA contained more C and N than FA.

Table 2.1 Ranges and means (indicated in brackets) for C and N composition of humic (HA) and fulvic (FA) acids extracted from soils from widely differing climatic zones (Schnitzer, 1982)

Element (%)	HA	FA
C	53.6 – 58 7 (56.2)	40.7 – 50.6 (45 7)
N	0.8 – 5.5 (3.2)	0.9 – 3.3 (2.1)

The proportion of HA to FA varies between soil types. Studies conducted by Kononova (1966) and MacCarthy *et al.* (1990) have suggested that the HA/FA ratios of soils are affected by native vegetation. Grassland soil are usually higher in HA than forest soils. Kononova (1966) had already indicated that grassland soils were high in HA as compared to the forest HA. Climate also appears to have an impact on the proportions of HA to FA in soils. Christopher (1996) reported higher amounts of FA in tropical soils than in temperate soils. In Peninsular Malaysia for example, 75-95% of organic C is derived from FA.

The HA/FA ratios of soil are seemingly reduced by cultivation. This observation is consistent with the work of Dormaar (1979), who found that following cultivation, HA-C as a percentage of total organic C had increased. Studies of Kononova (1966) also indicated that regular additions of manure to soil tend to widen the HA/FA ratios of soils. However these ratios were usually but not always found to decrease with depth.

Virtually every separation technique developed by chemists and biochemists have been applied to investigate humic substances. MacCarthy (2001) emphasized that none of these techniques have come even remotely close to isolating a material that could be called a pure humic substance. The result is that the classical fractionation technique of humic substances, as laid out by Aiken *et al.* (1985), is still used in many studies. However, it is the fractions rather than the whole of humic substances that are of immense interest. It should however be noted that most studies on humic substances have been conducted on FA and HA, while humin has been investigated to a lesser extent (Rice & MacCarthy, 1988).

2.2.2.1 Humic acid fraction

Humic acids comprise a fraction of humic substances that is not soluble in water under acidic conditions (pH<2) but is soluble at higher pH values. These acids can be extracted from soil by various reagents and they are the major extractable components of humic substances (MacCarthy *et al.,* 1990). They are dark brown to black in colour, and have higher molecular weight polymers compared to FA (MacCarthy *et al.,* 1990; MacCarthy, 2001). This fraction is thought to be complex macromolecules with amino acids, amino sugars, peptides and aliphatic compounds involved in linkages between aromatic groups. The aromatic structure depicts it as containing free and bound phenolic OH groups, quinine structures, N and O as bridge units and COOH groups, variously placed on aromatic rings (MacCarthy *et al.,* 1990).

2.2.2.2 Fulvic acid fraction

Fulvic acids comprise the fraction of humic substances that is soluble in water under all pH conditions. These acids remain in solution after removal of HA by acidification. They have a light yellow to yellow brown colour. Compared to HA, FA have lower molecular weight but higher oxygen content and as a result, they are more polar and mobile (Zalba & Quiroga, 1999). Thus this fraction is probably representative of the labile pool of organic matter. Most of the functional groups possessed by FA are of an acidic nature, particularly COOH, equating to 900-1400 meq/100g when compared to the 400-879 meq/100g of HA (Cresser *et al.,* 1993).

2.3 Factors determining organic matter content of undisturbed soils

The level of organic matter in any undisturbed soil at a given time is determined by the interaction among factors which determine its formation like climate, vegetation, topography and parent material (Fernandes *et al.,* 1997). Allison (1973) asserts that these factors exert their effect both individually and collectively and to varying degrees. Soil scientists unanimously agree that under natural conditions, organic matter levels of mature, undisturbed soils are almost constant. Marked changes in soil organic matter content only occur if there is a major change in the climate, which in turn affect the nature of the vegetation and also the innate nature of the soil and the topography of the land in question, thus all have an impact on the level of soil organic matter (Allison, 1973; Rasmussen & Collins 1991; Magdoff & Weil, 2004).

Temperature and precipitation are believed to be the major climatic factors responsible for determining soil organic matter levels via microbial activity (Smith & Elliot, 1990; Magdoff & Weil, 2004). Within limits, higher rainfall tends to increase plant growth and hence litter more than it does decomposition; therefore, soil organic matter tends to be positively correlated with high annual precipitation (Magdoff & Weil, 2004). In general, low annual temperature and high annual rainfall favours soil organic matter accumulation, and high annual temperature and low annual rainfall favours soil organic matter degradation.

Topography modifies the microclimate and influences the vegetation, thereby producing a strong effect on the amount of organic matter in the soil. The same climatic factors just mentioned above, change usually in favour of soil organic matter accumulation with higher elevations. Slope steepness and landscape facing position are also important factors, often accounting for large differences in soil organic matter accumulation within small distances. Aspect, *viz.* the direction a slope faces is of importance on steeply, sloping soils. The average temperature of a soil that faces towards the warm early afternoon sun may be several degrees higher than that of a soil facing in the opposite direction. More organic matter accumulates usually in the latter than the former soils (Troeh & Thompson, 1993).

In addition to these environmental factors, soil organic matter levels are also markedly influenced by inherent properties of the soil that can be attributed to the parent material like soil texture and mineralogy. Soil texture is particularly important in this regard (Kononova, 1966; Allison, 1973; Troeh & Thompson, 1993; Magdoff & Weil, 2004). Provided the environmental factors are homogeneous, finer textured soils tend to accumulate more organic matter than coarser textured soils. Nichols (1984) found that among soils in the southern Great Plains of the United States of America, organic matter levels were more closely related to clay content than to annual rainfall. The reason for this relationship is that high silt-plus-clay content provides a soil the capacity to hold water and nutrients for more plant biomass production while inhibiting the free circulation of air that would stimulate rapid decomposition of organic matter. These fine separates also have larger surfaces that chemically bind with organic compounds, resulting in aggregates that physically protect organic matter from microbial attack (Oades, 1995).

Considering the above mentioned it is not surprising that South Africa is characterized by soils with low organic matter levels. Based on the organic C content of undisturbed soils, only 4% of the soils contain more than 2% organic C and 58 % of the soils contain less than 0.5% organic C. The remaining 38% of the soils contain 0.5 to 2% organic C (Du Preez, 2002).

2.4 Influence of organic matter on soil quality

2.4.1 Soil quality

Soil quality can briefly be defined as the degree of fitness of a soil for a specific use (Gregorich *et al*., 1994). On a wider spectrum, Anderson and Gregorich (1983) described soil quality as the sustained capability of a soil to accept, store and recycle water, nutrients and energy. In addition to this, soil quality also addresses the capacity of a soil to disperse and transfer chemical and or biological materials and thus function as an environmental filter or buffer (Gregorich *et al*., 1994). Sharma *et al.* (2005) further described soil quality as a tool for evaluating the sustainability of management practices applied to cropping systems. The quality of soil depends in part on its natural or inherent composition (inherent soil quality), which is a function of soil formation factors referred to earlier and is also affected by human use and management (dynamic soil quality) (Pierce & Larson, 1993).

The quality of soil is usually quantified by measuring changes in selected key attributes over a prescribed period of time (Doran & Parkin, 1994; Larson & Pierce, 1994). Organic matter is such an attribute since it influences many other properties and processes in soil. For example organic matter plays an important role in the development and maintenance of physical, chemical and biological properties and processes that shall be elaborated upon in subsequent sections. Assessment of organic matter is therefore a valuable step towards identifying the overall quality of soil.

2.4 2 Influence of organic matter on soil properties and processes

2.4.2.1 Physical properties and processes

Organic matter promotes good soil structure, thereby improving tilth, aeration and retention of water. The deterioration of structure that accompanies intensive tillage is usually less severe in soils adequately supplied with organic matter. Organic matter acts as a ‘cement’ for holding silt and clay particles together, thus contributing to the crumb structure of soil (MacCarthy *et al.,* 1990; Troeh & Thompson, 1993). The frequent addition of easily decomposable organic residues, leads to the synthesis of complex organic compounds that bind soil particles into structural units called aggregates. These aggregates help to maintain a loose, open granular condition, thus maintaining large pores which ease aeration and favours infiltration and percolation of water downward through the soil (Schnitzer, 1991). Organic matter increases soils’ ability to resist erosion, in that it can absorb up to 90% of its weight as water, which substantially increases the water holding capacity of mineral soils (Smith & Elliot, 1990). Dark pigment conferred upon organic matter by humic substances, favours absorption of heat by the soil thus speeding the warming of the soil (Sikora & Stott, 1996).

2.4.2.2 Chemical properties and processes

Organic matter contributes to the acid-base buffering ability and exchange capacity of soils (MacCarthy, 2001). The colloidal nature of organic matter allows it to impart substantial buffering capacity to the soil through cation and anion exchange (Smith & Elliot, 1990). Soil organic matter is able to exhibit the buffering over a wide pH range. From 20 to 70% of the exchange capacity of many soils is due to colloidal humic substances.

Soil organic matter has both direct and indirect effects on the availability of nutrients for plant growth (Schnitzer, 1991). It serves as a storehouse for plant nutrients that are released slowly; it supplies nearly all the N, 50 to 60% of P and as much as 80% of S (Bohn *et al.,* 1985). The supply of nutrients from other sources is also influenced by soil organic matter, for example it is required as an energy source for N fixing bacteria. It also aids in trace element nutrition of the plant through chelation reactions with Fe, Cu, Zn and other polyvalent cations that might otherwise be leached out of the surface soil (Bohn *et al.,* 1985; Sikora & Stott, 1996). Organic matter also has an indirect role in soil through its effect on the uptake of micronutrients by plants and the performance of herbicides and other agricultural chemicals. Another role of organic matter is aiding in the solubilization of plant nutrients from insoluble minerals present in the soil. It achieves this by complexing with toxic ions such as Cd and Hg, as well as with micronutrient cations at high concentration and reduces their availability (Sikora & Stott, 1996). Organic matter also acts as an oxidizing and reducing agent, it supplies O_2 to plant roots and gives off CO_2 to the atmosphere.

2.4.2.3 Biological properties and processes

Soil organic matter plays a biological function in that it profoundly affects the activities of micro-flora and micro-fauna organisms by serving as a source for energy. Numbers of bacteria, actinomycetes and fungi in the soil are related in a general way to organic matter content. Earthworms and other faunal organisms are strongly affected by the quantity of plant residues returned to the soil. The humic substance portion of organic matter can serve as a reservoir for holding nutrients in the soil, and making them available later for plant root hairs (MacCarthy, 2001). Organic substances in the soil can have a direct physiological effect on plant growth. Some compounds such as certain phenolic acids have phytotoxic properties. Others such as auxins enhance plant growth. Factors influencing the incidences of pathogenic organisms in soil are directly or indirectly influenced, for example a plentiful supply of organic matter may favour the growth of saprophytic organisms relative to parasitic ones and thereby reduce population of the latter. Biologically active compounds in soil such as antibiotics and certain phenolic acids may enhance the ability of certain plants to resist attack by pathogens (Schnitzer, 1991). All these functions of soil organic matter are attributed to the humic substances it comprise of.

2.5 Influence of land use on soil organic matter levels

Organic matter accumulates in soil to the degree that C inputs (gains) exceed outputs (losses) or vice versa. This balance as described earlier is dependent on environmental factors but human interventions exert considerable influence on its direction. Soil organic matter usually reacts slowly to a change in land use, as a consequence changes are difficult to measure against a large background of organic matter. Therefore sufficient years have to elapse after a change in land use for differences to be larger than analytical variability (Rasmussen & Collins, 1991; Lobe, 2003). Idealistically, long-term experiments are required for such studies but they are rare in most countries and South Africa is no exception. Therefore studies of this nature rely in many instances on farmers who have good records of land use on their farms. The emphasis in this section will be on changes in soil organic matter resulting from cultivation of formerly virgin land, and reversion of cultivated land to perennial pasture, particularly for the area under investigation.

2.5.1 Cultivation of a formerly virgin land

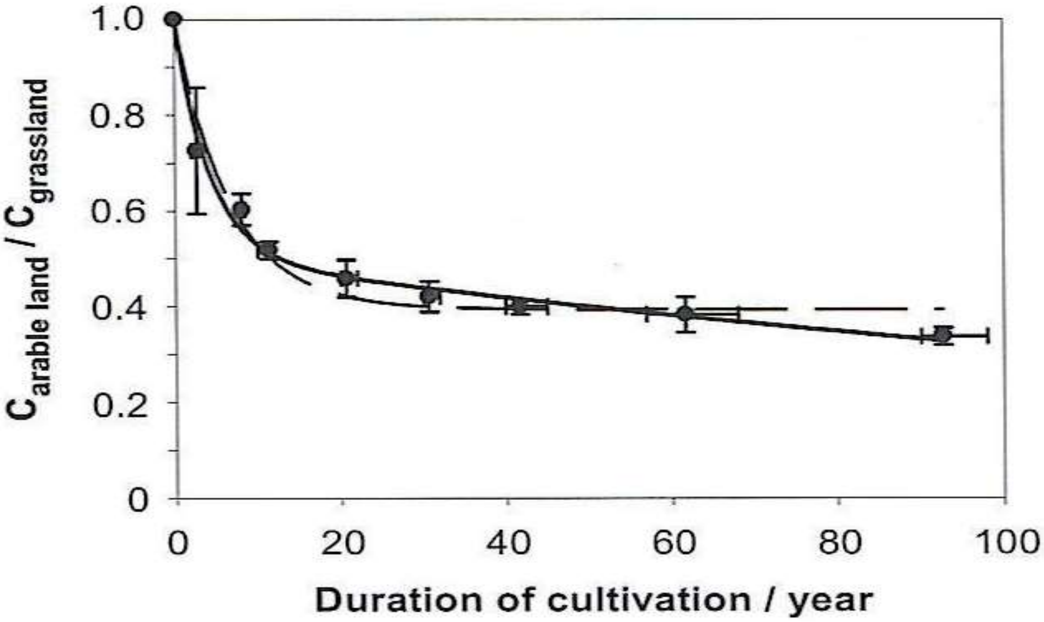
The activities of man, which usually include removal or marked modification of the vegetative cover and the use of intensive tillage systems like mouldboard ploughing, greatly speed up changes in soil organic matter levels (Allison, 1973). The level of organic matter present in soil is a function of the net input of residues by the cropping system practiced. Any factor that decreases the amount of substrate added to the soil or hastens the decomposition of the substrate in the soil will tend to decrease the equilibrium level of organic matter in the soil. As a result, cropping practices have considerable influence on the soil organic matter level (Janzen, 1987).

The shift in land use from natural vegetation to cropping generally results in a marked decline in soil organic matter levels. Cropping nearly always cause less C to be added to the soil and more to be lost (Magdoff & Weil, 2004). The lower input of C is usually not due to reduced net primary productivity under cropping, but rather to human appropriation and removal of much of the aboveground plant biomass produced. In addition, cropping practices, especially intensive tillage, accelerate the loss of C from the soil by microbial respiration and erosion. The magnitude and duration of the decrease in organic matter however, depends on the subsequent land use, climate, and soil physical and chemical properties (Fernandes *et al.,* 1997).

In South Africa anthropogenic factors that have contributed to the decline of soil organic matter are South Africa's isolation over many years, which resulted in monoculture cereal production, intensive tillage, short to no fallow and virtual absence of crop rotation systems in the commercial farming sector, and over utilization of cropped soils in the communal areas (Barnard & Du Preez, 2004). On account of these factors research by Du Toit *et al.* (1994) and Lobe *et al.* (2001) on the highveld showed significant losses of soil organic matter from distinct agro-ecosystems as indicated by either organic C and total N contents. An average loss of 44% C and 47% N was noted when grassland served as reference.

Data derived from Du Toit *et al.* (1994) and Lobe *et al.* (2001) on the three agro-ecosystems under investigation was used by Birru (2002) to express the degradation loss of organic C as percentage of the baseline values using the following equation $DL= [C_o - C_e]*100/C_o$. The results revealed that cultivation had caused a decrease in organic C of 60% for Harrismith after 35 years, 63% loss for Tweespruit after 44 years and 52% loss for Kroonstad after 14 years of cultivation. A similar pattern was discerned for loss of total N, using above mentioned equation with N substituted for C. Loss of total N was 53% for Harrismith after 34 years, 55% for Tweespruit after 35 years and 42% for Kroonstad after 10 years of cultivation.

