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Soil Organic Matter and Carbon Sequestration in Rehabilitated Mine Soils

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Abstract

Following the disturbance caused during the extraction of coal, landforms created with the overburden material and stockpiled topsoil must be rehabilitated and stabilized. Minesoils are not well studied but are generally of poor quality due to the loss of nutrients and overall structure caused by weathering and disturbance. Soil organic matter (SOM) improves soil quality in multiple ways and can be used as an indicator of soil quality. Improvement of minesoils is essential for rehabilitation success. By using soil organic carbon as a proxy for SOM, SOM levels can be monitored. However, common measurement methods do not distinguish coal and charcoal (a.k.a. black carbon (BC)) from more recent plant inputs. In order to assess the effect of rehabilitation management strategies on the quality of minesoils, a method to measure the SOM that distinguishes between newer plant inputs from coal and charcoal must be developed.

The objective of this research was to develop a method to measure the amount of carbon attributable to rehabilitation, test the applicability of DRIFT to predict this carbon pool, and make observations on any trends in carbon levels.

Sampling campaigns at coal minesites in the Bowen Basin, Queensland collected samples from four different mines with a range of rehabilitation ages and covering vegetation. Sampling focused on collecting small with increasingly larger increments with depth to allow detection of the movement of organic matter from the soil surface down into the soil.

Thermal analysis was selected from multiple methods that quantify coal and/or BC derived carbon based on their resistance to oxidation. By quantifying coal and BC, green soil organic carbon or “green carbon”, the carbon attributable to rehabilitation, can be calculated as the difference between the total organic carbon and the sum of coal and BC derived carbon.

Thermal analysis with evolved gas analysis (TA-EGA) using multivariate curve resolution (MCR) chemometric analysis was used to demonstrate the ability to distinguish between coal and BC in laboratory prepared mixed soil/coal/BC systems. MCR was able to separate components in the CO_2 thermograms without prior identification of the components.

TA-EGA with MCR was applied to minesoils to quantify green carbon, BC and coal and build a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs) prediction model. The DRIFT model did not yield good results as green carbon, BC,

coal, as well as other carbon measurements were poorly resolved in minesoils, indicating further work on the model and/or spectral library is required. The relatively high root mean square errors of prediction would mask small changes in green carbon; however, results suggest minesite specific calibrated models may improve predictions. As the three carbon pools are composed of a variety of materials, each with differing thermal oxidative patterns, the components identified by MCR varied somewhat from those identified in the laboratory prepared mixtures; however, the components were attributable to the pools due to their peak combustion temperatures. The BC and coal quantities attained through MCR did not concur with the recalcitrant organic carbon predictions from the Australia-wide Soil Carbon Research Programme (SCaRP) DRIFT model. This difference may be due to the use of a thermal definition as identified by MCR versus a molecular/spectroscopic definition as used by SCaRP. The use of different operational definitions of BC is reflective of the various methods used to measure BC by different laboratories and is the crux of why there is no consensus on a standard method. These methods are often biased towards measuring a particular window of the BC continuum suited for the purposes of that research field through the exploitation of a characteristic of the molecules that emerges in that window. However, as the BC continuum encompasses a wide range of thermally altered molecules, these windows often do not match each other, and as such, methods and operational definitions of BC proliferate.

The results of TA-EGA with MCR as applied to minesoils from two different mines and ages of rehabilitation ranging from non-surface mined to 20 years post rehabilitation showed a general trend of decreasing amounts of green carbon from the surface downwards into the soil profile. Amounts of coal within a sampling pit was relatively stable while varying greatly between pits. This may be attributed to the high level of local heterogeneity due to the use of heavy machinery to dump loads of spoil and topsoil during the formation of the landforms. While older (>10 years) rehabilitated soils could reach carbon levels similar to and greater than nearby non-surface mined soils, the contribution by green carbon was diminished, with significantly larger amounts of coal and BC compared to non-surface mined soils. Therefore, if rehabilitation goals include returning soil carbon levels to those pre-disturbance, carbon levels must surpass pre-disturbance levels to compensate for the increase in BC and coal. Thermally defined pools for green carbon, BC, and coal

produced by TA-EGA with MCR provides a new, promising method to monitor carbon changes in minesoils demonstrating the ability to differentiate the three pools concurrently and would prove useful in the monitoring of rehabilitation progress.

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Publications during candidature

Conference Abstracts

Chan, J., Baumgartl, T., Erskine, P. 2010, 'Soil organic matter and carbon sequestration in rehabilitated mine soils', poster presented to Organic Matter Stabilization and Ecosystem Functions Conference, Presqu'île de Giens, France, 19-23 September.

Chan, J., Baumgartl, T., Erskine, P., Peltre, C., Plante, A. 2014, 'Distinguishing Carbon Fractions in Coal Mine Rehabilitated Soils', paper presented to Life-Of-Mine Conference, Brisbane, Australia, 16-18 July.

Chan, J., Peltre, C., Plante, A., Baumgartl, T., Erskine, P. 2015, 'Comparing black carbon measurements from thermal analysis and national-scale MIR calibrations in minesoils', poster presented to Soil Interfaces For Sustainable Development, Montreal, Canada, 5-10 July.

Baumgartl, T., Glenn, V., Erskine, P., Chan, J. 2016, 'Spatial and temporal changes of soil organic carbon content since time of reclamation of mine soils in a semi-arid environment of Australia', poster presented to European Geosciences Union General Assembly, Vienna, Austria, 17-22 April.

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Publications included in this thesis

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Contributor	Statement of contribution
Author Jaclyn Chan	Designed experiments (60%) Wrote and edited paper (50%) Statistical analysis of data (10%)
Author Alain Plante	Designed experiments (10%) Statistical analysis of data (10%) Wrote and edited paper (40%)
Author Clément Peltre	Statistical analysis of data in (80%) Designed experiments (25%) Created graphs (100%) Wrote and edited paper (5%)
Author Thomas Baumgartl	Wrote and edited paper (2.5%)
Author Peter Erskine	Wrote and edited paper (2.5%)

Contributions by others to the thesis

Thomas Baumgartl (TB) and Peter Erskine (PE) proposed the idea to investigate black carbon in coal mine soils. TB was responsible for the decision to sample multiple depth fractions in each pit in an effort to show trends within a pit. Both TB and PE have edited this document.

Phill McKenna (PM), Vanessa Glenn (VG), TB and PE helped collect the minesoil samples in the field and in helping decide which sites to sample from as well as identifying the ground cover flora.

VG organised the field notes and photos to quickly be able to easily identify sites and with PM created maps to plot sampling points using ArcGIS software. Vinod Nath assisted with particle size analyses.

Clément Peltre and Alain Plante were responsible for the decision to use MCR to interpret the thermal evolved CO_2 data. They were also co-authors on the manuscript along with PE and TB, with Clément responsible for the majority of the statistical analysis and the creation of the graphs in Chapter 6.1 entirely. Maddie Stone created the R-script that extracted and aligned the thermal analysis data.

Phil Bloesch, Llew Rintoul, Serge Kokot, Romà Tauler and Tim Napier-Munn provided advice, assisted with the interpretation and proper use of the statistical analyses.

Statement of parts of the thesis submitted to qualify for the award of another degree

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Keywords

black carbon, coal, mine soil, rehabilitation, thermal analysis, soil organic matter, soil organic carbon

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Fields of Research (FoR) Classification

FoR code: 0503, Soil Sciences, 100%

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List of Abbreviations

BC	black carbon
CP/DP	cross polarization/direct polarization
DRIFTs	diffuse reflectance infrared Fourier transform spectroscopy
EC	electrical conductivity
FT-IR	Fourier transform infrared
GC	green carbon
HOC	humic organic carbon
IC	inorganic carbon
MCR-ALS	multivariate curve resolution – alternating least squares
MIR	mid infrared
PCA	principal component analysis
PLSR	partial least squares regression
POC	particulate organic carbon
RMSECV	root mean square error of cross validation
RMSEP	root mean square error of prediction
ROC	resistant organic carbon
SCaRP	Soil Carbon Research Programme
SNV	standard normal variate
SOM	soil organic matter
SOC	soil organic carbon
TA-EGA	thermal analysis – evolved gas analysis
TC	total carbon
TG-DSC	thermogravimetry – differential scanning calorimetry
TN	total nitrogen
TOC	total organic carbon

1 Literature Review

Introduction

Soil is recognized as a large reservoir of carbon in the global carbon cycle (Lal, 2004, Batjes, 1999, Lal and Follett, 2009). Globally, the upper meter of soils contains over 2000 Pg (petagram = gigatonne = 10^{15} grams) of carbon, excluding the litter layer and charcoal, as these sources of carbon could not be factored into the meta-analysis of global carbon stocks of Batjes (1996) due to differences in methods used by the source studies. The terrestrial carbon pool is estimated to be 3060 Pg with soil organic carbon (SOC) making up more than half at 1550 Pg, soil inorganic carbon (SIC) and the biotic pool containing 950 Pg and 560 Pg, respectively (Lal, 2008, Batjes, 1996). The soil pool (> 2000 Pg) contains more carbon than the vegetative biomass pool (830 Pg) and the atmosphere (760 Pg) combined (Post et al., 1990, Lal, 2008, Falkowski et al., 2000). Soils have a large capacity to sequester carbon, and it is estimated that agricultural soils in Australia have the ability to sequester 50 Pg CO_2-e over 20-50 years by altering land management practices (Garnaut, 2008). For context, the global CO_2-e emissions for the year 2010 is estimated to be ~47 Pg (Garnaut, 2008).

Like agricultural soils, the soils of rehabilitated mine sites have been altered by human activity. These activities disturb the soil and result in the loss of organic carbon through mineralization, weathering and erosion as well as through loss of regular organic inputs (Williamson and Johnson, 1990, Schwenke et al., 2000). The degree to which mine site soils (mine soils) have been altered, however, is much greater than agricultural soils in terms of the depth of disturbance in the soil profile and compaction. During the open cut coal mining process, heavy machinery is used to strip the topsoil and stockpile it in a series of heaps. The now exposed overburden spoil that lays on top of the coal seam is removed to expose the coal seam, hauled by mining dump trucks to a cleared dumping area and reshaped into large hills. These mesa-like dumping grounds are designed to allow maximum storage of overburden and landform stability and are large enough to support roads upon which mining dump trucks drive to higher areas to dump their loads. These newly formed hills are generally covered with a layer of the earlier stockpiled topsoil to promote plant establishment. Different management practices however, do not always include direct topsoil placement (Akala and Lal, 2001). Mine soils are therefore drastically different to naturally occurring soil as they have not been weathered and formed over geological timescales, but rather have been formed using heavy machinery from materials collected from potentially different locations and, due to mixing during stripping, generally lack the horizons that define natural soil types. Mine soils fall under the Anthroposol soil type, as they have been altered by human activity, with characteristics that are primarily determined by the parent material, a mix of materials formed at different times and conditions (CSIRO, 2011). The methods used to construct the landform and mine soils causes high local-scale (0-10 m) heterogeneity, often displaying a distinct change in characteristics at the topsoil-spoil interface (see Appendix C) and is influenced by micro-topography while also less influenced by landscape placement than natural soils (Akala and Lal, 2000, Banning et al., 2008, Schafer, 1979). Mine soils generally have low productivity due to characteristics such as higher levels of compaction from the use of heavy machinery, low pH, low nutrient levels, low SOM levels and high salinity, all from the mixing of topsoil with the spoil material as well as leaching and mineralization that occurs during the stockpiling of the bare topsoil heaps (Shrestha and Lal, 2006, Sencindiver and Ammons, 2000, Ussiri and Lal, 2005, Schwenke et al., 2000b). The amount of soil organic matter (SOM) and atmospheric carbon sequestered in SOM on rehabilitated open coal mine soils in Queensland is unknown. As SOM (and the amount of C contained therein) is an essential indicator for soil quality and is required to increase land productivity, it can be used to gauge coal mine site rehabilitation success and may be an important carbon emission offset (Lal, 2004, Sikora et al., 1996).

Since industrialisation, it is estimated that global soils have emitted 26 Pg and 52 Pg of carbon from erosion and mineralization, respectively (Lal, 2008). Changing the land use (e.g. forest to pasture) also causes SOM levels, and thus soil carbon levels, to change (Guo and Gifford, 2002). Disturbed soils tend to have low SOM levels (Ussiri and Lal, 2005). Losses in SOM are primarily attributed to weathering, mineralization, decomposition and erosion (Williamson and Johnson, 1990).

A soil with less SOM produces less biomass than it would with higher levels of SOM (Lal, 2006). In agricultural studies it has been found that the addition of SOM drastically improves productivity of degraded soil irrespective of nutrients (Kimetu et al., 2008). Addition of SOM improves the edaphic characteristics of soils such as cation exchange capacity, gas exchange and water retention properties (Stevenson, 1994). SOM is known to bind pesticides and slow their transport through waterways (Ahmad et al., 2001). It can also act as a source of nutrients, buffer soil pH and temperature fluctuations which can assist seed germination and plant development (Stevenson, 1994).

Mine soils have the potential to reach the same levels or surpass SOM levels at undisturbed sites based on land use and management practices (see Figure 1, Akala and Lal, 2001); therefore there is potential for comparing mine site management regimes for effectiveness at increasing mine soil SOM as a criterion of rehabilitation success (Anderson et al., 2008, Ussiri and Lal, 2005, Fettweis et al., 2005). For example, in Figure 1 the land management practices of the treatment "Reclaimed-III" would be considered the best at improving the soil carbon in rehabilitated soils.

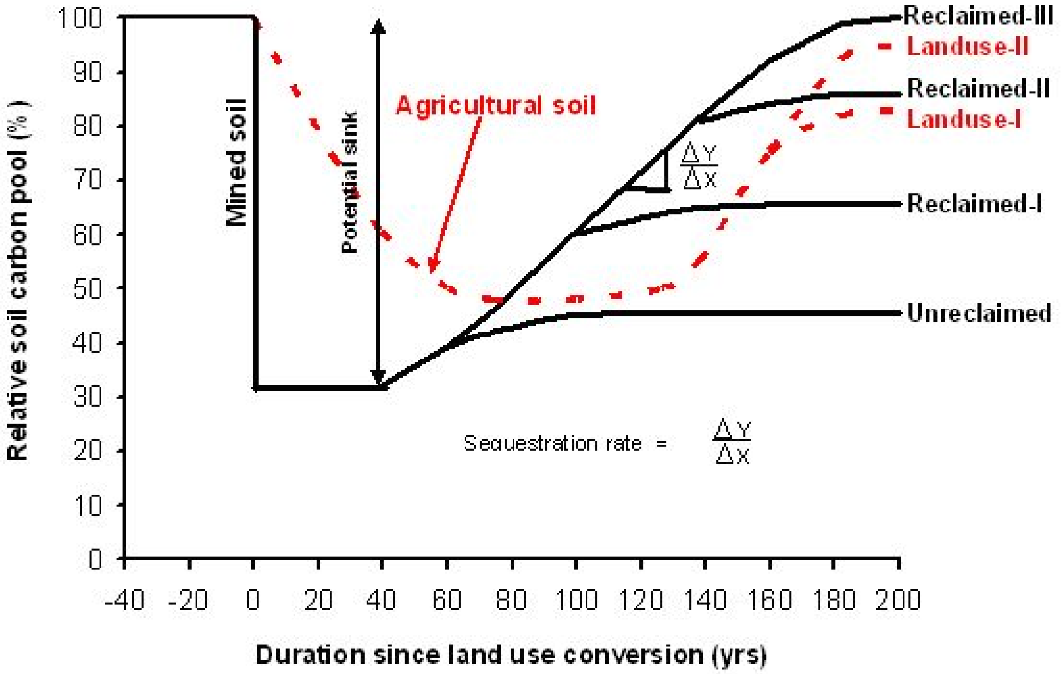

Figure 1 Conceptual model of carbon dynamics in reclaimed mine soil taken from Shrestha et al. (2009). The separately labelled "Reclaimed I-III" represent three different reclamation and land management scenarios. Landuse I and II represent two different soil/crop management scenarios to improve carbon levels in agricultural soil.

Mined land rehabilitation has two main goals, to revegetate and to manage erosion (Osterkamp and Joseph, 2000). Revegetation serves to stabilize slopes through reducing erosion, reducing soil compaction, and provides a source of SOM (Akala and Lal, 2000, Carroll et al., 2000). The accumulation of SOM in mine soils serves three purposes: it improves the soil structure, thereby improving further rehabilitation, increases productivity and it sequesters carbon. It has been hypothesized that aside from the beneficial influence due to the addition of nutrients, the addition of organic carbon to poor soils improves soil productivity due to surface features of SOC onto which bacteria cling and nutrients adsorb and become available to plants (Kimetu et al., 2008). The improved soil structure from the addition of SOM increases water retention and infiltration and reduces the risk of crust formation (Osterkamp and Joseph, 2000, Six et al., 1998). This can also lead to reduced runoff from rainfall events and in turn reduce erosion risk and ameliorate runoff water quality by conserving topsoil and reducing sediment load. Hence, SOM accretion is desirable and is critical for ecosystem stabilization on rehabilitated sites.

Mine soils are effectively young soils made of a mix of spoil rock and topsoil with little to no SOM (Sencindiver and Ammons, 2000, Ussiri and Lal, 2008b). The properties of mine soils are mainly determined by the parent material, mining technique and rehabilitation management practices (Schafer, 1979, Schwenke et al., 2000a). Rehabilitation management practices may include soil conservation and enhancement, liming, fertilizer application and use of mulches (Osterkamp and Joseph, 2000, Lee et al., 2009). Ripping of the soil surface is also sometimes done to relieve compaction caused by the heavy machinery. It has been thought that rehabilitated soils will not be as productive as natural soils because of compaction from machinery and low SOM levels. The loss of SOM from the mine soils is due to lack of plant litter, accelerated erosion and decomposition due to the aeration during the stockpiling of topsoil (Ussiri and Lal, 2008a). Furthermore, there is an early decrease in the levels of SOM following rehabilitation due to the disturbance caused by rehabilitation (Akala and Lal, 2000, Williamson and Johnson, 1990). However, newly rehabilitated mine soils can be expected to accumulate SOM rapidly until SOM input and decomposition rates reach equilibrium (Vindušková and Frouz, 2013, Roberts et al., 1988, Chaudhuri et al., 2012). Carbon sequestration rates in minesoils have been reported as ranging from 0.2-1.85 MgC ha^{-1} yr^{-1} dependant on land use and age (Ussiri and Lal, 2005, Acton et al., 2011).

The level of SOM in soils is dependent on organic matter input, climate and water availability and other ecosystem properties (Batjes, 1996, Krull et al., 2001). Soils have the capacity to store large amounts of carbon via accretion of SOM, such as microbial biomass, root exudates, and biodegraded organic matter. The carbon contained in SOM is known as soil organic carbon (SOC). SOC is thought to contribute 58% of SOM with the remainder composed of other elements, such as oxygen, hydrogen, etc. The actual amount that C accounts for has been observed empirically to vary from 40-58% depending on the soils (Tabatabai, 1996). The potential for soils to accumulate SOM is a function of the production of biomass by vegetation which enters the soil as root exudates and litter. Weathered soils disturbed during the process of open cut coal mining have been dug up, mixed with subsoil, stockpiled, and exposed to the elements also have low amounts of soil organic carbon and thus have the potential to accumulate and sequester carbon (Akala and Lal, 2001, Sperow, 2006). Published attempts to measure the rate of SOC sequestration in surface mined lands under rehabilitation has occurred overseas but not in Australia (Fettweis et al., 2005, Ussiri et al., 2006, Chatterjee et al., 2009a, Rumpel et al., 2001, Roberts et al., 1988). Carbon sequestration rates in minesoils have been reported as ranging from 0.2-1.85 MgC ha^{-1} yr^{-1} dependant on land use and age (Ussiri and Lal, 2005, Acton et al., 2011). These attempts however, often ignore the high local variability (0-10m laterally) in minesoils (Schafer, 1979, Nyamadzawo et al., 2008, Shukla et al., 2007). It is important to measure the amount of SOC accumulating in the soil to calculate carbon offsets, to compare the differences between different rehabilitation management strategies and inform management decisions. In 2016 ~1.9 x 10^9 bank cubic meters of overburden was moved at coal mines in Queensland that will require stabilization through rehabilitation (Natural Resources and Mines, 2016). SOC can be divided into two groups: recently sequestered carbon (as in SOM or “green” carbon) and old sequestered carbon (coal, and black carbon) (Maharaj et al., 2007b, Mackey et al., 2008).

Carbon Fractions: A problem of nomenclature

As carbon has been studied in atmospheric sciences, biological sciences, and soil and sediment sciences, terminology has been developed within each of these fields to describe different classifications of carbon in its many forms. However, these terminologies lead to confusion as they are not always consistent between fields or within fields. The following classifications and terminology will be used in this document.

Soil organic carbon (SOC) is a large class of carbon compounds found in the soil which excludes soil inorganic carbon forms (SIC), such as carbonates. Carbon is added to the terrestrial pool by fixation from the atmospheric pool. Carbon fixation, or sequestration, into the soil naturally occurs in two ways, photosynthesis and formation of secondary carbonates (Lal and Follett, 2009). The photosynthetic path, which continues with the senescence of plant tissues and microbial breakdown into soil organic matter, results in SOC (Figure 2). All SOC has at one time been part of plant matter and has since cycled through the food web.

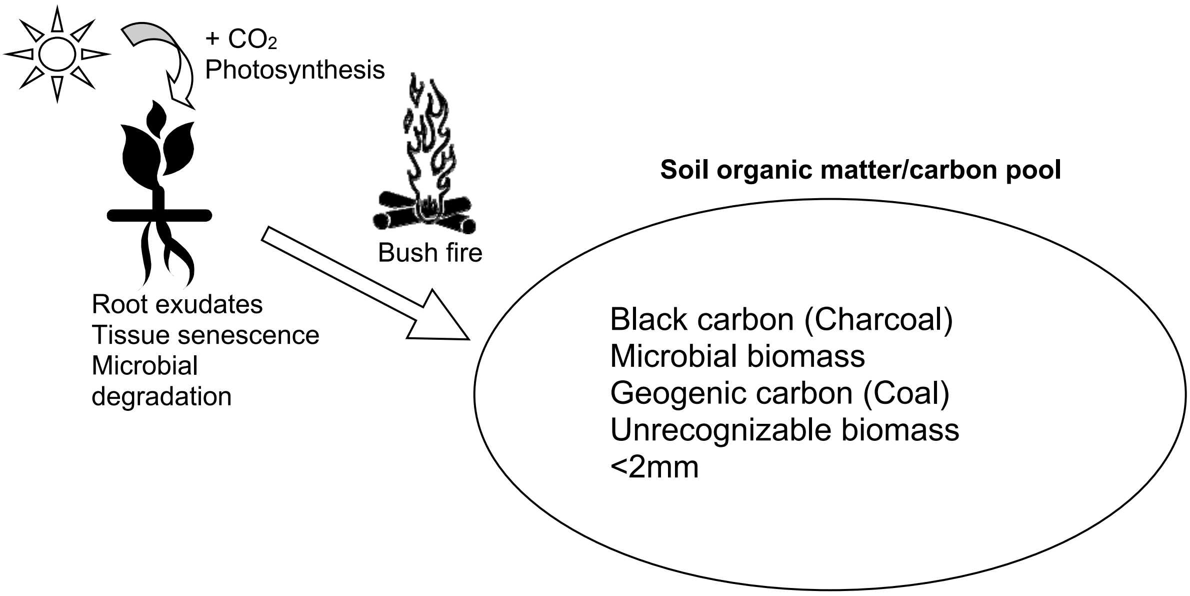

Figure 2 Conceptual model of soil organic matter/carbon pool

Coal is fossilised organic material that has withstood geophysical forces (Krevelen, 1993) and will herein be classified as geogenic carbon. It is still organic carbon since it was plant matter before the coalification process took place. Some studies have called coal “elemental carbon” (Han et al., 2007, Rumpel et al., 1998, Khan et al., 2009). Alternatively, some studies have included coal in the class called black carbon (BC) (Manning and Lopez-Capel, 2009, Brodowski et al., 2005).

Black carbon (BC) is the residue from incomplete combustion of organic matter and is known by different terms. It has been described as a continuum from slightly charred material to soot and in this study BC will be considered to include the whole continuum while excluding geogenic carbon (Schmidt et al., 2003) (Figure 3). Charcoal is a form of black carbon situated in the middle of the continuum. In atmospheric science BC forms have been called “elemental carbon” (Hammes et al., 2007, Han et al., 2007). BC and coal, when found in the soil, are both part of SOC (See Figure 2).

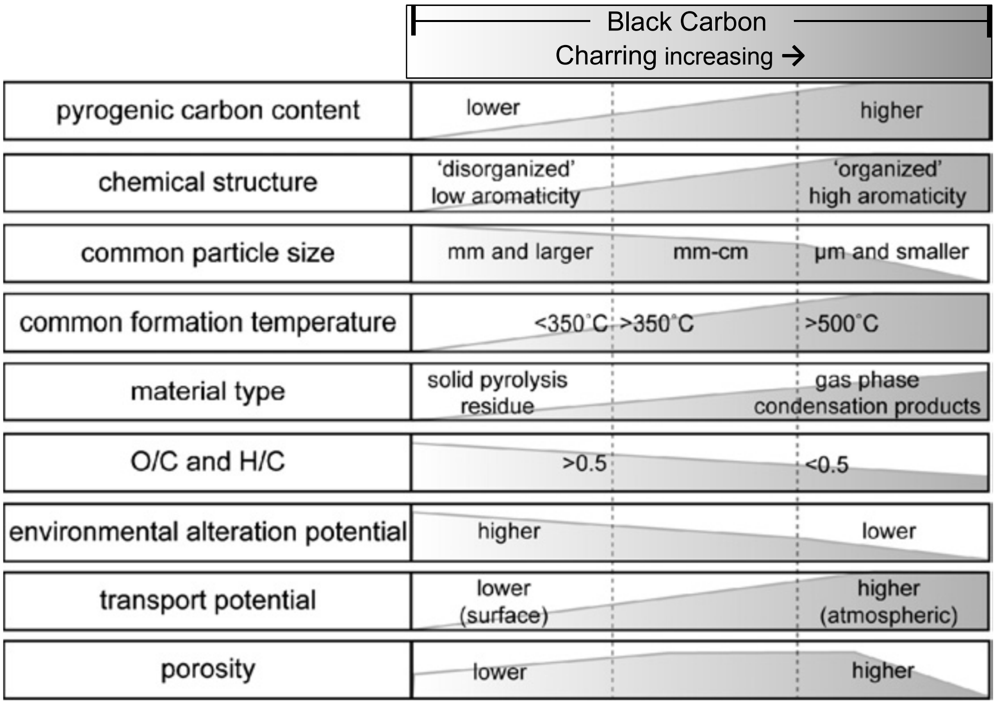

Figure 3 The pyrogenic carbon continuum modified from Bird and Ascough, 2012.

BC occurs in natural soils and is involved in many biogeochemical processes affecting the entire planet (Manning and Lopez-Capel, 2009, Schmidt et al., 2003). It has been found to contribute a significant amount of C in SOC and can account for 0.8-2.8% of the annual input of organic matter into the soil (Fang et al., 2010, Reeves III et al., 2008). BC is heterogeneous, chemically complex with chemical and physical properties that vary along the "combustion continuum" with structures which are not completely known (Han et al., 2007, Schmidt et al., 2003, Manning and Lopez-Capel, 2009, Simpson and Hatcher, 2004).

Previous studies to measure the amount of carbon plants sequester into the soil have noted the differences in the SOC fractions mentioned above, particularly the need to separate geogenic carbon (Sperow, 2006, Chatterjee et al., 2009a). Terminology for what they sought to study was named "recent" carbon (Ussiri and Lal, 2008a). This, however, does not make a distinction between BC from charred biomass and freshly biosequestrated carbon. Siavalas et al. (2013) has considered the need to include BC and geogenic carbon in carbon analysis. "Green" carbon, a term coined by Mackey et al. (2008) includes the living biomass in the soil, which is not what is being studied here. Thus a new classification, "green soil organic carbon" (herein redefining the term green carbon, for short), will refer to all SOC that passes through a 2 mm sieve, excluding geogenic carbon and BC. Green soil organic carbon includes the carbon contained in SOM that has been sequestered by organisms living in the immediate area and should exclude charcoal from bushfires.

The effect of vegetation type on carbon accumulation in minesoils is uncertain due to the low amount of data available (Vindušková and Frouz, 2013). However, it is uneconomical to collect and analyse sufficient samples to make statistically valid conclusions of the effect of vegetation type. Nyamadzawo et al. (2008) found carbon concentrations to vary greatly, with the coefficient of variation >35%. The influence of vegetation may also be obscured due to other factors, including the effects of microclimate and microtopography produced from the high heterogeneity existing at mine sites.

1.1 SOM Protection and Humus

SOM is a mixture of polysaccharides, proteins, resins, fats, waxes and humic substances, the products of chemical and microbiological degradation of organic inputs (Steelink, 2002). SOM accretes when the input exceeds the amount lost. The rates at which SOM is lost or biodegraded is dependent on environmental factors, such as moisture and temperature, and the material's ability to resist decomposition through biochemical recalcitrance, chemical interaction protection (often with minerals) and physical protection (Lorenz et al., 2009, Lützow et al., 2006). When the environment permits, the more labile fraction of SOM is quickly oxidized or incorporated into microbial biomass. The labile SOC fraction is removed from the soil in less than 10 years, if the residence time is 10-100 years or longer than 100 years, it is termed intermediate and stable, respectively (Lützow et al., 2006). Adequate oxygen, moisture and temperature range required for microbial biodegradation are the main factors governing decomposition.

SOM science has produced a method of considering SOM on a functional basis creating divisions based on the size or density of SOM particles. Studies have shown that similarly sized particles have shared characteristics. For example, it has been shown that the majority of charcoal in a soil sample may occur in the <53μm fraction (Skjemstad et al., 1996).

Some SOM molecules are considered naturally recalcitrant, able to withstand degradation due to properties of its chemical structure. These “biochemically recalcitrant biomacromolecules” are considered to contribute to long term C sequestration and are sometimes known as humic substances (Lorenz et al., 2009).

Physical protection of SOM is facilitated by minerals that limit the access of bacteria to the organic matter thereby slowing or preventing biodegradation. Clay has been hypothesized as protective of SOM (Jobbágy and Jackson, 2000, Verchot et al., 2011, Lützow et al., 2006, Kögel-Knabner et al., 2008). Wei et al. (2014) study using artificial soils with clay have found the opposite, that clay increased the degradation of fresh OM. It is possible that their artificial soil would not adequately reflect the activities of natural soils, however, it may be that the creation of mine soils would follow their findings.

Humus is believed to be a form of SOM that is resistant to biodegradation and is composed of “humic substances” including humic acids. Humic substances are associated with improvements of soil characteristics, including but not limited to water infiltration, increased cation exchange capacity and pH buffering (Stevenson, 1994). Humic acids are thought to be complex molecules including aromatic and aliphatic moieties (Steelink, 2002). ^{13}C NMR has indicated that the majority of aromatic C in soils can be attributed to lignin (Ahmad et al., 2001).

A note on SOM and particulate organic matter

The concept of the components of soil, organic matter and minerals, is simple to comprehend. However, in practice, the determination of whether organic matter is part of the soil or not is complicated as not everything found under the surface of the ground is part of the soil (Tabatabai, 1996). Living roots of plants are not soil as they are part of below ground primary productivity.

Sohi et al. (2001) include organic matter identifiable as plant matter in their free soil organic matter fraction. This free soil organic matter measured <10 mm in length. SOM does not have to be decomposed (Johnston et al., 2009, Yadav and Malanson, 2007). Thus, as a functional definition, SOM will consist of organic matter <2 mm in diameter and <10 mm in length that is not living or is unpractical to manually exclude from samples *i.e.* microbes.

Particulate organic matter is a classification of SOM based on particle size. It is believed that biological activity can be inferred through particle size (Sohi et al., 2001, Skjemstad et al., 2004b). Similarly, the carbon contained in the organic matter fraction >53 µm and <2 mm is considered biologically active or labile and is used as a measure of soil health, called particulate organic carbon (Rayment and Lyons, 2011).

1.2 Green Carbon Quantification

Green carbon, a term used herein to denote the soil organic carbon attributable to rehabilitation of minesoils through sequestration by plants and reestablishment of the soil ecosystem, is difficult to measure directly. SOM and SOC occur in a variety of different forms and molecules, some yet to be characterized, with varying chemical properties (Hedges et al., 2000, Ahmad et al., 2001, Grandy and Neff, 2008, González-Pérez et al., 2004). With respect to a sample, one approach to determining green carbon is by measuring the total carbon (TC), total inorganic carbon (TIC), geogenic carbon and BC. The difference between the total carbon and the total inorganic carbon is the total organic carbon (TOC) which is analogous to SOC (Eqn 1). TOC analysis is commonly done with an elemental analyzer, e.g. LECO CR-412 Carbon Analyzer. Green carbon is the difference between TOC and the sum of geogenic carbon and BC (Equation 2).

$$TOC = TC_{(Sample)} - TIC \qquad \textbf{Equation 1}$$

$$Green\ carbon = TOC - (\text{geogenic C} + \text{BC}) \qquad \textbf{Equation 2}$$

Thus, green carbon would be quantified indirectly through the measurement of BC and coal in soils. Research to quantify the amount of green carbon on rehabilitated coal mine soils has been done before at US coal mines (Akala and Lal, 2002, Maharaj et al., 2007b, Ganjegunte et al., 2009) and European sites (Sever and Makineci, 2009). However, these studies have either ignored geogenic carbon or BC or both (e.g. Ganjegunte et al., 2009); therefore, their results would have overestimated total green carbon. The ability to measure green carbon would allow land managers the ability to assess how the methods used in rehabilitation are improving soil health. If geogenic carbon or BC is included in green carbon measurements, changes in measured carbon levels may not correctly represent changes in soil health, but rather could be the result of contamination from geogenic carbon or black carbon, neither of which are attributable to rehabilitation. It is also desirable to be able to measure green carbon quickly and cost-effectively.

