# The Long-term Dynamics of Soil Organic Carbon in the Anthropogenic Soils of Scotland's Medieval Urban Landscape

By

Benneth O. I. Esiana

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**Supervisors:**

Dr W. Paul Adderley

Prof. Richard D. Oram

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# Author Declaration

I hereby state that I am the sole Author of this work, and all research materials used for its production has been cited and referenced accordingly.

Benneth O. I. Esiana

21/07/2015

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## ABSTRACT

In an interdisciplinary study requiring the synergistic association of historical evidence and chemical and biochemical analyses, this thesis investigates the properties and characteristics of historically modified soils known as anthrosols. These soils, developed through the anthropogenic addition of high volumes of organic-rich municipal waste materials to land, including human and animal waste, as part of the waste management practices in medieval urban communities in Scotland at St Andrews, Roxburgh and Elgin, offer an insight to the state and dynamics of these organic material.

Soil is one of the most sensitive environmental domains to transformation. These transformations are visible from the alterations to the physical and chemical properties of soil. Anthropogenic activities may leave behind signatures in the soil in the form of artefacts, ecofacts, elemental enrichment or depletion, enhancement in soil magnetic properties and organic matter content. In the historical dimension of this study, the observable features and measurable properties of soil profiles are exploited to reveal past organisation and functions of cultural landscapes by carefully studying the stratigraphic units of soil profile, and examining the association of each unit with settlement artefacts and soil properties. Through comparison with historical records of past events on the respective study sites, the relationship between the soils record of past human activities is observed through physical, chemical and biochemical properties. The historical record is used to assess if such evidence can be used reliably to develop the account of site use for the medieval burghs of Scotland.

In the environmental aspect, investigation focuses on the physical and chemical conditions of these soils in terms of their carbon content, composition, residence time estimates and their role in global C cycle and terrestrial carbon budgeting. Past investigations of anthopogenically-deepened soils have been interpreted with respect to historical site use, however, the

environmental implications of the resultant accumulated organic material or residue have not previously been considered in much detail. A particular novelty of this aspect of the project is that it is an in-depth examination of anthropogenic soils with known histories extending into the medieval period. This time-depth allows a new understanding of the processes and products of decomposition of known organic materials that were added to soil. The biophysicochemical data obtained from these soils such as their extant organic carbon content and variability with depth, the composition of the various carbon species that together constitute soil organic matter, and biological community and activity (microorganisms and enzymes) provides critical information on the relative recalcitrance, state of decomposition, and the mechanism of stabilisation of these materials in the soil.

## CONTENTS



## CHAPTER 1

### SOCIETY AND THE ENVIRONMENT

## CHAPTER 2

STUDY SITES



## CHAPTER 3

METHODOLOGY

**CHAPTER 7**

URBAN ANTHROSOL AS POTENTIAL HISTORICAL ARCHIVE: INTRA AND INTER SITE ASSESSMENTS OF SOIL RECORD DATA OF SCOTTISH MEDIEVAL URBAN LANDSCAPE

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## GLOSSARY

**Anthropogenic**: Events originating or caused by human activity

**Anthrosol**: Soils that have been modified profoundly by human activities such as addition of household wastes, organic materials, farming (livestock and crop growing)

**Amerindians**: Indigenous people of the pre-Columbian Americas

**Artefacts**: Cultural/historical objects made or constructed by human such as pottery etc.

**Backlands/garden**: A piece of land located behind properties where a range of activities occur including household activities and horticulture

**Burgesses**: The townsmen in a burgh/community

**Burgh**: An incorporated town in Scotland having its own charter, with some degree of self-governance/ political independence

**Buggage Plot/Hinterlands**: Large piece of land usually located outside the burgh (fringes) used primarily for cultivation

**Decomposition**: The gradual transformation of fresh litter (plant/animal) into amorphous carbon/humus.

**Degradation**: The breaking down (depolymerisation and oxidative reactions) of complex/large molecules (poly-aromatics, polysaccharides, lipids and proteins) in to simple, smaller molecules (amino acids, carboxylic acids, $CO_2$).

**Destabilisation**: The increase in the potential for SOM loss by respiration.

**Early modern period**: The $16^{th}$ to mid – $18^{th}$ Century

**Ecofacts**: Materials of plant or animal origin that has not been technologically altered such as bones etc.

**Epoch**: A subdivision of the geologic timescale that is longer than an Age and shorter than a Period

**Greenhouse gas** (GHG): A gas in an atmosphere that absorbs and emits radiation/heat causing a warming effect

**Hearth**: A brick or stone-lined fireplace, with or without an oven used for heating and cooking

**Hunter-gatherer/Nomadic**: A transient community that moves from one point to the other foraging.

**Labile/active C**: are materials that are more susceptible to microbial respiration or decomposition.

**Midden**: A refuse heap or dunghill which may contain shells, animal bones, animal and human excrement and other domestic waste and industrial effluent.

**Middle Ages**: The period from the $5^{th}$ – $15^{th}$ century

**Pastoral community**: Agricultural community, including livestock rearing

**Pedon**: The smallest unit of soil that contains all the soil horizons of a particular soil type

**Phenol oxidase** (PO): An enzyme that hydrolyses or breaks down phenolic compounds

**Physicochemical**: The physical and chemical properties of a material e.g. soil

**Pre-Columbian Americas**: Any period in the history of the Americas prior to European influence

**Pyrogenic**: Materials produced by partial or complete combustion or through exposure to heat

**Recalcitrant/passive C**: Carbon complexes that resist further transformation.

**Recalcitrance**: Refers to SOM with a longer mean resident time (MRT).

**Soil Focus Group** (SFG): A working group formulated in 2009 by the Scottish Government to advise in the implementation of the Scottish Soil Framework

**Stability/stabilization**: The combined effect of recalcitrance, interactions, and accessibility which leads to the decrease in the potential for SOM loss by respiration and/or leaching.

***Terra preta*/Amazonian Dark Earth** (ADE): Organic-rich soils that were formed from agricultural activities of the Amerindians in the pre-columbian America

## LIST OF FIGURES

## LIST OF TABLES

## THESIS STRUCTURE

This thesis is an inter-disciplinary study that employs a robust three-way approach to developing an understanding of the impacts of past historical soil management practices on the dynamics of the organic matter in the resulting extant soil. Investigation extends to the potential synergistic application of selected field and laboratory techniques for determining early settlement patterns, activity and organisation. The introductory chapter provides an overview of the framework on which the research conducted sits, with the chapters that follow spanning disciplinary boundaries including ethnographic history, anthropology, physical, biological and chemical sciences, soil conservation, management, and policy, and climate sciences. The thesis is structured to allow the continuity of the subjects and the various elements of discussion covered in the project.

Chapter one contains essential background to the project, consisting of several complementary and progressively laid out sections. The first section discusses mankind's interactions with the environment through time and its associated impacts, and continues on to look into the outcomes of past research studies on anthropogenically modified soils, and their contributions in anthropology and landscape history citing specific examples in South America. Subsequently, some of challenges of early research on manmade soil such as problems with earlier soil classification systems and general issues arising from the perception of what constitute soil are discussed. Explanations on the formation and history of anthropogenic urban soil in Scotland from medieval to contemporary period are given, followed by discussions on the cultural significance of such soils which defines the historical context of the project.

The subsequent section discusses the project in an environmental context highlighting the role of urban soil as carbon sinks. This provides the rationale for considering the impacts of climate-driven changes to the organic matter stored in urban soil and their responses which is

vital for managing carbon fluxes in terrestrial environment. Subsequent sections focus on global climate change effect, with discussions encompassing issues and challenges of greenhouse gas emissions reduction, carbon sink mitigation strategies and their potentials, and threats to soil carbon sequestration which together emphasises the imperative need for thorough scientific understanding of the various carbon stocks, store potential, and mechanisms governing this process in soils (natural and anthropogenic) in order to accurately predict future behaviour of all terrestrial sinks and their effects on future concentrations of atmospheric $CO_2$.

Chapter two outlines the set of criteria used in the selection of study sites, and provides detailed description and historical background to the study sites. Chapter three discusses the range of techniques that were applied in the project with emphasis on their suitability to complete specific analysis required to answer research questions throughout the project.

Chapter four discusses the impacts of historical activities on soil physicochemical properties, including the determination of, and characterisation of soil organic matter. In this chapter, the differences and similarities in key soil indicators were used to describe settlement organisation such as main activity areas, land-use type, intensity of exploitation and so on within the study site. Comparison of these anthropogenic soils with natural soils from around the study site was also made to determine the extent of modification of urban soils.

Chapter five focuses on the exploration of the biological impacts (microbial activity) of these foreign materials deposit on soil and their effects on enzymatic activity, nutrient dynamics and soil organic matter decomposition.

Chapter six explores the various mechanisms of stabilisation of soil organic matter at work and the degree to which they operate. This is relevant in soil carbon management policies because it identifies the degree of susceptibility of soil organic matter to various land-use types.

Finally, chapter seven focuses on the interpretation of historical settlement from soil record data, using various soil markers such as elemental signature, magnetic susceptibility, organic matter content, and soil pH, obtained from both field and laboratory analytical methods. The integration of soil-based evidence and historical records allows preliminary discussion of the activities associated with these settlements to be made and the cultural context within which the soils were formed. The final section summarises the thesis, outlining the key findings, contributions, and policy recommendations together with future research studies to build upon the foundations that has been established from this project to develop a better understanding of urban soil and its complexes.

# CHAPTER 1

## SOCIETY AND THE ENVIRONMENT

### 1.1 The Natural Environment

Soil is one of the domains most vulnerable to transformation in the environment. Humans and their ancestors have influenced their environment, in many ways directly and indirectly, over millions of years by deflecting the natural course of events of Earth systems (Golomb and Eder, 1964; Bridges, 1978; Ruddiman, 2003; Steffen et al., 2007, 2011). The impacts of prehistoric anthropogenic activities on the environment varied in intensity with time but generally increased. Prehistoric modifications which typically involved predation and landscape alteration usually by use of fire allowed ancient humans to gain advantage in acquiring sustenance (vegetative food sources) and aiding hunting (Steffen et al., 2007, 2011). These modifications to the natural environment may have been visible at various stages of Earth's history but were comparatively insignificant and unable to cause large-scale transformation.

Large-scale discernible transformation of the natural environment has been linked to the advent of agriculture (Ruddiman, 2003). The development of agriculture and its associated practice such as forest clearance, irrigation, and extensive use of fire, caused widespread alterations to soil, vegetation and the climate (Bridges, 1978; Ruddiman, 2003; Ellis et al., 2013). To these practices have been attributed the divergence from the natural trends in the atmospheric concentrations of $CO_2$ and $CH_4$ by 8000 years and 5000 years ago respectively. Crutzen and Stoermer (2000) have proposed the establishment of a new geological epoch called the "Anthropocene" to mark the time during which the impacts of anthropogenic activities on the environment have become apparent (see also Crutzen, 2002). The start of the proposed geological epoch the "Anthropocene" was placed by Crutzen and colleagues at around 1780 - 1800 A.D., the beginning of rapid increase in human population and of

industrial-era greenhouse gas emissions, but there is no consensus on this notion and questions still remain as to what date and period defines the beginnings of anthropogenic impact on the environment (Ruddiman, 2003; Certini and Scalenghe, 2011; Smith and Zeder, 2013) although supporting evidence for this period and transition is beginning to emerge (Wolfe et. al., 2013). Recent efforts to further this debate saw the introduction of the term "Palaeoanthropocene" by Foley et al. (2013) which is suggested to mark the period before the industrial era where an anthropogenic impact on the landscape and the environment is minor but discernible. Figure 1.1 below illustrates these proposed time frames.

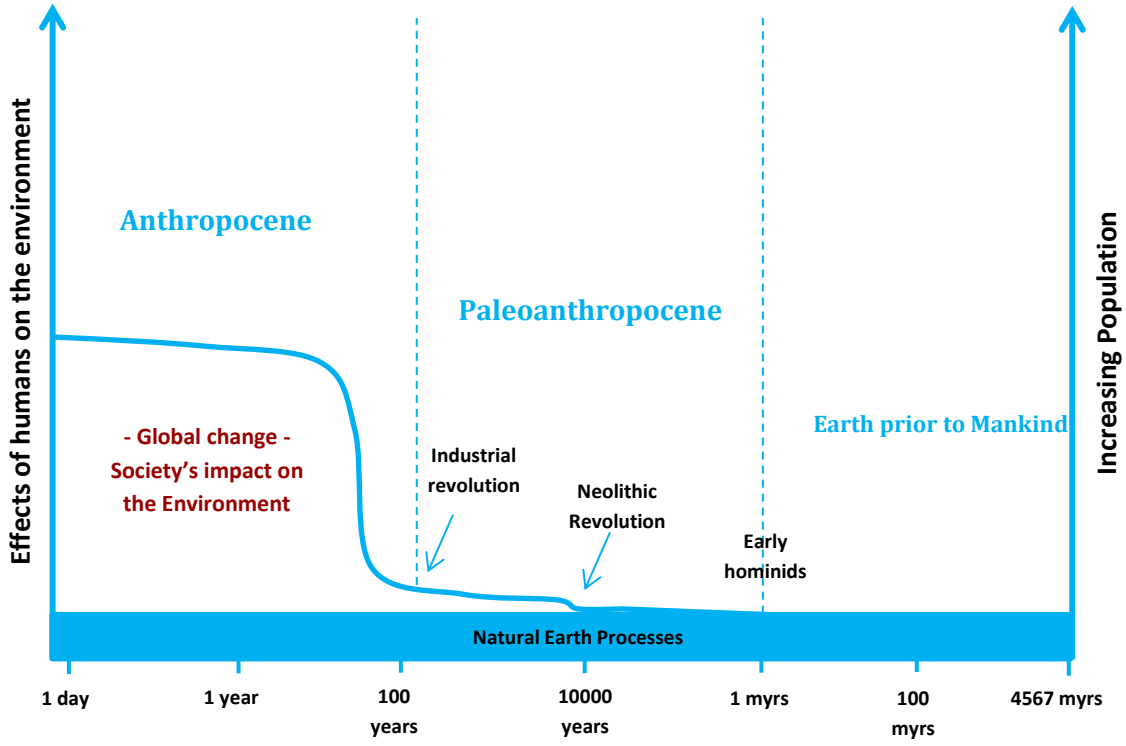



Fig. 1.1. Shows the degrees of anthropogenic processes (activities) on the environment and their suggested geological timescale (Adapted from Foley et al., 2013)

### *1.1.1 Soil Formation*

Soils are a natural dynamic body consisting of various assemblages of mineral particles and organic matter that covers the surface of the terrestrial domain. Formed initially by the physical, chemical and biological weathering of exposed rocks, the subsequent development of soil into differentiated horizons of varying depths with differing physical and chemical properties, composition, and biological characteristics is influenced by the various biotic and abiotic conditions to which they are subjected. These factors have been considered and are presented in Hans Jenny's famous equation of soil-forming factors:

$$s = f'(cl', o', r', p, t) \quad (1)$$

Soils and their inherent properties are determined by the soil-forming factors listed within the parentheses; where (*s*) stands for soil, (*f*) function of, (*cl*) climate, (*o*) organism, (*r*) topography, (*p*) parent material, and (*t*) time. Humans have been recognized as the major driving force within the 'independent variable' of organism (*o*) in the soil-forming factors (*cl, o, r, p, t*). Man's impact on soils are numerous and have been identified as an outstanding biological soil-forming factor capable of not only influencing soil formation in its category as an organism (*o*) but who can effectively alter other variables notably the vegetation and the climate (Jenny, 1941; Amundson and Jenny, 1991; Adler, 2003; Mason, 2003; Ruddiman, 2003; Adderley et al., 2010; Steffen et al., 2011).

### *1.1.2 Anthropogenic Soils*

Soil modification prior to the transition from hunter-gatherer to agricultural and pastoral community was prevalent but on small areas (Ruddiman, 2003; Hillel, 1992; Rowell, 1994). Changes in the cultural paradigm brought about by the adoption and development of agriculture gave rise to the establishment of permanently settled communities. With

increasing populations and specialisations associated with urbanisation, such communities were not without the associated problems of how to manage the increased production of waste materials generated. In contrast, the transient nature of the nomadic culture meant that waste disposal was not a problem in these communities as wastes produced were marginal in comparison and were readily disposed of (Rathje and Murphy, 2001; Marlowe, 2005). One commonly known strategy of managing such waste was its use in agriculture. Typically, in many contexts, mixtures of waste products such as faeces and urine, spoiled stored agricultural products, household rubbish, domestic food-processing waste, charcoal and ash, cesspit contents and debris, and other varieties of materials, were composted and applied on soils in backlands and fields to maintain fertility. In other contexts, specific selected materials were repeatedly applied. Such sustained practices resulted in the accumulation of organic materials or soil deepening to cumulative depths of over one metre in some locales (Hall, 1997; Davidson et al., 2006). Today these deep anthropogenic soils such as the Amazonian Dark Earth (*terra preta*), and plaggen soil, denotes a legacy of past agricultural practices/management systems but even more intriguing perhaps is the degree to which these soils represent a deliberate investment of human labour at the time of their formation or alternatively an inadvertent outcome of waste management/disposal (Woods et al., 2009; Fairhead and Leach, 2009; German, 2003).

### *1.1.3 Past Research on Anthropogenic Soil*

Studies investigating the development and management of anthropogenic soils are of growing significance in a time of increasing human activity such as expanding urbanization and agricultural intensification. An understanding of past management practices of early communities for example may provide a prospect for sustainable management of an increasing inventory of anthropogenically modified soils around the world. Although these

soils have been considered since the advent of modern pedology in the early 20th Century, early studies were rudimentary and typically restricted to aspects of contamination and, by association, to human health (Lehmann and Stahr, 2007). As these soils have long existed as components and characteristics of the landscape, their study, from a historical context for example, can provide information on the beginnings and end of a culture, it can reveal a great deal about the past lifestyle and occupation of early inhabitants, details of community size and phases of occupancy (if any), and perhaps more intriguing is its ability to acquire information on locales with otherwise no surviving historical record evidence. Additionally, environmental based research investigations on anthropogenic soils can provide understanding of the long-term sustainable settlement of ancient communities, land management practices which includes soil and waste management, climatic variations and community resilience, among other issues.

Soil analysis also provides evidence to support documented historical accounts which until recently have been over-relied upon for interpretations in some landscape. This increases the susceptibility to 'under' or 'over' interpretation that may or may not reflect the true nature of the event being described. A set of study that simultaneously illustrates the historical and environmental facets of anthrosols is the previous and on-going research on the hortic anthrosols (*terra preta*) of the Amazon. Through careful analysis of soil data, researchers have been able to establish that agriculture played an important role in the existence and flourishing of settlements in the region, which was previously considered as an unlikely scenario by archaeologist and environmental determinist alike due to the pre-conceived environmental limitations to the 'carrying capacity' of the region (Lehmann et al., 2003; Bruno and Woods, 2004; Kawa and Oyuela-Caycedo, 2008; Woods et al., 2009). The outcome of the above studies brought about the re-evaluation of the role of indigenous people (Amerindians) in the pre-Columbian Americas and consequently the dismissal of the consensus view that the

Amazon was incapable of supporting large farming communities due to its naturally infertile soil.

Additionally, preliminary assessment of the Amazonian soil showed that it contained unusually large amount of pyrogenic material or black carbon (Glaser et al., 2001a). Further examination of the soil revealed the potential of such management practice to serve as an approach to increasing terrestrial carbon sequestration given the soil's ability to hold organic carbon (char) for long period of time. Also due to its high fertility and self-sustaining nature, improved sustainable agriculture can be achieved (Woods and McCann 1999; O' Neil et al., 2009; Glaser, 2007); a legacy of the previous land management practice of the ancient dwellers. Conversely, it is arguable that such information may be obtained through careful studies of natural soils, but anthropogenic soils relate this information (climatic data, soil/land management data) in a manner that allows for the examination of impacts (direct or indirect) on mankind, an outcome that may be compared to modern day scenarios to gain understanding of such techniques that may be useful in ensuring the continued existence of our current civilisation. The study of anthropogenic soil can provide clues on how to address some contemporary issues such as climate change, food security (agriculture), and land degradation (land management issues), facing scientist today. As has been seen, research on Amazonian Dark Earth has provided invaluable evidence and demonstrated both the utilities and the practical aspect of the understandings obtained from its study. It is argued that the study of these soils could reveal more of the structural and functional dynamics of mankind's existence in such places.

*1.1.4 Soil Classification and Anthropogenic Soils*

In the early stage of soil science development, research studies on anthropogenic soils were uncommon, more so their environmental aspect and implications. This obscurity is probably due to the consensus view held at the time that anthrosols were generally not soils (Lehmann and Stahr, 2007). The absence of clear constructive classification of anthropogenic soils in the classification system, and the complications in understanding the processes of such soil formation or development due to the interaction of complex and diverse anthropogenic impacts (Manil, 1959; Kadar and Koncz, 1993; Hartman et al., 2004; Craul, 1994) contributed to this obscurity.

In soil classification, the perceived ambiguity in the operational definitions of terms and concepts, absence of detailed soil maps, and inflexibility in terms of practical value for use in multiple locales, made adoption of the system near impractical for use in many contexts (natural or anthropogenic) and regions alike (NCSS, 2002; Hartman et al., 2004). An example of this is the USDA Soil Taxonomy classification system that employs the concept of 'zonal' and 'azonal' soils. The absence of elements of specificity (i.e. the means of differentiating soils within and between taxa) within the existing classification system coupled with the scarcely understood properties of anthropogenic soils made soil identification a potentially contentious process. Such deficiencies in classification systems undoubtedly have hindered studies on anthropogenic soils and more so wide-spread recognition of these soils in scientific discussions and literature.

The development of an International Reference Base for Soil Classification (IRB) by the Food and Agricultural Organisation of the United Nations in the 1970s invigorated interest on the subject of anthropogenic soils, particularly on newly recognised soil groups (NCSS, 2002; WRB, 1998). The creation of an international framework for soil classification initially arose from problems with soil degradation and food production around the world, which became an

international concern that required harmonised soil information for effective problem solving and policy development. The problems were highlighted by the increased interdependence of countries for supply of various food and agricultural products. A comprehensive classification system that correlated and harmonised soil groups and definitions from different country-specific classification system was necessary to facilitate communication and understanding in soil science.

The development of the World Reference Base (WRB) classification system was greatly aided by the basis provided by soil maps such as Soil Map of the World Project which was also developed by the Food and Agricultural Organisation of the United Nations (FAO, 1971 – 1981), the Soil Map of Africa by D'Hoore, (1964) and the Soil Map of Europe, by Dudal and his team (Dudal et al., 1970). Later on, revisions to the previous versions of soil classification system (e.g. WRB, 1998, 2006, and 2014), and the introduction of new groups including the group technosols in 2006 by the World Reference Base remedied most operational issues detected in the previous classification scheme and introduced much clarity in distinguishing between the various forms of anthropogenic soils (i.e. anthrosols, technosols) which were absent in previous versions. The well-defined diagnostic horizons and features (differentiating criteria) allows for consistency in identification and description of soil by scientists from different backgrounds and regions, and with varying degree of experience. Other widely known classification systems such as the USDA Soil Taxonomy also saw revisions with increased consideration of anthropogenic soils in new editions as the system progressed (e.g; USDA Soil Taxonomy, 1975, 1983, 1990, 1998, 2003, etc., to the current edition in 2006). National soil classification systems were also developed in many countries and exist for specific domestic needs/use.

The adoption of WRB as the official reference soil nomenclature and soil classification for the European Commission, and acceptance by the West and Central African Soil Science

Association (WCASSA) as the preferred communication tool facilitated, to a degree, some harmony and a common technical terminology in exchange of soil information (e.g. in collaborative studies) between regions (ISRIC/IUSS/FAO, 2006). The same is true for the USDA Soil Taxonomy classification system after its endorsement by the International Union of Soil Sciences (IUSS) for international applications in 2014 (Hempel, 2014).

Soil classification has evolved into a sophisticated communication tool and remains an important resource in the discipline of soil science. The development of diagnostic parameters and quantitative definition of horizons and features is considered one of the greatest contributions to the subject in the last 50 years (NCSS, 2002). The growth and development in research on anthropogenic soils appreciated today is a result of the collective effort (past and current) of individual soil scientists, large groups of expert authors and organisational support provided by bodies such as; World Reference Base (WRB), German Pedological Society (AKS), Food and Agricultural Organisation of the United Nations (FAO), International Committee on Anthropogenic Soils (ICOMANTH), French Pedological Framework (Lehmann and Stahr, 2007).

The WRB and the other widely used classification system, USDA Soil Taxonomy, have made bold attempts to incorporate all currently known soils subject to human influence in their descriptions; but criticisms still remain on the absence of a single universal soil taxonomy system such as those for naming plant and animal species; a valid argument for consideration, for the future, that may yet provide more stability and unity within the discipline of soil science.

## 1.2 Urban Soils in Scotland

### *1.2.1 The Origin, Progression and Decline of Urban Soil in Scotland*

The disposal of waste and by-products of community living (domestic and industrial waste) is perhaps one of mankind's greatest problems, and still remains a current issue in various part of the world (Davidson et. al., 2006; Oram, 2011). The establishment of settlements, or any functional system or domain is almost always accompanied by waste production which must be disposed of. Previous studies that have investigated ancient settlements in cultural landscapes from around the world are in consensus on the system of early waste management practices which involved the use of refuse as fertiliser in agriculture (Macdonald, 1884; Hardy-Smith and Edwards, 2004; Golding and Davidson, 2005; Davidson et al., 2006; Herbert, 2009; Oram, 2011). Sources of waste materials have been identified as by-products from human habitation (faeces and urine, spoiled store products, household rubbish, domestic food-processing waste, cesspit contents and debris), residues from fire and hearths, stalled animals, slaughterhouses, metal-working, and other processing activities (Golding and Davidson, 2005; Golding et al., 2010; Oram, 2011).

The deepening of soil for agriculture, through the addition of organic rich materials, represents one of the oldest known management practices in the world. In Britain, urban waste composting for agriculture was well underway in the Middle Ages. Large scale use of urban waste as manure played an important role during the British agricultural revolution and earlier. In later years, scientific based improvements were made to processes of composting and field application to improve nutrient quality. In Scotland, until around late 1600s, and for smaller burghs until the nineteenth century, agriculture was as much a part of the socio-economic life of the community as was crafts and trade. The involvement of the townspeople in the process of primary food production contracted the boundaries between urban and rural lifestyle and activities. This societal inclination remained so after the establishment of Scottish

burghs in the twelfth century. Close association between burghs and the countryside meant that burgesses (townsmen) of diverse trade skills and other town-dwellers engaged directly in the cultivation of the surrounding arable and hinterlands, for the production of their dietary staples. Capitalization of soil assets was done primarily by utilising the most readily available natural fertiliser; their own waste products, composted in middens (Hall, 1997; Davidson et al., 2006; Oram, 2011).

Brothwell (1982), in his analysis of historical records on sources of waste, indicates that an estimated 182,000 litres of urine, 182,000 kilograms of solid waste, 8000 kilograms of ash from cooking and heating, and 36,000 kilograms of human faeces were produced annually per 100 households in pre-industrial societies. Urban waste management for use as fertilisers was by the fifteenth century a thriving trade. Domestic by-products (including faeces and urine), manufacturing (crafts, tanning) and processing (slaughter houses and fish gutting waste) were regarded as 'value commodity' and were highly sought after by both subsistence and commercial farmers. Parallels of this traditional soil management practice, the deposition and mixing of organic-rich materials on soil as manure; can be seen in the mainland European practice known as plaggen cultivation. This predominantly north-western European practice involved the enrichment of topsoil with organic rich material, such as turf, mud, peat, animal dung, and coarser materials such as beach sand (Guttmann et al., 2005).

By the late sixteenth century in Scotland, rising population, urban expansion and economic development led to a fall in the number of individuals directly involved in the production of their dietary staples. Shortages in cultivable urban and peri-urban land resource subsequently accelerated the process. Gradual severance of urban and rural activities in Scotland saw in the coming centuries rapid changes in the social and cultural attitudes towards urban waste from 'public good' to 'public ill' (Oram, 2011). The advancement in medical science in Britain in the late nineteenth century linked the use of refuse, especially human bodily waste, with food

contamination and spread of disease. The uncertainties associated with the health risk of consuming food grown in soils amended with refuse plus sanitary reforms taking place at the time provided a strong case for the discontinuation and devaluation of urban refuse (Goddard, 1996; Oram, 2011). Despite this fundamental cultural shift, urban waste and refuse nevertheless continued to be attributed significant economic value (cheaper source of soil amendments than foreign manure/fertiliser) and remained a popular soil improvement product amongst large-scale cultivators into the nineteenth century (Polprasert et al., 1982; Strauss, 1986; Davidson et al., 2006).

### 1.3 Urban Soils as Cultural Heritage

Anthropogenic activities such as the establishment of permanent settlements, agriculture and industry are known to cause substantial changes to the environment, particularly to soil. In medieval societies in Scotland, and in Britain in general, backlands or gardens held a different definition to modern day gardens. These spaces represented the hub of activity of their occupants where a range of undertakings including household tasks (e.g. cooking, food processing), industrial processing, livestock penning, urban horticulture and waste disposal were hosted. The precise nature and intensity of backland use differed between and within burghs, responding in space and time to economic change (Golding and Davidson, 2005; Oram, 2011). These past activities invariably leave behind traceable signatures in the soil in the form of artefacts, ecofacts and/or element enrichment which are often manifested in form of diagnostic horizons and features in soil profiles with time. These horizons and features can be defined in terms of their observable and measurable properties, which may be exploited to reveal past organisation and functions of cultural landscapes.

Many studies have employed a range of techniques in soil science such as micromorphology, image analysis, documentary sources, particle-size distribution, total phosphates, $\delta^{13}C$ values, $\delta^{15}$ N values, and lipid biomarkers (sitosterol, campesterol, and 5 β-stigmastanol) to investigate agrarian history (Bethell et al., 1994; Davidson and Carter, 1997; Evershed et al., 1997; Simpson, 1996; Simpson et al., 1998b; Bull et al., 1999b; Blume and Leinweber, 2004; Hubbe et al., 2007). These techniques are applied extensively in the studies of past infield management systems to understand the type of manuring episodes and cropping methods represented in early arable soils. For instance, in West Mainland Orkney, the identification of the presence of these biomarkers confirmed the utilisation of various types of manuring material, and the spatial variation in the intensity of application across the site (Simpson et al., 1999), and similarly in Pseira Island, Crete (Bull et al., 2001). The identification of specific signatures such as sitosterol, campesterol, and 5β-stigmastanol confirmed the use of composted turf and ruminant animal manure indicating a more plaggen-like system of management in Orkney whilst the presence of coprostanol indicates the use of human excrements for manuring. The results also confirmed the use of omnivorous animal manure (pig) indicated by the presence of coprostanol and bile acid, hyodeoxycholic acid, confirming pig farming in Orkney. Such studies have elucidated how soil modifications occur on farmed historical landscapes as well as providing supporting evidence to match and/or supplement documentary records (Simpson and Tveraabak, 1994; Evershed and Bethell, 1996; Simpson et al., 1998a; Bull et al., 1999a; Bull et al., 2001; Davidson et al., 2006).

The methodologies mentioned above, although popular in soil and archaeological science literatures, have not as yet been generally applied in the context of exploring the past organisational and occupational sequence in medieval urban communities. With careful application of these techniques in conjunction with magnetic susceptibility, electron microprobe analysis (EMPA) etc. on the stratigraphic units of a soil pedon, a chronological framework can be developed by examining the association of each unit with chemical

signatures and settlement feature (e.g. artefacts, ecofacts) of known cultural practices and age.

### *1.3.1 Soil Protection and Policy in Scotland*

A range of policy tools currently exist that protect against a variety of soil functions at both regional (Scotland) and continental (European) level. The increasing recognition of the central role of soil functions in our societies and the realisation that soil is a fragile and finite resource have prompted the enactment of several legislative measures against various element of degradation (pollution, erosion etc.) and devaluation (soil loss to development, over-exploitation etc.). In Scotland, following scoping studies by Adderley et al. (2004), the Scottish Soil Framework (SSF) developed in 2009 and The State of Scotland's Soil report published more recently in 2011 both represent active and on-going effort by the Scottish Government in the protection of soil resource (Dobbie et al., 2011). The Scottish Soil Framework is a tool that aims to promote the sustainable management and protection of soil. The Framework is set out in greater detail in Annex A of the report titled; *Policies for Soil Protection* (SSF, 2009).

The framework is a joint venture involving a range of public bodies such as the Scottish Natural Heritage (SNH), Scottish Environmental Protection Agency (SEPA), Historic Scotland (HS), and Forestry Commission Scotland (FCS) amongst others that together form the Soil Focus Group whose purpose is to advise the Scottish Government in the implementation of the Framework's directives. Whilst the Framework may appear robust in terms of the range of issues addressed, it does not provide adequate protection for historical/urban soils from potential loss of organic carbon from management change, and as potential historical 'archives'. Urban soils are often always overlooked in discussions on soil carbon management (conservation of organic matter) and almost never mentioned in landscape conservation. This

is echoed in previous and current editions of Soil Survey of Scotland maps, as well as in earlier classification systems as previously discussed, where soils in urban areas are not covered and, where attempts have been made to do so, they have been denoted by an ambiguous term 'brown soil'.

In the Scottish Soil Framework (2009), soil is defined as a medium within which artefacts and environmental evidence maybe embedded, but it is not in itself regarded as an archaeological resource. Historic urban soils are threatened from contemporary urban expansion largely due to their unappreciated value as historical archives and the ambiguity in the definition of what constitutes an archaeological soil in the Framework. Presently, soil record plays a marginal role in the designation of any locale as a site of archaeological interest. The designation of sites as an archaeological asset has no direct involvement with the soil within the area of interest and the basis of protection hinges upon the desire to preserve the below ground artefact, i.e. "preserve *in situ*". Anthrosols are relics of ancient settlements and should be viewed as more than simply a carrier vessel for archaeological deposits (artefacts). They are unique historical documents that contain detailed record evidence for past cultural practices. Urban soil deposits should therefore be preserved since they are, in many ways, partial artefacts of a past urban lifestyle that are seldom revealed in archaeology from structural vestiges.

### 1.4 Urban Soil as a Potential Carbon Store

Understanding the nature and quantity of the long-term carbon-store found in soils across Scotland is of key importance in developing policy tools pertinent to their management. In Scotland and around the world, carbon-rich urban and peri-urban soils have developed through many centuries of application of waste to soil of predominantly organic origin. The accumulation of these organic materials has resulted in soil deepening to depths of over one

metre in some locales (Hall, 1997; Davidson et al., 2006). Past investigations of the soils that have formed under these conditions have yet to consider in detail the fate of these soils in the environment with reference to their carbon stock and implications of management change. Recent publications on soil quality and vulnerability have identified climate change and loss of organic matter from soil as the most significant threats to Scottish soils; natural and anthropogenic (Scottish Soil Framework, 2009). To date, the composition and dynamics of the organic carbon in natural soils including peat are reasonably well understood but very little is known about anthropogenic deep soils despite their wide-distribution (Murray, 1982; Cachart, 2000; Carter, 2001; Bowler, 2004; Thomas et al., 2007). This is echoed in the UK inventory of terrestrial sinks and sources of carbon where references to carbon-rich and potentially carbon-rich soils are limited to remote upland soils with no mention of anthropogenic deep soils (Cannell et al., 1999).

Soil organic matter is an essential component of many soil functions and its dynamics has been the subject of focus of many studies (Sollins et al., 1996, Lutzow et al., 2006). Various mechanisms of stabilisation of soil organic matter in natural systems have been identified and studied due to their relevance in global C cycle and budgeting. Carbon storage and stability is broadly attributed to physical, chemical and biological processes in the soil that exert varying degrees of control at various stages of organic decomposition. Understanding the mechanisms of carbon stability across a range of soils, environment, and landscape enables the development of an appropriate management tool that seeks to increase carbon sequestration and maintain carbon storage capability in order to maintain the carbon sink potential of soils.

Carbon modelling has allowed the estimation of C reserve and flux in soils over periods of time. This has been used to study soil organic matter (SOM) dynamics and turnover rate in terrestrial systems (forest, grassland, arable) in different climatic scenarios and management systems however uncertainties on these estimations still exist due to inadequate data

availability and model assumptions therefore two questions can be asked. First, what are the dynamics of such a complex mixture of materials over time? Second, are we looking at a relatively balanced system given that these urban soils have been long exposed to elements of degradation? The UK national inventories of terrestrial carbon sources and sinks identified urbanisation (1.6 MtC $a^{-1}$) and cultivation (6.2 MtC $a^{-1}$), particularly of carbon-rich soils, as a source of increased atmospheric carbon compound concentration from the loss of soil organic matter. However there is a large uncertainty in the quantity and rate of soil carbon loss due to data deficiencies (organic matter content, carbon composition, rate of changes in soil carbon, land use area etc.) which results in potential error of about ± 50% on estimated values (Cannell et al., 1999). The in-depth understanding of the quantity and composition of the organic matter and the processes taking place are of vital importance in accurately accounting for terrestrial carbon reserve, predicting future behaviour of such terrestrial sinks, and thus their effects on soil-atmosphere interaction on future concentrations of atmospheric $CO_2$.

### 1.5 Global Green-House Gas Emissions and Climate Change

The ever increasing potential effect of global warming on weather patterns has necessitated the development of mitigation measures against its impact in the environment. This nature of activity is observed at many levels (governmental and non-governmental organisations, individuals) and across many countries around the world. The atmosphere contains around 380 ppm (parts per million) of carbon dioxide which, on the one hand, helps to keep the planet 33°C warm, essential for life on Earth, and on the other hand, a greenhouse gas (GHG) which causes the warming effect currently being experienced. Inclusive of this inventory of gases (GHG) are five others which are identified under the Kyoto Protocol as methane ($CH_4$), nitrous oxide ($N_2O$), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride ($SF_6$) (Forestry Commission, 2013; United Nations, 1998). One of several

collective actions taken by world governments, including the European Union, in tackling emissions is the agreement reached in the Kyoto Protocol which commits and binds all parties involved towards overall emission reductions by at least 5% from their respective 1990 levels in the commitment period 2008 to 2012 (United Nations, 1998; UNFCCC, 2008).

Around 11% of greenhouse gases emitted globally per year come from within the European Union. However legislation enacted at European level and by individual member states at national level has seen reductions in GHG emissions to comply with its Kyoto target and on-course to achieving the Commissions' unilateral emission reduction target of 20% below 1990 levels in the year 2020 (European Commission, 2012). In Britain, the Climate Change Act 2008 and Carbon Budgets requires that greenhouse gas emissions are reduced by at least 80% of 1990 emission level by 2050 (the National Archives; DECC, 2012). Although this Act represents the primary piece of climate change legislation in England alone, powers to implement measures to deliver on GHGs emission reduction across the country are presently devolved to governments in the individual states (the Scottish Parliament, the National Assembly for Wales, and the Northern Ireland Assembly) that together form the United Kingdom.

These administrations have to develop national climate change legislation, strategy, framework and targets commensurate with the overall 2050 emissions target of the UK. The chart below shows progress in the context of some of the UK's targets.

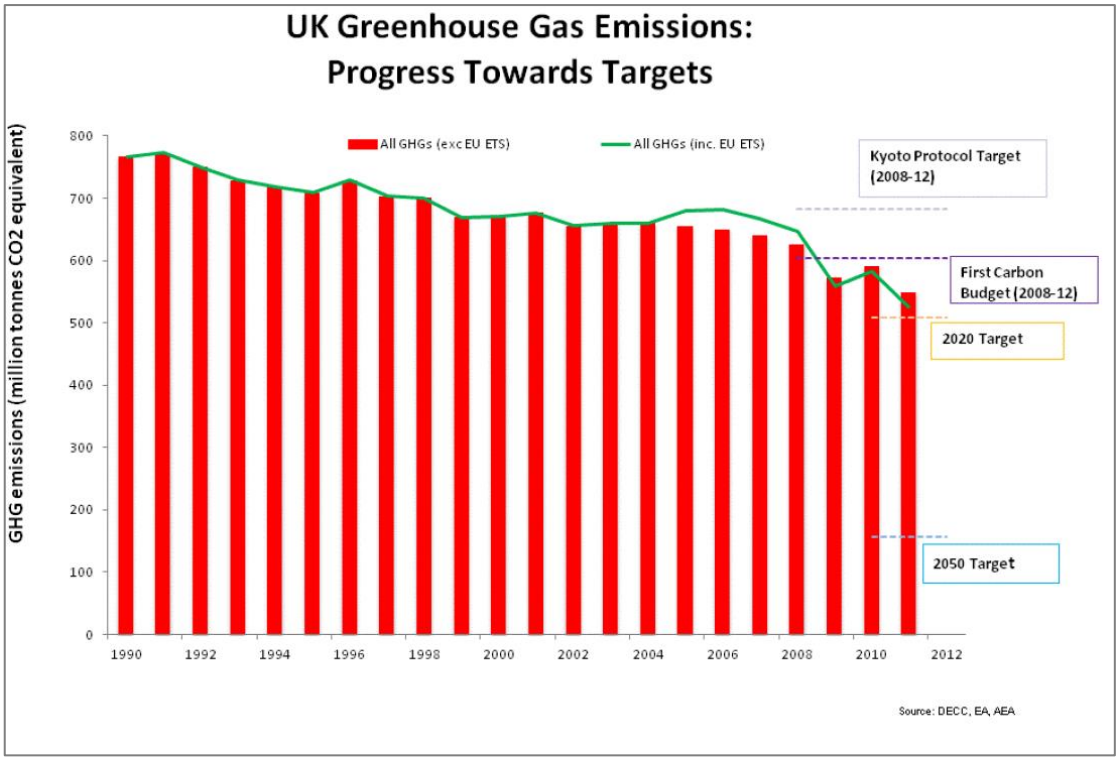



Fig. 1.2. UK greenhouse gas emissions progress towards the Kyoto Protocol target rate (Source: DECC, EA, and AEA)

In Scotland, the enactment of the Climate Change (Scotland) Act 2009 helps to provide a strong legislative platform for the enforcement of climate change duties on public bodies (the Scottish Government, 2009; the National Archives). Amongst several subsidiary policy tools developed to aid the implementation of the Act is the Scottish Soil Framework (SSF). The framework, developed by the Scottish Government in conjunction with the stakeholders in the Soil Focus Group, recognises contemporary pressures on soils particularly from climate change, as both a potential source and sink of carbon.

*1.5.1 GHGs Emission Sink Alternatives*

Soil is a major sink for carbon, as the global inventory of soil organic carbon shows it contains about 74% of the organic carbon in terrestrial ecosystems, hence an essential element in determining $C0_2$ flux in the atmosphere (Post and Kwon, 2000; Liu et al., 2009). Mainstream global climate change mitigation strategies involve the implementation of a range of measures with varying degrees of efficiency and uncertainties such as the forest biomass sink also known as woodland management, renewables (solar, wind, tidal turbines) and nuclear energy, and deep geological reservoirs of carbon. In any case, any successful strategy for alleviating climate change effects must create a 'carbon negative' or at the very least a 'carbon neutral' environment which would require the removal of more carbon dioxide from the atmosphere than current emission levels or equivalent. An accomplishment of this scale would require the involvement of a major terrestrial sink such as soil and the concerted action of other viable sink mechanisms.

Recently, the concept that the rapid warming is expected to increase plant growth in the Arctic, and result in gradual colonisation of the tundra by trees, which may help offset atmospheric $C0_2$ rise is being scrutinized. Models predict that enhanced carbon (C) storage in plant biomass may reduce rising temperatures, however, in some Arctic ecosystems, high plant productivity is associated with rapid carbon turnover and low storage of soil C; hence as plant growth increases, soil C may be lost through enhanced decomposition. A recent study by Hartley et al. (2012) in northern Sweden shows that high plant activity during the middle of the growing season stimulates the decomposition of older soil organic matter, a response termed positive-priming. Therefore expanding treeline (increasing forest biomass) in higher latitudes may lead to a net release of carbon from soil and hence is counter-intuitive to the notion of carbon sequestration in plant biomass.

*1.5.2 Soil Carbon and Land Use Change*

Soils represent the most important long-term organic carbon reservoir in terrestrial ecosystems, as they contain more C than plant biomass and the atmosphere combined (Raich and Potter, 1995; Schimel, 1995; Post and Kwon, 2000; Tarnocai et al., 2009). This large carbon reservoir is not permanent but results from a dynamic equilibrium in the processes that control material input – sequestration – and output in the soil. Consequently, soil carbon stock is affected by activities such as changes in vegetation cover (forest/grassland to cropland), farming practices (deep ploughing etc.), soil erosion, and disturbances arising from other activities including construction (Post and Kwon, 2000; von Lützow and Kögel-Knabner, 2009; Janssens et al., 2010).

Land use change represents the single greatest threat to soil carbon sequestration. This is reflected in the reports from National inventories of the parties (Countries) to the UNFCCC where soil carbon sink and source are interlinked and considerably dependent on land use change (Cannell et al., 1999). Soil mismanagement, regardless of carbon content, inevitably leads to an increase in carbon mineralisation and its subsequent loss to the atmosphere. The Intergovernmental Panel on Climate Change (IPCC) estimates that 10-30% of the increase in carbon dioxide emissions is due to land-use changes particularly deforestation. Similarly, it has been estimated that since the 1800s, more than 60% of the world's soil carbon has been lost due to land use change, management and environmental degradation (Prentice et al., 2001; BSSS, 2012). Therefore, scientific uncertainty on any process governing or involved in the soil carbon cycle or turnover cannot be overlooked if soils are to be fully exploited for their capability as global terrestrial carbon sink.

*1.5.3 Carbon Stock of Scottish Soils*

The development of climate change mitigation strategy through soil carbon management is an active area of research in Scotland. As discussed above, the effective management of soil organic matter is essential in achieving soil carbon sink potential. Scottish soils hold an estimated 3000 Mt of carbon, with a considerable amount held in peatlands and wetlands (SNH, 2009). Previous work by Chapman et al. (2009) on the carbon stocks of peatlands in Scotland estimated a fixed carbon deposit of 1620 Mt, which represents 56% of the total carbon stock in all Scottish soils. Although Scotland represents one third of the UK landmass, its soils hold approximately 50% of the total UK soil carbon stock.

As alluded to, previous and current works by the Scottish Government and its agencies such as Scottish Natural Heritage (SNH) have engaged mainly in peatlands as they contain a significant amount of carbon stock relative to other soil types. Whilst this is relevant for the management of carbon-rich soils and their conservation, very little attention is paid to understanding the rate of carbon loss and the carbon store potential of other potentially carbon-rich soils such as historically-deepened urban soils. As has been established and is now common knowledge, variations in soil properties can influence organic matter or carbon store potential; therefore some soils, although present in relatively small area, may have high carbon content, while others may have less so but cover a large area. The quantitative assignment of predetermined indices to various soils according to their carbon sink or source potential is lacking but, when achieved, will help to identify vulnerable soil types with high carbon sink potential meriting conservation.

Increasing concerns regarding food security and mounting demand for food to be grown, both issues partially driven by climate change, could potentially increase the area of agricultural land in Scotland suitable for cultivation to support increased food production (Figure 1.3). However, an extension of areas suitable for agriculture could impinge on areas of high

conservation (SSSIs, SACs, SPAs,) and / or biodiversity value, and other areas of high soil carbon stock reserve (anthropogenic deep soils and peatlands). Increasing agricultural production could also result in increased GHG emissions resulting in a positive feedback to climate change. The latest Scottish Greenhouse Gas Inventory estimated that soil carbon stock changes in land converted to cropland emitted 6.6 Mt of $CO_2$ eq for 2006 while converting arable land to grassland in the same time period removed 2.8 Mt $CO_2$ eq. from the atmosphere. Specific land use changes can therefore help offset GHG emissions whilst others can exacerbate them. Additionally, pressures from increasing land acquirement for development presents a potential threat to land areas with high or potentially high organic carbon stock (Cannell et al., 1999).

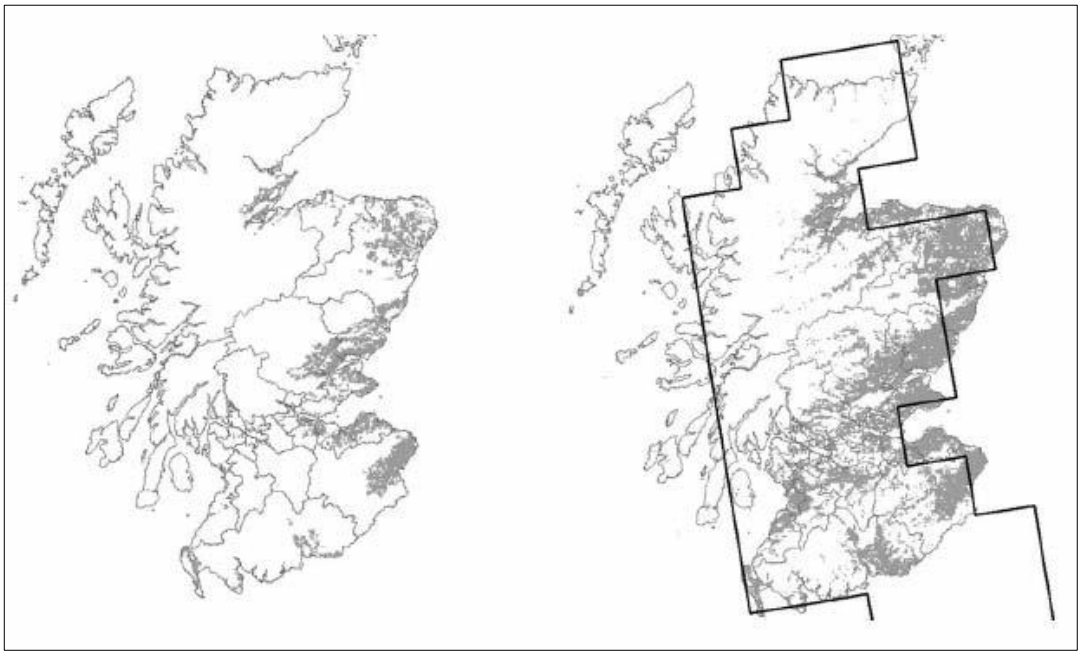


Fig. 1.3. Location of prime agricultural land (LCA classes 1, 2 and 3.1) a) current b) predicted under 2050's UKCIP02 Med-High Emissions (Macaulay Institute; Scottish Soil Framework, 2009)

Some of the initiatives of the Scottish Government and its agenicies in managing soil carbon include the intensification of the use of organic rich wastes (farm manures and slurries,

sewage sludge, composts and other non-agricultural wastes) on soils – a system in many ways analogous to waste management practices found from the medieval to early modern periods (11th – early 19th century). The Sewage Sludge Directive (86/278/ EEC) which is transposed into national legislation through the Sludge (Use in Agriculture) Regulations 1989 (as amended in 1990), complemented by a Code of Practice for Agricultural Use of Sewage Sludge 1996 seeks to regulate and encourage the use of sewage sludge and other organic wastes in agriculture. This practice is also advocated by Scottish Natural Heritage as a potential means of replenishment, burial, and therefore a sink for carbon in the soil. A paucity of data on the understandings of the long-term fate of these materials in the soil in terms of their resident period severely limits the attributed sustainability of implementing these measures as a long-term means of sequestering carbon in soils.

Climate change is a global affair that requires the synergistic approach of all parties (Governments and individuals) in order to combat its effects. Governments, in their national inventories, should aim to identify all anthropogenic (past and present), and natural disturbances that may be of potential source of carbon loss. Some of the mitigations suggested by Cannell et al. (1999) are the minimisation of urbanisation and expansion of forestry and cultivation into areas with high organic/carbon-rich soils, including the preservation of land areas that have been returned to semi-natural vegetation. The focus on reducing soil carbon emissions are warranted as they contain a significant portion of terrestrial carbon pool, and as well most vulnerable to disturbances however verification of sinks remains problematic. Evidently, policy tools to increase carbon sink potential and to reduce sources can be developed and implemented when their relative magnitudes can be determined.

## 1.6 Thesis Aim and Objectives

This introduction has sought to provide an overview of the importance of anthropogenic urban soils in past and contemporary settings as well as their anthropological and environmental significance within Scotland and for the wider research community. As discussed in preceding sections of this Chapter (*section 1.5.1 – 1.5.3*), soils are the largest carbon store in terrestrial environments. Soils also simultaneously represent a sink and source of carbon, and the direction of the flux between carbon in the atmosphere and carbon in soils rests upon the availability of suitable management tools that can operate in different soil and landuse types in order to increase the capacity of soil to sequester carbon.

As more research resources are directed towards understanding the processes that control and/or govern the dynamics of carbon in the various terrestrial systems, there are however, inaccuracies in the climate change model estimations due to uncertainties arising from inadequate data availability on soil properties (organic matter content, carbon composition, rate of changes in soil carbon, land use area etc.) across soil types (Cannell et al., 1999). Few studies have investigated the environmental significance of anthropogenic urban soils and their implications in terms of carbon store potential and management change given that large quantities of organic-rich materials were documented to have been deposited on soils within and around medieval urban environment for agriculture. Furthermore, as urban environment change in response to human development, investigation was extended to examine man's relationship with soil and the cultural significance of such soils as natural historical archives of human activity.

The aim of this thesis therefore is as follows:

1) To investigate the impacts and implication of historical soil management practices on soil organic matter storage and dynamics in anthropogenic urban soils. To address this, detailed biophysicochemical analysis of soil was undertaken to determine the following:

- The total organic carbon content of these soils (found within medieval urban areas) relative to the background content of the surrounding soil in order to recognise hotspots
- The composition of the soil organic matter by characterising them into their respective carbon species. This enables the relative recalcitrance of the organic matter to be known
- The various intricacies by way of stabilisation mechanism in operation and implications from management change and C dynamics

2) to examine the relationship between soil record of past human activity, as observed through soil geophysicochemical properties, and documentary accounts of past activities in a locale using soil-based evidence obtained from the integration of a range of field and laboratory methods, and ethnographic data. Accordingly it is hypothesised that differences in the landuse types, intensity of use, duration of exploitation etc., will be reflected in the occurrence, and/or variations in soil marker signatures such as elemental signature, magnetic susceptibility, organic matter content, soil pH, amongst others. The synthesis of these data may then be used to determine site organisation, functions, level of activity, of past cultural landscapes.

**CHAPTER 2**

# STUDY SITES

## 2.1 Site Selection

Study sites were determined based on various predefined criteria: a medieval urban settlement with limited contemporary urban disturbances, site in occupation for at least 300 years, a major market centre hosting a variety of activities, and dissimilar geographical location and geology between sites. St Andrew, Roxburgh and Elgin were initially selected in which to undertake this study. Elgin was eliminated from the list of sites after a preliminary visit to the site which involved soil test pit sampling and auger depth profiling confirmed the absence of deposits of urban-deep soils in the selected sample site (Cooper Park) in Elgin.

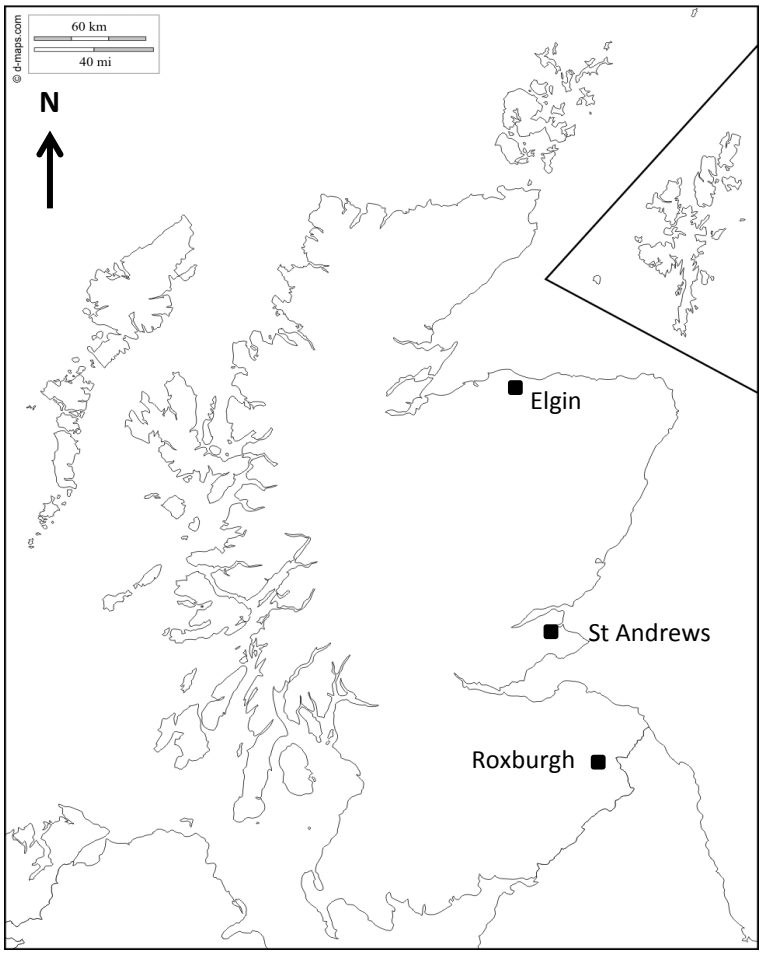



Fig. 2.1. Location of study sites across Scotland

St Andrews was especially chosen to be a reference site for the study. The suitability of St Andrew as a reference site is because it has preserved more of its medieval infrastructure (roads, buildings) and general layout than most other major Scottish settlements of the Middle Ages (Brooks and Whittington, 1977). It has many surviving medieval historical accounts and has also seen various archaeological works conducted, with each successive study providing more information into the database of the site's history (use, functionality etc.).