Researchers such as Jenny (1941) declared that the loss of soil organic matter owing to cultivation is usually exponential, *viz.* declining rapidly during the first 10-20 years and then continuing slowly until a new equilibrium is reached after 50-60 years. Representative degradation curves for the three agro-ecosystems under investigation were therefore established by Lobe *et al.* (2001) using either organic C or total N in an exponential decay model (Figure 2.1). The pattern of loss for both organic C and total N showed three distinct phases. The loss was rapid during phase one which was the first five years of cultivation. Thereafter the rate decreased in the second phase until an equilibrium was reached after about 35 years of cultivation. Following this very little or no further loss occurred, that marked the third phase (Du Toit *et al.,* 1994). The decomposition rate of organic matter because of cultivation in the warmest and driest Kroonstad agro-ecosystem was higher than in the coolest and wettest Harrismith agro-ecosystem. However, the percentage loss of organic matter was larger in the latter agro-ecosystem. This observation is supported by Mann (1986) who reported that soils initially high in organic C lost a larger proportion, and soils initially low in organic C lost a smaller proportion under the influence of cultivation. Thus organic matter from warmer, drier agro-ecosystems reached a new equilibrium much faster than that in cooler, wetter agro-ecosystems. In the agro-ecosystems under investigation, the organic matter content of virgin soils increased with increasing aridity indices (which implies luxuriant vegetation) and with increasing fine silt-plus-clay contents (which stabilizes organic matter) (Du Toit *et al.,* 1994).



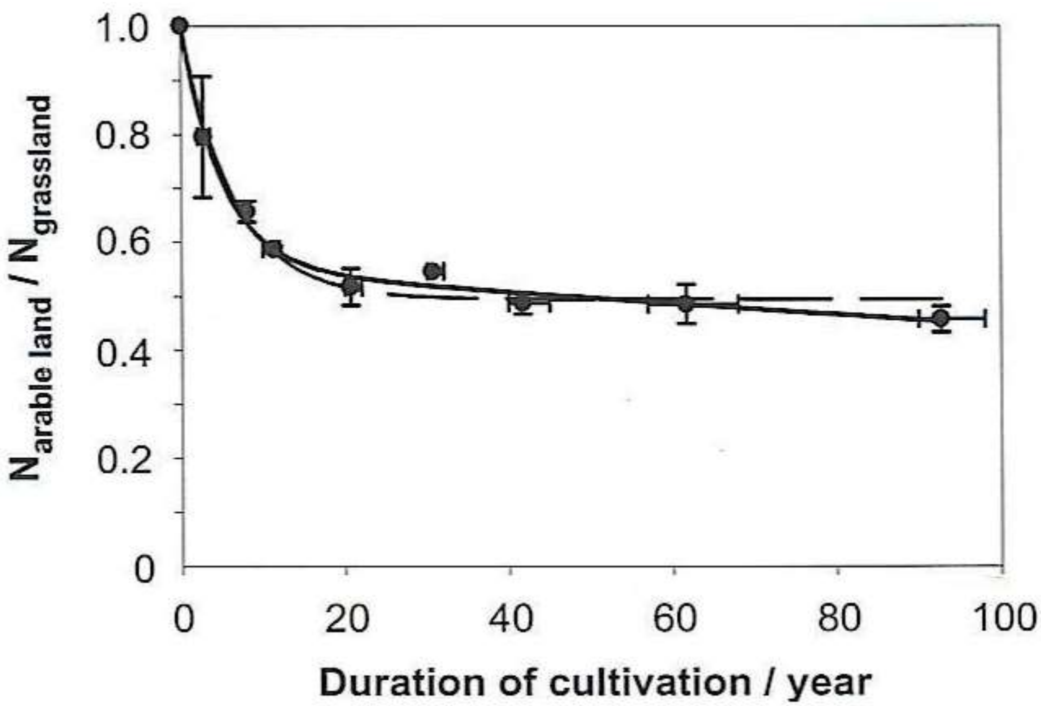


Figure 2.1 Effect of cultivation on the percentage loss of organic C and total N relative to the native grassland, shown as means of Harrismith, Tweespruit and Kroonstad agro-ecosystems. Horizontal bars represent the span of cultivation period between the three agro-ecosystems, vertical bars the standard error. The dashed line represents the fit of the exponential model.

2.5.2 Reversion of cultivated land to perennial pasture

Allowing cropland to return to natural grassland vegetation is one way by which the farmers can restore levels of soil organic matter. The pioneer in South Africa of this approach was Theron (1949; 1963; 1965). His findings gave some insight with regard to the function of grass as a means of rehabilitating worn-out soils. No fundamental differences in respect of the influence on the organic matter of the soil between a grass sward and ordinary farm crop has been observed. Living roots, be it grass or maize, are able to bring about complete cessation in the decomposition of the organic matter once the roots are properly established in the soil. The perennial grass does so permanently, whereas the action of the annual farm crop is intermittent, but neither is able to add unassisted, to the store of soil humus. The rehabilitation of worn-out soils must of necessity be based on restoration of the depleted humus. Thus a grass cover is not able to do so without our assistance in the form of nitrogen fertilizer addition (Theron, 1963).

More recently Birru (2002) investigated the restoration of soil organic matter in cultivated soils reverted to perennial pasture. This study comprised of the three agro-ecosystems under investigation, namely Harrismith, Tweespruit and Kroonstad. A substantial amount of the soil organic matter lost during 20 or more years of cultivation was restored under perennial pasture. However, it is likely to take up to 35 years for full restoration since organic C gains were found to be only 0.63, 0.28 and 0.54 Mg ha^{-1} yr^{-1} for Harrismith, Tweespruit and Kroonstad respectively. Although the factors on which soil organic matter restoration depend, such as climate, topography and soil appear to be correlated with mean organic C gains, that of Tweespruit is below comprehension due to a low N fertility level at all sites which did not receive N fertilization. Therefore Birru (2002) concluded that aggressively growing pasture grasses, which are closely linked to good management practices are vital for soil organic matter restoration.

This confirms the findings of Theron (1953) that upon recuperation of degraded cultivated land with perennial grass, management practices that entailed application of N fertilizer played a crucial part in the restoration of soil organic matter. Theron and

Haylett (1953) also reported that where perennial grass and lucerne were grown in a mix, accumulation of soil organic matter was apparent over time.

2.6 Soil organic matter management strategies

Despite increasing scientific understanding of the natural processes involved in soil organic matter dynamics, there are several factors that limit the adoption of management strategies to maintain or increase soil organic matter in the various agro-ecosystems. A major constraint is often an inadequate supply of organic inputs due to competing uses of organic materials as fodder, fuel and building materials. Management-induced changes in organic matter are usually attributed to differences in the amount, placement and composition of organic residues returned to the soil, and changes in the living environment (temperature, moisture, accessibility of energy source) of soil organisms. Several researchers have found microbial biomass to be a useful index for assessing the contribution of organic matter to aggregate stability in soil (Haynes & Swift, 1990).

Accelerated decomposition of soil organic matter due to cropping and the resulting loss of organic C to the atmosphere and its contribution to the greenhouse effect is a serious global problem. For example, in the early 1980's, land use changes were simulated to have resulted in the transfer of between 1 and 2 x 10^{15}g C yr^{-1} from terrestrial ecosystems to the atmosphere. Between 15 and 17% of this C came from the decomposition of soil organic matter (Fernandes *et al*., 1997). The reduction in soil organic matter content can be due to increased erosion, faster mineralization of organic substances, smaller quantities of organic inputs and/or more easily decomposed organic inputs in managed systems as compared to natural settings. However, in some managed systems, increases in soil organic matter contents have occurred due to improvements in plant productivity and the subsequent increase in additions of above and below ground organic inputs to the soil (Fernandes *et al.,* 1997).

2.6.1 Crop rotation

Fallowing significantly exacerbates the depletion of organic matter. In a long-term spring wheat rotation study, it was observed that lower organic C and N concentrations occurred in the wheat-fallow rotation than in treatments without fallow. The level and quality of organic matter retained over time in soil is also influenced by the selection of crops in the rotation (Janzen, 1987). In particular the inclusion of legumes or grass forages in the cropping sequence has been shown to reduce or even reverse organic C and N losses. These findings appear to tally with those of Theron (1953) that have been referred to earlier in the text. In 12 year-old wheat fallow fields of Western Nebraska it was found that losses of organic N decreased as the level of clean tillage decreased. Janzen (1987) also reported decreasing losses of organic matter with decreasing frequency of fallow for the cropping systems applied on Canadian Chernozemic soils.

2.6.2 Tillage practices

Tillage is often highlighted as the main cause of soil organic matter decline. This rests on the hypothesis that the disruption of soil aggregates leads to exposure of organic matter to microbial attack (Davison, 1986). Factors leading to soil organic matter loss through tillage, intensive grazing or frequent burning are similar in many respects and can probably be attributed mainly to erosion and vegetation removal (Mills & Fey, 2004).

Chan and Hulugalle (1999) studied organic matter changes in Alfisols caused by the conversion of native pasture to intensively tilled wheat with long fallow and stubble burning. The cultivated land had significantly lower organic C and total N in the 0-50 mm soil layer (Table 2.2). Mean organic C content of the cultivated land was about half of that in the pasture land. For the 50-100 mm soil layer, the organic C level was similar for both cultivated and pasture land. Examining the depth effect, it could be seen that under natural pasture there was a decline in organic C with depth. These led Chan and Hulugalle (1999) to conclude that conventional tillage implements such as disc plough, which pulverise and invert soil, lead to increased losses of organic C and total N. A study by Kang *et al.* (2003) concerning the effects of agricultural practices on levels of HA-C, revealed a higher C content in HA in the 0-50 mm soil layer under conservation than conventional tillage. The HA-C level was also found to decline with depth under both forms of tillage systems.

There is an abundance of data to show that grassland and forest soils in the United States of America tend to loose 20 to 50% of its organic matter within the first 40 to 50 years of cultivation. This is well illustrated in the studies of Mann (1985; 1986). Cultivation of grassland and forest soils result therefore in major losses of C in the atmosphere, contributing to the greenhouse effect (Jenkinson, 1990). For the soils of the Central United States of America, which include what is now the Corn Belt and a part of the Great Plains, Donigian *et al.* (1994) according to Swift (2001) studied the change in organic C to 200 mm depth between 1907, when soils were brought into long-term cultivation, and 1994. The results show a steep decline of organic C in the first 40 years of cultivation, and in that time, 47% of the organic C was lost. An equilibrium was achieved and maintained until reduced tillage operations were introduced in 1970, where after there has been a gradual accumulation of organic matter. On average soil organic matter content in the permanent grassland was 3.1% in 1949, and as a result of tillage and residue removal in the cultivated land it declined to 1.6%. There was no significant change in the organic matter content of the soils from 1949 to 1985.

Table 2.2 Changes in organic C and total N under conventional tillage wheat cropping in hard setting red Alfisols (Chan & Hulugalle, 1999)

Land use System	Depth (mm)	Organic C ($g\ kg^{-1}$)	Total N ($mg\ kg^{-1}$)	pH
Native pasture	0 -50	28.1^{a}	0.20^{a}	5.5^{a}
Cultivated		13.8^{b}	0.13^{b}	5.1^{b}
Native pasture	50 -100	13.6^{a}	0.11^{a}	5.3^{a}
Cultivated		12.2^{a}	0.10^{a}	4.9^{a}

*Values within the same column followed by different superscripts differ significantly at 95% level of probability for a soil layer.

2.7 Developments in soil organic matter characterization

The methods used in characterizing soil organic matter have developed under the influence of diverse scientific disciplines. However, functional aspects of organic matter have traditionally been explored by scientists associated with agricultural research because of its key role in soil productivity (Christensen, 1992). These aspects and the methodology used in establishing them have been reviewed regularly in recent years (Tisdale & Oades, 1982; Gregorich *et al.,* 1994; Potter *et al*., 1999; Hayes & Clapp, 2001; Swift, 2001).

It appears that in South Africa the chemical characterization of soil organic matter, in order to attain knowledge pertaining to the nature of its composition and turnover have not yet attracted the same attention as in some other countries. This may be due to the fact that some scientists believe that chemical fractionation has not proven very useful in following soil organic matter dynamics (Fernandes *et al*., 1997). Changes in organic C resulting from land use are currently often elucidated through the use of ^{13}C CP/MAS NMR spectroscopy, IR spectroscopy and pyrolysis. For the purpose of this study the classical chemical soil organic matter characterization procedure was used. This defines the humic substances on the bases of their solubility in alkali and acid extractants. Even though it is an old fashioned procedure and is labour intensive, it is still arguably the best method at providing the most interpretable data with regard to the components of humic substances (Hayes & Clapp, 2001).

2.8 Conclusion

A change in land use exerts a pronounced influence on the concentration and composition of soil organic matter. In general cultivated top soils have lower levels of organic C and total N than uncultivated top soils. The depletion of organic C and total N with cultivation can be attributed to changes in magnitude of the physical, chemical and biological processes in the soil (Stevenson, 1982). Increased microbial activity under aerated conditions caused by tillage, increases the decomposition rate of organic matter

(Rovira & Greacen, 1957). This is attributed to more favourable water and temperature regimes in the tillage inverted soil. Reduced rates of C inputs to the soil particularly root residue exudates, are also likely related to C depletion. Soil erosion has also been reported as a factor of organic matter loss from soil. Chemical fractionation techniques offer a significant potential for evaluating land use induced changes on humic substance fractions of organic matter when C and N are used as indices for measuring this change which ultimately has an impact on soil quality. This review provided a summary of the current knowledge and research activities in this area of soil science in South Africa and the world at large. Linkages between the various measurements of soil organic matter components and their application for soil quality interpretations were identified.

CHAPTER 3

MATERIALS AND METHODS

This study as mentioned in Chapter 1, complements earlier investigations (Du Toit, 1992; Birru, 2002; Lobe, 2003) into soil organic matter degradation and restoration on three agro-ecosystems in the Free State Province of South Africa. The collection of soil samples from each of these investigations was stored for further studies like this one. All soil samples used in the study were carefully selected from these collections with the listed objectives in mind. A concise description of the methodology employed by Du Toit (1992), Birru (2002) and Lobe (2003) in their investigations are therefore justified here.

3.1 Characteristics of studied agro-ecosystems

The three agro-ecosystems studied by Du Toit (1992), Birru (2002) and Lobe (2003) are at Harrismith, Kroonstad and Tweespruit (Figure 3.1). Their altitudes vary between 1400 and 1800 m above sea level with Kroonstad at the lowest and Harrismith at the highest location (Table 3.1). Mean annual rainfall ranges from 516 mm at Tweespruit to 625 mm at Harrismith of which most falls in summer from October to March. The mean annual temperature is 13.8 ^{o}C at Harrismith, 14.8 ^{o}C at Tweespruit and 16.6 ^{o}C at Kroonstad. All three agro-ecosystems have some native grassland used for stock farming. Harrismith is in the Moist Cold Highveld Grassland; Kroonstad in the Dry Sandy Highveld Grassland and Tweespruit in the Moist Cool Highveld Grassland (Bredenkamp *et al*., 1996). The botanical composition of the native grassland is dominated by *Cymbopogon plurinodis, Themeda trianda, Setaria sphacelata, Elionurus muticus* and *Erograstis curvula* at Harrismith, *Erograstis lehmanniana, Erograstis obtusa, Pancum coloratum, Stipagrostis uniplumis* and *Pentzia globosa* at Kroonstad, and *Themeda trianda* at Tweespruit. Stocking density is respectively 0.4, 0.5 and 0.6 large stock units per hectare at Harrismith, Kroonstad and Tweespruit (Lobe, 2003).

During the past century some of the grassland in the three agro-ecosystems was converted to cropland resulting in different ages under cultivation. This arable land had been ploughed to a depth of 200-300 mm and cultivated with a rotation of wheat, maize and occasionally sunflower. Fertilizer was applied annually (maize: 50-70 kg N, 10-25 kg P, 0-10 kg K ha^{-1}; wheat: 10-40 kg N,10-25 kg P, 0-15 kg K ha^{-1}; sunflower: 20-50 kg N, 10-20 kg P, 2-6 kg K ha^{-1} to the dryland crops. Average grain yields varied from 2.2-

3.75 t ha^{-1} for maize, 1.2-2.75 t ha^{-1} for wheat and 1.0-1.25 t ha^{-1} for sunflower. Soils are usually kept clear of vegetation for up to six months in the dry season so that the soils retain their stored water (Du Toit, 1992; Lobe, 2003).