Below a suite of tests cited in literature is presented and discussed explaining the possibilities for determination of various carbon fractions and their reliability.

1.3 Direct quantification of green carbon via Walkley-Black

The need for a quick and accurate method to measure green carbon in rehabilitated coal mine soils has been recognized; however, there is no known method to quantify green carbon directly (Maharaj et al., 2007b). The complication from the presence of coal and BC led to the suggestion that green carbon might be best quantified directly by using Walkley-Black (1934) organic carbon measurement results as a proxy (Dalal, 2010, pers. comm., September 9). Walkley-Black (1934) is a form of wet oxidation using dichromate without external heating. Walkley-Black (1934) has historically been used to determine the amount of soil organic matter/organic carbon. Determination of organic carbon is by colourimetry or titration of the reduced dichromate and the application of a correction factor to account for the incomplete oxidation (Rayment and Lyons, 2011). It is well established that Walkley-Black (1934) results in the incomplete oxidization of the organic carbon in a sample and it has been recommended that correction factors be recalculated for different soils (Lettens et al., 2007). Due to the inability to detect 100% of SOC, Walkley-Black (1934) has been considered unreliable and subsequently fallen out of favour as a SOC quantification method (Victoria Department of Primary Industries, 2009).

It is unclear what fractions of SOC that Walkley-Black (1934) measures. While Heanes (1984) heated dichromate oxidation completely oxidizes SOC, even in the presence of carbonates, there is variability in the oxidation of BC by Walkley-Black (1934) method (Schmidt et al., 2012). Oxidation of BC by Walkley-Black (1934) is dependent on the particle size of the black carbon and source material (Skjemstad and Taylor, 1999, Conyers et al., 2011). Recovery of up to 50% of BC was reported for particles 5-10 μm in size and up to 55% for acid washed charcoal < 250 μm but as low as 11% for biochar derived from plant waste materials (Skjemstad and Taylor, 1999, Conyers et al., 2011). Bird and Gröcke (1997) demonstrated that the heated dichromate oxidation of BC materials is a complex function of length of digestion time, degree of charring, and source material, among other factors. Furthermore, Knicker et al. (2007) determined that for the purpose of quantification of BC, dichromate oxidation would overestimate BC as hydrophobic SOM is not oxidized by being protected from the aqueous acid. Despite the variable oxidation of BC and the potential preservation of hydrophobic SOM, it has been suggested that what remains, COREC (chemical oxidation resistant elemental carbon), might serve as an estimate of BC (Siavalas et al., 2013). What has not yet been proven is whether results from Walkley-Black (1934) would agree and correlate with the difference between measurements of TOC and the sum of coal and BC (Eqn 2) (Dalal, 2010, pers. comm., September 9). In Chapter 6, where a novel method for differentiating and semi-quantifying carbon fractions using thermal analysis with subsequent chemometric analysis is presented, Walkley-Black carbon (1934) is reported to have a weak correlation with green carbon predictions.

1.4 Indirect quantification via quantification of BC

There is no gold standard method to quantify BC. An inter-laboratory experiment to compare BC quantification methods using common reference materials found a large range in the measurements with some as much as three times the average result (Figure 4) (Hammes et al., 2007). There are large variations in results between methods and materials. A key finding was that no correction factor could be applied to compare different studies, nor could any one method be considered correct as each method was biased toward a particular portion of the BC continuum that was appropriate for the operational definition of BC for each study.

Separating or removing coal and BC from samples is another general process to attempt to quantify green carbon. Flotation of coal is a common suggestion to remove it from a sample. However, it is unclear whether green carbon would be lost along with the coal as its properties are as yet undefined and may be similar to coal or whether all ranks and grades of coal would float (Shukla, 2010, pers. comm., August 6). In their recent review, Sohi et al. (2010) suggest that the successfulness of an attempt to physically separate BC from soils would be highly dependent on site characteristics. Alternatively, mine soils from open cut coal mines have been defined as soils containing coal particles which cannot be physically separated (Ussiri and Lal, 2008a).

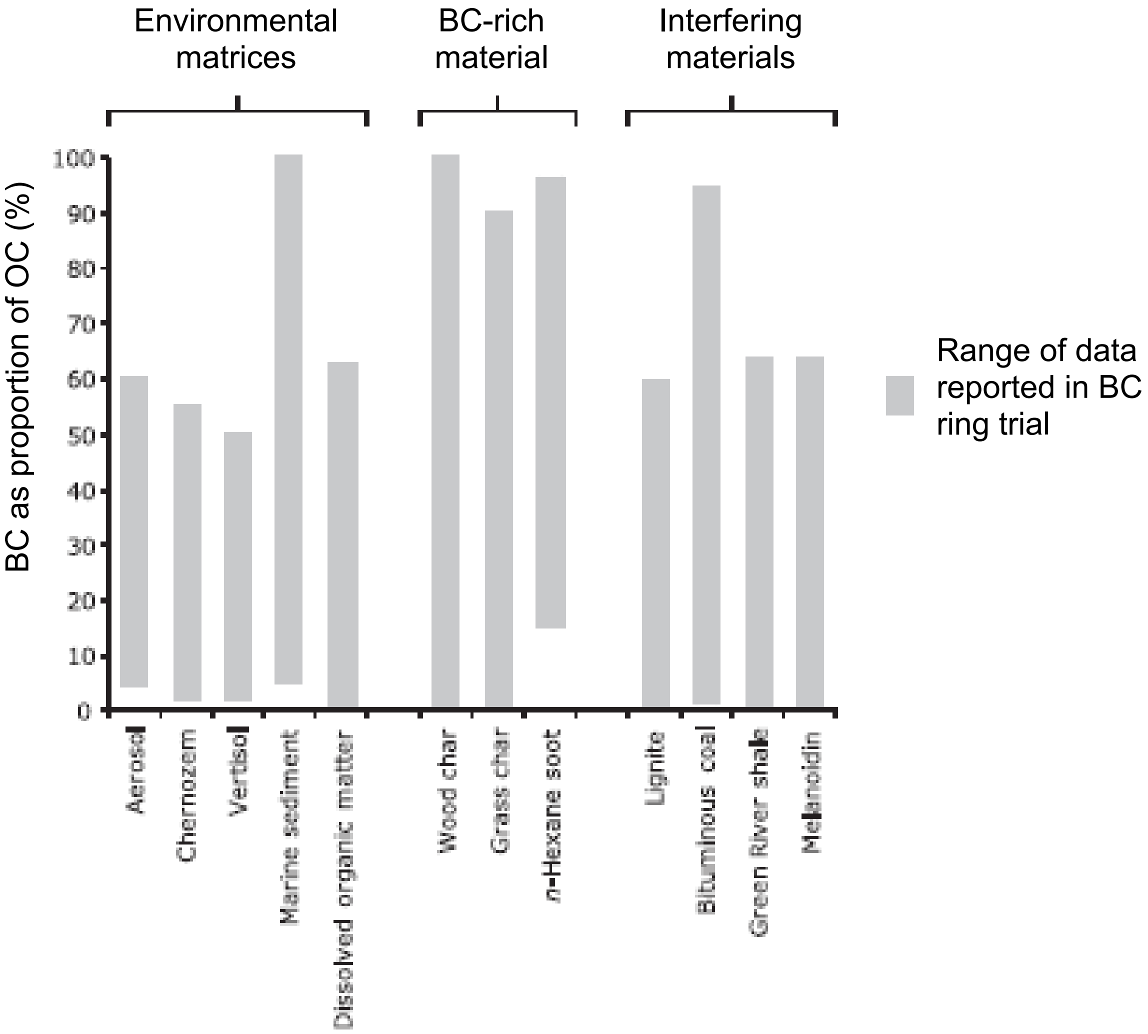

Figure 4 Range of BC quantification data reported by Hammes et al., 2007 (adapted from Meredith et al., 2012)

Some methods attempt to isolate BC by using its resistance to biodegradation or oxidation. Methods to quantify the amount of BC in soil have been categorized as thermal, chemical, molecular marker or optical (spectroscopic) (Poot et al., 2009, Simpson and Hatcher, 2004).

Thermal oxidation methods

Thermal methods rely on the ability of BC to withstand thermal oxidation. The simplest thermal method involves heating samples to a temperature where green carbon fully combusts but not BC. The green carbon will have been completely gassed off as CO_2. Thus green carbon can be measured as the difference in TOC before and after heating or “ashing” (Sarkhot et al., 2007). This method requires maintaining the sample at a temperature where BC remains stable, usually considered to be somewhere between 300-600˚C, but most commonly 340-375˚C (Poot et al., 2009).

Thermo-gravimetry (TG) is another thermal method where samples are heated at a constant rate and the weight loss of the sample and temperature is recorded. Using these two variables, the type of carbon containing substance can be determined.

All thermal methods result in the destruction of the sample. Thermo-gravimetric methods may overestimate the amount of BC in a sample because clay minerals release water from its crystalline matrix at temperatures characteristic for BC species (Manning and Lopez-Capel, 2009). Overestimation may also be the result of the creation of new BC from charring of organic matter during the heating process. Issues of charring can be overcome by promoting complete oxidation of organic carbon by finely milling samples to increase surface area and removing protection within aggregates and having a high oxygen environment.

Thermo-gravimetry can be combined with differential scanning calorimetry (TG-DSC) where the energy flux of the sample is measured during the heating process. It is possible to infer the chemical changes underway in the sample using this data. It has been shown that it is able to quantify BC in soil (Leifeld, 2007) and can distinguish new organic carbon additions in mine soils (Maharaj et al., 2007a). This method of carbon identification works of the basis that different carbon pools, such as fresh organic carbon, black carbon and coal, combust at different temperatures, using the peak combustion temperature to distinguish between pools.
TG-DSC has been used to quantify BC in soils and sediments (De la Rosa et al., 2008, Manning and Lopez-Capel, 2009). De la Rosa et al. (2008) used a functional definition for determining BC as the carbon oxidized between 475 and 650°C. However, they recognize that this temperature range is deficient because it excludes char formed by grasses (De la Rosa et al., 2008). This would suggest that a different definition for BC to include grass char and other less refractory portions of the BC continuum should be used.

An alternative to TG-DSC is the use of evolved gas analysis (EGA), where, instead of measuring weight loss and energy flux, this measures the oxidation of carbonaceous materials. This measurement has the benefit of directly measuring CO_2 evolved during the burning of soils and avoids the potential for water to inflate and interfere with mass loss attribution. EGA can be carried out by using a flame ionization detector to analyse flue gases from the TG unit. As neither gravimetry nor calorimetry is used with EGA, this alternative mode is more correctly named thermal analysis with EGA (TA-EGA).

Rock-Eval 6

Rock-Eval 6 (Vinci Technologies) analysis is similar to thermo-gravimetry where heating rate is constant but samples are first heated in an oxygen-free, then oxygen atmosphere from 250-850°C. The gases released during heating and formation of pyrolysis products are analyzed using a flame ionization detector and infrared detector (Copard et al., 2006). Rock-Eval technology has been in use since the 1980s for the analysis of hydrocarbon bearing rock (Krevelen, 1993, Verheyen et al., 1984) and was first used to analyze soils by Disnar et al. (2003).

There is increasing interest in using Rock-Eval for SOM characterisation (Hetényi et al., 2005, Saenger et al., 2013, Sebag et al., 2006, Nyilas and Imre, 2009). The benefits of using Rock-Eval includes low sample preparation requirements and ability to analyse multiple samples (Saenger et al., 2013). Samples do not need to be treated with acid to remove carbonates but requires the Rock-Eval machine and software. Poot et al. (2009) found that the results from Rock-Eval agree with the benzene polycarboxylic acid molecular marker and thermal optical reflectance/transmission measurements on BC standard materials (Hammes et al., 2007). These two methods, however, vary between overestimation and underestimation of BC content.

Saenger (2013) disagrees with Katz (1983) regarding the usefulness of a modified Van Krevelen diagram producible from the hydrogen and oxygen indices produced by Rock-Eval analysis. Traditionally the Van Krevelen diagram shows the richness of hydrogen and oxygen relative to the carbon richness in H/C and O/C atomic ratios whereas the modified diagram uses mg hydrocarbon/g TOC and mg CO_2/g TOC. It may be possible to use the placement of a sample on the modified Van Krevelen diagram to estimate the relative amount of BC/coal in a sample due to the carbon condensed nature of these similar materials if interpreted as a "qualitative fingerprint" (Copard et al., 2006).

This proposed use of the Rock-Eval data, by modified Van Krevelen diagram is not the normally studied method of estimating BC/coal concentrations in soils. What is seen in the literature involves the deconvolution of the Rock-Eval S2 thermogram, as detected by FID during the first pyrolysis heating step, and assigning the more thermally resistant curves as coal (Siavalas et al., 2013, Saenger et al., 2015, Copard et al., 2006). Whereas Poot et al. (2009) used the residual carbon fraction as a direct measurement of BC. Vindušková (2015) reports results agreeing with ^{13}C NMR by analysing the Oxygen Index measurement and also interpretation of the S_2 curve, a function of the thermal stability of the material being analyzed.

It may be possible to assign individual Gaussian curves to BC and coal on the basis of their peak temperatures, but this has not been tested. Copard et al. (2006) describes using Rock-Eval to fingerprint geogenic carbon.

The best method in which to interpret Rock-Eval results is not settled. As such, in cases where the thermogram is not available, the modified Van Krevelen estimation would need to be verified against other methods.

Hydrogen pyrolysis

A new tool in development which can quantify BC as well as the more labile fraction of SOC is hydrogen pyrolysis, where samples are heated in a high pressure hydrogen atmosphere (150 bar) to 550°C (Ascough et al., 2009, Meredith et al., 2012). The material that remains following the pyrolysis is believed to be BC fraction. This method is similar to Rock-Eval 6 in that samples are heated over a range of temperatures and it can be paired with radiocarbon analysis. Labile carbon fractions are turned into oil. Difficulties have been reported with distinguishing BC from high ranked coals and with underestimation of the less condensed part of the BC continuum (molecules with less than 7 carbon rings) (Meredith et al., 2012).

Chemical recalcitrance

A common method used to quantify the amount of BC operates on the basis of the recalcitrance of BC to chemical oxidation. Walkley-Black (1934) wet oxidation is the oldest method still in use. Labile carbon is oxidized with potassium dichromate and the remaining solution is titrated to determine the amount of carbon that was oxidized. The reaction is known to not be 100% effective and a correction factor must be applied to adjust for this. Alternatively, the method has been improved over time with the application of heat and other acids to remove silicates that may be physically protecting the organic carbon.

While relatively cheap, chemical methods result in the destruction of the sample and the creation of hazardous wastes (Walkley and Black, 1934).

Furthermore, there is criticism that chemical methods overestimate BC because some protected or stable green soil carbon is not oxidized and are included in the BC fraction (Ussiri and Lal, 2008a). Conversely, it has also been shown that a portion of sea-weathered coal is oxidized in sediments, thus potentially underestimating BC and coal contents (Siavalas et al., 2013) (Grossman and Ghosh, 2009)

Molecular Marker

Benzene polycarboxylic acids (BPCAs) are a family of compounds found in all BC and thus is not biased toward any one type of BC (Bornemann et al., 2008). The aromatic rings in BC are converted to BPCAs, which are then used to quantify the amount of BC. Carbon which does not form part of a ring structure is not converted into BPCAs and is subsequently not quantified. The method to isolate the BPCA in BC is a wet chemistry technique involving pretreatment digestions, multiple chemical conversions and is subject to significant inter-laboratory variation making the results difficult to compare with other studies using the same method (Hammes et al., 2007, Brodowski et al., 2005). This method also requires the use of gas chromatography and a correction factor to account for BC that is not converted into BPCA.

Optical

Thermal optical reflectance (TOR) is a method used in atmospheric sciences, where samples are collected on filter paper as airborne particulate. Samples undergo several 24h chemical digestion pre-treatments. In this analysis, samples are heated stepwise in a He atmosphere, then again in a He/O_2 atmosphere while reflectance/transmission is monitored with a laser. This method is susceptible to high levels of variation in results due to uneven application of samples to filter paper.

Spectroscopic

Spectroscopic techniques include a variety of analytical techniques including nuclear magnetic resonance and infrared spectroscopy. Spectroscopic methods using the infrared spectrum can be divided into three groups, transmittance, reflectance and photoacoustic techniques. The former two work on the basis of the vibration of molecular bonds which can be used to estimate the types of molecules in a given sample. The latter relies on the absorbance of a volatilized sample, the heating of which causes the sample to expand which can be detected by very sensitive microphones (Du et al., 2009).

Mid-infrared spectroscopy, using the infrared spectrum from 4000-400 cm^{-1}, is used in the Australian national Soil Carbon Research Programme (SCaRP), an Australia-wide soil carbon measurement standardization protocol as a means to quickly estimate several carbon measurements (Sanderman et al., 2011).

Nuclear magnetic resonance

Both liquid and solid-state ^{13}C Nuclear magnetic resonance (NMR) have been used to quantify resistant organic carbon (ROC or char carbon) by multiple authors (Rodionov et al., 2006, Baldock et al., 2013b, Krull et al., 2006, Ding and Rice, 2012, De la Rosa et al., 2008). ROC is defined as “organic carbon ≤ 2000 μm found in the coarse and fine fractions (≤ 2000 μm particles) having a chemical structure consistent with charcoal” as determined by the peak centred upon 130 ppm in the solid-state ^{13}C NMR spectra (Baldock et al., 2013b). This technique uses the “magnetic environment of each carbon atom in organic materials” (Ahmad et al., 2001). It is the method of choice for the SCaRP for identifying ROC (Sanderman et al., 2011, Baldock et al., 2013b). Poly-aryl carbon is used as a marker for ROC and it has been seen that charring increases aromaticity of organic matter (Czimczik et al., 2002, McBeath and Smernik, 2009). NMR infers the presence of BC in a sample by the distance of hydrogen from carbon atoms. NMR spectra are well enough understood for peaks to be ascribed to different chemical moieties. Furthermore, the chemical composition of thermally altered organic matter has been studied using NMR (Czimczik et al., 2002, Alexis et al., 2010, Filimonova et al., 2014).

The SCaRP method explicitly states that ROC is a measurable fraction that is similar to the inert organic carbon pool in the Rothamsted carbon turnover model (Sanderman et al., 2011, Skjemstad et al., 2004a). ROC may contain lignin but is considered to consist mainly of char (Page et al., 2013, Baldock et al., 2013b) as a lignin correction factor was applied to the SCaRP ROC calibration. The lignin calibration removes the average NMR signal of three lignin spectra from the ROC spectra.

Infrared spectroscopy

The use of infrared spectroscopy for analysis of soils has consistently been considered promising (Janik et al., 2007, Reeves III, 2010, Viscarra Rossel et al., 2006, Rumpel et al., 2001). There has been an exponential growth in the number of papers published using visual, near-infrared, and mid-infrared spectroscopy on soils successfully predicting TOC, TIC and soil texture (Guerrero et al., 2010, Grinand et al., 2012, Ge et al., 2014). The main draws of these methods include rapid analysis and minimal sample preparation in comparison to traditional analytical methods (Du et al., 2007a). Because of the potential for rapid analysis a spectroscopic technique is most likely to be useful in analyzing the large sample numbers required for statistically significant mine soil studies.

Diffuse reflection infrared Fourier transform spectroscopy (DRIFTs) in the mid-infrared range of the electromagnetic spectrum has shown great promise in the area of soil analysis including in predicting the coal content of mine soil (Reeves III, 2009, Rumpel et al., 2001). Spectral distortion caused by specular reflection off of minerals has resulted in the use of a non-reflecting medium, KBr, to be added during the preparation of soil samples in a ratio of 9:1 KBr to sample when used for quantification (Nguyen et al., 1991, Reeves III, 2010). Less than 1 cm^3 of material is scanned in DRIFTs. With soil contributing 10% of this small amount, the importance of representativeness and homogeneity of samples in DRIFTs is heightened. However, there is a movement towards the abandonment of KBr dilution (Viscarra Rossel, 2010, pers. comm., 18 June, Rumpel et al., 2001). This would increase the amount of sample which is scanned and has been shown to be more useful than diluted samples for calibration purposes (Reeves III, 2010).

Spectroscopic analyses of soils including chemometric techniques have successfully predicted SOC content, levels of SOM of different sizes, lignite coal content, distinguish between nitrogen from charred materials and forest litter, and distinguish between different types of coal (Michel et al., 2009, Rumpel et al., 2001, Bornemann et al., 2010). Using spectroscopic analyses to predict some other parameters of soil samples have varying levels of success. It is theoretically feasible to use spectroscopy to predict the ratio of $^{13}C/^{12}C$ isotopes (expressed as $\delta^{13}C$), however, it is impossible to state with confidence that spectral differences are due to the C isotopes and not other factors of the samples (Reeves III et al., 2006).

However, studies have shown that spectroscopic estimation methods of soil properties cannot be applied universally as the calibration set would need to encompass the many different types of soils that would be assayed and be in the order of many hundreds of soils large; thus local calibrations or the intentional inclusion of representative soils through spiking would produce more accurate predictions (Minasny et al., 2009, Guerrero et al., 2014, McCarty et al., 2002). Furthermore, spectroscopic methods to estimate different fractions of organic carbon require the use of chemometric analyses that require datasets to build a functional model as direct interpretation of spectra is not possible. The more diverse the set of soil types and parameters to be predicted, the larger the set of calibrating soils required to build the chemometric model (Reeves III et al., 2006). By using one soil type, it may be possible to create a functioning calibration set with as little as 25 samples, although with increasing sample size the prediction error would be reduced, with a recommendation of 50 samples to balance sampling effort to increased accuracy payoff (McBratney and Minasny, 2010, pers. comm. 3 Aug., Rumpel et al., 2001, Kuang and Mouazen, 2012). However, for large-scale estimates it was determined that no more than 20% of total samples should be used for the calibration set without losing efficiency (Grinand et al., 2012).

UV Photo-oxidation

This method developed by CSIRO involves the oxidation of C using high energy ultra violet light (UV) and quantification and characterization of the remaining C (assumed to be BC) by solid-state ^{13}C NMR and elemental analysis (Skjemstad et al., 1996, Skjemstad et al., 1993). Geogenic carbon can withstand the photo-oxidation treatment, making this a potential method to separate both BC and coal (Hammes et al., 2007). However, it has been noted that this method is time consuming, laborious, prohibitively expensive and may require the use of a unique and purpose built set up that cannot be easily replicated in other laboratories (Hammes et al., 2007, Baldock, 2010, pers. comm., 16 June).

Hybrid and other methods

Hybridization of methods is a trend in SOC analysis where methods from two types of analysis are combined, most notably chemi-thermal oxidation. There are other techniques which have been proposed for the purpose of SOC analysis which have not been developed to the extent where they are commercially available and can readily be applied in this study (Chatterjee et al., 2009b).

Chemi-thermal oxidation

When chemical pretreatments are used to improve the effectiveness of thermal oxidation it is called chemi-thermal oxidation (Poot et al., 2009). To overcome the positive bias of the basic thermal method due to the creation of new charred organic matter during the heating of samples, samples are pre-treated with chemicals to remove SIC and as much organic C as possible. The pre-treatment, however, is often too effective, leaving only the most refractory part of the BC continuum. This causes an underestimation of the amount of BC in samples. Quantification of carbon in the remaining sample is completed by C^{13} NMR or elemental analysis.

δ^{13}C Stable Isotope Analysis

The natural abundance of ^{13}C in soil can be used to determine the relative contributions of SOC from geogenic sources or more recent SOM (Ussiri and Lal, 2008b, Maharaj et al., 2007b). This method relies on the uptake of the ^{13}C isotope by vegetation from the air into plant tissues and the later inclusion of that carbon into the SOC pool. The $^{13}C{:}^{12}C$ ratio is compared against the ratio of a standard material, usually Pee Dee Belemnite (Eqn 3). $\delta^{13}C$ has been used to measure the ratio of C_3, and C_4 plants (Boutton et al., 1998), as a marker for geogenic C (lignite) in soils (Chabbi et al., 2007), has been found to be influenced by BC (Rumpel et al., 2006) and would be able to differentiate SOC sequestered by C_4 plants based on their ^{13}C isotope fixation rates (Ussiri and Lal, 2008a).

$$\boldsymbol{\delta^{13}C}\ (‰) = \left[\frac{^{13}C/^{12}C_{sample}}{^{13}C/^{12}C_{reference}} - \mathbf{1}\right] \times \mathbf{1000} \qquad \textbf{Equation 3}$$

This method may be promising as rehabilitated coal mine lands in the Bowen Basin tend to be dominated by buffel grass (*Cenchrus ciliaris*) which is a C_4 plant and the pre-disturbance forest trees, Brigalow (*Acacia harpophylla*) and *Eucalyptus spp.* are C_3 plants (Krull et al., 2003). The $\delta^{13}C$ measurement of C_3 plants range from -35 to - 22‰, C_4 plants range from-19 to -9‰ and bituminous coal from Ohio range from -23 to -25‰ (Ussiri and Lal, 2008a, Ussiri and Lal, 2008b). Geogenic C can be distinguished from green carbon from C_4 plants.

As the BC continuum is composed of a large variety of molecules with different characteristics and the objective in quantifying BC in this research was to capture as much BC as possible, a thermal definition of BC was seen to be promising. This avoided the focus on the array of different chemical moieties that contribute to BC and the need for NMR analysis that the use of a molecular definition for BC would require.

1.5 Considerations

Of the standard methods listed above, there is no one method which measures the entire continuum of BC quickly and accurately (Bornemann et al., 2008, Hammes et al., 2007). Furthermore, various methods produce results that differ greatly (De la Rosa et al., 2011).

Another consideration is the bias some methods have toward the more highly charred end of the BC continuum (Figure 5). Table 1 summarizes the principles upon which methods work and their outcomes on the quantification of BC is adapted from Hammes (2008).

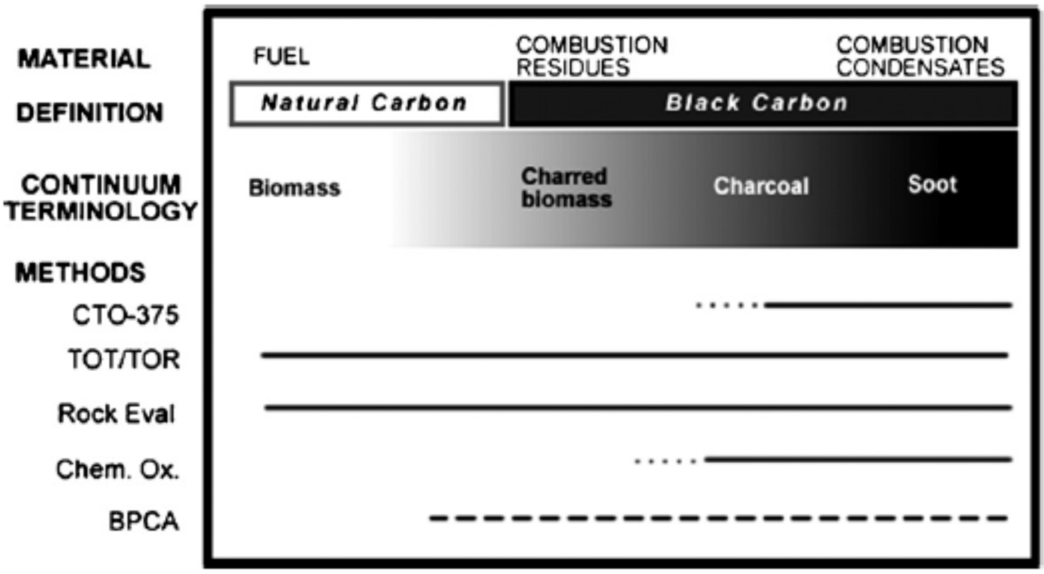

Figure 5 Black Carbon continuum and estimation of BC quantification method regions of effectiveness. Taken from Poot et al. (2009) and adapted from Hammes et al. and Masiello (2004, 2007).

Table 1 Summary of most common BC quantification methods and potential interferences affecting these methods (adapted from Hammes et al., 2008)

Method	Principle	Possible effects on the quantification of BC
Chemo-thermal oxidation at 375 °C	Sample oxidized at 375 °C for 18 h after acid pretreatment. Quantification of residual C as BC using elemental analysis	Overestimation: Mineral-associated and labile OM could be charred during oxidation Underestimation: Harsh oxidation; low temperature chars (<500 °C) oxidized almost completely
Adapted chemo-thermal oxidation method	Stepwise demineralization followed by hydrolysis of reactive OM prior to thermal oxidation at 375 °C	Underestimation: Hydrophobic particles could be lost during wash Harsh oxidation; low temperature chars (<500 °C) oxidized almost completely
Benzene polycarboxylic acid (BPCA)formation	Sample oxidized in HNO_3 for 8 h after removal of polyvalent cations with acid, to form BPCAs from aromatic C Quantification of BPCAs using GC/FID	Overestimation: Aromatic non-BC compounds are falsely detected as BC Underestimation: Large and highly condensed particles are not detected quantitatively
Acid dichromate oxidation (Cr_2O_7)	Sample oxidized in $K_2Cr_2O_7/H_2SO_4$ (Varying timing) after acid pre-treatment. Quantification of residual C as BC using elemental analysis	Overestimation: Aromatic non-BC compounds are detected as BC
Thermal optical transmittance and reflectance (TOT/R)	Sample heated stepwise to 900°C under oxygen/helium air mixture. Quantification of residual C using laser transmittance or reflectance, followed by FID	Overestimation: Dark coloured non-BC materials are falsely detected as BC during premature oxidation Over/Underestimation: Dark coloured materials can cause problems with split between OC and BC
UV photooxidation	Sample photo-oxidized at 2.5 kW for 2 h in O_2-saturated water. Quantification of residual C as BC using ^{13}C NMR and elemental analysis	Overestimation: Aromatic non-BC compounds (coal) are detected as BC
Thermogravimetry coupled with differential scanning calorimetry (TG-DSG)	Sample heated to 990°C. Measures carbonaceous species being thermally oxidized while recording	Overestimation: all chemical resistant carbon quantified as BC

	the mass difference recorded before and after heating	
Sodium chlorite oxidation	Sample oxidized three times with $NACIO_2$ for 4 hours after acid pretreatment. Quantification of residual C as BC using ^{13}C NMR and elemental analysis	Underestimation: Harsh oxidation; low temperature chars (<500 °C) oxidized almost completely
Rock-Eval 6	Sample heated Gas chromatography	Results agree with BPCA and TOT/R methods

Part of the difficulty of measuring the amount of SOC derived from plant growth and senescence at sites rehabilitated after coal mining is the presence of BC and geogenic C (Jacinthe et al., 2009, Shukla, 2010, pers. comm., 6 August). This problem is very vexing, leading some to try to exclude coal from their sample sites by choosing sites as far away from the mine as possible (Maharaj et al., 2007a). However, it has been shown that black carbon is ubiquitous in Australian soils and it seems implausible to choose sample sites free from coal particles since the area of study are rehabilitated coal mine lands (Skjemstad et al., 1996). Jacinthe et al. (2009) noted that due to the high C content of coal, even small amounts of contamination would have an overly large effect on SOC measurements. As coal can range from 50-98% in C content, 1 gram of coal in a 100 gram soil sample with 1 gram of SOM would have green carbon measurements without correction for geogenic C inflated by ~100-200%. BC has also been shown to make up a significant fraction of organic matter in soils in Iowa as well (Fang et al., 2010). If these two carbon bearing materials are not excluded from green carbon measurements, the effects of land management on the amount of SOM in minesoils could be overestimated.

Another difficulty in studying minesoils is the high level of spatial heterogeneity. The reported coefficient of variation for some minesoils have ranged from 0.5 - 22.4% for bulk density, 6.1- 112.2% for coal content, >35% for TC, and 0.7 – 82.3% for SOC (Nyamadzawo et al., 2008, Ussiri and Lal, 2008a). Due to the minesoils having been constructed using heavy machinery, mixing materials naturally deposited from different depths, times and locations resulting in high variability in SOC values across depths, has lead Ussiri and Lal (2008a) to suggest that sampling protocols normally used on undisturbed lands may not produce a representative sample set. Moreover, Myers (1997) calls for either larger samples or the local compositing of samples in minesoils to counter the high local heterogeneity. Assuming similar coefficients of variation in minesoils as those found above of 41% for SOC and an average TOC value of 2%, confidence and power of 80% (meaning the likelihood of rejecting a true null hypothesis and the likelihood of not rejecting a false null hypothesis being both 20%) in a two-sided, two-sample t-test (comparing means and not paired), in order to be able to distinguish a change of 0.2%C, ~380 000 samples would be required, to distinguish a 0.3%C change ~168 000 samples are required (Napier-Munn, 2015).

1.6 Chemometrics

The use of indirect quantification methods involves the interpretation of analytically complex chemical data. Chemometrics is the use of statistical methods on analytical results in the field of chemistry. Allowing computer algorithms to run the numerous calculations involved in multivariate statistics is the most efficient method to analyze large quantities of data.

There are numerous commercial and free chemometric software packages available and some are best used with certain types of data, e.g. spectroscopic or thermograms. The use of chemometrics to enhance the analysis of soil spectra from DRIFTs is necessary due to the large number of data points, as the mid-infrared range is 4000-400 cm^{-1}, and also the spectral interference from the mineral fraction of soil that prevents accurate direct interpretation of spectra (Reeves, 2012, Janik and Skjemstad, 1995). While the direct interpretation of DRIFT spectra to assess which chemical bonds are present is still possible, chemometric techniques was selected as there would not be enough time to develop the skills of spectral analysis and interpretation within the timeframe given. Chemometrics is capable of interpreting covariate data and provides a statistically based interpretation of data in comparison to rigidly set temperature ranges for operatively defining different soil carbon fractions.