Unlike St Andrews, Roxburgh has very little surviving records due to its turbulent past from series fire incidents to war invasion. Little by way of surface traces of the burgh now remain and although the site is now a scheduled monument and unlikely to be further disturbed, previous studies and assessment there revealed that there has been some level of disturbance from cultivation since its abandonment (Martin and Oram, 2007). The soil type investigated at all the study sites can be classified as a Technic Hortic Anthrosol under the revised WRB soil classification system (WRB, 2006). Anthrosols are defined as soils that have formed from profound modification of natural soil horizon as a result of human activities. The additional prefix qualifier 'Technic' was added to reflect the variety of Hortic soil because a diagnostic feature of "deep urban soils" is the presence of mixed material derived from building, household and industrial wastes and debris (Rossiter, 2007).

*2.1.1 St Andrews*

St Andrews (56° 20′ 29.15″ N, 2° 47′ 53.84″ W) is an extant Scottish urban settlement with medieval origins. It is a small coastal town located on the east coast of Scotland, UK. St Andrews has a temperate maritime climate with annual precipitation at 690 mm, and annual average temperature range of between 5.1 and 12.5 °C (Met Office). The naturally occurring soil in the area is podzol formed mainly from coastal raised beach deposits (mainly coarse and fine sand, silts, and gravel, and clay) (Soil Survey of Scotland, 1965; Wilson et al., 1981). The

present-day land use around the town is arable and improved grassland (Land Cover of Scotland, 1988). Within the medieval urban areas of St Andrews, where urban wastes were once deposited, are modern day garden areas dominated by grass cover which represents the only source of organic matter input to the soil.

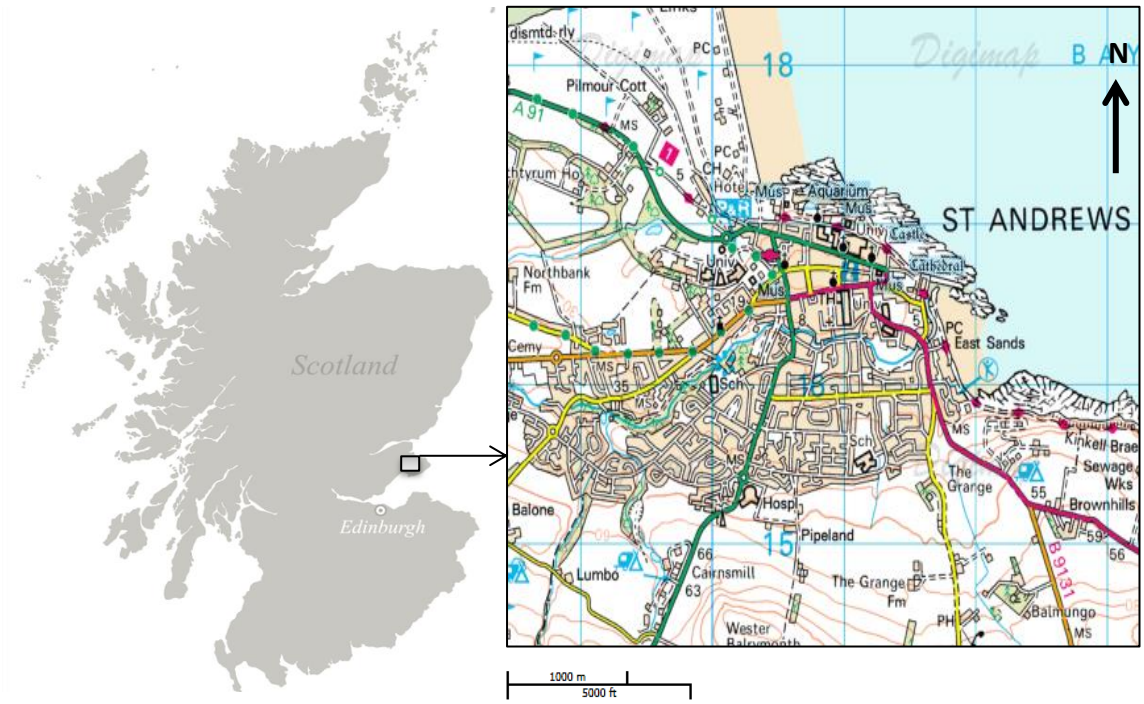



Fig. 2.2. Shows the location of St Andrews, Fife, Scotland [Digimap copyright]

According to Bishop Robert's foundation charter, the burgh of St Andrews was established in *circa* 1150 (Brooks and Whittington, 1977). St Andrews was a thriving medieval burgh which was a centre for a variety of functions, including ecclesiastical, educational and commercial functions. The burgh prospered due to the location of the shrine of the Apostle Andrew situated here, which was an international pilgrimage focus until the mid-sixteenth century. It was also the location of the cathedral of the senior Scottish bishop (and from 1472 archbishop). Its townsmen, or burgesses, were known to engage in a wide range of activities such as craftwork and trade, fishing was of note but farming was a more prevalent occupation.

Each burgess had exclusive possession of a large plot in the burgh on which to build their houses and workshops, the rear part of which was usually cultivated as vegetable garden, and they also had an equal share in the common arable and pasture land that lay outside the urban core (Oram, 2011). Although burgesses were primarily craftsmen and traders, they were also cultivators who grew their own dietary staples, mainly in the backlands of their own properties and on their 'rigs' in the burgh's common fields.

An important feature of burgess agriculture in St Andrews, and indeed in most other Scottish medieval towns, was the management of urban waste for use as manure. Documentary records of past land-use practice in St. Andrew from medieval to the early modern period (thirteenth to early nineteenth century) shows that high volume of organic waste materials were deposited on soils as ameliorates for horticultural and agricultural purposes (Macdonald, 1884; Murray, 1982; Clark, 1997; Hall 1997; Cachart, 2000; Carter, 2001; Bowler, 2004; Golding et. al., 2010; Oram, 2011). Although the use of urban waste as fertilizer continued until well into the nineteenth century in the hinterlands (Oram, 2011), its disuse within municipal areas began in the seventeenth century as new burgh regulations and urban expansion brought about changes in the cultural attitude of people towards waste from its perception as a valuable resource to a burden (Davidson et al., 2006; Oram, 2011).

*2.1.2 Roxburgh*

Roxburgh (55° 35' 54.59" N, 2° 26' 6.28" W) a now extinct royal burgh, is located south-west of the town of Kelso, an inland town situated in the Scottish borders to the south of Edinburgh. The study site lies on a fertile plain between the rivers Tweed and Teviot just before their confluence. The climate is temperate with an annual average temperature range of between 3.9 – 11.2 °C (Met Office). The soil mapped at Kelso is alluvium deposits in the Soil Survey of Scotland Map, with parent material derived from Lower Carboniferous sediments and basic

lavas, Upper Old Red Sandstones and Silurian greywackes. The present-day land use on the site is managed grassland.

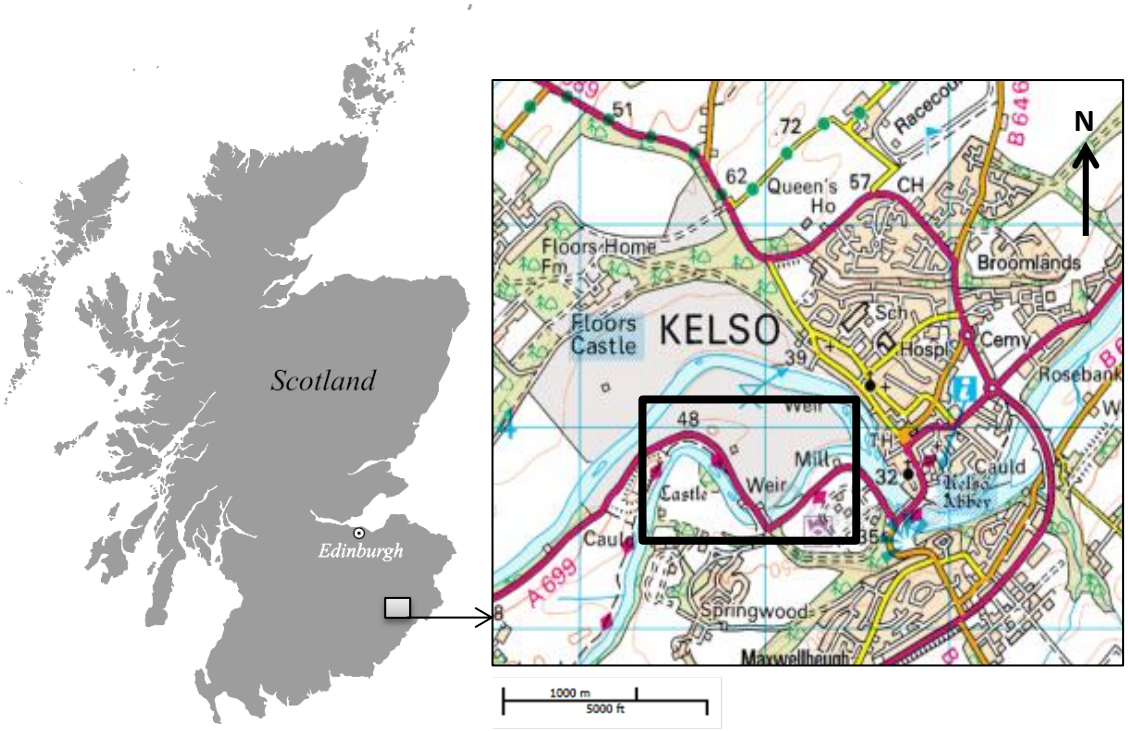



Fig. 2.3. Shows the location of Roxburgh in the Scottish Borders (highlighted with a polygon) [Digimap copyright]

The urban development that occurred at the royal burgh of Roxburgh (the new burgh) was comparatively short-lived due to the repeated devastation of the burgh in Anglo-Scottish conflicts after 1296 and the relocation of trade and administrative functions to more secure locations. First mentioned in the early 12th Century (ca. 1113) in the foundation charter of Selkirk Abbey, granted by the then Earl David (later King David I), the town flourished between the 12th to late 14th century AD, but went into rapid and terminal decline in early 15th century (Martin and Oram 2007). By the mid-15th century it had been abandoned and the site has been relatively undisturbed since this abandonment. Roxburgh in its prime was a thriving urban settlement with many trades, and the focal point for regional economic activity and international trade, the latter via the port of Berwick. Situated between the rivers Tweed and

Teviot, Roxburgh was well served with a riverine transportation route to the port as well as a natural defensive barrier in times of war.

Roxburgh had steadily prospered, since its establishment, throughout its period of activity, expanding its influence and status as a commercial hub of great importance across the region of Southern Upland Scotland. Roxburgh's development was however disrupted on three independent occasions by fire incidents in 1207, 1216 and 1244. Much structural damage to the infrastructure was caused, due to the susceptibility of the readily used construction material of the buildings (wood) to fire. The burgh regenerated and continued to thrive thereafter. Subsequent years saw increase in the frequency of raids, which together with the burgh's role in Anglo-Scottish conflict helped put Roxburgh firmly on the road to decline until its eventual abandonment in the early 15$^{th}$ century

*2.1.3 Elgin (Cooper Park) Site*

Elgin is a small coastal town located on the bank of the river Lossie in the North of Scotland. It was made a royal burgh by King David l of Scotland in 12$^{th}$ century, and was a thriving town with a defensive castle, and a Cathedral to the east of the town. The medieval street plan of Elgin is relatively well preserved; a main street widening into old cobbled market place, now known as the Plainstones, series to parallel streets linkages to the main street by narrow wynds and pends. A few buildings still retain the arched facades of early eighteenth century Elgin.

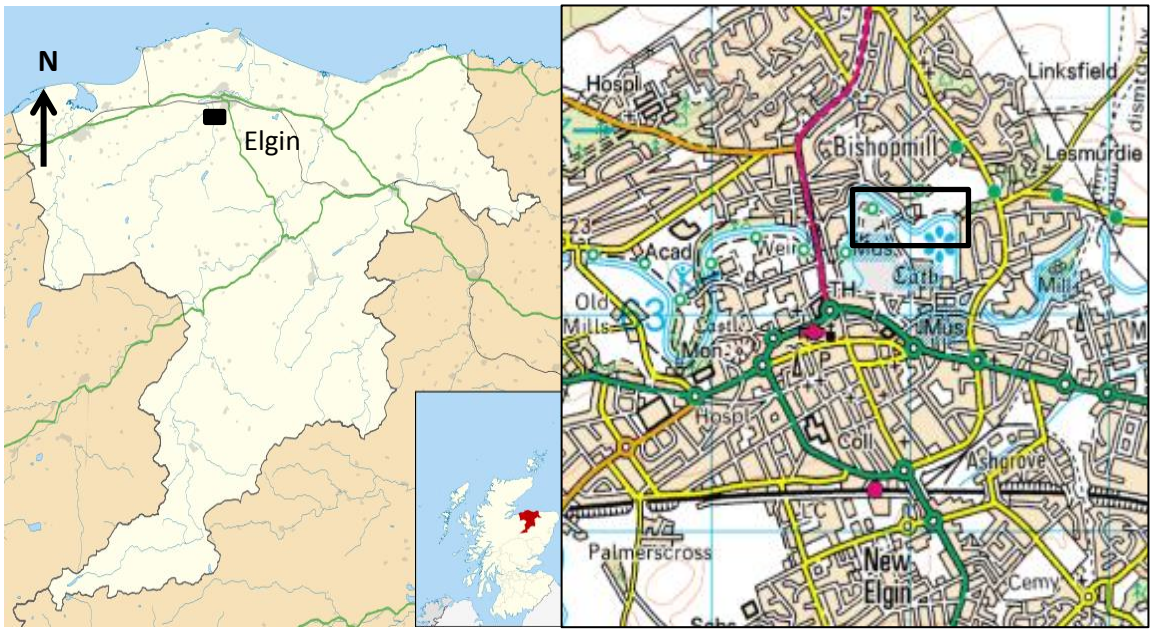



Fig. 2.4. Location of Moray council region in Scotland and of Elgin (Left), and Cooper Park (right) [highlighted with a polygon]

As alluded to in the preceding section, preliminary assessment of the study site (Cooper Park) confirmed the absence of urban soil deposits and therefore was excluded from the project (*see section 3.3.1* for more details)

**CHAPTER 3**

# METHODOLOGY

Undertaking this study required the use of a range of methodological tools available for both *in situ* and *ex situ* analysis. This chapter outlines these methods, and discusses their appropriateness in answering specific research questions in the study. The thesis explores the historical legacy of anthropogenic soils from medieval urban communities in Scotland principally through the physico-biochemical analysis of soil materials. The establishment of a robust three-way linkage between the scientific understanding of soil processes and their relationship to past land management practices and the more contemporary issue of climate change is vitally important to the development of policy tools relevant to the management of such soils or landscape. This project represents the first in Scotland to conduct a detailed physio-biochemical analysis of anthropogenic soils and by doing so developed a database upon which future work can be built. Except where otherwise stated, all soil samples collected were air-dried and sieved through a 2 mm aperture prior to laboratory analysis.

## 3.1 Field Methods

### *3.1.1 Soil Survey and Sampling*

#### *3.1.1.1 Auger Sampling (St Andrews)*

Auger samples were collected from four locations spread within the study area using the Edelman auger. The study area was sectioned into four sampling sites so that spatial variations in the intensity and extent of soil modification could be obtained. The physical expansion of St Andrews town was progressive and occurred in stages (Brooks and Whittington, 1977) therefore it could be expected that areas that were inhabited earliest will exhibit greater site use intensity (enhanced P concentrations, greater organic matter content), with lower use

intensity and modification as one moves further away from the burgh. Samples from site 1 (STM), 2 (SST), and 3 (SSJG) were collected at various points within the medieval town area, while those from site 4 (BGr) were collected at the outer fringes of the settlement, about two kilometres from the present town centre. Auger samples were taken at randomised locations in 10 and 20 cm depth increments until the auger could go no further. Within each site, between two to six points were sampled depending on the area of the site. Samples were labelled as follows: STM1 – 4, SST1 & 2, SSJG1 – 6, and BGr1 & 2. A total of 61 auger profile samples were collected and bagged for *ex situ* lab analysis. Samples were collected at similar depth where possible to aid comparison during data analysis.

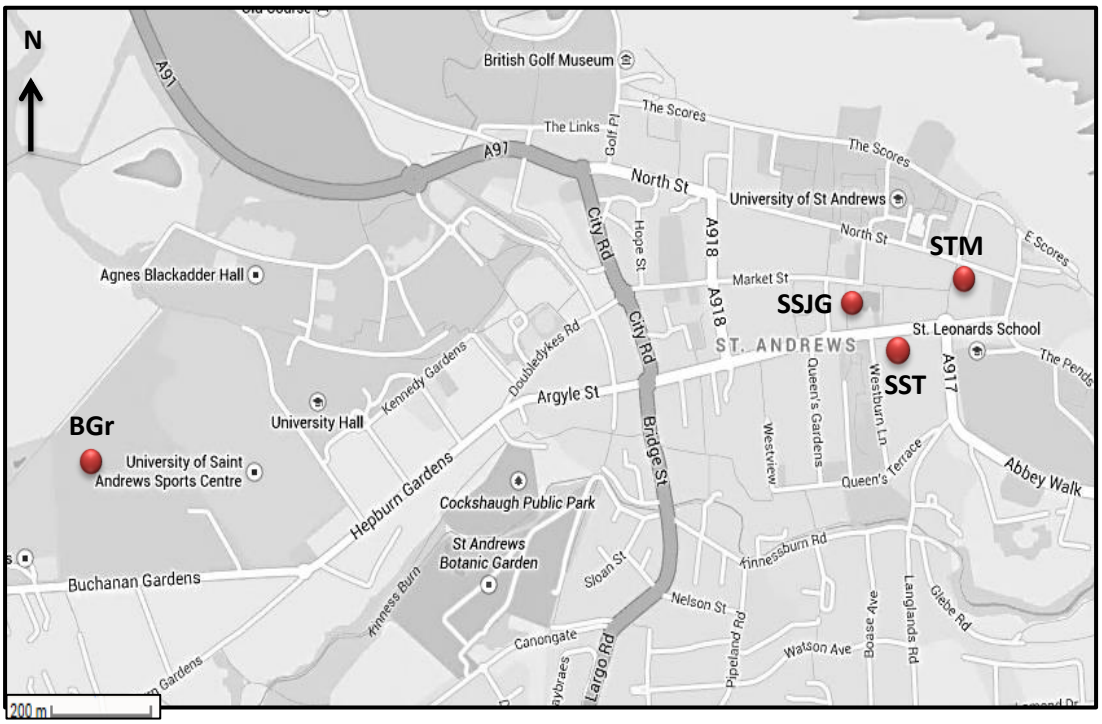



Fig. 3.1. Shows sample sites within St Andrews indicated on the map with red circles

Although records indicate that the area of site 4 (BGr) was located outside the town development boundary (Brooks and Whittington, 1977) which may have served as hinterland or fields during this period and therefore altered, it was nevertheless sampled for reference as it is presumed to comprise of more natural material (moderately modified) relative to soils

within the town area, as well as an effort to maintain uniformity in the geology and soil type for the study. All samples sites are located on areas of similar parent material and soil type.

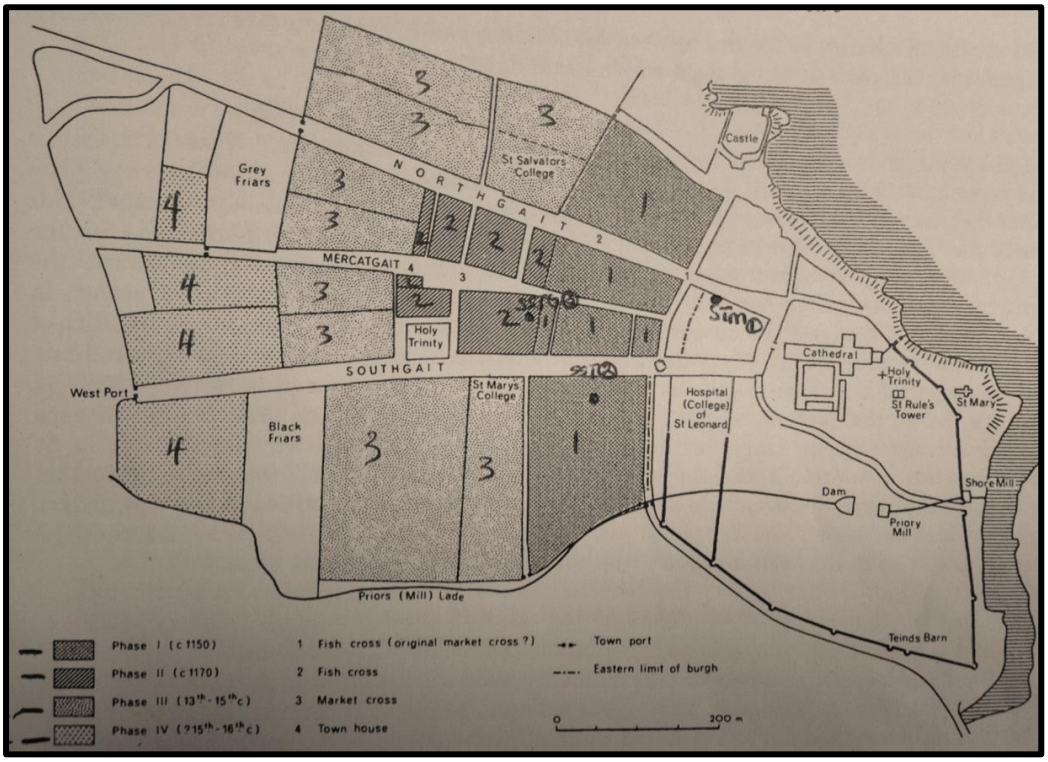



Fig. 3.2. Planning and growth phases of Medieval St Andrews; number 1 to 4, and corresponding shading represent the four stages of development of the burgh. Phase 1 (c. 1150); Phase 2 (c.1170); Phase 3 ($13^{th}$ – $15^{th}$ c); Phase 4 (~ $15^{th}$ – $16^{th}$ c) [map taken from Brooks and Whittington, 1977]

*3.1.1.2 Auger Sampling (Roxburgh)*

Auger samples were collected in the Friars Haugh area of the site. Transect sampling was deemed the most suitable sampling technique applicable from the view of the subject of the research study and due to the large size of the study area. Auger samples were obtained along a 300 m transect running east-west from trench 3 in the east to the defence works at the western end of the medieval settlement. Sample points were set at a regular 10 metre interval. A total of 82 samples were collected from 30 points (S1 to S30) along the 300 m

transect. Auger samples were taken at 20 cm depth increments until the auger could go no further. The transect line was purposefully positioned to run through what was putatively identified as the location of the medieval settlement's core area to attempt to capture and/or identify space use or divisions across the landscape.


Fig. 3.3. Shows location of trench 3 and the transect line running across the site (map from GSB prospection, 2004)

*3.1.2 Soil Pit Sampling*

*3.1.2.1 St Andrews*

A soil test pit was dug on 3 sites (STM-P, SSJG-P, and BGr-P). Soil pits were dug to a maximum of 1 m or until the topsoil could be clearly distinguished from underlying horizons in the case of site 4 (BGr-P). Field sketches were made at each location together with soil profile description following Hodgson (1974) and Schoeneberger et al. (2012) and are presented in Table 3.1 for the respective sites. Soil texture assessment (hand textured) and colour (Munsell Color, 2000) was also determined. A series of Kubiëna tins (8 cm high x 6 cm wide x 5 cm deep) were used to sample identifiable stratigraphic units from the respective soil pits for micromorphological analysis (Adderley et al. 2010). Undisturbed soil samples were collected from various depths along the profile corresponding to the profile stratigraphy identified. Bulk soil samples were also collected from positions coincident to where the Kubiëna tins were inserted. A total of 13 Kubiëna tin samples and associated bulk samples were collected. All samples were collected in dry weather conditions. Optically stimulated luminescence (OSL) samples of each profile's stratigraphy was also undertaken, and *in situ* magnetic susceptibility measurements of the exposed profile were made using a Bartington MS2F surface point probe at 10 cm vertical intervals.

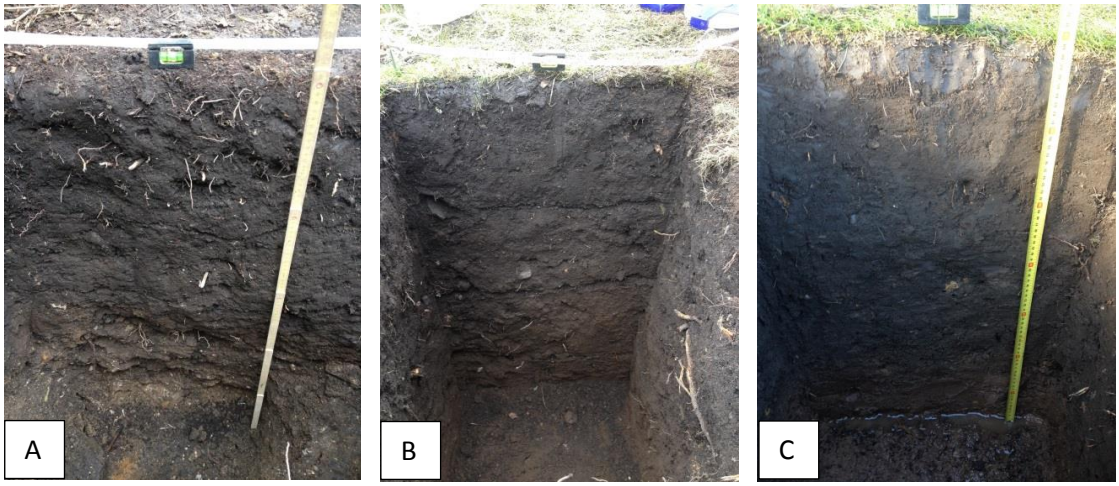



Fig. 3.4. Photographs of soil pit profile in: **a**) STM site; **b**) SSJG site; **c**) BGr site

Table 3.1. Profile description of soil pits at sample sites in St Andrews

| STM Profile | SSJG Profile | BGr Profile |
|---|---|---|
| **P001** 0–20 cm Ap1: Black (10YR 2/1) silty sandy loam with moderately developed coarse granular structure. Slightly gritty, with many fine and medium root penetration. Contains charcoal fragments. | 0–22 cm Ap1: Black (7.5YR 2.5/1) silty sandy loam with moderately developed medium granular structure. Contains many fine, fewer medium, and very few coarse root. Very slightly stony (2-6 mm), with small charcoal fragments. | 0–16 cm Ap1: Black (7.5YR 3/1) silty clay loam with fine granular structure and abundant fine roots. Very slightly stony (2-6mm). Moderately friable and contains charcoal fragments (1-10 mm). No artefact. |
| **P002** 20–40 cm Apu2: Very dark brown (10YR 2/2) sandy loam with medium granular structure. Moderately gritty with root penetration. 2% very small stones (2-6mm). Contains artefacts (pottery), ecofacts (bone and shells), and charcoal fragments. | 22–50 cm Apu2: Very dark gray (7.5YR 3/1) sandy loam with moderately developed medium granular structure. Contains few fine, and very few medium and coarse root. Slight stony (2-6 cm), with small charcoal fragments. | 16–37 cm Ap2: Very dark brown (10YR 2/2) silty clay loam with fine granular structure and medium roots. Very slightly stony (2-6mm). Moderately friable and contains charcoal fragments (1-10 mm). No artefact |
| **P003** 40–57 cm Apu3: Dark reddish gray (2.5YR 3/1) sandy loam with weakly developed coarse platy structure. Very few roots, with small stones (6 mm – 2 cm). Contains small Charcoal fragments. | 50–85 cm Apu3: Very dark grayish brown (10YR 3/2) sandy clay loam with weakly developed medium granular structure, and contains few medium roots. Moderately stony (2-6 cm), with small charcoal fragments. | 37–52 cm Ap3: Dark brown (7.5YR 3/2) silty clay loam with fine granular structure and very few roots. Very slightly stony (2-6mm). Moderately firm and contains charcoal fragments (1-10 mm). No artefact. |
| **P004** 57–78 cm Ap4: Dark reddish gray (2.5YR 3/1) sandy loam with weakly developed very coarse platy structure. No roots, with medium stones (2 – 6 cm). | 85–100 cm A: Dark brown (10YR 3/3) sandy clay with weakly developed granular structure. Contains no root. Moderately stony (2-6 cm), with small charcoal fragments. | 52–70 cm B: Reddish brown (5YR 4/4) clay. Apedal. Contains no root and stones. Very firm, with no charcoal fragments. No artefact. |
| **P005** 78–100 cm Bw: Light red (2.5YR 7/6) sandy clay with no roots. Contains large subangular stones (6-20 cm) | | |

Apu = (Mineral; organic matter (humus) accumulation, cultivated or with artificial disturbance, and presence of human-manufactured materials/artefacts.

*3.1.2.2 Roxbugh*

A soil pit – Trench 3 (RT3-P) of the Time Team's archaeological excavation work from 2003 – in the Friars Haugh area was re-excavated in 2013. Ground identification of Trench 3 was undertaken using a combination of measurements from site survey and from photographs taken during the initial excavation by the contractors working for a Channel 4 Time Team television production in 2003. In April 2013, a test trench (Figure 3.5; Trench A), measuring 2 m by 1m was dug by hand to a depth of 0.30 m onto undisturbed archaeology (stone floor or wall). The trench was backfilled and re-turfed as it was too far north relative to the desired deep ditch feature seen in Trench 3 when excavated by Time Team. A second trench (Figure 3.5; Trench B), was dug which corresponded to the south western end of Time Team Trench 3 to a depth of 1.2m, above the ditch feature which re-exposed suitable profile wall to sample as illustrated in the original trench excavated to 1.15m depth as reported by Wessex Archaeology.

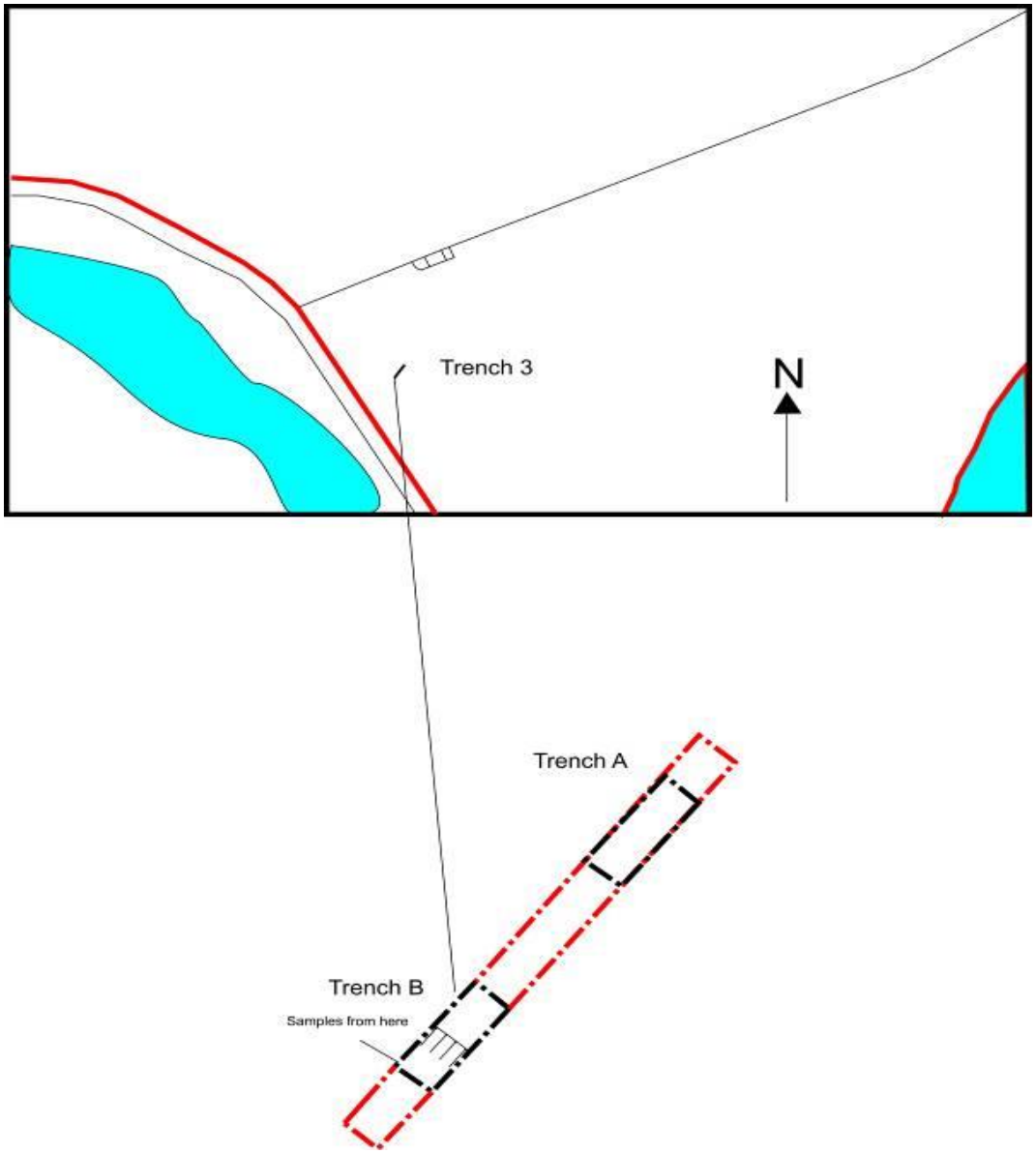



Fig. 3.5. Location of Trench 3 (scale 1:2500 cm), River Teviot in blue, Scheduled area boundary in red and expanded detail (scale 1:100 cm) showing re-excavated Trenches A and B and location of samples.

Samples were collected on the west wall (east-facing) of Trench B. Two sets of *in situ* analyses (Magnetic susceptibility, optically stimulated luminescence (OSL)) were undertaken on the same exposed profile prior to sampling, including near infra-red (NIR) analysis. Undisturbed materials for soil micromorphology analyses were collected as described above. OSL sampling

involved the use of 25 cm X 2 cm diameter copper tubes driven into the exposed profile at 10 cm intervals (Sanderson and Murphy, 2010). A total of 5 Kubiëna tin samples and 12 OSL samples were collected.

Fig. 3.6. Shows fully excavated Trench B looking north west showing section to be sampled to right of scale (highlighted); ditch edge visibly pointed by blue arrow

The profile was recorded by photographs (e.g. Figure 3.6) and a profile sketch (Figure 3.7) indicating the respective positions of all samples taken and noting the position of any visible archaeological ecofacts and artefacts.

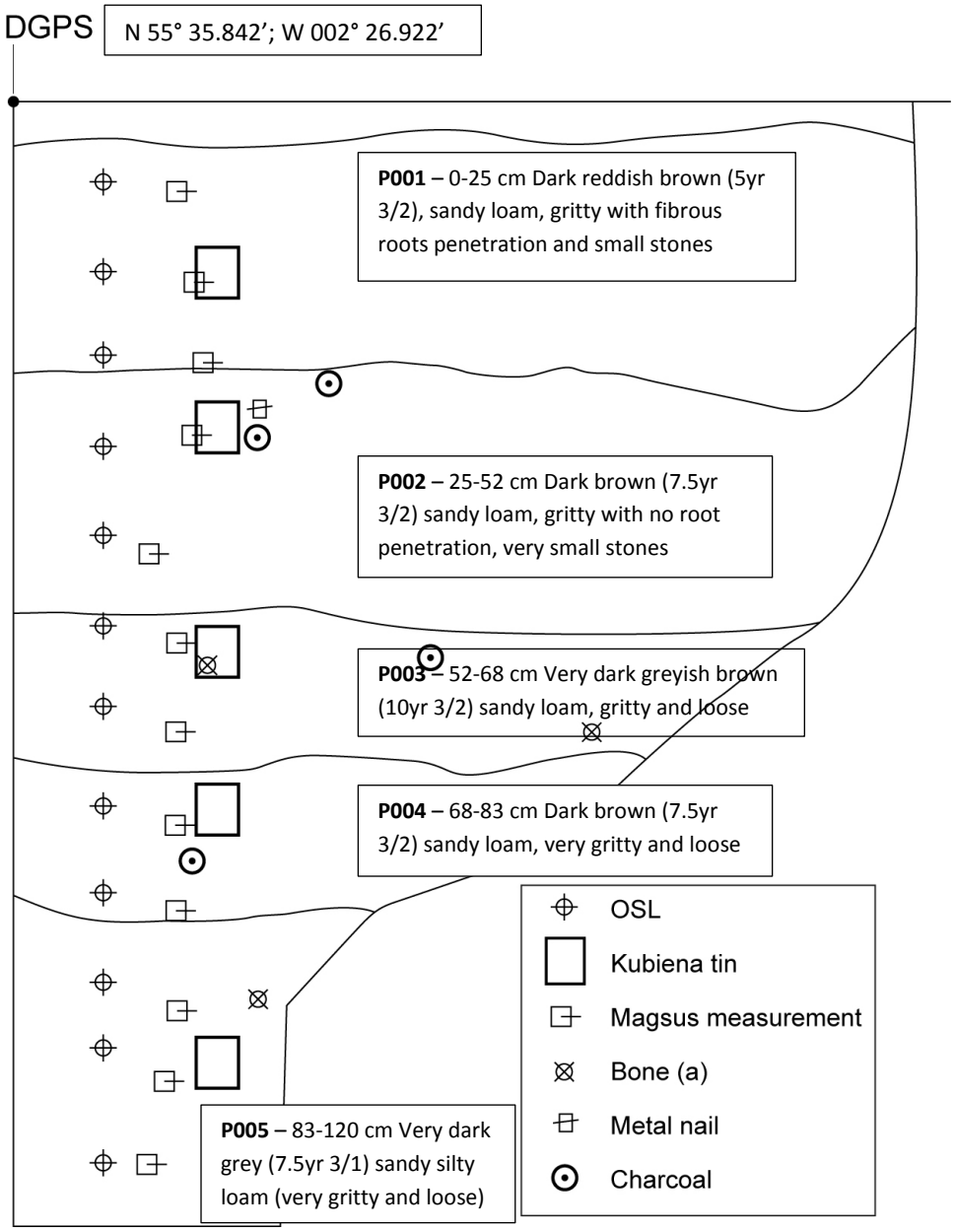



Fig. 3.7. Profile drawing of the sampled face of Trench 3 in Friars Haugh, Roxburgh

*3.1.3 Chronological Approach*

The chronological framework of this project is based upon the principle of superposition where in a sequence of sedimentary deposit, the layer of sediment is older than the one above it and younger than the one below (Grotzinger et al., 2007; Grotzinger and Jordan, 2010). In other words, younger materials are found closer to the surface while older materials are found farther from the surface at depth). Optically stimulated luminescence (OSL) was used to

explore the chronology and depositional history of the project sites. Briefly, portable OSL technique relies on the luminescence signal of mineral grains that may be partially bleached or reset to zero on exposure to light prior to deposition (Bokhorst et al., 2005; Lian and Roberts, 2006). Although this method can be influenced by factors such as local dose rates, initial bleaching, the inherited luminescence from prior materials, amongst others which are discussed in more detail in the following section, the depositional sequence, and hence the stratigraphic integrity of deposits can be determined which may be used as proxies for the age/period of deposit (Sanderson and Murphy, 2010; Munyikwa et al., 2012).

In urban environments, soils may not necessarily exhibit distinctive stratification due to the constant deposition and mixing of similar materials, however, sequences of deposits obtained from OSL analysis indicates the time-depth relationship of soil deposits relative to other sequence along a profile. This allows information such as the intensity of particular anthropogenic practice, and the consistency in the composition of materials deposited on soils to be obtained whether in agricultural or ordinary occupation deposits.

## 3.2 Analytical methods

This section gives a description of the methodological tools employed, both *in situ* and *ex situ*, during the course of the project, and discusses their application at various stages of this study in answering specific research question.

### *3.2.1 Solid-state $^{13}C$ CPMAS NMR Spectroscopy*

Nuclear magnetic resonance spectroscopy is a widely used technique for the study of chemical and structural composition of organic compounds and other chemical domains (Kögel-Knaber, 1997; Berns and Knicker, 2014; Preston, 2014). Despite this popularity with analytical and organic chemists, it is not so widely used to characterise naturally occurring or environmental

samples. However, as a non-invasive technique, its application in soil science enables the molecular-level characterisation of the chemical components of soil organic matter in bulk samples possible.

The development and application of NMR spectroscopy in the 1950s and 1960s led to major advancements in the understanding of organic matter composition and the processes, and mechanisms that may influence SOM decomposition. Prior to the discovery of nuclear magnetic resonance (NMR) spectroscopy, in the early 19$^{th}$ Century, humic acid (HA) fraction of soil organic matter were understood to consist of consolidated recalcitrant macro-geopolymers that have formed from the re-condensation a of previously degraded biopolymers (monomers) but current concepts achieved through NMR spectroscopy recognises the existence of partly degraded biopolymers due to the effect of physical and chemical stabilisation mechanisms (Berns and Knicker, 2014; Preston, 2014). Additionally, the development of various side-techniques such as magic-angle spinning (MAS), high-power decoupling, and cross polarization (CP) in NMR analysis has enhanced instrument sensitivity and quantitation; both of which have greatly facilitated the application of the technique in the SOM studies (Preston, 1996; Preston, 2014).


Fig. 3.8. A Varian Unity INOVA 7.05 T spectrometer

*3.2.1.1 Nuclear Magnetic Resonance (NMR) Technique*

*3.2.1.1.1 What is NMR?*

Nuclear magnetic resonance (NMR) spectroscopy measures the magnetic properties of nuclear spins of an atomic isotope. NMR relies on the interaction of the nuclei of atomic isotopes with an external magnetic field ($\mathbf{B}_0$). The nuclei of many elemental isotopes have a characteristic spin (**I**) which differs depending on the nuclei. Some nuclei have integral spins (**I** = 1, 2, 3, etc.), others may have fractional spins (**I** = 1/2, 3/2, 5/2) or no spin (**I** = 0). The most suitable isotopes for NMR spectroscopy are those nuclei which have I = ½ which includes $^{1}H$, $^{13}C$, $^{31}P$, $^{15}N$, $^{19}F$ etc.

When a nucleus with a spin property of **I** = ½ is placed in a magnetic field ($\mathbf{B}_0$), the nuclei may exhibit two spin states; + ½ or low energy state, and – ½ or high energy state. The low energy spin state (+ ½) is aligned with the external magnetic field while the high energy (- ½) state is

opposed to the applied external magnetic field (see Figure 3.9). The differences in energy between the two spin states is dependent on the strength of the external magnetic field therefore, on application of a radio frequency (rf) that matches the differences in the spin state of a specific group of nuclei, low energy state nuclei absorbs energy sufficient to cause excitation to the high energy spin state in much the same way an X-ray beam causes changes in energy state in the electrons of an atom.

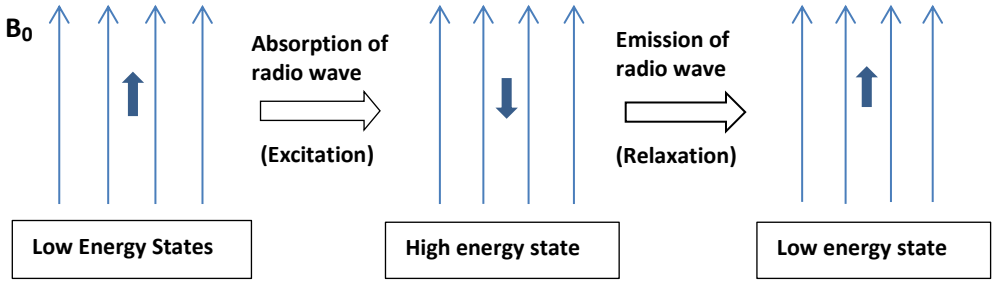



Fig. 3.9. Shows the changes in the state of nucleus (excitation and relaxation) on exposure to radio waves ($B_0$ – thin blue lines indicate direction of external magnetic field)

Receivers and amplifiers mounted on the equipment collect and record the energy absorbed and released as the nucleus relaxes back to a low energy state (Figure 3.10). These signals are subsequently processed to produce an NMR spectrum of the sample.

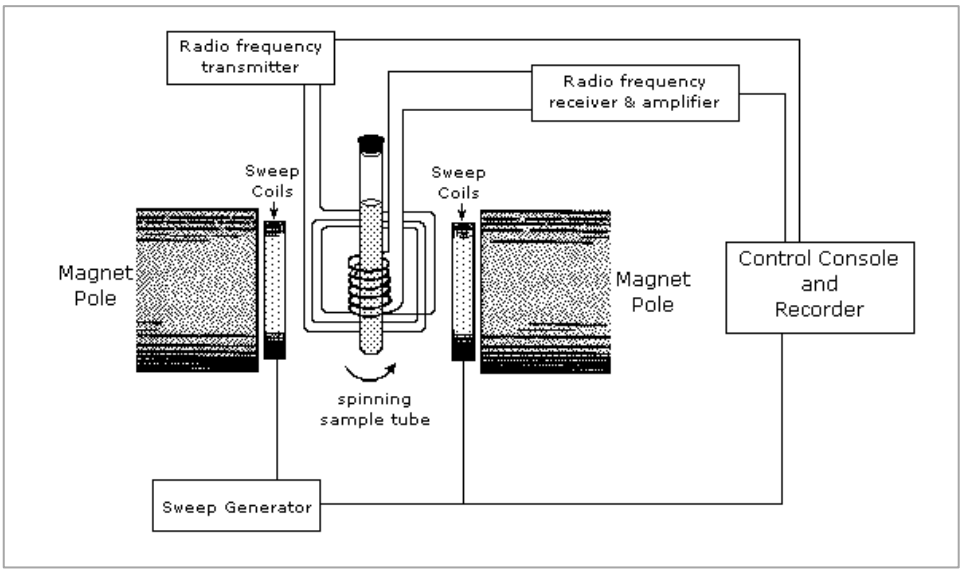



Fig. 3.10. A simplified diagram of the layout of an NMR spectrometer

*3.2.1.2 NMR Application*

Soil organic matter can be studied using a variety of spectroscopic (fluorescence spectroscopy, Infrared spectroscopy, X-ray spectroscopy, Nuclear magnetic resonance spectroscopy, mass spectroscopy) and wet-chemical techniques (e.g. acid hydrolysis). The progressive advancement and enhancement of these techniques, particularly spectroscopic techniques, has seen versatility increased in the number of applications allowing studies of SOM to be extended beyond molecular characterisation to exploring structural properties, in various medium; solids, intermediate physical states, solutions, and gaseous states (Preston, 1996; Bencze et al., 2007). Amongst these spectroscopic techniques, synchrotron radiation-based X-ray absorption spectroscopy (XAS) and its derivatives (XANES, NEXAFS, EXAFS), and nuclear magnetic resonance (NMR) spectroscopy are strongly emerging as the premier tool for investigating the chemical architecture, molecular properties, and functionalities of a range of substances including SOM. The selective advantage of both techniques is the high accuracy and resolution data that can be obtained, and when coupled, probing of local structural environments in molecules in various matrices (e.g. active, inactive, metabolites).

NMR spectroscopy can be performed in both liquid and solid state but what method is applied is dependent upon the nature of the material being analysed and the subject of the enquiry. An advantage of solid-state $^{13}C$ NMR over liquid-state, and wet-chemical techniques in SOM analysis is the ability to analyse insoluble samples. This is of particular importance since much of the macromolecular organic materials present in soil and sediment are insoluble, hence characterisation via liquid-state and wet-chemical methods is limited to only the soluble fractions of the sample being examined (Schmidt et al., 1997). The cross-polarisation magic-angle spinning (CPMAS) technique in NMR spectroscopy allows for a considerable signal enhancement during investigation of solid samples at natural $^{13}C$ abundance due to the cross-polarisation between $^{1}H$ and the dilute $^{13}C$ spins (Preston, 2014). The MAS technique is

essential to compensate for the chemical-shift anisotropy of solid samples (Wilson, 1987; Kögel-Knaber, 1997). Below is an example solid-state CP-MAS NMR spectrum of soil organic matter.

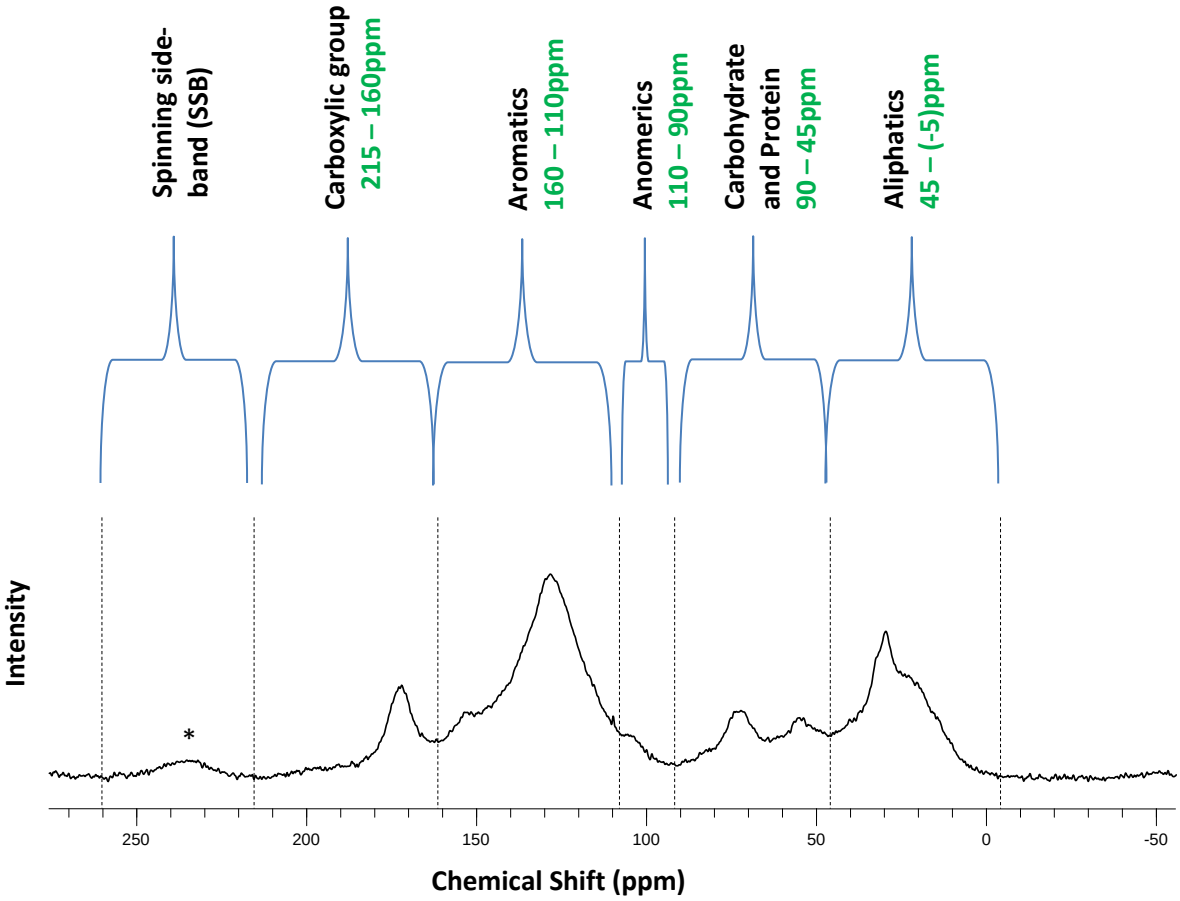



Fig. 3.11. A simplified representation of a typical NMR spectrum of SOM showing various chemical shift regions

The locations of various resonance signals on an NMR spectrum are dependent on the external magnetic field strength and radio wave frequencies; these differ between instruments. Therefore the location of the resonance signals in a spectrum is reported relative to a known reference signal using a standard compound. Tetramethylsilane, $(CH_3)_4Si$, or TMS for short, has become the reference compound of choice because it is relatively chemically unreactive and

hence does not interfere with the measurements. Additionally, to correct for frequency differences arising from the magnetic field dependence of the signal, the resonance signal frequencies are divided by the spectrometer frequency (Hz/MHz) and multiplied by one million. This result in uniformity in reporting resonance signals in an NMR spectrum; the chemical shift having units in parts-per-million (ppm) (Figure 3.11).

On the spectrum, distinct bands represent different chemical shifts which indicate specific organic compounds that are present in the sample. The resonance signal intensity of each chemical shift region generally indicates the proportion of a particular compound or groups in the sample although overlaps between regions can occur. The aliphatic region on the spectrum (45 – (-5) ppm) consist of compounds such as fatty acids, waxes, and resins which are derived from plant remains and microbial products. The (90 – 45 ppm) region represents O/N – substituted structures which contain materials that are easily decomposed by soil microbial community hence has a shorter turnover/residence period in the soil. Regularly fertilised soil such as arable soils will typically display high resonance signal intensity in this region due to constant inputs from fresh organic materials however this will be depleted in soils that do not receive new organic inputs.

The region between (90 – 110 ppm) represents di-O-alkyl C structures of anomeric C (polysaccharides and ketals) which sometimes overlaps with the aromatic C region. The aromatic C region represents recalcitrant component of soil organic matter relative to other compounds and there has a longer residence period in the soil. It is mainly enriched from pyrogenic materials such charcoal which may be of natural or anthropogenic source. Natural and anthropogenic soils that have been exposed to firing and/or received deposits from pyrogenic sources may display high resonance intensity in this region. From the spectrum, the organic matter is dominated by aromatic C structures and to a lesser extent by aliphatic

structures. The proportion of carbohydrate and protein is considerably low which is expected given that it is comprised of carbon components that are easily metabolised.

Farmed historical soils typically have an enhanced aromatic C region in their organic matter. Ash and charcoal from cooking, fire places, and ovens are known to form part of the component of organic waste that are composted and applied to soil as fertiliser. Additionally, the aliphatic region may also be enhanced due to the age of the soil deposits given the extended period of exposure to microbial decomposition and all other elements of degradation. Spinning side bands (SSBs) indicated with an asterisk on the spectrum results from increasing external magnetic field strength although higher magnetic field strength increases signal to noise ratio (Preston, 2001). SSBs generally obscure features on the spectrum and distort the relative resonance signal intensities of compounds but its effect can be mitigated with higher spin speed/rate, amongst other means, which was implemented in this study (see Section *3.2.1.4*).

Some applications of NMR spectroscopy in research studies have ranged from the investigation of the composition of organic matter of various organic compounds, and soil types of different ages to understand the impacts of various biotic and abiotic factors on the synthesis and hydrolysis of organic compounds in soils as summarised in the table below.

Table 3.2. Example research applications of NMR spectroscopy in soil science

| Study Aims | Key Results | Reference |
|---|---|---|
| The extent of OM decomposition in peat soil with depth; the carbon composition of organic-rich materials such as sewage sludge | Decrease in O-alkyl C with depth and increase in alkyl C, aryl C, and carboxyl C with depth. Ratio of alkyl C to O/N – alkyl C is indicative of high extent of decomposition with depth | Grover and Baldock, 2012; Kiem, et al., 2000; Smernik, et al., 2003 |
| The chemistry of organic carbon stored in different soil types, and clay fractions | Differences in the quantity and composition of carbon in different soil fractions | Kahle, et al., 2003; Hopkins, et al., 1993; Mathers and Xu, 2003; Kiem, et al., 2000 |
| The sources of refractory aromatic structures in soil organic matter and the effects of pyrolysis/ thermal treatment temperature on the degradability of char | Increases in the proportions of condensed aromatic structures (aryl C and O-aryl C ) with increase in thermal treatment temperature | Mcbeath and Smernik, 2009; Baldock and Smernik, 2002; Schmidt, et al., 1999 |
| Determination of organic matter composition, carbon storage capacity, and sources of biochemical recalcitrance of OM of historical soils (Neolithic soils, Amazonian Dark Earth, cumulic anthroposols) | High proportion of poly-aromatic structures (e.g. aryl C) from char relative to other C compounds | Downie, et al., 2011; Novotny, et al., 2009; Schmid, et al., 2001; Schmid, et al., 2002; Solomon, et al., 2007 |

*3.2.1.3 Data Quality and Quantitation in NMR Analysis*

As discussed above, NMR spectroscopy is an advanced technique for use in SOM studies. The effective application of the technique requires a thorough understanding of not only the instrument parameterisation but also the nature of the samples or materials being examined. Many factors including contact time, spinning side-band (SSBs), polarisation technique, paramagnetic species, sample carbon content, and line-broadening are known to influence quantitative potential in solid-state $^{13}C$ NMR spectroscopy (Preston, 2001). Several adjustments to equipment set-up and sample preparation have, therefore, been proposed. These include: sample pretreatment with hydrofluoric acid (HF) to minimise interference from

paramagnetic materials, dipolar-dephasing to alleviate problems with signal loss caused by protonated and non-protonated components in SOM, and spin counting to increase quantitation and data quality in NMR analysis (Berns and Conte, 2011; Preston, 2001; Schmidt et al., 1997; De Junet et al., 2012; Smernik and Oades, 2000b; Smernik and Oades, 2001; Smernik and Oades, 2003).