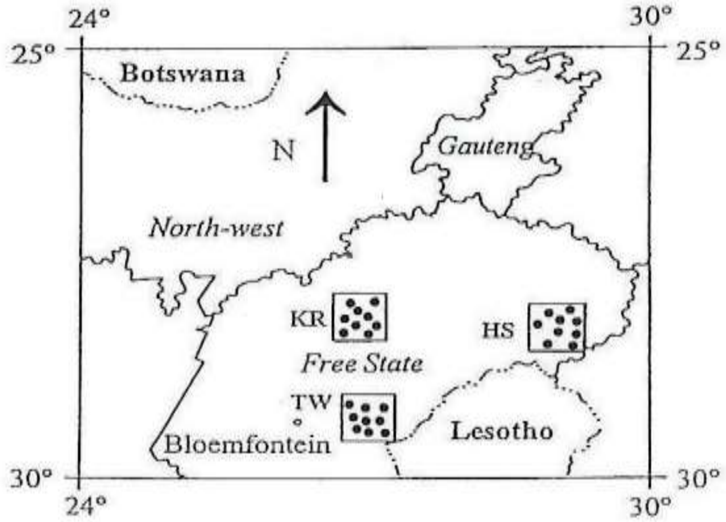


Figure 3.1 Location of the three agro-ecosystems Harrismith (HS), Kroonstad (KR), and Tweespruit (TW) in Free State Province in South Africa.

In the past three decades some cropland of all three agro-ecosystems was converted to perennial pasture resulting in different ages under conversion. The pasture comprised mostly of *Erograstis curvula* that is used either for grazing or haying. Inorganic fertilization is mainly restricted to the application of N at annual rates of 28-84 kg ha^{-1} at Harrismith, 0-75 kg ha^{-1} at Kroonstad and 0-46 kg ha^{-1} at Tweespruit (Birru, 2002).

Table 3.1 Environmental factors of the Harrismith (HS), Tweespruit (TW) and Kroonstad (KR) agro-ecosystems studied by Du Toit *et al*. (1994), Lobe *et al*. (2001) and Birru (2002)

Agro-ecosystem	Altitude (m)	Climatic data			Soil form	Clay %			Sampling depth (mm)
		[1]MAR (mm)	[2]AI	[3]Ta (^{0}C)		Du Toit	Lobe	Birru	
HS	1800	624	0.36	13.8	Avalon	9 - 16	13 -19	11 - 17	0 – 200
TW	1600	544	0.27	14.8	Westleigh	12 - 21	10- 16	9 - 16	0 – 200
KR	1400	566	0.28	16.6	Avalon	6 - 11	10 -15	7 - 14	0 - 200

[1]Mean annual rainfall; [2]Mean annual aridity index; [3]Mean annual temperature;

Soils of the agro-ecosystems are mainly of the Avalon and Westleigh forms (Soil Classification Working Group, 1991), which can be described also as Plinthosols (FAO, 1998) or Plinthustalfs (Soil Survey Staff, 1998). At Harrismith and Kroonstad the Avalon soil form (Figure 3.2) dominated. This soil has characteristically a brown to dark brown sandy loam orthic A horizon, followed by a yellowish brown to dark brown sandy clay loam apedal B horizon and then a grey mottled red sandy clay soft plinthic B horizon. At Tweespruit the Westleigh soil form (Figure 3.3) dominates. This soil has characteristically a very dark brown sandy loam to sandy clay loam orthic A horizon overlying a dark yellowish brown mottled sandy clay plinthic B horizon.

3.2 Site selection and soil sampling

The approach followed by Du Toit (1992), Birru (2002) and Lobe (2003) in the selection of sites and sampling of soils varied somewhat since their objectives differed. Du Toit (1992) sampled six sites at the Harrismith agro-ecosystem and five at both Kroonstad and Tweespruit agro-ecosystems. At each site six plots were sampled from a virgin and cultivated land. Twenty sub-samples were collected from each plot (10m x 10m) to 200 mm depth in obtaining a composite sample. This collection of soil samples represents cultivation periods of 0-59 years at Harrismith, 0-56 years at Kroonstad and 0-85 years at Tweespruit.

Lobe (2003) sampled nine sites at each of the Harrismith, Kroonstad and Tweespruit agro-ecosystems. The sites in each agro-ecosystem comprised arable land with varied lengths of time under cultivation and adjacent virgin land. Samples to 200 mm depth were taken from five sub-sites on each of these virgin and arable lands, using a radial sampling scheme with a horizontal distance of more than 3 metres. This collection of soil samples represents cultivation periods of 0-90 years at Harrismith, 0-98 years at Kroonstad and 0-90 years at Tweespruit.

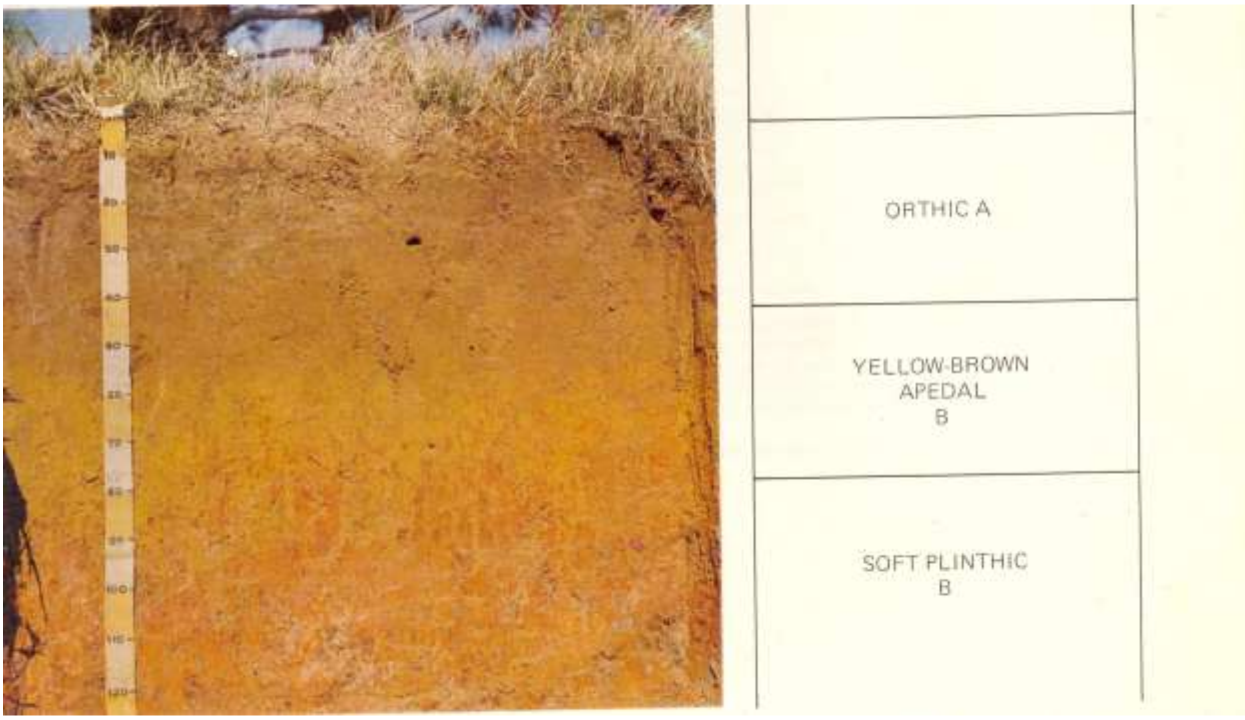


Figure 3.2 An example of an Avalon soil form profile (Soil Classification Working Group, 1991).

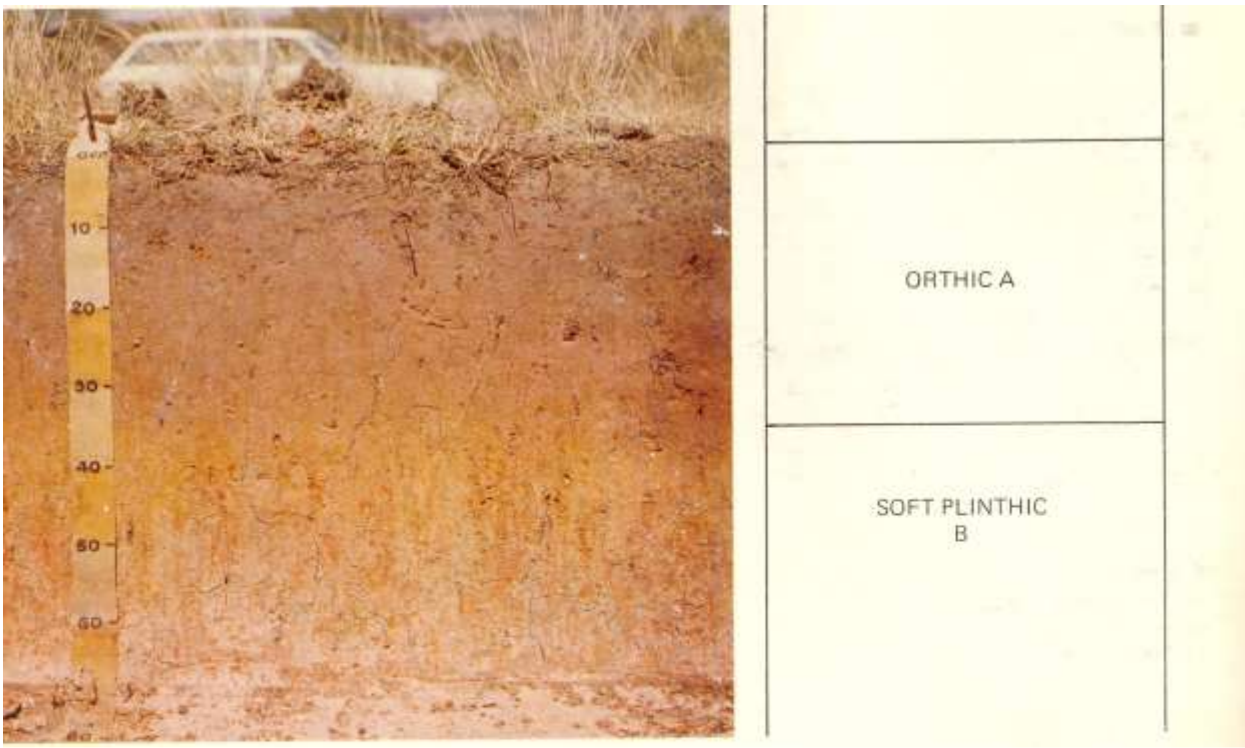


Figure 3.3 An example of a Westleigh soil form profile (Soil Classification Working Group, 1991).

Twenty eight perennial pasture sites, including eight from Harrismith, twelve from Kroonstad and eight from Tweespruit were sampled by Birru (2002). Sampling depths at each site were 0-50, 50-100 and 100-200 mm. Six replicate samples were collected from every site. Each of these samples was a composite of six sub-samples taken in a circle of 2 m radius. Only sites with perennial pasture older than five years that had previously been under continuous cultivation for more than 20 years were sampled. This collection of soil samples represents perennial pasture periods of 5-25 years at Harrismith, 4-20 years at Kroonstad and 5-25 years at Tweespruit.

3.3 Soil sample selection

In achieving the objective of this study soil samples were required from virgin, cultivated and restored land in each of the three agro-ecosystems. It evolved from the studies of Du Toit (1992), Birru (2002) and Lobe (2003) that either the depletion or restoration of organic matter resulting from land use is very sensitive to clay content. Thus for this particular study, selection of soil samples was based on consistence in clay content to ensure that results obtained would be a true reflection of the influence of the three land uses on the dynamics of humic substances in the three agro-ecosystems. Further prerequisites were that the soil samples from cultivated land be older than 20 years, and perennial pasture land older than 15 years, allowing for substantial organic matter depletion and restoration, respectively. Ultimately, virgin and cultivated land at sites 26 (Harrismith), 10 (Kroonstad) and 22 (Tweespruit) sampled by Du Toit (1992), and perennial pasture land at sites 7 (Harrismith), 11 (Kroonstad) and 6 (Tweespruit) sampled by Birru (2002) fulfilled these criteria. The soil samples collected and stored from the mentioned sites were therefore used in this investigation. Some characteristics of the soils are given in Table 3.2. The soil samples from Lobe *et al.* (2001) were not used as part of the investigation, instead the data obtained from their analyses was used as control.

Table 3.2 Characterization of sites in Harrismith, Tweespruit and Kroonstad agro-ecosystems from which soil samples were collected by Du Toit *et al.* (1994) and Birru (2002)

Agro-ecosystem (collected by Du Toit *et al*., 1994)	Sample No.	Soil form	Clay content (%)	Years under cultivation
Harrismith	26	Avalon	13.1	20
Tweespruit	22	Westleigh	12.1	85
Kroonstad	10	Avalon	10.6	20
Agro-ecosystem (collected by Birru, 2002)				Years under pasture
Harrismith	7	Avalon	13.5	25
Tweespruit	6	Westleigh	12.6	25
Kroonstad	11	Avalon	11.5	18

3.4 Analyses on soil samples

In total 144 soil samples, comprising respectively 36 and 108 from the collection of Du Toit (1992) and Birru (2002) were selected for this study. Records of data on these samples are available for referrals, for example particle size distribution, organic C and total N (Du Toit, 1992; Birru, 2002); total inorganic and organic S (Du Toit, 1993), and total, inorganic and organic P (Van Zyl, 1995).

The determination of organic C with the Mebius procedure (Nelson & Sommers, 1982) and organic N with Kjeldahl digestion (Bremner & Mulvaney, 1982) from crude soil were performed again on the selected samples. Concisely, the Mebius procedure entails oxidation of organic C by treatment with a hot mixture of 0.5N $K_2Cr_2O_7$ solution followed by concentrated H_2SO_4 according to Equation 3.1:

$$2Cr_2O_7^{2-} + 3C^0 + 16\,H^+ \leftrightarrow 4Cr^{3+} + 3CO_2 + 8H_2O \qquad 3.1$$

Excess $Cr_2O_7^{2-}$ is then titrated with 0.2N $Fe(NH_4)_2(SO_4)_2.6H_2O$. The $Cr_2O_7^{2-}$ reduced during the reaction is assumed to be equivalent to the organic C present in the sample.

In Kjeldahl digestion organic N is converted to NH_4^+-N with concentrated H_2SO_4 in the presence of a catalyst, *viz*. a mixture of $CuSO_4.5H_2O$, K_2SO_4 and $Na_2Se_2O_4$. This mixture is then steam distillated with 8.0N NaOH to convert the NH_4^+-N to NH_3-N, and the latter is then retained in H_3BO_3 according to Equation 3.2:

$$NH_3 + H_3BO_3 \leftrightarrow NH_4^+ + H_2BO_3^- \qquad 3.2$$

Titration of the distillate with 0.005N H_2SO_4 releases NH_3 from the ammonium borate.

A sequence of steps was followed for the extraction and fractionation of humic substances from crude soil (Figure 3.4). The procedure was used because most humic substances are linked in several ways to the minerals in soil. These linkages must be destroyed to convert humic substances into a soluble state (Kononova, 1966; Schnitzer, 1991; Swift, 2001). Various inorganic and organic solvents have been used for this purpose. However, much attention has been paid to neutral salts of mineral acids, in particular sodium pyrophosphate. The action of sodium pyrophosphate and some neutral salts of organic acids in isolating humic substances from the soil depend upon their ability to form insoluble precipitates or soluble complexes with Ca, Fe, Al and other polyvalent cations to which the humic substances in soil are linked. There is a lot of dispute with regard to the combination of extractants that could isolate the largest proportion of humic substances from a soil. The most recommended method of extraction employs a mixture of 0.1M $Na_4P_2O_7$ and 0.1N NaOH with a pH of 13 (Kononova, 1966; Schnitzer, 1982; Swift, 1996). This extraction mixture removes practically all humic substances from soil without altering its physical and chemical properties. Other advantages are that it is relatively quick because neither decalcification with HCl or H_2SO_4 nor repeated extraction is required (Kononova, 1966; Schnitzer & Khan, 1972; 1978; Swift, 1996). The fractionation of humic substances is based on the differences in their solubilities in aqueous solution (Schnitzer, 1982; Stevenson & Elliot, 1989; Hayes & Clapp, 2001).