Multivariate Curve Resolution-Alternating Least Squares

Multivariate Curve Resolution –Alternating Least Squares (MCR-ALS) is one chemometric technique used to estimate the relative contribution of components in mixed systems with no preparatory modeling (de Juan and Tauler, 2006). However, if available, including data on the pure components can improve the estimates of their relative contributions (Ruckebusch and Blanchet, 2013). Using MCR-ALS is appealing as the technique does not require any foreknowledge about the analytes or their concentrations. The technique relies on the iterative solving of the equation:

$$\boldsymbol{D} = \boldsymbol{C}\boldsymbol{S}^{\boldsymbol{T}} + \boldsymbol{E}$$

Equation 4

Where, D is the dataset

C and S^T are matrices of pure spectra and concentration profile, and

E is error

This relies on the signal data obeying Beer’s Law or in other words, that the signal response for the pure signal contributions can be described using a bilinear model (Ruckebusch and Blanchet, 2013, de Juan and Tauler, 2016).

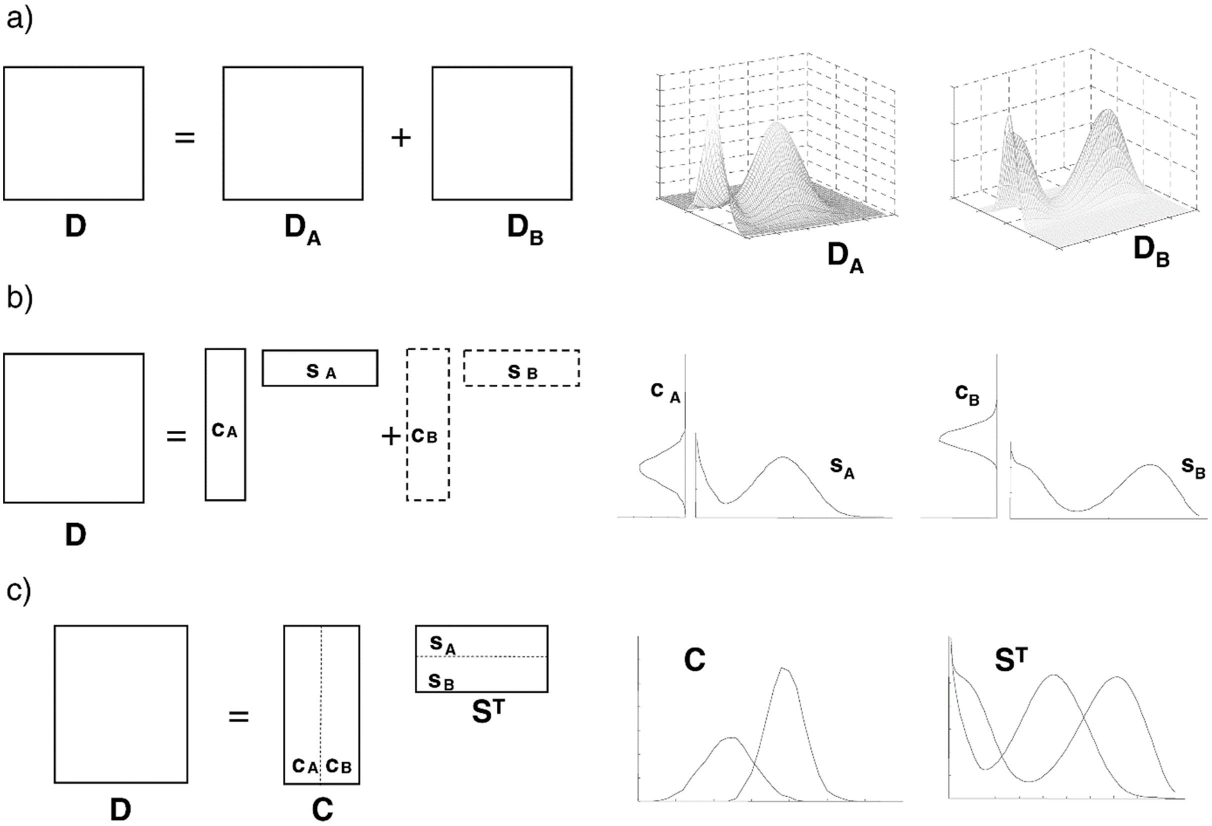

Figure 6 Taken from de Juan & Tauler (2006), this figure demonstrates the deconstruction of high-performance liquid chromatography with diode array detection data “D” into a) an additive model of pure signal contributions, b) a model of additive dyads of pure concentration profile and spectrum, and c) a bilinear model of concentration profiles and spectra. Note how in the bilinear model the data is now in the matrix form of Equation 4

Analysing continuous data, such as from spectral analysis, thermal analysis or evolved gas data with MCR-ALS allows the deconvolution of signal into constituents. In the application of this technique where the dataset is evolved gas thermograms, it can be considered a form of peak-fitting. MCR-ALS has been used in multiple applications, including biomedical, food science and applied chemistry (Le Dréau et al., 2009, Jaumot et al., 2002, Azzouz and Tauler, 2008, Garrido et al., 2008, Bosco and Larrechi, 2007)

However, there is difficulty in ascertaining the error in the solutions to the MCR-ALS equation. There is no formula to calculate the errors propagated when using MCR-ALS. Jaumot et al. (2004) attempts to visualize the error through resampling and notes that when the level of uncertainty is above 5%, a common analytical reporting error level, other sources of ambiguity must be considered in the interpretation of the results. There are two main forms of ambiguity: rotational and intensity. Rotational ambiguity exists where there are more than one solution that fits the data (i.e. the number of pure components) and intensity ambiguity is where the intensity of the components is uncertain. Intensity ambiguity of the components can be controlled through normalization of the data. Ruckebusch and Blanchet (2013) and de Juan and Tauler (2006) are two good review articles with more in depth information on MCR-ALS. Due to the difficulty in determining error in MCR-ALS, error will not be reported where it is used.

2 Research Questions

When quantifying soil organic carbon accretion from rehabilitation of coal mine lands, do indirect methods of distinguishing black carbon and coal carbon agree with direct measurement? Can the accretion of soil organic carbon over time from bioremediation be quickly and accurately distinguished from coal carbon and black carbon (BC) and be measured in rehabilitated coal mine soils from the Bowen Basin?

Hypothesis 1: Thermal analysis with evolved gas analysis in conjunction with multivariate curve resolution can distinguish and quantify Green Soil Organic Carbon (green carbon), black carbon and coal carbon.

Previous studies of similar lands (rehabilitated coal mine soils) attempting to quantify green carbon have ignored at least one of three different fractions of soil organic carbon (SOC). Whether it is possible to distinguish BC and coal carbon from green carbon is uncertain.

Hypothesis 2: Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs) can be used to quickly and accurately predict the amount of Green Soil Carbon in rehabilitated mine soils.

While DRIFTs has been shown to accurately and quickly estimate total organic carbon in soils, it has not been used to distinguish between green carbon, coal C and BC.

Hypothesis 3: There is a measurable difference in recently sequestered SOC in rehabilitated coal mine soils over time and depth.

Successful methods to distinguish the different SOC fractions aside, there may not be a large enough change in green carbon levels in rehabilitated coal mine soils that can be detected over time or across soil depths.

3 Research Plan

The objective of the research is to quantify the organic carbon attributable to remediation, herein called Green Soil Organic Carbon (green carbon or GC), in rehabilitated coal mine soils. These soils usually have low levels of soil organic matter, a suite of substances which improve soils properties for sustaining plant life, such as water retention, nutrient availability and bulk density (Ussiri and Lal, 2008b). These soils also may have low productivity due to characteristics such as high levels of compaction, low pH, low nutrient levels, or high salinity (Shrestha and Lal, 2006). The amelioration of the quality of minesoils would assist in promoting the growth and retention of plants that in turn should facilitate the establishment of a stable landform and ecosystem. These are essential requirements to relinquish mine leased lands back to the landholder. Thus, the ability to measure the accretion of GC is desirable for the purpose of monitoring rehabilitated soils and to determine the effects of land management and the trajectory of longer-term changes as an indicator for soil quality. However, rehabilitated coal mine soils can contain carbon from several sources, including carbonates from the parent material, coal, charcoal and other black carbon from bush fires. This complicates the determination of green carbon since common, standard methods to measure soil organic carbon do not distinguish between these groups (Wu et al., 1999). The project will also attempt to examine whether there is a difference in green carbon concentrations through time, soil depth, and types of vegetation.

Soil characterisation

As minesoils are highly disturbed and can be highly variable, it is important to begin with characterisation of the soil, including total carbon, total nitrogen, total organic carbon, soil texture, electrical conductivity, pH, and bulk density. The methods used to determine these are presented in Chapter 5. Testing of these methods is presented in Appendix G.

Carbon measurement

Walkley-Black method (1934) has been in use for decades and theoretically might be an adequate substitute for green carbon despite it potentially oxidizing some BC (Conyers et al., 2011). Theoretical benefits to measuring oxidisable carbon via Walkley-Black method (1934) include the avoidance of cumulative measurement error from multiple measurements required when using deductive quantification.

However, if the Walkley-Black method also oxidizes coal, due to the high C content of coal, even small amounts of contamination might have an overly large effect on SOC measurements.

There are other methods in literature, which may allow the quantification of some of the fractions of SOC and these are briefly described below:

- Thermogravimetry and differential scanning calorimetry has been shown to effectively quantify the carbon in soils from bituminous coal and black carbon, pyrogenic carbon ubiquitous in Australian soils (Skjemstad et al., 1996). Its sister technique, TA-EGA could potentially provide similar results without the confounding influence of water.

- Rock-Eval 6 pyrolysis analysis shows potential to be able to differentiate between different sources of carbon in soil samples (Behar et al., 2001, Poot et al., 2009). This technique involves using the difference in temperature of oxidation of different carbon containing molecules. It is commonly used in the hydrocarbon industry and is suitable for use in the analysis of carbon-rich substances, such as coal (Krevelen, 1993, Verheyen et al., 1984)

- Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs) has been shown to be able to predict the amount of lignite in rehabilitated coal mine soils in Germany with the use of chemometric analysis as well as physically separable resistant carbon fractions and changes in organic compounds from charring (Rumpel et al., 2001, Reeves III et al., 2008, Baldock et al., 2013b). To use this technique, the data from the other analyses (elemental analysis, etc.) must be input along with the spectra to form a calibration set. The calibration set is used to predict the levels of the different carbon groups in new samples by multivariate statistics (e.g. partial least squares regression) (Janik et al., 2007). It may be possible to use this technique to build a prediction model to quickly quantify different carbon pools.

Of the shortlisted techniques to measure the different SOC pools, TA-EGA was selected due to the low sample preparation requirements, the low cost associated with analysis, the potential to measure both BC and bituminous coal (Hammes et al., 2007) and the availability of the instrument to run the analyses.

While this research does not attempt to extrapolate findings to a larger scale, due to the high levels of heterogeneity in minesoils from their methods of genesis, numerous samples would need analysis to be able to draw field-scale conclusions. Thus, it was decided to investigate whether TA-EGA determined carbon pools could be predicted using DRIFTs to answer research question #2. This is presented in Chapter 7.4.

Figure 7 is a flowchart of the work presented in this dissertation including a few guiding questions.

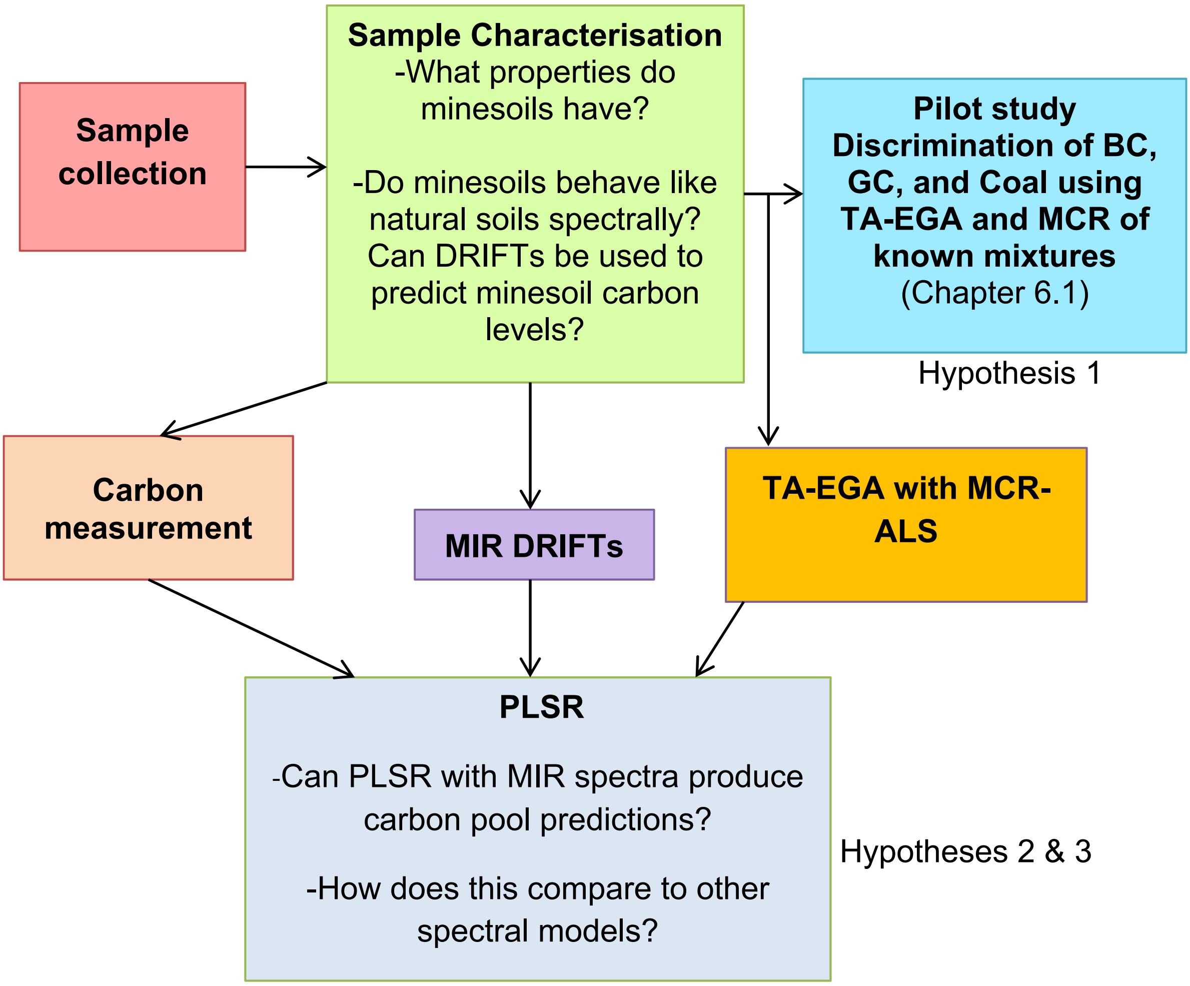

Figure 7 Research plan flowchart. Following sample collection and characterisation, thermal analysis with evolved gas analysis (TA-EGA) is tested for suitability to discriminate the different carbon pools in a pilot study (Hypothesis 1). Hypothesis 2 is investigated through the building and testing of MIR models using the carbon content determined by TA-EGA and other carbon measurements to test if a fast prediction for green carbon is possible. Using the best partial least squares regression (PLSR) MIR model determined in testing Hypothesis 2, minesoil samples across varying depths and lengths of

rehabilitation are analysed to inspect for trends (Hypothesis 3) Methods abbreviations: diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs); multivariate curve resolution (MCR); alternating least squares (ALS). Note: MCR-ALS and PLSR are chemometric techniques.

If successful, the research will enable the creation of a new rehabilitation success criterion and allow a baseline to be produced upon which rehabilitation can be measured and compared. Furthermore, different rehabilitation strategies can be compared in regards to the increase of green carbon and thus be used for remediation decision making.

Green soil carbon has not been researched before as soil organic carbon in coal mine rehabilitation context is usually considered “new carbon” and “old carbon”. What differentiates the proposed research is the exclusion of black carbon from the “new” carbon pool. This will reflect the carbon sequestered by remediation more accurately.

Alternatively, if approaching from the standpoint of being interested in BC or coal levels in soils, the research will provide a new method for quantifying BC and/or coal in soils. This would allow the monitoring of BC levels in soils to determine how management impacts those carbon pools.

4 Materials

Well characterized reference materials, minesoils, un-mined, or ‘natural’ soil and coal samples were used in this study. These materials were used to test the techniques in use in increasing complexity. Mixtures were created using different matrices, carbon-free sand and the reference Vertosol, with the addition of the reference charcoal and Bowen Basin collected coals. Soils and coal samples were collected at several different sites for the purpose of method testing and data collection. The majority of the sampling sites were on rehabilitated mine land, some were from land within the mine lease with soil profiles as yet undisturbed by mining (but probably containing coal dust from aeolian deposition) and one at some distance from any mining sites at the Brigalow Research Station in Theodore, Queensland. There were different sampling strategies employed that can be grouped as follows: precision stratified sampling, regular stratified sampling and bulk sampling.

Well characterized reference materials were also used for method development and concept testing. Chestnut char and Vertosol (Vertisols in USDA classification) used in an international BC ring trial were obtained as was laboratory grade sand (Natural Resources Conservation Service, 2013, McKenzie et al., 2004, Hammes et al., 2007).

4.1 Reference Materials

Materials with known carbon content were selected to create mixtures to test the sensitivity of TA-EGA with MCR to changing concentrations of BC and coal.

Charcoal

Chestnut (*Castanea sativa*) charcoal from southern Switzerland, used in the ring trial was chosen as the closest black carbon reference material to the historical black carbon from bush fires expected to be found in the Bowen Basin soils. Due to fire suppression within rehabilitated areas, it is believed that wood char would be the predominant source of black carbon over grass char. The study mine sites lie within the Brigalow Belt North interim biogeographic region, which prior to European settlement would have been densely covered with woody growth and litter from Brigalow (*Acacia harpophylla*) (Department of the Environment Water Heritage and the Arts, 2010, Dwyer et al., 2009). Despite a predominance of grass cover, usually buffel grass (*Cenchrus ciliaris*), in the region at present, due to the longevity of BC in environmental matrices the BC in the soil should reflect the BC derived from the historic Brigalow tree cover (Burrows et al., 1998).

This charcoal was added to different matrices (see below) to create mixtures with known concentrations of added BC.

Vertosol

The reference Vertosol, used in the Hammes (2007) international BC ring trial, was supplied by by CSIRO Land & Water, Adelaide where it was also assayed (Schmidt et al., 2001, Skjemstad et al., 1999). The top 10 cm of soil was sampled from Toowoomba, Queensland. A copy of the data sheet accompanying the sample detailing chemical properties, exchangeable cations, particle size analysis and NMR data is included as Appendix A.

This well-studied matrix represents a natural soil with known BC content that would be relatively similar to the soils of the Brigalow Belt. This soil would be mixed with coal and BC to create mixtures with known concentrations of added BC and/or coal C.

Carbon-free sand

Laboratory grade acid washed sand with reported impurities of 0.1% HCl soluble matter and 0.005% HCl soluble iron was washed with 4M HCl solution and monitored for effervescence that would indicate the presence of inorganic carbon. HCl solution was added drop wise until effervescence was not observed with agitation (Rayment and Lyons, 2011).

Following the acid wash the sand was rinsed 10 times with deionized water, dried and placed in a muffle furnace set at 600°C for 48 hours to oxidize any black carbon present in the sample.

This matrix represents a simple analogue of soil with no SOM or soil carbon content. Charcoal was added to create mixtures with known concentrations of BC.

4.2 Collected Material and Location (Methods)

Location

The Bowen Basin in Queensland is part of the interim biogeographic region, Brigalow Belt North (Department of the Environment Water Heritage and the Arts, 2010, Appendix B). The natural soils are usually clay Vertosols (Vertisols in USDA classification) McKenzie et al., 2004) and the climate is characterized as sub-humid

(Dwyer et al., 2009). Mature Brigalow contained high levels of aboveground biomass with a significant portion of that as dead matter (Dwyer et al., 2009).

Buffel grass is an invasive, weedy grass species that is prolific in rehabilitated mine lands. Other ground covers found in rehabilitated areas include grasses from the seed mixtures planted by the mine, shrubs and tree species.

The coal types in the Bowen Basin range from sub-bituminous to meta-anthracitic and can rank from graphite to sub-bituminous (Beeston, 1985, Dunstone, 1985). The area contains mudstone, siltstone and sandstone (Utah Development Co. Ltd., 1985).

Prior to mining, the land is stripped and the topsoil stockpiled. Upon rehabilitation, overburden spoil is generally covered with topsoil, deeply ripped and seeded with a variety of plant species. Previous studies have found the total amount of carbon in the soil of rehabilitated areas of Curragh Coal Mine to range from 1-4% (McKenna 2010, pers. comm., 12 May). This measurement would include inorganic, coal, charcoal and SOM carbon.

Minesoil sampling sites

Minesoil sampling sites were located in rehabilitated areas while non-mined "unmined" reference sites were within or near coal mine leases (Appendix C, specific Cartesian coordinates given in Appendix B). The sites are part of a monitoring program and were chosen on the basis of accessibility and proximity to certain types of vegetation (e.g. buffel grass, forest or brush). While grass classified sites (n = 24 pits) were predominantly *Cenchrus ciliaris*, brush and forested sites included a variety of plants including but not limited to *Senna artemisioides* for brush classified sites (n = 7 pits) and genus *Eucalyptus, Acacia flavescens* and *Acacia macradenia* for tree classified sites (n = 8 pits). A more extensive listing of the species present at each site is included in Appendix C. Distribution of sampling sites between cover types, age and mine sites can be found in Table 2.

One bulk sample of minesoil was collected by another party from Goonyella mine with little accompanying documentation. This soil was used in ancillary analyses and to initially test methods being developed.

"Natural" soil samples were also taken from the Brigalow Research Station located in Theodore, Queensland in a buffel grass-dominated paddock and a remnant Brigalow stand. At these two sites the surface vegetation and litter were removed and the top 10 cm of the dug pit were collected as a bulk sample. The samples were stored in paper bags for transport to the lab.

The natural soil samples were used in ancillary analyses to test the effect of time in storage on carbon content (see Appendix G).

Table 2 Pit distribution by age group, cover type and mine site. Mine site codes: CU-Curragh, NP-Norwich Park, BW-Black Water, GC-German Creek

Age of Rehabilitation (years)		Unmined	1-3	4-8	9-14	15-20	21+
Cover type / Mine site	Grass	1 NP	3 NP; 1 CU	2 CU	3 CU; 3 NP	1 CU; 3 NP; 2 BW	1 NP; 1 BW; 3 GC
	Bush	2 CU		3 CU	2 CU		
	Tree			1 CU; 2 NP; 1 GC	2 CU	1 CU; 1 BW	
Total number of pits		3	4	9	10	8	5

Coal sampling sites

Coal was collected by grab sampling from stockpiles at three coal mines: Goonyella, Blackwater and Curragh. Approximately 1 litre of coal was collected from each mine.

Soil sampling method

Precision stratified sampling

At each site, vegetation and litter were cleared and a pit was dug down to 30 cm or the spoil layer, whichever was reached first. A measuring tape was laid to gauge depth. Soil samples were collected using a trowel and placed in plastic bags before cold storage. The sites sampled in 2010 gathered seven increments per pit: 0-0.5, 0.5-1.0, 1-2, 2-5, 5-10, 10-20, and below 20 cm.

Regular stratified sampling

The series of depth increments collected changed between sampling years, resulting in two series of increments. The mined sites sampled in April and May of 2013 collected five increments: 0-2, 2-5, 5-10, 10-20 and below 20 cm.

Following collection, soil samples were processed to separate the soil from non-soil inclusions within the sample. Examples of non-soil organic matter organic matter include living roots, pieces of leaf litter >2 mm and bits of coal. Samples were dried in an oven at 40°C then sieved to 2 mm. Root fragments, grass and twigs were manually removed. Samples were stored in a cold room set at 4°C prior to and following processing to slow microbial degradation.

5 Materials Characterisation

To gain a sense of the properties of the minesoils collected and how they were similar as group, standard soils testing protocols were performed. Soils and reference materials were analysed for total carbon, total nitrogen, total organic carbon, soil texture (particle size), electrical conductivity, pH, Walkley-Black (1934) organic carbon, and bulk density. The carbon measurements are required for the calculations of green carbon. The other measurements will help in interpreting the overall qualities of the samples and in answering hypothesis 3 (see Chapter 2). Further methods, such as alternative TOC measurement techniques, were used to evaluate the sample handling and the methods used to characterise the samples. These are presented in Appendix G.

5.1 Total Carbon, Nitrogen and Total Organic Carbon

Carbon content is an important indicator of the health of soils and total organic carbon is an integral measurement for the indirect quantification of green carbon (see Equation 2).

Method

Processed soil samples were ground and sieved to pass a 0.5 mm screen. TC, TN and TOC were analysed using a high temperature combustion elemental analyser according to 6B2b, 7A5 and 6B3 methods from Rayment and Lyons (2011), respectively. To remove carbonates for TOC analysis either H_2SO_3 or H_2SO_4 acids were used depending on which of two laboratories analysed the samples. Some samples collected in 2010 were also analysed according to Heanes (1984) (6B1 in Rayment and Lyons, 2011), a heated dichromate oxidation similar to Walkley-Black (1934). A statistical comparison of the TOC results concluded they were similar once error was included (see Appendix G).

Results and discussion

Histograms of the TC and TOC values are presented in Figure 8 and Figure 9, while the individual results are in Appendix D. The carbon values for the minesoils are skewed towards lower values with a few samples with high carbon levels (>4 %C) as is seen in Figure 8 and Figure 9.

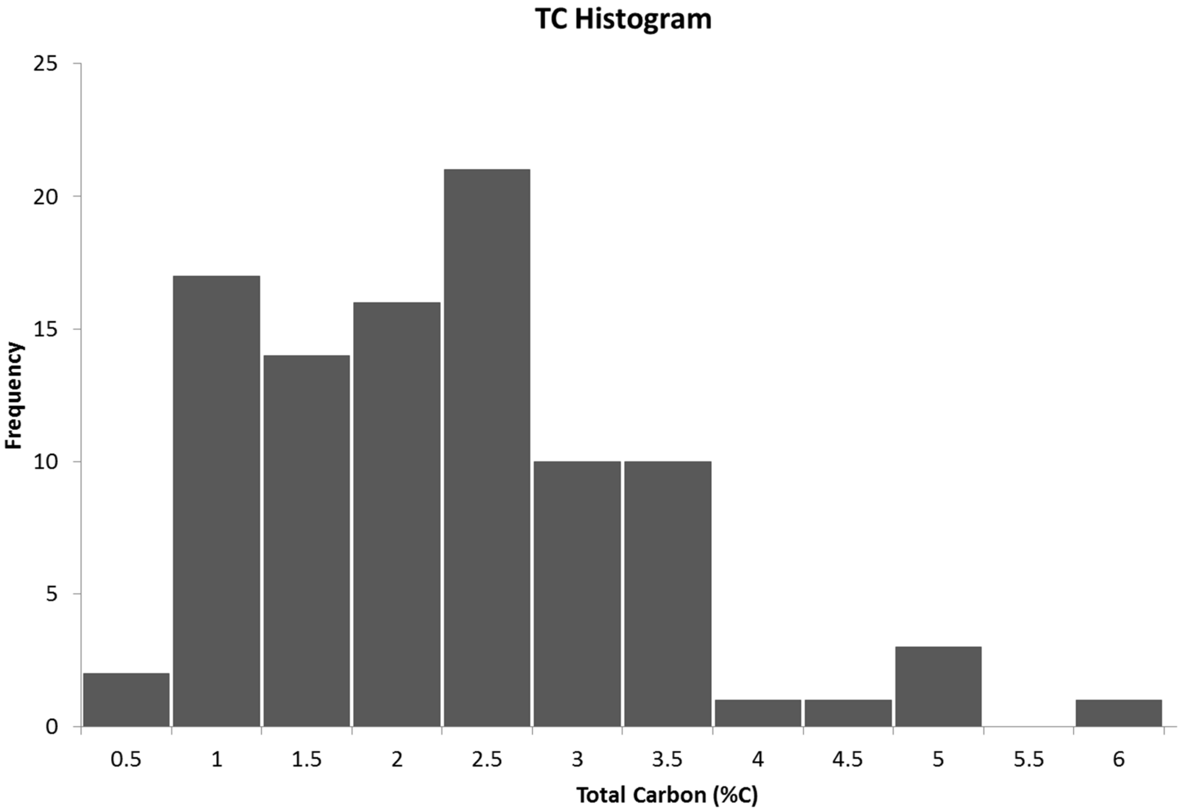

Figure 8 Histogram of the distribution of TC values in 0.5 %C increments. The largest grouping of samples fall in 2.0-2.5%C. A few samples have <4.0%C.

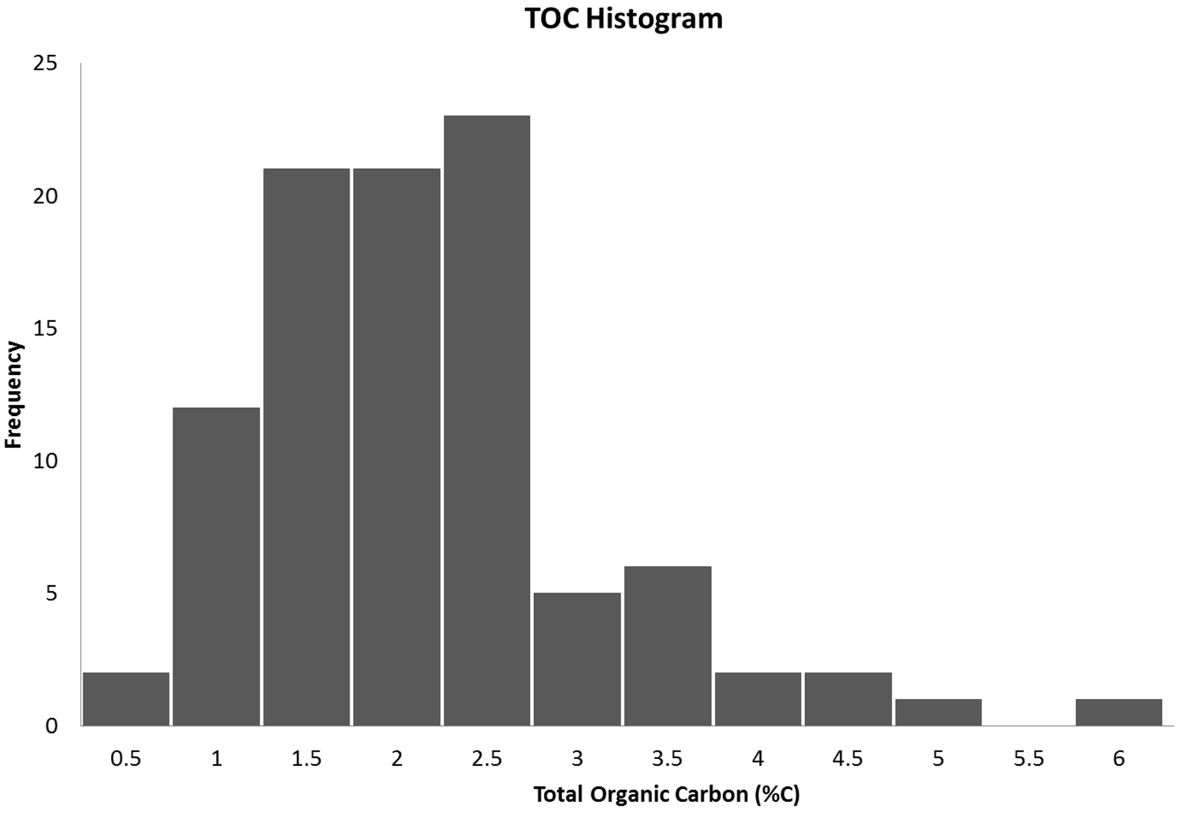

Figure 9 Histogram of the distribution of TOC values in 0.5%C increments. The majority of the samples have TOC values between 1-2.5 %C.

The larger number of samples with total organic carbon levels below 2%C would indicate that throughout the profiles of the various pits, there are not abundant amounts of carbon rich coal. In other words, there is not a high level of coal mixed in with the soil at the sites that were sampled, since coal may have as high as 50% C, if minesoils contained as much as 10% coal by weight, TOC levels could be higher than 5%C (Ussiri et al., 2014).

5.2 Particle Size Analysis

With many factors contributing to the weathering of soils and the oxidation of organic matter, soil texture could potentially assist with interpretation of carbon analysis results. Stumpe et al. (2011) found that sand and clay content were strongly predictive of SOC levels as predicted by partial least squares regression (PLSR) of MIR spectra. Clay is known to play a role in the stabilization of organic matter (Lützow et al., 2006, Verchot et al., 2011, Six et al., 2002) Also, as there is BC enrichment in the <53 µm size fraction, there may be a correlation in BC content and soil texture (Skjemstad et al., 1999).

Method

The hydrometer method was used on >2 mm, air dried soils (Bouyoucos, 1962). Two depth fractions per pit, one near the surface and one at 10-20 cm, were analysed to observe the difference in texture with increasing spoil contribution at depth. Sodium hexametaphosphate and sonification for 10 minutes was used to disperse the sample. Hydrometer readings were taken 8.5 hours apart to determine the clay content of the sample. The soil fractions are defined as below in Table 3.

Table 3 Soil Fraction Particle Size Definitions

Coarse Sand	Fine sand	Silt	Clay
2.00 – 0.20 mm	0.20 – 0.02 mm	0.02 – 0.002 mm	<0.002 mm

Results and discussion

Table 4 shows there is variability in the particle size distribution seen within pits and even within the few duplicates that were run (CU03_1a, CU08_3d, CU10_3a, CU17_2d, NP02_1a, NP06_1a, NP06_2d). These results should be considered indications of the particle size distribution instead of precise measurements as the replicates that were tested produced different results. The cause of the negative measurements could not be determined, but is probably a combination of operator error and fluctuating laboratory conditions. Despite the differences in measurements, the soil texture classification was not greatly changed where duplicates were run, and as such, the texture classifications are considered true (see Figure 10).

The soil texture is likely to reflect where the topsoil material had been harvested from prior to the construction of the landform. This is supported by the fact that the unmined sites consisted of the same soil types as is seen in the rehabilitated sites, assuming that the topsoil would have been collected and stockpiled from the mine lease area prior to mining.