*3.2.1.4 $^{13}$C CPMAS NMR Sample Analysis*

Solid-state carbon-13 Cross Polarisation Magic-Angle Spinning NMR Spectroscopy ($^{13}$C CPMAS NMR) was used to determine the composition and relative contributions of the various organic C compounds such as aromatic and aliphatic groups in the soil organic C pool. $^{13}$C NMR spectra were obtained on a 7.05 T Varian INOVATM Unity (Varian Inc., Palo Alto, CA, USA) (Figure 3.8) at a $^{13}$C resonance frequency of 75.4 MHz by applying the cross polarisation magic-angle spinning (CPMAS) technique. Samples were packed into a 6 mm diameter cylindrical zirconia Pencil® rotors with Vespel® drive tips and spun at 8000 ± 3 Hz in an HX Apex probe. A contact time of 1.5 ms and a 1.5 s recycle delay time were used. Optimal contact times and recycle delays were determined in separate experiments on several samples following the practice established by Conte et al. (1997). During cross-polarization the 1H radio frequency (RF) field strength was set to 48 kHz and the $^{13}$C RF field strength to 40 kHz. An ascending ramp of 16 kHz on the 1H-RF field was used during contact time to account for inhomogeneities of the Hartmann-Hahn condition (Berns and Conte, 2011). The spectra were collected with a sweep width of 25 kHz and an acquisition time of 20 ms. Proton decoupling was undertaken using a SPINAL sequence with a 1H field strength of 55 kHz, a phase of 4.5° and a pulse length of 12 µs.

The free induction decays (FID) – time-domain data converted to frequency domain spectrum by a fast Fourier transform algorithm (amplitude versus frequency) – were recorded with VnmrJ (Version 1.1 RevisionD, Varian Inc., Palo Alto, CA, USA) and processed by Mestre-C

software (Version 4.9.9.9, Mestrelab Research, Santiago de Compostela, Spain). Depending on the organic content of the samples the number of transients lay between 40000 and 250000. All FIDs were fourier-transformed with an exponential filter function with a line broadening of 20 to 50 Hz depending on the sample. Baseline correction was done using the manual baseline correction function of Mestre-C. The chemical shifts are reported relative to tetramethylsilane (= 0 ppm). The spectra were divided into five chemical shift regions: carboxyl/carbonyl C (215-160 ppm), aromatic C (160-110 ppm), anomeric C (110-90 ppm), O/N alkyl C (90-45 ppm), and aliphatic C (45-[-10] ppm). The relative intensities of the regions were determined using the integration routine of the MestReC software and subsequently, correction for the spinning side bands (SSBs) was done as described in Conte et al. (1997). Ratio of alkyl C to *O/N*-alkyl C [Eq. 1], and aromaticity index [Eq. 2] were calculated and used to assess the degree of decomposition (Baldock and Preston, 1995; Baldock et. al., 1997; Mathers and Xu, 2003).

$$\text{Alkyl C} : \textit{O/N}\text{-alkyl C} \;=\; \frac{\text{Alkyl C } (0-45 \text{ ppm})}{\textit{O/N}-\text{alkyl C } (45-110 \text{ ppm})} \qquad [1]$$

$$\text{Aromaticity } (\%) = \frac{\text{Aromatic C } (110-160 \text{ ppm})}{\text{Aromatic C } (110-160 \text{ ppm}) + \text{ Aliphatic C } (0-110)} \times 100 \qquad [2]$$

*3.2.2 Soil Pre-treatments*

The chemical pre-treatment of soil samples with hydrochloric and hydrofluoric acids (HCl/HF) are recommended procedure to remove paramagnetic material (Fe, Mn) and mineral matter (carbonates) from soil that allows specific element of soil to be studied, such as the organic carbon only fraction of soil, and organic carbon composition using nuclear magnetic resonance spectroscopy (Schmidt et al., 1997; Sánchez-Monedero et al., 2002; Salati et al., 2008). Removal of these materials increases the C/Fe ratio, and total organic carbon (TOC) in the samples presented.

*3.2.2.1 Hydrochloric Acid Pre-treatment*

A hydrochloric acid treatment adapted from Salati et al. (2008) was performed on all soil samples due to their relatively alkaline pH; this is more pronounced in St Andrews samples than in those from Roxburgh. The removal of carbonates from soil prior to undertaking total organic carbon (TOC) analysis allows that fraction (only organic carbon) of the soil to be studied (Heron et al., 1997) which is a vital soil property used for the assessment of the nutrient status and the decomposition of various organic assemblages in the soil. Approximately 5 g of 2 mm sieved air-dried soil was weighed into a 50 ml falcon polyethylene centrifuge tubes. 20 ml of concentrated HCl (12 M) was added to the soils and vortexed. The suspension was shaken for two hours at 250 rpm in an orbital shaker at room temperature. Samples were centrifuged for four minutes at 3000 rpm and the supernatant removed. The samples were re-suspended in 5 ml of fresh hydrochloric acid and shaken for another 2 hours. On completion, samples were centrifuged for two minutes at 3000 rpm and supernatant discarded. The samples were subsequently washed four times with 25 ml of distilled water until pH 6. Soils were then dried for 16 hours at 105°C and ground.

*3.2.2.2 Hydrofluoric Acid Pre-treatment*

Hydrofluoric acid pre-treatment has been shown in many studies to improve quantitation in solid-state NMR spectroscopy of soil organic matter (SOM) by reducing paramagnetic materials in the samples (Skjemstad et al., 1994; Preston and Newman, 1995; Schmidt et al., 1997). The presence of paramagnetic species such as iron and manganese in soil samples is a major hindrance to the use of solid-state $^{13}C$ NMR spectroscopy (Pfeffer et al., 1984; Hopkins et al., 1997; Smernik and Oades, 2000a; Smernik and Oades, 2000e). Paramagnetic interferences are most common in samples with low carbon to iron ratio (C/Fe < 1) (Schmidt et al., 1997; Salati et al., 2008) and treatment of such samples is recommended prior to NMR

analysis. Paramagnetic species affect NMR spectra by three mechanisms; i) signal loss and broadening, ii) increased relaxation rate, iii) changes in the chemical shift of resonances – see Smernik and Oades (2002) and references within for further detailed discussion.

Sample pre-treatment to improve solid-state NMR spectroscopy using other chemical methods such as citrate, sodium dithionite and stannous chloride have met with varying degree of success in terms of how much paramagnetic materials are removed (Vassallo et al., 1987; Arshad et al., 1988; Preston et al., 1989; Schmidt et al., 1997; Smernik and Oades, 2002). Treatment with 2% and 10% hydrofluoric acid has proven more reliable over these methods because it allows for the removal of majority of the mineral matter thereby concentrating carbon within the sample, as well as eliminating interfering paramagnetic particles without significantly altering the distribution and chemical composition of the organic matter (Skjemstad et al., 1994; Preston et al., 1994; Schmidt et al., 1997; Gonçalves et al., 2003). Although a few studies have reported some losses in organic C with HF treatment (Dai and Johnson, 1999; Rumpel et al., 2006; Salati et al., 2008), these losses are considered minimal and within acceptable limits for the improved data quantitation in solid-state NMR spectroscopy. Generally, sample pre-treatment with hydrofluoric acid prior to NMR spectroscopy leads to improvement in NMR sensitivity and spectral resolution, decrease in acquisition time, and hence cost of performing NMR analysis.

*3.2.2.3 Details of Procedure*

Hydrofluoric acid treatment, modified from Schmidt et al. (1997) was carried out on subsamples. Although C/Fe ratio of samples was generally less than one (C/Fe < 1), the NMR spectra of selected test subsamples were not quantitative, thereby necessitating the treatment of all samples prior to NMR analysis. 30 ml of 10% hydrofluoric acid was added to the 50 ml falcon polyethylene centrifuge tube containing the soil samples that had previously

undergone HCl treatment. The suspensions were shaken at room temperature for 20 hours at 260 rpm, centrifuged for 30 minutes at 3000 rpm and the supernatant removed. The procedure was repeated four times. The residue was washed five times with 30 ml of distilled water and vacuum filtered through a 0.45 µm Whatman cellulose nitrate membrane filter paper to remove salts and any residual HF. Finally, samples were freeze-dried and analysed. C/N ratio of subsamples was taken post HF pre-treatment and compared against values taken prior to the treatment to ensure that no significant loss of carbon occurred after treatment.

### *3.2.3 Optically Stimulated Luminescence*

Portable optically stimulated luminescence readers are a recent development that enable rapid field and laboratory measurement of luminescence properties of sediments which, in turn, can be used to determine the depositional sequence, and hence the stratigraphic integrity of deposits/sediments in both geological and archaeological landscapes. The use of the equipment to unravel complex depositional sequences has been demonstrated in a number of site profiling studies (Sanderson and Murphy, 2010; Munyikwa et al., 2012). Portable optically stimulated luminescence allows the direct measurement of bulk soils to be made, which helps to direct decision making on sampling strategy and positioning *in situ* during sample collection, and in the lab, negates the need to undertake the laborious mineral separation procedures involved in determining the suitability of samples for dating in regular detailed luminescence dating technique. Portable optically stimulated luminescence does not produce the absolute age of samples or deposits but its rapid data acquisition, low cost, and simplicity makes it a valuable tool in the study of deposits and sediment chronology.

OSL signal intensities respond to a combination of factors; i) the post-depositional age of the sediment (ii) the luminescence sensitivity (amount of light per unit dose, which is in turn linked

to mineralogical origin, grain size, clast content) (iii) local dose rates and (iv) initial bleaching and inherited luminescence from prior cycles of environmental irradiation (Bokhorst et al., 2005; Lian and Roberts, 2006; Wintle, 2008; Sanderson and Murphy, 2010). All of these variables can modulate luminescence signal intensity of sediments. The exposure of minerals such as feldspar and quartz, to natural radioactivity in the environment (Potassium ($^{40}$K), Uranium ($^{238}$U), Thorium ($^{232}$Th)) causes charges to be trapped within the crystal lattice (Lian and Roberts, 2006; Wintle, 2008). The stimulation of feldspar and quartz grains with infrared and blue light causes the release of accumulated charge which leads to the emission of light known as optically stimulated luminescence (OSL). The intensity of the trapped charge released, and the resulting OSL signal, reflects the total radiation dose that the sample has received. The sensitivity of OSL signal to light means that exposure of sediments to daylight, which may occur during and after deposition, will reduce or reset the OSL signal to zero (Bokhorst et al., 2005; Lian and Roberts, 2006). Therefore luminescence measurements estimate the radiation dose that the sample has received since its last exposure to daylight.

*3.2.3.1 OSL Sampling and Sample Analysis*

To obtain samples, twenty four 25 cm X 2 cm diameter copper tubes were driven into the exposed profile at 10 cm depth intervals or at each soil pedon, depending on site, to obtain sample set for optically stimulated luminescence (OSL) profiling (Sanderson and Murphy, 2010). Both ends of the tube were covered with grey plastic cap and sealed with duct tape. In the laboratory, the sediment at both ends of the tubes was discarded to prevent contamination of OSL signal from any materials that may have been exposed to light whilst sampling. Samples were analysed using a portable optically stimulated luminescence reader (SUERC, East Kilbride, UK).

For each measurement, about 10 g of the bulk sample was placed into the portable OSL reader in a 50 mm diameter Petri dish under subdued red-light conditions. All measurements were carried out in continuous wave mode. Signal separation during measurement is selectively done by the excitement of feldspar with infrared (IR) light (wavelength = 750 – 800 nm) and quartz with post-IR blue OSL (wavelength = 420 – 490 nm). Runs were configured to automatically perform a 15 second dark count (background) first followed by a 120 second IRSL measurement which predominantly relates to any feldspar component of the sample, followed by a 120 second blue-light (post-IR) OSL measurement which is predominantly related to the quartz fraction of the sample. These signals are plotted to produce luminescence profiles that depicts the variation of the luminescence signal with depth. During data analysis, to sufficiently discount the effects of mineralogy on background/natural radiation dose rate, IRSL/OSL ratio was used as a proxy for mineralogical similarities and dissimilarities within the profile section.

### *3.2.4 Near Infrared Reflectance Spectroscopy (NIRs)*

Near-infrared reflectance spectroscopy (NIRS) is an analytical technique that offers a rapid non-destructive and nearly instantaneous measurement of various soil properties such as organic matter, C, N, and P content, moisture content, pH, particle size, conductivity, cation exchange capacity (CEC) (Chang et. al., 2001; Cecillon and Brun, 2007). The technique is based on absorption of light in the region 780 to 2500 nm mainly by organic substances (Teixeira Dos Santos et al., 2013).

NIR spectroscopy is widely used in soil analysis as described above, and in the agro-food industry to determine the composition and functional properties of food products and other commodities (Chang et. al., 2001; Prieto et al., 2009; Teixeira Dos Santos et al., 2013). Field

portable/handheld NIR spectrometry is a proven analytical technique that permits rapid multi-parameter data collection with similar resolution to laboratory-based NIR instruments (Teixeira Dos Santos et al., 2013). Its additional advantage of portability, relative low cost and speed makes it an increasingly popular analytical tool.

*3.2.4.1 NIRS Sampling and Sample Analysis*

A field portable NIR spectrometer was used *in situ* to obtain soil data in field-moist "as is" condition. Data collection comprised of horizontal and vertical measurement at 10 cm interval across the exposed profile face using an ASD Labspec 5000 field portable Near-Infrared (NIR) analyser (Analytical Spectral Device Inc., Boulder, Colorado, USA). The contact probe was placed against the exposed profile surface, and spectral data were collected. The exposure time was for five seconds at each position, equating to fifty spectra being collected and then averaged.

The raw spectral data (not shown) were presented as the logarithm of the inverse of the reflectance [log (1/R)] in accordance with Chang et al. (2001). Data for statistical analysis by selected region from 1300 to 2400 nm to correlate with soil properties. This excludes an area of high 'noise' between 2400 and 2500 nm. Additionally, the spectral region from 1820 to 1840 nm was excluded from statistical processing as it represents the overlap between two of the spectrometers within the Labspec system, and can often manifest itself as a 'step' in the data (Parkin et al. 2013). The first derivative of the spectra was used for the statistical analysis of the data. In this study, Principal Components Regression of the NIRS spectra were used to correlate reflectance data and values for soil properties in order to estimate primary soil properties. Principal Components Regression was carried out on the selected spectral region highlighted in blue and grey below in Figure 3.12 using the GRAMS IQ program (Thermo Scientific).

| Depth | Profile | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
| 0 | | -0.12 | -0.1 | | -0.1 | | -0.18 | -0.11 | -0.16 | -0.13 |
| 10 | -0.17 | -0.11 | -0.09 | -0.16 | -0.09 | -0.09 | -0.09 | -0.02 | -0.2 | -0.18 |
| 20 | -0.11 | -0.08 | -0.08 | -0.16 | -0.05 | -0.1 | -0.14 | -0.23 | -0.07 | |
| 30 | -0.08 | -0.07 | -0.04 | -0.06 | -0.02 | -0.05 | -0.06 | -0.09 | -0.09 | |
| 40 | 0.074 | 0.043 | 0.031 | 0.03 | -0.04 | 0.036 | -0.07 | -0.11 | 0.15 | |
| 50 | 0.045 | 0.09 | 0.094 | 0.069 | 0.117 | 0.125 | 0.121 | 0.093 | | |
| 60 | 0.137 | 0.119 | 0.127 | 0.138 | 0.126 | 0.113 | 0.146 | 0.112 | | |
| 70 | 0.151 | 0.146 | 0.135 | 0.167 | 0.151 | 0.175 | | | | |
| 80 | 0.08 | 0.185 | 0.163 | 0.164 | | | | | | |
| 90 | 0.082 | 0.073 | 0.117 | | | | | | | |

Fig. 3.12. NIRS data collection format in trench 3; Grey and blue highlighted areas are used for PCR analysis. Black areas indicate areas where no data were collected; white areas are unresolved data points and were discounted from analysis (depth and distance in cm)

*3.2.5 Micromorphology*

Soil micromorphology is a well-established technique in pedology that allows the detailed examination of undisturbed soil and regolith samples using an optical microscopy (Stoops, 2003, 2010). Micromorphological investigations seek to understand the processes responsible for the formation and transformation of soil, and other features resulting from both natural (mottles, nodules) and artificial (burning, plough layer) cause. Consequently, it is applied in the study of soil genesis, classification and management of soil, and relative chronology. Micromorphology was already routinely used in archaeological science in the mid-nineteenth century in the investigation of palaeosols, and ancient materials (plasters, cements) (Kemp 1998; Macphail and Goldberg 1995; Kemp 1998; Stoops, 2003). Since then, it has been applied in the studies of natural and anthropogenic soil formation processes, and on a range of historical landscapes investigating past agricultural practices, land management systems and occupational deposits (Simpson 1997; Davidson and Carter 1998; Simpson et al., 1998b;

Simpson et al., 2003; Davidson et al., 2006; Golding, 2008; Golding et al., 2010; Adderley et al., 2010). The microscopic examination of soil materials is generally done on a thin section slide, a 30 micrometre thick section of the material to be probed that has been processed and mounted onto glass. The accurate interpretation of features observed in thin sections is a crucial aspect of this technique and requires objective analysis and detailed description.

*3.2.5.1 Thin Section Sample Preparation for Micromorphology*

Thin sections were manufactured at the University of Stirling (http://www.thin.stir.ac.uk/category/methods/) using the standard procedures developed by Murphy (1986). The samples were dried using vapour-phase acetone-exchange method to allow the hydrophobic resin to adequately fill soil pore spaces during impregnation The vapour-phase exchange was monitored by repeated by specific gravity measurement of acetone/water mixture. The blocks were impregnated under vacuum using Polylite polyester resin (Reichhold, Surrey UK) in styrene monomer and polymerisation catalysed by methyl ethyl ketone peroxide (MEKP). The mixture was thinned with acetone at a composition of (700 ml resin, 0.4 ml catalyst, and 200 ml acetone) used for all samples. Samples are left to cure for approximately 12 weeks, with the final few weeks in the oven at 40°C to ensure that any residual styrene and acetone solvents are removed. The impregnated soil blocks are cut with an abrasive rotary diamond saw to approximately 1 cm thick slices and bonded onto glass slides using epoxy resin (Logitech epoxy 301). Samples were lapped to 30 µm using 15 µm calcite aluminium oxide in water as a grinding medium and then polished with 3 µm diamond in oil suspension. The slides were not cover-slipped.

*3.2.5.2 Identification and Quantification of Features*

The identification and quantification of charcoal was prioritised in this study in order to investigate the linkages between the physical and chemical elements, i.e. if a correlation exist between the amount of pyrogenic materials (charcoal) and the high aromatic C abundance as seen from the NMR chemical analysis, soil colour and magnetic susceptibility. Additionally, charcoal was used as a proxy to investigate the degree of anthropogenic influence of the sites. Thin sections were examined using a petrological polarizing microscope (BX-50, Olympus Corp., Tokyo, Japan). Samples were examined under plain polarised illumination (PPL) using a 2 x magnification objectives. The quantitative determination of charcoal was undertaking by image analysis using AnalySIS-Pro image analysis Software (Olympus Corp., United Kingdom).

Observations were made at 1 cm intervals across each slide. A total of 20 observations were made on each slide. Areal proportions of charcoal were measured following a pre-set segmentation of the image (Russ, 1999; Adderley et al., 2006). The data generated were computed to produce a cumulative frequency distribution of charcoal at each soil pit and the area covered by charcoal in $mm^2$ per profile with depth across the sites.


Fig. 3.13. Olympus BX-50 petrological polarizing microscope, automated stage and software-controlled microscope camera used for thin section image analysis

*3.2.6 Elemental Microprobe Analysis (XRF analyser)*

Elemental microprobe analysis is a term that covers a range of techniques used to examine the elemental composition of substances which in turn provides information on the composition and concentrations of elements contained within the object being examined. Such multi-element analysis has been used since the last four decades in archaeology to investigate the

elemental compositional properties of stones (especially obsidian) and ceramic artefacts (Marwick, 2005; Shackley, 2010). Recent application of the technique in archeological prospection includes; the identification and interpretation of functional areas (byre, hearth, kitchen area, midden, garden and arable fields) in and around structures within historical landscapes using the elemental signature imprint of the respective study site (Entwistle et al., 1998; Wilson et al., 2007a; Wilson et al., 2009). Human activities can lead to physical and chemical alteration to soil properties. Chemical alterations are manifested by the enrichment or depletion of certain groups of elements (e.g. Pb, Zn, P, K, Ca, Ba, Sr, Mn, Hg, Cu, Mg) which can be explored to reveal past land use patterns (Wilson et al., 2007b). The patterns of enhancement and distribution of these suites of elements can be used as indicators of site use and functionality (Bull et al., 2001; Wilson et al., 2005; Wilson et al., 2006a).

Amongst these suites of elements, phosphorus is most commonly used in archaeological prospection due to its high retention rate in the soil (Leonardi et al., 1999; Oonk et al. 2009). Areas that have seen anthropogenic influence generally exhibit greater phosphate concentrations relative to their natural counterpart (Holliday and Gartner, 2007). However, although phosphorus can be a useful indicator of human activity, it does not discriminate between specific land use practices such as manuring and accumulated occupational deposits and debris as both activities can result in phosphorus enhancement (Entwistle et al., 2000a). Therefore, interpretations should be based on the pattern of relative enhancement of suites of elements across the sites rather than a single element (Wilson et al., 2006a).

Various field and laboratory methods to study elemental composition have been developed, ranging from simple qualitative colorimetric phosphate analysis to quantitative multi-elemental analysis using inductively coupled plasma mass spectrometry (ICP-MS), atomic emission spectrometry (ICP-AES), and X-ray fluorescence spectrometry (XRF) on bulk soils (Oonk et al., 2009). Portable XRF spectrometer was used in this study over inductively coupled

plasma spectrometry because it is relatively cheap, simple to use, with short sample preparation and processing time (Marwick, 2005; Shackley, 2010).


Fig. 3.14. Niton XL3t-Goldd+ X-ray fluorescence analyser used with helium purging (left) to enhance signal quality

The principle of X-ray fluorescence spectrometry involves the interaction of X-rays and the samples being examined. When the electrons of an element are excited by incident X-rays, they emit a spectrum of X-rays that is specific to that element, in other words, a signature of that particular element. The highly sensitive detector of the XRF instrument allow accurate detection of the elemental composition of a sample, and when used in conjunction with helium, detection is further enhanced for a range of elements such as phosphorus. Inductively coupled plasma spectrometry technique was not used due to potential problems arising from extraction techniques (different element retention rate within different soil fraction), detection limits, expense, and workload (long sample preparation time, washing and cleaning of equipment) (Entwistle and Abraham, 1997).

*3.2.6.1 Sample Processing and Discriminant Elements*

Soils were air-dried to reduce X-ray attenuation by moisture, sieved to <2 mm and homogenised. 10 g of soil was placed into a pellet press die and compressed vertically using a manual hydraulic press. Samples were analysed for their elemental composition and concentration using an X-ray fluorescence analyser (Niton XL3t-Goldd+, Thermo Scientific, Billerica, MA, USA). All measurements were carried out in the instrument's mining Cu/Zn mode, which increases the sensitivity and range of detectable elements. For each measurement, the pellets are placed on the surface of the detector with helium purging the space between sample and detector, to reduce detector attenuation, before activating the device. The instrument was configured to run for 60 seconds per sample in which time it goes through four selective filters (main, m-low, m-l-high, m-l-h-light). Results are calculated from a theoretical calibration (Niton Data Transfer PC software, Thermo Scientific) based on the relative self-absorbance and attenuations of a matrix dominated by iron-rich minerals such as soil. Results are displayed in parts per million (ppm) with elemental peaks displayed in accompanying spectra. The following suites of elements; barium (Ba), calcium (Ca), phosphorus (P), zinc (Zn), lead (Pb), potassium (K), manganese (Mn), sulphur (S), chlorine (Cl), magnesium (Mg), and strontium (Sr) were discriminated for interpretational purposes, because they have been shown to be the most useful in site delineation of functional areas (Wilson, et al., 2005; Wilson, et al., 2007a; Wilson, et al., 2009).

*3.2.7 Magnetic Susceptibility*

Environmental magnetism refers to the use of the magnetic properties and characteristics of minerals as proxy parameters with which to study the formation, transportation, deposition, and post-depositional modifications to substances that are/have been subject to a diverse range of environmental processes (Dekkers, 1997; Liu et al., 2012). Environmental magnetism

has advanced as a technique since the 1970s and is now widely applied in research studies in chemical, physical, biological, environmental, archaeological and geosciences (Dearing, 1994; Liu et al., 2012). The generic application of magnetism in many fields of discipline originates from the understanding that all matter responds in some manner to applied magnetic fields. Magnetic susceptibility measurements of materials, especially iron-bearing minerals are extremely useful for detecting signals associated with environmental processes in both natural and man-made environments (Crowther, 2003; Dalan, 2006; Schmidt, 2007). In archaeological prospection, thermoremanent magnetism is probably the best known magnetic effect caused by past human habitation. Thermoremanent magnetisation is acquired when a magnetic mineral or material rich in magnetic mineral (e.g. iron-oxide) cools from above its Curie temperature in a magnetic field. This thermoremanence property is stable and therefore can survive in the material with negligible change through geological time (Thompson and Oldfield, 1986; Schmidt, 2007).

The firing or burning of materials has long been associated with human habitation in archaeological sites because the resultant effect is visible from enhanced magnetic susceptibility in the area (Crowther, 2003; Dalan, 2006). During burning, weakly magnetic iron oxides (magnetite – $Fe_3O_4$, and maghemite – $Fe_2O_3$) in the clay and silt particles are heated above their curie temperature (~600-700°C). Similarly, fired bricks and pottery can also display thermoremanence and consequently enhanced magnetic properties. Since human habitation can lead to the enhanced magnetism, measurements of the magnetic property of soil are commonly used in archaeological survey for the identification of activity areas such as former hearths, kilns, furnaces and large fires as well as habitation layers.

*3.2.7.1 Volume Magnetic Susceptibility*

Magnetic susceptibility measurements can be carried out *in situ* or *ex situ* by collecting samples for laboratory analysis. The differences between both methods are often

distinguished by volume susceptibility or mass specific susceptibility. Volume susceptibility (ƙ) is defined by the relation ƙ = *M/H* (*M* = volume magnetisation induced; ƙ = susceptibility; *H* = applied field) and has a dimensionless unit (SI) however mass specific susceptibility ($\chi$) relates measured susceptibility values to the mass of the sample; $\chi$ = ƙ/$\rho$ ($\chi$ = specific susceptibility; ƙ = volume susceptibility; $\rho$ = density) with units expressed in $m^3$ $kg^{-1}$ (Thompson and Oldfield, 1986; Schmidt, 2007).

Magnetic susceptibility values of soil are often dependent on the inherent magnetic property of the parent material, and the degree of influence from post-depositional alterations (anthropogenic and natural influence); consequently absolute magnetic values can therefore vary extensively between sites. Although magnetic susceptibility of a material can be determined more accurately using mass specific susceptibility, but, since magnetic enhancement values can only be identified as a contrast between areas of higher susceptibility relative to the background measurements, and given the absence of established indices or threshold for this contrast, it is argued that field based volume magnetic susceptibility measurements are justifiable and suitable for archaeological investigations.

*3.2.7.2 Field Magnetic Susceptibility Measurement*

Volume magnetic susceptibility measurement was carried out for rapid *in situ* characterisation of soil profile properties within and between study sites. Magnetic susceptibility of the exposed soil profile pit was measured using an MS2F surface probe sensor coupled to a Bartington MS2 susceptibility meter (Bartington Instruments, Oxford, England). Similarly, downhole magnetic susceptibility was obtained at each auger sample point using Bartington MS2H downhole sensor. Measurements were made at every 10 cm interval down to the maximum depth of the profile (soil pit profile or auger profile).

Fig. 3.15. Field operation of the Bartington MS2 magnetic susceptibility meter with the MS2H downhole sensor

The MS2H downhole probe is calibrated by default to display the true volume magnetic susceptibility (k) for a 22 mm diameter hole. However, the Edelman auger used for sampling produces approximately 50 mm diameter hole which is beyond the maximum hole diameter of (25.4 mm) and the associated scale factor correction value of (1.74) for the probe (see Table 3.3 below).

Table 3.3. Bartington MS2H downhole probe scale factor (**k**) correction for different sample hole diameters

| **Hole diameter (mm)** | **Scale factor for k** |
|---|---|
| 22.0 | 1.00 |
| 24.0 | 1.42 |
| 25.4 | 1.74 |

An attempt was made to derive a scale factor for (k) for a 50 mm diameter hole but the result was not satisfactory and therefore was not used. Scale factor correction for (k) was done using the value stated for the maximum hole diameter (k = 1.74, hole diameter = 25.4 mm). This is to prevent the risk of overestimating the true volume susceptibility values displayed. Corrections were made for temperature drift experienced during measurement sequences for both sensors as described in the instrument booklet (Dearing, 1994). Magnetic susceptibility values are expressed as volume susceptibility (k) in dimensionless SI units ($10^{-5}$).

*3.2.8 Soil pH Analysis*

pH is a measure of the concentration of (more strictly the activity of) hydrogen ions ($H^+$) in a solution, defined as the negative logarithm of the hydrogen ions ($H^+$) concentration: the equation; $pH = - \log_{10} [H^+]$ (Cresser et al., 2013). pH is an important chemical property of soil and a factor relevant in the control of various chemical and biochemical processes in the soil such as element mobility, availability, reactivity, microbial activity, biomass, and community structure, mineralisation (Rowell, 1994; Brady and Weil, 2008; Cresser et al., 2013). Soil pH is affected by various factors of both natural (parent material, hydrology, vegetation, climate) and anthropogenic (addition and mixing of fertiliser, lime, shells and debris) origin (Rowell, 1994; Brady and Weil, 2008; Cresser et al., 2013). And therefore pH analysis can reveal information on soil condition and functioning of processes as mentioned above. Soil pH is routinely used in georarchaeology as an indicator of preservation conditions because high pH generally limits the presence and activity of organisms involved in degradative processes (Marwick, 2005).

Soil pH was measured in distilled water and in 0.01 M calcium chloride ($CaCl_2$) solution on a 1: 2.5 soil to water suspension using an Hl 209 pH meter (Hanna Instruments, Romania). Soil pH

measured in $CaCl_2$ provides a good approximation of the pH of the soil solution under field conditions than when measured in water (Rowell, 1994). When soil is diluted with water, some of the $H^+$ ions remain attracted to the soil colloids and are not released into the solution. The addition of small amounts of $CaCl_2$ provides $Ca^{2+}$ ions which displace H+ ions on the soil colloids allowing them to go back into the solution making their concentration in the bulk solution closer to field state. 10 g (± 0.1 g) of air-dry soil is weighed into a beaker containing 25 ml of distilled water. The mixture was stirred and allowed to settle for 10 minutes. The pH meter electrode was calibrated in the pH 7 and 4 buffer solutions respectively prior to measurement. The pH of the suspension was taken in water, and then in calcium chloride on addition of 1 ml of $CaCl_2$, when the electrode is stable, typically within 30 seconds (Rowell, 1994). Soil pH value was recorded to the nearest tenth and interpreted following the pH range criteria in Schoeneberger et al. (2012).

*3.2.9 Particle Size Analysis*

Soil/sediment consists of an assemblage of discrete particles of various shapes and sizes. Particle size distribution or gradation is the measure of the proportions by dry mass of the various particle size fractions. Soil particle size is generally determined from the basis of their diameter (Stokes' Diameter [$d_{St}$]) or volume diameter (Coulter's volume diameter [$d_V$]) depending on the method used (ISO 13320: 1999), which can be classified using scales such as the Wentworth (1922) grain size classification system mainly into clay, silt, sand, and gravel (Rowell, 1994). The distribution of particles determines soil/sediment texture which defines various soil properties and functions such as water holding capacity, bulk density, water conductivity and organic matter content (Rowell, 1994, pp. 9; Skaggs et al., 2001; Ryżak and Bieganowski, 2011). Particle size analysis can be performed by methods such as sieving, sieving and sedimentation, microscopy, and coulter counter (Coulter, 1990). The coulter

counter was used to determine the particle size distribution in this study because of its relative ease of use, precision, and speed (shorter sample processing time and less use of laboratory apparatus) (Arriaga et al., 2006).

*3.2.9.1 PSD Sample Processing and Analysis*

Subsamples were air-dried and sieved to 2 mm. 5 g of soil was put into a 50 ml plastic bottle containing 30 ml of distilled water. 2 ml of the dispersant sodium hexametaphosphate (Calgon) was added to aid deflocculation (Rowell, 1994, pp. 29; ISO 13320: 1999). Samples were agitated mechanically for 30 minutes using a magnetic stirrer to further deflocculate the sediments and to suspend particulates (Coulter, 1990; Ryżak and Bieganowski, 2011). Samples were analysed using a Coulter LS230 series Laser Diffraction Particle Size Analyser (Coulter Corporations, Miami, FL, USA). Measurement is performed after the appropriate concentration of sample is added (automatically determined by the instrument). The dispersed sample is illuminated by a series of light beams (laser beam and polarized light). The particles scatter the light in patterns determined by their respective sizes. A number of photo-detectors detect and measure the scattered lights which are scanned and the outputs converted to digital values. A computer analyses the flux pattern (light intensity per unit area) and computes the volume distribution of the sample (Coulter, 1994; pp. 4-1). Calibration of the instrument is done automatically by measuring electrical offsets and aligning the laser beam. Sample particle distribution was categorised using Wentworth (1922) classification system.

*3.2.10 CHNS-O Elemental Microanalysis*

CHNS-O elemental micro-analyser is a fast and relatively inexpensive technique used in investigating sample purity, with extensive industrial and research applications. Elemental

micro-analysis is one of a number of methods used in the studies of soil organic matter. Percentage loss on ignition (% LOI) is a widely known technique for measuring soil organic matter but it is prone to overestimation of organic matter content from loss of structural water from clay (sesquioxides) and carbonate minerals (calcite, dolomite) (Rowell, 1994). Oxidation method (dichromate solution) is also a valid technique for determining organic matter however it involves multiple stage procedures, reagents and equipment, and bulk calculations all of which increases the potential to introduce error. An elemental micro-analyser allows the percentage total carbon content ($T_C$) to be determined in both its inorganic, and organic forms by acid pre-treatment. Total nitrogen ($N_T$) content of soil sample is also obtained simultaneously saving considerable time and cost, and is more accurate in comparison to the process-laden Kjeldahl nitrogen determination method.


Fig. 3.16. Carlo Erba EA1108 CHNS-O elemental micro-analyser used to determine the total carbon and nitrogen of soil samples

*3.2.10.1 Elemental Microanalysis Sample Processing and Analysis*

Air-dried samples were sieved to 2 mm, oven dried for 20 hours at 105°C to further remove residual moisture before being ground. A properly dried sample is a prerequisite for this analysis because the determination of the mass percentage of CHNS-O elements of the sample is based upon the direct weight of the material sampled (Carlo Erba Instruments, 2009). Grinding is recommended as it decreases sample heterogeneity (Heron et al., 1997). 20 mg (± 0.2) aliquot of soil samples were weighed into pressed tin capsules (Elemental Microanalysis UK, product no. D1008) using an Oxford GM2505D precision balance (A & D Company Limited, Japan), folded into pellets ready for analysis. Total organic carbon ($T_{OC}$) and nitrogen ($N_T$) were determined using an elemental micro-analyser (EA1108 CHNS-O, Carlo Erba Instruments, Milano, Italy) coupled with PC-based Eager 300 data system.

The samples were placed inside an auto-sampler drum where they were purged with continuous flow of helium and then dropped into the combustion reactor, kept at 900°C, at pre-set intervals. The high temperatures and the temporary oxygen-enriched environment ensure that the sample is completely oxidised (flash combustion). Elemental composition and content is determined by gas chromatography coupled to the appliance. The instrument was calibrated with the analysis of standard compounds (Low Organic Content Soil analytical standard, B2152; C – 1.26%, N – 0.10%) supplied by Elemental Microanalysis UK (www.microanalysis.co.uk). Results for elemental analyses are displayed in percentage, and are calculated based on a known value of a standard (mass, C/N content) by using the K value factors calculation. This K value is determined by analysing an organic standard of a known elemental composition (Carlo Erba Instruments).

*3.2.11 Soil Respiration and Microbial Biomass*

Microbial biomass was determined indirectly using the substrate-induced method (Anderson and Domsch, 1978). Soil microorganisms are an essential component of soil and are of key importance in biochemical processes and global nutrient cycles (Bailey et al., 2002; Blagodastskaya and Kuzyakov, 2013). By measuring the size of microbial population of a given soil with known parameters (SOM content, composition), an estimate can be made for the residence period and rate of turnover of soil organic matter. Some of the most widely used methods for determining microbial biomass in soils are; chloroform fumigation extraction (CFE), substrate induced respiration (SIR), and phospholipid fatty acid (PLFA) all of which data reliability have been well demonstrated (Blagodastskaya and Kuzyakov, 2013). However caution must be exercised in the selection of methods used to ensure that the technique(s) selected suitably addresses the objectives of the study.

Blagodastskaya and Kuzyakov, (2013) consider that the microbial biomass in soils exist in four main physiological states grouped into living and non-living biomass. The *active*, *potentially active,* and *dormant* state, are the living components while *dead* is the non-living component. The active state corresponds to the pool of SMB that are constantly involved in driving ecosystem functions (utilisation of substrate, biochemical transformations,) and constitute about 0.1-2% of the total microbial biomass, hardly exceeding 5% in substrate rich soils. The potentially active pools of SMB are able to switch to the active state relatively quickly (within minutes to a few hours) on availability of substrate and constitutes between 10 and 40% (up to 60%) of the total microbial biomass. The dormant pool does not contribute to ongoing biogeochemical processes but can transition to the active pool under altered conditions or when incentivised and unlike the potentially active pool requires a considerably longer time period for the shift to occur (hours to days). The fourth state, the dead pool (lysed cells and microbial residue), is the non-living biomass and consequently does not directly contribute to

any ongoing processes but may affect the dynamics of organic material as potential sources of easily available substrate.

Chloroform fumigation extraction (CFE) and phospholipid fatty acid (PLFA) methods yields information on the chloroform sensitive total SMB, and total SMB and composition respectively and does not discriminate between living (active, potentially active, dormant) and non-living (dead biomass) predisposing them to error of overestimation of the portion of SMB involved in soil processes. Substrate induced respiration measurements on the other hand reflects the respiration of the living components of microorganisms in soil. With the objectives of this study being to investigate the dynamics of organic material (decomposition rate) the SIR technique was most advantageous as it allows for the quantification of the fraction of soil microbial biomass (active, potentially active, dormant) that influence and/or could influence the dynamics of processes in the soil.

Soil respiration and microbial biomass were determined using method described by Hopkins and Shiel, (1996) on STM-P, SSJG-5, and BGr-P samples. Approximately 5 g of field moist soil was weighed into a 15 ml glass vial and placed into a 60 ml syringe and plunged with a plunger. The nominal volume of the chamber was set to 50 ml and the outlet sealed with a 3-way tap fitted with a 1 ml syringe. The respiration chamber is shown diagrammatically below (Figure 3.17). The volume of the headspace was determined by displacement of equivalent mass (5 g of soil + vial) using a graduated measuring cylinder with a known volume of water. Total volume of the headspace is obtained by subtracting this volume (soil + vial) from the volume of the chamber (50 ml).

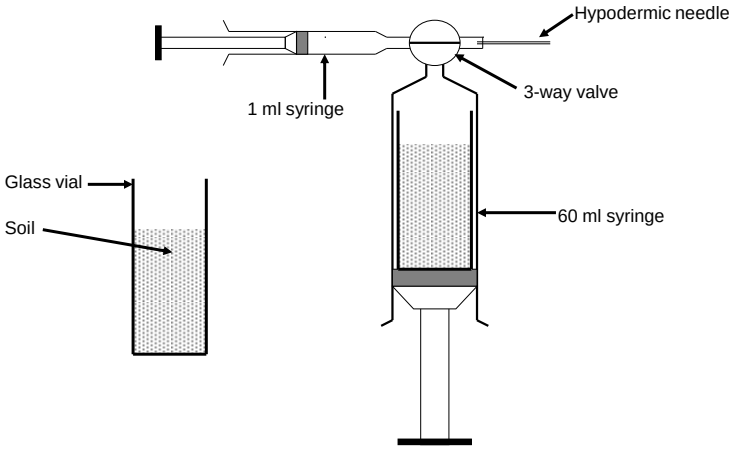



Fig. 3.17. Respiration chamber set-up for substrate-induced respiration experiment

The chamber is incubated at room temperature (21° C) for a period of 24 hours, and the concentration of $CO_2$ in a sample of gas from the headspace of the respiration chamber measured using a Varian aerograph 90-P gas chromatograph (Varian Aerograph, UK) coupled to an NGI Servogor 102 recorder (Cambridge Scientific, Watertown, MA, USA) after 24 hours. The gas chromatograph was calibrated by injecting 1 ml sample of gas containing a known concentration of $CO_2$ (CryoService, Worcester, UK; product no. 005-07-03020). To estimate microbial biomass, a second respiration chamber was set-up in identical conditions as the first but with the addition of 10 mg of glucose (2 mg glucose $g^{-1}$ of soil) (Hopkins and Ferguson, 1994). Anderson and Domsch, (1978) pointed out that when estimating microbial biomass using substrate-induced method, the minimum amount of substrate must be added in order to eliminate error from underestimation of microbial populations. Glucose was used as substrate because it is an easily utilisable carbon source for most soil organisms (Lin and Brookes, 1999). Moisture content was determined on a subsample as the difference in weight between fresh and oven dried (105°C) soil. Values are expressed as percentages.

Calculating Soil Respiration and Microbial Biomass: The respiration rate was calculated using the formula;

$$\text{Respiration rate } (\mu\text{mol C g}^{-1}\text{ soil hr}^{-1}) = \frac{(4.46\text{x } 10^{-7} \times \text{Sample peak height} \times \text{ Internal volume of chamber})}{(\text{Standard peak height} \times \text{dry mass of soil})}$$

$$= \frac{(\text{Formula 1 derivative})}{(24\text{ hr} \times 0.27)} \text{ X } 1000000$$

Respiration data obtained were assumed to be of absolutely microbial origin due to the absence of plant remains (roots). Soil microbial biomass was estimated using the regression equation obtained by Hopkins and Shiel (1996) from soils from north-east England to establish a calibration curve.

*3.2.12 Phenol oxidase Assay*

Microbial phenol oxidases and peroxidases are extracellular enzymes essential in biogeochemical processes in many ecosystems (Sinsabaugh, 2010). One of the main functions of phenol oxidase enzyme is to convert recalcitrant phenols that otherwise inhibit microbial access and therefore decomposition of organic material into their corresponding benzo-quinones - thereby decreasing their inhibitory effect on degradative enzymes such as hydrolases. Phenol oxidase enzyme activity is dependent on several environmental variables (pH, aeration, substrate availability (phenolic material) etc.) (Pind et al., 1994; William et al., 2000; Sinsabaugh, 2010) but it is primarily controlled by the anoxic conditions of the environment (Freeman, et al., 2001). This use of phenol oxidse enzyme activity in the study of nutrient dynamics and decomposition is gradually gaining momentum in research studies investigating nutrient dynamics and decomposition (Sinsabaugh, 2010) although much of this is focused on aquatic systems such as peatlands and wetlands (William et al., 2000; Freeman et al., 2004; Kang et al., 2011). Methods to assay phenol oxidase activity

spectrophotometrically in bulk soil samples have been developed (Floch et al., 2007; Bach et al., 2013) and applied in studies investigating OM decomposition in soils. However, variations in soil properties – most likely from the inherently low concentrations of phenolic compounds in soils relative to peatland and wetland environments – makes global scale correlation of PO oxidative activities and SOM contents and dynamics problematic; see Sinsabaugh, (2010).

The phenol oxidase assay was carried out on a number of predetermined experimental sites to investigate its potential control of organic carbon dynamics. Historical management practices saw high sustained inputs of diverse organic-rich materials to soils. The mixing of these materials, most of which are confirmed natural and anthropogenic sources of phenolic compounds (Michalowicz and Duda, 2007; Sinsabaugh, 2010; Li and Beta, 2013), are likely to have increased the inherent phenolic contents of the soils and the corresponding effect in the control of soil processes.

*3.2.12.1 Soil Sampling, Processing and Analysis*

A series of samples were collected from varying depths (0 cm to $\leq$ 120 cm) at the study sites (STM-P, SSJG-5, BGr-P, and RT3). Soil subsamples were air-dried, sieved to <2 mm and ground for 2 minutes at 20 MHz using a Retsch MM200 vibrating ball mill (F. Kurt Retsch GmbH & Co. KG, Haan, Germany). Moisture content and dry weight was calculated after drying approximately 1 g of soil at 105°C for 24 hours. Soils were stored at 4°C before use.

Spectrophotometric detection of ABTS oxidation: Phenol oxidase assays using ABTS as substrate (2,20-azino-bis (3-ethylbenzthiazoline-6-sulfonic acid)) were modified from Floch et al. (2007). Briefly, 5X modified universal buffer (MUB) was prepared by dissolving 12.1 g of tris (hydroxymethyl) aminomethane (THAM), 11.6 g of maleic acid, 14.0 g of citric acid, and 6.3 g of boric acid ($H_3BO_3$) in 488 ml of a 1 M sodium hydroxide (NaOH) and diluting the solution to 1 L with distilled water. 200 ml of the MUB solution was titrated to pH 3, with the final

volume adjusted to 1L using dH2O. ABTS solution was made by dissolving 27 mg ABTS in 500 µL of distilled water for a final concentration of 0.1 M ABTS.

0.1 g of soil was suspended in 10 ml of MUB solution pH 3 and mixed using a vortex for 10-15 seconds. A 1 ml representative sample was removed and substrate was added to a final concentration of 2 mM (ABTS). The sample was incubated at 30$^{o}$C for 5 minutes. After incubation, the sample was centrifuged at 10,500 g for 2 min. 200 µL of supernatant was collected and placed in a single well of a 96-well microtitre plate. Absorbance measurements were recorded at 420 nm using an MDS VERSA max tunable microplate reader (Molecular Devices, Sunnyvale, CA, USA), detecting ABTS product accumulation. Phenol oxidase activity is expressed as U $g^{-1}$; 1 U is defined as 1 µmol of $ABTS^{+}$ formed per minute, with an absorption coefficient for $ABTS^{+}$ at this wavelength (420 nm) of 18,460 $M^{-1}$ $cm^{-1}$. Assays were performed on at least 3 independent occasions: Heat-treated samples (121$^{o}$C for 1 h), and assay absent soils and/or substrate were used as controls.

*3.2.13 Differential Global Positioning System (DGPS): Field Application*

Differential Global Positioning System (DGPS) is a method that provides enhanced location accuracy to about 10 cm precision through performing differential corrections to a GPS receiver from a reference base station at a known location. The differential global positioning system (DGPS) was used in conjunction with field measurements and sampling for magnetic susceptibility and X-ray fluorescence microprobe elemental analysis. This allowed the investigate of the above and below ground features in the Friars Haugh area in Roxburgh to be precisely aligned to previous geophysical data of the site, undertaken by GSB prospection Ltd, shown as a base map in Figure 3.3. Sample data position and elevation are logged in and used to produce a map/layout of the relative distribution of elements, magnetic enhancement,

organic matter content and other soil physical and chemical properties across the site. Sample positions (auger) along the transect were defined using the Leica GS09 differential GPS unit (Leica Geosystems, Heerburg, Switzerland).

Fig. 3.18. Leica GS09 differential GPS unit being utilised in the field at Roxburgh

*3.2.14 Spatial Analysis*

The Ordinance Survey map of the study site at Roxburgh was obtained from Digimap (EDINA) as a background raster map. A site map containing the archaeological features generated by GSB prospection Ltd (2006) was then re-produced by importing the relevant figures-maps (JPEG images) into ArcMap (ESRI, ArcGIS v10) which were then geo-referenced to create Geo-TIFF files. This was subsequently overlaid with the OS map of the study site and incorporated into the map areas within ArcGIS. Spatial analysis was carried out on the Roxburgh map area by adding data points obtained from DGPS sampling (transect points). The result is a series of

visual maps showing the lateral and longitudinal distribution of the selected site markers (elemental signature, magnetic susceptibility, organic matter content, and soil pH) along the transact running across the site.

## 3.3 Methodology Development

This section briefly describes methodologies and experimental trials carried out whilst constructing the experimental design of the study. Experimental trials were undertaken to provide the boundary conditions for the different analyses that were to be carried out in order to provide empirical evidence for their applicability in the study.

The section begins with *section 3.3.1* which gives a more detailed description site investigation carried out in Cooper Park Elgin that subsequently led to the withdrawal of the site from the study. The following *section 3.3.2* investigates the effectiveness of various control methods applied in phenol oxidase assays in previous studies. This is to ensure accuracy in validating the origins of phenol oxidase enzyme activity in the study. The final *section 3.3.3* describes various works undertaken before and during CPMAS NMR analysis, including sample and instrument optimisation in order to improve overall data quality.

### *3.3.1 Site Investigations at Elgin*

Permission was obtained from Moray Council to undertake sampling at specific sections of Cooper Park, in Elgin. The area was selected in an attempt to sample away from areas affected by contemporary activities such as heavily sculpted public park features. In addition, records suggest that the area of Cooper Park, adjacent to the Cathedral may have been cultivated and

managed by similar soil management system practiced at the time; the use of refuse for soil improvement, however preliminary assessment of the site indicates otherwise.

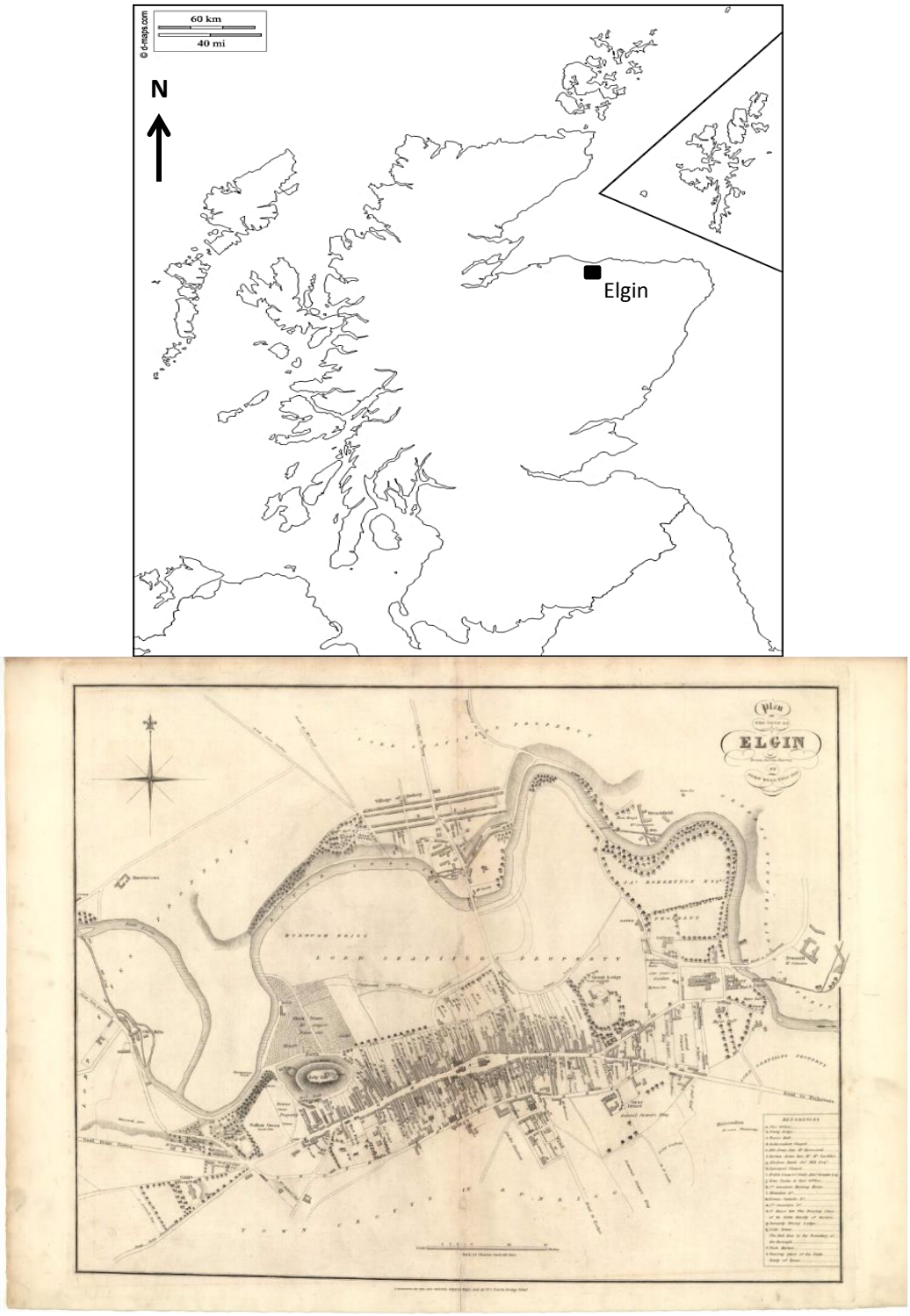



Fig. 3.19. Location of Elgin, Scotland UK (top), Wood 1822 - Plan of the Town of Elgin from actual survey (bottom) [National Library of Scotland (NLS)

The primary Elgin study site (Elgin site 1/ES-1) is located between the levees and the river bank (Figure 3.20), an unmanaged section of Cooper Park. Investigations involved augering at various points within the site to obtain spatial extent of soil deepening. A soil test pit (57° 39.294’ N, 3° 18.737 W) was also dug, to a depth of 60 cm, to gain a better appreciation of the depth of anthropogenic soil deepening. Optically stimulated luminescence (OSL) samples were collected to obtain profile stratigraphic sequence and relative age.

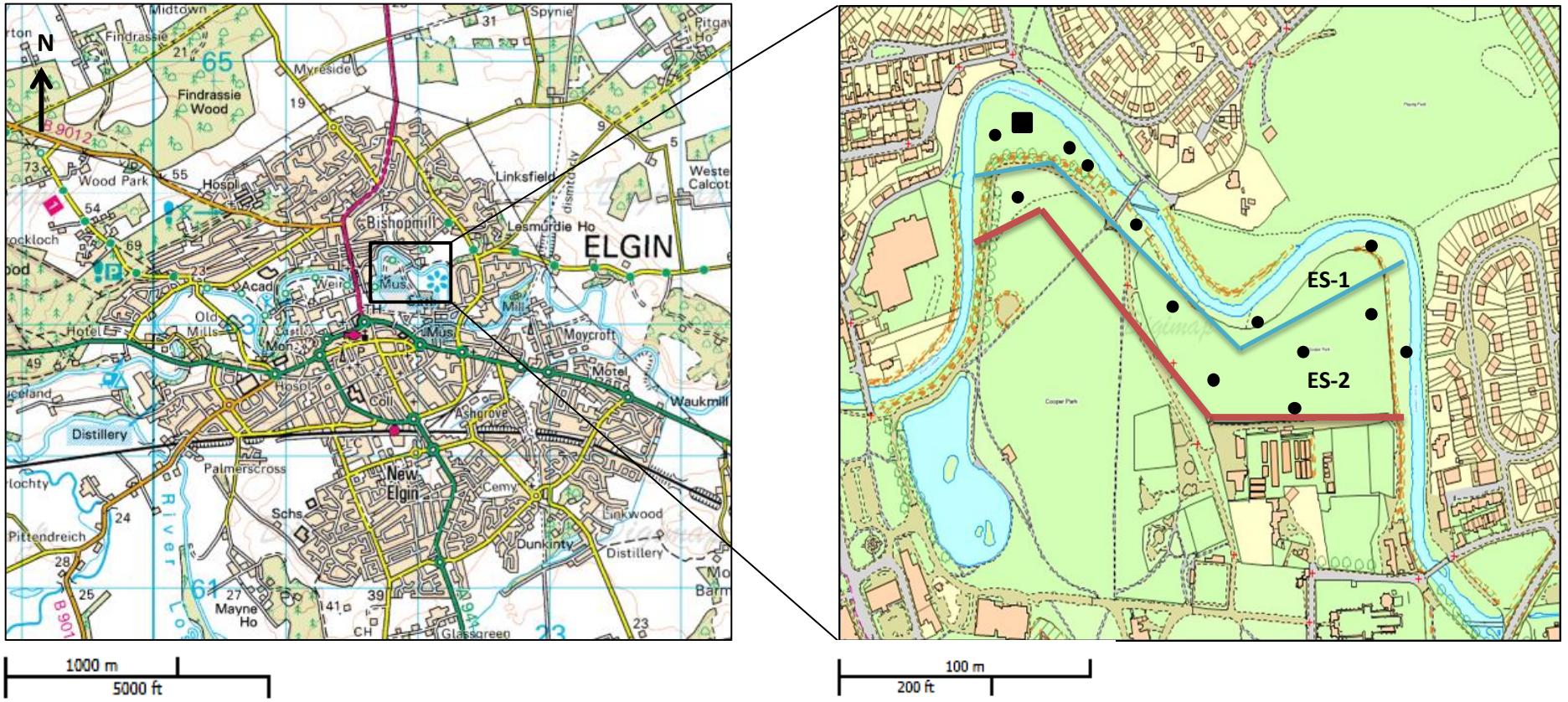



Fig. 3.20. Figure (left) shows the location of Cooper Park. The inset detail (right) shows the location and distribution of sample points in Cooper Park. The first demarcation, defined by the blue line, shows the southern boundary of the initial primary study site (ES-1), while the second demarcation, defined by the red line, depicts the extended sample area (ES-2). Round dots indicate auger test holes; the square block shows the location of soil test pit

Soils were primarily of a sandy texture, gritty and very loose, and low in organic matter judging from soil colour (visual inspection). Auger test samples (100 cm, maximum depth) displayed similar characteristics as seen in the test pit. Initial investigation was limited to the unmanaged section of the site (between the levees and the river bank) but initial findings prompted an extension of the site to the managed areas (ES-2) of the park (Figure 3.20). A series of test holes were dug, to similar depths as above, with an Edelman and a gouge auger to profile soils across the site. Results were in similar accord as seen in the initial site; no clear visual anthropogenic impact to soil – such soil deepening or artefacts such as charcoal – was evident on the site and therefore was subsequently withdrawn as an eligible site for the study.