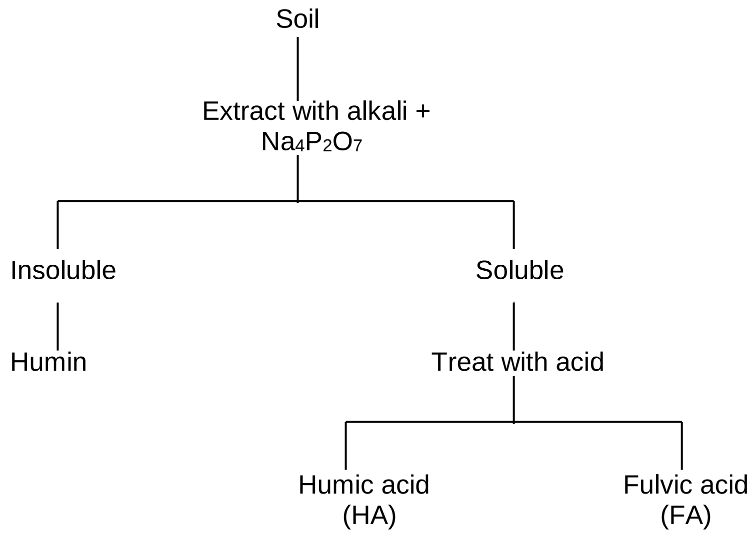


Figure 3.4 Extraction and fractionation of humic substances (Schnitzer, 1982).

Based on the above mentioned it was decided to use the procedure described by Schnitzer (1982). This implied that the humic substances were extracted with a mixture of 0.1N NaOH and 0.1M $Na_4P_2O_7$ of which the pH is 13. After extraction the supernatant was filtered and the filtrate was reserved for elemental (C and N) determinations and further fractionation into HA and FA. Concentrated H_2SO_4 was used to acidify the alkaline extract to pH 2. At this low pH HA precipitates and FA, which remained in solution, was decanted. The precipitated HA was dissolved in a warm 0.05N NaOH solution and filtered before C and N were determined. Determination of C and N in both instances was performed respectively with Mebius and Kjeldahl procedures outlined earlier. The concentrations and quantities of the reagents were adapted slightly. The C and N content of FA was obtained by difference between measured values of the humic substance extraction and HA.

3.5 Data processing and analysis

The measured C (g C kg^{-1} soil) and N (mg N kg^{-1} soil) contents for crude soil (Cs and Ns), humic substance extract (Ce and Ne), humic acid fraction (Ch and Nh) and fulvic acid fraction (Cf and Nf) were used to calculate C/N ratios after conversion to similar units. These measured and calculated data allowed for comparisons of cultivated soils (0-200 mm layer) with virgin soils (0-200 mm layer), and of restored soils (0-50 mm layer) with cultivated soils (0-200 mm layer). The intention of the latter comparison was to calculate weighted averages for the 0-200 mm layer of the restored soils. This was impossible due to very low C and N contents for the humic acid fraction in the 50-100 and 100-200 mm layers of especially the Kroonstad agro-ecosystem, resulting in unreliable data.

The NCSS software package (Hintze, 1997) was used for two way analyses of variance on mentioned indicators to test whether either agro-ecosystem or land use significantly influenced them. Comparisons of means was done with the least significant difference test of Tukey. Both analyses of variance and estimations of least significant differences were performed at a 5% probability level.

CHAPTER 4

RESULTS AND DISCUSSION

All data on C contents, N contents and C/N ratios for crude soil, humic substance extract, humic acid fraction and fulvic acid fraction are given in Appendix 1. These data are used as described in Chapter 3 to compare firstly, cultivated soils with virgin soils and secondly, restored soils with cultivated soils sampled from representative agro-ecosystems at Harrismith, Tweespruit and Kroonstad. Virgin, cultivated and restored soils have been defined in Chapter 1.

4.1 Comparison of cultivated soils with virgin soils

4.1.1 C contents

The summary of analyses of variance (Table 4.1) shows that the crude soil (Cs), extractable soil (Ce), humic acid (Ch) and fulvic acid (Cf) C contents differed significantly between agro-ecosystems (Harrismith, Tweespruit and Kroonstad) and land uses (virgin and cultivated). Effects of the interaction between land uses and agro-ecosystems on the Cs, Ce, Ch and Cf contents are displayed in Figure 4.1.

Table 4.1 Summary of the analyses of variance indicating the significant effects of agro-ecosystems (A: Harrismith, Tweespruit and Kroonstad) and land uses (B: virgin and cultivated) on crude soil (Cs), extractable soil (Ce), humic acid (Ch) and fulvic acid (Cf) C contents at 95% confidence level

	C fractions			
Treatments	**Cs**	**Ce**	**Ch**	**Cf**
A	*	*	*	*
B	*	*	*	*
AB	*	*	*	*

Crude soil C

The Cs of virgin soils ranged from 7.3 g C kg^{-1} soil in the Kroonstad agro-ecosystem to 21.6 g C kg^{-1} soil in the Harrismith agro-ecosystem (Figure 4.1). On a relative basis cultivation decreased Cs with 50.2 to 51.7% in the three agro-ecosystems.

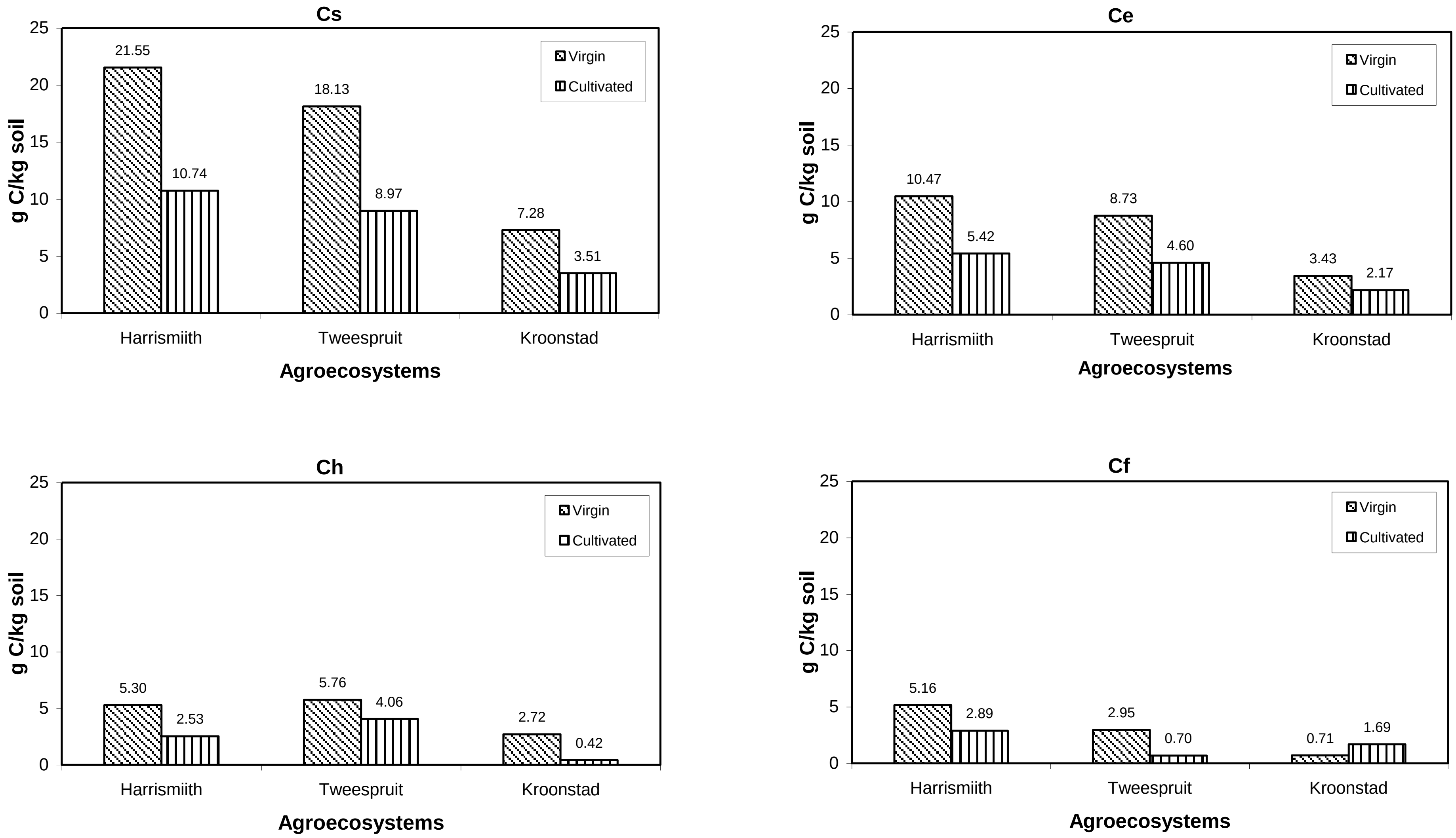


Figure 4.1 Effects of virgin and cultivated land use on crude soil (Cs), extractable soil (Ce), humic acid (Ch) and fulvic acid (Cf) C contents in Harrismith, Tweespruit and Kroonstad agro-ecosystems.

Hence Cs of the cultivated soils varied from 3.5 g C kg^{-1} soil in the Kroonstad agro-ecosystem to 10.7 g C kg^{-1} soil in the Harrismith agro-ecosystem. Losses of 40% or more in Cs on account of cultivation are common (Bowman *et al*., 1990; Magdoff & Weil, 2004).

Extractable soil C

A similar pattern to that of Cs content of virgin soils in the three agro-ecosystems was perceived in which Harrismith had the highest content of Ce, followed by Tweespruit and then Kroonstad (Figure 4.1). These Ce values constitute 47.1 to 48.6% of the Cs values. This is consistent with the theory that Ce makes up 50% of Cs in virgin soils of semi-arid regions (Allison, 1973; Kononova, 1966). On a relative basis the decline in Ce upon cultivation of formerly virgin soils was 48.2% at Harrismith, 47.3% at Tweespruit and 36.7% at Kroonstad. In the cultivated soils Ce constitutes more to Cs than in the virgin soils, *viz.* 50.5, 51.3 and 61.9% in Harrismith, Tweespruit and Kroonstad agro-ecosystems respectively.

Humic acid C

The Ch content of virgin soil in the Kroonstad agro-ecosystem was lower than that in the Tweespruit and Harrismith agro-ecosystems which were almost similar (Figure 4.1). These Ch values constitute 50.7, 65.9 and 79.3% of the Ce values at Harrismith, Tweespruit and Kroonstad respectively. The loss of Ch due to cultivation was highest at Kroonstad (84.4%), followed by Harrismith (52.3%) and then Tweespruit (29.4%).

Fulvic acid C

In the virgin soils Cf declined similar to Cs and Ce from the Harrismith to Tweespruit agro-ecosystem, and then to the Kroonstad agro-ecosystem (Figure 4.1). The Cf constituting Ce in the virgin soils complements Ch in the three agro-ecosystems, viz. 20.7, 33.7 and 49.3% at Kroonstad, Tweespruit and Harrismith respectively. Contrasting to Cs, Ce and Ch that decreased in all three agro-ecosystems upon cultivation Cf increased in Kroonstad agro-ecosystem with 57.9%. Cultivation resulted however in Cf losses of 44.0% at Harrismith and 76.3% at Tweespruit.

4.1.2 N contents

The summary of analyses of variance (Table 4.2) displays that there were significant differences between agro-ecosystems (Harrismith, Tweespruit and Kroonstad) and land uses (virgin and cultivated) concerning crude soil (Ns), extractable soil (Ne), humic acid (Nh) and fulvic acid (Nf) N contents. Effects of the interaction between land uses and agro-ecosystems on the Ns, Ne, Nh and Nf contents are shown in Figure 4.2.

Table 4.2 Summary of the analysis of variance indicating the significant effects of agro-ecosystems (A: Harrismith, Tweespruit and Kroonstad) and land uses (B: virgin and cultivated) on crude soil (Ns), extractable soil (Ne), humic acid (Nh) and fulvic acid (Nf) N contents at 95% confidence level

	N fractions			
Treatments	**Ns**	**Ne**	**Nh**	**Nf**
A	*	*	*	*
B	*	*	*	*
AB	*	*		*

Crude soil N

The Ns of virgin soils varied from 694 mg N kg^{-1} soil in the Kroonstad agro-ecosystem to 1918 mg N kg^{-1} soil in the Harrismith agro-ecosystem (Figure 4.2). Cultivation reduced Ns with 33.3, 40.8 and 45.9% in the agro-ecosystems of Kroonstad, Tweespruit and Harrismith to 462, 969 and 1037 mg N kg^{-1} soil respectively. Losses of this magnitude in Ns upon cultivation are often reported (e.g. Blair *et al*., 1995; Magdoff and Weil, 2004).

Extractable soil N

The content of Ne in virgin soils of the agro-ecosystems at Harrismith, Tweespruit and Kroonstad amounted to 1677, 799 and 490 mg N kg^{-1} respectively (Figure 4.2). Hence, Ne constitutes 87.4% at Harrismith 48.8% at Tweespruit and 70.6% at Kroonstad of the Ns in these virgin soils. A pattern of decline, similar to that experienced for Ns, was noticed for Ne when the virgin soils in the three agro-

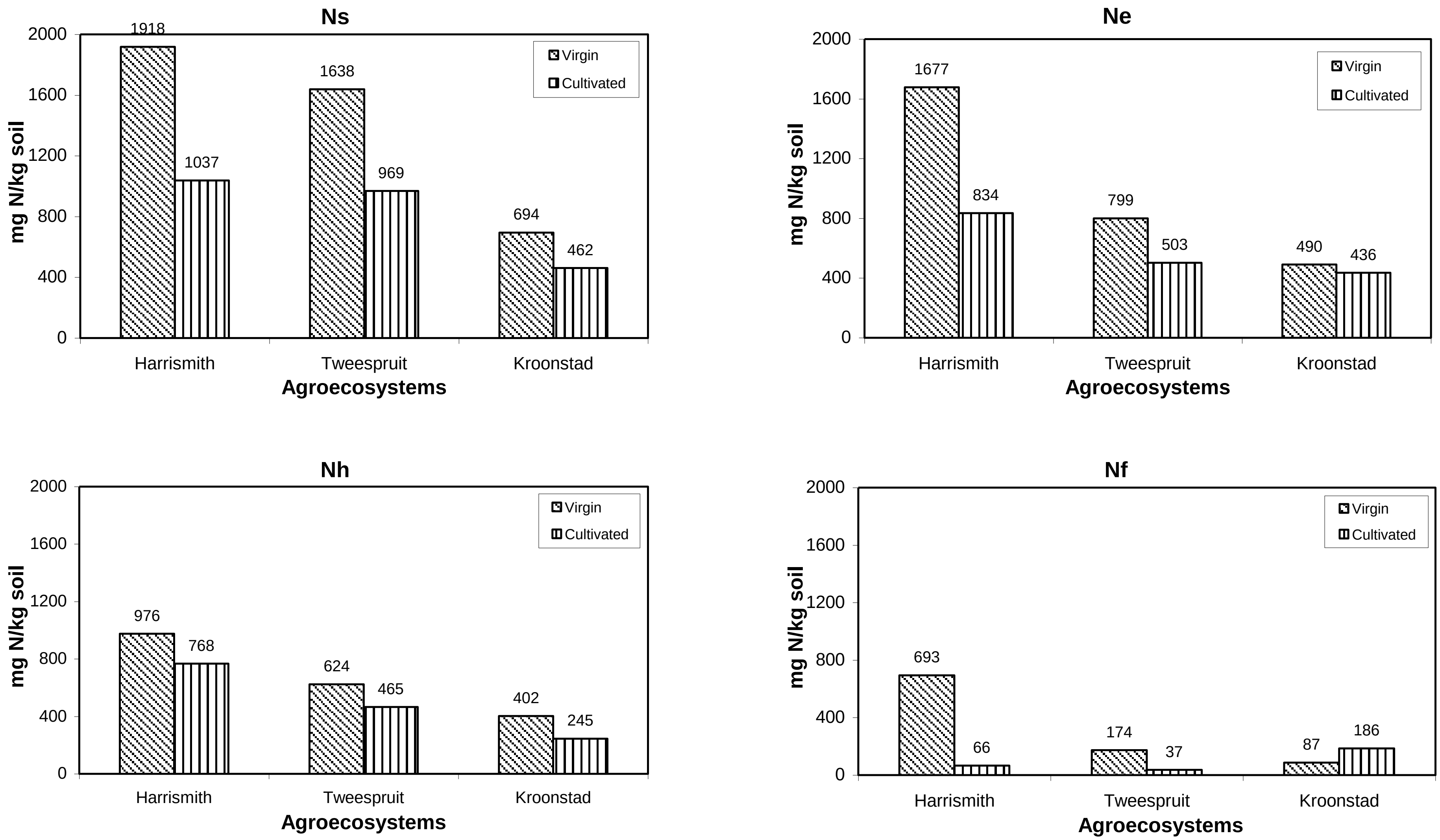


Figure 4.2 Effects of virgin and cultivated land use on crude soil (Ns), extractable (Ne), humic acid (Nh) and fulvic acid (Nf) N contents in Harrismith, Tweespruit and Kroonstad agro-ecosystems.

ecosystems were cultivated. These losses were 10.8% for Kroonstad, 37.1% for Tweespruit and 50.2% for Harrismith.