Table 4 Soil texture of minesoils

Sample ID	%Coarse sand	%Fine sand	%Silt	%Clay
BW19_2c	35%	41%	4%	20%
BW31_1c	9%	31%	4%	56%
CU00_2a	12%	20%	44%	24%
CU00_2d	4%	24%	16%	56%
CU00_3a	26%	38%	12%	24%
CU00_3d	23%	41%	16%	20%
CU03_1a	5%	27%	24%	44%
CU03_1a	5%	19%	60%	16%
CU03_1b	6%	34%	-2%	62%
CU03_1c	5%	19%	30%	46%
CU03_1d	6%	22%	20%	52%
CU05_1a	7%	33%	20%	40%
CU05_1d	8%	22%	26%	44%
CU07_1a	4%	20%	24%	52%
CU07_1d	4%	16%	28%	52%
CU08_2c	13%	31%	4%	52%
CU08_3a	5%	31%	20%	44%
CU08_3d	6%	18%	32%	44%
CU08_3d	7%	33%	24%	36%
CU08_4a	5%	23%	20%	52%
CU08_4a	5%	35%	4%	56%
CU08_4d	4%	28%	12%	56%
CU08_4d	6%	14%	24%	56%
CU10_2c	3%	21%	0%	76%
CU10_3a	5%	19%	16%	60%
CU10_3a	8%	27%	16%	48%
CU10_3d	5%	35%	12%	48%
CU10_4a	6%	30%	24%	40%
CU10_4b	5%	51%	-14%	58%
CU10_4c	4%	36%	15%	45%
CU10_4d	4%	16%	30%	50%
CU11_1a	6%	30%	16%	48%
CU11_1d	4%	20%	20%	56%
CU11_2a	11%	25%	28%	36%
CU11_2d	3%	25%	16%	56%
CU17_1a	4%	20%	16%	60%
CU17_1d	4%	24%	24%	48%
CU17_2a	4%	28%	24%	44%
CU17_2d	5%	15%	0%	80%
CU17_2d	4%	24%	-12%	84%
GC26_1c	9%	55%	12%	24%
GC26_2c	13%	59%	4%	24%
NP00_1a	13%	35%	30%	22%
NP00_1d	9%	31%	16%	44%
NP01_1a	16%	20%	36%	28%
NP01_1d	13%	19%	28%	40%
NP01_2a	5%	15%	12%	68%
NP01_2d	6%	18%	16%	60%
NP02_1a	26%	42%	4%	28%
NP02_1a	24%	51%	6%	18%
NP02_1d	20%	40%	14%	26%
NP06_1a	19%	21%	16%	44%
NP06_1a	15%	38%	12%	34%
NP06_1d	19%	29%	12%	40%
NP06_2a	14%	2%	36%	48%
NP06_2d	13%	19%	16%	52%
NP06_2d	13%	33%	6%	48%
NP10_1a	9%	23%	12%	56%
NP10_1d	8%	24%	16%	52%
NP10_2a	5%	19%	20%	56%
NP10_2d	5%	15%	8%	72%
NP10_3a	9%	31%	16%	44%
NP10_3d	7%	13%	14%	66%
NP20_1a	14%	38%	24%	24%
NP20_1d	11%	29%	32%	28%
NP20_2a	18%	48%	10%	24%
NP20_2d	22%	54%	3%	21%
NP20_3a	20%	56%	4%	20%
NP20_3d	20%	30%	22%	28%
NP27_1a	18%	30%	28%	24%
NP27_1d	17%	31%	16%	36%

The 10-20 cm depth (sample identifications ending with d) often had a higher clay content than the surface 0-2 cm depth (samples ending with a). This may indicate high clay levels in the overburden, as mixing between the spoil layer and the applied topsoil would be more likely to occur in the 10-20cm depth increment as the topsoil settles following application and if sites underwent ripping.

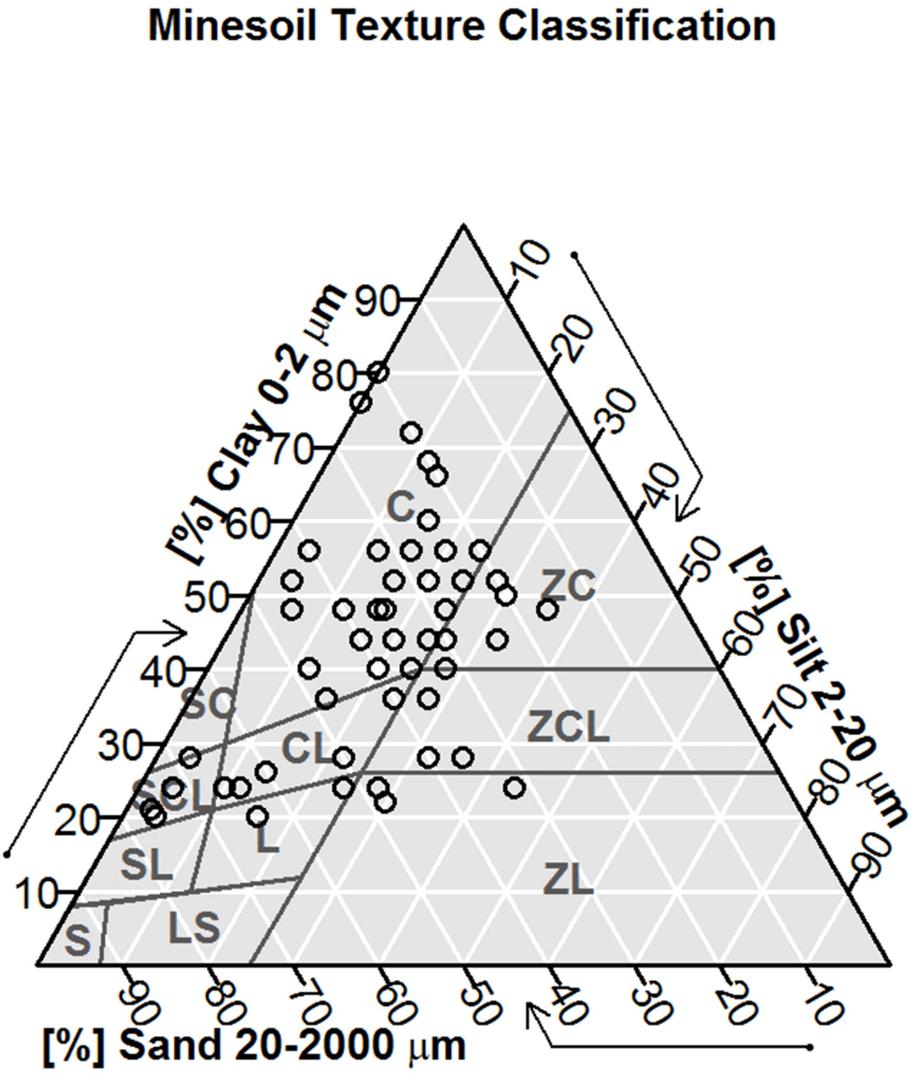

Figure 10 Minesoil samples plotted on an Australian texture triangle. The majority of samples were classified as clay soils. Classification abbreviations: C-Clay, ZC-Silty clay, ZCL-Silty clay loam, ZL-Silty loam, LS-Loamy sand, S-Sand, SL-Sandy loam, L-Loam, SCL-Sandy clay loam, CL-Clay loam, SC-Sandy clay

Table 5 Soil texture classification of collected samples

Clay/clay loam	Clay	Loam/Clay loam	Sandy clay loam	Sandy loam/sandy clay loam	Sandy clay/clay	Loam	Clay/silty clay
5	32	2	10	4	3	2	2

The mine soils tested had significant levels of clay and the majority of which were found to be clays according to the Australian soil texture triangle (Figure 10) shows the texture class distribution of the mine soils. Unmined sites were evenly split between clay, loam and sandy clay loam/sandy loam. At most pits, two depths were tested, 0-2 and 10-20 cm, dependant on there being sufficient sample (*e.g.* Figure 11).

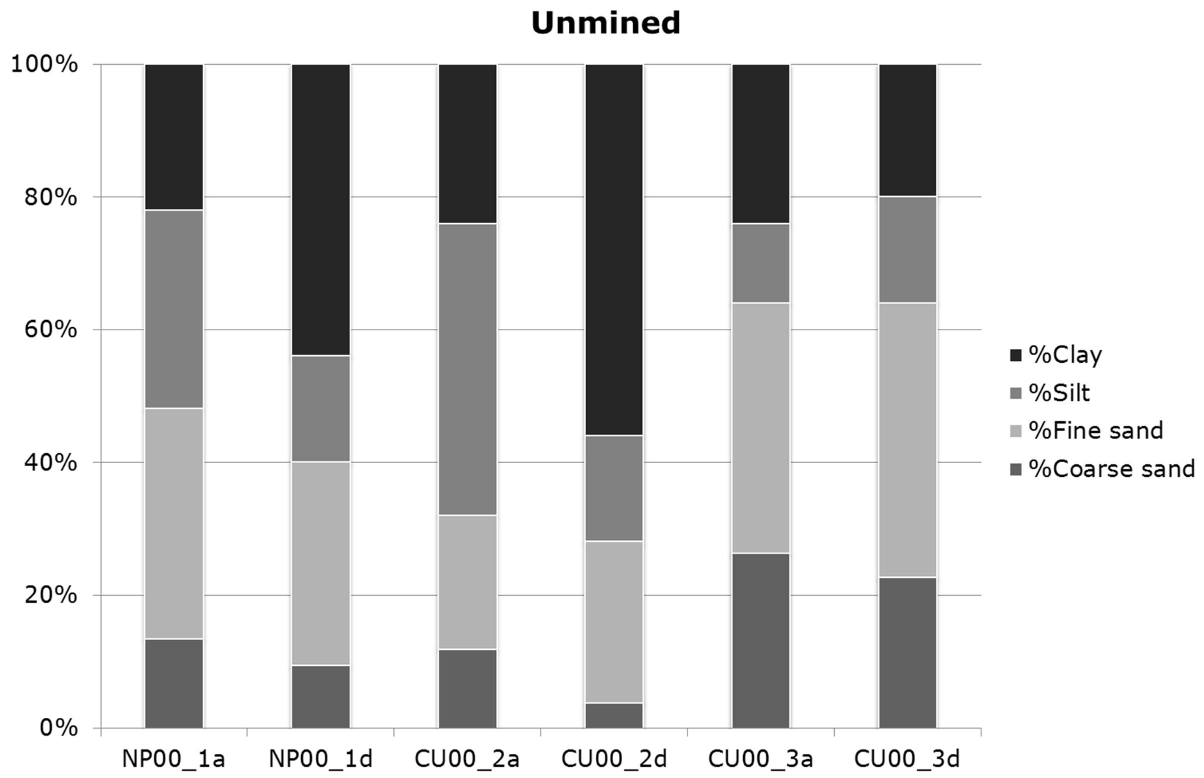

Figure 11 Particle size distribution for three unmined sites at 0-2 cm and 10-20 cm depths

There was no discernable pattern in soil class according to mine site or depth. Samples aged over 21 years post rehabilitation often contained more sand, with 4 out of 5 of the samples being sandy clay loam and the one clay sitting nearer the sandy loam placement. Of the total 60 samples, 32 samples were clays, 5 verging on clay loam, 3 verging on sandy clay.

5.3 Electrical conductivity and pH

The electrical conductivity (EC) and pH were determined according to methods 3A1 and 4A1 (Rayment and Lyons, 2011), respectively. Briefly, aliquots of soil were mixed end-over-end with deionized water in a ratio of 1:5 soil/water for one hour. After allowing 30 minutes for solids to settle, EC and pH probe was immersed in the supernatant and allowed to come to equilibrium. The salinity and pH of the soils are important contributing characteristics that determine its suitability for sustaining plant growth. EC was converted to total dissolved solids using Equation 5.

Total dissolved solids (mg/L) = 0.64 x Electrical conductivity (μS/cm) **Equation 5**

It is worthwhile to note that clay has a positive relationship with EC as the particles increase surface conduction (Choo et al., 2016).

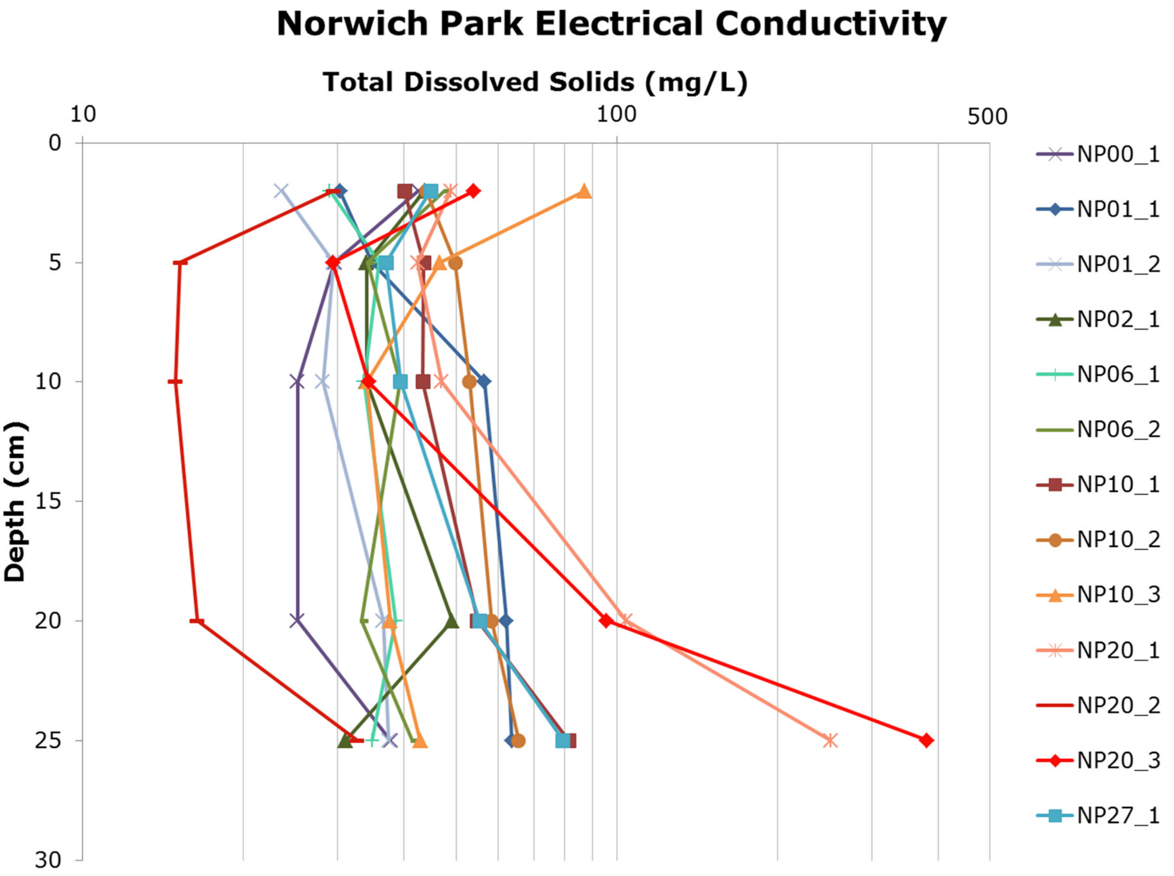

Figure 12 Changes in electrical conductivity of Norwich Park samples along depth. The establishing sites (1-3 years since rehabilitation) exhibit a zig-zaggy pattern reflective of the newly created profile. Older rehabilitation and non-mined sites have a curving trend with higher conductivity near the surface, perhaps from inputs. The rise in conductivity further down the profile may be due to leaching and the effect of the increasing proportion of spoil.

Figure 12 shows there was a general trend of EC initially dropping from the surface to the 2-5 cm depth, then increasing with depth or not changing greatly down the profile (70% of the sample have a standard deviation less than 20 mg/L).

The pH of the samples ranged from 4.5 to 9.7 pH. Higher pH levels were expected at some Curragh sites as white rocks, suspected to be secondary carbonates, were observed in some samples.

5.4 Walkley Black

Walkley-Black (1934) is a dichromate oxidation that uses the heat generated from the dilution of concentrated H_2SO_4 to drive the oxidation reaction and has historically been used to measure organic carbon. It has been suggested that this technique may be used to estimate BC (see Chapter 1.3 Direct quantification of green carbon via Walkley-Black).

Method

Processed mine soils were sent to Queensland State Government's Department of Science, Information Technology and Innovation Ecosciences Prescinct Boggo Road soil laboratory to undergo Walkley-Black (1934) organic carbon analysis according to method 6A1 in Rayment and Lyons (2011). Briefly, weighed samples were wetted with a $Cr_2O_7^{2-}$ solution to which concentrated H_2SO_4 is added. A colorimeter is used to determine the absorbance at 600 nm and thereby the concentration of Cr^{3+} and of the amount of carbon oxidized during the reaction according to the Beer-Lambert Law and Equation 6. The results are found in Appendix D.

$$2Cr_2O_7^{2-} + 16H^+ + 3C \rightarrow 4Cr^{3+} + 8H_2O + 3CO_2$$ **Equation 6**

5.5 Bulk density

In 2010, one bulk density sample per pit was collected using a 55 mm diameter x 40 mm height soil core at 20 cm depth at mined sites. This depth was in the applied soil layer, above the spoil level. If the spoil layer was encountered, another sample without spoil was collected as the rocky nature of spoil made it too difficult to cut an even face to the core. If a piece of rock was discovered partially within the core, an equivalent volume of soil taken from the same depth was added to replace the volume of rock removed and the sample re-leveled. It is assumed that bulk density sample collection is sufficiently imprecise, such that the replacement of <20% of the volume of the core with soil from the same depth without excessive compaction would not significantly change the bulk density measurement (Hartge and Horn, 2009, Baumgartl 2010, pers. comm., 23 August). Nyamadzawo et al (2008) found the coefficient of variation for bulk density in minesoils in Ohio to be <15%.

In 2013 two bulk density samples were collected using a soil core with the same dimensions as in 2010, one at the soil surface after removing the litter layer and one at 20 cm depth. The soil bulk density of points between the two sampling depths was interpolated assuming the change was linear (see Appendix D). The core samples were bagged in oven proof bags and dried in an oven at 105°C overnight and weighed. Bulk density was not sampled at natural sites.

Results

Values ranged from 0.51 – 1.58 g/cm^3 at the surface and 1.00 – 1.58 g/cm^3 at 20 cm depth. The greatest change in bulk density between the surface sample and 20 cm depth was 0.96 g/cm^3. Unmined soils ranged from 1.13-1.29 g/cm^3 at the surface and 1.24-1.50 g/cm^3 at 20 cm depth (n=3).

Conclusion

The rehabilitated mine soils had similar bulk densities to the unmined soil. Unlike Shrestha and Lal (2011), whose sites containing larger amounts of sand displayed significantly higher bulk density in rehabilitated soils over undisturbed sites, the Bowen Basin mine soils displayed higher average bulk densities at the two different depths than the average of unmined sites while ranging from clay to sandy clay loam (see Chapter 5.2).

6 Discrimination of carbon fractions

Soil organic carbon can be divided into three different fractions: coal, black carbon and green carbon. Coal is organic matter that has undergone coalification. Black carbon (BC) is organic matter that has not combusted completely, e.g. charred wood, charcoal and soot. Green carbon is any organic matter that is not coal or black carbon. It should be noted that black carbon and green carbon both exist in the black carbon combustion continuum with green carbon being at one extreme as it has not been charred (Hedges et al., 2000).

An international ring study comparing different BC quantification methods found there was little consensus between methods in terms of the range of the BC continuum measured and ability to exclude non-BC carbon (Hammes et al., 2007). The study showed thermogravimetry with differential scanning calorimetry (TG-DSC) and UV photo-oxidation to be the most promising methods to use for the purpose of quantifying BC and coal as they both measured C3 plant char and bituminous coal carbon more effectively than other methods studied. C3 plants include woody plants, such as Brigalow; thus, BC from before the groundcover change to C4 plants, i.e. grassy pastures, could be measured. This would facilitate the calculation of green carbon as the difference between total carbon and the combination of char and coal using one measurement method.

Enquiries determined that UV photo-oxidation would be prohibitively costly and not replicable as there is only one laboratory in the world that carries out the procedure. However, collaborators for TG-DSC were found, Dr. Alain Plante and Dr. Clément Peltre, and analyses were carried out at The University of Pennsylvania on a set of reference charcoal spiked samples of Vertosol, both materials used in the Hammes et al. (2007) ring trial.

A modified TG-DSC analysis was tried by the addition of an infrared gas monitor. Thermal analysis with evolved gas analysis (TA-EGA) uses the same machine as in TG-DSC without the use of neither gravimetric nor calorimetric data, but rather, measuring the evolved CO_2 to assess carbon loss. Differential scanning calorimetry did not contribute much additional information to the analysis of the soils as the DSC profiles were seen to closely follow the evolved gas profile, so DSC data was not used. Testing of whether TA-EGA could distinguish BC and coal in a soil-like matrices is described in the manuscript titled: *Quantitative differentiation of coal, char* *and soil organic matter in an Australian coal minesoil* that has been submitted for publication to Thermochimica Acta, and is presented in Chapter 6.1. Additional information that was not included in the manuscript and pertaining to the application of DRIFT spectroscopy is presented in Chapter 7. Further information on the chemometric technique used, multivariate curve resolution, a form of signal deconvolution or peak fitting can be found in Chapter 1.6.

6.1 Thermal analysis with multivariate curve resolution carbon partitioning in mine soils

Introduction

Minesoils are the soils created during the rehabilitation of mined lands, typically covering the newly constructed landforms (Sencindiver and Ammons, 2000, Ussiri et al., 2014). The landforms created with the overburden must be stabilized and rehabilitated before relinquishment.

Increased organic inputs from plant establishment are part of the rehabilitation process in restoring soil quality and function (Kimetu et al., 2008). Improved soil quality can reduce erodibility and stabilize these landforms, thus fulfilling rehabilitation objectives. Soil organic matter (SOM) derived from the accumulation of recent plant and microbial inputs could therefore potentially be used as an indicator of rehabilitation success. In addition, disturbed minesoils also represent an opportunity to act as an important sink for atmospheric CO_2 as SOM levels increase (Akala and Lal, 2000, Lal, 2004).

Minesoils at coal mines have variable amounts of coal fines from spoil containing coal reject and dust from aeolian deposition. This complicates the assignment of measured soil carbon to recent SOM inputs attributable to rehabilitation. The quantification of SOM accumulation in Australian coal minesoils is further complicated by the potential presence of pyrogenic C derived from the incomplete combustion of biomass from wildfires. This black carbon (BC) has been investigated for its potential to remain in the soil for centuries (Schmidt et al., 2002). Black carbon is found commonly in soils globally (Krull et al., 2008, Schmidt et al., 2001, Skjemstad et al., 2002) (Krull et al., 2008, Schmidt et al., 2001) and is nearly ubiquitous in Australian soils and especially in Vertosols (Krull et al., 2008, Skjemstad et al., 1996). Vertosols and Sodosols are the predominant soil type in the coal mining region of interest to this study – the Bowen Basin, Queensland, Australia

(CSIRO, 2011). Quantifying SOM carbon accumulated in mined lands during rehabilitation therefore requires distinguishing this carbon from that which is inherited from the starting materials used for reclamation.

In studying coal-minesoil rehabilitation, several methods have been used to differentiate coal carbon from more recent carbon inputs, including C/N ratios (Ganjegunte et al., 2009), high energy UV photo-oxidation, ^{13}C-NMR spectroscopy and radiocarbon measurements (Rumpel et al., 2000), and combined chemical and thermal oxidation (Ussiri and Lal, 2008b). Similarly, methods to quantify BC generally involve elemental analysis after removal of more labile organic matter either by chemical or thermal oxidation (Hammes et al., 2007, Schmidt et al., 2001) or direct detection by pyrolysis-GC/MS, ^{13}C-NMR or thermogravimetry (De la Rosa et al., 2008). More recently, Rock-Eval analysis uses ramped pyrolysis and combustion to discern different types of organic materials in soil and sediment samples (Carrie et al., 2012, Disnar et al., 2003, Sebag et al., 2006), and has been compared to conventional methods for distinguishing BC from SOM (Poot et al., 2009, Saenger et al., 2015, Siavalas et al., 2013).

As geogenic C, pyrogenic C and soil organic matter C combust at different temperatures, the application of ramped combustion to distinguish among them is an attractive approach. However, each of these components is actually composed of a spectrum of materials that combust over a range of temperatures, making the distinction with a single temperature cut-off challenging. The interpretation of thermograms, as the primary result from ramped combustion of carbon-containing substrates, may be carried out qualitatively or (semi-)quantitatively. Multivariate curve resolution - alternate least squares (MCR-ALS) is defined as a group of statistical techniques that help resolve mixtures by determining the number of constituents, their response profiles (e.g., spectra) and their estimated concentrations, using a minimal number of assumptions about the nature and composition of these mixtures (de Juan and Tauler, 2003, de Juan and Tauler, 2006, Jaumot et al., 2005). MCR-ALS has been successfully applied to a variety of biological and chemical processes with near infrared (NIR) spectroscopy (Blanco et al., 2006, González-Sáiz et al., 2008), FTIR spectroscopy (Le Dréau et al., 2009, Spegazzini et al., 2009) and discrete data such as concentrations of different pollutants (Terrado et al., 2010). However, this technique has not been applied to resolve thermal analysis curves or to the characterization of organic matter in surface soils.

The objectives of this study were to first provide a proof-of-principle test of whether thermal analyses combined with the MCR-ALS chemometric technique are able to distinguish between and quantify proportions of geogenic C, pyrogenic C and soil organic matter C in model mixtures of increasing complexity. A series of experimental mixtures combining various mineral matrix and organic C end-members were subjected to CO_2 evolved gas analysis (CO_2-EGA) during ramped combustion (i.e., thermal analysis). MCR-ALS analyses were applied to the resulting thermograms to generate modeled estimates of the different forms of organic C. A second objective was to test the approach against a set of minesoils of unknown composition to generate estimates of the proportional contributions of geogenic C (coal), pyrogenic (or black) C (BC) and soil organic matter C (SOC) to the total organic C content. The ultimate goal is to provide a robust method for quantifying soil organic matter C accumulations during the rehabilitation of minesoils, and in other similar applications.

Materials and Methods

6.1.1 Reference materials and mixture end-members

Geogenic carbon

Bituminous coal from the BHP Billiton Mitsubishi Alliance Goonyella coal mine and from the Anglo American German Creek coal mine were selected as the reference materials for geogenic C. As these coal samples originated from mines within the Bowen Basin, they were assumed to be similar to coal particles found in rehabilitated minesoils in the vicinity of the mined resource. The samples were oven dried at 40 °C, and homogenized by ball milling.

Reference materials

The reference chestnut charcoal, Vertosol and carbon-free sand described in Chapter 4 were selected to represent pyrogenic carbon, a carbon-free mineral matrix and a coal-free, BC-containing soil matrix. The sand was ball milled to improve homogeneity of mixtures and is used as a simplified model mineral matrix. Vertosol was selected as a soil matrix because Vertosols and other high clay containing soils are common to the Bowen Basin.

Minesoil matrix

Rehabilitated minesoil collected from BMA Blackwater coal mine (BW19_2d) was selected as a reference minesoil matrix for experimental mixtures because of its low organic and inorganic carbon concentrations. Minesoil samples were collected from 0.1-0.2 m depth. The soils were oven dried at 40°C, sieved to pass a 2.0-mm mesh, ground to pass a 0.5-mm mesh for Walkley-Black (1934) organic C and elemental analyses, and ball milled for improved homogeneity prior to thermal analysis.

6.1.2 Experimental mixtures

A total of 31 experimental mixtures containing Goonyella coal and BC, individually and combined, were created with three different mineral matrices: sand, Vertosol and Blackwater minesoil (Table 6). All mixtures, with the exception of the sand+BC, were made with ball milled materials and homogenized in a vial by end-over-end shaking for 30 minutes. The sand+BC mixtures underwent elemental analysis shaken, but unground, and were manually ground with mortar and pestle just prior to thermal analysis.

Table 6 Experimental mixtures generated of pyrogenic C (chestnut char, BC) and geogenic C (Goonyella coal) mixed with three mineral matrices used in proof-of-principle thermal analyses

Matrix	BC	Goonyella Coal	BC+Coal
Sand	1%, 2%, 3% by mass		0.5%C 1:1, 1:2, 2:1 1%C 1:1, 1:2, 2:1 2%C 1:1, 1:2, 2:1
Vertosol	0.5%, 1%, 1.5%, 2%, 2.5%, 3% by mass	1%, 5%, 11% by mass	0.5% + 0.5% by mass
Blackwater minesoil			2%C 1:1, 1:2, 2:1 3%C 1:1, 1:2, 2:1 4%C 1:1, 1:2,

Three sand+BC mixtures were made to target 1%, 2% and 3% weight proportions of BC. The true weight proportions of the mixtures were 1.007%, 2.451%, 3.205% of BC by weight. Using a reported C concentration of 682.0 g C kg^{-1} for the BC (Hammes et al., 2006), the resulting estimated C concentrations of the mixtures were 6.87 g C kg^{-1}, 16.7 g C kg^{-1} and 21.9 g C kg^{-1}. These simple mixtures were not subsequently used in the MCR analyses, but used along with the mixtures of Vertosol+BC (see below) to test the efficacy of combustion-based elemental analyses in quantifying pyrogenic C.

Nine different sand+BC+coal mixtures were made to generate target C concentrations of 0.5%, 1% and 2%, using the reported C concentrations of 682.0 g C kg^{-1} for BC (Hammes et al., 2006) and a measured C concentration 655.6 g C kg^{-1} for the Goonyella coal (see below). For each target C concentration, the concentration was achieved by adding BC and Goonyella coal in 1:1, 1:2 and 2:1 mass ratios. The mixtures were made by weighing out the sand, adding the coal, reweighing the partial mixture, then calculating how much BC to add to generate the desired target C concentrations.

Six different Vertosol+BC mixtures were designed to target 0.5%, 1%, 1.5%, 2% 2.5% and 3% weight proportions of BC. Actual weight proportions were 0.510%, 0.995%, 1.466%, 2.086%, 2.556% and 3.097%. Using the reported C concentrations of 26.7 g C kg^{-1} for the Vertosol (Schmidt et al., 2001) and 682.0 g C kg^{-1} for the BC (Hammes et al., 2006), the estimated total C concentrations of the mixtures were thus 30.04 g C kg^{-1}, 33.22 g C kg^{-1}, 36.31 g C kg^{-1}, 40.37 g C kg^{-1}, 43.45 g C kg^{-1} and 46.99 g C kg^{-1}, where the proportions of mixture C attributable to the added BC ranged from 11.6% to 44.9%. It is important to remember that the C contained in the Vertosol itself was a combination of BC and soil organic matter.

Three Vertosol+coal mixtures were designed for target coal proportions of 1%, 5% and 11% by weight of Goonyella coal. Actual weight proportions were 0.996%, 5.323% and 11.189%. Using the reported C concentrations of 26.7 g C kg^{-1} for the Vertosol (Schmidt et al., 2001) and a measured C concentration of 655.6 g C kg^{-1} for the Goonyella coal, the resulting estimated C concentrations of the mixtures were 6.53 g C kg^{-1}, 34.9 g C kg^{-1} and 73.4 g C kg^{-1}. The added coal represented 19.8% to 75.6% of the mixture C.

One Vertosol+BC+coal mixture was made using an aliquot of the Vertosol+0.5%BC mixture described above and adding Goonyella coal to achieve a target proportion of 0.5% coal by weight. The actual mixture was 0.510% BC by weight and 0.549% coal by weight. The resulting estimated C concentration of the mixture was 25.27 g C kg^{-1}, of which 21.1% of the mixture total C was attributable to the added BC and coal.

Nine different minesoil+BC+coal mixtures were made to generate target C concentrations of 2%, 3% and 4%, using the reported C concentrations of 682.0 g C kg^{-1} for BC (Hammes et al., 2006), and measured C concentrations of 655.6 g C kg^{-1} for the Goonyella coal and a measured C concentration of 11.9 g C kg^{-1} for the Blackwater minesoil (see below). For each target C concentration, the concentration was achieved by adding BC and coal in 1:1, 1:2 and 2:1 mass ratios. The mixtures were made by weighing out the minesoil, adding the coal, reweighing the partial mixture, then calculating how much BC to add to generate the desired target C concentrations. The proportions of total mixture C attributable to the added BC ranged from 13.2% to 49.7%, and the added coal represented 13.5% to 48.3% of the mixture C.

6.1.3 Reclaimed minesoils of unknown composition

The efficacy of the analytical and statistical approaches developed using the experimental mixtures of known compositions was tested on a series of minesoil samples of unknown composition. A soil from a 26-year-old rehabilitation site at the Capcoal AngloAmerican German Creek coal mine was chosen and samples collected with precision stratified sampling (see Soil sampling method subheading under section 4.2).

Analytical techniques

6.1.4 Elemental analyses

Literature values were used for the carbon concentrations of the BC and Vertosol, while C concentrations of the Goonyella and German Creek coals, sand and minesoils were measured. Multiple techniques for the quantification of C in these samples were used because of the highly recalcitrant nature of the pyrogenic and geogenic C expected to be in the samples. Total and organic C in the coal samples were determined by Rock-Eval 6 (Lafargue et al., 1998). Since Rock-Eval is used routinely in the petroleum industry, it was decided that this analysis would provide better accuracy than regular elemental analysis (Lafargue et al., 1998, Verheyen et al., 1984), which may combust samples at too low a temperature for complete C recovery. Total C concentrations of the sand and minesoils were determined by dry combustion using a LECO TruSpec CHN autoanalyser. For comparison, organic C concentrations of the minesoil samples were also determined using the Walkley-Black (1934) method, which was expected to generate substantially smaller C concentrations than the combustion-based methods, but were more closely representative of soil organic matter exclusive of pyrogenic and geogenic C (Siavalas et al., 2013).