Results from *ex situ* analysis of OSL samples from the soil test pit shows materials of much greater age on the site than values from other study site (Table 3.4). Typical values of OSL signals ranges from 280 counts for the youngest profile to just under 82000 counts, however luminescence signal intensity in Elgin far exceeds this range (several 10 folds) at all depths suggesting materials of natural origin than anthropogenic. Luminescence signal of comparable intensity can be found only in Roxburgh at a depth of 110 cm. The lower luminescence signal values at the profile base suggest an old deposit that has either been completely or partially bleached from re-exposure to sunlight before subsequent burial.

Table 3.4. Comparison of luminescence signal data of soil pit samples from all study site

| Sample and Location | Depth (cm) | IRSL (photon counts/min) | Post IR-OSL (photon counts/min) |
|---|---|---|---|
| STM-P | 14 | 2462 ± 69 | 6363 ± 93 |
| (*St Andrews*) | 34 | 10443 ± 113 | 42839 ± 212 |
| | 50 | 1095 ± 58 | 4338 ± 81 |
| | 71 | 4368 ± 82 | 25102 ± 165 |
| | 88 | 7316 ± 98 | 29803 ± 179 |
| SSJG-P | 16 | 280 ± 51 | 804 ± 56 |
| (*St Andrews*) | 44 | 445 ± 52 | 1033 ± 58 |
| | 62 | 538 ± 53 | 1367 ± 60 |
| | 94 | 639 ± 54 | 1508 ± 62 |
| BGr-P | 6 | 1495 ± 61 | 2823 ± 71 |
| (*St Andrews*) | 29 | 960 ± 57 | 3003 ± 73 |
| | 42 | 3824 ± 78 | 11718 ± 118 |
| | 61 | 66564 ± 262 | 81771 ± 290 |
| **EGr-P** | **3** | **151622 ± 392** | **307620 ± 557** |
| **(*Elgin*)** | **18** | **451709 ± 674** | **764678 ± 876** |
| | **33** | **1470561 ± 1214** | **1838590 ± 1357** |
| | **48** | **763552 ± 875** | **1000770 ± 1002** |
| RT3-P | 10 | 6245 ± 93 | 3042 ± 74 |
| (*Roxburgh*) | 20 | 390 ± 53 | 1031 ± 59 |
| | 30 | 1159 ± 60 | 12688 ± 123 |
| | 40 | 677 ± 55 | 4242 ± 81 |
| | 50 | 556 ± 54 | 1270 ± 61 |
| | 60 | 544 ± 54 | 1625 ± 63 |
| | 70 | 6830 ± 96 | 10032 ± 111 |
| | 80 | 3825 ± 79 | 11100 ± 116 |
| | 90 | 28067 ± 175 | 100047 ± 320 |
| | 100 | 29395 ± 178 | 106333 ± 330 |
| | 110 | 776102 ± 882 | 1894169 ± 1377 |
| | 120 | 5439 ± 89 | 13761 ± 127 |

*3.3.2 Phenol oxidase enzyme activity – determining suitable controls for phenol oxidase assays*

Many studies that report on methods for determining the phenol oxidase enzyme activity in soil have recommended the use of autoclaved soil as a suitable control in validating the enzymatic origin of phenol oxidase enzyme activity (Floch et al., 2007). The rationale is that enzymes will be denatured at temperatures sustained during autoclaving (121$^{o}$C), however

unconformities to this generalisation is possible because enzymes bound to the mineral matrix of soil can retain functionality even after autoclaving or after undergoing similar heat treatment (Sinsabaugh, 2010). Recent studies by Bach et al. (2013) reported that enzymatic activity was detected in autoclaved soil assay. To determine a suitable control soil sample, phenol oxidase assay was carried out as follows:

Phenol oxidase assays were performed on at least 3 independent occasions and results averaged to eliminate the effects of single localised events/factors on the samples. Three treatments assays; 1) heat-treated samples (autoclaved at 121$^{o}$C for 1 h), 2 & 3) without ABTS and/or soil added to the reaction mixture, were performed, including a control assay (untreated sample). Phenol oxidase activity was expressed in units defined as µmoles of $ABTS^{+}$ formed from ABTS $min^{-1}$ (U) and $g^{-1}$ of dry matter (U $g^{-1}$ DM). Results are displayed in Table 3.5.

Table 3.5. Phenol oxidase assay treatments on enzyme activity. ABTS only (treatment 3) was 3.03 U/g. BGr – P1 & P4, STM – P1 & P5, and RT3 – P1 & P2 are profile samples while SSJG-5 – 1 & 8 are auger samples.

| **Sample** | **Depth (cm)** | **Control samples - (U/g)** | **Autoclaved samples (1) - (U/g)** | **Sample without ABTS substrate (2) - (U/g)** |
|---|---|---|---|---|
| BGr-P1 | 10 | 21.24 | 4.48 | 1.84 |
| BGr-P4 | 60 | 49.77 | 23.65 | 0.40 |
| STM-P1 | 12 | 35.18 | 7.95 | 3.83 |
| STM-P5 | 87 | 50.02 | 16.14 | 2.60 |
| RT3-10 | 0-10 | 43.59 | 10.55 | 2.82 |
| RT3-120 | 110-120 | 155.00 | 59.08 | 6.43 |
| SSJG-5 (1) | 0-20 | 44.02 | 12.21 | 5.06 |
| SSJG-5 (8) | 85-100 | 103.76 | 51.28 | 4.73 |

No notable oxidative activity was detected in treatment 2 and 3 (without ABTS substrate and/or soil added to the reaction mixture). In treatment 1 (autoclaved samples), substrate oxidation was detected albeit 2 – 4 fold less than in the experimental samples. This result contradicts Floch et al. (2007) report on the use of autoclave-sterilised samples as suitable controls, but is in agreement with the findings of Bach et al., (2013) that sterilizing soil samples by autoclaving may not be a suitable method of negative control. Accordingly, autoclaving was not used as a control method in subsequent experimental analysis in the study.

### *3.3.3 $^{13}$C CPMAS NMR Analysis – Enhancing Pre-treatments and Sample Spectra Quality*

The potential to determine quantitative distributions of functional groups in soil organic matter (SOM) is a major attraction of this technique in soil science. Its effectiveness, however, requires careful control of the experimental set-up, an understanding of the samples being investigated, and post-analysis processing operations. As discussed in Chapter 2, many factors such as contact time, spinning side-band (SSBs), recycle delay & signal-to-noise (S/N) ratio, etc. can influence quantitation in solid-state $^{13}$C NMR spectroscopy therefore optimisation of instrument set-up for soil samples was explored together with treatment methods.

#### *3.3.3.1 The Effect of HCl/HF Pre-treatment on $^{13}$C CPMAS NMR Spectra*

Hydrofluoric acid pre-treatment has been shown in many studies to improve quantitation in solid-state NMR spectroscopy by reducing and/or eliminating the effects of paramagnetic materials during analysis. Paramagnetic species can lead to signal loss and broadening, increased relaxation rate, and changes in the chemical shift of resonances. Paramagnetic interferences are most common in, but not exclusive to, samples with a low carbon to iron ratio (C/Fe < 1) (Schmidt et al., 1997; Salati et al., 2008) and treatment of such samples is recommended prior to NMR analysis.

The C/Fe ratio of soil samples was generally less than one (C/Fe < 1), therefore, a subset of untreated samples were analysed to determine the need for sample treatment. The NMR spectra of selected test subsamples obtained from the initial analysis were not quantitative (Figure 3.21) due to high signal to noise ratio and indistinguishable peaks, even though the C/Fe ratio of samples was generally less than one (C/Fe < 1). HCl/HF pre-treatment was therefore subsequently carried out on all samples prior to analysis. Spectra quality was greatly improved after HF treatment (Figure 3.22 and 3.23).

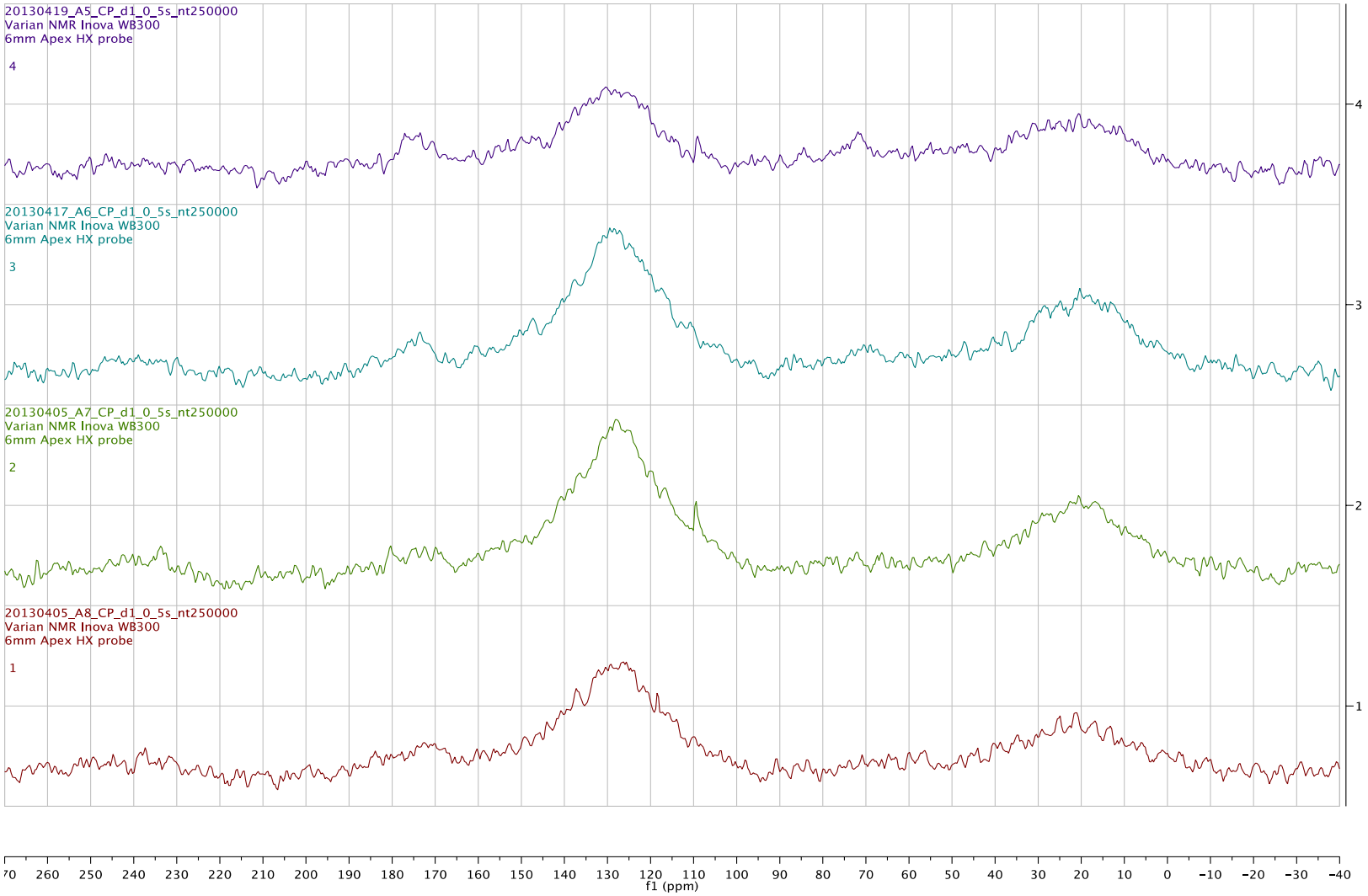



Fig. 3.21. Shows the NMR spectra of soil samples (STM-2) before HCL/HF treatment [base axis – chemical shift – in ppm]

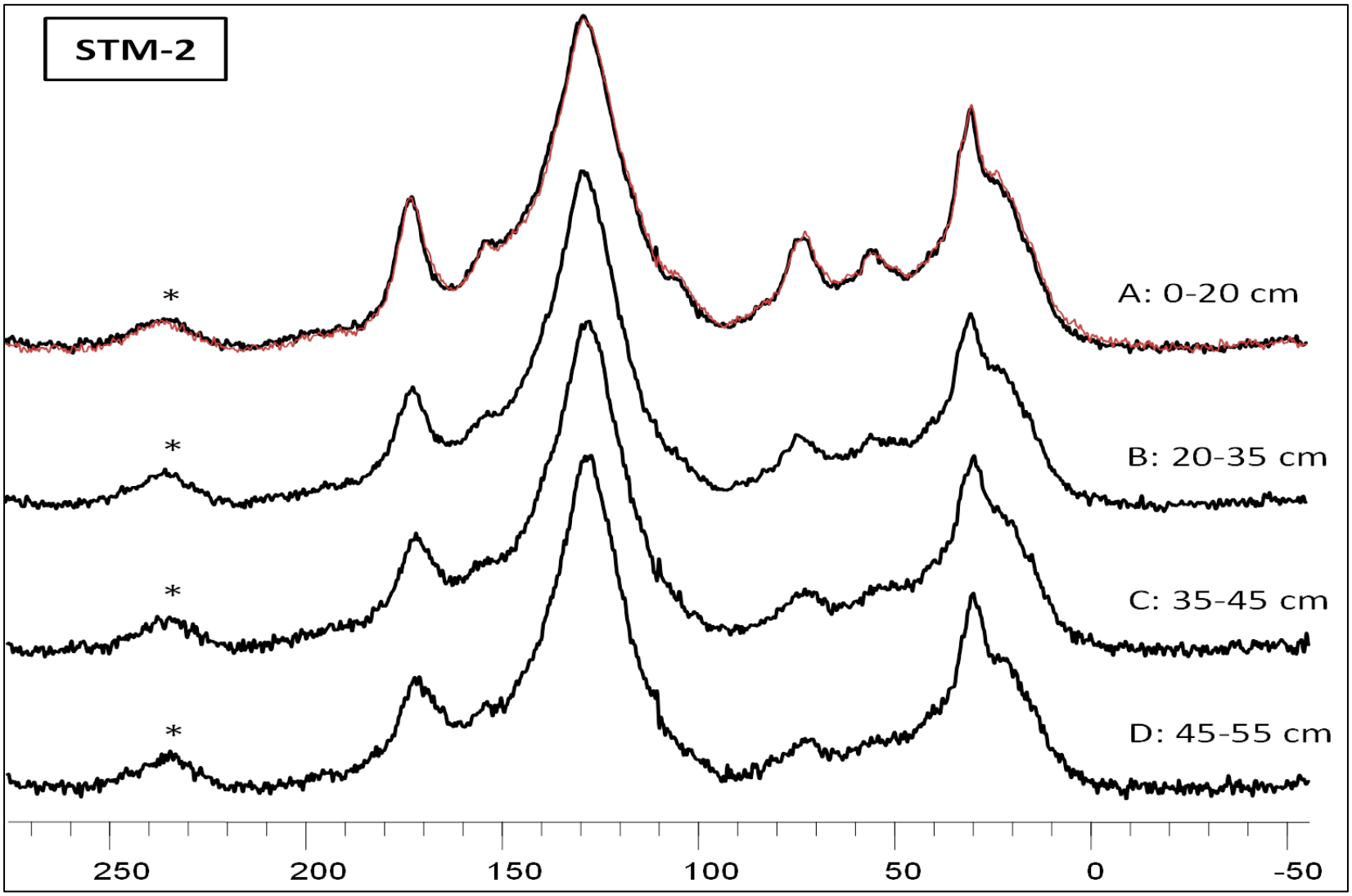



Fig. 3.22. NMR spectra of STM-2 soil sample after HCl/HF treatment [base axis – chemical shift – in ppm]

The alterations to the distribution and chemical composition of the soil organic matter after treatment with hydrofluoric acid are not uncommon and have been reported, although losses are relatively insignificant (Schmidt et al., 1997; Gonçalves et al., 2003). Accordingly, C/N ratio of soil samples before and after treatment were used to semi-quantitatively determine the loss and changes in composition of carbon species in the soil samples. Excessive deviation between the two ratios would indicate that some loss occurred. A comparison of C/N ratio of the samples broadly showed no excessive changes in the ratios (Table 3.6), although some losses may have occurred in SST-1 30-40 cm and BGr-1 30-40 cm sample profile respectively.

Table 3.6. Ratio of carbon to nitrogen content before and after sample treatment with hydrofluoric acid

| **Sample** | **Depth (cm)** | **C/N Ratio - Before (HF) treatment** | **C/N Ratio – After (HF) Treatment** |
|---|---|---|---|
| STM-2 | 0-20 | 8.19 | 7.56 |
| | 20-35 | 8.72 | 8.70 |
| | 35-45 | 9.39 | 10.31 |
| | 45-55 | 13.25 | 11.36 |
| SST-1 | 0-20 | 5.67 | 7.28 |
| | 20-30 | 8.33 | 10.24 |
| | 30-40 | 18.00 | 13.05 |
| | 40-50 | 10.41 | 11.92 |
| SSJG-1 | 0-20 | 10.08 | 7.98 |
| | 20-35 | 8.67 | 9.18 |
| | 35-50 | 13.02 | 10.06 |
| | 50-60 | 8.76 | 10.55 |
| BGr-1 | 0-20 | 8.21 | 7.37 |
| | 20-30 | 9.82 | 9.57 |
| | 30-40 | 17.00 | 11.31 |
| | 40-50 | 10.86 | 12.42 |

Based on C/N ratio and the distribution of signal intensity of the chemical shifts on the spectra, excessive loss of and/or changes in organic matter composition was considered low, except for possible loss of carbohydrates, however, these losses are considered minimal and within acceptable limits for improved data quantitation in solid-state NMR spectroscopy.

*3.3.4 Determining $^{13}C$ CPMAS NMR Instrument Parameterisation Appropriate for the Study Samples*

In order to optimize instrument operation, data acquisition process and quality, several adjustments to instrument set-up were performed. Standard cross polarisation (CP) technique was applied on all samples. Samples were experimented on parameters such as (i) contact time to ensure that all $^{13}C$ nuclei in the sample are resonating at or near their maximum intensity, and (ii) the delay time (d1) is sufficient enough to allow for optimum relaxation between pulses. The superimposed coloured spectrum represents the use of different delay and contact times, to improve spectra quality. The red spectra in SSJG-1 (Figure 3.23) represents a shorter delay time (d1) of 0.5 s and a contact time of 1500 µs. The green spectrum represents a delay time of 0.5 s and a shorter contact time of 1000 µs. A delay time of 1.5 s and a contact time of 1500 µs were used for all samples as standard CP spectrum.

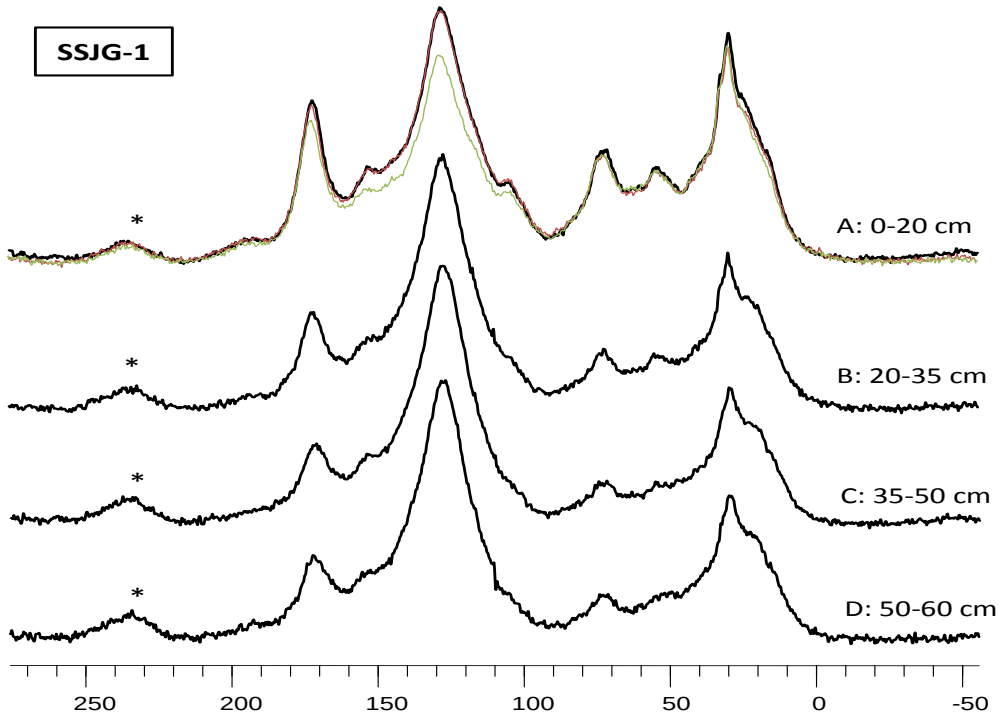



Fig. 3.23. NMR spectra of SSJG-1 soil samples labelled by depth of sample. All samples pre-treated by HCl/HF treatment [base axis – chemical shift – in ppm]

**CHAPTER 4**

# Impacts of Historical Land Management Systems on the Physical and Chemical Characteristics of Soils within Medieval Urban Site

## 4.1 Introduction

Anthropogenic activities are major agency of change to the environment besides natural courses and occurrences. Humans and their ancestors have influenced the environment from their inception through both minor and major, and direct and indirect modifications. One of the main contributors to these events was the discovery of agriculture and the subsequent associated changes in practices such as burning, forest clearance etc. that accompanied it. These cultural changes inevitably led to widespread alterations to not only soils but to vegetation and the climate (Bridges, 1978; Ruddiman, 2003; Ellis et al., 2013).

In this chapter, the chemical composition of the organic matter, resulting from past land management practices found in the medieval burgh of St. Andrews, Scotland is explored using a variety of techniques. Documentary records have shown that historical waste management practices involved the deposition of a variety of waste material, predominantly organic, to soil within and outside the municipality as fertiliser to improve soil conditions. We applied solid-state $^{13}C$ CPMAS NMR spectroscopy to determine the chemical composition of the resultant soil organic matter. *In situ* magnetic susceptibility measurement of exposed profiles is used to ascertain the influence if any of the pyrogenic materials deposited, particularly ash/charcoal, to the soil's inherent magnetic properties. Finally, soil micromorphology and image analysis were used to investigate the micro distribution of materials, especially organic residues (e.g. charcoal) within the soil profiles.

### *4.1.1 Man's Activity and the Environment*

Man's impact on the environment has been very much underrepresented in past pedological studies however his influence is no longer disputable (Dudal et. al., 2002). The intensity and impacts of these activities have increased with the passage of time to the present day as population increased and technology advanced (Bridges, 1978; Price et al., 2011). As discussed in Chapter One, *section 1.1.1*, man is recognised in the fundamental equation of soil-forming factors by Hans Jenny as a potent biological soil-forming factor capable of not only influencing soil formation but can equally alter the actions of other variables (Jenny, 1941; Bidwell and Hole, 1965; Bridges, 1978; Dudal et. al., 2002; Adler, 2003; Mason, 2003; Ruddiman, 2003; Hillel, 2008; Adderley et al., 2010; Steffen et al., 2011). However, the capacity of man's activities to alter the environment to such a degree makes a very good case for the consideration of humans as a separate biotic factor in soil formation (Bidwell and Hole, 1965).

### *4.1.2 Anthropogenic Soil Modification*

The development and spread of agriculture is routinely associated with periods of observable anthropogenic impacts on the environment (Ruddiman, 2003; Steffen et al., 2011). Soil modification prior to the transition from hunter-gatherer to agricultural and pastoral community was prevalent but at a small-scale (Ruddiman, 2003; Hillel, 1992; Rowell, 1994). More importantly, the transient nature of the nomadic culture meant that waste disposal was not a problem in these communities as wastes produced were marginal in comparison and were readily disposed of (Rathje and Murphy 2001). Changes in the cultural paradigm brought about by the adoption and development of agriculture gave rise to the establishment of permanently settled communities. These communities were not without the associated problems of how to manage the increased production of waste materials generated. One

commonly known strategy of managing waste was its use in agriculture. The large-scale utilisation of wastes for soil amendment almost certainly began with the development of agriculture, and despite the development and use of industrial fertilizers in the 20th century, continues to the present-day (Polprasert et al., 1982; Strauss, 1986; Oram, 2011). Documentary records of past management practices have confirmed the use of waste for soil improvement in agriculture. A variety of soil analyses have been applied to examine the time-depth of such amendment at a variety of locations worldwide.

The routine use of waste in cultivation have been traced to as far back as 2300 years in Pseira Islands, Crete, where household rubbish were applied to cultivated terraces (Bull et al., 2001). Similarly, the formation of Amazonian Dark Earth (*terra preta* and *terra mulata*) in South America provides evidence for enduring pre-Colombian practices of soil enhancement through application of domestic waste (Sombroek et al., 2002; Woods and McCann, 1999). The use of waste as fertiliser is not restricted to ancient cultures. Studies have indicated that this practice was ongoing in many historic Scottish and British towns until the early-modern periods (Macdonald, 1884; Bridges, 1978; Murray, 1982; Clark, 1997; Hall 1997; Cachart, 2000; Carter, 2001; Bowler, 2004; Davidson et al., 2006; Herbert, 2009; Golding et al., 2010; Oram, 2011). Mechanisms of waste production include by-product of domestic, manufacturing (crafts, tanning) and processing activities (slaughter houses and fish gutting) (Oram, 2011). Studies by Brothwell (1982), on the urban man and his environment, indicates that an estimated 182,000 litres of urine, 182,000 kilograms of solid waste, 8000 kilograms of ash from cooking and heating, and 36,000 kilograms of human faeces were produced annually per 100 households in pre-industrial societies. Composted urban waste which generally consist of human bodily waste (faeces and urine), food waste, animal dung, fuel residue (ash, charcoal), butchery shambles (bones, flesh, shells), and other debris, were valued commodity and highly sort after by both subsistence and commercial farmers (Oram, 2011).

Parallels of this anthropogenic practice can be seen from the North Western European practice of plaggen cultivation. Dating back to more than 3000 years in the island of Sylt, Germany, soil enrichment was accomplished by the addition of organically rich material, such as turf, mud, peat, animal dung, including coarser materials such as beach sand (Pape, 1970; Simpson, 1997; Blume and Leinweber, 2004; Guttman et al., 2005). Evidence of plaggen cultivation has been found in other parts of Germany, in France, Netherlands, Belgium, Denmark, Norway, Russia and north Atlantic islands; Shetland, Orkney (Pape, 1970; Simpson, 1997; Davidson and Carter, 1998; Simpson et al., 1998b; Blume and Leinweber, 2004; Bokhorst et al., 2005; Davidson et al., 2006; Hubbe et al., 2007; Thomas et al., 2007; Oram, 2011). Other examples of deep anthropogenic soils have also been found in Australia (Downie et al., 2011), Africa (Lehmann, 2009; Fairhead and Leach, 2009) and in various other locations around the world with history of early anthropogenic occupation (see also Blume and Leinweber, 2004). Overtime, cultural and geographical differences gave rise to variations in management practices which are visible today from the development of different diagnostic horizons (terric, plaggic, irragric, anthraquic, hydragic, and hortic horizons) (WRB, 2006). Today these soils denote a legacy of historical agricultural and waste management practices.

The distribution, and degree of modification of deep anthropogenic soils in Scotland and elsewhere in the United Kingdom are generally known to be greatest within settlement core areas, with diminishing occurrence away from the settlement (Oram, 2011; Golding 2008, pp.189, 276) although significant deepening of soil outside the settlement core areas is not uncommon and have been reported (Davidson et al., 2006). This pattern of distribution where soils with higher nutrient statues (e.g. organic matter) and artefacts are found in or within closer proximity to the settlement is widespread and can be seen in plaggen (black and brown) soil distribution in Europe (Pape, 1970), and in Amazonian dark earth (*terra preta* and *terra mulata*) in South America (Woods and Denevan, 2009; Balee, 2010) similar modes of formation for such soils have also been reported in West Africa (Fairhead and Leach, 2009).

Geoarchaeological investigation of these soils (anthrosols) have elucidated on the practices that have led to their formation and the sources and nature of the transformative agents in the soil.

One of the general characteristic features of anthropogenically modified soil is the occurrence of charred material such as charcoal and ash and although not exclusive to anthropogenically disturbed soils and can be found in various measures in natural soils, levels are generally lower than in their modified counterpart (Schmidt and Noack, 2000; Solomon et al., 2007). The presence of pyrogenic material in natural soils arise from direct and indirect sources; direct sources may be from forest fire, and/or bush fires while indirect sources arise from movement of allochthonous materials such as (waste from fossil fuel burning, coal, wood etc) through various transported medium (wind, river, rain). Source of charred material in anthrosols are due to deliberate addition of autochthonous materials such charcoal and ash from fires and hearth onto soil although other indirect sources may also contribute to this albeit a small amount. High levels of charred organic carbon, sometimes visible from soil colour, are characteristic properties of heavily modified anthropogenic soils found around the world (Pape, 1970; Davidson and Carter, 1998; Schmid et al., 2001; Schmid et al., 2002; Davidson et al., 2006; Hubbe et al., 2007; Fairhead and Leach, 2009; Balee, 2010). Spectroscopic examinations of these soils have associated their relatively high charcoal contents, and dark colour, to high aromatic C carbon peak in Carbon-13 NMR spectra analysis (Schmidt et al., 1999; Novotny et al., 2009; Downie et al., 2011).

In this Chapter, we investigate the impacts of historical practices on the physical and chemical properties of soil, with particular focus on the chemical composition of soil organic carbon and relate the results to the research outcomes reported on other anthropogenic soils around the world. To do this, a series of questions were devised;

1) Is there a difference in the organic matter content and composition between soils within and outside the settlement core area (hinterland)?
2) Does variation in soil colour with depth arise from the differences in the amount of charred organic material in the soil, and is this reflected in the signal intensity of the aromatic C region of the respective NMR spectra?

## 4.2 Materials and Methods

This study was carried out in St Andrews, Scotland (see Chapter 2, *section 2.1.1* for details on the study site). The study area was sectioned into four sampling sites (STM, SST, SSJG, and BGr), beginning from what is believed to be the medieval town core and extended towards the outer perimeters of the medieval town, the hinterlands/fields (see *section 3.1* in Chapter 3 for more details on sampling). *In situ* magnetic susceptibility measurements were undertaken on auger holes and soil pit profile face. A series of laboratory analysis were carried out on auger profile sub-samples (STM-2, SST-1, SSJG-1, and BGr-1) and their corresponding soil pit profile samples (STM-P, SSJG-P, and BGr-P); details of which are provided in Chapter Three. A total of 29 samples were analysed.

## 4.3 Result and Discussion

### *4.3.1 Elemental Analysis, pH values*

Table 4.1 shows the results of the elemental analysis on STM-2, SST-1, and SSJG-1 sites located within St Andrews' medieval core area and BGr-1 site located outside the medieval town. The organic carbon content and nitrogen content on the sample sites from within the core areas (STM-2, SST-1, SSJG-1) are considerably higher than in samples outside the town (BGr-1) at all depths. The differences are more pronounced at depths of between 40 – 60 cm depending on the site's overall profile depth. This pattern of enrichment is not uncommon on historical sites

and is in-line with observations from previous works carried out in Nairn, Perth, Pittenweem, Lauder and Wigtown where soil modification was reportedly more intense within burgh backlands (gardens) than in the surrounding burgh acres (fields) (Clark 1997; Carter 2001; Bowler 2004; Dercon et al., 2005) although significant modification of soil outside the settlement core areas is not unusual and has been reported (Davidson et al., 2006).

Table 4.1. Total organic carbon and nitrogen content, C/N ratios, pH, and phosphorus concentrations of soils in all 4 sample sites within the study area

| Sample | Depth (cm) | $C_{org}$ (%) | $N_T$ (%) | C/N ratio | pH ($CaCl_2$) | P (mg/kg) |
|---|---|---|---|---|---|---|
| STM-2 | 0-20 | 8.44 | 1.03 | 8.19 | 6.58 | 9209 |
| | 20-35 | 5.23 | 0.60 | 8.72 | 6.33 | 8041 |
| | 35-45 | 3.38 | 0.36 | 9.39 | 7.00 | 8420 |
| | 45-55 | 3.71 | 0.28 | 13.25 | 6.77 | 9326 |
| SST-1 | 0-20 | 7.83 | 1.38 | 5.67 | 6.82 | 8004 |
| | 20-30 | 4.58 | 0.55 | 8.33 | 6.85 | 6967 |
| | 30-40 | 2.88 | 0.16 | 18.00 | 7.20 | 6332 |
| | 40-50 | 3.02 | 0.29 | 10.41 | 7.24 | 5080 |
| SSJG-1 | 0-20 | 7.26 | 0.72 | 10.08 | 6.71 | 7098 |
| | 20-35 | 5.20 | 0.60 | 8.67 | 6.88 | 6695 |
| | 35-50 | 5.73 | 0.44 | 13.02 | 7.16 | 8589 |
| | 50-60 | 3.33 | 0.38 | 8.76 | 7.16 | 8420 |
| BGr-1 | 0-20 | 3.45 | 0.42 | 8.21 | 5.98 | 2943 |
| | 20-30 | 3.24 | 0.33 | 9.82 | 6.13 | 2785 |
| | 30-40 | 2.21 | 0.13 | 17.00 | 6.22 | 1639 |
| | 40-50 | 0.76 | 0.07 | 10.86 | 6.31 | 995 |

The contrast in the organic carbon and nitrogen content between sites located within and outside the historic burgh core is attributed to the beginning of utilisation of urban waste, the volume of materials deposited, and period of accumulation, all of which are associated with and to a degree dependent upon the establishment of the settlement in *circa* 1150. According to Brooks and Whittington (1977), the development of the medieval burgh of St Andrews involved a four stage development phase, expanding westward away from the cathedral

precinct (see Figure 4.1). Consequently it is logical to assume that impacts to soil (modification) visible from the higher organic carbon enrichment in soils within the core area will be more pronounced in areas of the settlement that were first inhabited (phase 1), with diminishing intensity of alteration in areas that were later occupied as the burgh expanded.

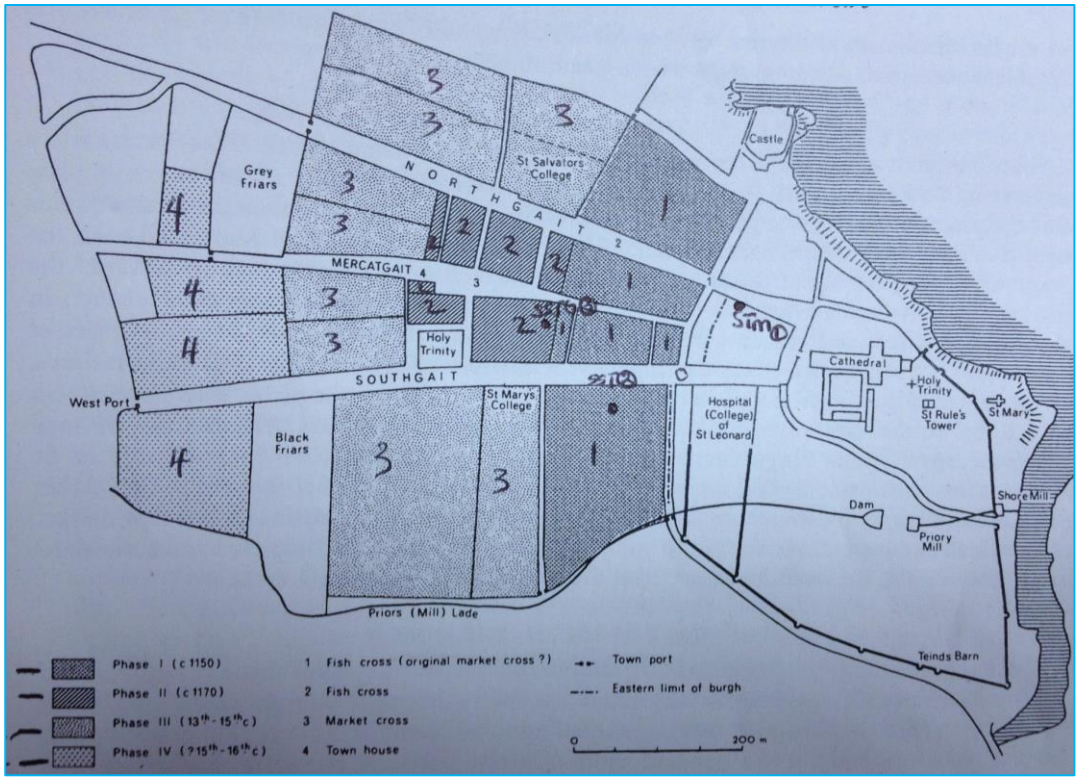



Fig. 4.1. Planning and growth phases of Medieval St Andrews; numbers 1 to 4 and corresponding shading represent the four stages of development of the burgh (map from Brooks and Whittington, 1977)

The anomalous variations in the organic carbon and nitrogen content with depth within sites arise from the differences in inputs and management strategy of individual plots at various stages of soil development and periods of land ownership or leasehold (Oram, 2011). Documentary records reveal that burgesses were allocated plots of land in the surrounding fields, in addition to their own backlands, which were principally used for the cultivation of their own dietary staples. Whilst many burgesses utilised their allocated fields either by themselves or cultivated on their behalf by employing labourers, some chose to lease it out to

other burgesses and/or in-dwellers i.e burgh residents who lacked the economic privileges of full burgess status (Davidson et al., 2006; Golding et al., 2010; Oram, 2011). The upkeep of each plot of land in terms of replenishment and maintenance of soil nutrient to maximise output becomes a responsibility of the keeper. Factors such as the volume of materials (fertiliser) accessible and therefore deposited, the composition of the mixtures (nutrient status), the area of the plot, which are in turn influenced by the social status of the individual by how much of these fertiliser can be procured, in addition to their own waste production, would result in large spatial variations in soil properties within relatively small distances.

The generally high total P concentrations in STM-2, SST-1, and SSJG-1 sites within the burgh are indicative of the degree of anthropogenic influence in these locales. This provides evidence to support the use of domestic refuse and human waste for soil enrichment. Additionally, the elevated total P concentrations found within the burgh core areas over lower concentrations found in BGr-1 site, outside the historic burgh core, also reflects the scale and length of time over which they have been exploited (Davidson et al., 2006; Golding 2008, pp.189, 276). Soil pH values on all sites are within similar pH range of between 6.0 and 7.3 (slightly acidic to neutral) although values for BGr-1 samples outside the historic burgh core area are typically on the lower end of the range (slightly acidic) but are not overly discordant. Weak correlation between pH and total P concentration (not shown) suggests that element retention has not been significantly influenced by post depositional effects. Similar to organic carbon content, total nitrogen content is greater on sites located within the historic burgh (0.16 to 1.38 %) than those outside the burgh (0.07 to 0.42 %) (Table 4.1). The C:N ratio follows no clear discernible pattern in all study sites and it varies between 5.67 and 18. These values, however, do indicate the relative degree of humification of the organic material (Tan, 1993; Schmid et al., 2001).

The particle size distribution data (Table 4.2) shows the dominance of silt and fine sand. The general decrease in clay and silt content and corresponding increase in sand content towards the surface is atypical to reported distribution patterns in deepened soils where an increase in the proportion of clay, silt and fine sand in upper horizons of deepened soil has been associated with anthropogenic inputs of finer material into soil (Dercon et al., 2005; Davidson et al., 2006). The distribution pattern of grain size across the study sites is interpreted here as being indicative of the homogeneity in the composition of material and the relative lack of deviation in the system of management through time, as well as suggestive of the inputs of coarser material.

Table 4.2. Grain size distribution pattern of soil in sample area

| Sample | Depth (cm) | Clay (%) | Silt (%) | Fine Sand (212µm) (%) | Medium Sand (630µm) (%) |
|---|---|---|---|---|---|
| STM-2 | 0-20 | 3.39 | 51.71 | 33.30 | 11.60 |
| | 20-35 | 3.08 | 51.42 | 30.50 | 14.60 |
| | 35-45 | 4.77 | 47.13 | 34.70 | 13.40 |
| | 45-55 | 5.17 | 62.93 | 29.80 | 2.10 |
| SST-1 | 0-20 | 4.09 | 64.01 | 30.60 | 1.30 |
| | 20-30 | 5.99 | 71.01 | 22.50 | 0.50 |
| | 30-40 | 11.00 | 89.00 | 0.00 | 0.00 |
| | 40-50 | 10.10 | 89.86 | 0.04 | 0.00 |
| BGr-1 | 0-20 | 6.60 | 68.60 | 24.30 | 0.50 |
| | 20-30 | 7.28 | 69.52 | 22.70 | 0.50 |
| | 30-40 | 8.36 | 55.64 | 34.60 | 1.40 |
| | 40-50 | 17.70 | 82.30 | 0.00 | 0.00 |

*4.3.2 Site Depositional History*

Optically stimulated luminescence data profiling of the soil pit samples (STM-P, SSJG-P, BGr-P) are displayed in Table 4.3. In Figure 4.2 below, the IRSL and post-IR OSL signals are plotted to show variation of the luminescence signal with depth which can be used to construct the depositional history or sequence of sediments in a given location (Sanderson and Murphy,

2010; Munyikwa et al., 2012). Site stratigraphic integrity and relative age of individual stratigraphy can therefore be determined on the bases of Steno's principle of superposition which states that each layer of an undisturbed sedimentary sequence is younger than the one beneath it and older than the one above it (Coch and Ludman, 1991; Grotzinger et al., 2007; Grotzinger and Jordan, 2010).

Table 4.3. Luminescence signal data of soil pit samples; STM-P, SSJG-P, and BGr-P

| Sample | Depth (cm) | IRSL (photon counts/min) | Post IR-OSL (photon counts/min) | IRSL/OSL Ratio |
|---|---|---|---|---|
| STM-P | 14 | 2462 ± 69 | 6363 ± 93 | 0.39 |
| | 34 | 10443 ± 113 | 42839 ± 212 | 0.24 |
| | 50 | 1095 ± 58 | 4338 ± 81 | 0.25 |
| | 71 | 4368 ± 82 | 25102 ± 165 | 0.17 |
| | 88 | 7316 ± 98 | 29803 ± 179 | 0.25 |
| SSJG-P | 16 | 280 ± 51 | 804 ± 56 | 0.35 |
| | 44 | 445 ± 52 | 1033 ± 58 | 0.43 |
| | 62 | 538 ± 53 | 1367 ± 60 | 0.39 |
| | 94 | 639 ± 54 | 1508 ± 62 | 0.42 |
| BGr-P | 6 | 1495 ± 61 | 2823 ± 71 | 0.53 |
| | 29 | 960 ± 57 | 3003 ± 73 | 0.32 |
| | 42 | 3824 ± 78 | 11718 ± 118 | 0.33 |
| | 61 | 66564 ± 262 | 81771 ± 290 | 0.81 |

The luminescence signal intensities of a depositional sequence are influenced by variables such as dose rate, luminescence sensitivity, mineralogy, burial age, depositional rate, and level of bleaching experienced prior to burial. When all these variables other than time are held constant, the relative variation of luminescence signals up a stratigraphic profile would be a function of the burial ages of the depositional units.

The luminescence signal of individual sites differed. Of all the sample sites, SSJG-P site produced the lowest luminescence signal suggesting that its materials are of a relatively young age than those from STM-P and BGr-P sites. The gradual increase in the luminescence signals with depth in SSJG-P site indicates that the stratigraphic sequence at the site has not been

disturbed since it was last emplaced (Figure 4.2). IRSL and post-IR OSL signal in STM-P site fluctuates with depth most notable between 34 – 50 cm, indicating mixing of sediments of different ages. The luminescence signal intensity is generally highest in STM-P site than in SSJG-P and BGr-P sites. This is expected since soil modification would have initially begun in the core area (STM-P) from when the settlement was first established so that the accumulation and subsequent burial of material occurred at an earlier period on the site, prior to subsequent burgh expansion into areas where site three is currently located where similar transformation and burial of material would have occurred at a later stage. Furthermore the occurrence of soil deposits of younger depositional age in SSJG-P site at similar profile depth (100 cm) as in STM-P site is indicative of the different rate of accumulation in both sites. In SSJG-P, this is suggestive of rapid accumulation of materials with relatively short intervals between each successive deposition, and vice versa in STM-P.

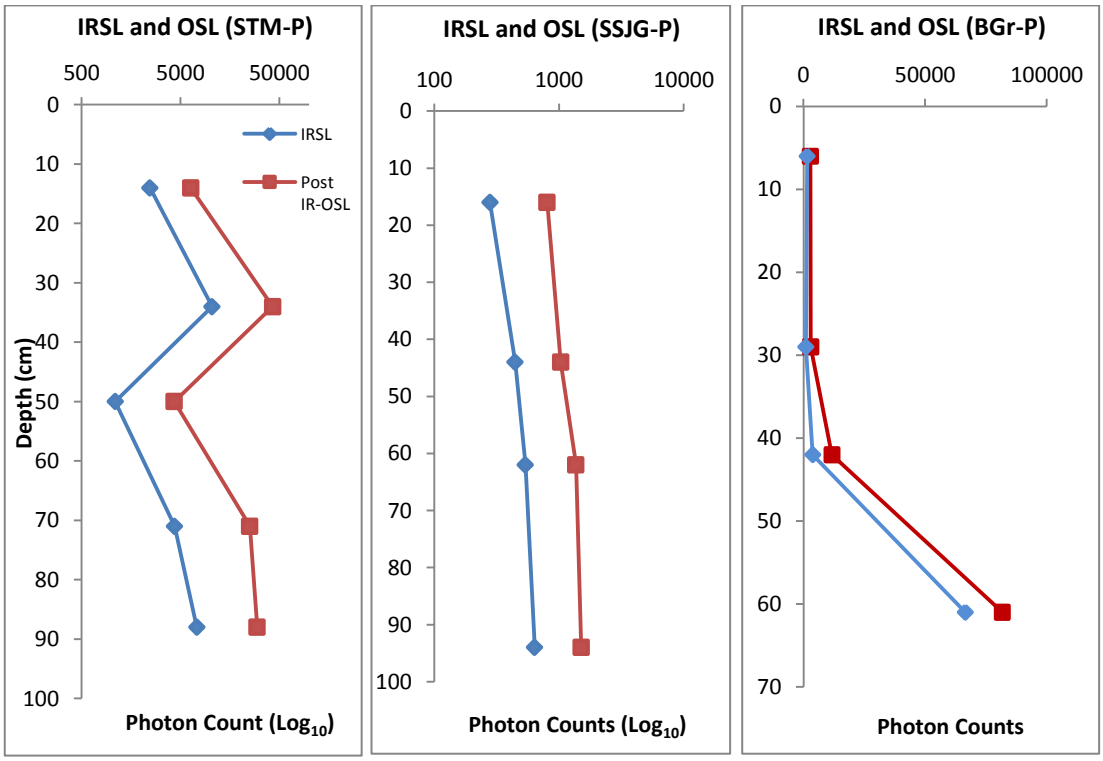



Fig. 4.2. Graph illustrating the optically stimulated luminescence signal of soil profile on sample sites from St Andrews

BGr-P site is located outside the maximum expansion range of the medieval settlement, an area which would have served as burgage plot or hinterland used for either cultivation (arable, pasture) or livestock grazing. The luminescence signal on the site generally increased with depth until 45 cm where a sharp increase in signal intensity is observed. The noticeable increase in IRSL and post-IR OSL luminescence signal at 60 cm from just under 12000 counts at 45 cm to over 80000 counts at 60 cm suggest that the maximum depth of anthropogenic influence on the site was at 45 cm, below which is a transition to more natural parent material (clay) of much older age (Table 4.3; Figure 4.2). This finding also corresponds with the elemental data of the site where sharp decreases in organic carbon content, nitrogen content and total P content were observed at similar depth (60 cm) (Table 4.1). Also in agreement is the particle size distribution data as significant increase in the clay proportion in the profile is evident at 60 cm (Table 4.2). Given the relatively constant IRSL/OSL ratio in all the sites and until 45 cm in BGr-P site (Figure 4.3), the variations in luminescence signal down the profile most likely reflects the burial age of the sediments (Sanderson and Murphy, 2010; Munyikwa et al., 2012), than variations in the mineralogical characteristics and by extension the dosimetry of the site.

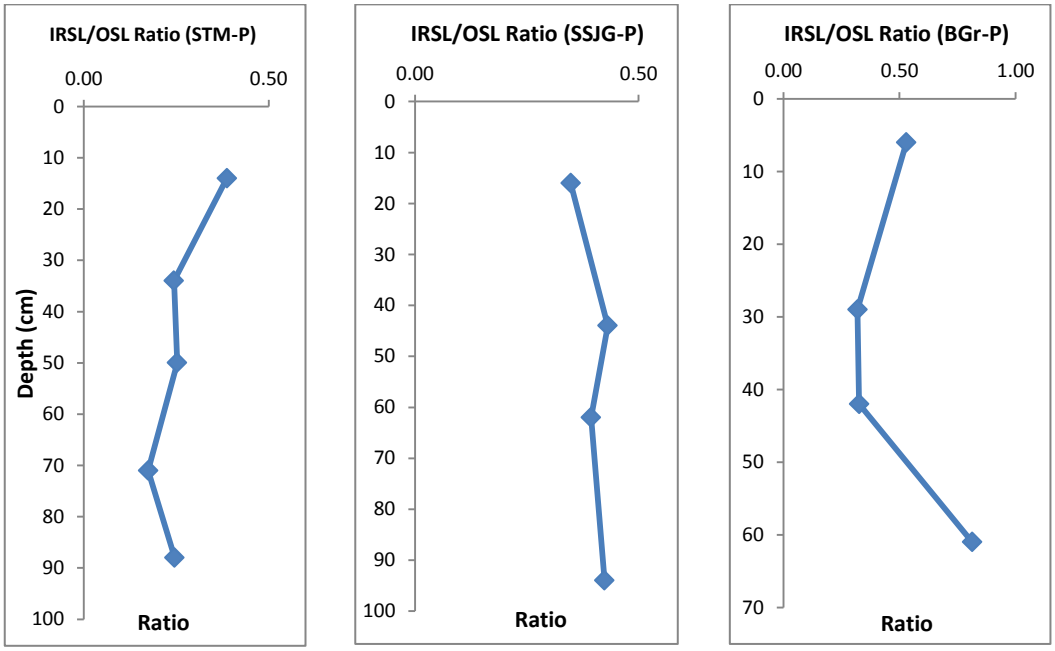



Fig. 4.3. Ratio of infra-red (IRSL) luminescence to blue light (Post-IRSL)

Generally, soil deepening is greatest in STM-P and SSJG-P sites and lowest in BGr-P site. The relative range of luminescence signal intensity of individual sites, until 45 cm for BGr-P site, suggest that the profiles in STM-P and SSJG-P site are still within anthropogenic deposits rather than into natural material as seen in BGr-P site (Figure 4.2). As previously mentioned, the relatively constant IRSL/OSL ratio throughout the profiles on all the sites, other than after 45 cm in site three where there is a noticeable deviation, confirms this assessment as the ratio of IRSL to OSL is used as a proxy to indicate changes in mineral characteristics within sediment stratigraphy. The greater variation in IRSL/OSL ratio between 45 and 60 cm in BGr-P sit may indicate changes in mineral composition within the profile.

### *4.3.3 Magnetic Susceptibility and Colour*

Table 4.4 shows the volume magnetic susceptibility (ƙ) of soil pit samples with depth on all the sample sites. Enhanced magnetic susceptibility values were observed in samples within the settlements (STM-P, SSJG-P) than in those outside the settlement (BGr-P).

Table 4.4. Volume magnetic susceptibility of soil profiles with depth

| **Depth (cm)** | **Volume magnetic susceptibility (ƙ) in SI ($10^{-5}$)** | | |
|---|---|---|---|
| | **STM-P** | **SSJG-P** | **BGr - P** |
| 10 | 253 | 258 | 7 |
| 20 | 413 | 262 | 96 |
| 30 | 229 | 226 | 56 |
| 40 | 223 | 252 | 56 |
| 50 | 258 | 211 | 150 |
| 60 | 285 | 211 | 15 |
| 70 | 340 | 321 | 14 |
| 80 | 210 | 273 | - |
| 90 | 192 | 171 | - |
| 100 | 240 | 248 | - |

The firing or burning of materials have long been associated with human habitation in archaeological sites because the resultant effect to soil is visible from the enhancement of magnetic susceptibility termed 'thermoremanent magnetism' (Crowther, 2003; Dalan, 2006; Schmidt and Noack, 2000). During burning, weakly magnetic iron oxides (magnetite – $Fe_3O_4$, and maghemite – $Fe_2O_3$) in the clay and silt particles heated above their curie temperature (~600-700°C) can gain an enhanced magnetic signature. Similarly, fired bricks and pottery can also display thermoremanence and consequently enhanced magnetic properties.

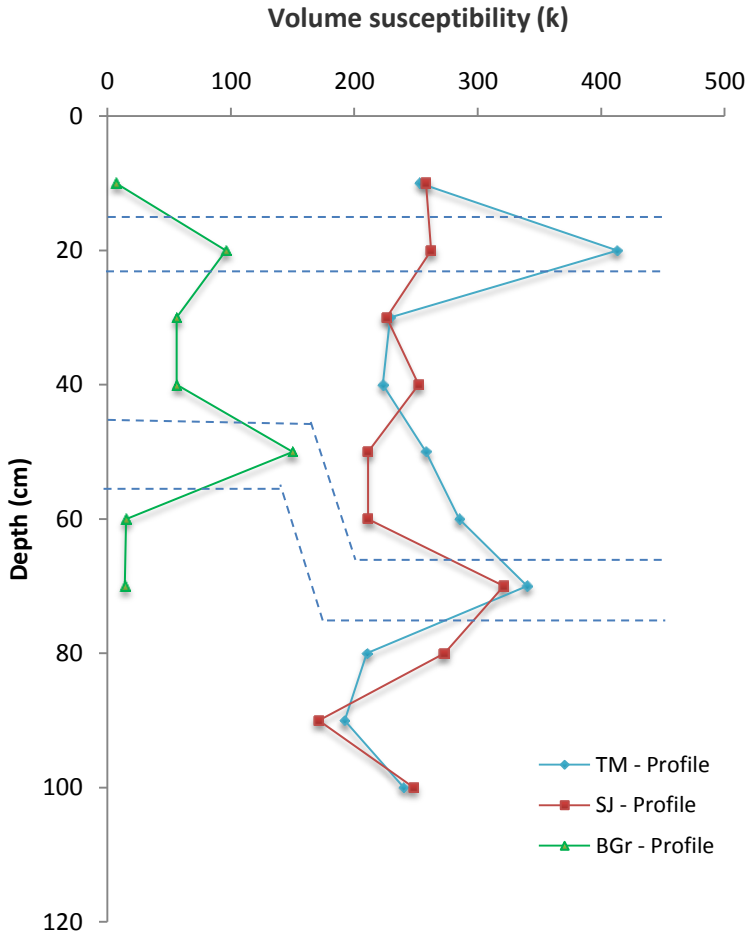



Fig. 4.4. Variation in volume susceptibility of soil profiles with depth (TM = **STM-P**, SJ = **SSJG-P**, and BGr = **BGr-P**).

Marked differences in magnetic susceptibility between sites are primarily attributed to the differences in the volume of autochthonous and allochthonous inputs of pyrogenic material to the soil (Figure 4.4). Although magnetic properties are typically enhanced by onsite burning, it is conceivable that sufficient addition of fragments of fired pottery and bricks, including ash and/or charcoal can alter the magnetic properties of soil (James, 1999). Also a contributing factor to the magnetic enhancement observed is the plausible presence of small bacterial magnetosome components (biomagnetism). The activities of magnetotactic bacterium, found in organic-rich materials such as in midden content, are known to increase magnetic signatures from the production and accumulation of magnetic crystals such as magnetite (Peter et al., 2000; Schmid et al., 2002). Magnetic anomalies (peaks) highlighted at 70 cm in both STM-P and SSJG-P, and manifested at 50 cm in BGr-P profile may be interpreted as variations in the composition of midden content deposited on soil, that is, the deposition of high content of material of pyrogenic origin, during the period of such practices and reflects the similarities in anthropogenic land use and therefore management system across the settlement (Figure 4.4). The small peaks observed at 20 cm depth across all sites, more pronounced in STM profile, further supports the view. This assessment is in agreement with reports from previous studies in prehistoric sites where higher magnetic values were found in archaeological soils than those of the surrounding soil.

Soil colour is widely associated with the relative content of organic material in the soil. Darker colours are often associated with high organic matter content while lighter colours are indicative of low organic matter content. Schmid et al. (2001; 2002) and Downie et al. (2011) reported a correlation between darker soil colour and organic carbon content in anthropogenically modified soil in Neolithic settlement sites in Germany and Aboriginal sites in Australia. $^{13}C$ NMR analysis of these sites revealed that this relationship was mostly due to the

considerably high contributions of aromatic C in the region of the spectra of the respective soils compared to the surrounding contemporary soils.