Humic acid N

In the virgin soils of the agro-ecosystems, Nh increased from Kroonstad to Tweespruit and then to Harrismith (Figure 4.2). The content of Nh in Harrismith, Tweespruit and Kroonstad were tantamount to 69.4, 83.7 and 69.9% of Ne in the respective agro-ecosystems. With cultivation, Nh contents decreased within the agro-ecosystems in the order Harrismith, Tweespruit and Kroonstad. The losses of Nh on a relative basis equated to 21.3% at Harrismith, 25.5% at Tweespruit and 39.1% at Kroonstad.

Fulvic acid N

There are marked differences in the contents of Nf in virgin soils ranging from 87 mg N kg^{-1} soil in the Kroonstad agro-ecosystem to 693 mg N kg^{-1} soil in the Harrismith agro-ecosystem (Figure 4.2). In these soils Nf constitute 41.4, 21.8 and 17.9% of Ne in the Harrismith, Tweespruit and Kroonstad agro-ecosystems respectively. On account of cultivation there was tremendous decrease in the content of Nf at the Harrismith (90.4%) and Tweespruit (78.5%) agro-ecosystems. The Nf content at Kroonstad agro-ecosystems on the other hand increased by 53.0%, following cultivation.

4.1.3 C/N ratios

The summary of analyses of variance (Table 4.3) indicates that the crude soil (Cs/Ns), extractable soil (Ce/Ne), humic acid (Ch/Nh) and fulvic acid (Cf/Nf) C/N ratios differed significantly among agro-ecosystems (Harrismith, Tweespruit and Kroonstad) and land uses (virgin and cultivated). Effects of the interaction between land uses and agro-ecosystem on the Cs/Ns, Ce/Ne, Ch/Nh and Cf/Nf ratios are presented in Figure 4.3.

Table 4.3 Summary of the analyses of variance indicating the significant effects of agro-ecosystems (A: Harrismith, Tweespruit and Kroonstad) and land uses (B: virgin and cultivated) on crude soil (Cs/Ns), extractable soil (Ce/Ne), humic acid (Ch/Nh) and fulvic acid (Cf/Nf) C/N ratios at 95% confidence level

	C/N fractions			
Treatments	**Cs/Ns**	**Ce/Ne**	**Ch/Nh**	**Cf/Nf**
A	*	*	*	*
B	*	*	*	*
AB		*	*	*

Cs/Ns ratio

The Cs/Ns ratios of the virgin soils laid within a narrow range from 10.48 for the Kroonstad agro-ecosystem to 11.24 for the Harrismith agro-ecosystem (Figure 4.3). Cultivation decreased the Cs/Ns ratios at all three agro-ecosystems. On a relative basis the decrease amounted to 8.2% at Harrismith, 16.3% at Tweespruit and 26.8% at Kroonstad.

Ce/Ne ratio

The Ce/Ne ratios of the virgin soils ranged from 6.24 for the Harrismith agro-ecosystem to 10.92 for the Tweespruit agro-ecosystem (Figure 4.3) This range is wider than that of Cs/Ns. Compared to Cs/Ns that decreased in all three agro-ecosystems on account of cultivation, Ce/Ne increased slightly with 3.8% at Harrismith. However, at Tweespruit (16.3%) and Kroonstad (30.1%) Ce/Ne decreased similar to Cs/Ns.

Ch/Nh ratio

The Ch/Nh ratio of virgin soil in the three agro-ecosystems were low, namely 5.45 for Harrismith, 9.22 for Tweespruit and 6.80 for Kroonstad (Figure 4.3). These ratios decreased upon cultivation with 39.4% at Harrismith to 3.30, 5.5% at Tweespruit to 8.72, and 74.3% at Kroonstad to 1.74.

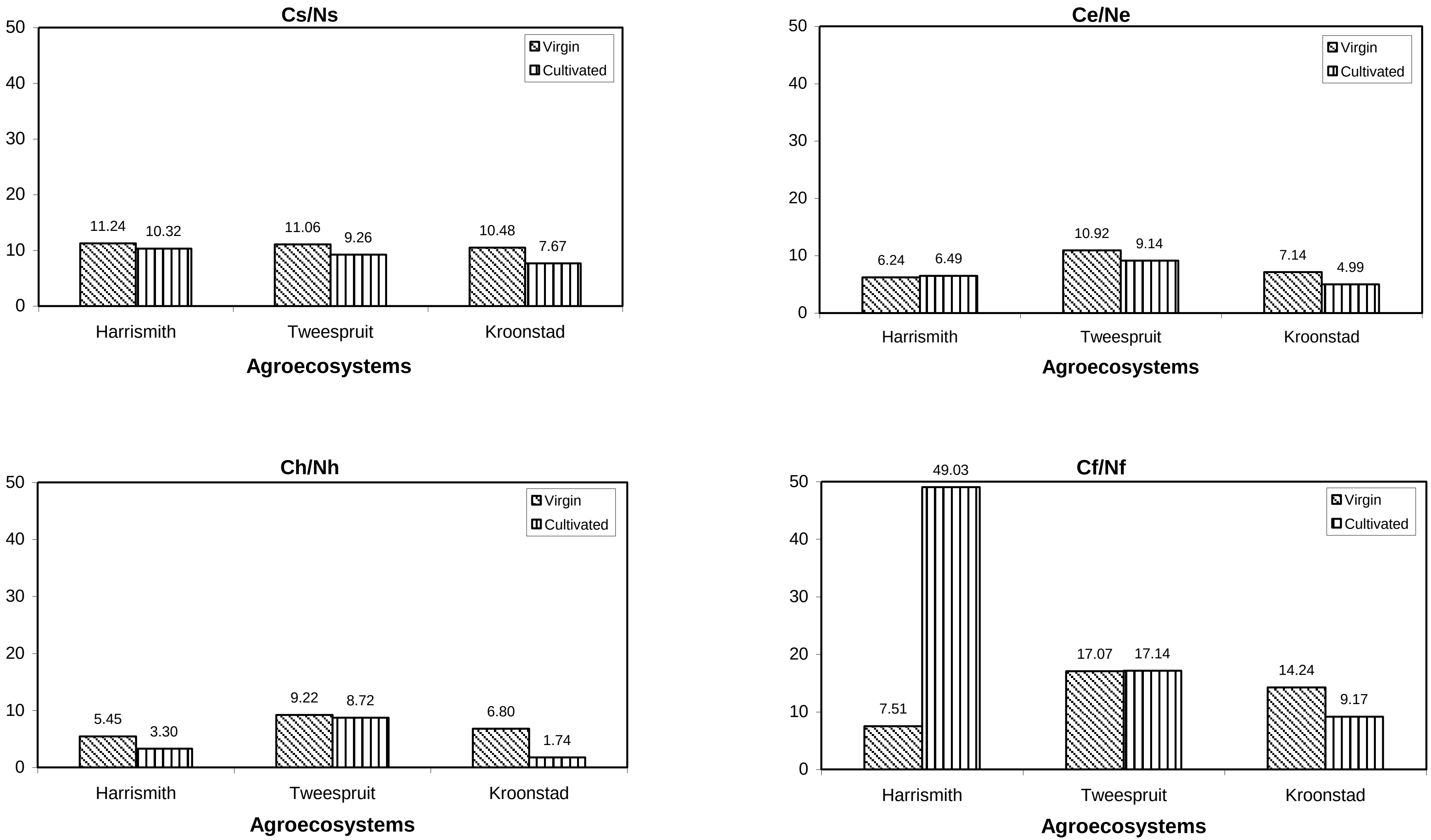


Figure 4.3 Effects of virgin and cultivated land use on crude soil (Cs/Ns), extractable soil (Ce/Ne), humic acid (Ch/Nh) and fulvic acid (Cf/Nf) C/N ratios in Harrismith, Tweespruit and Kroonstad agro-ecosystems.

Cf/Nf ratio

Compared to Ch/Nh, Cf/Nf were substantially higher in the virgin and cultivated soils of the three agro-ecosystems (Figure 4.3). The Cf/Nf of the virgin soils were 7.51 at Harrismith, 17.07 at Tweespruit and 14.24 at Kroonstad. Cultivation increased Cf/Nf to 49.03 in the Harrismith agro-ecosystem and decreased Cf/Nf to 9.17 in the Kroonstad agro-ecosystem. This ratio was not affected by cultivation in the Tweespruit agro-ecosystem.

4.2 Comparison of restored soils with cultivated soils

4.2.1 C contents

The summary of analyses of variance (Table 4.4) displays that there were significant differences between agro-ecosystems (Harrismith, Tweespruit and Kroonstad) and land uses (cultivated and restored) regarding crude soil (Cs), extractable soil (Ce), humic acid (Ch) and fulvic acid (Cf) C contents. Effects of the interaction between land uses and agro-ecosystems on Cs, Ce, Ch and Cf contents are displayed in Figure 4.4.

Table 4.4 Summary of the analyses of variance indicating the significant effects of agro-ecosystems (A: Harrismith, Tweespruit and Kroonstad) and land uses (B: cultivated and restored) on crude soil (Cs), extractable soil (Ce), humic acid (Ch) and fulvic acid (Cf) C contents at 95% confidence level

	C fractions			
Treatments	**Cs**	**Ce**	**Ch**	**Cf**
A	*	*	*	*
B	*	*	*	*
AB	*	*	*	*

Crude soil C

The pattern portrayed by Cs is that this parameter was higher in the restored soils than the cultivated soils of the three agro-ecosystems (Figure 4.4). On a relative basis the increase equated to 42.2% for Harrismith, 34.9% for Tweespruit and 60.4% for Kroonstad.

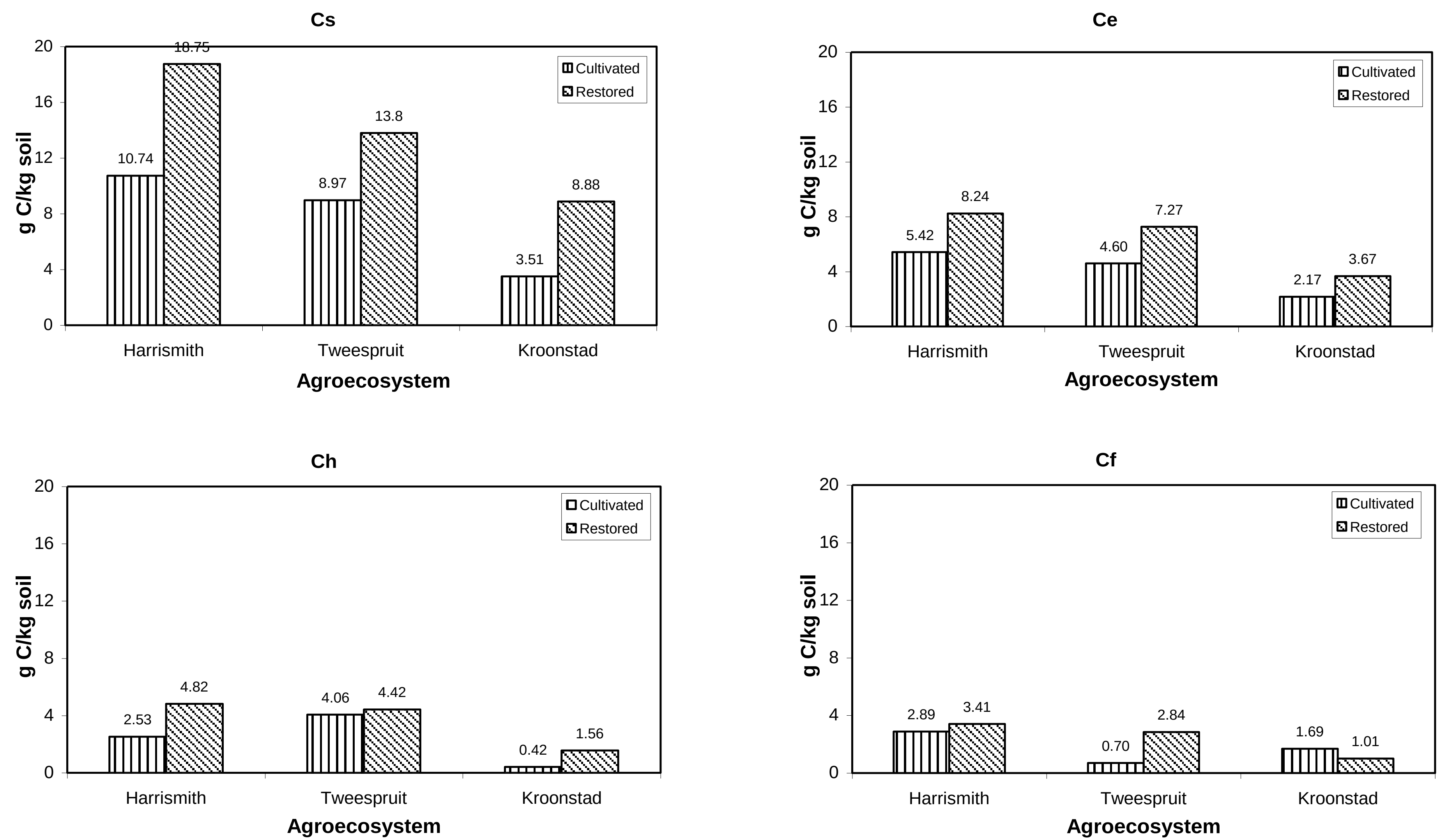


Figure 4.4 Effect of cultivated and restored land use on crude soil (Cs), extractable soil (Ce), humic acid (Ch) and fulvic acid (Cf) C contents in Harrismith, Tweespruit and Kroonstad agro-ecosystems.

Extractable soil C.

The gain of Cs in restored soils from the three agro-ecosystems manifested to a large extent in their Ce contents (Figure 4.4). On a relative basis, the Ce content of restored soils at the Harrismith, Tweespruit and Kroonstad agro-ecosystems was respectively 52.0, 52.4 and 68.4% higher than in cultivated soils. In the restored soils the contribution of Ce to Cs is 43.9% for Harrismith, 52.7% for Tweespruit and 41.3% for Kroonstad.

Humic acid C

Content of Ch in all three agro-ecosystems was positively affected by conversion of cultivated land to perennial pasture (Figure 4.4). In terms of percentages, gains in Ch were the largest at Kroonstad (72.7%), followed by Harrismith (47.5%) and then Tweespruit (8.1%). The Ch content in the restored soil comprised 58.5, 60.9 and 42.5% of Ce in Harrismith, Tweespruit and Kroonstad agro-ecosystems respectively.

Fulvic acid C

The Cf contents of restored soils were higher than that of the cultivated soils in the Harrismith and Tweespruit agro-ecosystems (Figure 4.4). This trend was opposite in the Kroonstad agro-ecosystem where the Cf content of restored soil was lower than that of the cultivated soil. In the restored soils of the Harrismith, Tweespruit and Kroonstad agro-ecosystems Cf constitutes 41.4, 39.1 and 27.6% of Ce respectively.

4.2.2 N contents

The summary of analyses of variance (Table 4.5) shows that the crude soil (Ns), extractable soil (Ne), humic acid (Nh) and fulvic acid (Nf) N contents differed significantly between agro-ecosystems (Harrismith, Tweespruit and Kroonstad) and land uses (cultivated and restored). Effects of the interaction between agro-ecosystems and land uses on Ns, Ne, Nh and Nf contents are illustrated in Figure 4.5.

Table 4.5 Summary of the analyses of variance indicating the significant effects of agro-ecosystems (A: Harrismith, Tweespruit and Kroonstad) and land uses (B: cultivated and restored) on crude soil (Ns), extractable soil (Ne), humic acid (Nh) and fulvic acid (Nf) N contents at 95% confidence level

	N fractions			
Treatments	**Ns**	**Ne**	**Nh**	**Nf**
A	*	*	*	*
B	*	*	*	*
AB		*	*	*

Crude soil N

The Ns like Cs increased upon the conversion of cultivated land to perennial pasture at all three agro-ecosystems (Figure 4.5). These gains in Ns amounted on a relative basis to 29.7, 32.3 and 44.8% in the Harrismith, Tweespruit and Kroonstad agro-ecosystems respectively.