6.1.5 Analytical thermal analysis

Thermal analyses (i.e., simultaneous thermogravimetry, differential scanning calorimetry, evolved-gas analysis) were performed to characterize the thermal stability of the different end-member reference materials and experimental mixtures, with the expectation that thermal stability of the various forms of C could be used to distinguish among them. German Creek minesoil samples were subsequently subjected to thermal analysis as the true unknown samples to test the method. Analyses were performed according to Fernández et al. (2012) using a Netzsch STA 409PC Luxx equipped with a type-S (Pt/PtRh) TG-DSC sample carrier supporting a PtRh10-Pt thermocouple (Netzsch-Gerätebau GmbH, Selb, Germany). Evolved gas analysis (EGA) during ramped combustion was performed using a LI-840 CO_2/H_2O infrared gas analyzer (IRGA, LI-COR Biosciences, Lincoln NE, USA) coupled to the outlet of the STA instrument. Samples were weighed into 85-µL Pt crucibles with pierced lids to a mass of approximately 30 mg for soils and mixtures, and 2-4 mg for BC and coal. Samples were heated from 30 to 800 °C at 10 °C min^{-1}, with an isothermal pause at 105 °C to eliminate sample moisture, under a flowing atmosphere of CO_2-free Ultra-Zero air. Resulting CO_2-EGA thermograms are expressed in units of ppm_v of CO_2 per mg of sample. Prior to MCR analysis (see below), the thermograms were normalized by the area under the CO_2-EGA curves (i.e., by the total CO_2 detected by the IRGA).

6.1.6 Statistical analyses

Multivariate curve resolution - alternate least squares (MCR-ALS) techniques were applied to the CO_2-EGA thermograms as an empirical, quasi-quantitative means of determining the concentrations of SOM, BC and coal in the experimental mixtures as proof-of-principal, then applied the technique to a set of minesoils of unknown composition. MCR-ALS is a multivariate deconvolution technique allowing the separation of one or several end-members (also called pure components), which in this case corresponded to CO_2-EGA thermograms of coal, BC and SOM, from unresolved mixtures when no prior information is available about the nature and composition of these mixtures (de Juan and Tauler, 2003). When available, providing initial guesses for the pure components helps the algorithm converge to finding pure components as close as possible to the prescribed ones. MCR-ALS analyses were run with and without initial guesses to determine the robustness of the resulting models. When initial guesses were used, the CO_2-EGA thermograms of BC, coal, or Vertosol and Blackwater minesoil without additional BC or coal were provided as the pure components to be separated by the MCR-ALS. In the case of the unknown minesoils, initial guesses of the SOC pure components were not possible because they were the desired results, but pure German Creek coal and BC were included in the analytical set.

MCR-ALS analyses were run using The Unscrambler® software v10.1 (Camo Software AS, Oslo, Norway). Four MCR analyses were performed during the proof of principle phase, each with and without initial guesses of pure components provided. The first MCR was performed to separate BC and coal from a simple matrix not containing organic C using the sand+BC+coal mixtures ($n = 9$), with BC and Goonyella coal provided as pure components when initial guesses were used. When initial guesses were not provided, the BC and coal thermograms were included as samples in the analytical set. The second MCR was performed to separate SOC and BC using the Vertosol+BC mixtures ($n = 6$), with Vertosol and BC provided as pure components when initial guesses were used, or included in the analytical set when initial guesses were not used. The third MCR was performed to separate SOC, BC and coal using the Vertosol+coal mixtures ($n=3$), Vertosol+BC mixtures ($n = 6$) and the Vertosol+BC+coal mixture ($n = 1$) for a total of 10 samples, with Vertosol, BC and coal provided as pure components when initial guesses were used, or included in the analytical set when initial guesses were not used. The fourth MCR was performed to evaluate the separation of SOC, BC and coal in a minesoil with a different SOC composition than the Vertosol, using the Blackwater minesoil+BC+coal mixtures (n = 9), with Blackwater minesoil, BC and coal provided as pure components when initial guesses were used, or included in the analytical set when initial guesses were not used. The outputs of the MCR-ALS analyses are modeled thermograms of the constituent components resolved from the experimental mixture thermograms (*i.e.*, SOC, BC and coal) and the areas under these curves, which are then expressed as relative concentrations in the initial unresolved mixture (Gargallo et al., 1996).

MCR-predicted C proportions of total organic C were calculated as the modeled area assigned to a specific component (*e.g.*, BC) divided by the total area modeled for all components combined, and expressed as a percentage. The relationships between the MCR-predicted C proportions and the calculated C concentrations of the various mixtures, based on the proportions of added BC and coal, were evaluated using least-squares linear regression. The ability of the regression models to explain the variance in the data was assessed using the coefficient of determination (R^2). Ideal MCR-predicted versus calculated C values would follow the 1:1 line with no significant deviations (*i.e.*, non-zero intercept and/or slope different from 1). Deviation of the MCR-predicted values from the 1:1 line was assessed using root mean square error (RMSE), which is expressed in % of total organic C.

Results

6.1.7 Organic C concentrations of reference materials, experimental mixtures and unknown minesoils

Elemental analysis of the sand confirmed minimal contamination (0.006% C), and thermal analysis did not detect any evidence of thermally stable C indicative of pyrogenic or geogenic C (data not shown). Organic C concentrations in the Blackwater minesoil used in the experimental mixtures was relatively low (1.2%, Table 8). Its composition was dominated by SOM as indicated by the fact that Walkley-Black organic C represented 94% of the total. The high C concentrations in coal samples exceeded the reliably determinable levels of the LECO analyzer, which produced unusually low results (data not shown). Rock-Eval analysis found that the

Goonyella and German Creek coals differed in C concentration (Table 8), but ramped combustion by thermal analysis data showed that the CO_2-EGA thermograms of the two coals were similar, thereby justifying the use of the Goonyella coal in the experimental mixtures as a substitute for the German Creek coal (see Appendix F). Similar to coal, the BC material was known to have high concentrations of recalcitrant C that may result in low yields from the LECO analyzer. Evidence for this was provided by correlation analysis of estimated versus LECO-measured C concentrations in the Sand+BC and Vertosol+BC mixtures (data not shown). Values were highly correlated (R^2 = 0.988), but biased (slope = 0.845) and thus indicated that measured values underestimated the true values. The proportions of Walkley-Black organic C to total C in the German Creek minesoil samples ranged from 67% to 84% (Table 8), indicating substantial contributions from recalcitrant components. As a result, the measured total C concentrations of these samples should be considered underestimates. It is therefore difficult to attribute confidence to absolute concentrations of the various components determine by the MCR-ALS method, and therefore only relative proportions are reported.

Table 7 Measured carbon concentrations of end-member materials used in mixtures and minesoils. Total C concentration of the coals were determined using Rock-Eval, while dry combustion elemental analysis was used for the sand and minesoils. Values of "nd" indicate that sample was not analysed using the particular method.

Sample	Total C (g C kg^{-1} soil)	Walkley-Black organic C (g C kg^{-1} soil)
Sand	0.06 ±0.04 (n=2)	nd
Goonyella coal	656	nd
German Creek coal	604	nd
Blackwater minesoil (10-20cm)	11.9	11.2
German Creek minesoil (0-0.5 cm)	18.0	11.9
German Creek	16.4	11.0

minesoil (0.5-1 cm)		
German Creek minesoil (1-2 cm)	19.8	13.3
German Creek minesoil (2-5 cm)	20.4	13.9
German Creek minesoil (5-10 cm)	10.0	8.4
German Creek minesoil (10-20 cm)	19.0	12.0
German Creek minesoil (20-30 cm)	12.0	8.6

6.1.8 MCR analysis for the separation of BC from coal in unresolved sand mixtures

Thermograms of BC and coal reference materials were relatively simple, with a single dominant peak at 531 °C for BC (Figure 13a) and at 545 °C for coal (Figure 13b). The major distinctions between the two thermograms were a more pronounced shoulder at around 400 °C for the coal, and greater thermal stability for coal than for BC, as indicated by a higher peak temperature and higher end temperature of the exotherm, which exceeded 600 °C for the coal. These small differences are exploited in the MCR analysis to partition the carbon sources despite the relative similarity of the CO_2-EGA thermograms.

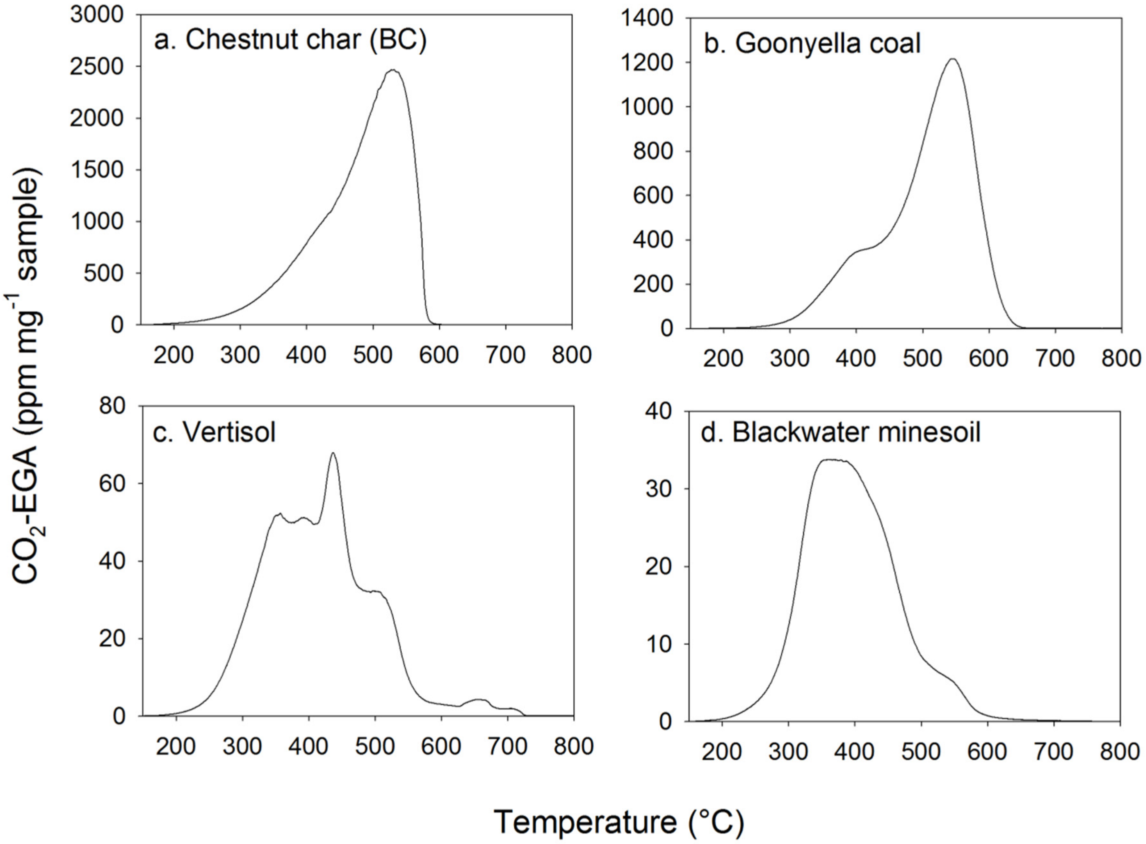

Figure 13 CO_2 evolved gas analysis (CO_2-EGA) thermograms of reference end-members used in experimental mixtures: (a) pyrogenic carbon in the form of chestnut wood char black carbon (BC), (b) geogenic Goonyella coal C, (c) Vertosol and (d) Blackwater minesoil.

When no pure component initial guesses were provided, the MCR-ALS analysis was able to distinguish the BC and coal in sand+BC+coal mixtures (Figure 14a). However, while the MCR-generated thermogram of BC was similar to the actual, this was less so for the coal thermograms (Fig. 17a). As might be expected, when initial guesses were provided the MCR-generated thermograms were much more similar to actual thermograms (Figure 14b), with maximum peak temperatures of 529 °C for component 1 (corresponding to BC) and a maximum peak temperature of 545 °C for component 2 (corresponding to coal).

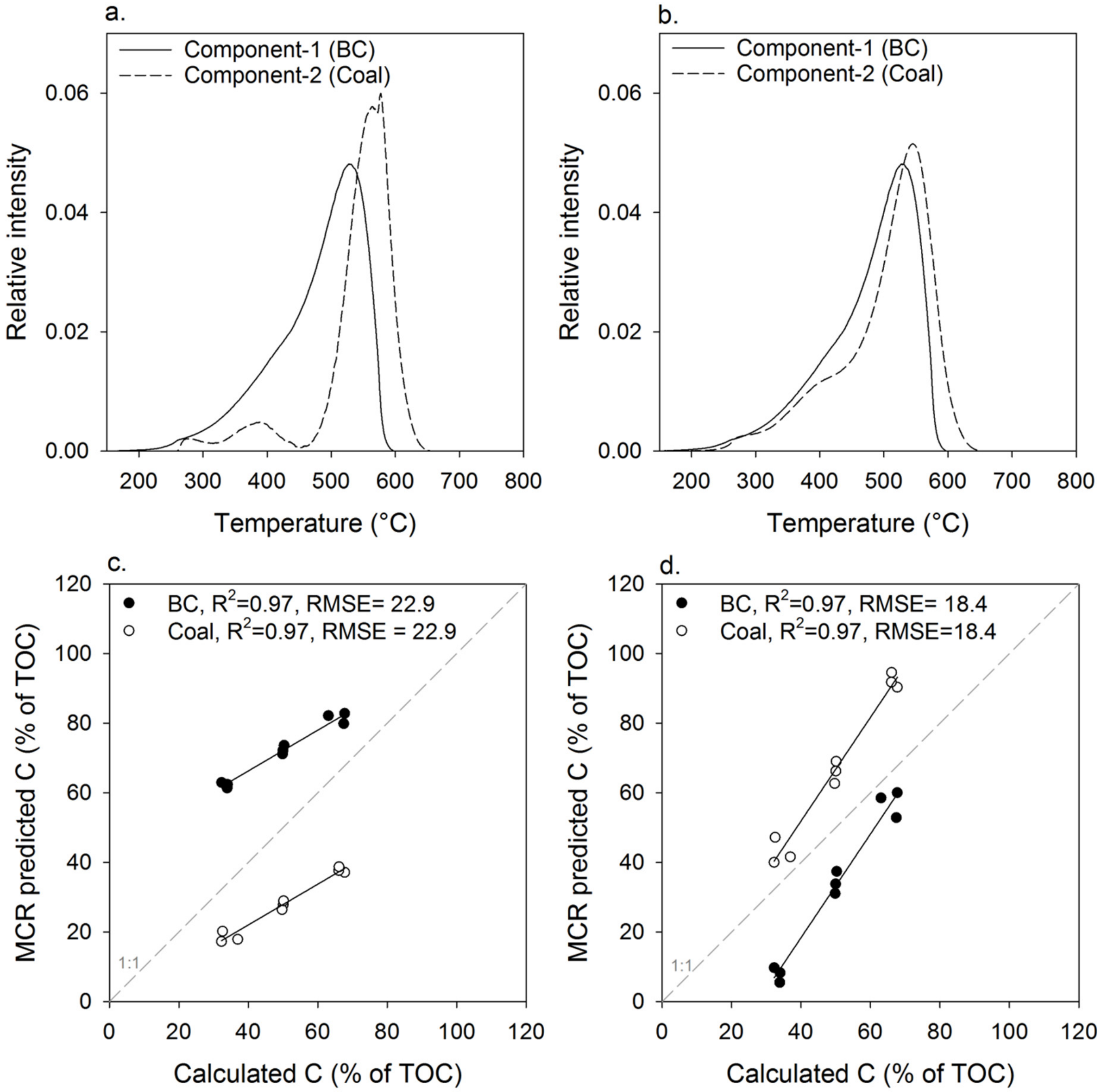

Figure 14 MCR analysis for the separation of black carbon (BC) and coal from sand+BC+coal experimental mixtures. Thermograms of the pure components separated by MCR without (a) and with (b) initial guesses provided, and MCR predicted BC and coal contents without (c) and with (d) initial guesses provided. Clusters of three data points having similar proportions of calculated C are not replicates, but mixtures made with differing ratios of BC and coal (*i.e.*, 1:1, 1:2, 2:1).

The regression between calculated and MCR-predicted proportions of total carbon corresponding to BC and coal showed a good performance of the MCR model, with an R^2 of 0.97 and RMSE of 22.9 % of total C, though the slopes were substantially different from the 1:1 line (Figure 14c). When the thermograms of BC and coal were used as initial guesses of the pure components, RMSE decreased to 18.4% of total C (Figure 14d) and slopes were closer to the 1:1 line. Deviations of the regression lines from the 1:1 line (deviation of the slope from 1 and deviation of the intercept from 0) indicated the necessity to correct the MCR-predicted values using the linear regression equation before the MCR model could be used in practice.

6.1.9 MCR analysis for the separation of BC from SOC in unresolved Vertosol mixtures

The Vertosol SOM had a more complex thermogram compared to BC and coal, with a major peak at 450 °C and smaller peaks and shoulders at 350 °C, 380 °C and 525 °C (Figure 13c). Additions of BC to Vertosol resulted in the largest increases in the thermogram peak near 525 °C, but also smaller increases in other smaller peaks (Figure 15). Increases in smaller, low temperature peaks were generated by the low temperature tail of the BC thermogram (Figure 13a).

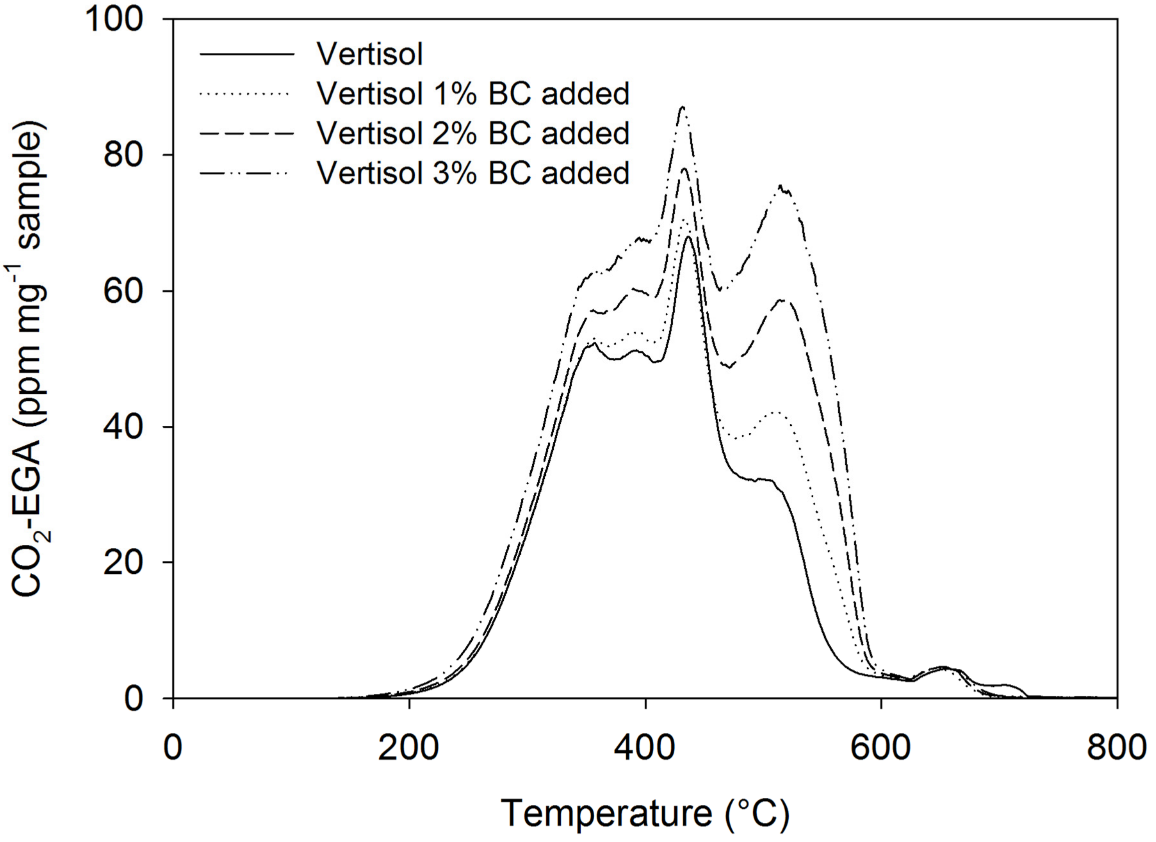

Figure 15 CO_2 evolved gas analysis (CO_2-EGA) thermograms of experimental mixtures composed of a Vertosol with different amounts of chestnut wood char black carbon (BC) added.

MCR was able to clearly distinguish between SOC and BC in the Vertosol mixtures, whether or not initial guesses for pure components were provided (Figure 16). MCR-generated thermograms were similar to actual thermograms, as would be expected when pure components are identified (Fig. 19b). When pure components were not provided, the MCR-generated thermograms remained similar, but a larger portion of the CO_2 emissions from 500-600 °C were attributed to the BC than the SOM components (Fig. 19a).

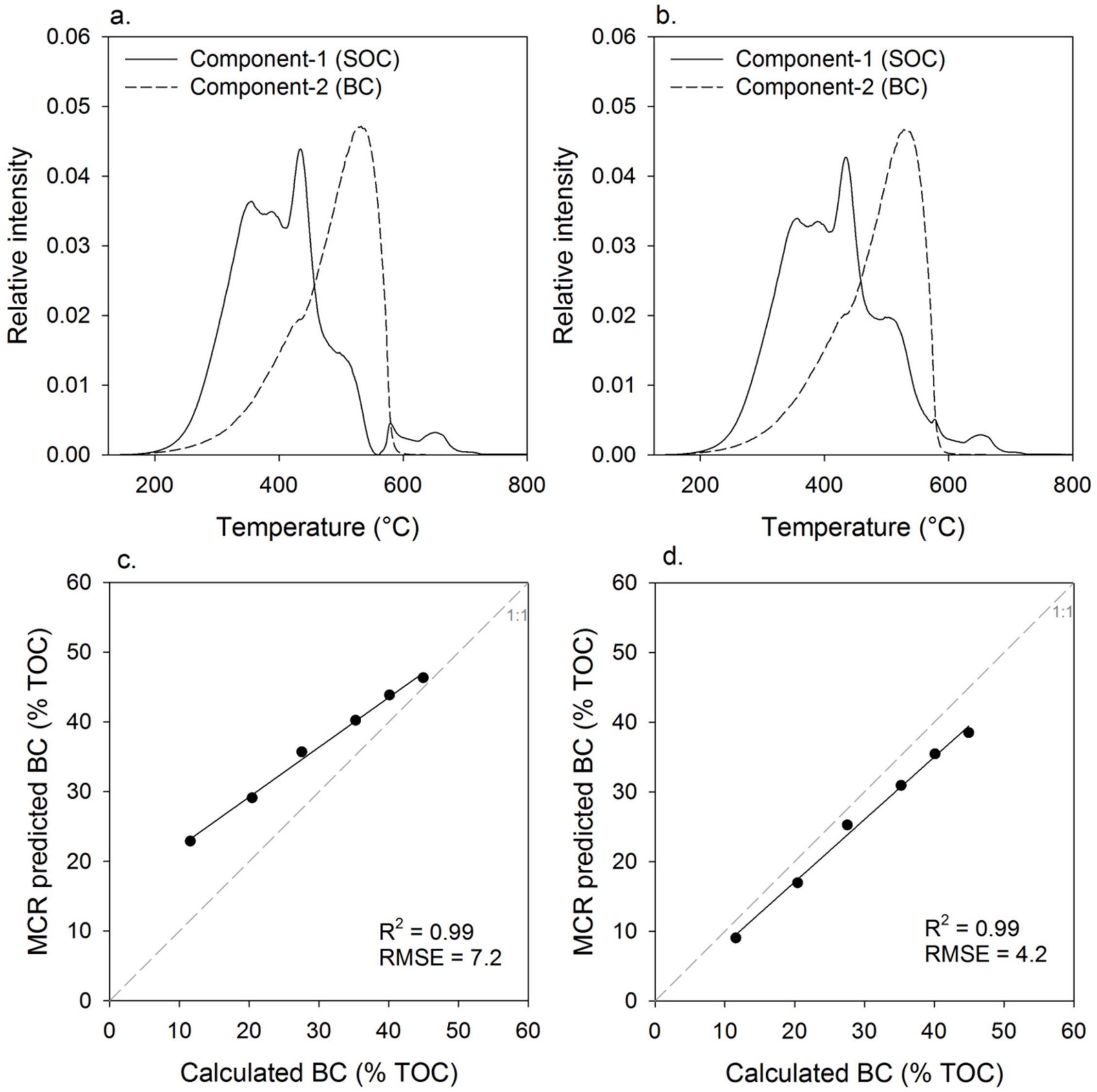

Figure 16 MCR analysis for the separation of soil organic carbon (SOC) and black carbon (BC) from Vertosol+BC experimental mixtures. Thermograms of the pure components separated by MCR without (a) and with (b) initial guesses provided, and MCR predicted BC content without (c) and with (d) initial guesses provided.

Slopes of the regressions between calculated and MCR-predicted proportions of total carbon corresponding to BC were similar both with and without provided pure components, but the intercepts changed substantially. When the pure component initial guesses were provided, MCR under-predicted the amount of added BC, and RMSE increased slightly (Figure 16d). This is likely attributable to the fact that the Vertosol also contains some BC carbon, which is not accounted for in the analysis.

6.1.10 MCR analysis for the separation of BC and coal from SOC in unresolved Vertosol mixtures

With increased complexity of adding coal to the Vertosol+BC mixture, MCR was still able to generate distinct end-members whether or not pure component initial guesses were provided (Figure 17a and b). However, the provision of initial guesses substantially improved the similarity between MCR-generated and actual thermograms, particularly for the coal component (Fig. 20a and b).

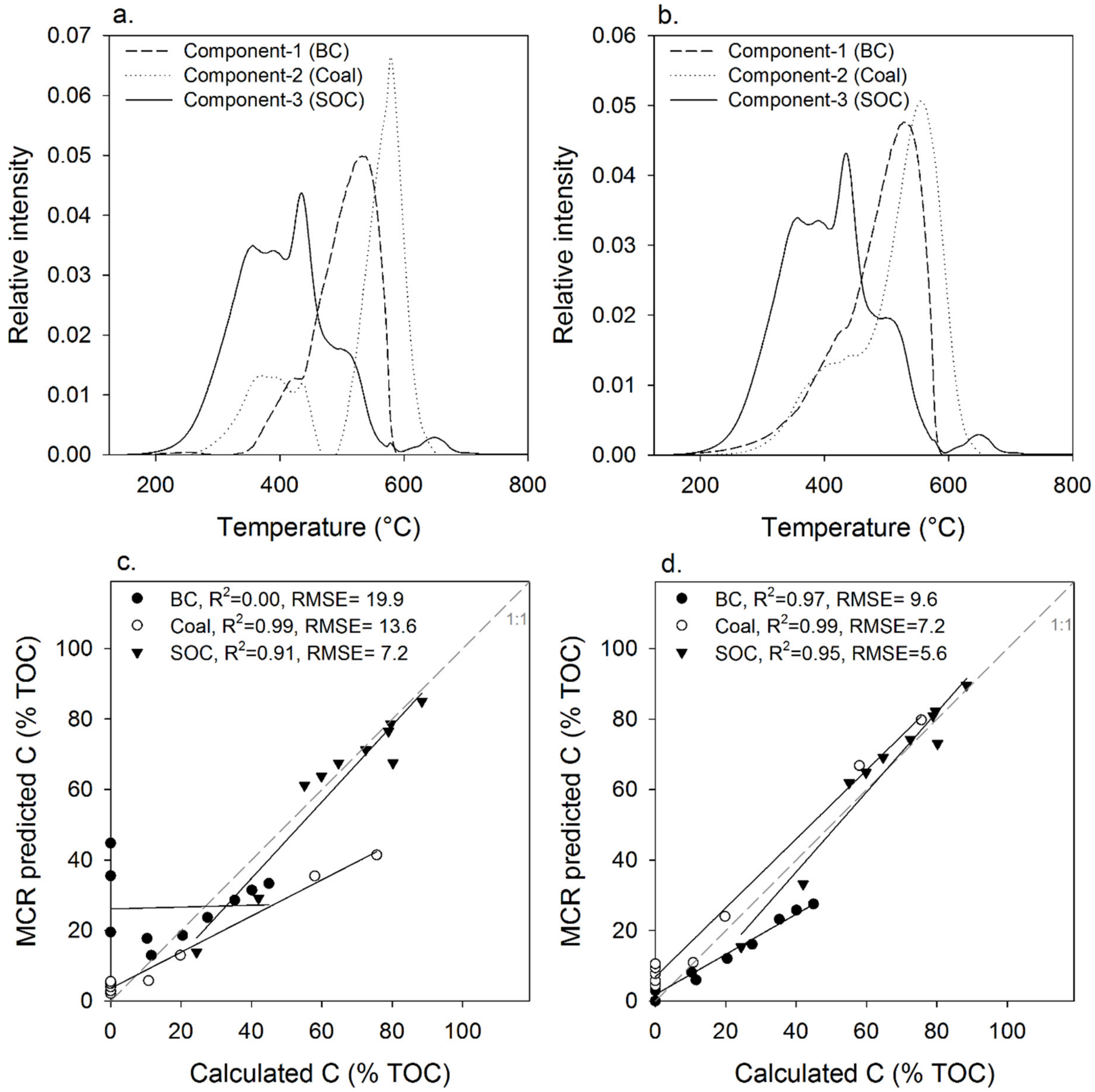

Figure 17 MCR analysis for the separation of soil organic carbon (SOC), black carbon (BC) and coal from Vertosol+BC+coal experimental mixtures. Thermograms of the pure components separated by MCR without (a) and with (b) initial guesses provided, and MCR predicte predicted BC, coal and SOC contents without (c) and with (d) initial guesses provided.

Provision of the initial guesses also substantially improved MCR-generated estimates of the proportions of coal, BC and SOC (Figure 17c and d). Without the initial guesses, no relationship was found between calculated and MCR-generated proportions of BC, while the correlation was much stronger (R^2=0.97) when initial guesses were provided. The initial guesses also reduced RMSE values for BC, coal and SOC. Slopes of the regressions were also substantially closer to 1 and intercepts were substantially closer to 0 when initial guesses were provided.

6.1.11 MCR analysis for the separation of BC and coal from SOC in unresolved minesoil mixtures

The thermogram of the Blackwater minesoil consisted of a single broad peak near 370 °C (Figure 13d). Consistent with the Walkley-Black organic C results (Table 8), the thermogram showed little contribution of thermally recalcitrant C. The Blackwater minesoil thermogram contrasts substantially with the more complex Vertosol thermogram, which may reflect the relatively short developmental age and lack of organic inputs in the minesoil.

MCR was able to distinguish between coal, BC and SOC in the minesoil mixtures with or without the provisions of initial guesses despite coal and BC having similar peak combustion temperatures and a large overlap (Figure 18a and b). The provision of initial guesses substantially improved the similarity of MCR-predicted and actual thermograms, particularly for the coal end-member (Figure 18a and b). MCR estimates for SOC were improved by the provision of initial guesses, decreasing RMSE from 18.2% to 4.4% of TOC (Figure 18c and d), though the parameters of the regressions were not substantially changed. Estimates for BC and coal were, in a sense, reversed when initial guesses were provided. Without initial guesses, BC was overestimated but was underestimated when initial guesses were provided, and the phenomenon was reversed for coal. Under optimal conditions (when guesses were provided), the correlation of BC was the weakest (R^2 = 0.43) among the components, likely due to its intermediary nature and similarity to coal.

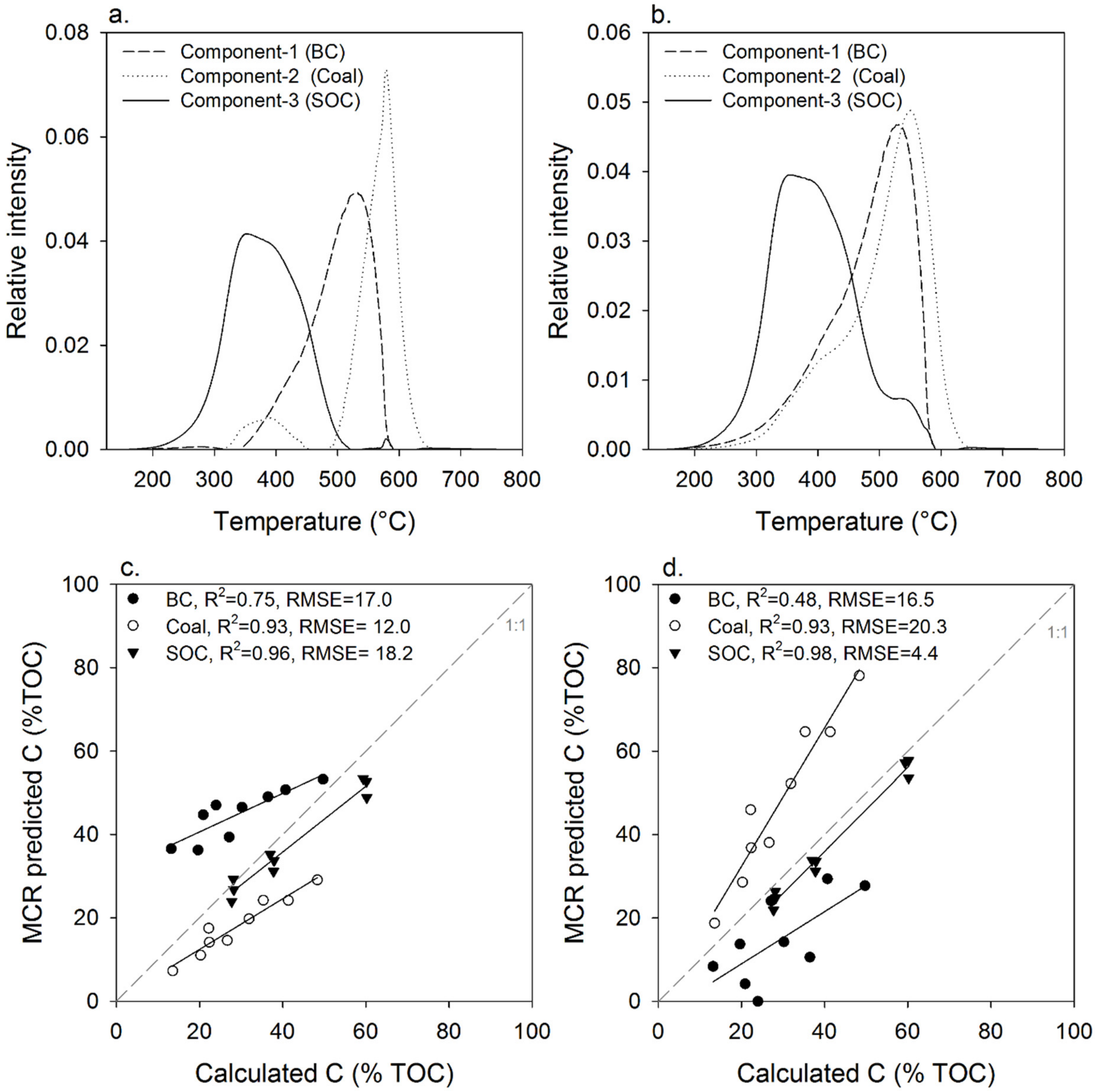

Figure 18 MCR analysis for the separation of soil organic carbon (SOC), black carbon (BC) and coal from Blackwater minesoil+BC+coal experimental mixtures. Thermograms of the pure components separated by MCR without (a) and with (b) initial guesses provided, and MCR predicted BC, coal and SOC contents without (c) and with (d) initial guesses provided.