Table 4.5. Soil profile colour and charcoal content

| Sample | Depth (cm) | Colour (Munsell) | Charcoal content (Area covered ($mm^2$)) |
|---|---|---|---|
| STM-P1 | 12 | 10YR 2/1 (black) | 4.66 |
| P2 | 30 | 10YR 2/2 (very dark brown) | 6.90 |
| P3 | 48 | 2.5YR 3/1 (dark reddish gray) | 35.38 |
| P4 | 71 | 2.5YR 3/1 (dark reddish gray) | 23.54 |
| P5 | 87 | 2.5YR 7/6 (light red) | 30.77 |
| SSJG-P1 | 15 | 7.5YR 2.5/1 (black) | 61.24 |
| P2 | 35 | 7.5YR 3/1 (very dark gray) | 23.32 |
| P3 | 58 | 10YR 3/2 (very dark grayish brown) | 25.27 |
| P4 | 87 | 10YR 3/3 (dark brown) | 36.68 |
| BGr-P1 | 10 | 7.5YR 2.5/1 (black) | 7.86 |
| P2 | 23 | 10YR 2/2 (very dark brown) | 15.24 |
| P3 | 46 | 7.5YR 3/2 (dark brown) | 8.32 |
| P4 | 60 | 5YR 4/4 (reddish brown) | 5.08 |

Soil colour *values* (Munsell) were similar in all samples, becoming progressively lighter with depth (Table 4.5). In the Munsell colour notation, a Value of 0 denotes absolute black whilst a value of 10 denotes absolute white. For all soils investigated, the surface horizons are darker, with a Munsell Value of 2, than corresponding subsoils which is in discordance with the charcoal content of the respective soil profiles. Additionally, results from the $^{13}C$ NMR analysis of the samples do not reflect such relationships of darker soil colour with high aromatic C regions. This observation shows that soil colour is not directly dependent on the contributions of charred organic material/high aromatic C contributions and that other organic and inorganic pigments contribute to soil colour (Schmidt et al., 1999).

*4.3.4 Chemical Composition of SOC ($^{13}$C CPMAS NMR)*

The solid-state $^{13}$C CPMAS NMR spectra of soil profile samples investigated are given in Figure 4.5, and their relative signal intensities presented in Table 4.6. STM-2, SST-1, SSJG-1 depicts the NMR spectra of samples located within the St. Andrews medieval burgh core area while BGr-1 displays the spectra of samples located outside the historic burgh core area. In the spectra of all the samples, the resonance line around 30 ppm, in the region of alkyl C (0 – 45 ppm) can be assigned to methylene structures (fatty acids, waxes, resins) (Baldock et al., 1992; Kiem et al., 2000; Schmid et al., 2002). The small peak around 56 ppm, in the region of *O/N* – substituted alkyl C (45 – 90 ppm) can be ascribed to methoxyl groups and/or N-substituted alkyl C (Preston et al., 1997), while signal peak at 72 ppm are assigned to O-alkyl C structures representing carbohydrates. The resonance signal intensity between 90 – 110 ppm represents di-O-alkyl C structures of anomeric C in polysaccharides and ketal (Wilson, 1987; Schmid et al., 2001; Solomon et al., 2007). The prominent signal in the region of aryl C (110 – 160 ppm), peaking at 130 ppm may originate from C- or H- substituted aromatic carbon, as well as from unsaturated alkyl structures. The resonance near 170 ppm in the chemical shift region of carbonyl/carboxyl C (160 – 215 ppm) can be ascribed to carboxyl and amide functional groups.

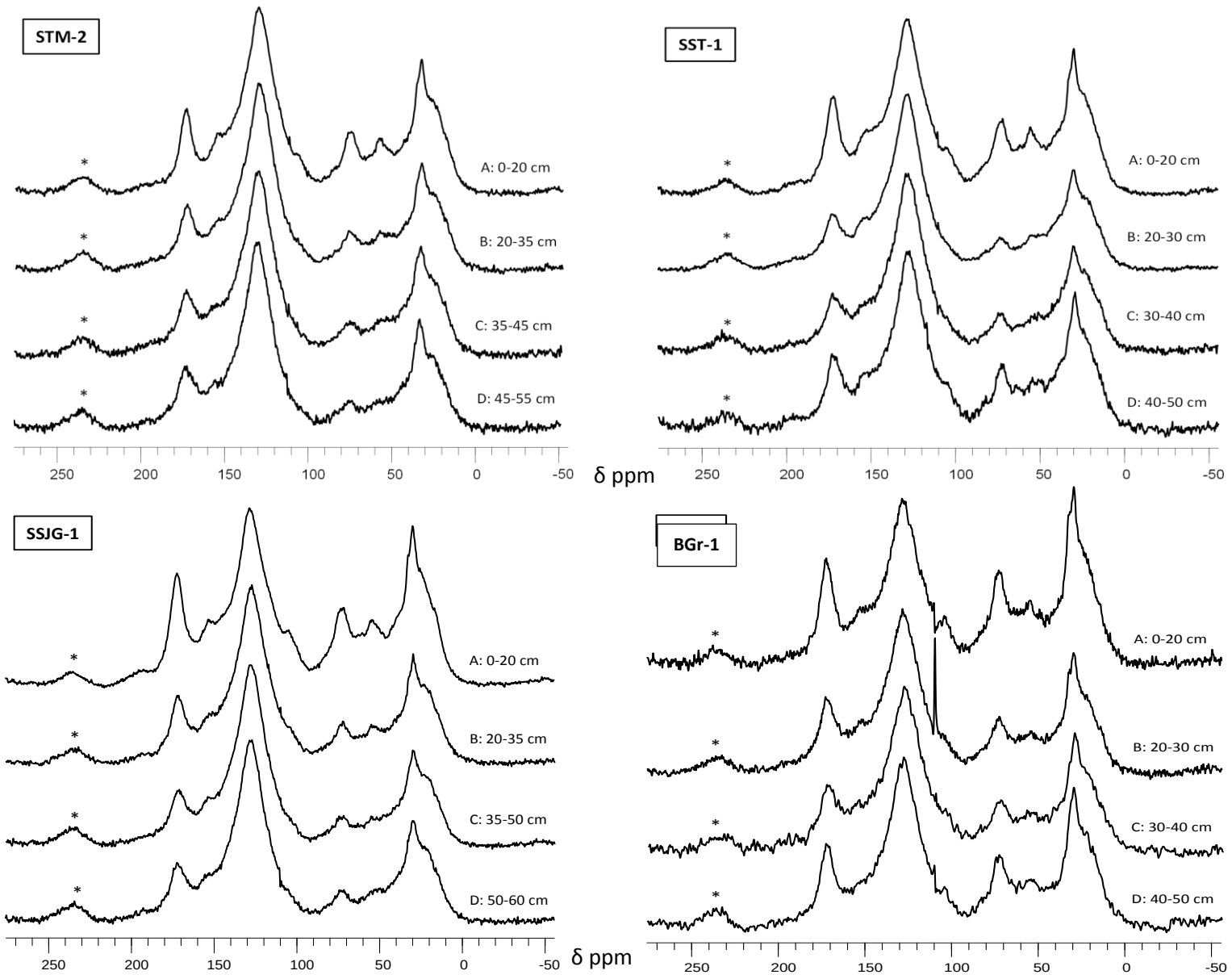



Fig. 4.5. CPMAS $^{13}C$ NMR spectra of soil samples from within core areas (STM-2, SST-1 and SSJG-1), and in the hinterland (BGr-1), outside the town in St Andrews [Spectra were graphically normalised to the dominant aromatic region centred at 130 ppm]

The patterns of distribution of carbon species in the spectra of soil samples between the sites investigated share similar characteristics (Figure 4.5). Surface and sub-surface spectra of soil profile show little discordance despite containing materials of varying age. The relative contribution of the signal intensity in the aromatic C region (110 – 160 ppm), at 130 ppm, dominates the spectra of soils from all of the sample sites, accounting for between 42 % - 58 % of total signal intensity (Table 4.6). The contribution of alkyl C region accounts for between 18 % – 24 % of the signal intensity while *O/N* – alkyl C comprises between 10 % - 19 %. The carboxyl C group contributions ranged from between 10 % - 13 %, while anomeric C region exhibits a relatively low contribution of 3 % - 5 % to the overall signal intensity of spectra in the respective sites. Analogous pattern of resonance signal distribution in the NMR spectra of soils, particularly the enrichment of the aromatic C region, have been reported in historic soils from Neolithic settlement sites in Europe (Schmid et al., 2001; Schmid et al., 2002), and in Amazonian Dark Earth (*terra preta*) in the Brazilian Amazon Basin (Solomon et al., 2007).

The strong similarities in the signal distribution of the spectra of surface and sub-surface soil profile positions on all the sample sites suggest that the composition of materials deposited onto the soil and the ratio of the various constituents of these material did not change significantly throughout the duration of the practice of the use of composted urban waste for soil improvement. The observed higher organic matter content in samples within the settlement core area (STM-2, SST-1, and SSJG-1) compared to samples outside this area (BGr-1) cannot be explained by the relative signal intensities of NMR spectra. This suggests that the differences originate from the variations in the volume of initial materials deposited and the period of accumulation. This interpretation is also supported by the associated elevated P concentration in the sites within the settlement than in sample site outside the settlement (Table 4.1).

The contributions of alkyl C (0 – 45 ppm) and *O/N* – alkyl C (45 – 90 ppm), in the soil samples from within the medieval core area, are lower than in soil samples from the hinterland and generally decreases with depth, more so in the *O/N* – alkyl C region. The lower contribution of *O/N* – alkyl C signal intensity relative to aromatic C and aliphatics (0 – 45 ppm) suggest that fresh plant material did not constitute a major part of urban waste, although it is also possible that they have been degraded over time due to the action of microorganisms since this region arise from compounds that are easily degradable by microbes (e.g. carbohydrates, proteins and peptides). The contributions of the carboxyl C and anomeric C regions are relatively unchanged with depth but values are generally higher at surface profiles. Aromatic C contributions are higher in samples within the settlement core area (STM-2, SST-1, and SSJG-1) and lower in samples outside the core area (BGr-1), however, no particular trend was discernible with depth although surface profiles tend to have lower contributions than subsurface soil profiles. Variations in the relative signal intensity distribution between surface soil and subsoil in the *O/N* – alkyl C region, diminishing with depth, indicate low organic input to subsoil than on surface soil. Kiem et al. (2000) also reported similar trend where the relative contributions of *O*-alkyl decreased concomitantly with low organic input. The changes in the distribution of the resonance signal intensity of *O/N* – alkyl C (45 – 90 ppm) region with depth was found to correlate negatively with aromatic C region (110 – 160 ppm). Previous studies undertaken on a wide variety of soil types have reported similar correlations between these regions, in agreement with our observations (Kiem et al., 2000).

Table 4.6. Relative contributions of carbon species to the total signal intensity in $^{13}C$ NMR spectroscopy of soil samples from different sites and sampling depth

| Sample & Depth (cm) | % Alkyl C (0-45 ppm) | % O/N-Alkyl C (45-90 ppm) | % Anomeric C (90-110 ppm) | % Aromatic C (110-160 ppm) | % Carboxyl C (160-220 ppm) | Alkyl C / O/N-Alkyl C | Aromaticity (%) | Clay (%) | Silt (%) |
|---|---|---|---|---|---|---|---|---|---|
| **STM-2** 0-20 | 21 | 15 | 4 | 50 | 11 | 1.40 | 55.56 | 3.39 | 51.71 |
| 20-35 | 19 | 12 | 3 | 54 | 11 | 1.58 | 61.36 | 3.08 | 51.42 |
| 35-45 | 20 | 11 | 3 | 54 | 12 | 1.82 | 61.36 | 4.77 | 47.13 |
| 45-55 | 19 | 10 | 3 | 57 | 11 | 1.90 | 64.04 | 5.17 | 62.93 |
| **SST-1** 0-20 | 22 | 17 | 4 | 45 | 12 | 1.29 | 51.14 | 4.09 | 64.01 |
| 20-30 | 20 | 11 | 3 | 54 | 11 | 1.82 | 61.36 | 5.99 | 71.01 |
| 30-40 | 21 | 12 | 4 | 53 | 10 | 1.75 | 58.89 | 11.00 | 89.00 |
| 40-50 | 22 | 15 | 4 | 48 | 11 | 1.47 | 53.93 | 10.10 | 89.86 |
| **SSJG-1** 0-20 | 23 | 17 | 5 | 43 | 13 | 1.35 | 48.86 | - | - |
| 20-35 | 21 | 12 | 4 | 52 | 11 | 1.75 | 58.43 | - | - |
| 35-50 | 18 | 10 | 3 | 58 | 11 | 1.80 | 65.17 | - | - |
| 50-60 | 20 | 10 | 4 | 56 | 11 | 2.00 | 62.22 | - | - |
| **BGr-1** 0-20 | 24 | 19 | 4 | 42 | 12 | 1.26 | 47.19 | 6.60 | 68.60 |
| 20-30 | 19 | 15 | 4 | 50 | 12 | 1.27 | 56.82 | 7.28 | 69.52 |
| 30-40 | 20 | 14 | 5 | 50 | 12 | 1.43 | 56.18 | 8.36 | 55.64 |
| 40-50 | 22 | 17 | 4 | 46 | 11 | 1.29 | 51.69 | 17.70 | 82.30 |

Lignin units are generally represented by the combination of resonance signals from methoxyl C region (56 ppm), O – alkyl C (72 ppm) and phenolic C (150 ppm) (Preston et al., 1997). Distinct signal intensity indicative of lignin compounds cannot be identified in the spectra region of methoxyl C and O – alkyl C, however a small peak is visible at 150 ppm (Figure 4.5). The contribution of the signal intensity of this region is very low and decreases with depth indicating that lignin is not a major component of the soil organic matter in urban anthrosols and that virtually all of the signal intensity at ~ 130 ppm (aromatic C) can be attributed to charred organic material (ash and charcoal) (Kiem et al., 2000; Downie et al., 2011). The dominance of the aromatic C region and the associated high aromaticity indices of soils (47 % - 65 %) from the entire study site are attributed to the autochthonous inputs of charred material unto soil. The additions of pyrogenic materials such as ash and charcoal unto soil are not uncommon, and are well documented component material of urban waste added to soil.

Previous research by Brothwell (1982) reported an estimated 8100 kilograms of ash from cooking and heating were generated annually per 100 households in pre-industrial societies. Ash and charcoal from hearth, kilns and cooking fires are composted together with other waste materials in middens and applied to soil (Davidson et al., 2006; Golding et al., 2010; Oram, 2011). This is consistent with the widely-reported observations of the enrichment of anthropogenically modified soils with charred organic material around the world (Pape, 1970; Davidson and Carter, 1998; Schmidt et al., 1999; Novotny et al., 2009; Downie et al., 2011). The strong resonance intensity of aromatic C species (110 – 160 ppm) in soil samples indicates that charred organic residues deposited on soil were produced under high pyrolysis temperature. Previous study by Mcbeath and Smernik (2009) showed that the degree of aromatic condensation, the amount of aromatic C structures (aryl C), increases with increasing thermal treatment.

According to Baldock and Preston (1995) and Baldock et al. (1997), the ratio of alkyl C to *O/N*-alkyl C can be used as an indicator for assessing the extent of decomposition of organic materials. Higher proportions of alkyl C relative to O/N-alkyl C are associated with higher level of decomposition. The ratio of alkyl C to *O/N*-alkyl C is higher in samples within the settlement than in samples outside the settlement area. The ratios generally increased with depth except for SST-1 site where no particular pattern is discernible however ratios are lower in surface soil than in subsoil. The higher ratio of alkyl C to *O/N*-alkyl C observed in samples with the settlement indicates that decomposition has progressed further on this site than on BGr-1 site. The depth dependent increase in the ratio also suggests that subsoils have undergone a greater extent of decomposition than surface soils (Kiem et. al., 2000; Mathers and Xu, 2003). The low contribution of the resonance signal around 150 ppm that is assigned to lignin units which are typically found in plant materials during the initial phase of decomposition also indicates that decomposition is at a higher state.

**4.4 Summary and Conclusion**

Anthropogenic activity generally leads to the alteration of the natural conditions of soil which are visible from the residual soil properties in modified areas relative to those of the surrounding area. These changes which are defined by the nature, intensity and period of sustained activity alter specific aspect of soil characteristics and/or a variety of soil aspects. Minor alterations to the natural conditions of soil are often difficult to detect in areas susceptible to high post-depositional effects (dynamic environment) and signals can be concealed and/or erased by post-depositional processes. However, signals from soil modifications arising from longstanding practices such as burning, and the inputs of waste products on soil can persist in the soil and it is this signals that can be exploited to reveal details of past anthropogenic activities and their various impacts on soil.

In the sites investigated, evidence of soil modification arising primarily from the addition of substantial volume of organic-rich material from domestic and industrial refuse are still visible to the present day. Variations in the physicochemical properties of soil such as organic matter content and composition, colour, pH, and magnetic susceptibility were observed between experimental sites. Sample sites within the settlement area, where activities are said to be more pronounced, are characterised by enhanced phosphate concentrations, higher organic carbon content, and higher magnetic susceptibility values relative to sites located outside the settlement; and although soil modification was evident in the site outside the settlement, as indicated by results obtained, this is at a comparatively lower degree than found in sites within the settlement.

Solid-state $^{13}C$ NMR spectroscopy was used to investigate the chemical composition of organic material beyond the ordinarily observable differences in soil organic matter content. Using NMR spectra display and integrated values, the identification and distribution of various organic carbon functional components of SOM was possible. The molecular level information generated by $^{13}C$ NMR analysis, complemented with other physicochemical examination of soil carried out in this study, confirms that the soil in St Andrew were significantly altered by past anthropogenic activities particularly the deposition of municipal waste unto soil for enrichment purposes. As documented in ethnographic records, soil capitalisation was achieved primarily by the addition of composted urban waste including materials from pyrogenic origin to maintain and/or increase production output. The high organic carbon content, P concentrations, and magnetic enhancement of soils in sites within the settlement and the depth at which they occur reflects the scale of material input, the length of time over which they were added, and by extension the concentration of activity and land-use intensity in St Andrews.

Having elucidated on the compositional properties of soil organic matter in buried anthropogenic soils and their distribution, the subsequent Chapters explore the processes of degradation of such materials in Chapter five, and the various processes of SOM stabilisation, in Chapter six.

**CHAPTER 5**

# The relationship between Phenol oxidase Enzyme Activity, Organic Carbon Content, and Decomposition in Buried Anthrosols

## 5.1 Introduction

Phenol oxidase is an extracellular enzyme and one of the few known enzymes capable of degrading recalcitrant phenolic materials and compounds. However phenolic compounds are inhibitors of enzyme activity and have been shown in many studies to decrease the rate of enzymatic decomposition of organic material. In temperate peatland, waterlogged conditions limit oxygen availability which decreases phenol oxidase activity. This allows for the accumulation of phenolic compounds that inhibit the activity of hydrolytic enzymes thereby slowing decomposition. Conversely, studies carried out in tropical marsh soils with different water regime and organic matter content reported decreases in enzyme activity including phenol oxidase in drier soils than in wet soils. This indicates the potential for phenol oxidase activity to respond to not only changing anoxicity but to other environmental variables. We investigated the relationship between phenol oxidase enzyme activity, organic carbon content, and microbial activity in buried anthrosols (St Andrews, UK) that likely contains elevated phenolic and organic matter content from historical land use practices.

## 5.2 Phenols and Phenol oxidase Enzyme: Sources, Activity and Function

Phenolic compounds are one of the constituents of soil chemical properties and are active agents in a number of ecosystem processes. Phenolic compounds accumulate in the soil through various natural and anthropogenic processes (Barlow and Johnson, 2007; Michalowicz and Duda, 2007; Li and Beta, 2013). Natural sources of phenolic compounds are derived from plant residues and by-products of microbial metabolism while anthropogenic sources are

mainly through industrial processes such as the production and degradation of pesticides, and generation of industrial and municipal sewages (Pind et al., 1994, Rimmer, 2006; Barlow and Johnson, 2007; Michalowicz and Duda, 2007; Sinsabaugh, 2010; Li and Beta, 2013). Phenols have been implied to play an active role in a range of processes in the environment, such as: in the defence mechanisms of various plants and animals, the termination of oxidative processes (reactive free radicals to non-reactive stable free radicals), and decreased rate of decomposition of organic material (Steinberg, 1984; Steinberg, 1986; Wetzel, 1992; Appel, 1993; Pind et al., 1994; Freeman et al., 2004; Halliwell and Gutteridge, 2007; Favaron et al., 2009; Sinsabaugh, 2010).

Martens (2002a and 2000b) investigated the relationship between phenolic compounds in crop residues and soil processes such as decomposition, nutrient availability and aggregate formation, and concluded that phenolic compounds have a slower degradation rate relative to carbohydrates and proteins during decomposition processes in soil. The association of phenolic compounds with a low rate of breakdown of organic matter is attributed to their antioxidant properties, their inhibitory actions on enzymatic activity and their ability to further stabilise the carbon-carbon bonds of aromatic rings, rendering such materials potentially inaccessible to microbes (Appel, 1993; Pind et al., 1994; Freeman et al., 2001, 2004). Therefore the presence and content of phenolic compounds in soils, acting in tandem with various other soil organic matter (SOM) stabilisation mechanisms could further decrease carbon loss from soil, thus increasing the role of soil as a major global terrestrial sink for carbon.

However, phenol oxidase, an extracellular enzyme, is one of the few known enzymes capable of degrading phenolic compounds (Freeman et al., 2004). Phenol oxidase activity has been studied under field and laboratory conditions, and in various aquatic (riparian, peatlands, wetlands, marshlands, streams) and terrestrial (grass/shrublands, and forest) systems in relation to litter decomposition, and the decomposition rate of the general body and

assemblage of organic matter (Freeman et al., 2001, 2004; Sinsabaugh, 2010; Kang et al., 2011; Liu et al., 2014). Freeman et al. (2001) investigated the role of phenolic compounds and phenol oxidase enzyme activity in controlling the rate of decomposition of organic material in temperate peatland and found that oxygen constraint on the enzyme phenol oxidase slows the decomposition of organic material by preventing the degradation of phenolic compounds that inhibit the activity of hydrolytic enzymes; this mechanism is called the 'enzyme latch mechanism'. Biodegradative hydrolase enzyme activity (sulphatase, phosphatase, β-glucosidase, chitinase, xylosidase) that have no oxygen requirements are constrained in the presence of phenolic material but significant increases in activity were observed upon removal of phenolic compounds. On the contrary, similar studies by Kang et al. (2011) looked at this mechanism in tropical marsh soils with different water regime and with less organic matter content. The authors concluded that a decrease in water level led to a corresponding decrease in enzyme activity and hence a decrease in decomposition rate. Other studies, including those reviewed by Sinsabaugh, (2011), on this subject have also reported both positive and negative feedback regulation of phenol oxidase activity in different systems involving varied biotic (vegetation type) and abiotic components (pH, moisture, oxygen, temperature, N availability, OM content, litter quality, microbial community).

This present study assessed the effect of phenol oxidase enzyme activity on nutrient dynamics and microbial activity in anthropogenically modified soils with known histories of high inputs of organic-rich waste materials. Historical management practices saw sustained recurrent inputs of diverse organic-rich materials to soils. The mixing of these materials, most of which are natural and anthropogenic sources of phenolic compounds (Michalowicz and Duda, 2007; Sinsabaugh, 2010; Li and Beta, 2013), are likely to have increased the phenolic content of soil above the natural background levels, and their corresponding associative effects/influence on soil processes. We hypothesize that decreases in soil organic matter content with depth may

stimulate the production and release of phenol oxidase enzymes by microorganisms to degrade phenolic compounds in response to nutrient availability, or lack thereof.

Microbial nutrient cycle

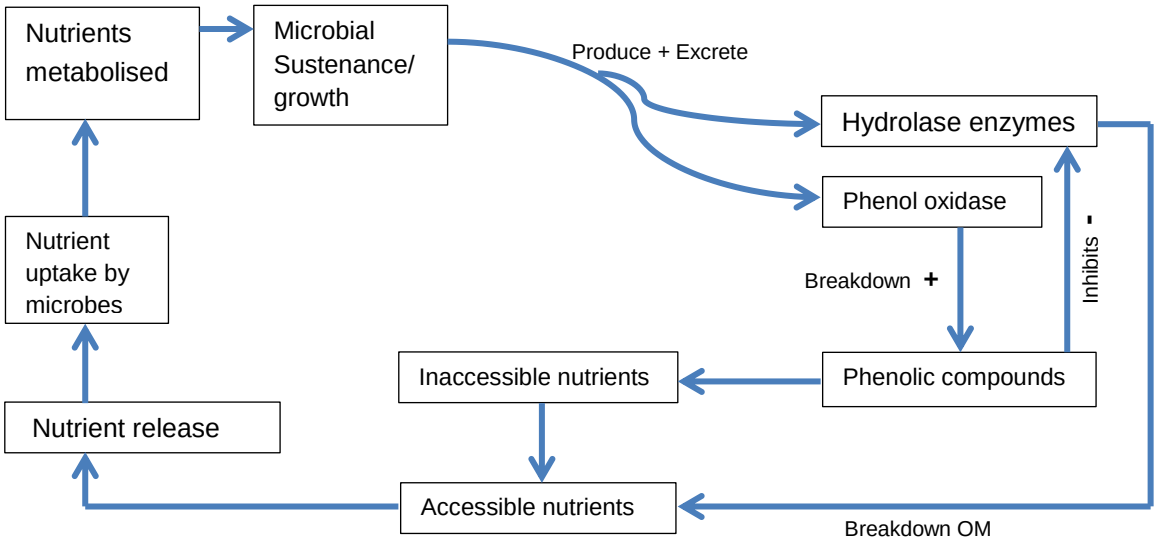



Fig. 5.1. Schematic representation of the role of phenol oxidase enzyme in nutrient cycling. Plus and minus signs indicate positive (breakdown) and negative (inhibitory) effects on the system

**5.3 Materials and Methods**

Sampling was carried out in St Andrews in the manner described in Chapter Three. Soil profile samples STM-2, SSJG-1, BGr-1, STM-P, SSJG-5, and BGr-P were collected and bagged for *ex situ* analysis. Subsamples (STM-P, SSJG-5, and BGr-P) for biological analysis – phenol oxidase assay, soil respiration and microbial biomass – were stored at 4°C before use.

A total of 17 samples were assayed for phenol oxidase enzyme activity using the procedure outlined in Chapter Three, *section 3.2.12*. This was complimented by soil respiration and microbial biomass analysis as also detailed previously in *section 3.2.11* of Chapter 3. Samples

undergoing soil respiration and microbial biomass were analysed in field state condition, and therefore were not air-dried and sieved.

### *5.3.1 Statistical Analysis*

Second order Polynomial regression analysis (which produced the best fit for all data sets) was carried out on the selected factor(s) to investigate the interdependence of variables. Best subsets multiple regressions were carried out on Minitab 17 statistical software (Minitab 17 Statistical Software 2010. State College, PA: Minitab, Inc.) to differentiate between the effects of variables and to determine which select factor(s) are most important in influencing phenol oxidase activity. *P*-values of $< 0.05$ were used for significance test where applicable. Possible relationships among moisture content, microbial biomass, soil respiration, organic matter content and composition, C/N ratio, soil pH, and particle size distribution were evaluated by correlation analysis and calculated ratios.

**5.4 Results**

The tables below summarises the physical and chemical properties of the sub-sample of soils used in the study.

Table 5.1. Summary of soil physical and chemical properties (phenol oxidase samples)

| Sample | Depth (cm) | $C_{org}$ (%) | $N_T$ (%) | C/N ratio | pH ($CaCl_2$) | Moisture Content (%) |
|---|---|---|---|---|---|---|
| STM-P | 12 | 5.19 | 0.28 | 18.54 | 5.58 | 23.01 |
| | 30 | 4.34 | 0.32 | 13.56 | 5.92 | 20.54 |
| | 48 | 2.83 | 0.23 | 12.30 | 6.06 | 20.87 |
| | 71 | 2.61 | 0.12 | 21.75 | 5.70 | 17.27 |
| | 87 | 4.02 | 0.17 | 23.65 | 5.89 | 18.35 |
| SSJG-5 | 0-20 | 8.22 | 0.85 | 9.67 | 5.48 | 25.93 |
| | 20-30 | 7.85 | 0.62 | 12.66 | 5.80 | 25.00 |
| | 30-40 | 6.73 | 0.39 | 17.26 | 5.84 | 21.82 |
| | 40-50 | 7.25 | 0.50 | 14.50 | 5.91 | 22.43 |
| | 50-65 | 6.75 | 0.39 | 17.31 | 5.77 | 21.24 |
| | 65-75 | 6.75 | 0.39 | 17.31 | 5.84 | 22.81 |
| | 75-85 | 4.47 | 0.36 | 12.42 | 5.71 | 20.35 |
| | 85-100 | 2.99 | 0.23 | 13.00 | 5.66 | 21.70 |
| BGr-P | 10 | 2.32 | 0.51 | 4.55 | 5.58 | 22.12 |
| | 23 | 3.31 | 0.36 | 9.19 | 5.95 | 15.60 |
| | 46 | 2.43 | 0.26 | 9.35 | 5.61 | 16.04 |
| | 60 | 0.45 | 0.11 | 4.09 | 5.84 | 16.50 |

Table 5.2. Summary of soil physical and chemical properties ( - no data) (NMR samples)

| Sample | Depth (cm) | Clay (%) | Silt (%) | Fine Sand (212µm) (%) | Medium Sand (630µm) (%) |
|---|---|---|---|---|---|
| STM-2 | 0-20 | 3.39 | 51.71 | 33.30 | 11.60 |
| | 20-35 | 3.08 | 51.42 | 30.50 | 14.60 |
| | 35-45 | 4.77 | 47.13 | 34.70 | 13.40 |
| | 45-55 | 5.17 | 62.93 | 29.80 | 2.10 |
| SSJG-1 | 0-20 | - | - | - | - |
| | 20-35 | - | - | - | - |
| | 35-50 | - | - | - | - |
| | 50-60 | - | - | - | - |
| BGr-1 | 0-20 | 6.60 | 68.60 | 24.30 | 0.50 |
| | 20-30 | 7.28 | 69.52 | 22.70 | 0.50 |
| | 30-40 | 8.36 | 55.64 | 34.60 | 1.40 |
| | 40-50 | 17.70 | 82.30 | 0.00 | 0.00 |

*5.4.1 Relationship between **Depth** and Soil variables: Moisture content, Microbial biomass, Soil respiration, and Organic matter content*

Moisture content, microbial biomass, soil respiration, and organic matter content decreased with increasing depth. BGr-P soils have lower organic matter and moisture content than found in STM-P and SSJG-5 but other parameters are comparatively similar. Polynomial regression analyses of these variables show strong inverse correlations with depth as shown in Figure 5.2, 5.3, and 5.4. Predictably, these factors also show a negative but variable correlation with phenol oxidase activity (graph not shown).

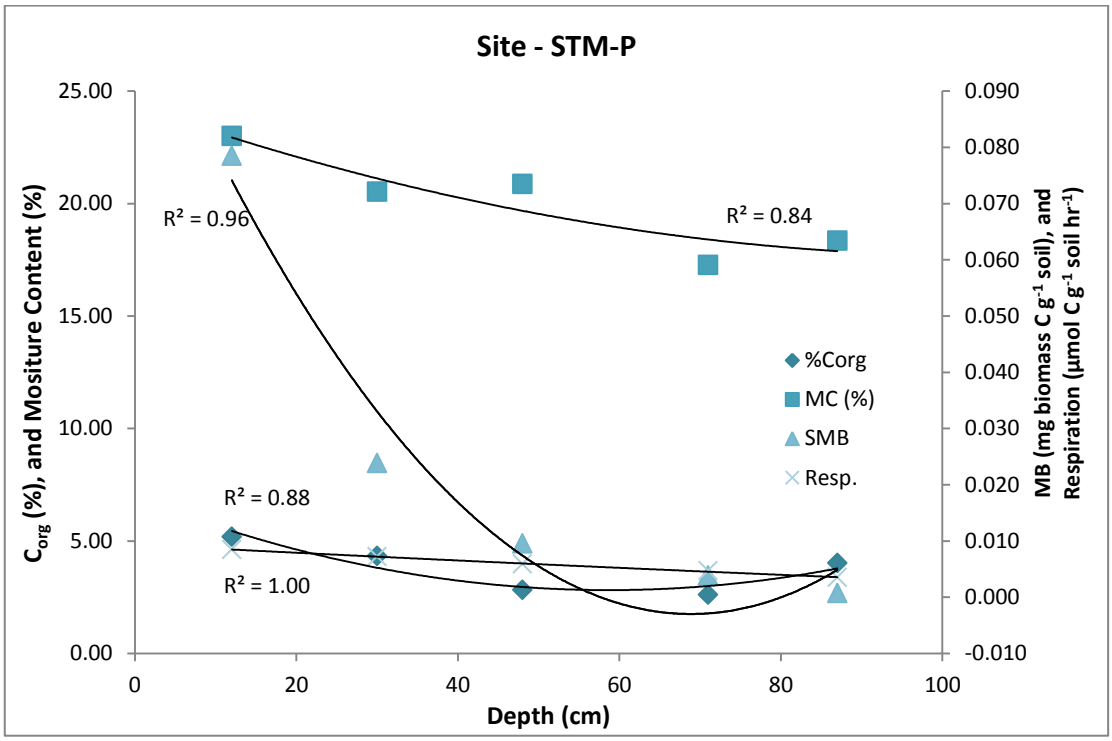



Fig. 5.2. Relationship between soil variables and depth on site STM-P

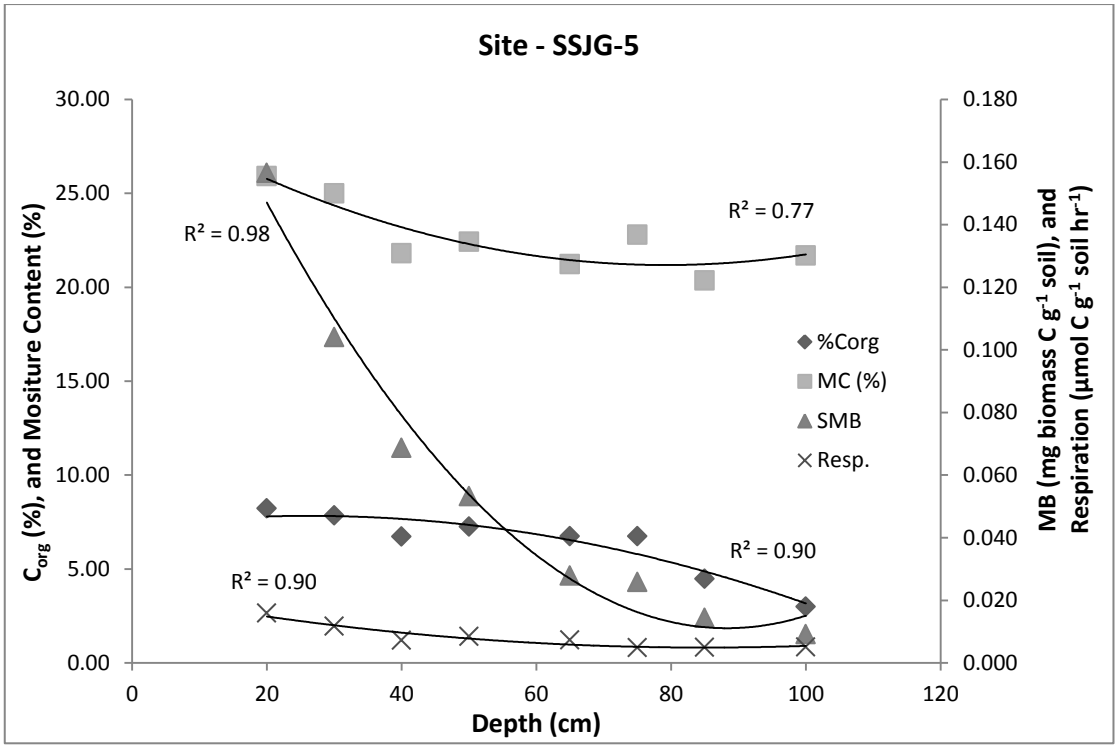



Fig. 5.3. Relationship between soil variables and depth on site SSJG-5

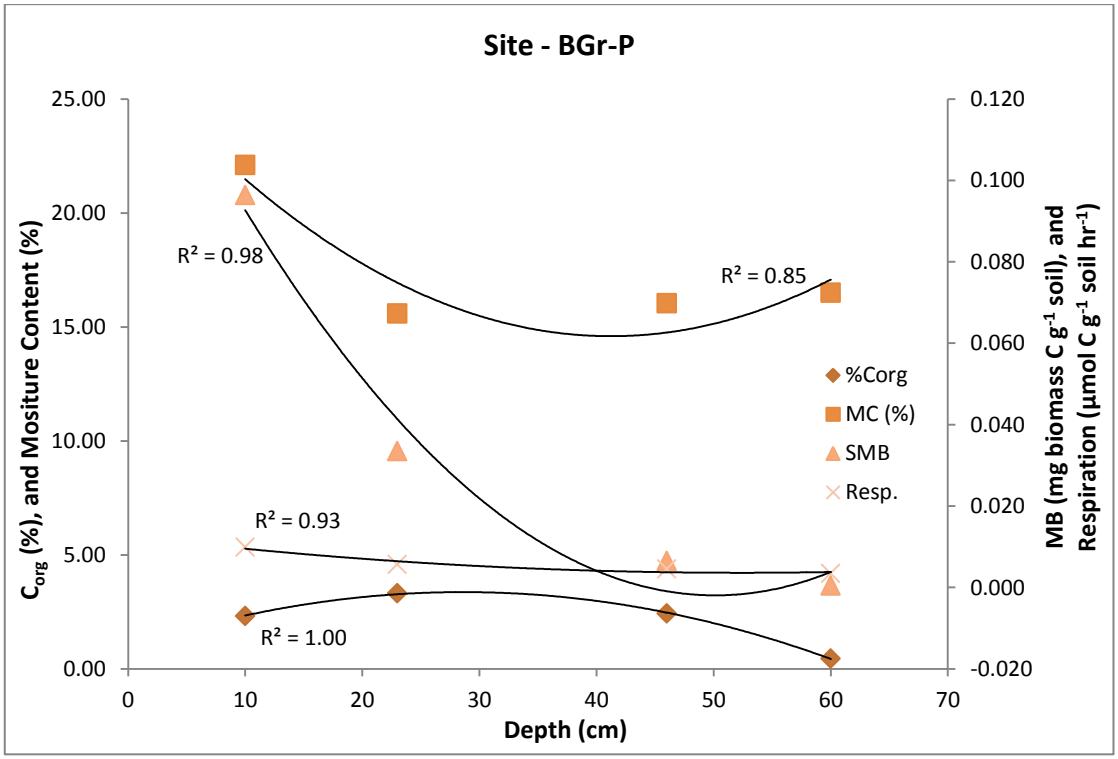



Fig. 5.4. Relationship between soil variables and depth on site BGr-P

*5.4.2 Relationship between Phenol oxidase activity and Depth*

Phenol oxidase enzyme activity was generally higher in sub-soils than in topsoil. Phenol oxidase activity was lowest in BGr-P samples on the top 3 profiles but similar to values for STM-P and SSJG-5 at subsoil depths, between 40-50 cm. Phenol oxidase activity correlated positively with depth on all three sample sites assayed: STM-P, SSJG-5, and BGr-P, with *R-square* values of 0.58, n = 5; $R^2$ = 0.93, n = 8; $R^2$ = 0.66, n = 4 respectively (Figure 5.5). Polynomial regression analysis of the relationship was only significant in site SSJG-5 (*p*-value = 0.001).

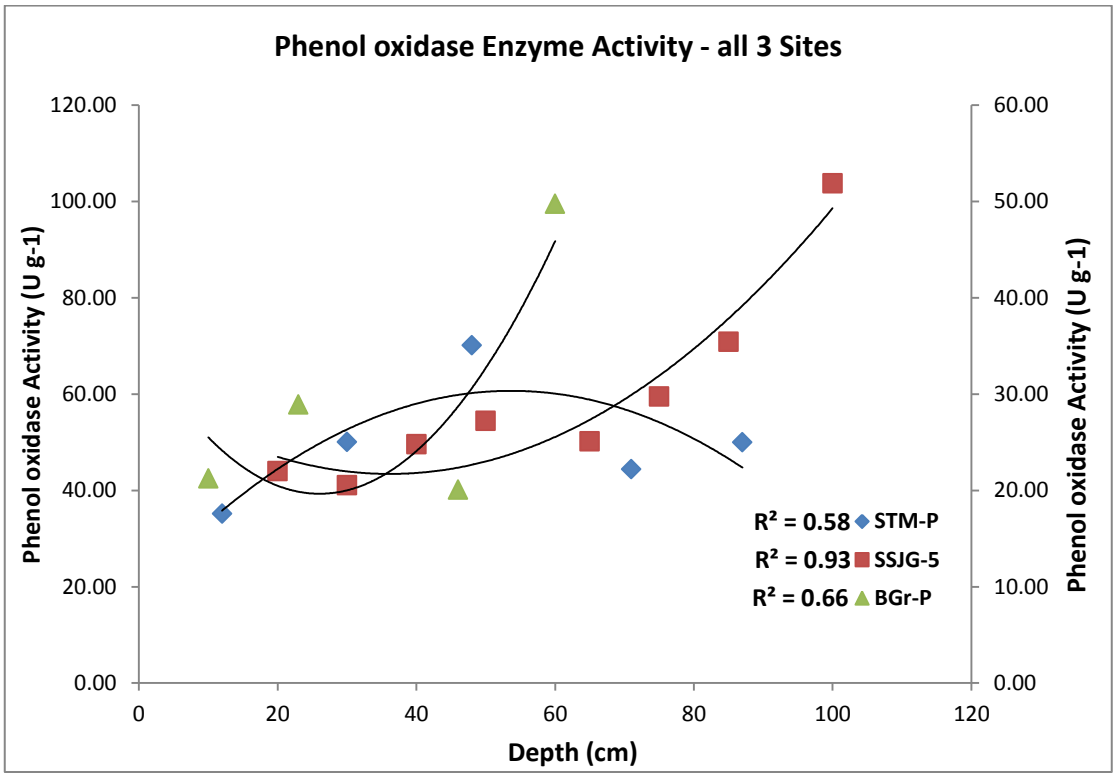



Fig. 5.5. Polynomial regression of depth against phenol oxidase activity on all three sample sites: STM-P ($y = -0.01x^2 + 1.54x + 19.43$), SSJG-5 ($y = 0.01x^2 - 0.98x + 61.19$), and BGr-P ($y = 0.02x^2 - 1.19x + 35.09$)

*5.4.3 Relationship between **Phenol oxidase activity** and Soil variables: Moisture, Microbial biomass, Respiration, and Organic matter content*

Statistical analysis by best-subsets multiple regression of phenol oxidase activity and soil variables revealed that soil organic matter content was the best single predictor variable that accounts for the variation in phenol oxidase activity observed on all three sites (Table 5.3).

Table 5.3. Values for Best subset multiple regression analysis

| Site | $R^2$ value | $R^2$ (adj) value | Cp | S value | No. of variable |
|---|---|---|---|---|---|
| STM-P | 0.37 | 0.16 | 0.6 | 11.770 | 3 |
| SSJG-5 | 0.91 | 0.89 | 0.5 | 6.6960 | 5 |
| BGr-P | 0.62 | 0.43 | 1.3 | 10.359 | 2 |

Phenol oxidase activity correlated inversely with organic matter content in all sites (Figure 5.6). Polynomial regression analysis of organic matter content against phenol oxidase activity was significant for site SSJG-5 and BGr-P (*p*-values = 0.001, and 0.038, respectively) but was not significant for STM-P (*p*-value = 0.480).

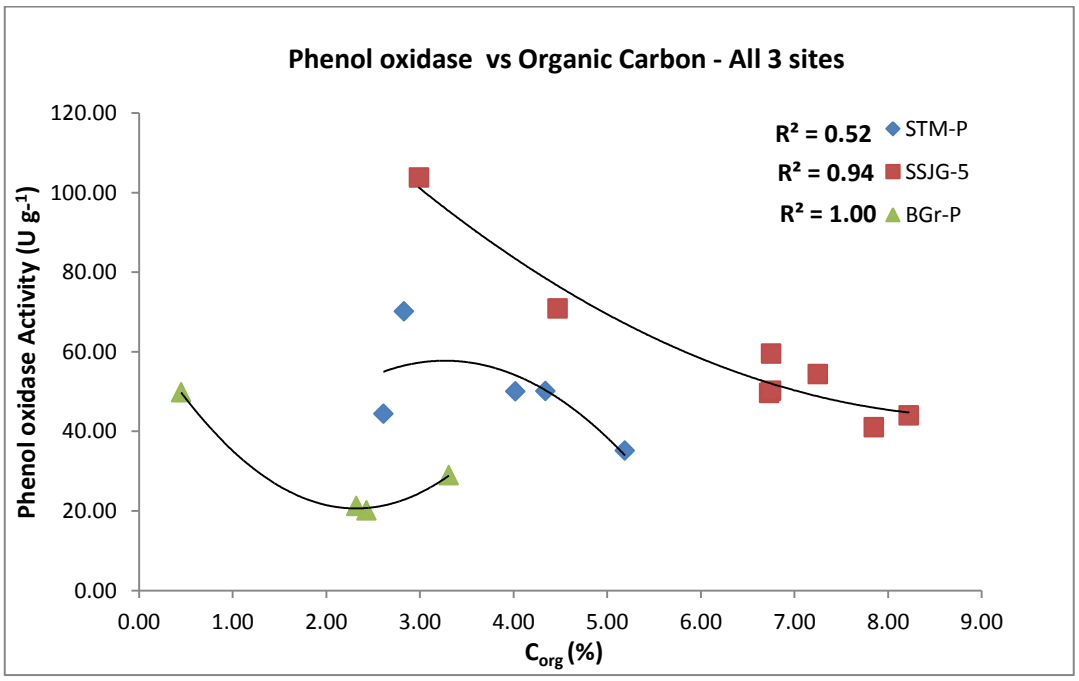



Fig. 5.6. Polynomial regression of phenol oxidase activity and organic matter in all three sites: STM-P ($y = -6.43x^2 + 42.03x - 10.90$), SSJG-5 ($y = 1.56x^2 - 28.25x + 171.76$), and BGr-P ($y = 8.37x^2 - 38.77x + 65.53$)

*5.4.4 Organic matter content, Composition, and Particle size distribution*

As has been reported in *section 5.4.1*, organic matter generally declined with depth, however, characterisation of carbon species using $^{13}C$ NMR spectroscopy revealed that the decline in total organic matter content corresponds with a decrease in the *O/N*-alkyl C region in all sites except at 50 cm depth (the deepest section of the profile) in BGr-1 where the only increase was seen (Table 5.4). Aromatic C generally increased with depth in all sites except at 60 cm and 50 cm in SSJG-1 and BGr-1, respectively where the only increase was detected. A similar trend was observed in the aromaticity index as seen in aromatic C. The ratio of alkyl to *O/N*-alkyl C increased with depth in all sites albeit a decrease was seen at 50 cm depth in site BGr-1.

Particle size distribution of soil profile samples show an increase in clay content with increasing depth in STM-2 and BGr-1. This trend is more pronounced in BGr-1 especially at 40-50 depth where the clay content is over double the value for the topsoil. The increase in clay content corresponds to the relatively higher amount of residual *O/N*-alkyl C on the site relative to STM-2 and SSJG-1, and the increase in *O/N*-alkyl C at the subsoil (40-50 cm) than at the topsoil (Table 5.4 and Figure 5.7). Although the absolute amount of organic matter is lower in the BGr-1 site, the proportions of carbon species generally follows a similar trend as seen in STM-2 and SSJG-1.

Table 5.4. Relative contributions of carbon species to the total signal intensity in $^{13}C$ NMR spectroscopy of soil samples in study sites

| Sample & Depth (cm) | % O/N-Alkyl C (45-90 ppm) | Alkyl C / O/N-Alkyl C | Aromaticity (%) | Clay (%) |
|---|---|---|---|---|
| **STM-2** 0-20 | 15 | 1.40 | 55.56 | 3.39 |
| 20-35 | 12 | 1.58 | 61.36 | 3.08 |
| 35-45 | 11 | 1.82 | 61.36 | 4.77 |
| 45-55 | 10 | 1.90 | 64.04 | 5.17 |
| **SSJG-1** 0-20 | 17 | 1.35 | 48.86 | - |
| 20-35 | 12 | 1.75 | 58.43 | - |
| 35-50 | 10 | 1.80 | 65.17 | - |
| 50-60 | 10 | 2.00 | 62.22 | - |
| **BGr-1** 0-20 | 19 | 1.26 | 47.19 | 6.60 |
| 20-30 | 15 | 1.27 | 56.82 | 7.28 |
| 30-40 | 14 | 1.43 | 56.18 | 8.36 |
| 40-50 | 17 | 1.29 | 51.69 | 17.70 |

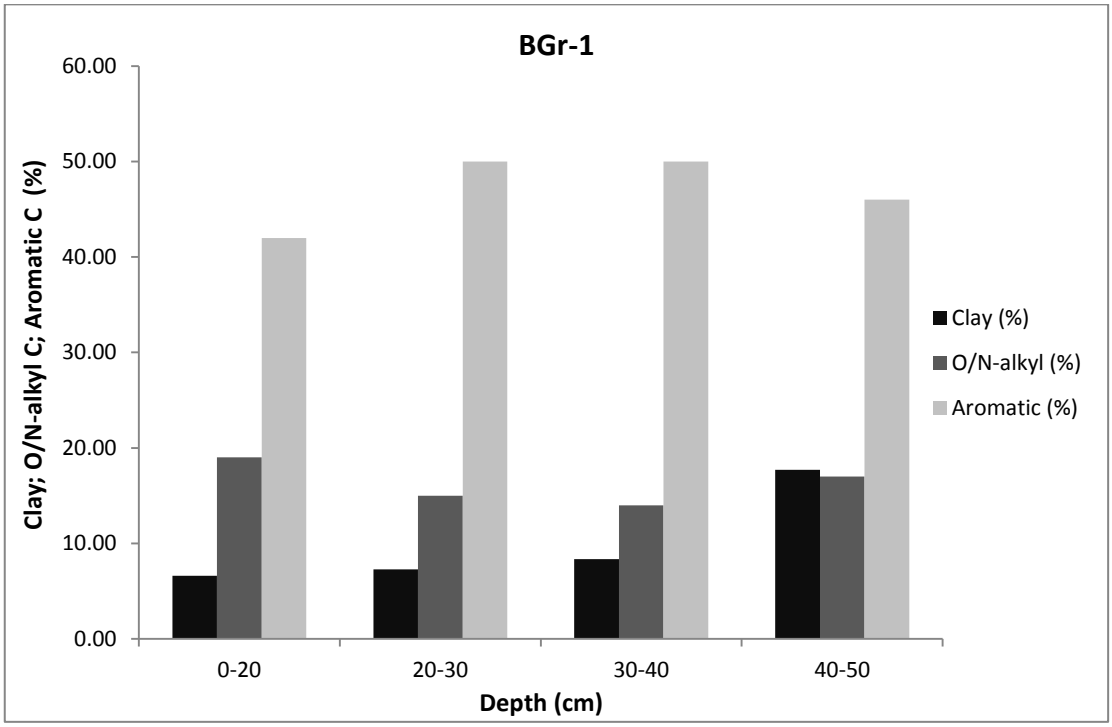



Fig. 5.7. Relationship between soil clay content, *O/N*-alkyl C and aromaticity in profile BGr-1

*5.4.5 Relationship between Microbial biomass, Basal respiration, C/N ratio and pH*

Microbial biomass and basal respiration decreased with depth, however, the rate of biomass decrease was disproportional to decreases observed in basal respiration (Figure 5.8, 5.9, and 5.10). Microbial biomass followed an exponential decrease with depth increments, while respiration showed a steady decline with increasing depth. This trend is visible on all sites, albeit less so in SSJG-5 site.

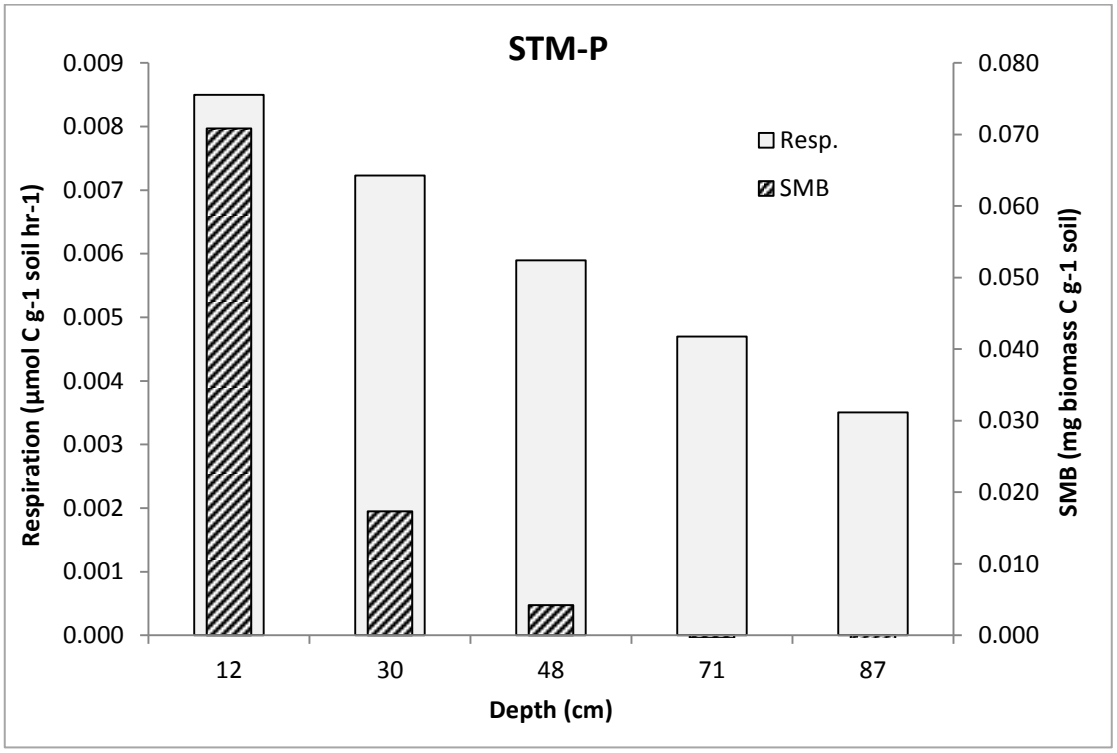



Fig. 5.8. Basal respirations (Resp.) versus soil microbial biomass (SMB) measurements STM-P sample site

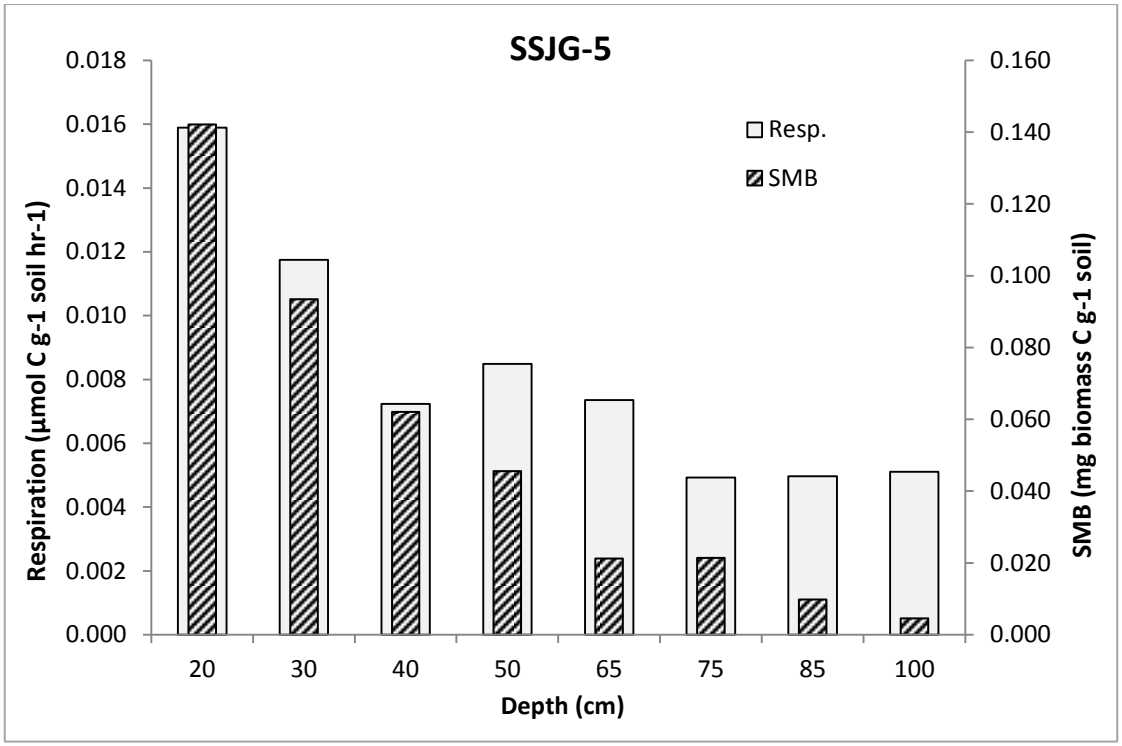



Fig. 5.9. Basal respirations (Resp.) versus soil microbial biomass (SMB) measurements in SSJG-5 sample site

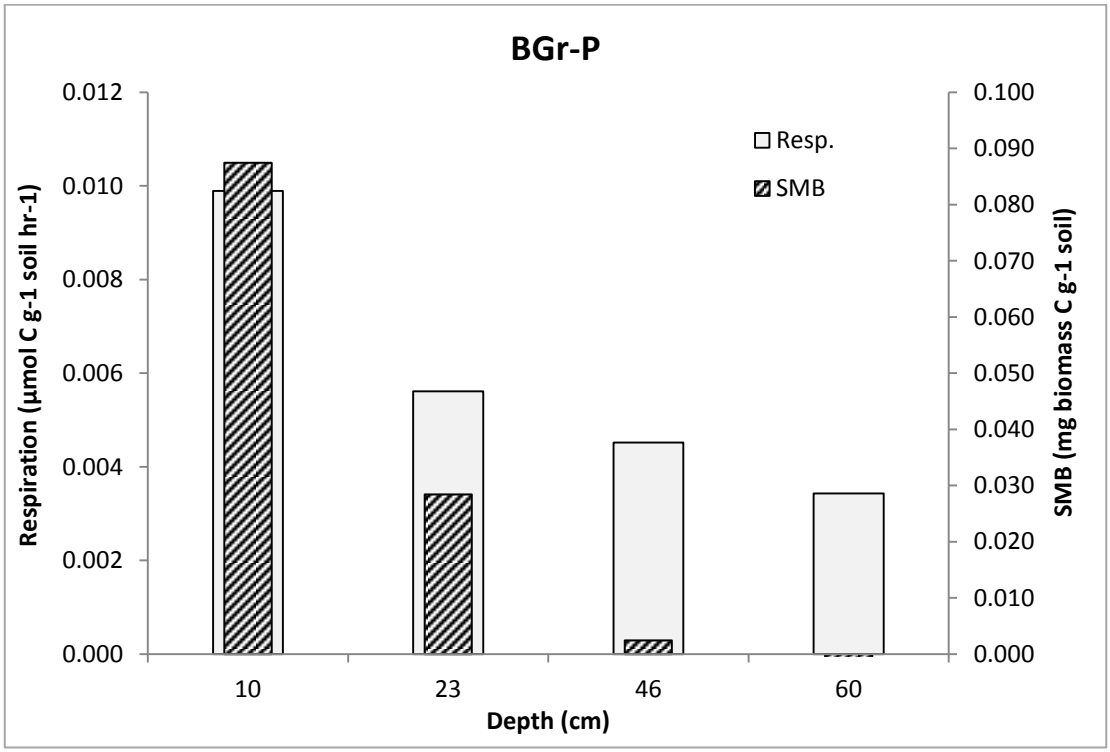



Fig. 5.10. Basal respirations (Resp.) versus soil microbial biomass (SMB) measurements in BGr-P sample site

The low values for microbial biomass in STM-P at 71 and 87 cm, and BGr-P at 60 cm (Figure 5.8 and 5.10) are due to the limits of detection and/or sensitivity of SIR-method because changes in the peak height of $CO_2$ evolved were evidently higher in the substrate-induced samples than in the control samples after 24 hours (data not shown) which indicates the presence of microorganism.