Extractable soil N

Gains of Ne in restored soils from the Harrismith, Tweespruit and Kroonstad agro-ecosystems amounted to 93.5, 65.4 and 28.4% respectively (Figure 4.5). These gains are of a much wider range than that of Ce, probably due to N fertilization of the perennial pasture in the Harrismith agro-ecosystem. In the agro-ecosystems of Tweespruit and Kroonstad N fertilization of perennial pasture is not common.

Humic acid N

The pattern discernable for the change of Nh content with establishment of perennial pasture on cultivated land in all three agro-ecosystems is that of ascend (Figure 4.5). Highest gain was at Tweespruit (22.1%), followed by Harrismith (6.9%) and then Kroonstad (1.7%). The contribution of Nh towards Ne in the restored soils are 51.1, 71.8 and 44.5% for the Harrismith, Tweespruit and Kroonstad agro-ecosystems respectively.

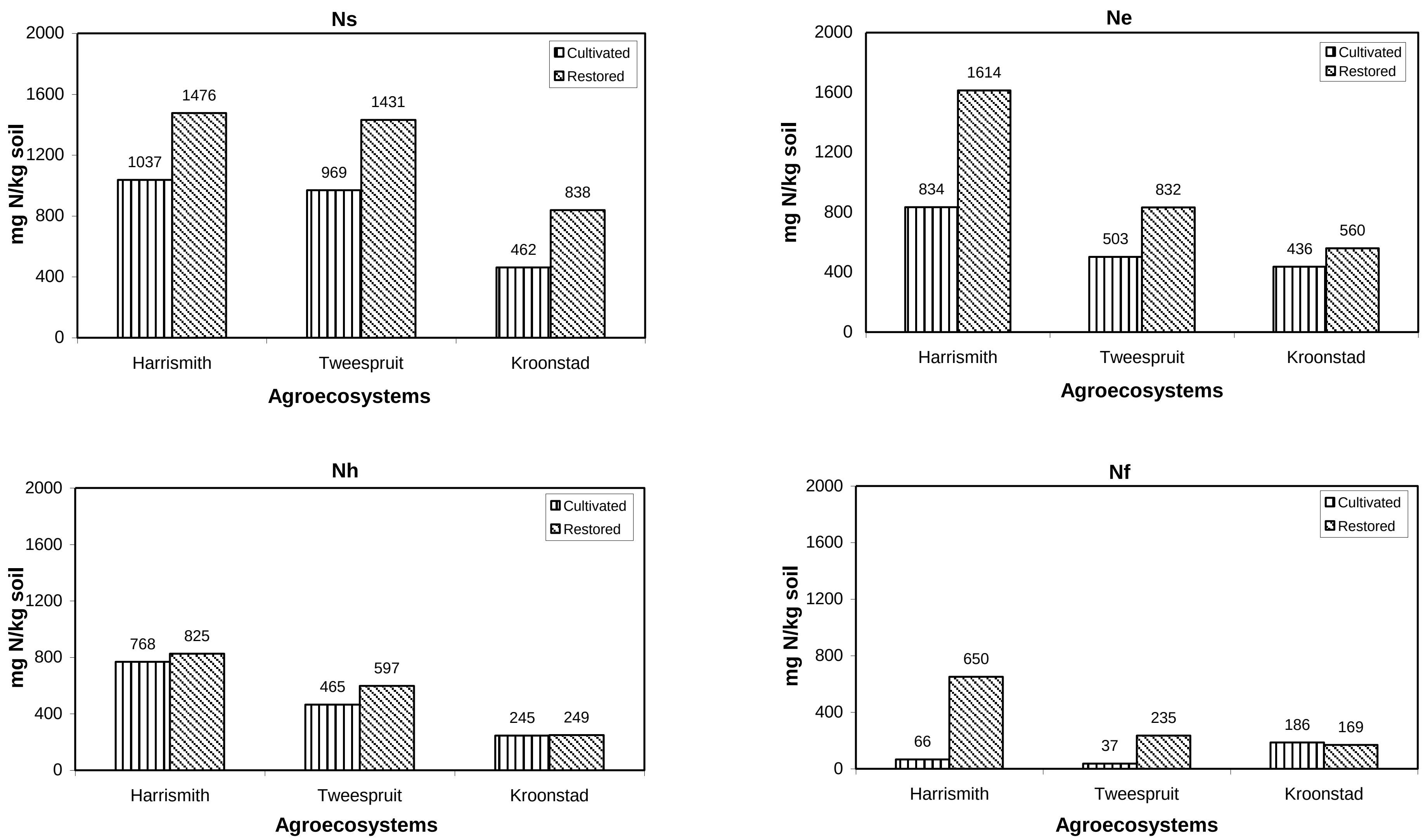


Figure 4.5 Effect of cultivation and restored land use on crude soil (Ns), extractable soil (Ne), humic acid (Nh) and fulvic acid (Nf) N contents in Harrismith, Tweespruit and Kroonstad agro-ecosystems.

Fulvic acid N

The contents of Nf in the cultivated soils of the Harrismith and Tweespruit agro-ecosystems were very low (Figure 4.5). Establishment of perennial pasture on these soils resulted therefore in six-fold (Tweespruit) and ten-fold (Harrismith) increases of Nf. Contrasting, the Nf content of restored soil in the Kroonstad agro-ecosystem was slightly lower than that of the cultivated soil.

4.2.3 C/N ratios

The summary of analyses of variance (Table 4.6) indicates that the crude soil (Cs/Ns), extractable soil (Ce/Ne), humic acid (Ch/Nh) and fulvic acid (Cf/Nh) C/N ratios differed significantly between agro-ecosystems (Harrismith, Tweespruit and Kroonstad) and land uses (cultivated and restored). Effects of the interactions between land uses and agro-ecosystems on Cs/Ns, Ce/Ne, Ch/Nh and Cf/Nf ratios are depicted in Figure 4.6.

Table 4.6 Summary of the analyses of variance indicating the significant effects of agro-ecosystems (A: Harrismith, Tweespruit and Kroonstad) and land uses (B: cultivated and restored) on crude soil (Cs/Ns), extractable soil (Ce/Ne), humic acid (Ch/Nh) and fulvic acid (Cf/Nf) C/N ratios at 95% confidence level

	C/N fractions			
Treatments	**Cs/Ns**	**Ce/Ne**	**Ch/Nh**	**Cf/Nf**
A	*	*	*	*
B	*		*	*
AB	*	*	*	*

Cs/Ns ratio

The Cs/Ns ratios of the restored soils ranged between 9.64 at the Tweespruit agro-ecosystem to 12.56 at the Harrismith agro-ecosystem (Figure 4.6). At all three agro-ecosystems, restored soils had higher ratios of Cs/Ns in comparison with cultivated soils. The higher Cs/Ns at Tweespruit although significant appeared to be negligible, as it was only 3.9%. However, at Harrismith and Kroonstad Cs/Ns was respectively 17.9 and 27.9% higher.

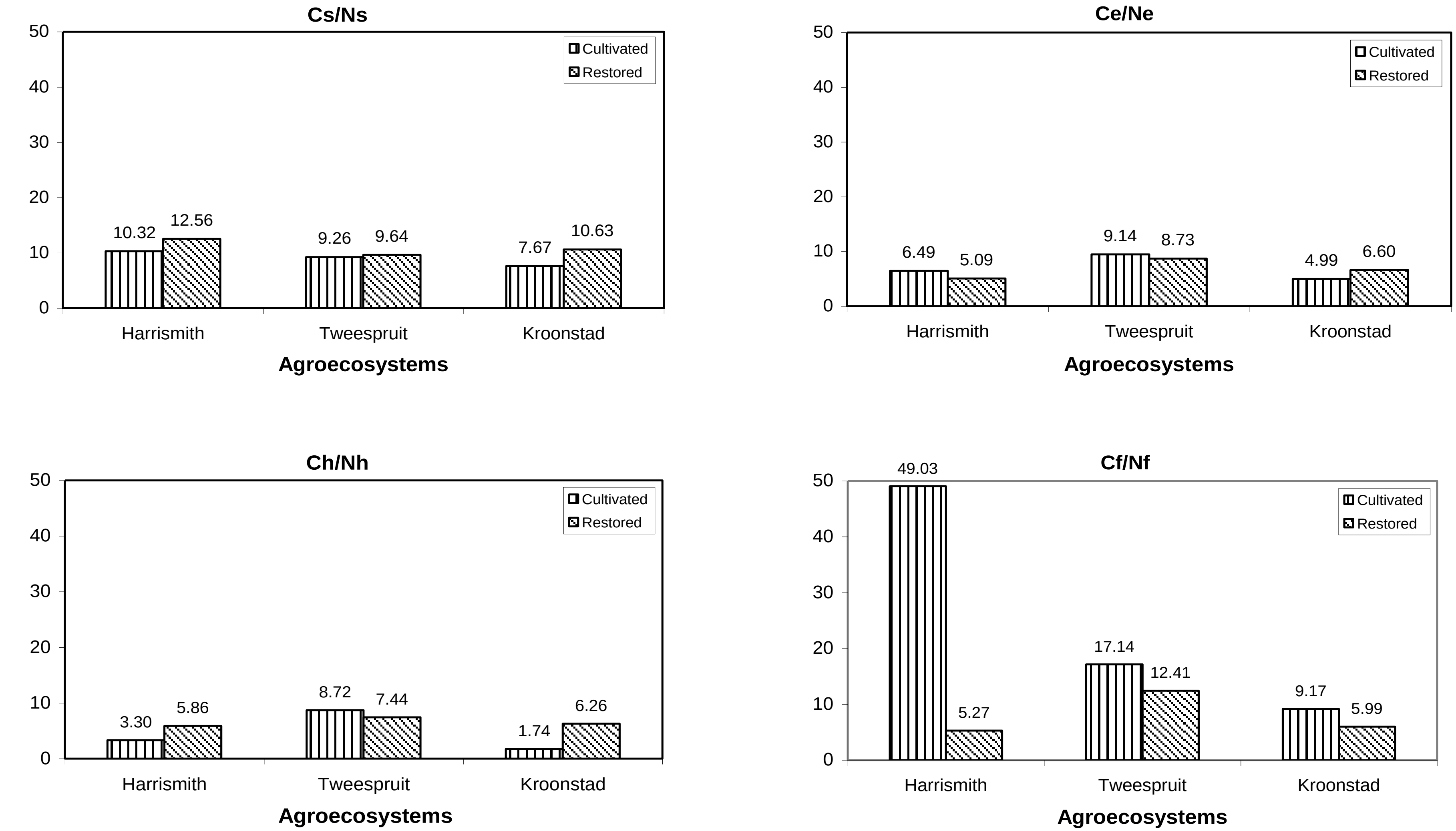


Figure 4.6 Effects of cultivation and restored land use on crude soil (Cs/Ns), extractable soil (Ce/Ne), humic acid (Ch/Nh) and fulvic acid (Cf/Nf) C/N ratios in Harrismith, Tweespruit and Kroonstad agro-ecosystems.

Ce/Ne ratio

The differences in Ce/Ne ratios between cultivated and restored soils at all three agro-ecosystems were smaller than that of the Cs/Ns ratios (Figure 4.6). At Harrismith and Tweespruit agro-ecosystems the Ce/Ne ratios of the restored soils were slightly lower than that of the cultivated soils. The opposite is observed at the Kroonstad agro-ecosystem.

Ch/Nh ratio

At both Harrismith and Kroonstad agro-ecosystems, the Ch/Nh ratios for the restored soils were higher compared to that of the cultivated soils (Figure 4.6). Differences are approximately two-fold at Harrismith and four-fold at Kroonstad. The opposite was depicted at Tweespruit agro-ecosystem, where the Ch/Nh ratio of the cultivated soil was slightly higher than that of the restored soil.

Cf/Nf ratio

At all three agro-ecosystems the restored soils had lower Cf/Nf ratios than the cultivated soil (Figure 4.6). The diffence at Harrismith was extremely large, *viz.* more than nine-fold. At Tweespruit and Kroonstad the differences were less than two-fold.

The results presented on crude soil, extractable soil, humic acid and fulvic acid C contents, N contents and C/N ratios provide substantial evidence that the different combinations of land uses and agro-ecosystems influenced humic substances in soils to varying degrees. Despite of this some noteworthy trends evolved, justifying further discussion of the results to put them in perspective.

All measured C and N contents on humic substances in the virgin soils from Harrismith, Tweespruit and Kroonstad appear to emanate from the MAR (mean annual rainfall) and Ta (mean annual temperature) prevalent at each of the agro-ecosystems. Lowest values were recorded at Kroonstad (MAR = 566 mm and Ta = 16.6°C), followed by Tweespruit (MAR = 544 mm and Ta 14.8°C) and then Harrismith (MAR = 624 mm and Ta = 13.8°C). Several researches showed that organic matter content of grassland soils which have almost similar clay contents (10.6 to 13.1%) like in this study increased with higher MAR and lower Ta (Stevenson, 1982; Magdoff

& Weil, 2004). This phenomenon is attributed to higher primary production resulting in more residues whereof the rate of decomposition is slower.

In the virgin soils of all three agro-ecosystems the contribution of Ce to Cs was almost the same, ranging between 47.1 and 48.4%. This is slightly lower than the 50 to 60% several investigators (Kononova, 1966; Schnitzer, 1978; Stevenson, 1982; Hayes *et al*., 1989; Zalba & Quiroga, 1999) reported. Variations of this magnitude may be the result of procedures used for extraction and fractionation since they differ somewhat as pointed out in Section 3.4. Contrasting to the very consistent contribution of Ce to Cs, that of Ch to Ce decreased and that of Cf to Ce increased from the warmer, drier Kroonstad agro-ecosystem to the cooler, wetter Harrismith agro-ecosystem.

The contribution of Ne to Ns in the virgin soils of the three agro-ecosystems was surprisingly variable, namely from 50.6% at Harrismith to 79.5% at Kroonstad. No obvious explanation can be given for this phenomenon. However, the contribution of Nh to Ne and of Nf to Ne confirmed the trends reported in the previous paragraph for the contributions of either Ch or Cf to Ce.

The Cs/Ns ratio of the virgin soils declined slightly from 11.24 in the cooler, wetter Harrismith agro-ecosystem to 10.48 in the warmer, drier Kroonstad agro-ecosystem. This was not the case with the Ce/Ne, Ch/Nh and Cf/Nf ratios which were highest in the Tweespruit agro-ecosystem. Based on MAR and Ta, Tweespruit has the intermediate climate of the three agro-ecosystems.

Against this background the effects of cultivation on humic substances of formerly grassland soils will be discussed now. Cultivation reduced Cs in the three agro-ecosystems with 50.2 to 51.8%, confirming that degradation of organic matter probably stabilized in the studied soils as reported by Du Toit *et al*. (1994). Loss of Ce was more variable ranging from 36.7% in the warmer, drier Kroonstad agro-ecosystem to 48.2% in the cooler, wetter Harrismith agro-ecosystem. Trends of this nature were non-existent for either Ch or Cf losses.

The loss of Ns was not as consistent as that of Cs since it ranged from 33.4% in the warmer, drier Kroonstad agro-ecosystem to 45.9% in the cooler, wetter Harrismith agro-ecosystem. A similar trend evolved for Ne loss, but no obvious trends for losses of either Nh or Nf could be observed.

All Cs/Ns, Ce/Ne, Ch/Nh and Cf/Nf ratios of the cultivated soils were, with one exception equal or lower than that of the virgin soils. This exception is at the Harrismith agro-ecosystem where the Cf/Nf ratio of the cultivated soil exceeded that of the virgin soil substantially. No obvious explanation can be given for this phenomenon.

The absence of trends for HA (Ch and Nh) and FA (Cf and Nf) indices in cultivated soils across agro-ecosystems may be ascribed to their nature (See Section 2.2.2). Nowadays it is generally accepted that FAs and HAs are a continuous series of compounds that are procedurally defined. As a result of this it is possible that HAs and FAs are affected in such a manner by cultivation, that their observed trends in the virgin soils across agro-ecosystems are extinguished.

As mentioned, relative losses of Cs were almost similar across the three agro-ecosystems. This implies that absolute losses of Cs increased from the warmer, drier Kroonstad agro-ecosystem (3.77 g C kg^{-1} soil) to the cooler, wetter Harrismith agro-ecosystem (19.81 g C kg^{-1} soil). The two mentioned agro-ecosystems were both subject to 20 years of cultivation and hence the rate of Cs loss at Harrismith (0.54 g C kg^{-1} soil yr^{-1}) was almost three times higher than at Kroonstad (0.19 g C kg^{-1} soil yr^{-1}). Similarly, the rate of Ns loss was also lowest at Kroonstad (12 mg N kg^{-1} soil yr^{-1}) and highest at Harrismith (44 mg N kg^{-1} soil yr^{-1}) inspite of relative Ns losses that were variable across agro-ecosystems. These rates of Cs and Ns losses manifested in that of Ce and Ne but not in that of the HA (Ch and Nh) and FA (Cf and Nf) indices.