6.1.12 MCR analysis for the quantitative distinction of coal, BC and SOC in minesoil unknowns

MCR analysis of the thermograms of the German Creek minesoil samples did not include initial guesses, but thermograms of German Creek coal and the chestnut wood char BC were included in the analysis dataset. MCR-generated BC and coal thermograms were similar to those generated in previous MCR analyses without initial guesses provided (Figure 19a compared to Figure 17a and Figure 18a). The MCR-generated thermogram for BC was reasonably similar to its actual thermogram, while the thermograms for German Creek coal differed substantially (Fig. A1). The

MCR-generated thermogram for SOC (Figure 19a, solid), which has no known/actual analog was more similar to that of the Vertosol than the Blackwater minesoil in that it had two main peaks. The second, smaller peak could be thermally stable (i.e., strongly mineral-adsorbed) soil organic matter, a form of BC or coal that is dissimilar to the identified pure components, or inorganic (carbonate) C. The SOC thermogram also has a prominent shoulder near 350 °C, which might indicate the presence of a distinct pool of easily oxidized/combusted SOM. MCR-estimated partitioning of the total C of the German Creek minesoils resulted in the largest proportion contributed by SOC, followed by BC, and the smallest contribution by coal (Figure 19b). C contributions from BC and coal also appeared to decrease with soil depth, though this trend was not statistically significant.

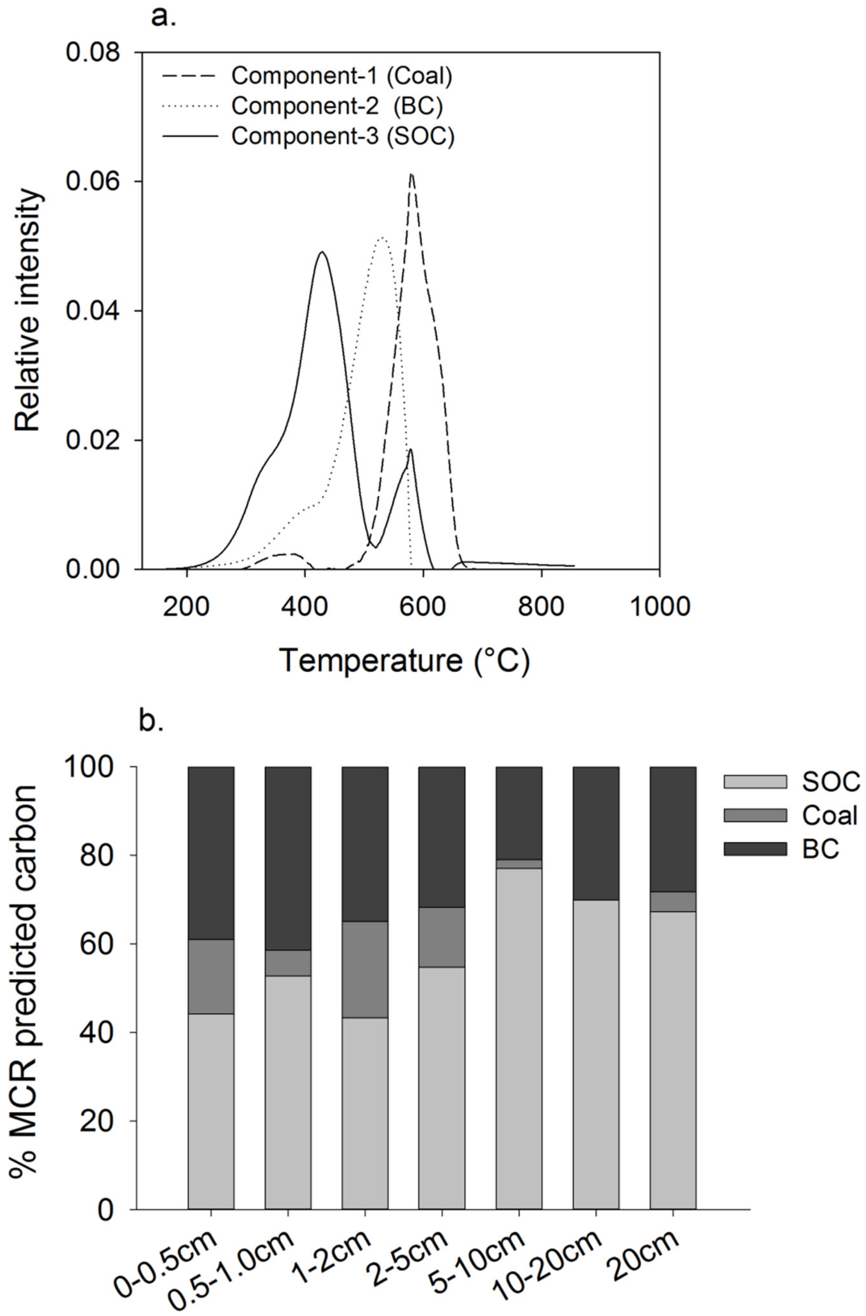

Figure 19 MCR analysis for the separation of black carbon (BC), coal and soil organic carbon (SOC) from a depth profile of a minesoil of unknown composition. Thermograms of the pure components separated by MCR (a) and MCR predicted BC, coal and SOC contents (b).

6.1.13 TA-EGA predicted BC compared with theoretical BC additions

A comparison of the estimated total carbon (TC) content of samples analyzed by TA-EGA and Dumas TC found TA-EGA underestimated the carbon content of soils tested. The estimation of the added BC content of the reference mixtures was also below calculated BC content (Figure 20)

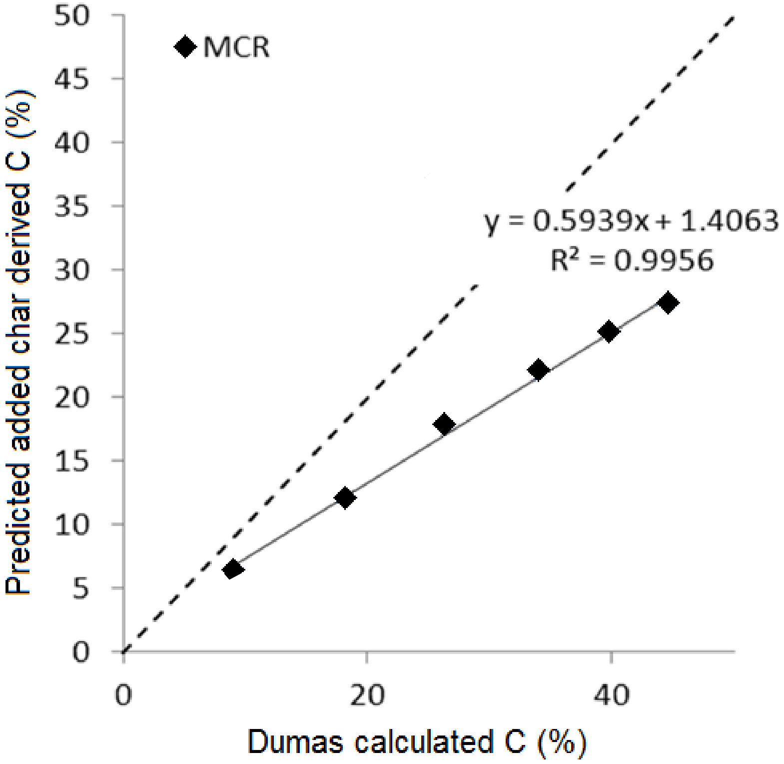

Figure 20 Predicted added char content versus Dumas calculated char content

Calculation of the background level of BC in the Vertosol was possible from the standard addition series as the y-axis intercept of the line of regression of the measured BC vs. predicted BC values (Elmquist et al., 2004, Roth et al., 2012). The Vertosol was determined to have 30% BC which corresponded with the reference material information from a UV-photo oxidation measurement (see Appendix A).

Discussion

Direct and indirect measures of SOM content are frequently used in assessments of agricultural soil quality and health (Gregorich et al., 1994, Karlen et al., 2001). Similarly, SOM accumulation can be used as an indicator of rehabilitation success during minesoil reclamation (Kimetu et al., 2008), as it is often the result of increased vegetation cover. However, the quantification of SOM accumulation in reclaimed coalmine soils is hampered by the presence of various forms of organic C. Ussiri et al. (2014) provide a comprehensive overview of the methods for quantifying geogenic C (i.e., coal) in rehabilitated minesoils, which they classify as: optical/microscopic, thermal, chemical, spectroscopic, molecular markers, isotopic, or some combination of these. The most reliable method to quantify geogenic C is radiocarbon analysis, owing to old age and lack of radiocarbon activity, but the analysis is prohibitively expensive for routine use, particularly in cases requiring large sample numbers such as carbon stock assessment in rehabilitated land. ^{13}C-NMR spectroscopy has also been used (Rumpel et al., 2000), but frequently requires sample pre-treatments and long run times thus also making it time-consuming, expensive, and impractical for high sample numbers. In response, infrared spectroscopy (FTIR, DRIFT) combined with multivariate data analysis (partial least squares (PLS)) was proposed as a more rapid and practical approach (Rumpel et al., 2001), but this approach requires substantial calibration data that might be soil-specific or only locally applicable.

The most common methods for differentiating recent (i.e., SOM) and geogenic C pools involve chemical, thermal or combined methods to remove SOM followed by subsequent analysis of the residue. Chemical methods for SOM removal include hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl), disodium persulfate ($Na_2S_2O_8$), among others (Ussiri et al., 2014), and rely on the fact the geogenic C is resistant to chemical oxidation due to its highly condensed aromatic chemical structure. Thermal oxidation methods rely on the fact that geogenic C is more thermally resistant than SOM owing to diagenetic processes, and temperatures between 300 and 400 °C are typically used as a cut-off (Gélinas et al., 2001, Schmidt et al., 2001, Ussiri and Lal, 2008b, Gustafsson et al., 1996). The challenge with these methods is that a single chemical or temperature cut-off between recent and geogenic C does not account for the wide spectrum of properties of each of these components. That is, in some cases highly recalcitrant SOM is not adequately oxidized or conversely some portion of coal is oxidized, leading to over- or underestimation of one pool or the other. Adding to the complications is the frequent presence of pyrogenic C (i.e., recent, fire-derived BC). The quantification of BC in soils and sediments varies greatly between methods (Hammes et al., 2007), largely due to a wide continuum of BC properties attributable largely to the properties of the fire that produced it. While BC frequently represents an intermediary form of organic matter between SOM and coal, many of the methods outlined above are unable to distinguish between BC and coal (Ussiri and Lal, 2008b). For the purposes of minesoil reclamation, the differentiation of BC is important as it would be considered more recent C than coal and might be included as arising from rehabilitation if fires are known to have occurred post-reclamation.

Deconvolution of EGA-CO_2 thermograms using MCR-ALS can directly apportion different components of the soil C pool (See Hypothesis 1 in Chapter 2), and avoids the interference of water mass loss experienced using thermogravimetry as well as the problems associated with empirical cut-off temperatures. The MCR results show a distinct separation of the coal and char but overestimated the coal contribution (Figure 14b and Figure 18b) in some cases. This bias towards the material with a higher temperature of combustion may be due to some interference by the mineral matrix if it protects BC materials, thus increasing the combustion temperature (Flessa et al., 2008, Lützow et al., 2006, Plante et al., 2009). The provision of initial estimate thermograms for end-member components improved the MCR model fits as expressed by smaller RMSE, calculated MCR-estimated regression slopes closer to 1, and regression intercepts closer to zero. The one exception to this was that RMSE for the regression for coal content increased from 12.0 to 20.3 when initial guesses were provided for the Blackwater minesoil+BC+coal experimental mixtures (Figure 18c versus d). It is unclear what produced this anomaly because the MCR-predicted thermograms for coal were substantially more similar to the measured thermogram when initial guesses were used (Fig. S1b versus S2b).

Thermal analysis results indicated that geogenic C represented a small proportion of the total organic C in the unknown minesoils (*e.g.*, up to 21%, with mean = 9.2%), and a larger contribution from pyrogenic C (*e.g.*, up to 41%, with mean = 32.4%). This is consistent with the findings of Skjemstad et al. (1996) of the presence of high levels of BC in Australian soils. However, this technique is vulnerable to the issue of under-estimating total organic C concentrations.. Even Rock-Eval analysis, which has been well correlated to elemental analysis, have been shown to under-estimate total organic C in soils (Saenger et al., 2015).

Trends in the estimated proportions of SOM based on thermal analysis and MCR-ALS were consistent with proportions of Walkley-Black (1934) measurements of organic C (Table 8), though the correlation was not especially strong ($p = 0.17$, $R^2=0.35$; data not shown). Walkley-Black values were greater than the thermal analysis-derived values for SOM, which is not surprising as the Walkley-Black procedure is known to oxidize a varying portion of BC, depending on particle size, C concentration and source material, making it possible to overestimate SOM in recently rehabilitated minesoils with low total organic C (Conyers et al., 2011, Siavalas et al., 2013, Skjemstad and Taylor, 1999). Walkley-Black also significantly underestimates C in many organic substrates and is influenced by soil texture and soil depth (Conyers et al., 2011, Lettens et al., 2007). As such, while Walkley-Black might serve to give an indication of plant-derived, new organic carbon accumulation and has been used for this purpose in coal-containing sediments (Siavalas et al., 2013), there is a long history of recommending against the method for the purposes of distinguishing between SOM carbon stocks and pyrogenic and geogenic forms of C (Bremner and Jenkinson, 1960).

Conclusion

Thermal analysis using ramped combustion has been used for the quantification of BC in sediments and soils (De la Rosa et al., 2011, De la Rosa et al., 2008) and in quantification of coal in mine soils (Maharaj et al., 2007a). However, as noted above, a single cut-off temperature to distinguish between two components during ramped combustion can be problematic, and thermogravimetry can be problematic because some mass loss during ramped combustion is not associated with organic matter oxidation. Through a series of experiments, it was demonstrated that materials with similar thermal properties (*i.e.*, BC and coal) can be distinguished and proportionally quantified in natural soils as well as in minesoils using ramped combustion measuring CO_2-EGA paired with chemometric analysis using MCR-ALS. While the inclusion of known end-members in the MCR-ALS analysis improved the estimates, results suggest that the approach may be appropriate when no such initial guesses are available. However, there are limitations to the use of this method, such as the presence of carbonate and other inorganic carbon sources. Carbonates frequently decompose at temperatures similar to the combustion temperatures of pyrogenic and geogenic organic C. This poses a potential problem in distinguishing these pools. Greater total carbon concentrations attributable to carbonates could inflate the MCR estimates for pyrogenic and geogenic C, and therefore be less reliable. However, sample pre-treatment with acid to remove carbonates (which was not performed in the current study) may alleviate this problem. In addition, the unknown soils tested appeared to have relatively low geogenic C concentrations. It is unclear whether MCR estimates would be more or less robust if there were greater proportions of geogenic and pyrogenic C, and further testing with other soil types, including carbonate-containing soils, is needed to extend the applicability of this technique to other soils.

7 Diffuse Reflectance Infrared Fourier-Transform Spectrometry

There has been growing interest in using infrared spectral analysis to predict the properties of soils in order to replace wet chemical analysis (Du et al., 2007b, Ge et al., 2014, Reeves III, 2010). While spectroscopic analysis has not yet advanced to the point where soil property predictions are accepted without further wet chemical analysis, spectral libraries are continuing to be developed (Baldock et al., 2013a). With the possibility of developing a spectral library for the prediction of different carbon pools in minesoils in mind, a subset of the minesoils were scanned in the mid-infrared spectrum. Sample similarity, handling methods, including additional sieving and spectral pre-processing were investigated.

For small datasets (n<40), it is beneficial for the samples to be similar, to improve the accuracy of predictions (McBratney and Minasny 2010, pers. comm., 3 August). While there are high levels of variability in minesoils due to the methods of their creation, a PCA run on the MIR spectral dataset can determine which samples are more similar to each other to assist in selecting which samples to include in a PLSR model (Baldock and Hawke, 2010, Baldock et al., 2013a). Models built with large datasets of more dissimilar soils (e.g. country scale MIR models) do not perform as well as smaller sized, local models at predicting soil properties at a field scale as the prediction accuracy decreases unless actions such as sample spiking or extra-weighing is used (Sankey et al 2008, Guerrero et al. 2014, Grinand et al., 2012).

Methods

Aliquots of dried and sieved soils were ground in a Retsch 2000 planetary ball mill for 180 seconds using zirconium oxide cup and 10mm diameter zirconium oxide balls. Samples were analysed in DRIFTs at two facilities, Queensland University of Technology (QUT) to build a mine soil spectral database and the Queensland State Government's Department of Science, Information Technology and Innovation Ecosciences Prescinct Boggo Road soil laboratory to predict soil properties using the SCaRP model.

At QUT, powdered samples were loaded into the spectrometer sample cup and leveled. A KBr blank was subtracted from the measured spectra to remove atmospheric and instrument artefacts. The blank was refreshed at least once every two hours of scanning to compensate for changing humidity within the local environment.

Samples were scanned on a Thermo Nicolet Nexus 870 FT-IR with the DRIFT attachment from 4000-400 cm^{-1} at 8 cm^{-1} resolution in transmission and taking the average of 128 scans.

Spectral preprocessing

Spectra were loaded onto The Unscrambler (CAMO Software AS, 2011), visually inspected for abnormal spectra clipped from 4000-1072 cm^{-1}. To further remove atmospheric effects, particularly the effects of the ambient CO_2 levels, 2441-2380 cm^{-1} were down weighted to zero in further analyses. Following this, the spectra were analyzed and compared in their raw format, baseline corrected and transformed with the standard normal variate function.

Results and discussion

A PCA on the raw spectra showed the Blackwater and German Creek samples, both collected in 2010, separating from the bulk of the Curragh and Norwich Park samples (Figure 10). If this trend continues following spectral pre-processing, this suggests that the German Creek and Blackwater samples should not be used in building a model for predicting the soil properties of the other mines as they would be too dissimilar to the other soils and skew the model. The building of a spectral model with this data is presented in Chapter 6.3.

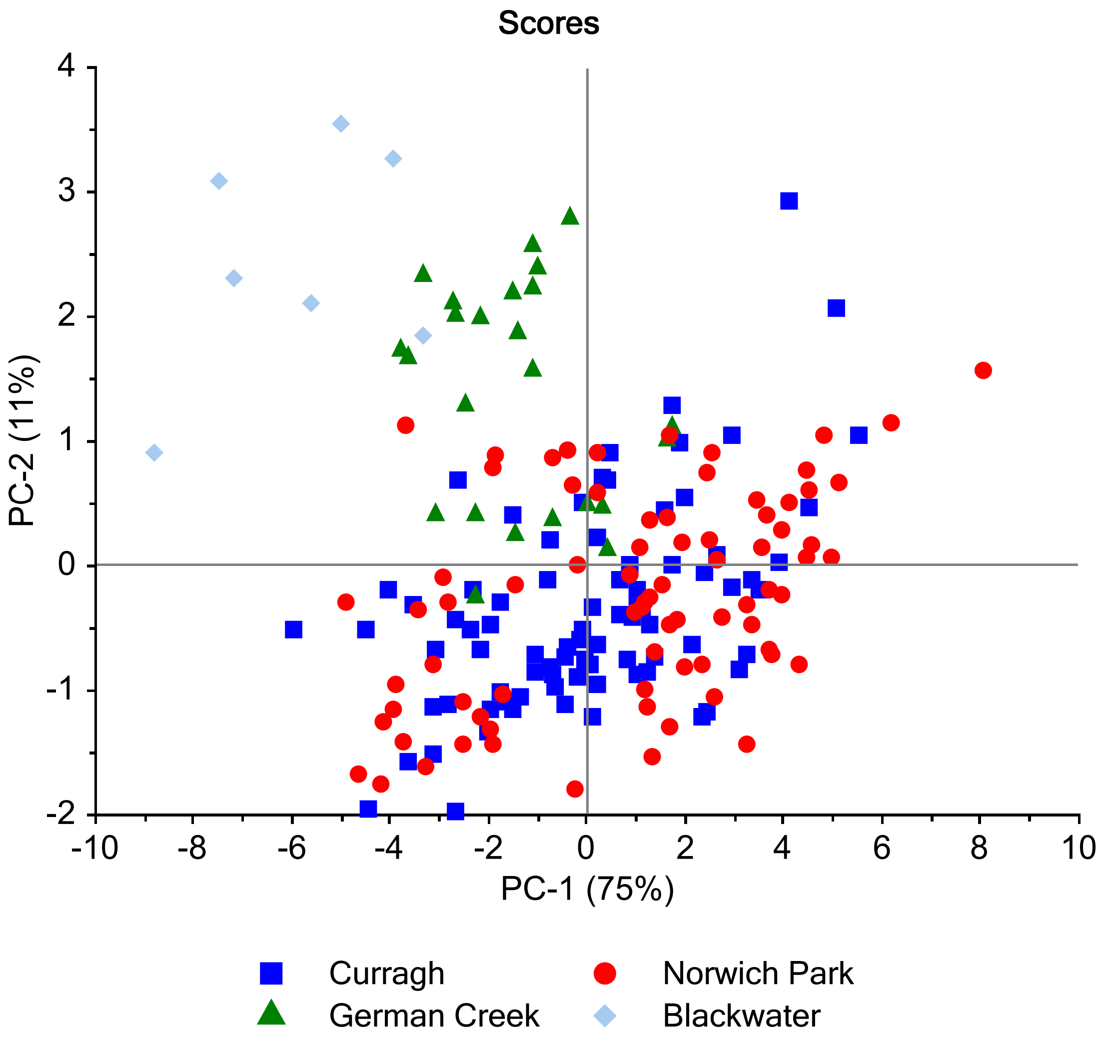

Figure 21 PCA scores plot of DRIFT spectral data of minesoils

7.1 The effects of removal of coarse particles from milled soils

The benefits of standardized soil preparation protocols on the quality of spectra and spectral analysis is known to reduce spectral variance, variance in predictions and error of prediction (Stumpe et al., 2011, Baldock and Hawke, 2010, Baldock et al., 2013a, Bellon-Maurel et al., 2010). Also, particle size is known to have an inverse relationship with quality of spectra (Fuller and Griffiths, 1978). Fine milling improves homogeneity within a sample, making it more representative of the bulk sample by preventing one large particle from being over-represented within the small DRIFT sample holder.

However, some materials, such as rocks or plant matter, can survive the milling process and remain as distinct particles. It is believed that the larger surviving grains, some as large as 1-2 mm, are derived from hard rocks within the soil sample.

These rocks are assumed to not contain notable concentrations of organic carbon or BC. Therefore, the removal of these grains in effect concentrates the organic carbon within the fines that pass sieving.

Method

Ball milled samples were sent to Queensland State Government's Department of Science, Information Technology and Innovation Ecosciences Prescinct Boggo Road soil laboratory for DRIFTs analysis using the SCaRP calibration (see NMR section of Chapter 1.4), including aliquots of five samples that were re-sieved to remove larger particles (<0.2 mm) that had survived milling. Particle size is known to reduce spectral quality as large particles reduce homogeneity of samples and can occupy a significant portion of the sample in the sample holder.

SCaRP calibration predictions for all carbon fractions of both neat and sieved (corrected and uncorrected) samples were compared by paired t-test. The DRIFT PLSR predictions for of the sieved compared to neat samples (n-12) to see if there was a difference in the prediction that they produced. (see Chapter 7 for DRIFT methods).

Results and discussion

The neat and re-sieved samples were analysed by paired t-test of all four predicted carbon fractions (humic organic carbon (HOC), particulate organic carbon (POC), ROC, TOC) the one-tailed p-values were 0.46, 0.47, 0.37, 0.49 and for all measurements combined in one paired t-test, p = 0.50 (n=20). For all measurements, neat against corrected values, one paired t-test p = 0.005; and uncorrected against corrected values, one paired t-test p = 0.001.

These results indicate that sieving and removal of harder particles <0.2 mm does not change the results significantly, meaning that the mass removed was relatively small. Furthermore, the hard, sand-sized, assumed pieces of rock are not enriched in organic carbon. When the carbon fraction concentrations of the samples are corrected for mass loss from the removal of the larger particles, the average change in the values predicted using the SCaRP calibration for all values was -1.071 mg/g the median change -0.678 mg/g and ranged from -5.254 (for an unusually hight TOC of 26 mg/g NP41) to -0.028 mg/g. The average correction factor used was 0.820 and the median was 0.813.

Conclusion

It was deemed that leaving non-soil organic matter in samples did not substantially change the organic carbon content of those soils as the mass of the organic matter did not account for much of the total mass of the soil in which it was found.

7.2 Partial Least Squares Regression

Partial least squares regression (PLSR) is a common model building method used with soil spectral data for the prediction of soil carbon although other methods, such as neural networks have been found to produce more robust models (Knox et al., 2015, Mouazen et al., 2010, Kuang and Mouazen, 2012). PLSR has been used in conjunction with mid and near-infrared spectroscopy to predict particulate organic matter (Bornemann et al., 2010), nitrogen content (Yang et al., 2012) as well as different carbon fractions in soils (Baldock et al., 2013a). Total carbon has been predicted using infrared spectra by many researchers and is generally well modelled. As such, TC was chosen as a test property to assess the predictive power of PLSR on DRIFT spectra of minesoils.

Method

The samples (n=70) consisting of samples from Norwich Park and Curragh mines were divided roughly into 2/3 calibration and 1/3 validation (49:21) set by running a PCA to determine groupings of similar samples. The calibration set was selected from all of the groups to ensure it would better represent the whole collection samples. This was achieved by using the Kennard-Stone function in The Unscrambler X (CAMO Software AS, 2011) on the baseline corrected MIR spectra and TC measurements using the first three PCA components. The weighting of the data was normalized using the inbuilt mean-centering and division by the standard deviation function. The Kennard-Stone algorithm (1969) selects an even subset of samples that reflects the overall frequency and distribution.

The PLS function in The Unscrambler X (CAMO Software AS, 2011) was employed using the calibration samples to build a model to predict TC from the DRIFT spectra. The validation samples were used to test the model.

Results and discussion

An $R^2 = 0.82$ was achieved using three factors, and explained 81% of the variance (Figure 22). The root mean square error of prediction (RMSEP) is 0.5%C. The mean TC is 2.3%C and the standard deviation is 1.2%C.

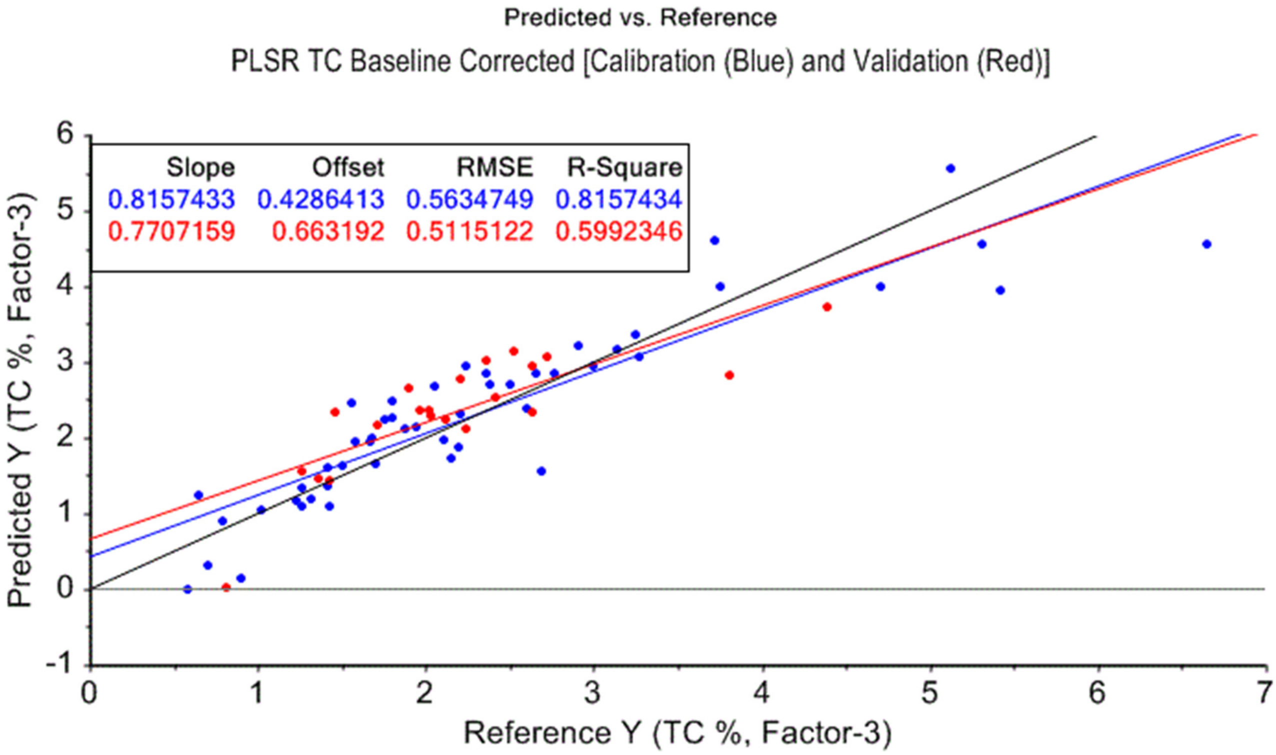

Figure 22 Predicted TC vs Reference TC for baseline corrected DRIFT spectra. The calibration set is in blue and the validation set in red.

Conclusion

As the RMSEP is greater than 20% of the mean TC value and 42% of the standard deviation the RMSEP is unacceptably high for predicting TC from this model built on minesoils. However, it should be noted that the spectral library is quite small and the minesoils are not homogenous as can be seen in the PCA scores plot of the DRIFT spectra. It is possible that better results could be achieved with a larger spectral library, or if the library consisted of sample that are more similar.

Comparing MIR results/Anecdote

It is known that individual spectrometers can have idiosyncratic responses and spectra from one instrument should not be directly compared to spectra from another instrument (Ge et al., 2011). Similarly, when using chemometrics with spectra from multiple instruments does not provide best results as the differences in the spectra due to the different machines would be included in the analysis, introducing a source of noise.

As such, when comparing results from different instruments, it should be noted what chemometrical analytical method was used when comparing the separate predictions. Furthermore, the pre-processing required for different analyses, including the increased handling may change samples.

Aliquots of three samples were analysed on DRIFTS at the Queensland State Government's Department of Science, Information Technology and Innovation Ecosciences Prescinct Boggo Road soil laboratory. There were two treatments – milling to 0.5 mm as per Dumas TC methods and standard soil pre-processing. After ball milling the samples were analysed using the SCaRP database for particulate organic carbon (POC), humic organic carbon (HOC), ROC and TOC. Of the three samples, one sample showed significant differences beyond the accepted variation (± 10%) in all of the predictions. Also, the predicted HOC for all three soils were significantly different.

While such a small sample set cannot definitively support the hypothesis that milling to 0.5 mm prior to ball milling alters the carbon make up of a soil sample, it highlights the sensitivity of spectral analyses and the fragility of soil carbon forms.

7.3 Effects of Spectral Pre-processing

There are multiple spectral pre-processing methods for the purpose of improving accuracy of predictions. These include, but are not limited to clipping, using a derivative, mean-centering, smoothing, and various scatter and baseline corrections. The purpose of these manipulations is to improve the data to noise ratio. The choice of which pre-processing methods to use is a somewhat individual decision arrived at through trial-and-error or "empirically" (Sanderman et al., 2011, Bloesch, 2015, pers. comm. 14 April). The raw spectra can serve to indicate which pre-processing techniques are most beneficial when common artefacts are observed, such as multiplicative scatter effect or specular reflection.

In this subchapter, the pre-processing used in the SCaRP calibration (spectral clipping, baseline offset, and mean centring) are applied to a set of minesoils from Curragh and Norwich Park mines (Baldock et al., 2013a). The PLSR predictions resulting from that are compared to other preprocessing methods.

Methods

Samples were ball milled in a Retsch 2000 planetary ball mill using zirconium oxide cup and 10mm diameter zirconium oxide balls.

Powdered samples were loaded into the spectrometer sample cup and leveled. A KBr blank was subtracted from the measured spectra. The blank was refreshed at least once every two hours of scanning to compensate for changing humidity within the local environment.

Samples were scanned on a Nexus 870 FT-IR spectrometer with the KBr beam splitter attachment from 4000-400 cm^{-1} at 8 cm^{-1} resolution in transmission and taking the average of 128 scans.

Spectral pre-processing

Sample spectra were recorded and transformed to absorbance by OMNIC™ software (Thermo Fisher Scientific) from 4000-400 cm^{-1}. Spectra were uploaded into The Unscrambler (CAMO Software AS, 2011) and analytical data was appended. The raw spectra were plotted to see if there were obvious differences between the samples and to examine methods of preprocessing that would improve the data (Figure 23).