C/N ratio was lowest in BGr-P, medium for SSJG-5 and highest in STM-P. Total nitrogen generally declined with depth as in organic matter but no particular pattern or trend was discernible for C/N ratio to explain the higher respiration to biomass ratio observed with depth. Soil pH values on all three sites were similar, with marginal increases with depth. Soil pH ranged from 5.85 to 6.41 in water, and 5.48 to 6.06 in calcium chloride which are conducive for microbial activity and extracellular enzyme activity.

*5.4.6 Other Observations*

Phenol oxidase enzyme activity assays were performed on at least 3 independent occasions and results averaged to eliminate the effects of single localised events/factors. Three control assays were performed in order to verify the enzymatic origin of the phenol oxidase activity detected; A) heat-treated samples (autoclaved at 121$^{o}$C for 1 h), B & C) without ABTS and/or soil added to the reaction mixture.

No oxidative activity was detected in the control assay B and C (without ABTS substrate and/or soil added to the reaction mixture). In control assay A (autoclaved samples), substrate oxidation was detected albeit 2 – 4 fold less than in the experimental samples. This result contradicts Floch et al. (2007) report on the use autoclave-sterilised samples as suitable controls, but in agreement with Bach et al. (2013) findings that sterilizing soil samples by autoclaving may not be a suitable method of negative control. The rationale for the use of

autoclave treated samples for control is that enzymes will be denatured at temperatures sustained during autoclaving (121$^{o}$C), however unconformities to this generalisation is possible because enzymes bound to the mineral matrix of soil can retain functionality even after autoclaving or after undergoing similar heat treatment (Sinsabaugh, 2010).

## 5.5 Discussion

### *5.5.1 Relationship between **Depth** and Soil variables*

The differences in depth between surface and subsurface conditions or environments in both terrestrial and aquatic ecosystems is one of the key determining factor influencing diversity and variations in these system processes; natural or anthropogenic. Strong positive and negative correlations between the depth of sample and various soil-process dependent elements such as moisture content, organic matter, microbial biomass, soil respiration, and phenol oxidase enzyme activity were detected on all sites (Figure 5.2, 5.3, and 5.4)

### *5.5.2 Relationship between Phenol oxidase activity and Depth*

Phenol oxidase enzyme activity was positively correlated with depth in all sites ($R^2$ = 0.58, 0.93, 0.66) (Figure 5.5). Enzyme activity generally increased with depth and was highest in subsoil than in topsoil, about 2 fold more at the base of the profile than at the surface. The rate of phenol oxidase activity was similar in STM-P and SSJG-5 but lower in BGr-P although activity rates were similar at 40-50 cm depth.

An earlier study by Pind et al. (1994) on the enzymatic activity of phenol oxidase in northern peatlands found that phenol oxidase activity fell rapidly with depth and correlates with oxygen availability. The increase in phenol oxidase activity with depth in our sites, where conditions

are much drier, suggest that oxygen supply is not a limiting factor on phenol oxidase in the system and although soil moisture content generally decreased with depth (Table 5.1; Figures 5.2, 5.3, and 5.4), it does not correlate in any form with phenol oxidase activity. These supports the view that the pattern of phenol oxidase enzyme activity detected was in response to other factors such as substrate availability – i.e. organic matter content – and accessibility rather than oxygen constraint.

*5.5.3 Relationship between Phenol oxidase activity, Depth and SOM content*

Previous work by Freeman et al. (2001, 2004) on the role of phenol oxidase enzyme in decomposition in northern temperate peatlands found that decreases in phenol oxidase activity led to a decline in the activity of hydrolases [sulphatase, phosphatase, β-glucosidase, chitinase, xylosidase]. This outcome was attributed to shortages in oxygen supply to the system due to waterlogged conditions which decreased the activity of the enzyme phenol oxidase. The waterlogged conditions allow phenolic compounds, which are strong inhibitors of hydrolytic enzymes, to accumulate thereby decreasing microbial decomposition. This phenomenon is known as the 'enzymatic latch mechanism' (Freeman et al., 2001).

In our sites, where oxygen supply does not appear to be a constraint on enzyme activity, phenol oxidase activity increased with depth, concomitantly with decreasing organic matter content. The increase in phenol oxidase enzyme activity with depth can be interpreted as a microbial response to an increasingly nutrient poor environment found at lower depths, as it is well established that organic matter content is one of the key controlling variables for enzyme activity (Kang et al., 2011). Best-subset multiple regression analysis showed that organic matter content had the strongest effect on phenol oxidase activity (Table 5.3). Second order polynomial regression analysis was subsequently carried out to further investigate this

relationship. Phenol oxidase activity exhibited a strong negative correlation with organic matter in site SSJG-5 and BGr-P ($R^2$ = 0.94; 1.00), and a reasonable correlation in site STM-P ($R^2$ = 0.52) (Figure 5.6). Similarly, the regression was significant in site SSJG-5 and BGr-P (*p*-value = 0.001, 0.038) but was not significant in STM-P site (*p*-value = 0.480).

The increase in unfavourable conditions generally associated with depth may be caused by a host of factors such as low organic matter content, pH, anoxicity, changes in mineral contents, particle/pore size and phenolic contents limit nutrient (organic carbon) availability and accessibility to microorganisms (Leified et al., 2008; Chiti et al. 2009, Schmidt et al., 2011). As mentioned earlier, phenolic compounds are potent inhibitors of enzyme activity, but they are also associated with the stabilisation of C-C bonds in aromatic carbon structures (Freeman et al., 2004). It is the view that microorganisms synthesize and release phenol oxidase enzyme in order to degrade phenolic compounds that are present in the soil so as to increase microbial access to substrate (organic matter), and to reduce the inhibitory effect of phenolics on hydrolytic enzymes involved in microbial metabolism and/or decomposition.

### *5.5.4 Relationship between Microbial biomass, Basal respiration, Decomposition and Phenol oxidase activity*

The effects of elevated phenol oxidase enzyme activity with depth can also be seen from patterns of soil microbial biomass activity. Soil microbial biomass and respiration both decreased with depth as expected, however the depth dependent decline in microbial biomass was exponential while soil respiration declined almost steadily (Figure 5.8, 5.9, and 5.10). Low ratio of microbial biomass to respiration as determined by the respiratory quotient with depth indicates a relatively high nutrient-rich environment and/or the presence of highly active microbial community at depths.

The latter may be considered as an adaptation of organisms to their surrounding environment. However, this may not be the case as adaptation typically involves the alteration of an organism's metabolism, and in extreme cases morphology, so as to increase nutrient use efficiency, survival and habitat sustainability. These requirements were not met, and although microbial community structure was not investigated it is unlikely that change in community structure is attributable due to the similarity in the environmental and edaphic conditions other than organic matter and depth, in the profiles and sites (Table 5.1).

Although the concept of adaption is not entirely dismissed, we propose that it is most plausible that the localised increases in nutrient availability at the various depths through increased accessibility by the mechanisms discussed in *section 5.5.3* has led to an increase in the activity rate of microorganisms by proportion, in deeper soil horizon relative to their surface counterpart. In addition, the observation of highly active microbial biomass by mass at depth without an associated increase in community size suggests that the nutrients made available to the system is utilised primarily to maintain biomass health rather than increase biomass size and that phenol oxidase enzyme production is independent of microbial community size. The stoichiometric requirements for optimal microbial health in soils are known to decrease with high C/N ratio and vice versa with lower C/N ratio. This is due to decreases or increases in protein synthesis which in turn is dependent on nitrogen availability (Yuste et al., 2007). C/N ratio on all sites show neither a discernible trend nor pattern to suggest that the higher microbial activity observed at depth may be sustained by high nitrogen availability (Table 5.1). Also of note is the activity of phenol oxidase enzyme in surface and near surface profile samples that receive fresh litter in conditions that are easily available for microorganisms to metabolise. The expression of phenol oxidase enzyme by microbes at these profiles may be seen as mitigation response against the toxicity of phenolic molecules by actively reducing soil phenolic content (Michalowicz and Duda, 2007; Sinsabaugh, 2010).

The influence of phenol oxidase enzyme activity on decomposition rate can be seen through its impacts on nutrient dynamics, and enzyme activity (Pind et al., 1994; Freeman et al., 2001, 2004). Decomposition rate is generally understood to decline with depth due to reduced energy availability to sustain heterotrophic microbial biomass and their associated activities (Chiti et al., 2009; Schmidt et al., 2011); however, research by Kemmitt et al. (2008) showed that the rate of organic matter decomposition was not proportional to the size, activity or composition of the microbial biomass. The authors hypothesised that mineralisation of organic matter is regulated by abiological processes that transforms non-bioavailable soil organic matter to bioavailable substrates. On our site, the general decline in microbial biomass and respiration with depth initially suggest a higher decomposition and/or activity rate at the surface than at depth when considered in absolute terms, however when measured in relative term to the biomass size, microorganisms at depth appear to be metabolically more active than their surface counterpart (Figure 5.8, 5.9, and 5.10).

According to Baldock and Preston (1995) and Baldock et al. (1997), the ratio of alkyl C to *O/N*-alkyl C can be used as an indicator for assessing the extent of decomposition of organic materials. The ratio of alkyl C to *O/N*-alkyl C increased with depth in all sites except at 40-50 cm depth in BGr-1 indicating a higher degree of decomposition at depth than on the surface (Kiem et al., 2000; Mathers and Xu, 2003). The decrease in alkyl C to *O/N*-alkyl C ratio in BGr-1 is attributed to the higher percentage of clay content at 40-50 cm depth (Table 5.4; Figure 5.7). Clay minerals are well known to slow decomposition of organic material in soil through the association of SOM with mineral components (adsorption) which in turn reduces substrate availability and/or accessibility to microbes thereby slowing decomposition (Sollins et al., 1996; Baldock and Skjemstad, 2000; Wang et al., 2003; Chiti et al., 2009; Schmidt et al., 2011; Saidy et al., 2012; Pronk et al., 2013).

*5.5.5 The Variability of Phenol oxidase enzyme activity in different Environments*

Phenol oxidase enzyme have been shown in many studies to assume an active role in a range chemical and biochemical processes in different ecosystem (Wetzel, 1992; Appel, 1993; Pind et al., 1994; Freeman et al., 1996; Williams et al., 2000; Freeman et al., 2001, 2004; Sinsabaugh, 2010). Its activity is not determined by a single factor but by multiple variables (moisture, aeration, organic matter, pH, $Fe^{2+}$, phenolic content) depending on the physicochemical profile of the individual systems. Kang et al. (2011) examined the rate of microbial enzyme activity including phenol oxidase in tropical marsh soils with different water regime to determine mechanisms associated with decomposition in such ecosystems. They found that enzyme activity was higher in waterlogged soils than in dry soils, however, this effect was attributed to higher nutrient and organic matter availability in the wet soils than in drier soils. They also demonstrated that depth had no discernible effect on enzyme activity and that water supply was a limiting factor in the system although only 2 depth profiles (0 – 5 cm and 5 – 10 cm) were studied. Similarly, Liu et al. (2014) examined the effects of flooding on soil phenol oxidase activity during rice straw decomposition and concluded that enzymatic activity was higher in flooded soils than non-flooded soils.

These results are in contradiction to previous reports on enzyme activity in temperate marsh and peatlands where water-table drawdown stimulates enzyme activity (Freeman et al., 1996; Kang et al., 1998); however the studies by Kang et al. (2011) and Liu et al. (2014) demonstrate that the oxygen content of the systems was not sub-optimal for enzyme activity and therefore not a limiting factor in the wet system, and that nutrient and organic matter content constrained enzyme activity in the dry system. Furthermore, Williams et al. (2000) investigated the phenol oxidase activity in *Sphagnum* and *Carex* wetland in New York. They reported that pH and phenolic contents had more effect on phenol oxidase activity than aeration. In our site, the patterns of phenol oxidase enzyme activity observed show a closer relationship with

organic matter content than other factors investigated (aeration, pH, and microbial abundance). Soil pH ranged between 5.85 and 6.41 in water and 5.48 - 6.06 in calcium chloride both of which are not sub-optimal for phenol oxidase enzyme activity (Pind et al., 1994; Sinsabaugh, 2010, Bach et al., 2013).

**5.6 Conclusion**

The overall result of this study indicates that phenol oxidase activity is dependent on organic matter content in our sample sites (St Andrews, Scotland, UK), and therefore demonstrates for the first time that such activity plays a major role in the nutrient dynamics in anthropogenically modified soils. Historical practices saw high inputs of diverse organic-rich materials to soils. The mixing of these materials of diverse origin, most of which are natural and anthropogenic sources of phenol, would have elevated the concentrations of phenolic compounds in the soil above natural levels. Phenol oxidase enzyme is produced and deployed by soil microorganisms to counter the effects phenolic materials on general enzyme activity within soil. Future investigations should focus on determining the abundance of phenolic compounds present *in situ*, as well as microbial community structure, to better understand the effects of substrate concentration and the associated microbial response.

# CHAPTER 6

## Carbon Stock and Dynamics of Buried Anthrosols in Scotland

### 6.1 Introduction

In Scotland and around the world, carbon-rich urban and peri-urban soils have developed through many centuries of application of bio-wastes (human and animal waste, vegetable waste, bones etc.) to soils. Organic waste materials were composted and reapplied to gardens and hinterlands for horticultural and agricultural purposes. At present, no studies have attempted to understand the various decay processes that have taken place in time as well as the potential implications of their carbon store in the environment, particularly in respect of changing climate. Here, we investigate the fate of the organic-rich materials that were deposited on soil by examining the organic matter content and composition in relation to decomposition and the processes that may control the dynamics and stability of the organic matter.

### 6.2 Carbon Accumulation in Historical Soils and Environmental Implication

The enrichment of soil with organic waste for cultivation in the medieval and early-modern periods was a common management practice in Scottish towns (Macdonald, 1884; Murray, 1982; Clark, 1997; Hall 1997; Cachart, 2000; Carter, 2001; Bowler, 2004; Golding et al., 2010; Oram, 2011). Commercial and subsistence food production were heavily reliant upon the recycling of community waste to improve soil conditions and productiveness (Cachart, 2000; Carter, 2001; Golding and Davidson, 2005; Golding et al., 2010; Davidson et al., 2006; Oram, 2011). Mechanisms for production of these wastes include products from human habitation, stalled animals (dung), fire and hearth residues (ash), craftwork and other processing activities (fish gutting, butchery shambles etc.). The human habitation contribution can be further

broken down into enrichment through inputs of human bodily wastes (faeces, urine), re-deposition of cesspit contents, domestic food processing waste and household rubbish such as spoiled food and debris (Davidson et al., 2006; Golding et al., 2010; Oram, 2011). The accumulation of these organic materials has resulted in soil deepening to depths of over 1 metre in some locales across Scotland (Hall, 1997; Davidson et al., 2006).

The carbon store and dynamics of soils that have formed under these circumstances is one of the least understood processes. Past geo-archaeological investigations have identified these anthropogenically-deepened soils and interpreted them in respect to site activity but the implication of management change and the fate of these soils in the environment with respect to their carbon store potential, processes and dynamics of organic carbon, in response to changes in environmental conditions, has received relatively little detailed investigation. Many studies have used the CENTURY soil organic carbon (SOM) model (Parton et al., 1987, 1988) and RothC model (Coleman and Jenkinson, 1995; Jenkinson and Rayner, 1977) to study soil organic matter (SOM) dynamics and turnover rates in a variety of terrestrial ecosystems (forest, grassland, arable) for different past and future climate change scenarios, management systems, and in different regions (Parton et al., 1989; Smith et al., 1997; Falloon et al., 1998; Farage et al., 2007; Liu et al., 2009; Barancikova et al., 2010; Xu et al., 2011; Hashimoto et al., 2012) whilst others have used various other SOM models (SOMM , ITE, Verberne, CANDY, DNDC, DAISY, NCSOIL) to investigate the same subject (Smith et al., 1997; Coleman et al., 1998).

The implications and outcome of these model assessments and predictions are germane to developing management systems that would attenuate the effects of climate change on carbon loss, but uncertainties on these estimations still exist (Cannell et al., 1999), and more so on anthropogenic deep soils, due to inadequate data availability and assumptions made in model simulations; therefore questions can be asked: (i) what are the dynamics of such

complex mixtures of materials over time; (ii) are we looking at a relatively balanced system given that these urban soils have been long exposed to elements of degradation?

The physical, chemical, and biological mechanisms of control of soil organic matter dynamics have been studied in great detail due to the relevance of soil as a source and sink in global C cycle and budgeting (Sollins et Al., 1996; Baldock and Skjemstad, 2000; Lutzow et al., 2006). These mechanisms are comprised of various other processes that can be viewed as resulting from four sets of characteristics: (i) recalcitrance; (ii) accessibility; (iii) interaction; and (iv) biological state. Protection due to *recalcitrance* involves the inherent chemical properties of an organic compound that influences microbial and enzyme degradation. *Accessibility*, however, is the protection due to occlusion, intercalation, encapsulation, and hydrophobicity that affect degradation rate. Protection by *interaction* comprises of the inter-molecular interactions of organic matter with soil minerals (aluminium, iron and manganese oxides, phyllosilicates), metal ions and other organic substances, while protection arising from *biological state* refers to the size, community structure, and the capacity of microbial community (Sollins et al., 1996; Baldock and Skjemstad, 2000; Baldock et al., 2004; Lutzow et al., 2006). These control processes of SOM stabilisation mechanism can operate, in varying degrees, on one or more different components of soil organic matter fractions as well as in the different particle size fractions of soil (different clay size fractions, silt, and sand) (Baldock and Skjemstad, 2000; Kahle et al., 2003).

Studies on the long-term dynamics and stability of soil organic matter in many natural systems have used measured $^{14}C$ ages of whole soil organic matter or its fractions (humins, humic and fulvic acids) together with various spectroscopic techniques to chemically characterise the forms of the resultant soil organic carbon species after 'X' number of years of decomposition (Martel and Paul, 1974; Wang et al., 1996; Paul et al., 1997; Bruun et al., 2005; Chiti et al., 2009), others have considered this in a shorter-term on organically amended soils on either

experimental field plots or in a controlled environment in laboratories to study various transformational pathways of organic material during decomposition (Šimon, 2005; Smidt et al., 2005; Busato et al., 2012). Urban soils present a rare site, a form of natural laboratory, to study the long-term product of the decomposition of known organic materials added to soils under natural environmental conditions and processes. We investigated the fate of the organic-rich materials that were introduced to soil as part of the waste management practices in medieval urban communities by studying soil physical, chemical and biological properties, including SOM content, and its chemistry. We adopt a meso-level approach to examine the relationship between C content in different horizons and various other deterministic elements of decomposition and stabilisation including phenol oxidase enzyme synthesis and activity rate, soil respiration and microbial biomass, soil pH, mineralogy and particle size distribution.

## 6.3 Materials and Methods

The study site is located within the town of St Andrews, on the east coast of Scotland. Please refer to Chapter Two, *section 2.1.1* for more details on site description and sampling. The samples (STM-2, SST-1, SSJG-1, BGr-1, STM-P, SSJG-5, and BGr-P) used in this Chapter have previously been analysed and discussed in context of the investigations in Chapters Four and Five. As also stated previously, samples were analysed following the procedures detailed in Chapter Three. A total of 33 bulk soil profile samples were collected and analysed.

## 6.4 Result and Discussion

### *6.4.1 SOM Stabilisation and Protection Mechanisms*

The consequence of the heterogeneous nature of soil organic matter is the differences in the rate of accumulation and decomposition as they are acted upon by various biotic and abiotic factors. These control factors includes temperature, moisture, rate of microbial activity, enzyme activity, microbial community size, pH, mineral constituents, soil texture (grain size)

and structure (aggregation) (Sollins et al., 1996; Baldock et al., 2004). As alluded to, SOM stabilisation is broadly considered under three main mechanisms; physical, biological and chemical mechanisms. The actions of these mechanisms have no defined operational boundary in which one mechanism terminates and another activates but acts in a synergistic manner where one or two of the processes of stabilisation are active via either bio-chemical or physio-chemical mode (Sollins et al., 1996). Changes in organic matter with time therefore represent the combined interaction of these mechanisms. The extant content of organic matter and its chemical composition as found in the study sites are discussed in the framework of SOM stabilisation mechanisms as described above.

### *6.4.2 The Effect of Intrinsic Chemical Structure on Carbon Dynamics*

Soil organic matter comprises of a wide range of organic substances exhibiting different structural and functional characteristics that influence their predisposition to degradation by microorganisms and extracellular enzymes. The inherent molecular properties of organic materials such as charcoal or black carbon confers some degree of resistivity against microbial hydrolysis due to the highly condensed poly-aromatic nature of the molecules, that allows them to survive in the environment (soil) for long periods of time (Lutzow et al., 2006). Black carbon has an estimated residence period of between 500 – 10000 years in the soil, depending on soil and environmental conditions (Kuzyakov et al., 2009). Due to this apparent long residence time, the occurrence of black carbon in the soil can be viewed as an effective means of prolonged carbon retention and storage and therefore a process of carbon stabilisation/equilibration (Schmidt and Noack, 2000), although some reports have shown that black carbon can undergo some natural degradation (Bird et al., 1999) and biological degradation (Hamer et al., 2004).

The solid-state NMR spectra of the samples indicate that large proportions (42 % - 58 %) of the organic C of the soil are in the aromatic C form (Figure 6.1, and Table 6.1), a product of pyrogenic processes, which are considered recalcitrant in the soil due to their high resistance to thermal oxidation, and to chemical photo-oxidation. The selective accumulation of these highly resistant aryl-C structures (aromatic C) (Figure 6.1) suggests that the relative chemical recalcitrance of charcoal to degradation or its relatively slow decomposition rate contributes to the extant residual organic matter content seen in urban anthrosols (Solomon et al., 2007). Charred organic residues derived from high combustion temperatures have been demonstrated to have higher resistance to biological degradation relative to those obtained from lower thermal treatment. Baldock and Smernik (2002) showed that the rate of C mineralisation of carbon contained in charred residues decreased with increasing pyrolysis temperature of organic C. Similar study by Bruun et al. (2008) also confirms this relationship.

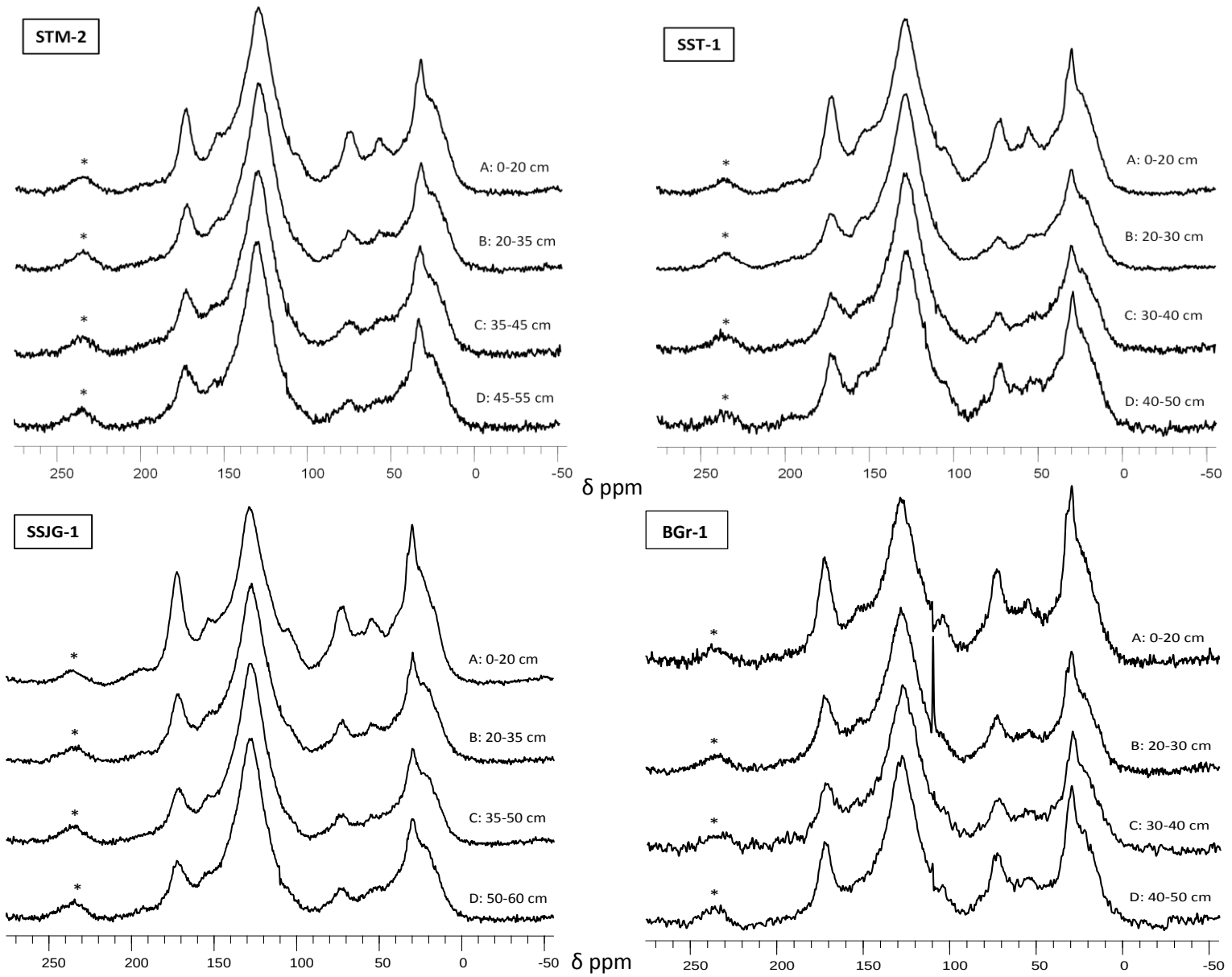



Fig. 6.1. CPMAS $^{13}C$ NMR spectra of soil samples from within (STM-2, SST-1 and SSJG-1) and outside (BGr-1) the settlement core areas of St Andrews [Spectra were graphically normalised to the dominant aromatic region centred at 130 ppm]

High contents of condensed aromatic C structures of SOM as observed from the spectra (Figure 6.1) indicates black carbon derived from high thermal alteration of the precursor organic material which may have a negative influence (decrease) in the degradability of char (black carbon) in the soil. As cited above, the variability in the conditions (heat intensity, parent material, duration of heating) involved in the formation of charred residue can result in the creation of diverse products of chemical state whose catabolic pathways differ from the conventional process thereby influencing their ability to act as microbial substrate (Baldock and Smernik, 2002; Kleber, 2010; Mcbeath and Smernik, 2009). The postulated inertness of black carbon in the soil results from the interaction between molecular properties, the microbial ecology, and a host of environmental factors amongst which anoxicity conditions has been implicated as an important determinant factor in their catabolism (Kleber, 2010). The oxidation conditions of organic C compounds expectedly vary, and the degree of oxidation of these compounds in the soil is determined by the oxidation capacity of the soil environment (oxygen availability). Therefore high oxygen-containing compounds with low activation energy should have a faster turnover rate than those with low molecular oxygen content and high activation energy because they do not require large energy investment from the decomposer community to metabolise.

Table 6.1. Relative contributions of carbon species to the total signal intensity in $^{13}C$ NMR spectroscopy of soil samples from different sites and sampling depths

| **Sample & Depth (cm)** | **% Alkyl C (0-45 ppm)** | **% O/N-Alkyl C (45-90 ppm)** | **% Anomeric C (90-110 ppm)** | **% Aromatic C (110-160 ppm)** | **% Carboxyl C (160-220 ppm)** | **Alkyl C / O/N-Alkyl C** | **Aromaticity (%)** | **Clay (%)** | **Silt (%)** |
|---|---|---|---|---|---|---|---|---|---|
| **STM-2** 0-20 | 21 | 15 | 4 | 50 | 11 | 1.40 | 55.56 | 3.39 | 51.71 |
| 20-35 | 19 | 12 | 3 | 54 | 11 | 1.58 | 61.36 | 3.08 | 51.42 |
| 35-45 | 20 | 11 | 3 | 54 | 12 | 1.82 | 61.36 | 4.77 | 47.13 |
| 45-55 | 19 | 10 | 3 | 57 | 11 | 1.90 | 64.04 | 5.17 | 62.93 |
| **SST-1** 0-20 | 22 | 17 | 4 | 45 | 12 | 1.29 | 51.14 | 4.09 | 64.01 |
| 20-30 | 20 | 11 | 3 | 54 | 11 | 1.82 | 61.36 | 5.99 | 71.01 |
| 30-40 | 21 | 12 | 4 | 53 | 10 | 1.75 | 58.89 | 11.00 | 89.00 |
| 40-50 | 22 | 15 | 4 | 48 | 11 | 1.47 | 53.93 | 10.10 | 89.86 |
| **SSJG-1** 0-20 | 23 | 17 | 5 | 43 | 13 | 1.35 | 48.86 | ND | ND |
| 20-35 | 21 | 12 | 4 | 52 | 11 | 1.75 | 58.43 | ND | ND |
| 35-50 | 18 | 10 | 3 | 58 | 11 | 1.80 | 65.17 | ND | ND |
| 50-60 | 20 | 10 | 4 | 56 | 11 | 2.00 | 62.22 | ND | ND |
| **BGr-1** 0-20 | 24 | 19 | 4 | 42 | 12 | 1.26 | 47.19 | 6.60 | 68.60 |
| 20-30 | 19 | 15 | 4 | 50 | 12 | 1.27 | 56.82 | 7.28 | 69.52 |
| 30-40 | 20 | 14 | 5 | 50 | 12 | 1.43 | 56.18 | 8.36 | 55.64 |
| 40-50 | 22 | 17 | 4 | 46 | 11 | 1.29 | 51.69 | 17.70 | 82.30 |

The contribution of alkyl C (0 – 45 ppm) accounts for between 18 % – 24 % of the signal intensity while *O/N* – alkyl C (45 – 90 ppm) comprises between 10 % - 19 %. The selective degradation of soil organic matter is evident from the lower contribution of *O/N* – substituted alkyl C and a higher contribution of alkyl C. Previous studies by Smernik et al. (2003) on the chemical composition of 3 – 5 yr old sewage sludge using solid-state $^{13}C$ NMR revealed the dominance of *O/N* – alkyl C and alkyl C in sewage sludge organic matter. The depletion of *O/N* – alkyl C signal intensity, and the enrichment of the alkyl C region corresponds with the preferential utilisation of oxygen and nitrogen-containing aliphatic (*O/N* – alkyl C) compounds by microorganism during humification process (Novotny et al., 2009). This is because the signal intensity from this chemical shift region arise from compounds that are easily degradable by microbes, such as carbohydrates (~72 ppm), methoxyl (~58 ppm), proteins and peptides (~53 ppm). Given the chemically analogous composition of the organic substances deposited on urban soils to sewage sludge and the period of time in which these materials have undergone transformation and/or decomposition in the soil, the change in the dynamics of carbon, the decrease of *O/N* – alkyl C compounds relative to alkyl C, as seen from the NMR spectra of urban anthrosols provides evidence for the selective degradation of the less resistant (*O/N* – alkyl C) compounds in relation to other carbon species, more so aromatic C (Sollins et al., 1996). The resonance signal intensity of alkyl C region generally consists of materials from microbial neo-synthesis or products resulting from decomposition process. Plant materials such as resins, waxes, and cutins, however, which have some resistance to degradation, are also constituent material of this region and may also contributes to the signal intensity of the chemical shift region of alkyl C (Baldock et al., 1992; Preston, 1996; Lutzow et al., 2006). As previously discussed, the intrinsic chemical characteristic of black carbon decreases its susceptibility to biological degradation which results in the gradual accumulation of black carbon in the soil. In addition to its chemically advantageous properties, black carbon can also

influence the dynamics of organic matter by acting as sorption sites for SOC to fixate as seen in clay minerals (Solomon et al., 2007; Schmidt and Noack, 2000).

*6.4.3 Physical Control of Soil Organic Matter Dynamics*

The physical protection of soil organic matter from degradation is a well-recognised mechanism of stabilisation in the study of organic matter dynamics and turnover. Soil physical (texture, structure) and chemical (mineralogy) properties can influence substrate availability (OM) to microorganisms and therefore influence the residence period of organic matter regardless of their biochemical predisposition to microbial degradation (Kahle et al., 2003; Wattel-Koekkoek et al., 2004; Kiem and Kögel-knabner, 2002). Various processes such as occlusion, intercalation, encapsulation, hydrophobicity and OM interaction with mineral assemblages (aluminium, iron and manganese oxides, phyllosilicates) have all been implicated in the protection of organic matter from biological attack (Baldock et al., 2004; Saidy et al., 2012; Wilson et al., 2013). Solid-state NMR spectra of soil samples shows an overall decline in the O/N – alkyl C region with depth (Figure 6.1) which is expected since the OM at subsoil is older and therefore will have undergone a greater extent of decomposition than those at the surface, from the longer period of exposure to biochemical degradation.

However, a higher proportion of O/N – alkyl C was observed in subsoil profiles of samples from SST-1 and BGr-1 sites which signify the operation of an active transport system. In SST-1, O/N – alkyl C contributions declined with depth from 17 % at 0 – 20 cm to 11 % at 20 – 30 cm (Table 6.1), before increasing to 12 % and 15 % between 30 – 40 cm and 40 – 50 cm depth respectively. In BGr-1, the contributions of O/N – alkyl C also declined with depth from 19 % to 14 % between 0 – 40 cm before rising to 17 % at 40 – 50 cm depth. Samples from BGr-1 site also exhibited a higher content of O/N – alkyl C in all of its profile than found on the other sites.

The higher contributions of O/N – alkyl C compounds to surface soil profiles are understandably attributable to the direct seasonal inputs of fresh organic material (litter) to topsoil, a process which is relatively absent in subsoil. Although, subsoils may also receive fresh organic material through bioturbation and translocation of dissolved organic C (DOC) from the surface (Chiti et al., 2009), this, however, does not explain the higher retention or content of such compounds at subsurface profiles, particularly at depths, as observed in BGr-1 site, given that such products are readily-mineralisable microbial substrates.

Table 6.2. Relative contribution of O/N-Alkyl C and sample grain size distribution of soil samples from study sites (ND – no data)

| Sample/Depth (cm) | O/N-Alkyl C (45-90 ppm) (%) | Clay (%) | Silt (%) |
|---|---|---|---|
| **STM-2** 0-20 | 15 | 3.39 | 51.71 |
| 20-35 | 12 | 3.08 | 51.42 |
| 35-45 | 11 | 4.77 | 47.13 |
| 45-55 | 10 | 5.17 | 62.93 |
| **SST-1** 0-20 | 17 | 4.09 | 64.01 |
| 20-30 | 11 | 5.99 | 71.01 |
| 30-40 | 12 | 11.00 | 89.00 |
| 40-50 | 15 | 10.10 | 89.86 |
| **SSJG-1** 0-20 | 17 | ND | ND |
| 20-35 | 12 | ND | ND |
| 35-50 | 10 | ND | ND |
| 50-60 | 10 | ND | ND |
| **BGr-1** 0-20 | 19 | 6.60 | 68.60 |
| 20-30 | 15 | 7.28 | 69.52 |
| 30-40 | 14 | 8.36 | 55.64 |
| 40-50 | 17 | 17.70 | 82.30 |

The presence of labile organic carbon compounds that are preferentially utilized by decomposer communities at depths is suggestive of the presence of an active mechanism of protection against hydrolysis. Soil horizons with higher O/N – alkyl C compounds than the preceding horizon have an associated increase in clay content at corresponding depth (Table 6.2). In STM-2 and SSGJ-1 samples where O/N – alkyl C contributions declined with depth, the percentage contribution of clay size fractions along the profile did not vary greatly (3.08 % - 5

%), whereas variations in this parameter (% - clay) were more pronounced in SST-1 and BGr-1 samples varying from 4 % to 11 % for SST-1, and 6.60 % to just under 18 % for BGr-1. Much indirect evidence exist for the role of clay minerals in soil organic matter stabilisation from studies on carbon and nitrogen dynamics of manure and crop residue in soils of textural disparity (Solins et al., 1996; Saidy et al., 2012). Positive correlations have been obtained between clay and organic C content in soils, as well as the amount of residual C substrate retained in a soil after designated period of decomposition (Baldock et al., 2004). Clay mineral complexes and assemblages provide the vast majority of sorbent surface area in soil for sorption of various organic compounds protecting them from biological attack.

As discussed above, the percentage clay content of soil can alter C mineralisation by limiting microbial access to substrate (Wang et al., 2003). The degree of these interactions is influenced by particle size, which increases with smaller particle size (Baldock et al., 2004; Kiem and Kögel-knabner, 2002). The spatial arrangement of pores spaces and particles, which is determined by the structural configuration of soil fabric, can limit the hydrolysis and diffusion of organic molecules in soils where a significant portion of the available pore spaces exists in pores less than 0.5 µm in diameter (Baldock et al., 2004). The proportion of total soil porosity formed by pores less than 0.5 µm increases with increasing clay content and results in the protection of any organic material associated with particles in these pores because microorganisms are not able to enter pores less than 0.5 µm. Soil samples from BGr-1 site have higher percentage clay content than other samples investigated and it is presumed that the impact of this mechanism will be more pronounced on the site as a result. The impact of clay mineralogy on OM is not apparent from examination of gross organic carbon content of soil samples because these interactions occur at a much finer scale, at molecular level, as illustrated by $^{13}C$ NMR spectra.

*6.4.4 Biological Control of Soil Organic Matter Dynamics*

The biological control of C mineralisation rate in soil is dependent on the condition of the decomposer community, if other factors that may influence substrate availability and accessibility are kept constant. This condition is defined by the proportion of active microbial biomass, activity/metabolic rate, community structure and stoichiometric requirements that together determines the rate of decomposition and the amount of $CO_2$ released in the process (Solins et al., 1996; Lutzow et al., 2006; Mazoni et al., 2008, 2010). The operation and potency of the biological control mechanism is to an extent subject to the degree of physio-chemical mechanism of stabilisation in operation. As previously discussed, the intrinsic chemical structure of certain organic compounds such as charcoal prevent rapid degradation by microorganism resulting in accumulation, while physical stabilisation, before reaching C saturation point, limits the accessibility of organic matter, irrespective of their forms, (labile or refractory) (Solins et al., 1996, Pérez-Cruzado et al., 2014). Thus, the biological control of organic C mineralisation can be considered to be greatest in soils with little or no active mechanisms of stabilisation such as in less-structured sandy soils, but biological mechanism is noticeably limited in silty-clay or clay type soil where physio-chemical interactions are prevalent.

Table 6.3. Relative contributions of carbon species to the total signal intensity in $^{13}C$ NMR spectroscopy of soil samples from different sites.

| Sample & Depth (cm) | $C_{org}$ (%) | O/N-Alkyl C (45-90 ppm) (%) | Alkyl C / O/N-Alkyl C | Aromaticity (%) | pH ($CaCl_2$) |
|---|---|---|---|---|---|
| **STM-2** 0-20 | 8.44 | 15 | 1.40 | 55.56 | 6.58 |
| 20-35 | 5.23 | 12 | 1.58 | 61.36 | 6.33 |
| 35-45 | 3.38 | 11 | 1.82 | 61.36 | 7.00 |
| 45-55 | 3.71 | 10 | 1.90 | 64.04 | 6.77 |
| **SST-1** 0-20 | 7.83 | 17 | 1.29 | 51.14 | 6.82 |
| 20-30 | 4.58 | 11 | 1.82 | 61.36 | 6.85 |
| 30-40 | 2.88 | 12 | 1.75 | 58.89 | 7.20 |
| 40-50 | 3.02 | 15 | 1.47 | 53.93 | 7.24 |
| **SSJG-1** 0-20 | 7.26 | 17 | 1.35 | 48.86 | 6.71 |
| 20-35 | 5.20 | 12 | 1.75 | 58.43 | 6.88 |
| 35-50 | 5.73 | 10 | 1.80 | 65.17 | 7.16 |
| 50-60 | 3.33 | 10 | 2.00 | 62.22 | 7.16 |
| **BGr-1** 0-20 | 3.45 | 19 | 1.26 | 47.19 | 5.98 |
| 20-30 | 3.24 | 15 | 1.27 | 56.82 | 6.13 |
| 30-40 | 2.21 | 14 | 1.43 | 56.18 | 6.22 |
| 40-50 | 0.76 | 17 | 1.29 | 51.69 | 6.31 |

As described in section *6.4.3*, the overall decline in O/N – alkyl C compounds with depth is associated with the duration of exposure of the SOM in each profile to elements of decomposition, and the reduced input of new organic matter. The higher retention of O/N – alkyl C compound observed at depths in BGr-1 (40 – 50 cm) and SST-1 (30 – 40 cm; 40 – 50 cm) sites were attributed to physical mechanism of protection; the association of SOM with mineral which reduces substrate availability to microbes (Chiti et al., 2009). From the integration values of NMR spectra of soil samples (Table 6.1), the percentage contribution of aryl C (110 – 160 ppm) decreased with increase in O/N – alkyl C content and vice versa. Previous studies by Kiem et al. (2000) observed a similar inverse correlation between these chemical shift regions and attributed it to diminishing organic input. It is suspected, however, that this relationship may also result from '*priming effect*' from the presence of easily metabolisable substrate (O/N – alkyl C) on microbial degradation of compounds of higher chemical resistance (char). Although charred organic matter (black carbon) is considered to be

relatively inert with long residence time in the soil, Hamer et al. (2004) and Kuzyakov et al. (2009) showed that charred plant materials amended with an easily utilisable C source (glucose) were metabolised at a faster rate by microorganisms through co-metabolism.

The ratio of alkyl C to O/N – alkyl C, and aromaticity (Table 6.3) are used as indicators for assessing the extent of decomposition of SOM (Baldock and Preston, 1995; Baldock et al., 1997). The increase in both alkyl C to O/N – alkyl C ratio and aromaticity values with depth indicates higher degree of humification of SOM with depth with exceptions to BGr-1 and SST-1 samples where values tend to be lower at depth and/or the proceeding horizon; these values are nevertheless still greater than surface values. Soil microbial biomass (SMB) and respiration both decreased with depth but the rate of decline is more pronounced for SMB relative to respiration. This difference in the reduction quotient with depth suggests that the smaller pool of SMB at depth/subsoil may consist of more active microbial populations (Figures 6.2).

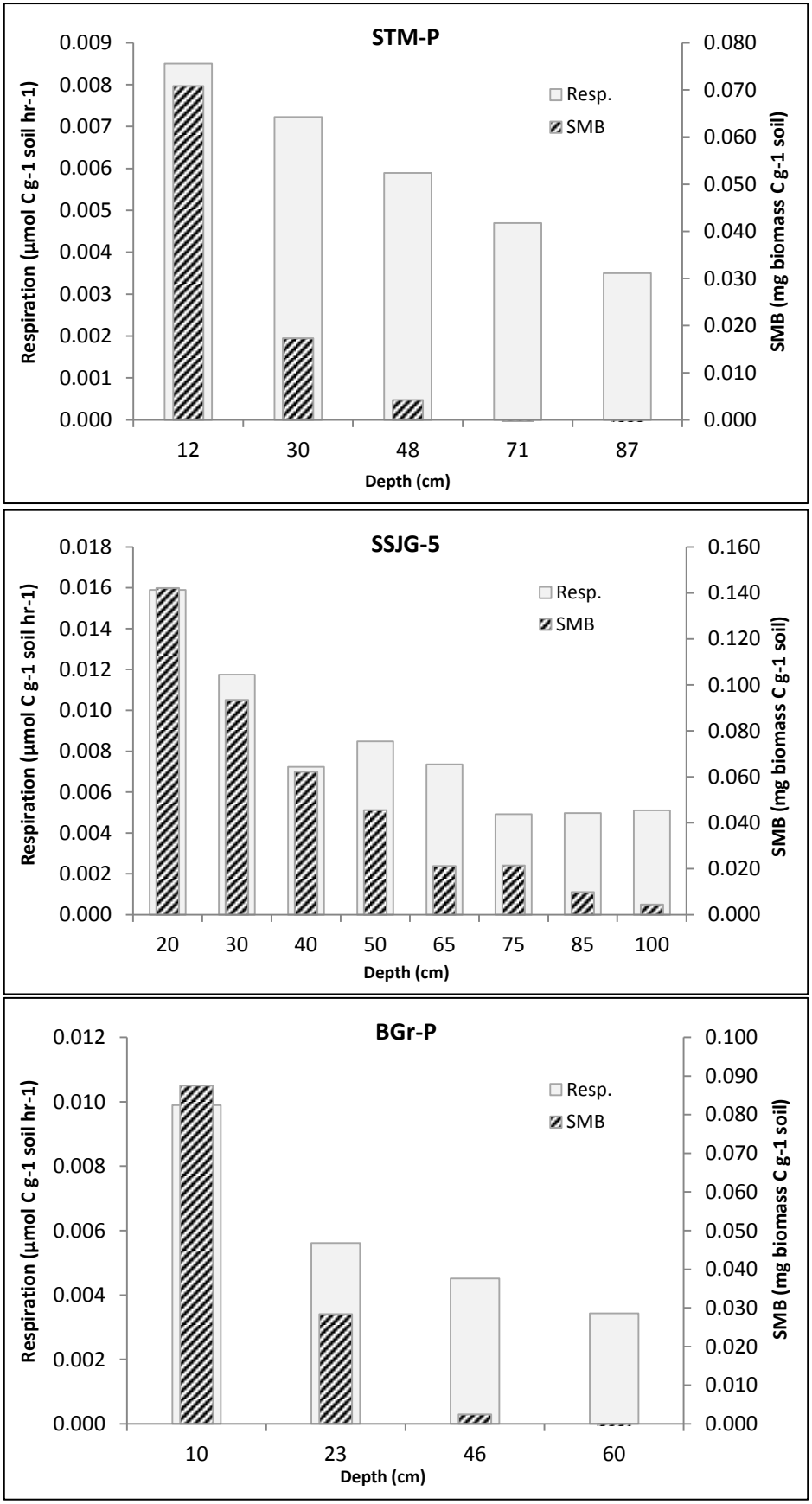



Fig. 6.2. Respiration rate versus microbial biomass measurements in study sites

An aspect of biological control of organic matter dynamics in urban anthrosol was discussed in chapter five, where in response to a nutrient poor environment, microorganisms synthesise and release the extracellular enzyme phenol oxidase to degrade phenolic compounds which are known inhibitors of hydrolase activity. Phenolic compounds occur naturally in soils, however, secondary sources of phenolic enrichment in urban soils arise from the addition of household waste to soil (*Section 6.2*), some of the contents of which are known natural and anthropogenic source of phenolic compounds (Michalowicz and Duda, 2007).

Table 6.4. Phenol oxidase activity of soil profile from sample site STM-P, SSJG-5, and BGr-P

| **Sample** | **Depth (cm)** | **Phenol oxidase Enzyme Activity (U g-1)** |
|---|---|---|
| STM-P | 12 | 35.18 |
| | 30 | 50.09 |
| | 48 | 70.17 |
| | 71 | 44.42 |
| | 87 | 50.02 |
| SSJG-5 | 0-20 | 44.02 |
| | 20-30 | 41.06 |
| | 30-40 | 49.62 |
| | 40-50 | 54.42 |
| | 50-65 | 50.20 |
| | 65-75 | 59.52 |
| | 75-85 | 70.86 |
| | 85-100 | 103.76 |
| BGr-P | 10 | 21.24 |
| | 23 | 28.93 |
| | 46 | 20.08 |
| | 60 | 49.77 |

Elevated concentrations of phenolic compounds result in a corresponding increase in its influence on substrate availability. Phenol oxidase activity was noticeably greater at depths than at the surface responding to reduced nutrient availability, but the expression of phenol oxidase enzyme by microorganisms in surface soil (Table 6.4) that regularly receives fresh litter which is a source of easily available substrate may be seen as a mitigation response to the toxicity of phenolic molecules by actively reducing soil phenolic content (Sinsabaugh, 2010).

*6.5 Summary and Conclusion*

As discussed, various mechanisms of stabilisation of soil organic matter are at work at varying degrees in soils and soil horizons of different textural, structural and mineralogical properties. The rate of decomposition of SOM is co-determined by the complex set of interactions between the physical, chemical, and biological mechanisms of protection and a range of environmental variables. Soil organic matter was dominated by H- and C- substituted aryl C aromatic structures amounting to between 42 % and 58 % of the total resonance signal intensity. This is followed by aliphatic C moieties (18 % – 24 %), and the more labile O/N – alkyl C functionalities (10 % - 19 %). The similarity in the solid-state NMR spectra of surface and subsurface soil samples is suggestive of the stabilisation of soil organic matter although the ratio of alkyl C to O/N – alkyl C and aromaticity indicates that subsoil samples have undergone a greater extent of decomposition.

Soil enrichment by anthropogenic additions of charred organic C residues is the primary source of condensed aromatic structures found in historical urban anthrosols. The abundance of the aromatic C functional group in SOM suggests that selective accumulation of these relatively recalcitrant compounds is a major contributing factor to the residual extant organic C content observed. Molecular oxygen constraint on the decomposer communities may reduce the rate at which organic C molecules with high stoichiometric oxygen demand are metabolised. The presence of O – containing organic C species and potentially labile aliphatic C functionalities, both of which have been long exposed to decomposition processes in the soil, shows the importance of active stabilisation mechanisms. Also highlighted is the complementary role that may be played by black carbon as an additional source of protection in physically stabilising OM in their capacity to act as sorption sites for SOM potentially limiting microbial access to labile components of organic matter.

**CHAPTER 7**

# Urban Anthrosol as Potential Historical Archive: Intra and Inter Site Assessments of Soil Record Data of Scottish Medieval Urban Landscape

## 7.1 Introduction

Human activities can cause significant changes to the landscape, particularly to soil (Grieve, 2001). The establishment of settlements and the associated occupational activities and functions of the settlement can result in deliberate and/or inadvertent changes to the original soil conditions. The degree of this change and the features of the resulting soils are determined by the nature and intensities of particular anthropogenic processes and activities and/or longevity of such practices which are in turn influenced by geographical and cultural differences (Holliday, 2004). The development of distinctive horizons (terric, plaggen, irragric, anthraquic, hydragric, and hortic) in anthrosols demonstrates the influence of these modifier factors on soil pedogenic processes (WRB, 2006).

The tendencies of horizon differentiation in anthrosols are greater on arable fields than in backlands and gardens found within settlement core areas because they represent the main agricultural land. As discussed previously, these features can be explored to reveal details of past agrarian history in cultivated landscapes (Simpson and Bryant, 1998; Davidson and Carter, 1998; Dercon et al., 2005), however, other occupational activities such as craft work, ovens, cooking, butchery, and middens may also leave traceable signatures that can equally serve as indicators for site use, and for determining the organisational history of urban landscapes.

## 7.2 Relict Anthropogenic Soils

Soils have long been used as a natural archive in climatic and anthropological studies to understand past environmental conditions and their effects on both terrestrial dynamics and on human developmental history (Glaser et al., 2003). As mentioned above and discussed in

preceding chapters, urban dwellings, particularly back gardens, represents hubs for a range of domestic and industrial activities in the medieval period, responding to changes in economic and environmental conditions in space and time. Through the analysis of accumulated soil materials, the association of occupational deposits and debris (physical and chemical) resulting from these activities, some of which are distinctive signature-bearing activity, allows a time-depth construction of landscape history and when augmented with historical and archaeological records, provides a more comprehensive account as well as a platform on which models of urban soil use can then be built.

In Scotland, the protection of historical sites does not currently take into account the cultural significance of historical urban soils. The presence of above-ground artefacts almost entirely determines the designation of a site as a cultural heritage site (see Chapter 1, sub-section 1.3.1 for full discussion). The prioritisation of visible artefacts undoubtedly excludes other sites without such features, including sites within extant medieval urban centres/cities that may be of cultural significance, with potentially rich cultural history embedded within its soil pedon/stratigraphy. To this end, it is argued that consideration should be given to the preservation of urban soil deposits since they are, in part, an aspect of our history that may not be reflected in visible structural remains or archaeological excavation.

### 7.3 Past Settlement History of Roxburgh and St Andrews

The royal burgh of Roxburgh and the ecclesiastical burgh of St Andrews are both medieval urban settlements that were established in the 12$^{th}$ century but they have very different histories. Whilst St Andrews has thrived and prospered in relatively peaceful conditions down to the present, Roxburgh's past was one of conflict which led ultimately to its failure; most modern awareness of it is limited to the history book. Roxburgh in its prime was a thriving urban settlement with many trades, and the focal point for regional economic activities and international trade (Martin and Oram 2007). The burgh steadily prospered since its

establishment in 1120s, but this was disrupted by a series of fire incidents – both accidental and deliberate - in 1207, 1216 and 1244. Much structural damage was caused in those events, mainly due to the largely wood-built character of the structures at the time but the burgh regenerated and continued to function. The outbreak of Anglo-Scottish conflict in 1296 led to nearly seven decades of hostilities which is arguably the single biggest overarching factor that led to the terminal decline of Roxburgh and its eventual abandonment before 1460, when the Scots finally recaptured and destroyed its English-held castle.

St Andrews on the other hand flourished during the medieval period, largely due to it being the location of the cathedral of the senior Scottish bishop and consequently a centre of commercial activities. From 1411 it was also the location of Scotland's first university, further boosting its economic power. Most of its residents, like in Roxburgh, engaged in a range of activities such as farming, craftwork, and trade, fishing was of note, but farming was more prevalent. Generally, soil capitalisation in medieval and early modern Scotland were done by recycling composted domestic and industrial wastes which were then later applied to cultivated areas such as back gardens and fields (Macdonald, 1884; Golding et al., 2010; Oram, 2011). In Roxburgh, whilst this soil management practice, including other anthropogenic signature-bearing activities, was in decline during the final stages of the burgh and at a complete halt after abandonment, they however continued in St Andrews until the mid-nineteenth century, approximately 450 years after their cessation in Roxburgh, and until present-day for other anthropogenic activities.

### 7.4 Predicted Impacts of Past Settlement History in Roxburgh and St Andrews

The objective of this study is to assess the relationship between the soil records of past human activities, as observed through physical, chemical and biochemical properties, and historical records of past events on the study sites by utilising soil-based evidence and historical records.

The evidence is subsequently interpreted to allow preliminary discussion of the activities associated with soil formation and the spatial distribution pattern of various soil markers such as elemental signature, magnetic susceptibility, organic matter content, and soil pH.

In St Andrews where site occupation has continued to the present, a suite of factors such as organic matter content, and/or elements e.g. phosphorus that are indicative of land use intensity is expected to be enhanced more substantially than in Roxburgh. Settlement core areas are also expected to show increased enhancement relative to areas around the periphery (Oram, 2011; Golding 2008, pp.189, 276). In Roxburgh, the study specifically focuses on the spatial analysis of these markers (elemental signature, magnetic susceptibility, organic matter content, and soil pH) to investigate the below ground features in the Friars Haugh area of the site that was putatively identified as the location of the medieval settlement's core area by GSB Prospection geophysical survey data obtained during the Time Team excavation in 2003.


Fig. 7.1. Shows below ground features across the site as identified by GSB prospection ltd (map from GSB prospection, 2004)

## 7.5 Materials and Methods

Sampling was carried out in St Andrews and Roxburgh. Details of the study sites are provided in *sections 2.1.1* and *2.1.2* of Chapter Two. In St Andrews, samples were collected in the manner described in Chapter Three and similarly in Roxburgh. Also provided in Chapter Three are the details of subsequent *ex situ* laboratory analyses. Samples labelled STM1 – 4, SST1 & 2, SSJG1 – 6, BGr1 & 2, STM-P, SSJG-P, and BGr-P were collected in St Andrews while those labelled S1 – S30, and RT3-P were collected in Roxburgh. A total of 86 and 99 samples were collected respectively from both sites, and analysed.