Establishment of perennial pasture on formerly cultivated soils of the three agro-ecosystems resulted in gains of organic matter as indicated by C and N contents of the 0-50 mm layer. The magnitude of gains in this layer is not at all representative of that accomplished to the assumed ploughing depth of 200 mm. This is because organic matter gains are usually far more pronounced near the surface (Mann, 1986; Kumada, 1999). However, for reasons given in Section 3.5, the mentioned data illustrates the gains achieved in the restored soils as the best.

The gains of Cs varied from 5.37 g C kg^{-1} soil in the warmer, drier Kroonstad agro-ecosystem to 8.01 g C kg^{-1} soil in the cooler, wetter Harrismith agro-ecosystem. This trend manifested also in Ce as gains were lowest at Kroonstad (1.50 g C kg^{-1} soil) and highest at Harrismith (2.82 g C kg^{-1} soil). Neither Ch nor Cf showed trends of this nature.

Gains of Ns were also lowest in the Kroonstad agro-ecosystem (376 mg N kg^{-1} soil) but highest in the Tweespruit agro-ecosystem (462 mg N kg^{-1} soil). Like Ce, gains of Ne were greater in the agro-ecosystem of Harrismith than in the one of Kroonstad. No trends of this nature evolved for either Nh and Nf.

At the time of sampling the soils at the Tweespruit and Harrismith agro-ecosystems were under perennial pasture for 25 years. The rate of Cs gain equated therefore to 0.19 g C kg^{-1} soil yr^{-1} at Tweespruit and 0.32 g C kg^{-1} soil yr^{-1} at Harrismith. However, Ns was gained at a rate of 18 mg N kg^{-1} soil yr^{-1} at the two agro-ecosystems. Based on their MAR and Ta given earlier, Tweespruit is slightly warmer and drier than Harrismith.

Evidence of this study shows therefore, that over the same period larger amounts of organic matter is either lost (due to cultivation of formerly grassland soils) or gained (due to establishment of perennial pasture on formerly cultivated soils) from cooler, wetter agro-ecosystems than from warmer, drier agro-ecosystems when the soils are comparable (Plinthustalfs with 10.6 to 13.5% clay in A horizon). In an agro-ecosystem, evidence suggested that the rate of organic matter loss when formerly grassland soil is cultivated, exceeded the rate of organic matter gain when formerly cultivated soil is put under perennial pasture. These aspects are of great importance and should be considered in any debate on the role that cropping plays in global warming through the release or sequester of CO_2 through organic matter.

CHAPTER 5

SUMMARY AND CONCLUSIONS

This study was initiated to compliment earlier investigations (Du Toit, 1992; Birru, 2002; Lobe, 2003) into soil organic matter degradation and restoration on account of agricultural land use in the Free State Province of South Africa. In these studies no attention was given to the response of humic substances which represent the most active fraction of organic matter. The aim with this study was therefore to quantify the influence of agricultural land use on humic substances in soils of semi-arid regions.

Topsoil (0-200 mm) samples of Du Toit (1992) and Birru (2002) from distinctive agro-ecosystems at Harrismith (MAR = 624 mm and Ta = 13.8°C), Tweespruit (MAR = 544 mm and Ta = 14.8°C) and Kroonstad (MAR = 566 mm and Ta = 16.6°C) were selected for use in this study. An agro-ecosystem implies a region where the three environmental factors affecting yield, namely climate, slope and soil are for practical purposes homogeneous. The selected samples represent a virgin (grassland soil never cultivated before), cultivated (formerly grassland soil cultivated for at least 20 years) and restored (formerly cultivated soil converted to perennial pasture for at least 15 years) Plinthustalfs (10.6 to 13.5% clay) at every agro-ecosystem. Parameters quantified comprise crude soil, extractable soil, humic acid and fulvic acid C contents, N contents and C/N ratios. Concerning these parameters cultivated soil was compared with virgin soil and restored soil with cultivated soil.

The Cs of virgin soil ranged from 7.3 g C kg^{-1} soil in the warmer, drier Kroonstad agro-ecosystem to 21.6 g C kg^{-1} soil in the cooler, wetter Harrismith agro-ecosystem. Across agro-ecosystems the contribution of Ce to Cs was almost constant, namely 47.1 to 48.4%. The contribution of Ch to Ce decreased and that of Cf to Ce increased from the Kroonstad to Harrismith agro-ecosystem.

Cultivation reduced Cs in the three agro-ecosystems with 50.2 to 51.8%. This is equivalent to absolute losses of 3.8, 8.2 and 10.8 g C kg^{-1} soil at Kroonstad, Tweespruit and Harrismith agro-ecosystems respectively. Loss of Ce was more variable ranging from 36.7% or 1.3 g C kg^{-1} C in the warmer, drier Kroonstad agro-ecosystem to 48.2% or 5.1 g C kg^{-1} soil in the cooler, wetter Harrismith agro-ecosystem. Trends of this nature were non-existent for either Ch or Cf losses.

Gains of Cs varied from 5.4 g C kg^{-1} soil in the warmer, drier Kroonstad agro-ecosystem to 8.0 g C kg^{-1} soil in the cooler, wetter Harrismith agro-ecosystem. This trend manifested also in Ce as gains were lowest at Kroonstad (1.5 g C kg^{-1} soil) and highest at Harrismith (2.8 g C kg^{-1} soil). Neither Ch nor Cf showed trends of this nature.

The N contents although more variable than the C contents are to a large extent supportive concerning organic matter in the virgin, cultivated and restored soils of the three agro-ecosystems. Further elaboration on the N contents is therefore not justified here except for the variability. The data gave no indication whether the more variability in N than C contents is attributable to fertilization or not, since insensitive measuring procedures may also contribute to the phenomenon. This aspect should be investigated properly in future.

The Cs/Ns ratio of the virgin soils decreased slightly from 11.24 in the cooler, wetter Harrismith agro-ecosystem to 10.48 in the warmer, drier Kroonstad agro-ecosystem. This was not the case with the Ce/Ne, Ch/Nh and Cf/Nf ratios which were highest in the Tweespruit agro-ecosystem, which has the intermediate climate of the three agro-ecosystems.

All Cs/Ns, Ce/Ne, Ch/Nh and Cf/Nf ratios of the cultivated soils were with one exception equal or lower than that of the virgin soils. No trend evolved for these ratios between cultivated and restored soils.

Based on above mentioned indices it can be stated that humic substances did not show explicit trends on account of land use as was the case with organic matter *per se*. The rate at which organic matter is either lost or gained seems very much dependent on prevailing climatic conditions. Loss and/or gain rates of Cs at some agro-ecosystems were therefore calculated for comparison. This was possible because during sampling soils at Kroonstad and Harrismith were cultivated for 20 years and soils at Tweespruit and Harrismith were under perennial pasture for 25 years. Loss (0.54 g C kg^{-1} soil yr^{-1}) and gain (0.32 g C kg^{-1} soil yr^{-1}) rates were higher in the wetter, cooler Harrismith agro-ecosystem than in the warmer, drier Kroonstad (0.19 g C kg^{-1} soil yr^{-1}) and Tweespruit (0.19 g C kg^{-1} soil yr^{-1}) agro-ecosystems respectively. Another interesting feature evolving from the rates for Harrismith agro-ecosystem is that loss of Cs was quicker than its gain.

REFERENCES

ADU, J.K. & OADES, J.M., 1978. Physical factors influencing decomposition of organic materials in soil aggregates. *Soil Biol. Biochem.* 10, 109-115.

AIKEN. G.R., McKNIGHT, D.M., WERSHAW, R.L., MACCARTHY. P., 1985. Humic substances in soil, sediments and water: Geochemistry, isolation and characterization. John Wiley & Sons, New York.

ALLISON, F.E., 1973. Soil organic matter and its role in crop production. Elsevier, Amsterdam.

ANDERSON, D.W. & GREGORICH, E.G., 1983. Effect of soil erosion on soil quality and productivity. In: Soil erosion and land degradation. Proc. of 2nd Annual Western Provincial Conference on Rationalization of Water and Soil Research and Management, Saskatoon, Canada.

BARNARD, R.O. & DU PREEZ, C. C., 2004. Soil fertility in South Africa: the last twenty five years. *S. Afr. J. Plant Soil.* 21, 301-315.

BIRRU, T.C., 2002. Organic matter restoration by conversion of cultivated land to perennial pasture on three agro-ecosystems in the Free State. M.Sc. Dissertation, University of the Free State, Bloemfontein.

BLAIR, G.J., ROD, D.B.L & LISLE, L., 1995. Soil carbon fractions based on the degree of oxidation and the development of a carbon management index for agricultural systems. *Aust. J. Agric. Res*. 46, 1159- 1466.

BOHN, H.L., McNEAL B.L. & O'CONNOR, G.A., 1985. Soil chemistry. John Wiley & Sons, New York.

BOWMAN, R.A., REEDER, J.D. & LOBER, R.W., 1990. Changes in soil properties in a central plains rangeland soil after 3, 20 and 60 yrs of cultivation. *Soil Sci.* 150, 851-857.

BRADY, N.C. & WEIL, R.R., 1996. The nature and properties of soil, 11th edn. Prentice-Hall International, Upper Saddle River, New Jersey.

BREDENKAMP, G., VAN ROOYEN, N. & LUBKE, R.A., 1996. Moist Cold Highland Grassland (40); Dry Sandy Highveld Grassland (37); Moist Cool Highveld Grassland (39). In A.B. Low and A.G. Rebelo (eds.). Vegetation of South Africa, Lesotho and Swaziland. Department of Environmental Affairs and Tourism, Pretoria.

BREMNER, J.M. & MULVANEY, C.S., 1982. Nitrogen-total. In A.L. Page (ed.). Methods of soil analysis. Part 2. Chemical and microbiological properties. Am. Soc. of Agron., Madison, Wisconsin.

BROWN, S.A., COOK, H.F. & MCRAE, S.G., 1993. Investigation into soil organic matter as affected by organic farming in South-East England. In H.F. Cook and H.C. Lee (eds.). Soil management in sustainable agriculture. Wye College Press, London.

CAMPBELL, C.A. & SOUSTER, W., 1982. Loss of organic matter and potentially mineralizable nitrogen from Saskatchewan soils due to cropping. *Can. J. Soil Sci.* 62, 651-656.

CHAN, K.Y. & HULUGALLE, N.R., 1999. Changes in some soil properties due to tillage practices in rainfed hardsetting Alfisols and irrigated Vertisols of eastern Australia. *Soil Till. Res*. 53, 49-57.

CHRISTENSEN, B.T., 1992. Physical fractionation of soil organic matter in the primary particle size density separates. *Adv. Soil Sci*. 20, 1-90.

CRESSER, M., KILLHAM, K. & EDWARDS, T., 1993. Soil chemistry and its applications. Cambridge University Press, Cambridge.

CHRISTOPHER, T.B.S., 1996. Humic substances. http://agri.upm.edu.my/~chris/as/om_humic-subs.html.

DALAL, R.C. & MAYER, R.J., 1986. Long-term trends in fertility of soils under continuous cultivation and cereal cropping in Southern Queensland. II. Total organic carbon and its rate of loss from the soil profile. *Austr. J. Soil Res*. 24, 265-279.

DAVISON, S., 1986**.** Cultivation and soil organic matter. *Rural Res*. 131, 13-18.

DORAN, J.W. & PARKIN, T.B., 1994**.** Defining and assessing soil quality. In J.W. Doran, D.C. Coleman, D. F. Bezdicek & B.A. Steward (eds.). Defining soil quality for a sustainable environment. Soil Sci. Soc. of Am., Madison, Wisconsin.

DORMAAR, J.F., 1979. Organic matter characteristics of undisturbed and cultivated chernozemic and solonetzic A horizon. *Can. J. Soil Sci*. 59, 349-356.

DU PREEZ, C.C., 2002. Agricultural land use and changes of soil organic matter in arid to semi arid South Africa. Proc. of 17th World Congress of Soil Science, Bangkok, Thailand.

DU TOIT, M.C., 1993. Effect of cultivation on the sulphur fractions in selected dryland soils. M.Sc. Agric. Dissertation, University of the Free State, Bloemfontein.

DU TOIT, M.E., 1992. Effect of cultivation on organic carbon and total nitrogen in selected dryland soils. M.Sc. Agric. Dissertation, University of the Free State, Bloemfontein.

DU TOIT, M.E., DU PREEZ, C.C., HENSLEY, M. & BENNIE, A.T.P. 1994. Effect of cultivation on the organic matter content of selected dryland soils in South Africa. *S. Afr. J. Plant Soil* 11, 71-79.

FAO, 1998. World reference base for soil resources. World Soil Resource Report 84, FAO, Rome.

FERNANDES, E.C.M., MOTAVALLI. P.P., CASTILLA, C. & MUKURUMBIRA, L., 1997. Management control of soil organic matter dynamics in tropical land-use systems. *Geoderma.* 79, 49-67.

GREGORICH, E.G., CARTER, M.R., ANGERS, D.A., MONREAL, C.M. & ELLERT, B.H., 1994. Towards a maximum data set to assess organic matter quality in agricultural soils. *Can. J. Soil Sci.* 74, 367-385.

HAAS, H.J., EVANS, C.E. & MILES, M.L., 1957. Nitrogen and carbon changes in Great Plains soils as influenced by cropping and soil treatments. U.S. Dept. Agric. Tech. Bull.1164, Washington.

HAYES, M.H.B. & CLAPP, C.E., 2001. Humic substances: Consideration of compositions, aspects of structure, and environmental influences. *Soil Sci.*166, 723-737.

HAYES, M.H.B., MACCARTHY, P. MALCOLM, R.L. & SWIFT, R. S. 1989. Humic substances. II. In search of structure. John Wiley & Sons, London.

HAYNES, R.J. & SWIFT R.S., 1990. Stability of soil aggregates in relation to organic constituents and soil water content. *J. Soil Sci.* 4, 73-83.

HINTZE, J.L., 1997. Number cruncher statistical systems 2000, Kaysville, Utah.

JANZEN**,** H.H., 1987. Soil organic matter characteristics after long-term cropping to various spring wheat rotations. *Can. J. Soil Sci.* 67, 845-856.

JENKINSON, D.S., 1990. The turnover of organic carbon and nitrogen in soil. *Phil. Trans. R. Soc. Lond*. 329, 361-368.

JENNY, H., 1941**.** Factors of soil formation: A system of quantitative pedology. McGraw-Hill, New York.

KANG, S., AMARASIRIWARDENA, D., VENEMAN, P. & XING, B., 2003. Characterization of ten sequentially extracted humic acids and humin from a soil in western Massachusetts. *Soil Sci. 168*, 880-887.

KONONOVA, M.M., 1966. Soil organic matter: Its nature, its role in soil formation and in soil fertility. Pergamon Press, Oxford.

KUMADA, K., 1999. Chemistry of soil organic matter. Developments in Soil Science 17, Elsevier, Amsterdam.

LARSON, W.E. & PIERCE, F.J., 1994. The dynamics of soil quality as a measure of sustainable management. In. J.W. Doran, D.C. Coleman, D.F. Bezdicek and B.A. Steward (eds). Defining soil quality for a sustainable environment. Soil Sci. Soc. of Am., Madison, Wisconsin.

LOBE, I., 2003. Fate of organic matter in sandy soils of the South African Highveld as influenced by duration of arable cropping. Ph.D. Thesis, University of Bayreuth, Germany.

LOBE, I., AMELUNG. W. & DU PREEZ. C.C., 2001. Losses of carbon and nitrogen with prolonged arable cropping from sandy soils of the South African Highveld. *Eur. J. Soil Sci.* 52, 93-101.

MACCARTHY, P., 2001**.** The principles of humic substances. *Soil Sci*. 166, 738-751.

MACCARTHY, P., MALCOLM, R.L., CLAPP, P.R. & BLOOM, C.E., 1990. An introduction to soil humic substances. In: Humic substances in soil and crop sciences: Selected readings. Soil Sci. Soc. of Am., Madison, Wisconsin.