From Figure 23 it could be seen that there is a baseline shift, indicating that baseline offsetting could improve analyses. Further interrogation of the spectra showed some multiplicative scatter as seen by the larger differences in spectra at either extreme of the wavelength window than the middle. Multiplicative scatter could be corrected for using standard normal variate correction, the formula for which is:

$$\boldsymbol{\widehat{X}_k = \frac{x_k - \bar{x}}{\sigma}} \qquad \textbf{Equation 7}$$

Where, k is the wavelength

$\widehat{X}_k$ is the corrected absorbance value at wavelength k;

x_k is the raw absorbance value;

σ is the raw absorbance; and

$\bar{x}$ is the mean absorbance value of that spectra

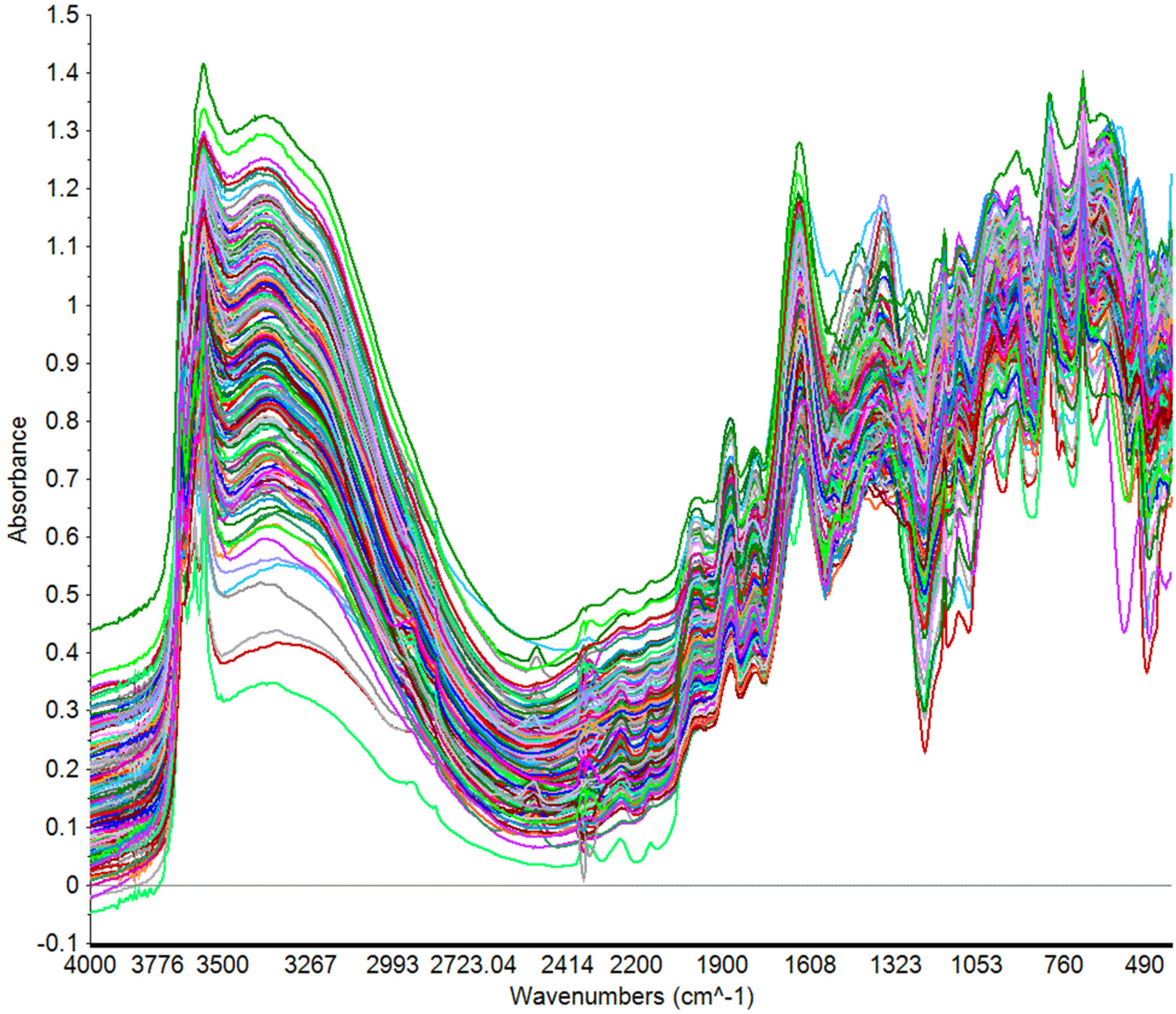

Figure 23 Raw MIR DRIFT minesoil spectra

The SCaRP preprocessing used was as follows: spectral clipping to 4000-1030 cm^{-1} followed by baseline correction through the in-built baseline offset and mean centring functions in The Unscrambler (Baldock et al., 2013a, CAMO Software AS, 2011). The SCaRP preprocessing is compared to using spectral clipping with baseline offset and linear baseline correction, standard normal variate (SNV), spectral clipping with standard normal variate, and standard normal variate with linear baseline correction.

PLSR was performed on a sample set n = 121 with cross validation of 20 random segments using the standard settings in The Unscrambler (CAMO Software AS, 2011) to predict TC. Total carbon was chosen as the measurement to test since the method is well established and has shown to be well predicted using MIR (Knox et al., 2015, Minasny et al., 2009). The spectral preprocessing used and the results on the PLSR models produced are presented in Table 8. As cross validation, instead of a separate validation set was used, the models can be compared using root mean square error of cross validation (RMSECV), which is similar to RMSEP. The optimal factor number is the number of factors used in the PLSR model and was chosen based on the amount of variance explained in that model. The greater the amount of variance explained by the model, the better

Results

Table 8 shows that the PLSR models produced a linear fit but could be improved. It is desirable to minimize the number of factors used in the model to avoid over fitting while also maximizing the amount of variance explained. Thus the majority of the "optimal factor number" selected were well below the maximum number of seven created by The Unscrambler (CAMO Software AS, 2011).

Table 8 MIR spectral preprocessing and PLSR response for predicting TC

Preprocessing	**R^2**	**RMSECV (%C)**	**Optimal factor number**	**Variance explained**
Spectral clipping, baseline offset, linear baseline correction	0.754	0.76	3	75%
SNV	0.817	0.74	5	81%
Spectral clipping, SNV	0.810	0.74	4	75%
SNV, linear baseline correction	0.825	0.74	4	73%
SCaRP	0.81	0.75	4	70%

Conclusion

The limiting of the sample set to only minesoils from Curragh and Norwich Park mines was to avoid the skewing of the transformed spectra by the coal and BC samples whose spectra greatly differ to minesoils as well as the spectrally different minesoils from Blackwater and German Creek mines. While already reduced, it is possible that the pool of samples used were not sufficiently similar, in soil texture (Table 4) or in mineral composition, resulting in a poorer fit (Knox et al., 2015). Norwich Park samples had on average a lower clay content, with nearly 50% of the samples tested having clay values ranging from 18-30%, whereas the Curragh samples had slightly more than 10% of the samples testing falling in that clay range. The majority of the Curragh samples had clay levels <40%. While the precise clay levels may be questionable, it can be concluded that the Curragh samples had higher clay levels than Norwich Park.

While all of the preprocessing treatments produced similar RMSECV, SNV as a preprocessing step can be seen to improve the R^2 values. The SCaRP treatment does not produce significantly improved values to the other preprocessing treatments. While SNV may be a beneficial spectral preprocessing technique for minesoil MIR spectra for further PLSR, the importance of soil similarity should be considered. Due to the high heterogeneity of mine soils, as can be seen in the carbon and electrical conductivity measurements, this may support the limiting of spectral models to mine specific if the soils are highly similar or the need for a significantly larger sample set to broaden the applicability to multiple mine sites.

7.4 Prediction of Green Carbon by Diffuse Reflectance Infrared Fourier-Transform spectrometry (DRIFTs)

Diffuse reflectance infrared Fourier-transform spectrometry is a technique where samples are scanned with infrared energy in a spectrometer that detects the vibration of chemical bonds. It is fast, non-destructive and has been shown, when coupled with multivariate analysis (chemometrics), to be able to predict total organic carbon and charcoal content of soil samples (Janik et al., 2007, Hobley et al., 2014), and characterize coal (Bona and Andrés, 2008a). Samples of charcoal, coal, spoil, mine soil and agricultural soil were scanned at Queensland University of Technology.

The resulting spectra showed visible peaks in areas correlating to carbon ring structures in the mine soil. Since carbon rings are found in black carbon and coal it was believed that these peaks could be used as proxies for BC and coal.

This was encouraging as DRIFTs could potentially be used semi-quantitatively through the comparison of the areas underneath peaks as done by

Hobley et al. (2014). However, it is much more common to use multivariate analysis (partial least squares regression) to predict quantities of any compound under study.

Historically, solid samples would be diluted with a non-absorbing material (i.e. KBr) to allow the energy to diffuse into the sample and refract. There is now a movement towards less sample preparation, including scanning samples neat, or undiluted (Reeves III et al., 2005, Sanderman et al., 2011, Hobley et al., 2014).

During milling of the soils, it was noted that many samples adhered and caked onto the walls of the milling jar, resulting in grit remaining. Some samples would still contain grit even after being milled twice. Due to the ineffectiveness of re-milling at reducing grit and little change in carbon values (see subchapter 7.1) it was decided to standardize sample handling by milling all samples once. Likewise, coarse particles were not removed by wet-sieving or wet-milling for fear of altering the sample by introducing water or other chemicals.

The inclusion of larger particles in the DRIFT assay is known to cause baseline sloping and introduce noise (Chalmers, 2006, Faix and Böttcher, 1992) as well as reduce the homogeneity of the sample resulting in higher variability in the spectra (Baldock and Hawke, 2010). However, as the spectra are not being directly interpreted as done by Hobley et al. (2014) but rather by chemometrics, it is believed that spectral pre-processing and the statistical analysis should compensate for this and other artefacts (Bona and Andrés, 2008a).

It is known that water masks DRIFT spectra at certain bands. Despite this, no extra drying step after initial soil processing was done. It was deemed too difficult to maintain artificially low moisture levels due to the high amounts of clay in the samples (see Figure 10),as its hygroscopic nature combined with the time required to transport samples to the spectroscopy laboratory would mean samples would begin absorbing atmospheric water upon removal from the drying oven. As earlier studies have not reported an additional drying step, it is assumed that the effect of water will be overcome by the use of chemometrics in analysing the spectra (Hobley et al., 2014, Sanderman et al., 2011).

A treatment of the spectra similar to what was done in Sanderman et al. (2011) was selected to best approximate results. Subchapter 7.3 investigating other spectral preprocessing techniques indicated that SNV may improve results.

Method

Processed soils were finely milled using grinding jars and 10 mm diameter milling balls of zirconium oxide in a Retsch PM 200 planetary ball mill. The ball number, duration and RPM settings for grinding (10, 3 minutes, 550 RPM) were developed from suggestions by the manufacturer after their analysis of a few exploratory samples sent to their laboratory.

At the Queensland University of Technology spectroscopy laboratory, the samples were analyzed on a Thermo Nicolet NEXUS 870 FT-IR averaging 128 scans from 400-4000 cm^{-1}, 8 cm^{-1} resolution and a KBr beam splitter. The DRIFT sample cup was loosely filled with soil and the surface smoothed. The soils were tested milled, neat and not pelleted. Samples of coal and charcoal were diluted with KBr at roughly 1:9 by volume to reduce absorbance. A pure KBr background was subtracted from the resulting spectra.

Analysis

Data pre-processing

Spectra were visually inspected using The Unscrambler X (CAMO Software AS, 2011) and underwent PCA to identify similar soils. The PCA loadings were also noted and inspected for their resemblance to noise. The spectra were observed to display scatter and variable baselines (see Chapter 7.3).

Baselines were corrected using The Unscrambler X (CAMO Software AS, 2011) baseline offset function. It was visually obvious that correcting the baseline shift improved the alignment of the spectra. In Figure 21a, a selection of soils were repeatedly scanned with their raw spectra plotted all together. The replicate spectra would ideally be identical to each other. However, due to baseline shift and scatter effects, the raw spectra of replicates differ from each other. In Figure 24b where the baseline has been corrected, scatter is more evident as seen by the spread at the extremities of the spectral window.

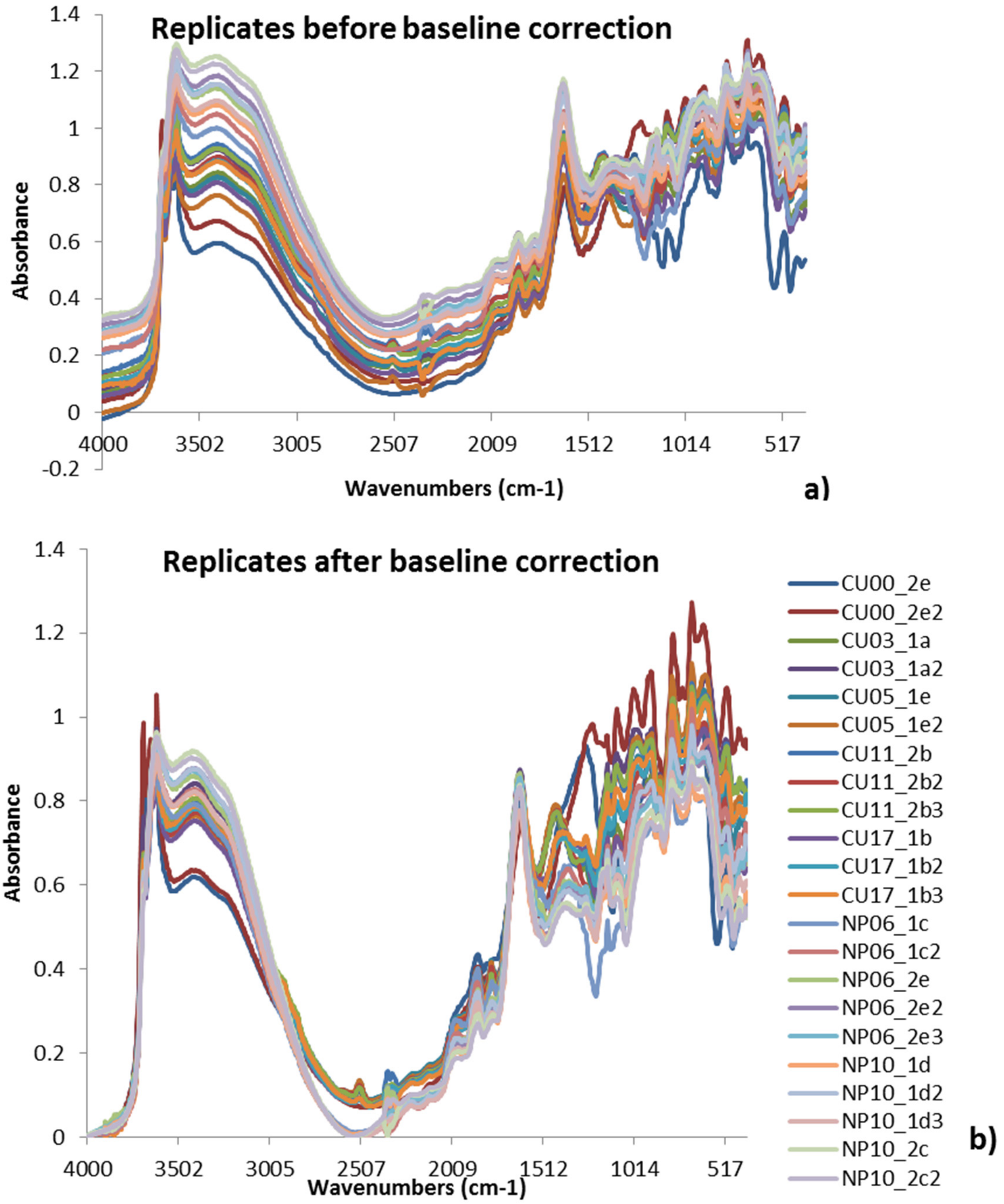

Figure 24 A set of soils repeatedly scanned a) before and b) after baseline correction

As a preliminary analysis, samples that had undergone TA-EGA were used as a calibration set for partial least-squares regression (PLSR) on the rest of the samples. Wavelengths known to correlate with carbon bonds, 1580-1610 cm^{-1}, were up-weighted by 20 percent while wavelengths associated with CO_2, 2441-2380 cm^{-1} were down-weighted in an attempt to mitigate the effects of operator error due to breathing during sample loading (Chalmers, 2006).

Soils were grouped by similarity of their spectra as determined by PCA to maximize the MCR analysis accuracy. The results were converted to weight percent of the different carbon compounds, green carbon, coal, BC, and IC. Using these amounts, this was added to the DRIFT spectra data matrix and was used as the response variable in the PLSR.

Other analytical results, such as TC and TOC were added to the matrix and where the measured amounts were below the detection limits an amount was input to avoid blank spaces and zero-values (e.g. total nitrogen was input as 0.04%). The HOC, POC, ROC and TOC predictions from the SCaRP calibration were also input and where those values were below their threshold for certainty the limit was used (i.e. <0.10 mg/g HOC was 0.10 mg/g). Where twice-sieved samples were analysed, correction factors were used to compensate for the removal of hard materials (see subchapter 7.1). Where replicate scans existed (separate DRIFT spectra of the same soil), the calibration set were checked to make sure that both spectra were not in it thereby spiking the calibration.

The wavenumbers corresponding to the presence of H_2O were not downweighted and no attempt to minimize the amount of water in the soils after initial drying during processing of the soils was done. Therefore, soils with high levels of clay would likely have higher levels of H_2O. It is known that the presence of H_2O masks certain wavenumbers that correspond to the presence of organic carbon bonds. It was anticipated that the number of samples included in the analysis would compensate for the masking caused by higher moisture content. Furthermore, it was decided that efforts to maintain the samples as dry as possible prior to DRIFT analysis was unreasonable due to time and distance to travel between laboratories and the number of samples to be analyzed. It is known that the levels of clay within the different samples was highly variable (see Table 4 in Chapter 5.2).

Results and discussion

When the PCAs of the minesoil spectra were completed, there was no clustering seen of the samples high in clay. The samples were best separated by minesite as there were insufficient numbers of independent samples if separated by depth, age of rehabilitation or covertype. It cannot be ruled out however, that clay content plays a role in sample similarity although not a major component. Clay content has been speculated to covariate with carbon content and may protect the organic matter. This was not seen to hold true with the minesoils under study with clay content having Pearson correlation coefficients of -0.24 and -0.23 for TC and TOC.

The soils were analysed in groups according to minesite to improve sample similarity. Furthermore, the whole library was used together to predict carbon fraction levels. Validation sets of ~70% of the samples were selected by Kennard-Stone algorithm (1969) of the transformed spectral data. The different groupings produced the following results at predicting BC+Coal, TOC, GC, and SCaRP ROC (Table 9).

Table 9 Partial least squares regression model metrics for different spectral pretreatments and sample groupings

Treatment /Grouping	PLSR metrics: Number of factors, RMSEP, R^2			
	BC+Coal	TOC	GC	ROC
SCaRP/Whole	2 factors, 0.40%C, R^2=0.536	4 factors, 0.54%C, R^2=0.805	3 factors 0.37%C, R^2=0.850	3 factors, 0.08%C, R^2=0.941
SCaRP /Norwich Park	2 factors, 0.39%C, R^2=0.75	3 factors, 0.30%C, R^2=0.89	3 factors 0.20%C, R^2=0.957	2 factors, 0.05%C, R^2=0.897
SCaRP /Curragh	5 factors, 0.13%C, R^2=0.849	5 factors, 0.45%C, R^2=0.912	3 factors 0.43%C, R^2=0.903	4 factors, 0.06%C, R^2=0.895
SNV /Whole	6 factors, 0.17%C R^2=0.766	4 factors 0.31%C R^2=0.786	3 factors 0.36%C, R^2=0.829	2 factors 0.09%C R^2=0.936
SNV /Norwich Park	5 factors, 0.45%C R^2=0.855	3 factors 0.33%C R^2=0.875	2 factors 0.12%C, R^2=0.931	2 factors 0.03%C R^2=0.945
SNV /Curragh	5 factors, 0.14%C R^2=0.858	4 factors, 0.54%C R^2=0.899	3 factors 0.42%C, R^2=0.905	3 factors, 0.06%C R^2=0.917

Table 9 shows the number of factors chosen in the model, the resulting root mean square error of prediction (a goodness of fit parameter) and the linearity of the regression by the R-squared value. Increasing the number of factors would reduce the RMSEP and increase the R-squared value, however it also risks overfitting the data. Often, the improvement in the R-squared would be minimal above the value 0.8 thus lower factor numbers were usually selected after this value had been reached. Factor numbers were also selected to be similar to each other to facilitate comparison between treatments/carbon pool models.

When a larger dataset was used for predicting carbon pools greater errors were produced and lower R^2 values. This indicates that it is better to limit the calibrations to within a minesite as the minesoils from different mines are too different from each other. Similarly, it would not be advisable to use calibrations from any individual minesite to predict carbon levels of minesoils outside of that minesite.

Of GC, TOC, and combined BC and coal, GC was the best modelled, requiring fewer factors to produce greater R^2 and smaller RMSEP values. The RMSEP values however, are unacceptably high at four to five times the RMSEP of the ROC predictions, indicating high levels of uncertainty around the carbon levels predicted by the models. The high TOC RMSEP supports the questioning of the accuracy of MIR-TOC predictions (Page et al., 2013).

ROC was well modelled as can be seen by the low RMSEP values and high R^2. That this carbon pool was well modelled from the minesoil spectra indicates how strongly the ROC pool is tied to the molecular vibrations. It should be remembered that ROC was originally quantified using ^{13}C NMR, which, along with MIR both function based on detecting chemical bonds (Forouzangohar et al., 2015).

Replicability of DRIFT (Measurement and operator error)

There are multiple sources of variation during the DRIFT analysis. From the amount of moisture in a sample, as affected by the relative humidity in the laboratory, the concentration of CO_2 in the atmosphere as affected by the breathing of the operator to the variability within an aliquot of sample depending on the homogeneity of the sample.

The error can be divided into operator error and experimental error. The operator error includes, CO_2 levels obscuring sections of the spectra, irregularity of the scanned sample surface within the sample cup effecting the ability of the collector from detecting radiation and sample heterogeneity due to ineffective milling or mixing of the soil sample.

Experimental error may originate from the changing characteristics of the laboratory like CO_2 levels and humidity. There can also be instability of the laser beam from power fluctuation.

In order to give a measure of the error in the spectra, several randomly selected soils were scanned multiple times. The variation in the spectra of the different aliquots of the same soil were quantified by calculating the standard deviation across each measured wavelength (Bona and Andrés, 2008b). Soils scanned on different days with different laboratory conditions were also included in this analysis.

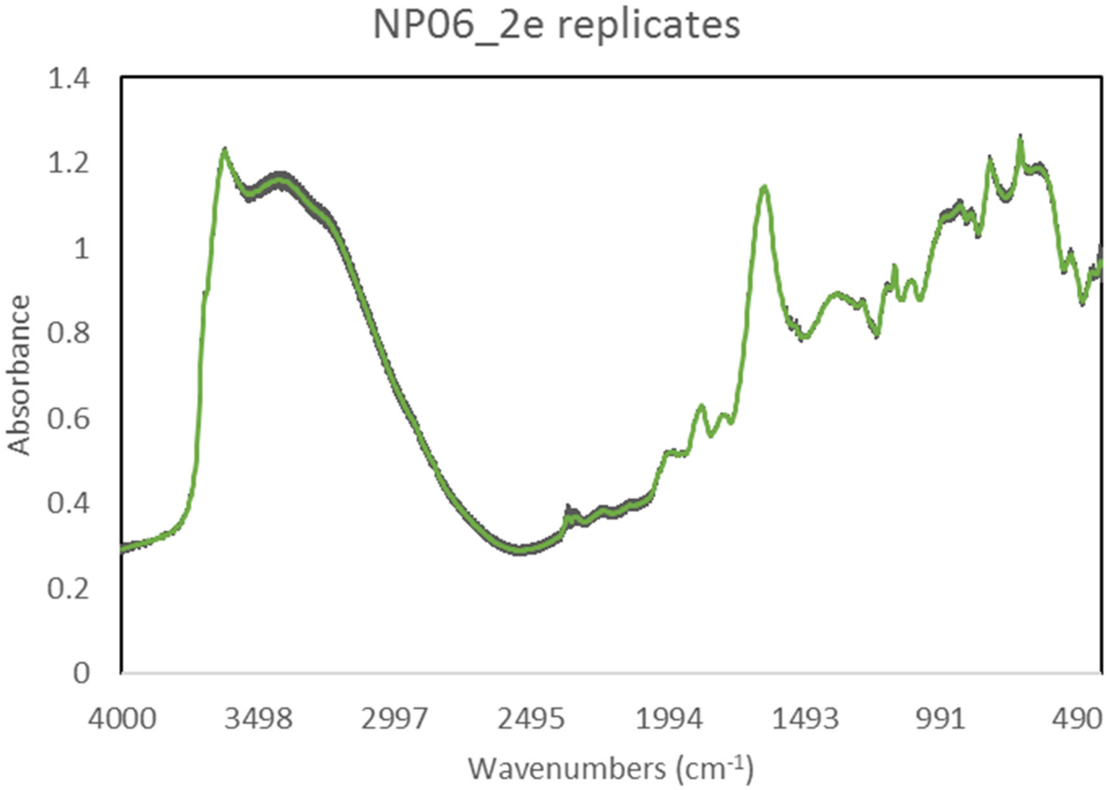

Figure 25 Average spectra of NP06 2e (n=3) with standard deviation shown in grey. The replicate spectra were consistent, with the greatest variance appearing in the 3500-3200 cm^{-1} area, known for water absorbance and 2360-2330 cm^{-1} wavenumbers, known for CO_2 absorbance. The variation present may be attributable to differences in the laboratory environment and operator error, particularly the relative humidity in the laboratory and the CO_2 present in the sample chamber; either from the operator exhaling when placing the sample in the sample chamber or a change in the length of time a sample was left in the chamber before the spectra was recorded. As these sources of error could not be easily excluded, it was concluded that they were acceptable.

There is also a question of the effect of the KBr background milling state on the spectra. Some soils were scanned with a milled KBr background and some were scanned with an unmilled KBr background. The differences in these samples could also be attributed to the difference in time between scannings (years). However, common practices around soil samples hold that following drying and processing, soils would change minimally, despite the directions in Schumacher (2002) and the finding of the change in TOC over time in Appendix G.

It is concluded that the error in the DRIFT analysis is acceptable and that the imperfect milling noted of some soil samples would be of little consequence, or does not significantly change the spectra of mine soils. It is noted that the larger particle sizes in a sample would change the path length of the beam reflecting within the sample and it could be argued that the background should be milled and that the soils are different for this reason.

8 MCR on unknown minesoils

Chapter 6 demonstrated that TA-EGA with MCR can produce good predictions of BC and coal using CO_2-EGA data of soils with known BC and coal composition. In this chapter, MCR is applied to a larger set of minesoils with unknown BC and coal composition. The carbon fractions are then compared to SCaRP resistant organic carbon (ROC) for validation (Sanderman et al., 2011).

8.1 Application of TA-EGA with MCR to minesoils

TA-EGA with MCR is applied to minesoils from different coal mines along a depth profile to determine if any patterns can be observed with depth, in soils with varying age of rehabilitation and cover type. An illustrative example of the variability in the carbon pools quantities is also presented.

Methods

The TA-EGA thermograms were visually inspected to gain a sense of what the data was like. Both mass and area under the curve normalizations were inspected (see Figure 26 and Figure 27).

For further analyses, the TA-EGA CO_2 thermograms of 2013 collected minesoils were baseline corrected, area-normalised (CO_2 detected), and truncated using the PeakFit (Systat), Proteus (Netzsch), and R software packages (R Development Core Team, 2008) to the range between 120-800°C. This temperature range was chosen as most H_2O has been removed and significant amounts of CO_2 are released between ~200-800°C. These were loaded into The Unscrambler X (CAMO Software AS, 2011) for principal component analysis (PCA) and MCR analysis. The PCA was run on the thermograms to identify similar sample groupings in an attempt to optimize MCR analysis by reducing the noise in the data. As there is variability in the rate and temperature of combustion for different coals, their CO_2-EGA thermograms also differ. Since MCR produces curves of the pure components, the more similar the shape of the thermograms of the different carbon fractions within their grouping, the better the MCR prediction will be. Additionally, PCA gives an indication of the optimal number of components for the following MCR-ALS analysis. The standard settings for PCA were mean centering, NIPALS algorithm, cross validation with randomly selected sets (n=82) with 20 segments.

Multiple MCR-ALS analyses were performed, varying the number of samples included, EGA curve normalization by sample mass or CO_2 detected (area normalization), the way in which the samples were grouped (by minesite, by cover type, etc), the inclusion of the coals and BC samples, and whether to identify initial guesses for pure components or not.

The MCR analyses were performed on the EGA thermograms from soil samples collected from two mines, Curragh and Norwich Park in 2013 and the coals and BC described in Chapter 4. MCR components were assessed on the shape of the curves and peak temperatures. MCR solutions were judged on the basis of solution convergence and total residuals.

Results and discussion

The choice of normalization for the EGA can have a strong influence on the MCR solution. Although the peak combustion temperatures of the pure components should not change, the relative contribution of each component would change in order to fill the differently shaped EGA curves best. Also, the use of mass normalization would introduce intensity ambiguity in the MCR resolved pure component magnitude (Abdollahi and Tauler, 2011) (CAMO Software AS, 2006). The difference between these two normalizations is that the relative contributions of carbon materials with different thermal resistance is more evident in the area normalized samples, whereas the sample mass normalization reflects the true carbon richness of the samples.

Despite the ease of interpretability of the PCs for mass normalized data, area normalization was selected for the subsequent MCR-ALS as area normalization showed better separation of the samples in the PCA. The use of area normalized data simplified the interpretation of the MCR-ALS component contributions; since component contribution as given by the program are relative (i.e. intensity ambiguity is removed) quantitative contributions can be calculated by multiplying the relative contribution of the component by the total carbon for each sample.

The mass-normalized thermograms made the difference between the samples from different mines more evident (see Figure 26). The EGA curves showed four main peaks in the samples at ~350°C, 450°C, 560°C and above 700°C with some smaller features within the first three peaks (see Figure 27). The third peak above 700°C indicated that these samples contained inorganic carbon.

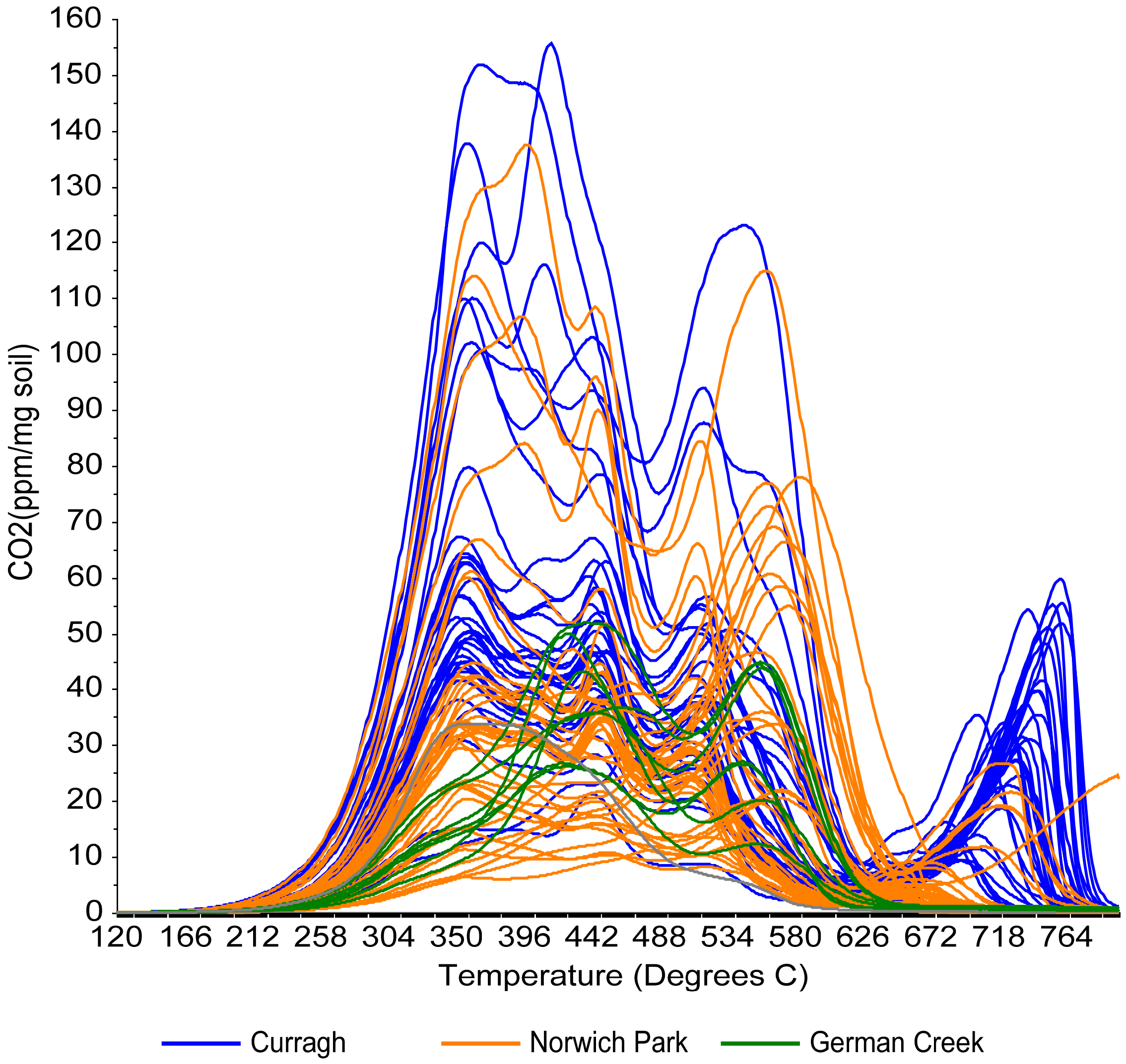

Figure 26 Minesoil CO_2 EGA curves normalized by sample mass and grouped by minesite. German Creek samples were included to demonstrate the difference between mines. Most Curragh samples have a peak >700 °C indicating the presence of inorganic carbon. The German Creek samples contained significantly less carbon than the samples from the other mines as the green coloured curves are engulfed by the yellow and blue curves. The Norwich Park samples generally appear to have more carbon in the >500°C peak than most Curragh samples.