### *7.5.1 Statistical Analysis*

Principal component analysis was carried out in order to determine the principal components or set of variables that best explicates the variability observed in the distribution pattern of elements across the sites. Prior to undertaking factor analysis, KMO (Kaiser-Meyer-Olkin) and Bartlett's Test of Sphericity was carried out to check for sample adequacy. To proceed with the analysis, it is recommended that the Kaiser-Meyer-Olkin Test result should be .6 or greater and the Bartletts's Test should be statistically significant with p-value of <0.05. Values are displayed in Table 7.1 below.

**Table 7.1. KMO and Bartlett's Test analysis output**

| | | |
|---|---|---|
| Kaiser-Meyer-Olkin Measure of Sampling Adequacy. | | .713 |
| Bartlett's Test of Sphericity | Approx. Chi-Square | 579.091 |
| | df | 55 |
| | Sig. | .000 |

The number of components extracted was determined by using Kaiser's criteria; only the components with an Eigen value of 1.0 or greater were used. A factor of two component solution of the five components that met the Eigen value requirement of 1.0 or greater was

used for further analysis because 61.522% of the total variance is explained by these two components.

## 7.6 Result and Discussion

The time-depth sampling approach adopted was intended to permit intra and inter site linkages to be made with the various marker-parameters measured at specific profile depths. The vertical and horizontal continuity or discontinuity of key anthropogenic markers such as organic matter content, soil pH, and elemental concentrations across the sites are investigated. The potential outcome of this application is such that detailed chronological history of landscape may be obtained. For example, the occurrence of dominant cultural practices taking place at a specific period of time, and changes in settlement phase through time may be revealed by examining the association of each soil pedon with the presence or absence off, and/or enrichment and depletion of certain routine anthropogenic groups of elements. However, where this is not possible due to factors such as the absence of deep soil stratigraphy, post depositional disturbances from physical activities, or indeed nature of the diversity (uniformity) in activities taking place within the settlement, broader yet useful conclusions such the delineation of site and the intensity of use can be made where such is the case.

### *7.6.1 Site Variability: St Andrews*

Soil record evidence presented in Table 7.2, indicates that areas within the medieval core areas (STM, SST, and SSJG) exhibit greater enhancement in the properties measured relative to areas outside (BGr). As discussed in Chapter 4, this pattern of enhancement is commensurate with occupational deposits where strong modifications are concentrated within and/or in close proximity to core functional areas, with diminishing intensity with

distance away from the settlement core (Oram, 2011; Golding 2008, pp.189, 276). Varying degrees of enhancement in soil properties found in the sites located within the settlement core areas are evident due to differences in the activity type, intensity and/or duration as has been previously stated.

Table 7.2. Variations in soil properties within and between study sites in St Andrews [underlined values are not mean values]

| Sample Site & points | Depth (cm) | n | **Organic Matter (%)** | Mean | StDev | **Soil pH ($CaCl_2$)** | Mean | StDev | **Phosphorus (mg/kg)** | Mean | StDev |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Site 1** | | | | | | | | | | | |
| *STM 1 - 4* | 0-20 | 4 | | 7.02 | 1.337 | | 6.71 | 0.140 | | 9261 | 984 |
| | 20-35 | 4 | | 5.37 | 1.136 | | 6.88 | 0.364 | | 8106 | 355 |
| | 35-45 | 4 | | 3.87 | 0.704 | | 7.02 | 0.073 | | 8232 | 259 |
| | 45-55 | 4 | | 3.62 | 0.900 | | 7.03 | 0.177 | | 7718 | 1752 |
| | 55-65 | 1 | | 2.39 | - | | 7.35 | - | | 4282 | - |
| **Site 2** | | | | | | | | | | | |
| *SST 1 - 2* | 0-20 | 2 | | 6.79 | 1.460 | | 6.96 | 0.191 | | 7787 | 308 |
| | 20-40 | 2 | | 5.34 | 1.075 | | 7.10 | 0.346 | | 7157 | 268 |
| | 40-55 | 2 | | 4.27 | 1.970 | | 7.14 | 0.085 | | 7334 | 1415 |
| | 55-65 | 2 | | 3.33 | 0.431 | | 7.20 | 0.057 | | 7100 | 2856 |
| | 65-80 | 1 | | 3.35 | - | | 7.03 | - | | 7783 | - |
| **Site 3** | | | | | | | | | | | |
| *SSJG 1 - 6* | 0-20 | 6 | | 6.89 | 1.108 | | 6.25 | 0.626 | | 7407 | 504 |
| | 20-35 | 6 | | 5.84 | 1.131 | | 6.52 | 0.726 | | 7779 | 1310 |
| | 35-50 | 6 | | 6.36 | 1.046 | | 6.46 | 0.742 | | 8555 | 694 |
| | 50-60 | 6 | | 5.99 | 1.432 | | 6.36 | 0.722 | | 9319 | 1360 |
| | 60-80 | 2 | | 5.93 | 0.460 | | 5.84 | 0.106 | | 8905 | 1039 |
| | 80-100 | 1 | | 2.99 | - | | 5.66 | - | | 10534 | - |
| **Site 4** | | | | | | | | | | | |
| *BGr 1- 2* | 0-20 | 2 | | 2.89 | 0.799 | | 5.55 | 0.035 | | 2682 | 370 |
| | 20-30 | 2 | | 3.78 | 0.050 | | 5.83 | 0.177 | | 2820 | 48.8 |
| | 30-40 | 2 | | 2.32 | 0.156 | | 5.70 | 0.120 | | 2178 | 763 |
| | 40-50 | 2 | | 0.61 | 0.219 | | 5.85 | 0.007 | | 1174 | 253 |

*7.6.1.1 Soil pH*

Soil samples from STM and SST sites have higher pH values (6.71 – 7.35) than those found in SSJG (5.66 – 6.25), and in BGr (5.55 – 5.85). These neutral – alkaline pH possibly results from the deposition of substances rich in carbonate such as animal bones and shells of various types although primarily seashells given the proximity of the settlement to the coast. In BGr site, much fewer shells were found which may have contributed to the lower pH value on the site. The abundance of sea shells as found in the soil profiles in STM, SST, and SSJG, and its underlying effect on pH is also indicative of the nature of the local diet and the amount consumed.

*7.6.1.2 Organic Matter Content*

The mean values for OM content and pH measurements taken at each sample point and depth profile per site was used for ease of data interpretation. The organic matter content and pH values differed between sites, and generally decreased with depth on all the sites. This difference in the parameters is sufficiently distinct to discriminate between samples located within the central area of the settlement (STM, SST, and SSJG) from those located outside (BGr) without additional consideration. The organic matter content in STM, SST, and SSJG sites have similar values at the topsoil until 20 – 40 cm but continues to decline in STM and SST until the maximum profile depth whereas in SSJG, OM content remained steady until 65 – 80 cm before decreasing significantly to similar level as seen in the other two sites (STM and SST). OM content in BGr remains consistently lower at all depths relative to other sites (Table 7.2).

The variation in the organic matter distribution across the sites results from differences in the accumulation rate and composition of materials that were deposited on soils as have been previously alluded to in preceding chapters. The accumulation of occupational debris such as

pottery, and organic debris from manuring activities both result in soil modification from changes in the composition and enhancement of various soil markers however areas that have received inputs primarily from organic debris and residues will display greater overall organic matter content than areas where deposition is composed of ordinary occupation debris or a combination of both.

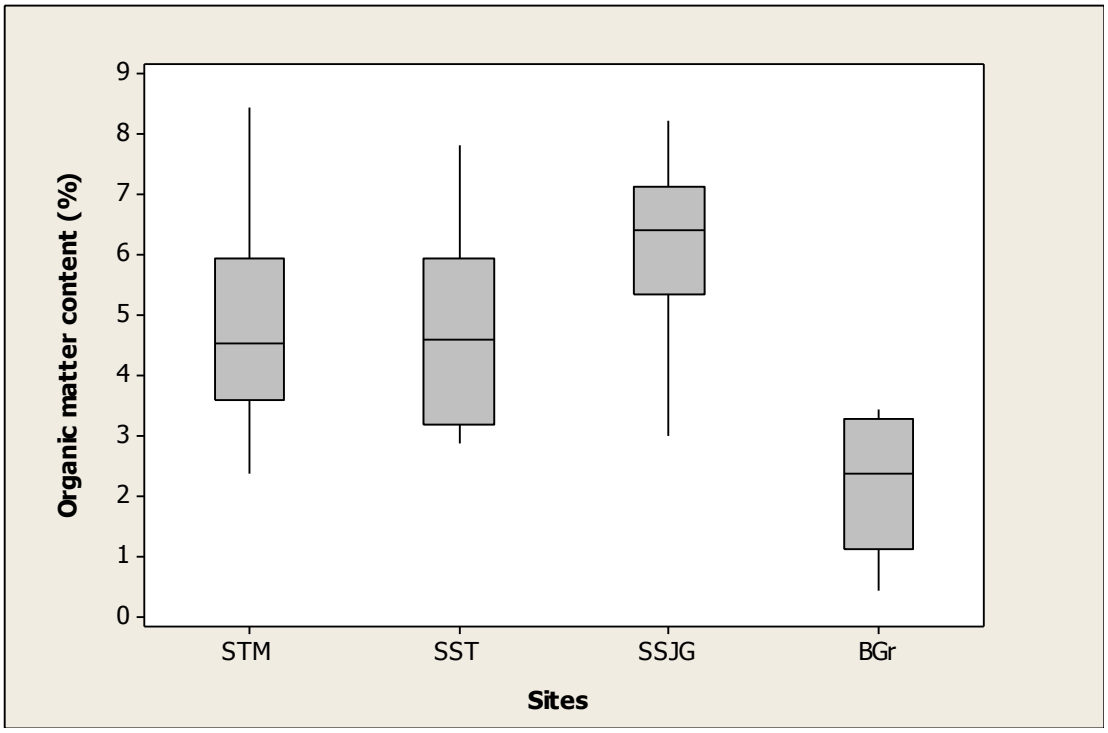



Fig. 7.2. Boxplot showing the differences in the combined total of organic matter content on the sites

The absolute combined quantity of soil organic matter across SSJG site is greater than found in STM and SST. This is indicative of the potential function of the site as an intensively managed farmed plot relative to the other two sites (Figure 7.2). Micromorphological analysis of charcoal content in thin section slides also supports this view. Results confirms that samples from SSJG site contain greater amount of charcoal than in both STM and BGr although charcoal content in STM site is greater than in BGr site (Figure 7.3).

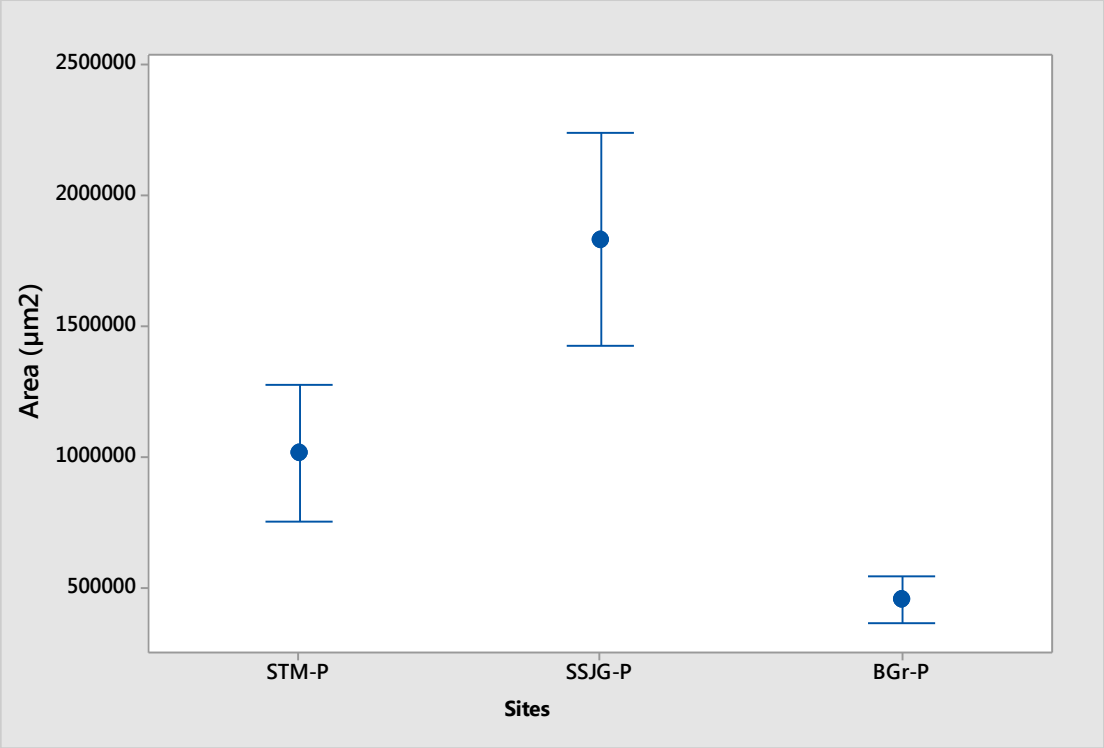



Fig. 7.3. Interval plot of charcoal content of soil pit samples in St Andrews sites [Individual standard deviations were used to calculate the intervals; 95% CI for the Mean]

Evidence for greater rate of material accumulation in SSJG which is suggestive of the intensive use of site/turnover is also visible from optically stimulated luminescence data (Figure 7.4).

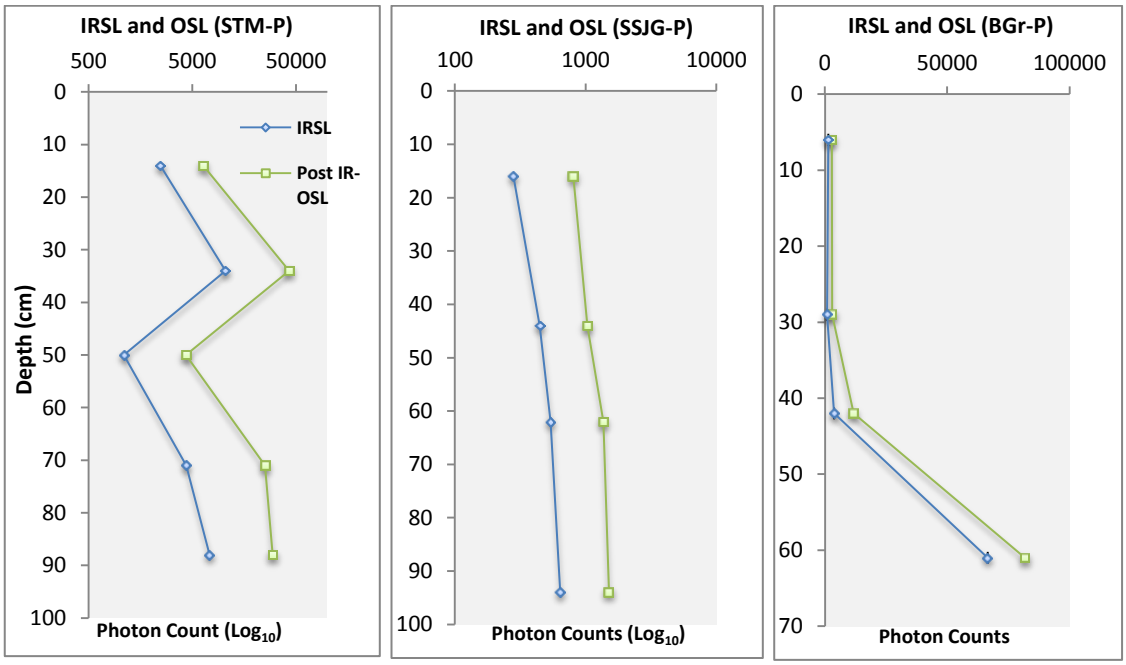



Fig. 7.4. Optically stimulated luminescence signal of soil profile on sample sites

OSL analysis reveals the relative age of sediments based on the depositional sequence since younger deposits will display lower luminescence signal and vis versa for older deposits. This can be used as a proxy for the accumulation rate because materials deposited at similar time-frame will have concordant luminescence signal, and discordant with those deposited at different period. In SSJG, the deposits occurring at the different depths along the profile (0 – 100 cm) are of relatively similar age, and younger than those in STM at all depth. This suggests that the deposits on the site have accumulated more rapidly with short interval between each event. Additionally, although the subsoils have greater luminescence intensity and are therefore older, the relative concordance in luminescence intensity throughout the profile could also have resulted from differences in individual manuring practices where new materials are likely thoroughly mixed with older deposits sufficient enough to allow repeated bleaching of materials.

Thin-section analysis of charcoal size distribution showed similar pattern of distribution across the sites (Figure 7.5). This suggests similarities in the source and composition of materials deposited on the sites and that differences in the extant residue observed is due to the difference in the quantity of initial materials deposited on the individual sites.

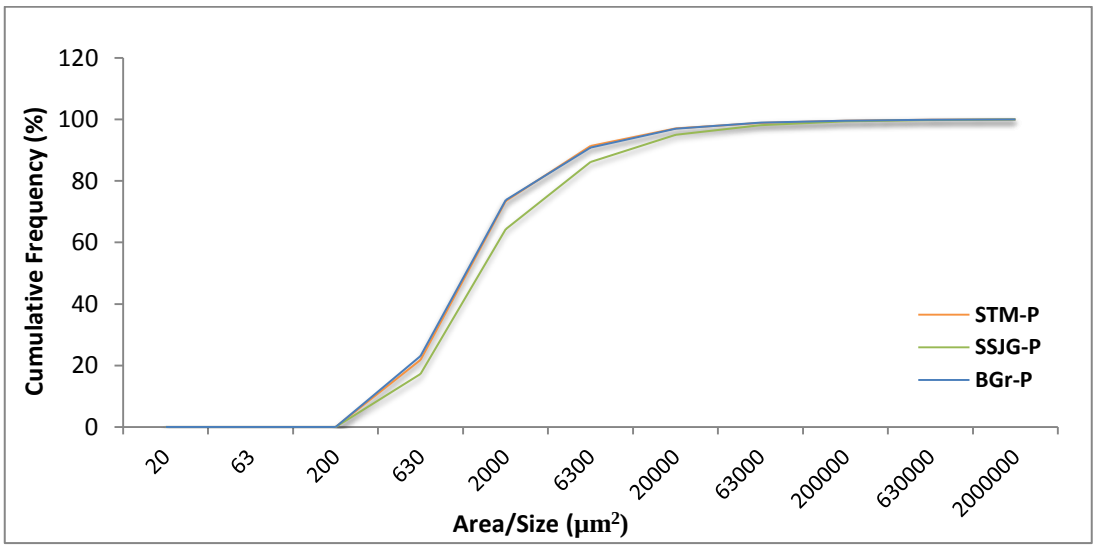



Fig. 7.5. Size distribution of charcoal particles in St Andrews

Other factors that may have influenced organic matter distributions includes the following: i) the occurrence of other types of activities on the site, ii) social status of the landowner, and iii) and size of land/plot.

I. Other than the influence of the varying levels of organic matter content in occupational debris and organic waste, areas dominated by craft activities such as joiners, fletchers, coopers, shoemakers and other non-organic matter associated activities may show low levels of residual organic matter enrichment relative to areas used primarily for cultivation of food crop which require constant fertilisation. Additionally, lower-level organic matter associated activity such as cultivation of non-food crops such as grass and ornamental trees and plants may also influence the level of residual organic matter available.

II. High status areas such as in SST as indicated by the presence of large buildings three storey tall (Figure 7.6) and their associated large backlands (Figure 7.7a and 7.7b) in comparison to the smaller two storey and one storey buildings found in SSJG and STM (Figure 7.6) may have been used for low-intensive cultivation (ornamental gardens) as a matter of preference in order to reduce the malodorous odour that would result from constant use of highly organic household refuse and human waste habitually referred to as ‘fulzie’ or ‘failyie’ within their property.

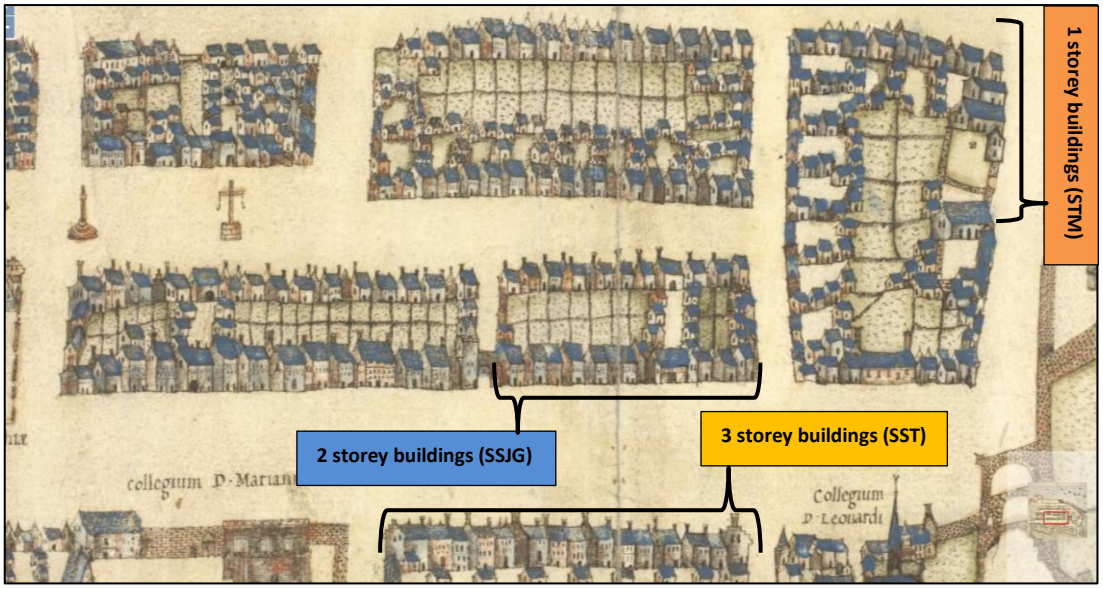



Fig. 7.6. 1580-1919 town plans/views of St Andrews by John Geddy, 1580 [National Library of Scotland]

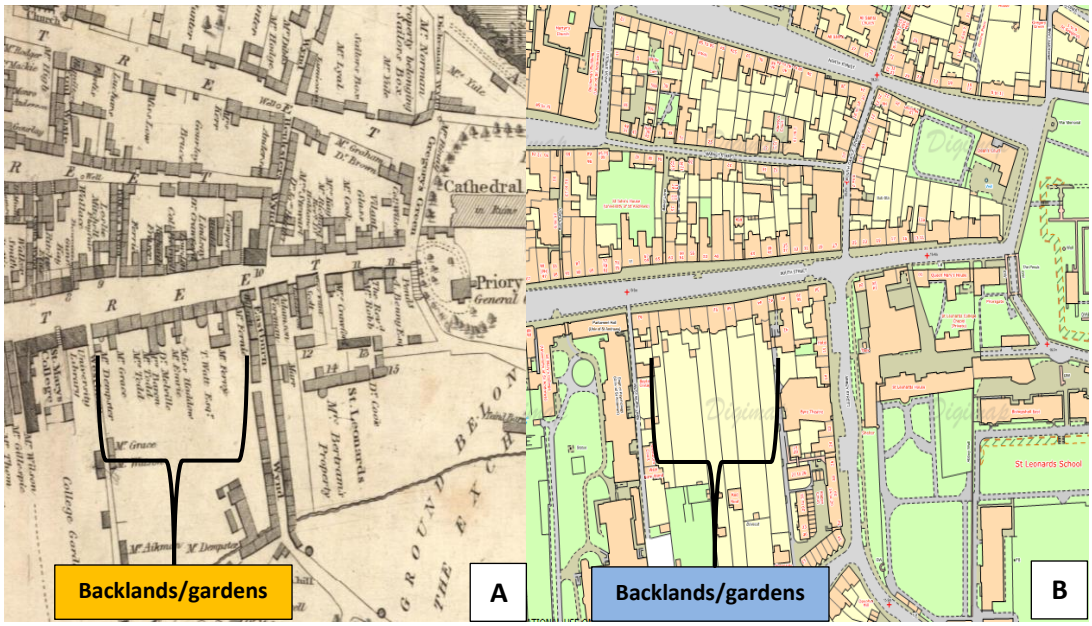



Fig. 7.7a. (Left) Woods' 1820 town plans/views of St. Andrews [National Library of Scotland]; Fig. 7.7b. (Right) Contemporary map of St Andrews showing the sizes of backlands (garden area) on the sites [Digimap Roam, Edina]

III. Areas with similar management strategy can also have different organic matter content and accumulation rate depending on the quality and quantity of materials deposited. For example, the deposition of comparable quantities of material with high organic content on a small plot of land will result in higher residual OM content and accumulation of material compared to where similar application is made on larger plot. Similarly, smaller plots that have received high quantity of low quality organic material may have similar residual organic matter to a larger plot that has received low-quantity high-quality material because of the concentration of material deposited per point.

*7.6.1.3 Elemental Concentrations*

The occupation and establishment of settlement can alter the natural concentration of certain groups of elements in the soil from the accumulation of occupational debris from daily living (Holliday and Gartner, 2007; Oonk et al., 2009). Among the suites of anthropogenic-marker elements, phosphorus is most routinely used in archaeological prospection as indicator for human activity due its relatively high retention rate and stability in the soil (Bull et al., 2001; Wells 2004; Leonardi et al., 1999; Oonk et al., 2009). Although phosphorus can be useful in simple contrasting exercise between potential anthropogenic sites and reference/natural sites, no single element however can provide a clear signature for any specific activity but the examination of the patterns of enhancement of relevant suites of elements across the landscape. The following suites of elements; barium (Ba), calcium (Ca), phosphorus (P), zinc (Zn), lead (Pb), potassium (K), manganese (Mn), sulphur (S), chlorine (Cl), magnesium (Mg), and strontium (Sr), were used as indicators to determine type of land-use activity across sites.

Principal component analysis was used to determine the driver of variability in the patterns of element enhancement. Soil profile depth and sample sites both of which are interrelated with

activity types were used to define element distribution pattern in St Andrews based on the assumption that layers of occupational deposits will contain within it signatures that are indicative of specific, including dominant, cultural activity taking place across the settlement at the time and/or signatures relating to the occupation history of particular site. Results indicate on the one hand that patterns of element distribution across St Andrew at all depths are relatively uniform with no particular clustering of any groups of elements at any one depth (Figure 7.8). This uniformity indicates that the variability in the enhancement of elements as observed on the sites is not attributable to profile depth, and that the mere presence of these anthropogenic suites of elements is insufficient to identify differences in land-use but the concentrations of these elements.

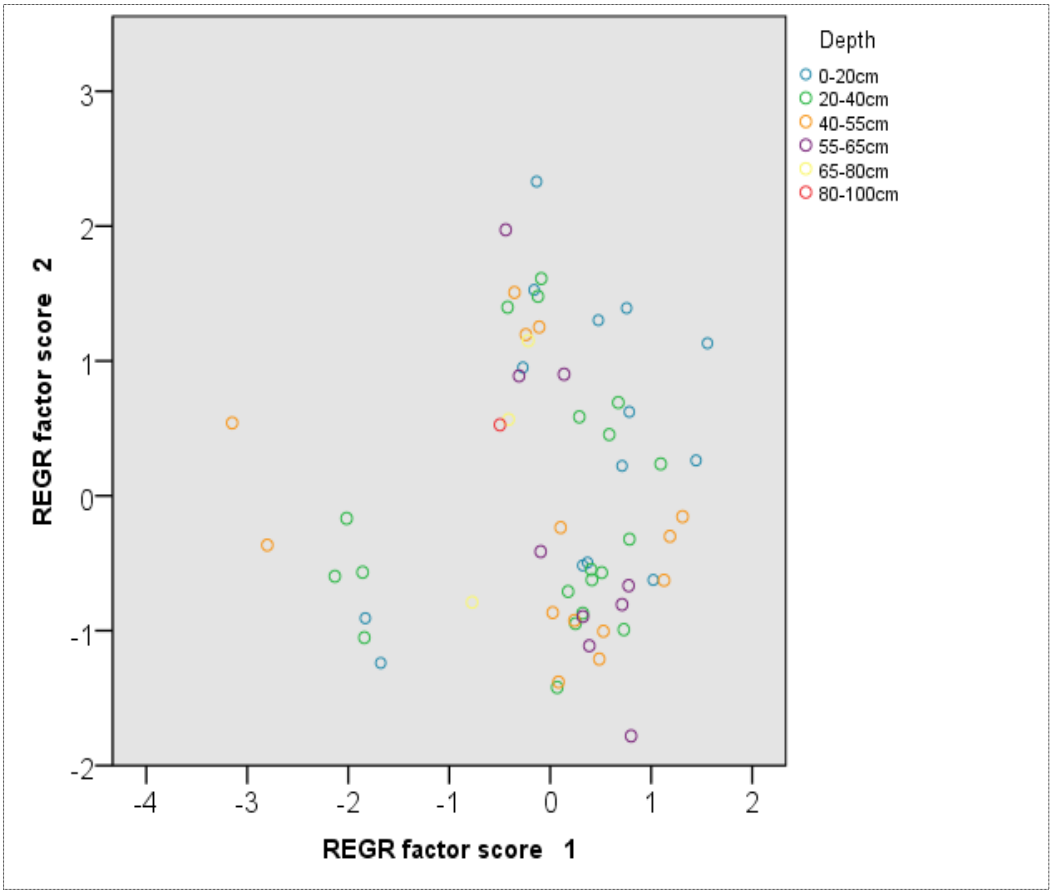



Fig. 7.8. Element distribution by depth

On the other hand, variations in the distribution of elements across the landscape appear to be driven by site. The distinction of background elements from signature anthropogenic element is clear from the clustering of various groups of elements as shown in Figure 7.9. Magnesium (Mg), potassium (K), and barium (Ba) are strongly associated with BGr-1 or background reference site which attributes these elements to site geology rather than anthropogenic. The anthropogenic-associated elements are spread within all the sites located within the centre of the burgh although specific clustering of groups of elements such as zinc (Zn), lead (Pb), manganese (Mn) among others which are signature elements for organic waste deposits and craft production area suggests that SSJG site could have been used for such, or related activities, particularly areas around SSJG-5 samples (Wilson et al., 2007).

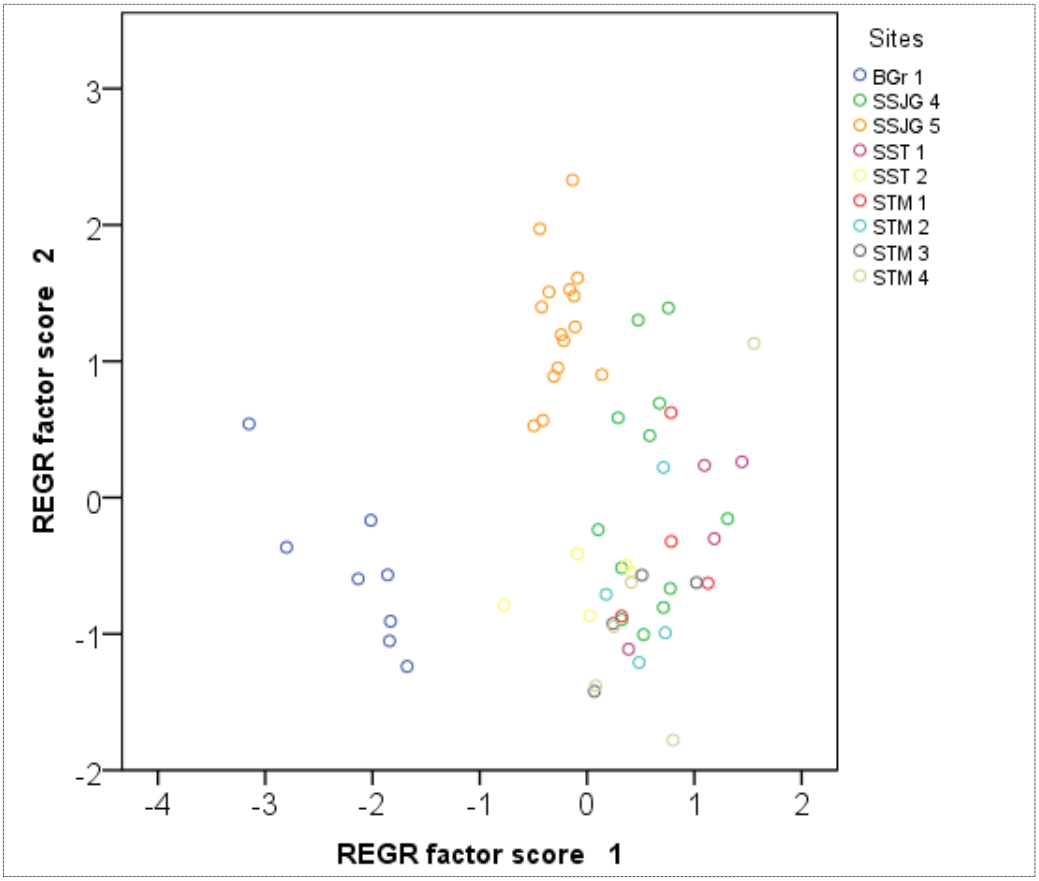



Fig. 7.9. Element distribution by site

*7.6.1.4 Magnetic Susceptibility*

Soil magnetic properties varied extensively along the profiles on all sites with no discernible pattern or trend in the enhancement although sample sites located within the burgh centre (STM and SSJG) show more enhancement values (Table 7.3). Volume susceptibility ranged from between 8.12 ƙ to 273.18 ƙ in STM and SSJG, and 1.74 (ƙ) to 10.44 (ƙ) in BGr site. The magnetic properties of soils/sediments may be enhanced through specific autochthonous activities such as in hearth area (fireplaces, ovens, cooking places) and/or allochthonous inputs of materials that have been subjected to heat such as charcoal, pottery, and ash. Magnetic enhancements for *in situ* activities generally have higher susceptibility values due to the concentration of magnetic minerals on the site of activity relative to the dilution effect in allochthonous deposits due to mixing with other material substances. In this case, the magnetic enhancements on the sites are suggestive of enhancement obtained from deposition of materials with firing history rather than enhancement from onsite activities due to the generally low values (see Table 7.3).

Table 7.3. Volume susceptibility (ƙ) values of sample sites in St Andrews [underlined values are not mean values]

| Sample site and point | Depth (cm) | n | Mean (ƙ) | StDev |
|---|---|---|---|---|
| **Site 1** | | | | |
| *STM 1 - 4* | 10 | 4 | 24.8 | 25.5 |
| | 20 | 4 | 22.2 | 20.4 |
| | 30 | 4 | 42.6 | 20.4 |
| | 40 | 4 | 31.8 | 22.6 |
| | 50 | 4 | 189.2 | 141.2 |
| | 60 | 1 | 121.80 | - |
| **Site 3** | | | | |
| *SSJG 4 - 6* | 10 | 3 | 103.24 | 14.17 |
| | 20 | 3 | 29.58 | 7.97 |
| | 30 | 3 | 13.9 | 19.6 |
| | 40 | 3 | 39.4 | 65.3 |
| | 50 | 3 | 8.12 | 8.76 |
| | 60 | 3 | 15.08 | 17.17 |
| | 70 | 2 | 51.3 | 25.8 |
| | 80 | 1 | 83.52 | - |
| | 90 | 1 | 81.78 | - |
| | 100 | 1 | 273.18 | - |
| **Site 4** | | | | |
| *BGr 1* | 10 | 1 | 5.22 | - |
| | 20 | 1 | 10.44 | - |
| | 30 | 1 | 5.22 | - |
| | 40 | 1 | 1.74 | - |
| | 50 | 1 | 6.96 | - |

*7.6.2 Site Variability: Roxburgh*

Prior to the archaeological evaluation carried out on the site of medieval Roxburgh, the landscape was presumed to be free from external disturbances other than natural soil processes and the post-burghal agricultural activity (strip-cultivation) that occurred in the eastern edge of Vigorous Haugh outside the settlement's core areas as shown in Wyeth's 1736 survey. However, the results from the survey study conclusively dismisses this assumption by revealing the extent of physical disturbances from ploughing resulting from wider more-significant agricultural activity that took place after Wyeth's 1736 survey in 1780 as noted by

Jeffery (1859, 152), and in the 1940s for war-time agricultural production (Anon, 1947). Therefore data interpretation is focused on subsoil samples (from 20 cm depth and below) in an effort to reduce and/or eliminate interferences from these disturbances including any contemporary activity such as the point-to-point racing event frequently hosted on the site. Table 7.4 below shows the mean values of the soil marker-parameters (elemental signature, magnetic susceptibility, organic matter content, and soil pH) used for interpretation.

Table 7.4. Variations in soil properties at sample points across the study site in Roxburgh

| Sample points | Depth (cm) | n | Mean | StDev |
|---|---|---|---|---|
| ***S1 – S30*** | | | | |
| **Organic Matter (%)** | 0-20 | 30 | 2.925 | 0.746 |
| | 20-40 | 29 | 2.123 | 0.497 |
| | 40-60 | 15 | 1.491 | 0.211 |
| | 60-80 | 6 | 1.283 | 0.413 |
| **Soil pH** | 0-20 | 30 | 5.5253 | 0.1664 |
| | 20-40 | 29 | 5.5321 | 0.2446 |
| | 40-60 | 15 | 5.5647 | 0.1754 |
| | 60-80 | 6 | 5.6550 | 0.1504 |
| **Magnetics Susceptibility (k)** | 0-10 | 30 | 43.62 | 30.92 |
| | 10-20 | 30 | 44.20 | 25.61 |
| | 20-30 | 29 | 389 | 691 |
| | 30-40 | 20 | 224 | 496 |
| | 40-50 | 15 | 198 | 426 |
| | 50-60 | 10 | 533 | 764 |
| | 60-70 | 6 | 482 | 487 |
| | 70-80 | 4 | 28.8 | 26.2 |
| **Phosphorus (mg/kg)** | 0-20 | 30 | 5974 | 983 |
| | 20-40 | 29 | 5782 | 1367 |
| | 40-60 | 15 | 5856 | 1674 |
| | 60-80 | 6 | 6461 | 2528 |

*7.6.2.1 Soil pH*

Soil pH value varied between sample points across the site however the pattern of distribution is similar along all three profile depths. Although the pH range across the site are not overly discordant, ranging from 5.05 – 5.95, trends in the distribution is nonetheless evident across the site as displayed on the map. pH values are generally highest at the western end of the site from S1 to S7, and lowest at the Eastern part from S8 to S19 around where has been suggested to have been the likely location of the medieval burgh core area (Figure 7.10).

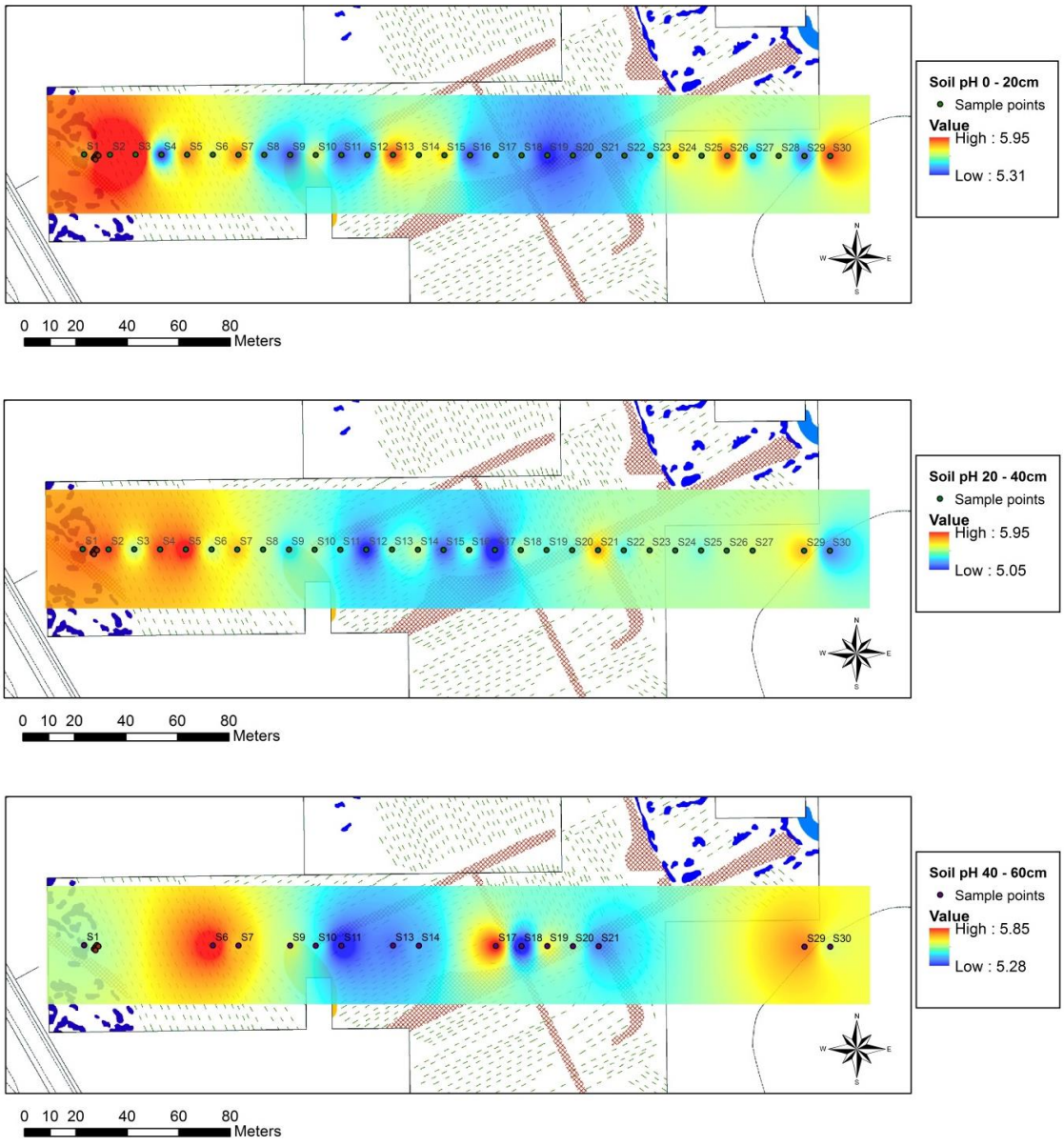



Fig. 7.10. Spatial distribution of soil pH across the site

The extremities of the eastern part of site towards Vigorous Haugh, outside the tentative burgh core area, has moderately high pH value relative to the areas within the burgh core although isolated spots of high and low values exist along the transect. Mean values of soil pH of the individual depths in Table 7.4 above, and on the third order polynomial regression in Figure 7.11 below shows strong similarities in the overall pH values of the profiles.

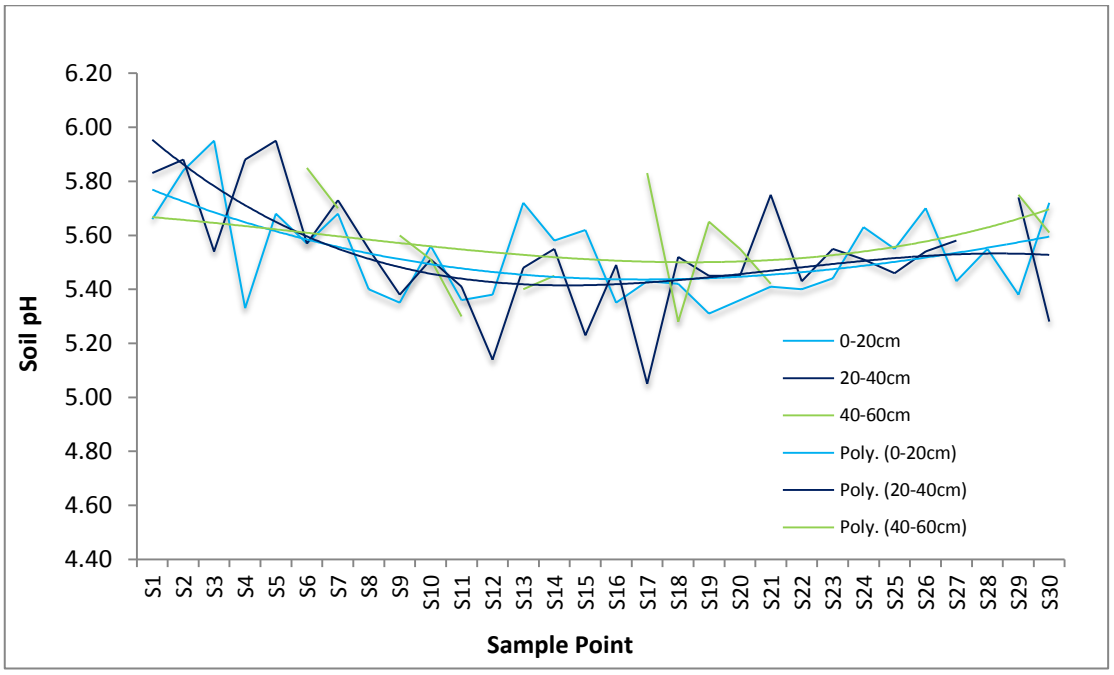



Fig. 7.11. Shows the distribution of soil pH values at various depths across the site

*7.6.2.2 Organic Matter Content*

The soil organic carbon content fluctuates heavily across the site, and declines with depth. The distribution of soil organic carbon follows similar trend across all profile depths despite the differences in the overall content of organic material at the various depths (Figure 7.12).

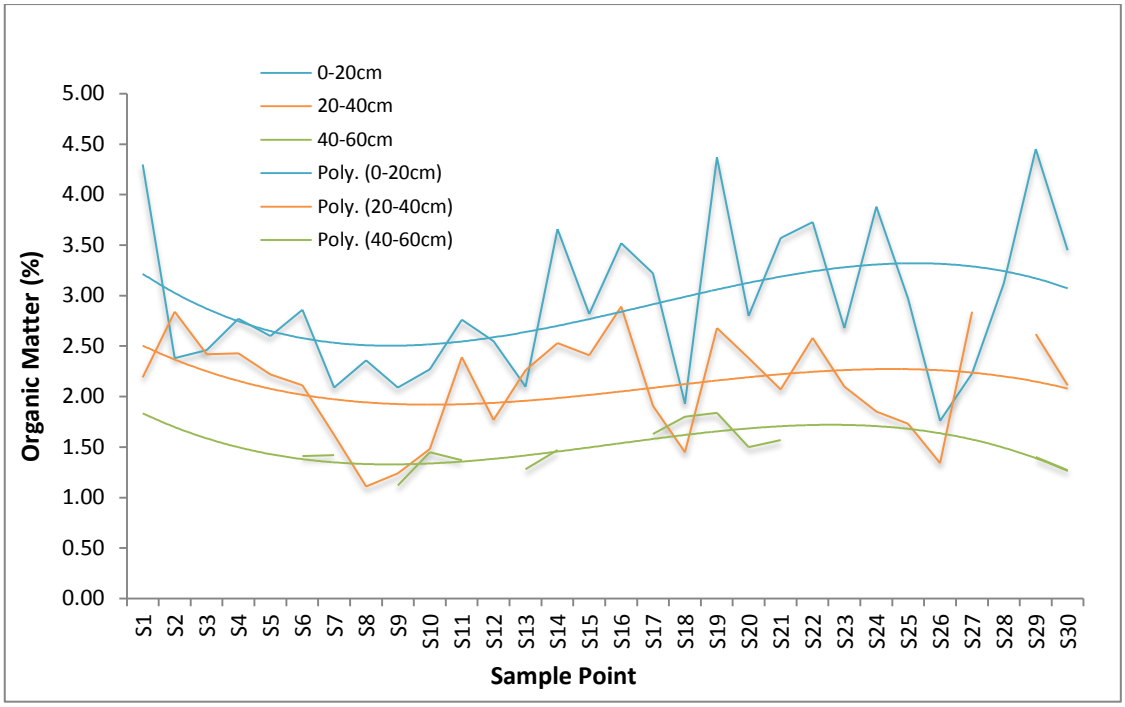



Fig. 7.12. Shows the pattern of distribution of soil organic matter at different depth across the site

The area to the west of the site, over which was putatively identified by previous study as the location for the old burgh core, shows higher residual OM content than the eastern part of the burgh (Figure 7.13). This trend is consistent at all profile depths and across the transect. The contrast in the boundary areas between bands of high and low SOM content are broader and more diffuse at 0 – 20 cm and 40 – 60 cm relative to 20 – 40 cm depth where this is sharper and narrower. Few isolated spots of low organic matter content are visible at 0 – 20 cm (S18, S26, and S27), and at similar location at 20 – 40 cm depth (S18, S24, S25, and S26). It is anticipated that areas that were subjected to cultivation will show higher residual enrichment relative to uncultivated areas so that field areas may be discriminated from the burgh core living areas.

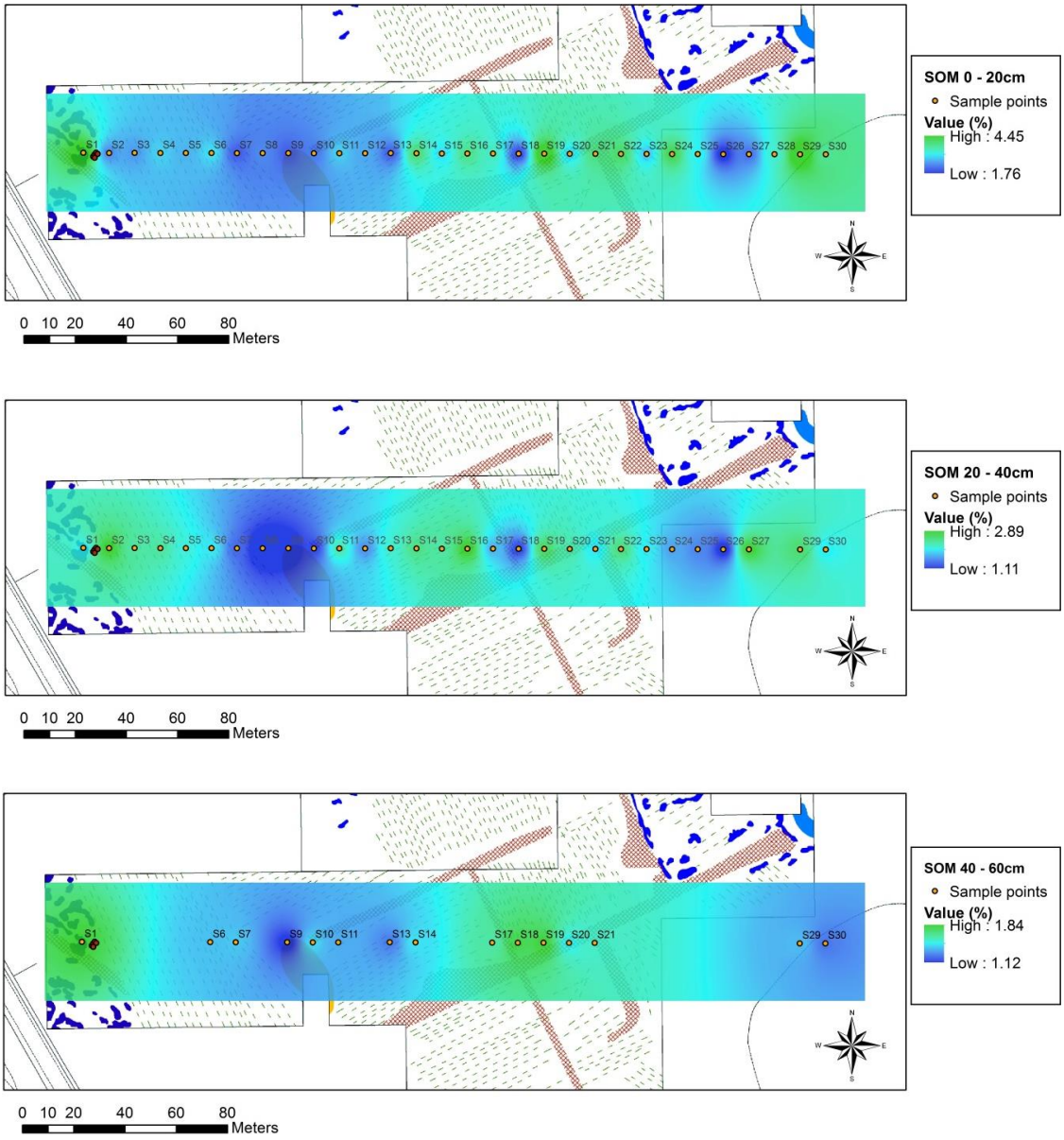



Fig. 7.13. Spatial distribution of soil organic matter content across the site

*7.6.2.3 Elemental Concentration*

The enhancement pattern of the suites of elements selected for site discrimination follows a near-identical distribution across the sites at all depths. As a result, the element phosphorus was selected amongst the suites of elements for further site examination because it is most strongly influenced by anthropogenic activity. Site interpretation was based on a general concept where 'low enhancement indicates low activity areas and high enhancement indicates

high activity areas'. This simplistic approach to the data interpretation was adopted in order to reduce the danger of over-interpretation taking into consideration the sample size and resolution.

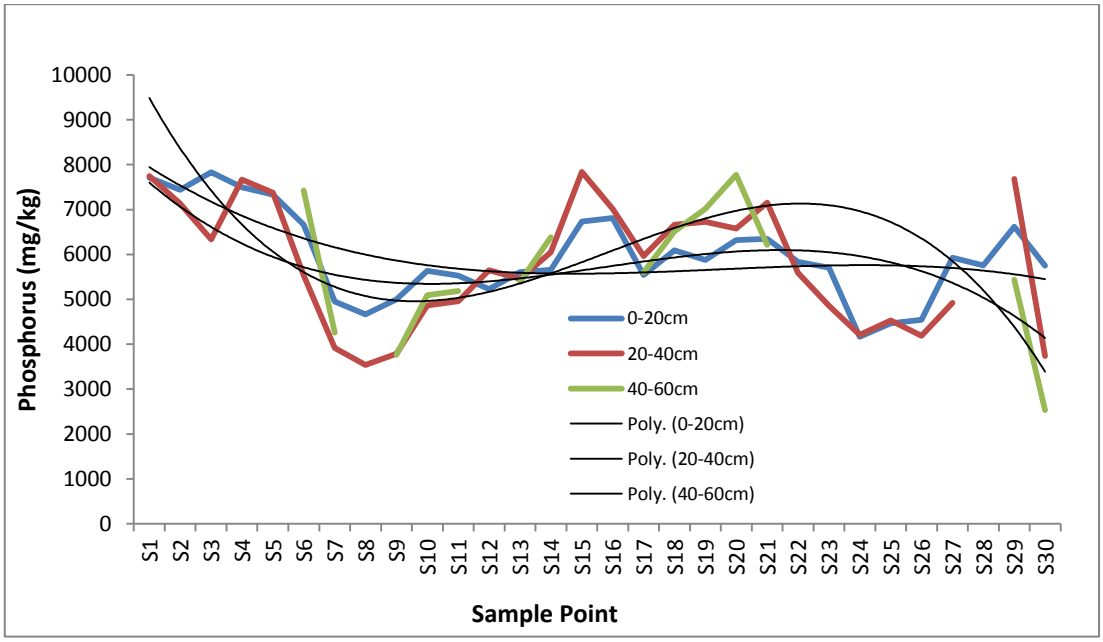



Fig. 7.14. Shows the pattern of distribution of phosphorus at different depth across the site

Phosphate concentration follows a similar pattern of distribution as previously seen in soil pH and organic matter content (Figure 7.14). From the spatial interpolation, phosphorus can be seen to be enhanced in two distinct bands; high and moderately high and low and moderately low concentrations taking into account the relative differences in enhancement between profiles (see Figure 7.15). Phosphorus enhancement is highest in the western end of the site, between S1 and S5, and between S14 and S21, the area that was identified as the medieval burgh centre in the respective profiles. Conversely, the eastern end of the site from between S22 to S30, and the section along the transect situated between the western end and the putative medieval burgh centre (S6 to S13) are regions of low P enhancement (Figure 7.15).