MACVICAR, C.N., SCOTNEY, D.M., SKINNER, T.E., NIEHAUS, H.S. & LAUBSCHER, J.H., 1974. A classification of land (climate, terrain form, soil) primarily for rainfed agriculture. *S. Afr. J. Agric. Extension* 3, 21-24.

MAGDOFF, F. & WEIL, R.R., 2004. Soil organic matter management strategies. In F. Magdoff and R.R. Weil (eds.). Soil organic matter in sustainable agriculture. CRC Press, Boca Raton.

MALCOLM, R.L., 1990. Variation between humic substances isolated from soils, stream waters and groundwaters as revealed by ^{13}C-NMR spectroscopy. In: Humic substances in soil and crop sciences: Selected readings. Soil Sci. Soc. of Am., Madison, Wisconsin.

MANN, L.K., 1985. A regional comparison of carbon in cultivated and uncultivated Alfisols and Mollisols in central United States. *Geoderma* 36, 241-253.

MANN, L.K., 1986. Changes in soil carbon storage after cultivation. *Soil Sci.* 142, 279-288.

MILLS, A.J. & FEY, M.V., 2004. Declining soil quality in South Africa: effects of land use on soil organic matter and surface crusting. *S. Afr. J. Plant Soil.* 21, 388-398.

NELSON, D.W. & SOMMERS, L.E., 1982. Total carbon, organic carbon and organic matter. In A.L. Page (ed.). Methods of soil analysis. Part 2. Chemical and microbiological properties. Am. Soc. of Agron., Madison, Wisconsin.

NICHOLS, J.D., 1984. Relation of organic carbon to soil properties and climate in the Southern Great Plains. *Soil Sci. Soc. Am. J.* 48, 1382-1384

OADES, J.M., 1995. Recent advances in organomineral interactions: Implications for carbon cycling and soil structure. In P.M. Huang (ed.), Environmental impact of soil component interactions. Volume I. Natural and anthropogenic organics. Lewis Publishers, Boca Raton.

PIERCE, F.J. & LARSON, W.E., 1993. Developing criteria to evaluate sustainable land managements. In J.M. Kimble (ed.). Proc. of the 8th International Soil Management Workshop on Utilization of Soil Survey Information for Sustainable Land Use, Sacramento, California.

PRINSLOO, M.A., 1988. Effect of cultivation on the content and availability of nitrogen in selected Orange Free State soils. M.Sc. Agric. Dissertation, University of the Free State, Bloemfontein.

POTTER, K.N., TORBERT, H.A., JOHNSON, H.B. & TISCHLER, C.R., 1999. Carbon storage after long-term grass establishment on degraded soil. *Soil Sci.* 164, 718-725.

RASMUSSEN, P.E. & COLLINS H.P., 1991. Long-term impact of tillage, fertilizer and crop residue on soil organic matter in temperate semi-arid regions. *Adv. Agron*. 45, 93-134.

RICE, J.A. & MACCARTHY, P., 1988. Comments on the literature of humin fractions of humus. *Geoderma* 43, 65-73.

ROVIRA, A.D. & GREACEN, E.L., 1957. The effect of aggregate disruption on the activity of microorganisms in the soil. *Aust. J. Agric. Res.* 8, 317-659.

SANCHEZ, P.A., BANDY, D.E., VILLACHICA, J.H. & NICHOLAIDES, J.J., 1982. Amazon Basin soils: management for continuous crop production. *Sci*. 216, 821-827.

SCHNITZER, M., 1977. Recent findings on the characterization of humic substances extracted from soils from widely differing climatic zones. In Proc. of a Symposium on Soil Organic Matter Studies, Braunsweig, Germany.

SCHNITZER, M., 1978. Humic substances: Chemistry and reactions. In M. Schnitzer and S.U. Khan (eds.) Soil organic matter. Elsevier, New York.

SCHNITZER, M., 1982. Organic matter characterization. In A.L. Page (ed.). Methods of soil analysis. Part 2. Chemical and microbiological properties. Am. Soc. of Agron., Madison, Wisconsin.

SCHNITZER, M., 1991. Soil organic matter - the next 75 years. *Soil Sci.* 151, 41-59.

SCHNITZER, M. & KHAN, S.U., 1972. Humic substances in the environment. Marcel Dekker, New York.

SCHNITZER, M. & KHAN, S.U., 1978. Soil organic matter. Elsevier, New York.

SCOTNEY, D.M. & DIJKHUIS, F.J., 1990. Changes in the fertility status of South African Soils. *S. Afr. J. of Sci.* 86, 395-402.

SHARMA, K.L., MANDAL, K.U., SRINNIVAS, K., VITTAL, K.P.P., MANDAL, B., GRACE, J.K. & RAMESH, V., 2005. Long term soil management on crop yields and soil quality in dryland Alfisol. *Soil Till. Res*. 83, 246-259.

SIKORA, L.J. & STOTT, D.E., 1996. Soil organic carbon and nitrogen. In J.W. Doran and A.J. Jones (eds.). Methods of assessing soil quality. Soil Sci. Soc. of Am., Madison, Wisconsin.

SMITH, J.L. & ELLIOT, L.F., 1990. Tillage and residue management effects on soil organic matter dynamics in semi-arid regions. *Adv. Soil Sci.* 13, 69-89.

SMYTH, A.J. & DUMANSKI, J. 1995. A framework for evaluating land management. *Can. J. Soil Sci.* 75, 401-405.

SOIL CLASSIFICATION WORKING GROUP. 1991. Soil classification, a taxonomy system for South Africa. Memoirs on the Agricultural Resources of South Africa No.15, Department of Agricultural Development, Pretoria.

SOIL SURVEY STAFF. 1998. Key to soil taxonomy. 8th edn. Pocahontas Press, Blacksburg, Virginia.

STEVENSON, F.J., 1982. Humus chemistry: Genesis, composition, reactions. John Wiley and Sons. New York.

STEVENSON, F.J. & COLE, M.A., 1999. Cycles of soil: carbon, nitrogen, phosphorus, sulfur, micronutrients, 2nd edn. John Wiley & Sons. New York.

STEVENSON, F.J. & ELLIOT, E. T., 1989. Methodologies for assessing the quality and quantity of soil organic matter. In D.C. Coleman, J.M. Oades and G. Uehara (eds.). Dynamics of soil organic matter in tropical ecosystems. University of Hawaii Press, Honolulu.

SWIFT, R.S., 1996. Organic matter characterization. In D.L. Sparks (ed.). Methods of soil analysis. Part 3. Chemical methods. Soil Sci. Soc. of Am., Madison, Wisconsin.

SWIFT, R.S., 2001. Sequestration of carbon by soil. *Soil Sci.* 166, 858-871.

TATE, R.L., 1992. Soil organic matter: Biological and ecological effects. Krieger Publishers, New York.

THERON, J.J., 1949. The restoration of organic matter in worn-out soils under dryland cultivation. African Regional Scientific Conference Communications, Johannesburg.

THERON, J.J., 1953. The recuperation of soils under grass pastures. In D. Meredith (ed.). The grasses and pasture of South Africa: Pasture management in South Africa. Central News Agency, Johannesburg.

THERON, J.J., 1963. The mineralization of nitrogen in soils under grass. *S. Afr. J. Agric. Sci*. 6, 155-164.

THERON, J.J., 1965. The influence of fertilizers on the organic matter content of soil under natural veld. *S. Afr. J. Sci.* 8, 525-534.

THERON, J.J. & HAYLETT, D.G., 1953. The regeneration of soil humus under grass ley. *Empire Journ. Exper. Agric.* 21, 86-98.

TISDALE, J.M. & OADES, J.M., 1982. Organic matter and water stable aggregates in soils. *J. Soil Sci*. 33, 141-163.

TROEH, F.R. & THOMPSON, L.M., 1993. Soils and soil fertility. Oxford University Press, Oxford.

VAN ZYL, A.J., 1995. Effect of cultivation on the phosphorus fractions in selected dryland soils. M.Sc. Agric. Dissertation, University of the Free State, Bloemfontein.

WEIL, R.R. & MAGDOFF, F., 2004. Significance of soil organic matter to soil quality and health. In F. Magdoff and R.R. Weil (eds.). Soil organic matter in sustainable agriculture. CRC Press, Boca Raton.

ZALBA, P. & QUIROGA, A.R., 1999. Fulvic acid carbon as a diagnostic feature for agricultural soil evaluation. *Soil Sci.*164, 57-61.

ZINCK, J.A. & FARSHAD, A., 1995. Issues of sustainability and sustainable land management. *Can. J. Soil Sci*. 75, 407-412.

Appendix I: Data on C contents, N contents and C/N ratios for crude soil (Cs and Ns), humic substance extract (Ce and Ne), humic acid fraction (Ch and Nh) and fulvic acid fraction (Cf and Nf) for samples from three land uses (V = Virgin, C = Cultivated and R = Restored) per agro-ecosystem (HS = Harrismith, TW = Tweespruit and KR = Kroonstad).

Agro-ecosystem	Sample No.	Replication	Land use	C contents (g C kg^{-1} soil)				N contents (mg N kg^{-1} soil)				C/N ratios			
				Cs	Ce	Ch	Cf	Ns	Ne	Nh	Nf	Cs/Ns	Ce/Ne	Ch/Nh	Cf/Nf
HS	26	1	V	22.09	10.95	5.64	5.31	1938	1690	1027	618	11.40	6.48	5.49	8.59
		2		21.26	10.63	5.23	5.40	1957	1653	1003	650	10.86	6.43	5.21	8.31
		3		22.40	10.73	5.29	5.44	1997	1845	1010	835	11.22	5.82	5.24	6.52
		4		23.24	11.13	5.40	5.73	1996	1694	968	726	11.64.	6.57	5.58	7.89
		5		21.82	10.63	5.47	5.16	2021	1674	1031	643	10.8	6.35	5.31	8.03
		6		18.49	8.77	4.82	3.95	1604	1506	817	689	11.53	5.82	5.9	5.73
Mean				**21.55**	**10.47**	**5.31**	**5.16**	**1918**	**1677**	**976**	**693**	**11.24**	**6.24**	**5.45**	**7.51**
HS	26	1	C	12.66	5.89	2.62	3.27	1116	852	754	98	11.34	6.91	3.48	3.34
		2		12.25	5.75	2.33	3.42	1034	869	834	35	11.85	6.62	2.79	9.77
		3		10.10	5.30	2.50	2.80	1012	819	765	54	9.98	6.47	3.27	5.19
		4		10.70	5.28	2.62	2.66	1072	850	772	78	9.98	6.21	3.39	3.41
		5		9.84	5.14	2.47	2.67	1022	783	707	76	9.63	6.56	3.49	3.51
		6		8.86	5.17	2.64	2.53	971	836	776	60	9.13	6.18	3.40	4.22
Mean				**10.73**	**5.42**	**2.53**	**2.89**	**1037**	**834**	**768**	**66**	**10.32**	**6.49**	**3.30**	**4.90**
HS	7	1	R	22.23	9.86	5.46	4.40	1600	1699	854	746	13.89	5.80	6.39	5.90
		2		17.93	8.27	4.59	3.67	1495	1643	843	652	11.99	5.03	5.44	5.63
		3		18.03	7.63	4.96	2.66	1424	1581	747	677	12.66	4.83	6.64	3.93
		4		18.09	8.08	4.64	3.43	1469	1583	822	693	12.31	5.10	5.64	5.37
		5		17.24	7.41	4.29	3.11	1428	1561	767	662	12.07	4.75	5.59	4.70
		6		17.91	8.18	4.98	3.20	1440	1622	915	525	12.44	5.04	5.44	6.10
Mean				**18.57**	**8.24**	**4.42**	**2.84**	**1431**	**1614**	**825**	**650**	**12.56**	**5.09**	**5.86**	**5.27**
TW	22	1	V	19.12	8.92	5.3	3.62	1705	842	647	195	11.21	10.59	8.19	18.56
		2		19.24	9.51	6.60	2.91	1698	819	676	143	11.33	11.61	9.76	20.35
		3		18.45	8.87	6.22	2.65	1656	816	671	145	11.14	10.87	9.27	18.28
		4		17.29	8.17	5.40	2.77	1564	773	587	186	11.06	10.57	9.20	14.89
		5		16.99	8.19	5.76	2.34	1582	770	598	172	10.74	10.64	9.63	13.61
		6		17.71	8.75	5.29	3.46	1625	777	570	207	10.90	11.26	9.28	16.72
Mean				**18.13**	**8.73**	**5.76**	**2.95**	**1638**	**799**	**624**	**174**	**11.06**	**10.92**	**9.22**	**17.07**

TW	22	1	C	9.27	3.90	3.59	0.31	911	479	450	29	10.18	8.14	7.98	10.69
		2		8.4	4.45	4.15	0.30	932	501	462	39	9.01	8.88	8.98	7.69
		3		8.64	4.74	3.48	1.26	958	492	450	42	9.02	9.63	7.73	30.0
		4		8.69	5.2	3.91	1.29	1009	538	484	54	8.61	9.67	8.08	23.89
		5		9.93	4.45	4.45	1.00	1018	510	474	36	9.75	8.73	9.39	27.78
		6		8.92	4.88	4.81	0.07	990	499	474	25	9.01	9.78	10.15	2.80
Mean				**8.97**	**4.60**	**4.06**	**0.70**	**969**	**503**	**465**	**37**	**9.26**	**9.14**	**8.71**	**17.14**
TW	6	1	R	14.04	7.80	4.34	3.45	1422	865	615	250	9.87	9.02	7.06	13.8
		2		14.66	7.92	4.78	3.13	1454	867	632	235	10.08	9.13	7.56	13.32
		3		13.72	6.92	4.04	2.91	1389	808	623	185	9.88	8.56	6.48	15.73
		4		12.79	6.83	4.75	2.07	1355	772	594	178	9.44	8.85	8.00	11.63
		5		13.52	6.99	4.46	2.52	1460	831	519	312	9.26	8.41	8.59	8.08
		6		14.05	7.13	4.17	2.95	1509	851	603	248	9.31	8.38	6.91	11.89
Mean				**13.8**	**7.26**	**4.42**	**2.84**	**1431**	**832**	**597**	**235**	**9.64**	**8.72**	**7.43**	**12.41**
KR	10	1	V	8.47	3.58	2.58	1.00	770	433	398	35	11	8.27	6.48	28.57
		2		6.89	3.40	2.70	0.70	634	418	382	36	10.87	8.13	7.07	19.44
		3		6.03	3.36	2.78	0.58	674	429	406	23	8.95	7.83	6.85	25.22
		4		7.52	3.62	3.55	0.07	704	535	403	132	10.68	6.77	8.81	0.53
		5		6.50	3.29	3.12	0.17	697	538	405	133	9.33	6.12	7.7	1.28
		6		8.27	3.37	1.63	1.74	685	588	421	167	12.07	5.73	3.87	10.42
Mean				**7.28**	**3.44**	**2.72**	**0.71**	**694**	**490**	**402**	**87**	**10.48**	**7.14**	**6.80**	**14.24**
KR	10	1	C	4.34	2.13	0.64	1.49	399	386	225	131	10.88	5.52	2.84	11.37
		2		2.53	2.33	0.58	1.40	467	457	268	189	5.42	5.10	2.16	7.41
		3		3.41	1.99	0.41	1.58	482	445	253	192	7.08	4.47	1.62	8.23
		4		3.85	1.94	0.28	1.66	489	438	250	188	7.87	4.43	1.12	8.83
		5		2.42	2.35	0.30	2.05	470	454	253	201	5.15	5.18	1.19	10.2
		6		4.53	2.31	0.34	1.97	470	441	222	219	9.64	5.24	1.53	9.00
Mean				**3.51**	**2.17**	**0.42**	**1.69**	**462**	**436**	245	**186**	**7.67**	**4.99**	**1.74**	**9.17**
KR	11	1	R	8.74	3.43	1.50	0.82	739	613	251	165	11.83	5.6	5.98	4.97
		2		9.56	3.42	1.62	0.84	838	588	257	154	11.41	5.82	6.30	5.45
		3		7.64	3.67	1.42	1.18	827	594	255	160	9.24	6.18	5.57	7.37
		4		9.24	3.81	1.95	0.83	813	534	252	176	11.36	7.13	7.74	4.72
		5		8.93	3.82	1.63	1.03	882	525	235	177	10.12	7.28	6.94	5.82
		6		9.14	3.87	1.24	1.38	929	508	247	182	9.84	7.62	5.02	7.58
Mean				**8.87**	**3.67**	**1.56**	**1.01**	**838**	**560**	**249**	**169**	**10.63**	**6.60**	**6.26**	**5.99**