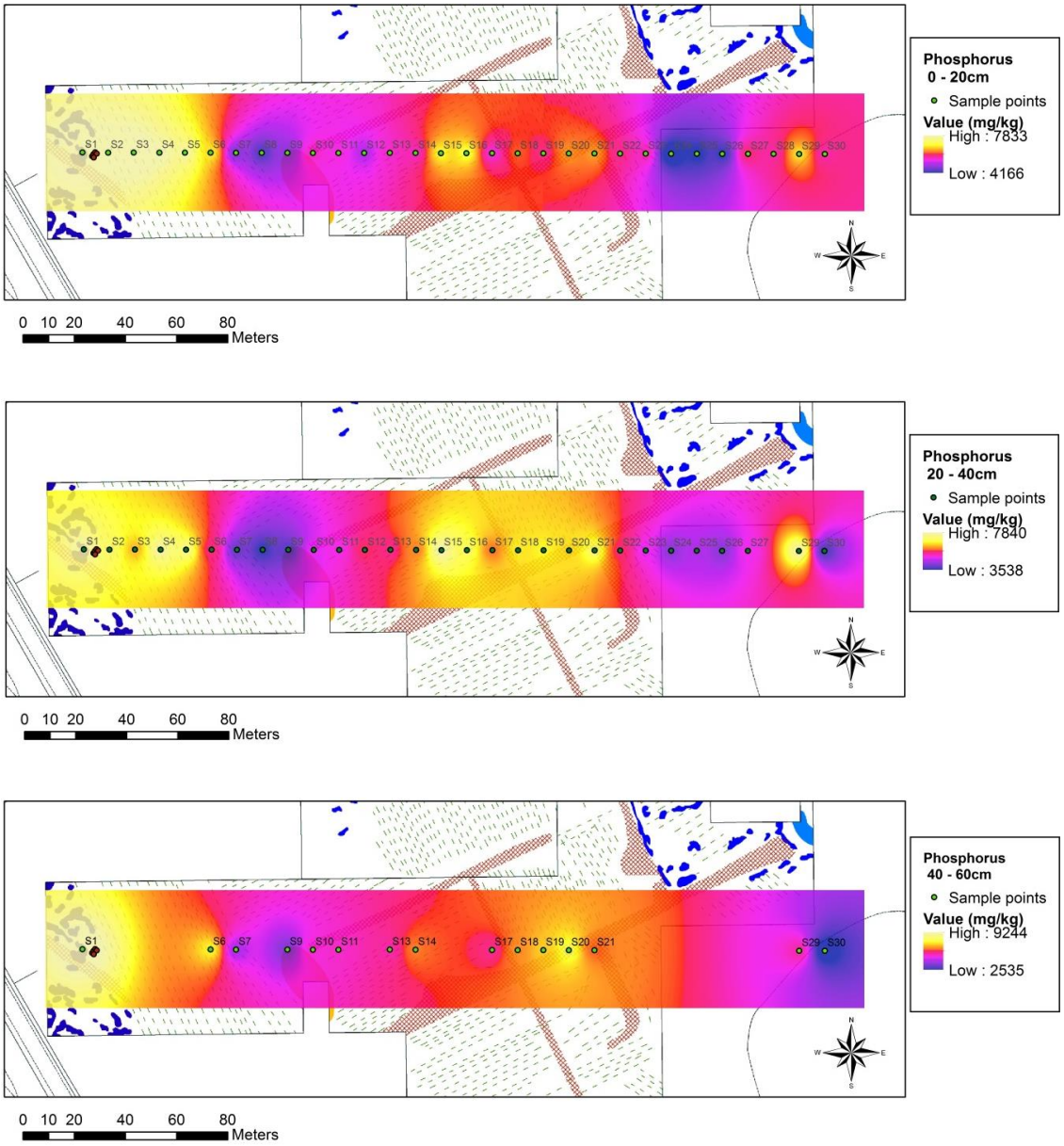
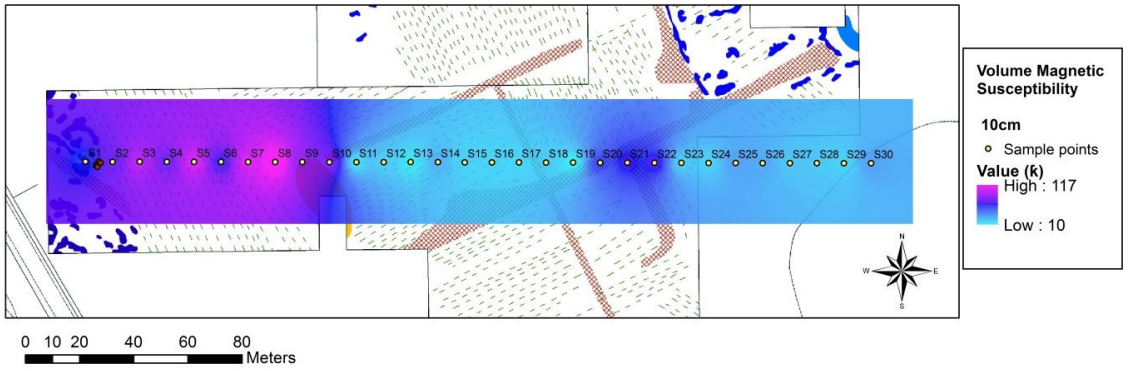


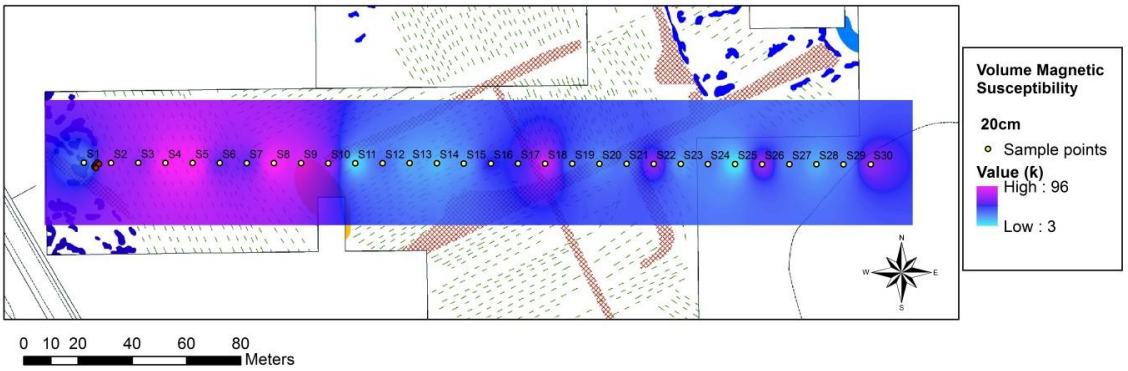

Fig. 7.15. Spatial distribution of phosphorus across the site

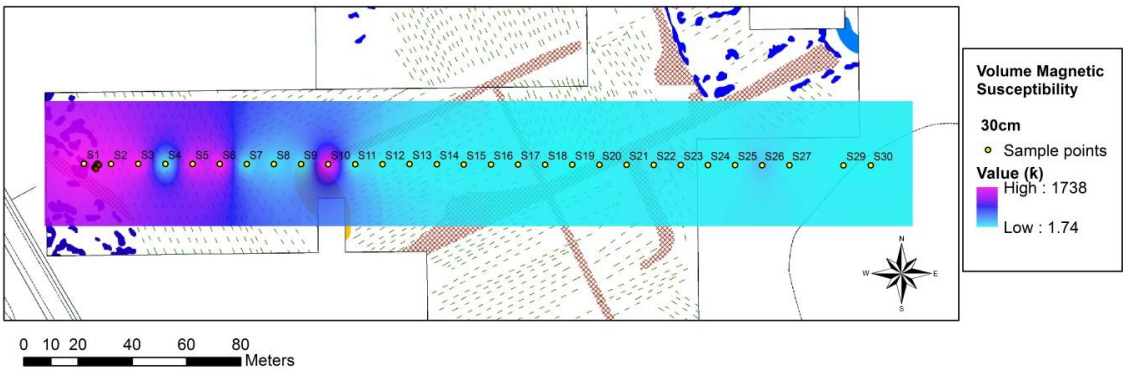
*7.6.2.4 Magnetic Susceptibility*

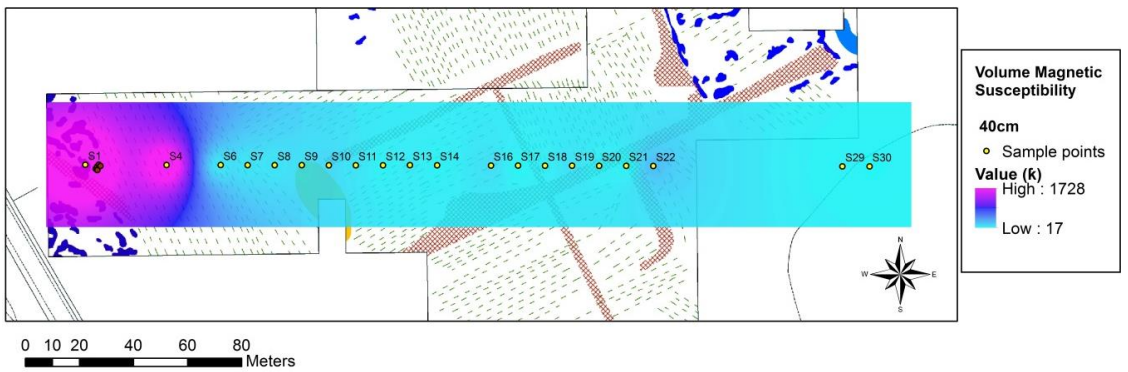
The magnetic susceptibility signal across the landscape is displayed in Figure 7.16. Magnetic enhancement is heavily concentrated on the western end of the site towards the modern A699 road. Sample points from S1 to S10 have higher enhancement values than at the other points along the transect at their respective profile depth although this range decreases to S7, S4, and S2 for 60 cm, 40 cm, and 50 cm. Sample points beginning from S11, for 10 to 30 cm

profile depths, and for other profile depths, S9 (60 cm), and S6 (40 cm and 50 cm) to S30, encompassing the putative medieval core area, have low magnetic susceptibility.



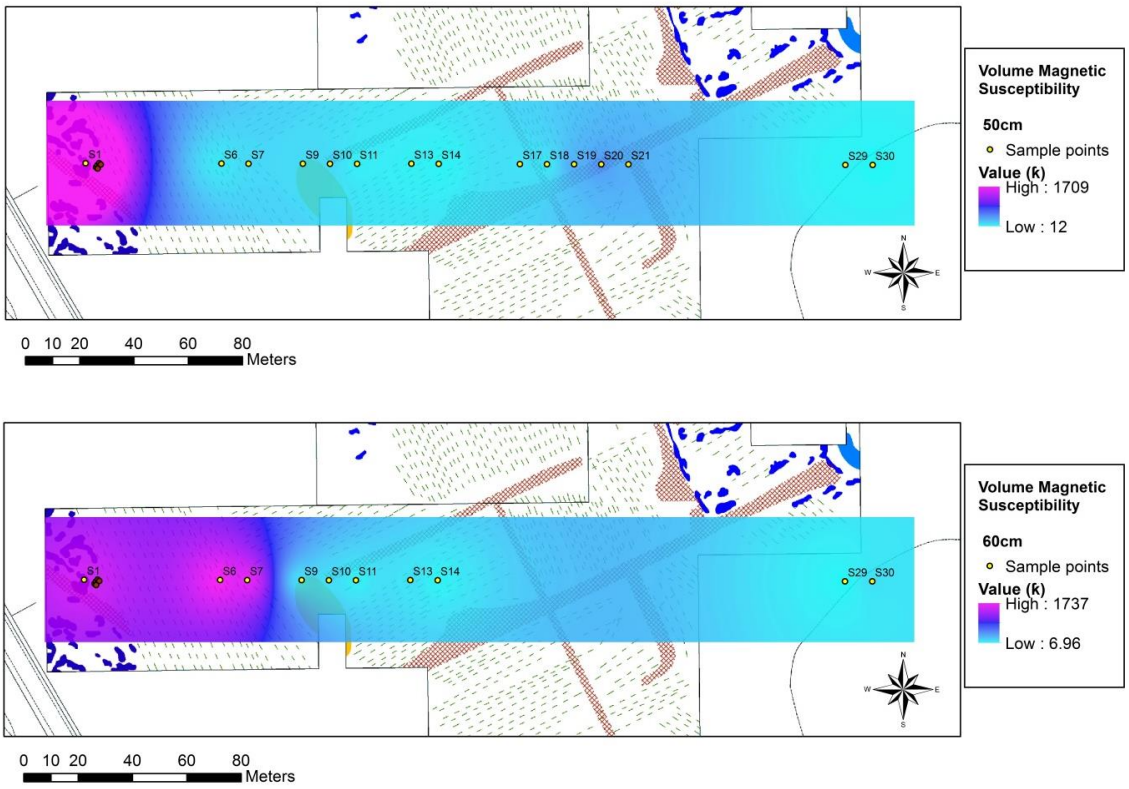



Fig. 7.16. Spatial distribution of magnetic susceptibility across the site

The absolute magnetic susceptibility values expressed per sample point across the site for 10 cm and 20 cm profiles are several orders of magnitude less than values obtained from between 30 cm to 60cm. The 30 cm profile depth has the highest number of points with high susceptibility value of all the profiles (Figure 7.17).

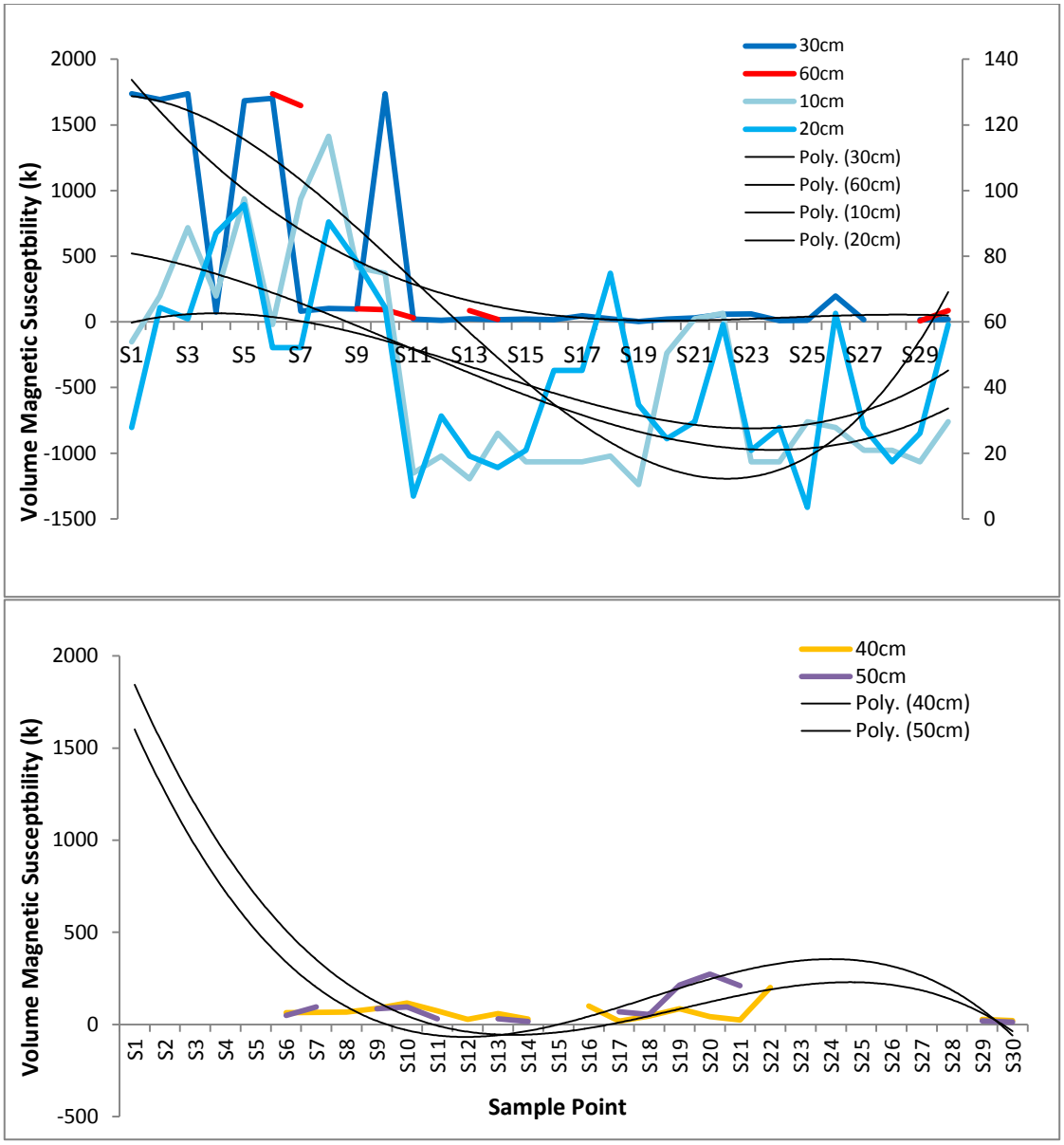



Fig. 7.17. Depth distribution of soil magnetic susceptibility values across the Roxburgh site [10 cm and 20 cm profiles are on the secondary axis on the right side of the graph]

*7.6.3 The Medieval Burgh of Roxburgh as Seen from Soil Records*

The medieval royal burgh of Roxburgh was abandoned by the 15$^{th}$ century, over 550 years ago, but its surviving archaeological features, now mostly buried, are relatively close to the surface, and as shallow as 20 cm in some locales. The proximity of its underlying archaeology to the surface renders it susceptible to disturbances. The archaeological assessment of the site by

Wessex Archaeology in 2003 revealed extensive disturbance to the below ground archaeology on most of the site due to ploughing that occurred post burgh abandonment. Figure 7.18 below shows a tentative reconstruction of the area enclosed by the burgh.

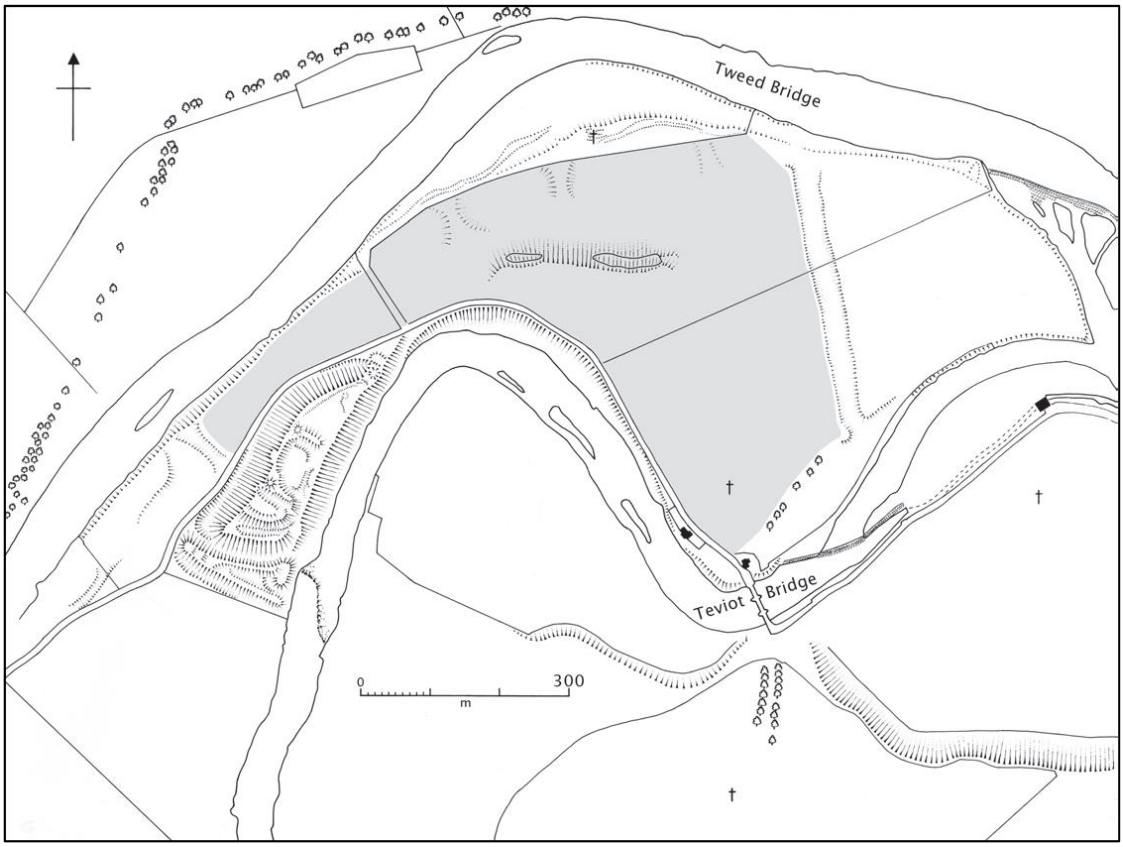



Fig. 7.18. A reconstruction of the area enclosed by the burgh (in grey) [Martin and Oram, 2007]

Soil pH values at the sample points within the settlement core areas (S9 to S20) are generally lower than values on either side of this region, more so on the western extremities. Interestingly, areas of high soil organic matter content, around similar region (S11 and S23), overlaps with regions of low soil pH although sample points S1 to S6 on the west side of the site equally has high SOM content. The distribution of soil pH values and organic matter content across an anthropogenic landscape may serve as indicators, amongst others, for site use, particularly activities associated with farming (cropping and livestock rearing, e.g. kailyard). pH and organic matter content are two soil properties that are most readily modified

during cultivation due to their important role in crop yield and productivity. High soil pH values and organic matter content can therefore be used to reasonably distinguish between cultivated/arable areas and uncultivated areas. The trends in pH and organic matter distribution on the site suggests that some level of agricultural activity may have occurred in areas within the perimeter of the settlement such as minor cropping or gardening on the backlands. This provides a possible explanation for the low pH and high organic matter trend found within the core areas relative to high pH and high organic matter on the west, and east side of the burgh, more so for the former, where more significant cropping activity would have occurred. In other words, backlands and garden areas represent secondary production area while areas to the west, towards the A699 and Kay Brae, and east towards Vigorous Haugh would have been the primary agricultural fields (Figure 7.19).

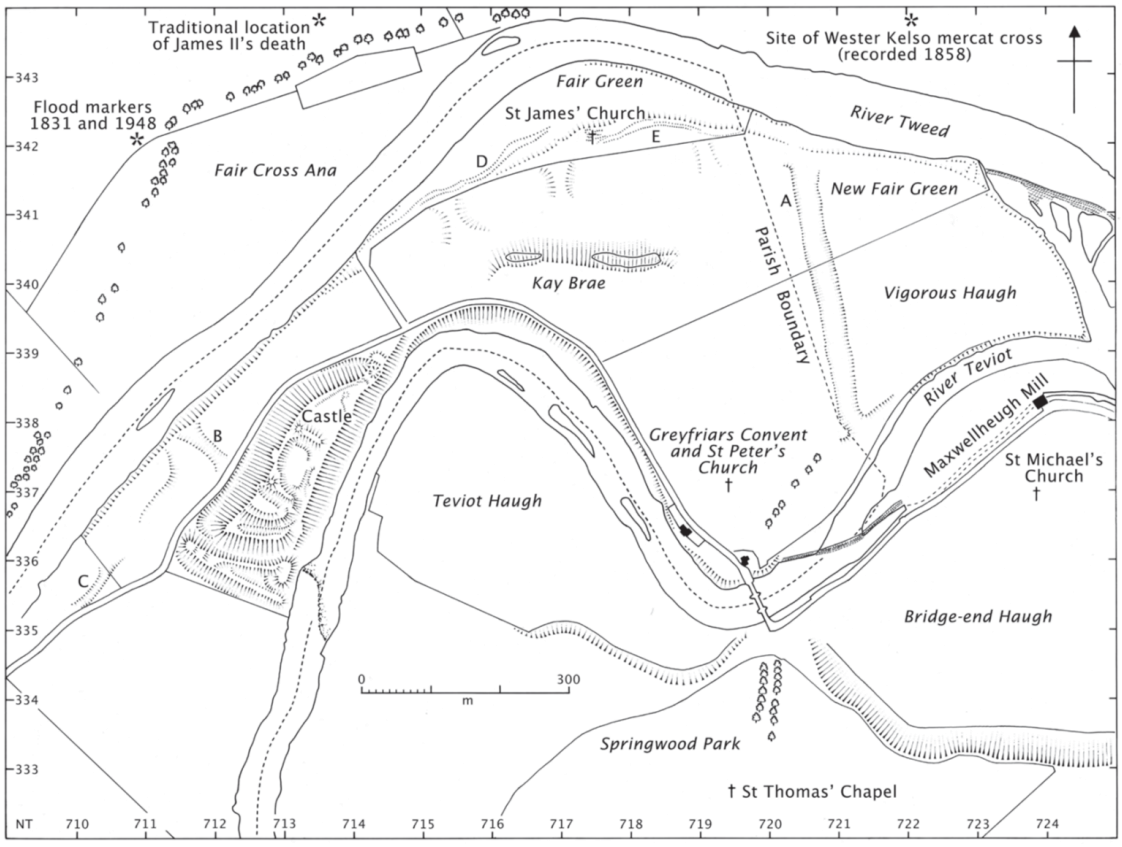



Fig. 7.19. General plan of the burgh site, showing the locations of various features [Martin and Oram, 2007]

Elemental analysis of the site, using phosphorus as the single discriminant element, is in agreement with this interpretation. Phosphorus is enhanced in two very distinct bands of high and low regions (Figure 7.15). The distribution is such that high areas of enhancement are concentrated within the putative burgh core areas (S14 to S21) as well as on the west end of the site (S1 to S6) between which are areas of low concentration. As discussed previously, phosphorus enhancements can be successfully used as proxy indicators for identifying areas that have been impacted by anthropogenic activity. High concentration of phosphorus within the regions S14 to S21 and S1 to S6 suggests that these were centre points for activity, in other words, high activity area within the site although the high P enhancement in S1 to S6 on the west side of the site may have resulted from the deposition of organic waste material because it is unlikely to have been the centre of the burgh due to its proximity to the road (A699).

The magnetic properties of soil across the site are strongly enhanced on the west side and fringes of the landscape (Figure 7.16). Areas of low magnetic enhancement, beginning from S6 at 40 and 50 cm depth, S9 at 60 cm, and S11 at 10 to 30 cm profile depth, encompasses the putative settlement core site along the transect to the east side of the site around Vigorous Haugh at S30. This pattern of distribution is unconventional given the pyrogenic history of the site. Roxburgh was devastated by a series of major fire incidents in the 12$^{th}$ century (1207, 1216, and 1244), and on two occasions in the 14$^{th}$ century. These fire events would have progressively increased the magnetic susceptibility of the soil in the affected areas beyond the background levels. Consequently, soils around the burgh core areas are expected to be magnetically enhanced relative to the surrounding areas but this was not observed. The likely cause for this anomaly is due to possible clearance activity that may have occurred post these incidents. It is probable that deposits of burnt wood, charcoal, ash, and soil materials with enhanced organic matter content and high phosphorus concentrations etc., from within the settlement were moved to the outer fringes of the burgh, in this case, to the west side

towards the A699, to make way for reconstruction. This assessment is consistent with interpretations made on historical landscapes from past studies assuming that the outlined area identified within the landscape is indeed the true centre of the medieval Roxburgh which is supported by current and previous dataset.

The maximum depths of individual profile points along the transect were recorded to determine topsoil depth, and to afford additional prospect for further discrimination between zones across the site. Depth distribution across the site was categorised into three separate zones of high, intermediate and low depth. Zone one (S2 – S5; S23 – S28) are shallow areas, zone two (S12 – S22) are moderately deep areas while zone three (S6 – S11; S29) are the deepest sections on the site (Figure 7.20).

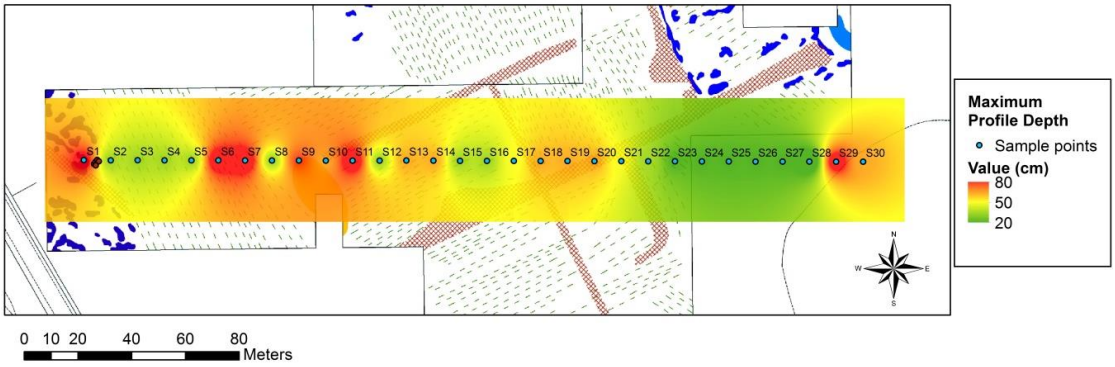



Fig. 7.20. Depth distribution across the site

It was anticipated that living quarters and street zones within and around the burgh centre will have shallower depth relative to zones outside this perimeter such as field areas due to the presence of floor layers, walls and building foundations. Figure 7.21 shows the depth distribution across the site.

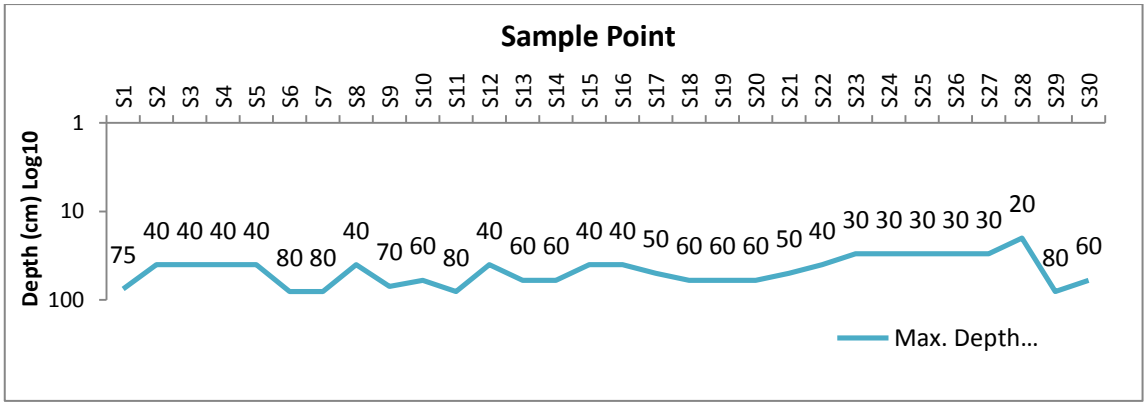



Fig. 7.21. Maximum profile depth of individual sample points across the site

The maximum depth in zone one on the west of the site is 40 cm, and 20 cm on the east side. The maximum site depth in zone one (S2 – S5) was confirmed in field sampling during the re-excavation of trench 3 in this study and in previous archaeological work by Wessex Archaeology in 2003. During the initial attempt to excavate trench 3, a maximum depth of 30 cm was reached in this area (Trench A) below which lies undisturbed archaeology (stone floor or wall) (see Figure 7.22). The location was adjusted in order to excavate the deep ditch feature of the original trench 3 (Trench B). Hence the depth distribution data displayed on the figures can be regarded to reasonably represent the true depth outline of the site. Shallow areas on the map (zone 1) indicate the presence of the structural remains of buildings or road network while intermediate and deep zones indicate areas with few or no structural presence. Zone two within which lies the burgh core is an area of intermediate depth bordered on the west by a deep zone (zone 3), and by a shallow zone (zone 1) on the east. This pattern of distribution on the one hand suggests that the burgh core area may have been further to the east, closer to the defence ditch than previously understood although this is not conclusive given the limits on the number of data points. On the other hand, the redistribution or movement of materials post burgh abandonment.

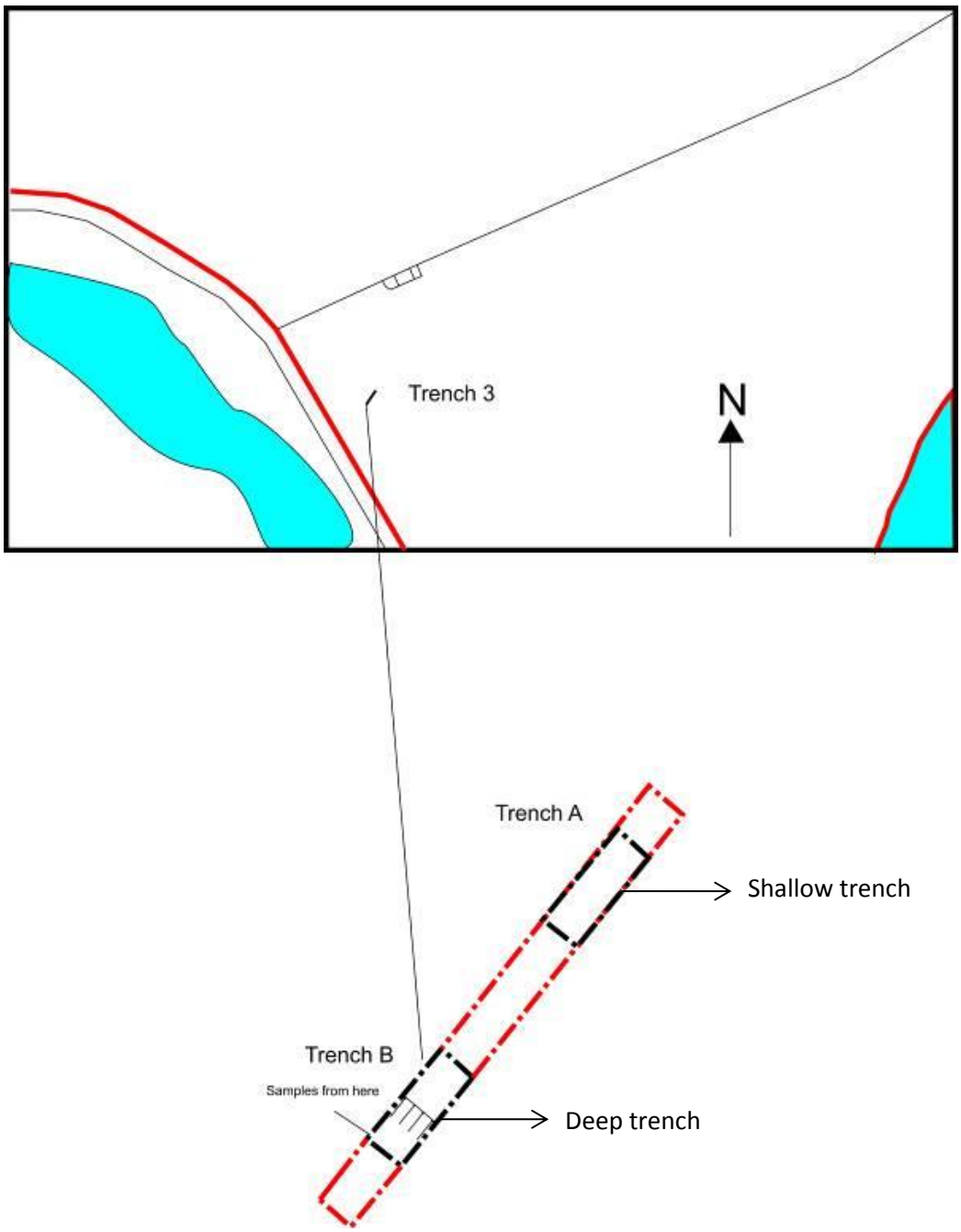



Fig. 7.22. Location of Trench 3 (scale 1:2500 cm), River Teviot in blue, Scheduled area boundary in red and expanded detail (scale 1:100 cm) showing re-excavated Trenches A and B and location of samples

Optical stimulated luminescence analysis was carried out in trench 3 to examine the stratigraphic integrity of the deposits. In Figure 7.23, both IRSL and OSL signals fluctuate with depth indicating some mixing of sediments of different ages. The sequential reduction in IRSL

and post IR-OSL signals from 110 cm to 50 cm suggests periodic or gradual deposition of new (completely or partially bleached) sediments of relatively similar mineralogy given the fairly constant IRSL/OSL ratio, except the slight increment experienced at 70 cm but not overly discordant. Higher variation in IRSL/ OSL ratio between 10 cm to 50 cm is perhaps attributable to mineralogy, largely the proportion of feldspar to quartz (Sanderson and Murphy, 2010). The lower luminescence signal values at the profile base suggest an old deposit that has either been completely or partially bleached from re-exposure to sunlight before subsequent infilling with older sediments. This interpretation is consistent with a ditch infill.

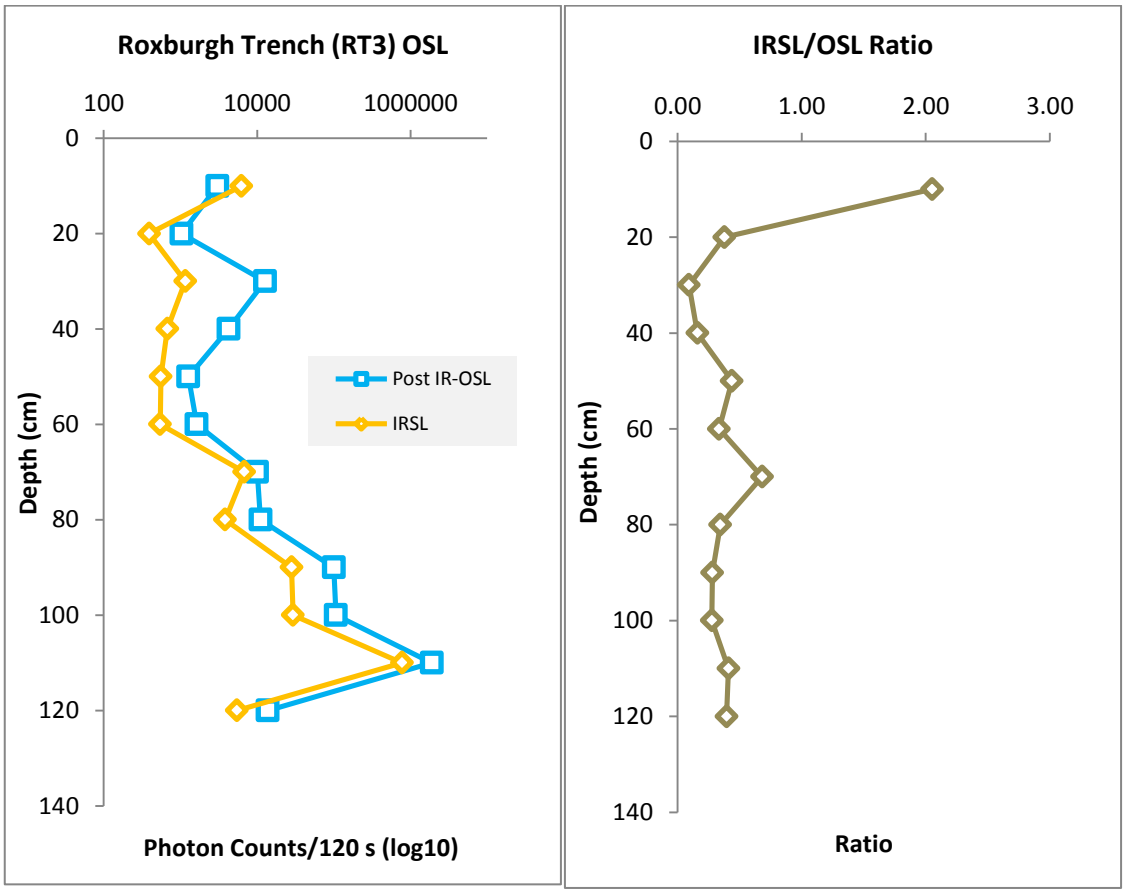



Fig. 7.23. Luminescence profiles (IRSL, Post IR-OSL and IRSL/OSL ratio) of Trench 3, Roxburgh

Previous archaeological work on the site identified the south-west end of trench 3 as a roadside ditch beside which lay a possible street and a stone building. Examination of the deposits and horizons indicates that the ditch deposits had accumulated naturally and not anthropogenic deposition. Optical stimulated luminescence of the profile suggests that materials have accumulated gradually which supports this assessment.

Near infrared reflectance analysis was carried out *in situ* on the ditch stratification/profile to investigate the differences in soil properties along the profile deposits that may hold signatures to various or specific anthropogenic activity. Figure 7.24 below shows changes in soil properties with the key determining factor attributed to variations along the vertical axis/lattice; depth, rather than horizontal influence. Dominant factor(s) inducing this variation is mainly attributed to the magnetic properties given that profile 20 – 40 cm represents the busiest depth on the analysis undertaking on the site.

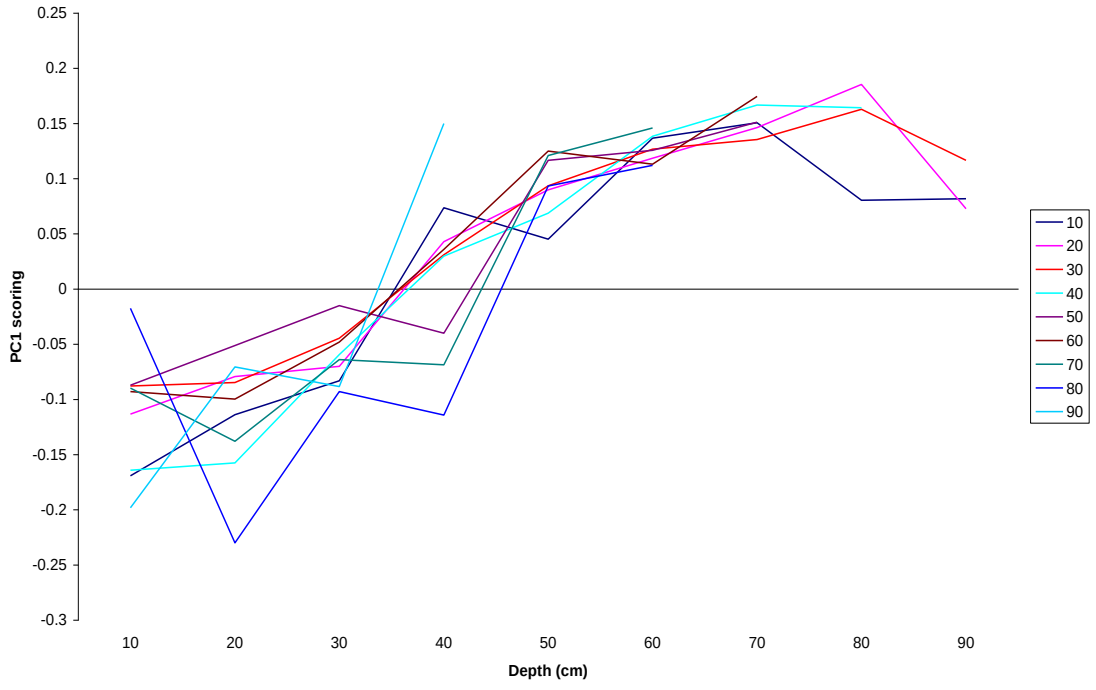



Fig. 7.24. Principal component regression analysis showing variation in soil properties with depth at Roxburgh Trench 3

*7.6.4 Site Comparison of St. Andrews and Roxburgh*

The degree of enhancement of soil indicator parameters differs between both burgh. Soil pH, organic matter content, and phosphorus concentration are considerably enhanced in the medieval core areas in St Andrews relative to Roxburgh. Thin section analysis of charcoal content which can be used as a proxy for human occupation shows that Roxburgh has similarly low charcoal content as in BGr site in St Andrews.

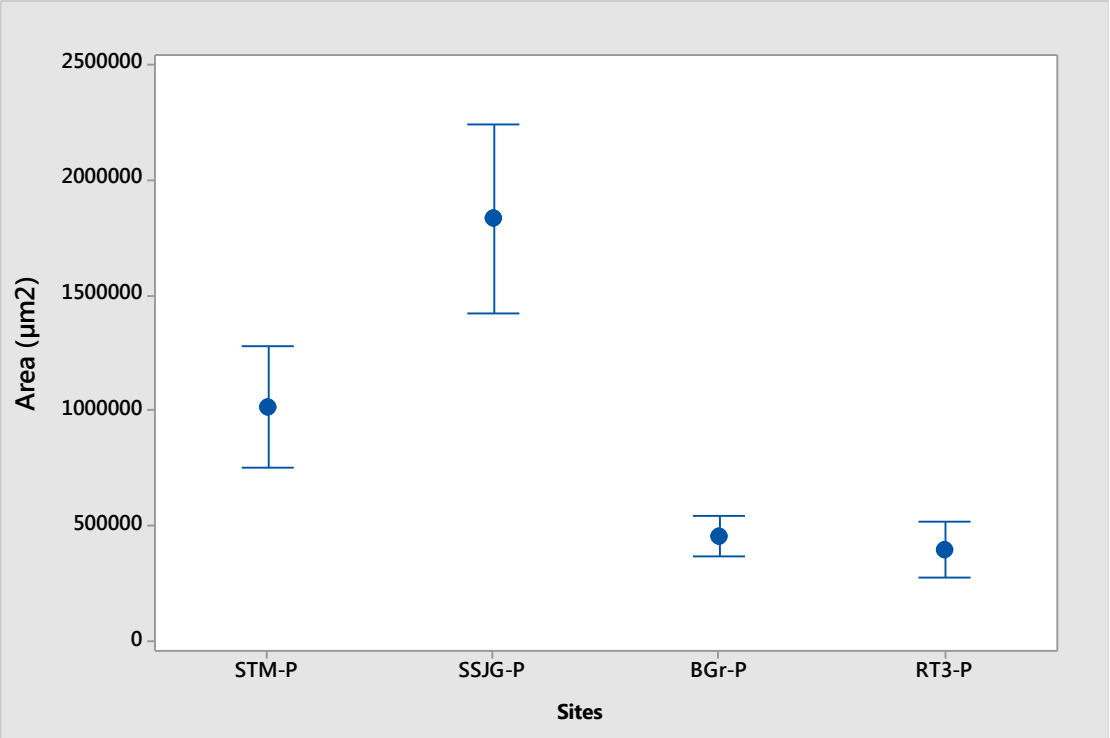



Fig. 7.25. Interval plot of charcoal content in St Andrews (STM, SSJG, and BGR) and Roxburgh (RT3) [Individual standard deviations were used to calculate the intervals; 95% CI for the Mean]

The enhancement values of these parameters in Roxburgh more closely match those found in the reference site (BGr) in St Andrews, a semi-natural area with less anthropogenic influence (Figure 7.25). The difference in the degree of expression of these anthropogenic signatures is not arbitrary and has been attributed primarily to the duration of site occupation. The

documentary accounts of both settlements indicate that the burghs as opposed to the religious site and royal castle at St Andrews and Roxburgh respectively were established at relatively similar period, in the 12th Century (Brooks and Whittington, 1977; Martin and Oram, 2007) and whilst St Andrews has continued until present, Roxburgh went into decline and eventual abandonment in the 15th Century.

Site use intensity and period of occupation are two factors that define the degree of modification and the resultant residual anthropogenic signatures in the soil. High intensity use and short occupation period is analogous to low/moderate intensity use and long occupation period. Roxburgh and St Andrews were both commercial centres where a range of activities such as trading, farming, craft etc. occurred albeit at a higher scale in Roxburgh relative to St Andrews. Roxburgh's short lifespan, however, would have resulted in the discontinuation of these activities and the corresponding truncated extent of soil modification, whilst it continued in St Andrews. The continuation of various cultural practices and activities in St Andrews until the early nineteenth century, and its occupation until present, has resulted in the high enhancement values observed in the soil compared to Roxburgh where such activities were in decline and then came to a complete halt in the 15th century.

The soil magnetic properties in Roxburgh differ substantially to those found at St Andrews. High residual magnetic enhancement in Roxburgh is associated to the site occupation activity as in St Andrews but primarily to the pyrogenic history of the site as have been discussed. Although magnetic susceptibility values are higher within the burgh core areas (STM, SST, and SSJG) in St Andrews relative to areas around the periphery (BGr), this increase is insignificant when compared to enhancement values in Roxburgh.

### 7.7 Conclusion

The various elements and processes of past occupation at St Andrews and Roxburgh sites all have potential impacts and imprints on the soil. These impacts are visible from changes in a number of soil parameters within and around settled areas, as discussed, can be explored to investigate the history of past landscapes, and when combined with documentary accounts, a more comprehensive narrative of site histories is developed.

In St Andrews, analysis of the distribution of anthropogenic signatures indicates strong site influence over profile depth; consequently, establishing a chronological sequence for occupational history was not possible. This is due to the homogenous nature of the deposits on each respective site that resulted from mono-cultural practices which is not uncommon. Further analysis of site deposit allowed the distinction between the background and anthropogenic enhancements to be made. Indication of site use, and intensity of use is also evident from the similarities or differences in the enhancement of particular signatures as well as from the rate of the accumulation of materials.

In Roxburgh, although most of the built settlement remnants now lie below the surface, attributed to its tumultuous past, previous investigations on the site have been able to confirm the general, albeit tentative, outline and internal structure of the burgh. From this study, the spatial distribution of soil markers across the site indicates high and low activity zones. High activity areas as indicated on the map, overlaps with the putative medieval core area identified by the geophysical survey data undertaken previously by GSB Prospection. Also of note is the relatively high enhancement values observed on the west side of the site, particularly for the magnetic properties distribution. The elevated soil magnetic properties in Roxburgh relative to St Andrews are highly likely to result from the pyrogenic history of the

site. The bias in the magnetic properties to the west side of the burgh suggests the inputs of materials of pyrogenic nature possibly from the burgh. The site would now benefit from absolute dating analysis of soil profiles to better understand the time frame in which these materials were deposited.

Overall, this study forms part of the continuum of the series of studies on the site that incorporates newly obtained datasets to previous database to boost the interpretive power and therefore enhance our understanding and/or stimulate further discussions on the history of this arguable one of the most important burgh in medieval Scotland.

# CHAPTER 8

SUMMARY

## 8.1 Project Aims and Main Conclusions

This thesis has employed three broad scientific approaches (physical, chemical, and biochemical), augmented with historical and archaeological records to develop a new understanding for anthropogenic-deepened soils in the medieval burgh of Scotland. This development allows a continuous narrative and a contextualisation of these extant soils to be made – from their historical inception to the contemporary period – by correlating the documentary records of bio-waste application to present-day soil-based evidences.

This study has revealed, from the physicochemical analysis of soils, the impacts of historical land use practices on the dynamics of soil processes, including mechanisms of organic carbon store, and decomposition of such materials that were deposited onto soils. Chemical analysis by solid-state $^{13}C$ CPMAS NMR spectroscopy has revealed that a significant proportion (42 – 58 %) of the soil organic carbon of anthropogenic-deepened urban soil is composed of thermally-altered organic material (black carbon), derived from high temperature pyrolysis/burning. Materials formed by pyrolysis (black carbon) therefore represent the primary source of high aromatic C assemblages found in the soil.

The depletion of organic matter is more evident in the non-pyrogenic components of soil organic matter relative to the black carbon components, a conclusion that reinforces understandings of its relative recalcitrance. Furthermore, soil profile analysis of organic matter relative to profile depth revealed that the soil organic matter contents in anthrosols have reached a relatively stable state, or approaching a steady state in the case of topsoil. Given the elapsed time, and the similarities in the pattern of distribution of carbon species in both

subsoil and surface soil profiles, organic carbon found in these soils is considered relatively stabilised although subsoils have undergone a greater extent of decomposition.

The biochemical analysis of soil samples has revealed several key insights into the dynamics of organic matter by assessing the potential role of phenol oxidase in organic matter decomposition. For the first time, phenol oxidase enzyme activity was demonstrated to influence organic carbon dynamics in urban anthrosols. In response to poor nutrient environment, microorganisms synthesise and release the enzyme phenol oxidase to degrade phenolic compounds that inhibit the activities of hydrolytic enzymes. This action compensates for the lower nutrient environments typically found in subsoils by the release more phenol oxidase enzyme. Additionally, the stabilisation of organic carbon results from the synergistic interaction of the active mechanisms of stabilisation identified; selective accumulation/degradation resulting from chemical recalcitrance, organic matter interaction with soil matrix (particles, clay minerals and charcoal), and possibly the presence of specialised isolated biological community/pool of microorganisms adapted to the catabolism of the old (recalcitrant) organic carbon compounds.

In the historical context of the study, the data obtained from the analysis of soil records shows that soils hold records of past human activity and represent an alternative means for understanding past cultures and landscape utilisation where documentary records are incomplete or unavailable.

### 8.2 Contributions and Policy Recommendations

This study is among the first in Europe to consider, in detail, the nature and properties of the organic matter in soils within and around historical urban settlements. This advancement increases our understanding for urban soils beyond basic soil reference/series data and brings

it in-line with international knowledge-base and research from elsewhere around the world on anthropogenic soils that have developed under similar conditions.

Through the analysis of anthrosol soils sourced from medieval urban environments, this research has:

1. elucidated on the long-term product of decomposition of known organic-rich substances that were added to soil. This information provides insight into the relative recalcitrance of such materials which in-turn informs decision-making process on the development of viable long-term strategies for soil carbon management aimed at increasing soil capacity as a sink for carbon; and,

2. increased the measure of data available on anthrosol soils that would allow better estimates of soil carbon content, depth and spatial variability, and C turnover, all of which allows for better calibration of climate model calculations that would improve predictions of organic carbon responses to climate-induced changes; and,

3. shown that anthrosols of different age (period of formation) have relatively similar chemical properties in terms of the composition and distribution of carbon species of the soil organic matter. This allows us to infer the stabilisation state of the organic carbon of the younger more contemporary anthrosols; and,

4. identified some of the active mechanisms of stabilisation that control the dynamics of the organic matter in anthrosol soils. This provides insight into the potential impact of changes to present soil conditions that may arise from management change (external disturbances); and finally,

5. provide a deeper understanding of urban landscape, divisions, patterns, and intensity of land utilisation at medieval burgh sites.

### *8.2.1 Policy Recommendations*

The use of animal manure, sewage sludge, and other municipal waste in agriculture are practices that are endorsed by the European Commission and applied in member states under The Sewage Sludge Directive (86/278/ EEC). This practice is analogous to historical methods of soil improvement where similar municipal materials are composted and reapplied to soil to maintain fertility and production.

In 2009, the Scottish Government announced a framework – The Scottish Soil Framework – that sets out to protect Scotland's soils from various forms of degradation, particularly climate induced, and to inform policy leads on management. The loss of soil organic matter was identified as one of the major threats to the environment to which various carbon management strategies were developed to sequester carbon in soil. One of the strategies proposed by the agencies involved in the implementing this policy framework involves the modification of existing practice (as discussed above) where high volumes of these organic-rich materials are buried underground in order to increase soil carbon sequestration.

From the research outcome, it is evident that the burial of organic-rich material in soils is not a viable means of sequestering carbon in the long-term due to the relatively short residence period of these materials as they are gradually mineralised, however, burial with mixtures of pyrogenic material (char) may increase survival sufficient for medium-term conservation. For long-term management, the burial of pyrogenic materials represents a feasible mechanism of carbon sequestration although it is worth noting that charcoal is not entirely immune to physical and biological degradation.

As urban environments change in response to human development, the changes and/or transitions are often documented and archived for future reference. Soils in urban areas are predisposed to these elements of change and therefore can conceal records of urban development history within it as shown in this project. Current soil policy on the protection of cultural landscapes does not accommodate locales without visible above ground structures or known below ground artefacts. A possible means of achieving this would be to change the criteria of the standard archaeological works carried out prior to landscape development – as part of the requirements for the Environmental Impact Assessment (EIA) – to be extended to incorporate detailed soil physical and chemical analysis in order to further assess soil historical significance, in other words, to uncover additional cultural legacy contained within its stratigraphy that are not conveyed in structural vestiges and artefact.

### 8.3 Future Work

Further explorations of the linkages and interactions between phenol oxidase enzyme activity, phenolic content, substrate availability and accessibility are required across a wider range of site types to better understand the interdependence of these variables in organic matter decomposition. This coupled with investigations of the microbial community structure in subsoil and topsoil will be greatly advantageous in determining their influence on phenol oxidase enzyme production and increase our understanding of soil enzymes generally.

### 8.4 Closing remarks

The absence of scientific data (physical and biochemical) on soils conditions prior to and during anthropogenic urban soil development obviously makes timed contextual comparisons impossible. Therefore, the datasets generated from this research on various aspects of urban soil are expected to serve as baseline information upon which successive analysis will be

interpreted. This will allow for the long-term monitoring of the organic carbon of anthrosols which will provide new understanding into the dynamics of carbon in real-time. Soil is an interface between society and the environment. Man's dynamic relationship with soil has long been recognised through investigations of our past interactions with the environment during the course of mankind's development. The impact of man's colonisation of his landscape is apparent in the environment, particularly in the soil. These impacts are only expected to rise with the passage of time as resource utilisation and exploitation expands.

Society's influence on Earths' natural processes are now clearly apparent in the environment from the current reported rises in the CO2 levels in the atmosphere and as well the rate and intensity of soil and/or landscape alterations as has been discussed in Chapter One. Consequently, questions can be asked regarding the limits of society's alterations and therefore the tolerance and breaking point of the various Earths' systems to support our existence. Such questions include: 1) should manmade alterations to any natural systems be permitted? 2) Should drastic actions be taken to immediately curtail any further alterations to natural processes regardless of the immediate and future impacts to our development? 3) Do we learn to understand the changes occurring around us and adapting our lifestyle accordingly? and finally, 4) to what extent can adaptation to the presently changing systems ensure sustainability of nature and society? The current debate on the establishment of a new geological epoch "Anthropocene" and its sister term "Paleoanthropocene" to mark periods where anthropogenic activity became sufficiently extensive as to make an imprint on the environment is very appealing, however, Earth's processes are still predominantly driven by natural events and the impacts of our activities, although visible in this natural cycle of events, are not currently sufficient as to be major drivers of Earth's processes to permit this new classification.

Now to revisit the series of questions stated earlier, it is undoubtedly an attractive option to restrict any anthropogenic activity that would impact on the environment however, it is even more so to develop an understanding of Earth's processes to a degree that allows society to very accurately predict potential activities that will result in unwanted changes and where this is inevitable, strategies for adaptation can be developed to minimise disturbances and to ensure sustainability. Some of the earlier more significant environmental-change causing activities such as agriculture, the extensive use of fire and so on carried out by society were perhaps undertaken at the time unconsciously aware of the future effects of these activities due to their inability to do so. Presently, however, we are well equipped to thoroughly investigate our environment and the capacity to do this continues to increase with development. It is therefore to this aim that this research has been conducted to further our understanding of anthropogenic urban soils, its processes and dynamics.

Soils are natural reservoirs containing valuable records of natural and man-induced changes to the environment within it and therefore are an essential component in climatic and anthropological studies. Greater understanding of the influence of past environmental change, and its mechanisms, on mankind and vice versa is key to the future management and sustainability of this dynamic environment in which we live. It is hoped that the conclusions from this research will help enable the future understanding of historical landscapes, soil conservation, and for the development of soil management policies for the growing inventory of urban landscapes around the world in the changing climate of this present century.

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