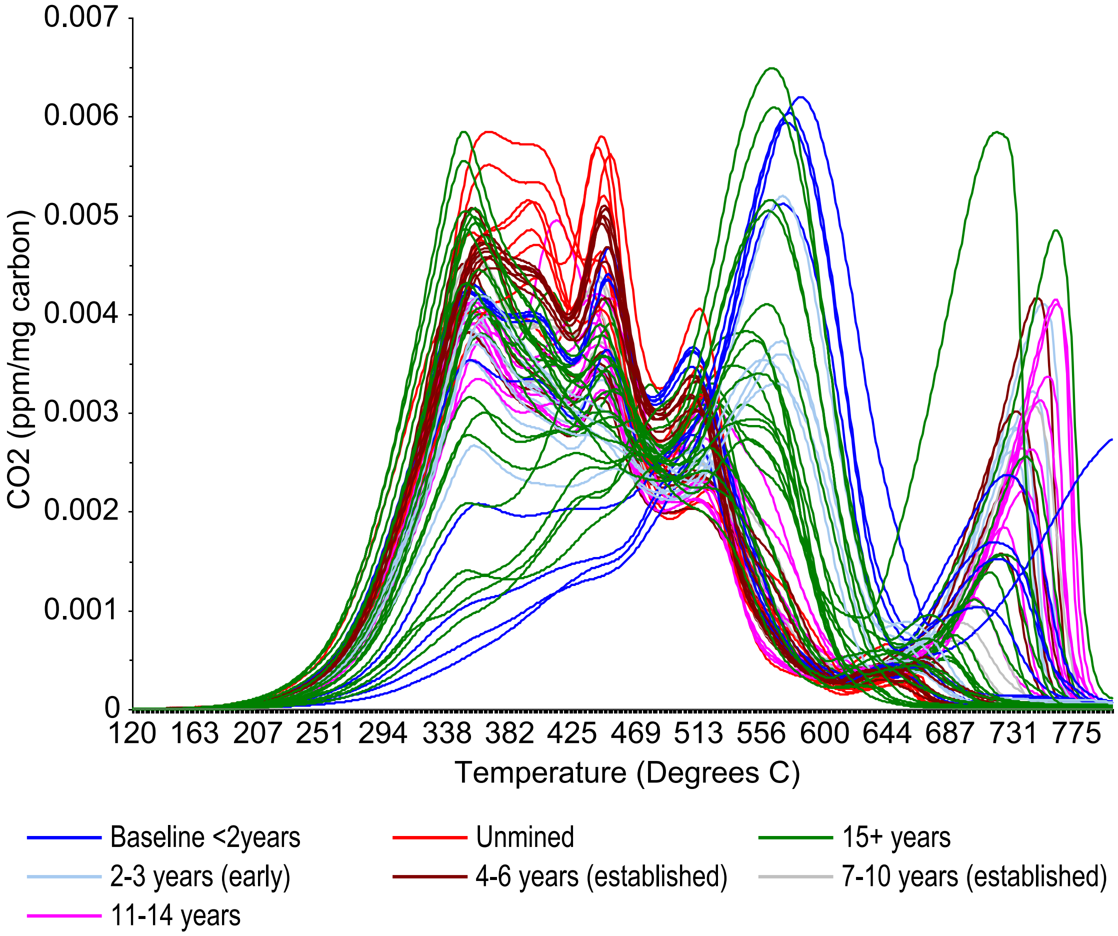

Figure 27 Minesoil CO_2 EGA curves normalized by carbon detected (area normalization) and grouped by age of rehabilitation. The unmined samples included show a greater proportion of carbon in the <400°C range than the mined samples. Some baseline years show a strong peak at 560°C indicating a high proportion of more thermally stable organic matter, such as BC and coal. This is to be expected as the baseline sites have had little organic inputs due to its low developmental age. However, the depicted curves show multiple samples from the same pits, explaining the high similarity between those samples and why broader conclusions cannot be drawn from this figure.

PCA for the determination of sample groupings in MCR

To optimize MCR-ALS resolved pure components, soils were grouped by similarity prior to MCR-ALS analysis. Highly similar soil CO_2 EGA curves would increase the weight of the differences between curves, thereby reducing noise and allowing the pure components solution to reach convergence with lower residuals. To identify similar samples, PCA was run on the CO_2 EGA data.

The PCA scores plots showed the samples were largely separated by the principal component (PC) that explains the second most amount of variance (24%), PC2. Between the two normalizations, the scores plots showed a clearer separation between the two minesites with area normalization (Figure 28). A few samples from Norwich Park were amongst the Curragh samples, mostly from one reference (unmined) pit. The other Norwich Park samples that were not separating from the

Curragh samples were one 20-year old spoil layer sample (NP20_3e) that the influence plot showed was an outlier, and a younger, 0-2cm sample (NP01_2a). The Curragh samples highest along PC-2 are from the spoil layer, while the lowest were from the 0-2 cm depths. The scores plot, along with the loadings plot of PC-2 (Figure 29b), that shows how that principal component was weighted, indicate that the Curragh samples tended to proportionally have more inorganic carbon since the peak of PC-2 is above 700°C and everything below that had negative loadings. Therefore, it appears that the area normalized samples PCA is more sensitive to the underlying mineral matrix than the mass normalized EGA data when samples with carbonates are present (Figure 30). More plainly, PC2 from area normalized data (Figure 29b) is mainly representing carbonates.

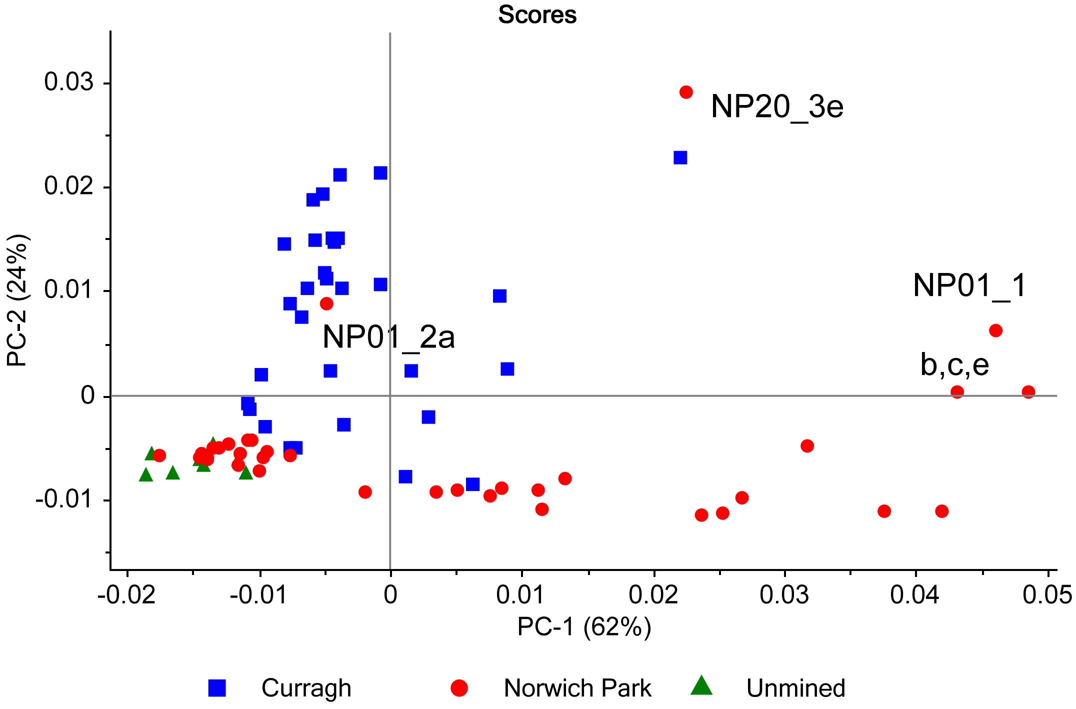

Figure 28 PCA of 2013 collected samples scores plot of CO_2-EGA data area normalized. Unmined sites are comprised of samples from both mines and have minimal surface disturbance. Thus, they are somewhat similar to natural soils in that the profile has not been removed and replaced for the purpose of mining.

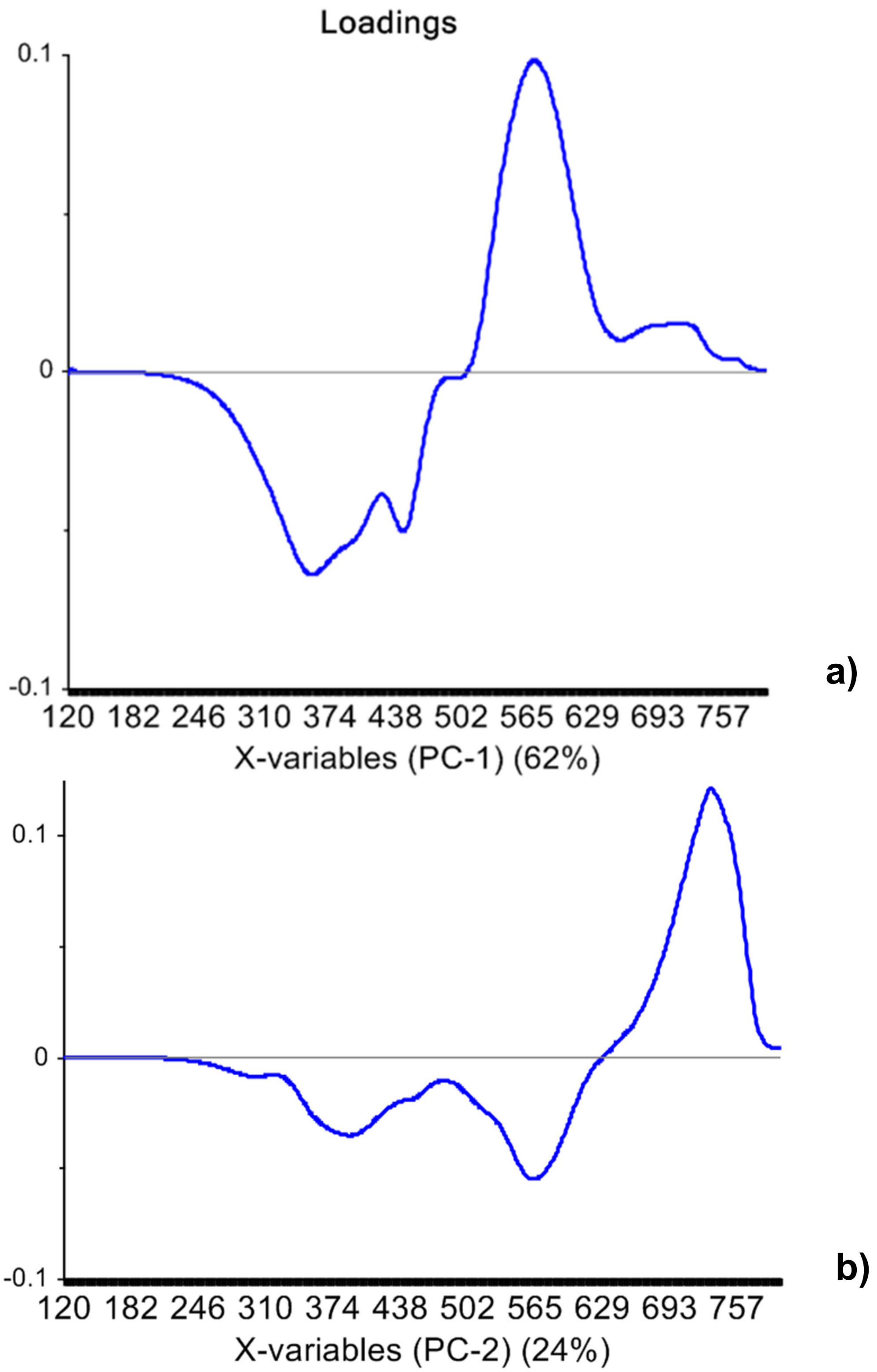

Figure 29 a) PC-1 and b) PC-2 loadings for CO_2-EGA area normalized samples, the x-variables units is temperature in °C

The loadings of the principle components showed that for area normalization, PC-1 (Figure 29a) that explains 62% of variance is of thermally stable carbon materials, as the peak is at ~570°C.

Outliers

If the samples used in the MCR are dissimilar, the MCR pure components may be calculated to fit the variance in the data set caused by the dissimilar samples or the analysis will produce larger residuals. As the CO_2 thermograms are dependent on the content of the mixture of carbon containing matter and its interaction with the mineral matrix, if thermograms differ from the majority of samples, it is indicative that a variation exists in the carbon containing matter or possibly, in the matrix (Peltre et al., 2013; Ascough et al., 2011).

To detect whether the MCR pure components are overly influenced by potential outliers, thereby producing poorer carbon pool apportioning, outlier samples were removed from the MCR analysis to examine the impact on the pure components and carbon apportioning.

The influence plot provided in the PCA overview graphs (Appendix H) showed that three spoil layer samples, NP01_1e, NP20_3e, and CU17_1e were outliers as they appeared in the upper right of the graph. When outliers were removed from the MCR-ALS analysis, five samples had changes in the carbon pools of <1%C. The most notable change was in German Creek coal, where all carbon was attributed to either BC or GC instead of as coal carbon. The component peaks remained at the same temperature with minor changes in the tails of Component -1, which accounted for inorganic carbon. As the difference was minor, it was decided to keep the outliers in the dataset, but it was noted that the prediction for these samples would be relatively poor since they did not fit the model well.

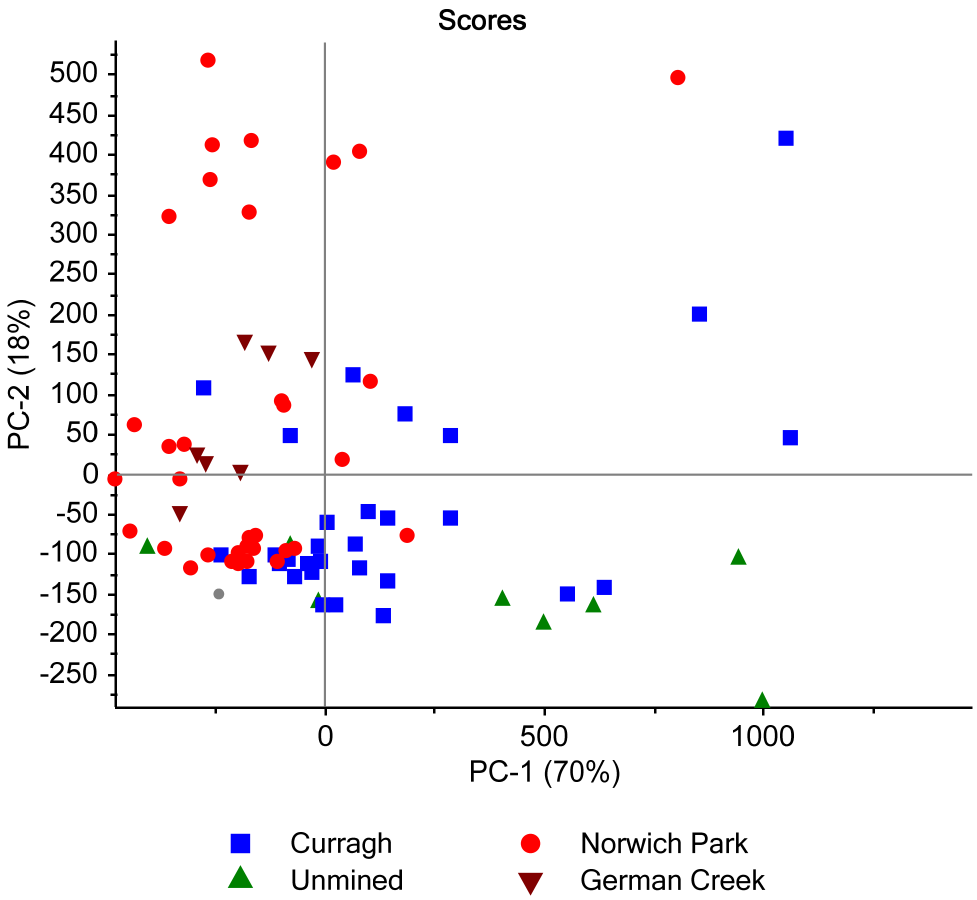

Figure 30 PCA of 2013 collected samples scores plot of CO_2-EGA mass normalized

For comparison to area normalizion, a PCA was performed on the mass normalized EGA data (Figure 30). PC-1 explained 70% of variance and was representing more labile carbon materials, as can be seen by the loadings plots. PC-3 was the inorganic carbon, and this PC explained 6% of variance (Figure 31).

The mass normalized PCA was optimized at 3 components with 94% of the variance explained while the area normalized PCA was optimized at 4 components.

Table 10 PCA explained variance by number of principal components for mass and area normalizations

Normalization		PC-1	PC-2	PC-3	PC-4	PC-5
Mass	Calibration set	70.12	88.13	94.50	96.44	97.60
	Validation set	68.14	86.97	93.39	95.36	96.33
Area	Calibration set	62.27	85.89	90.14	93.85	95.75
	Validation set	62.23	84.81	87.06	92.24	94.02

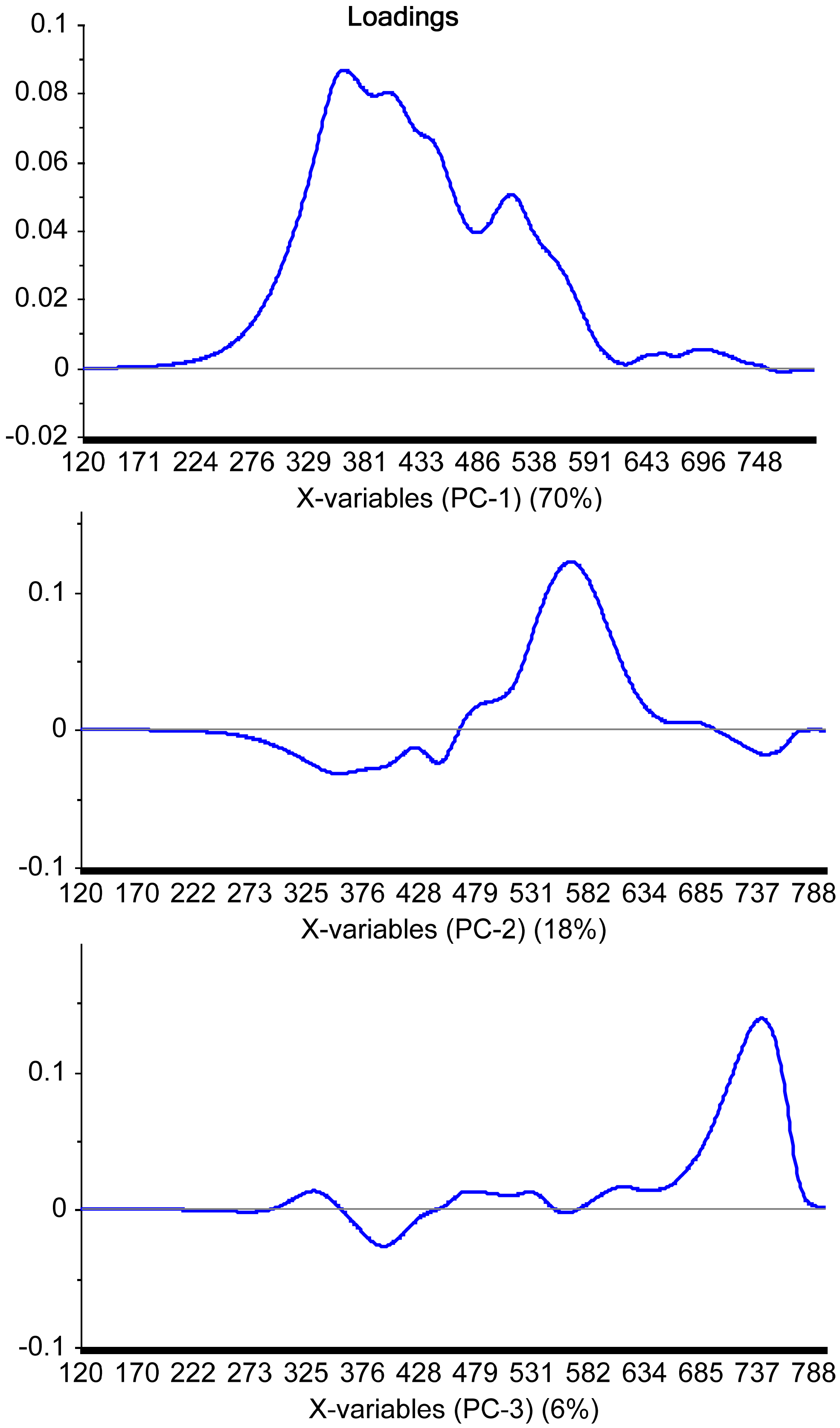

Figure 31 PC-1,2,3 for mass normalized CO_2-EGA PCA, the x-variables units is temperature in °C

The difference in the pure components identified from the two normalizations can be seen when running MCR-ALS (See Figure 32). In both cases the coals and char were included in the sample set, but not identified as pure components and component number set to six.

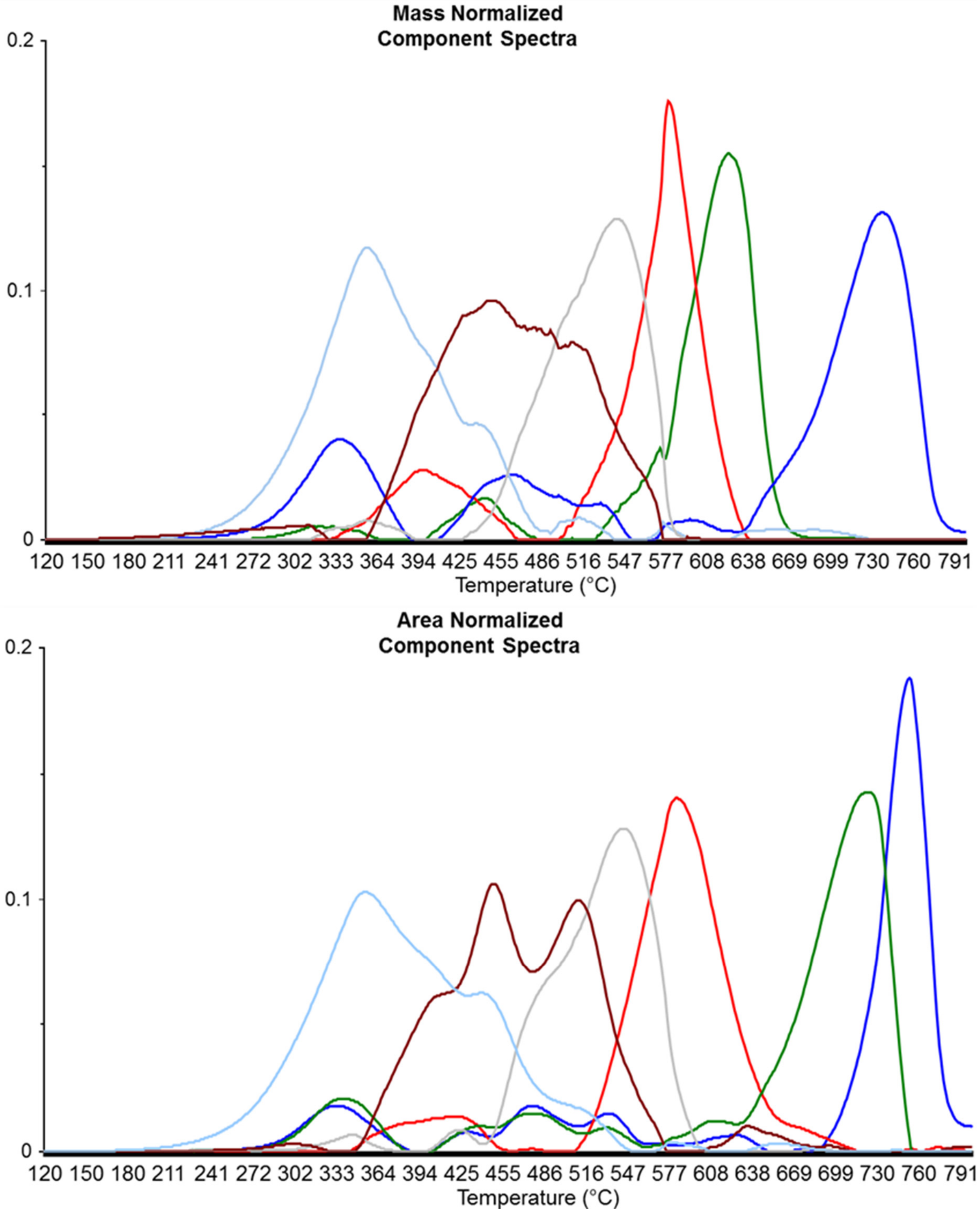

Figure 32 6-Component solutions for MCR-ALS of mass and area normalized CO_2-EGA data with coals and char included but not identified

Along with the change in the shape of the components, the sample residuals change. This means that the models fit their respective datasets quite differently as the residuals change for each sample. Samples that are not well described by the MCR-ALS solution will also have high residual values.

MCR Optimization and Interpretation

In this application of MCR-ALS, when optimizing the solution, it is important to visually inspect the components to determine if they can be interpreted. Another source of information on the optimal number of components in the solution, when rotational ambiguity exists, is to look at the total residuals. Area normalization was chosen to control intensity ambiguity, as area normalization effectively makes all samples equal in carbon richness. When MCR-ALS is run with coals included in the analysis, but not identified as pure component estimates, the analysis finds convergence at 5 and 6 components when sensitivity to pure components is lowered and the number of iterations is increased (Figure 33 and Figure 34). The y-axis is arbitrary as the component curves are unit-vector normalized (Tauler, 2016).

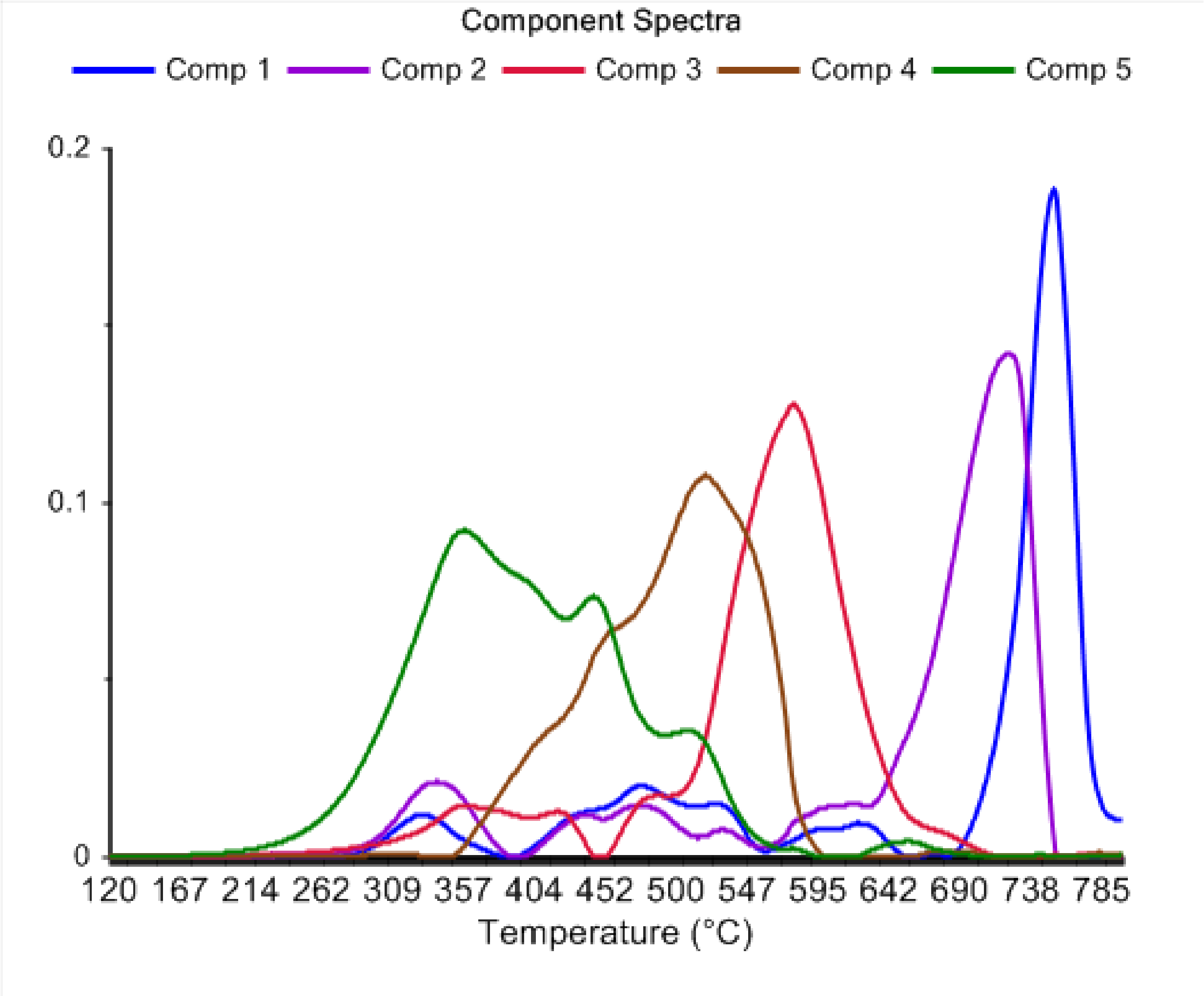

Figure 33 MCR-ALS component spectra for all soils from area normalized, coals and char included but not identified

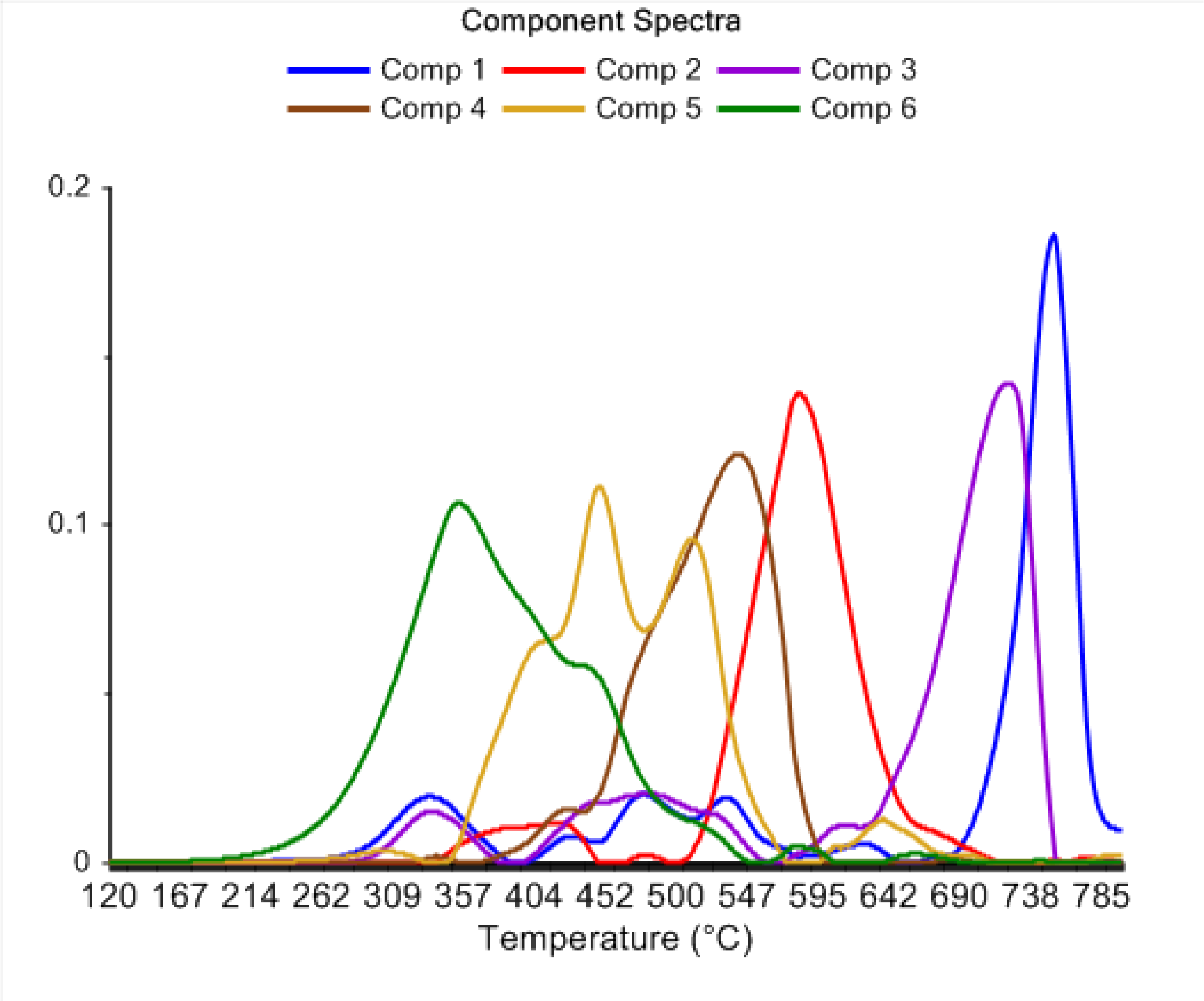

Figure 34 MCR ALS component spectra for all soils area normalized, coals and char included but not identified

A comparison of the component spectra of area normalized MCR-ALS with coals and char included in the sample set versus excluding them (soils only) is below. The number of components was decided based on the total residuals (Figure 35). As the CO_2-EGA data had been area normalized, there are no units for the y-axis of the residuals plots, but rather the intensities of total residuals should be considered.

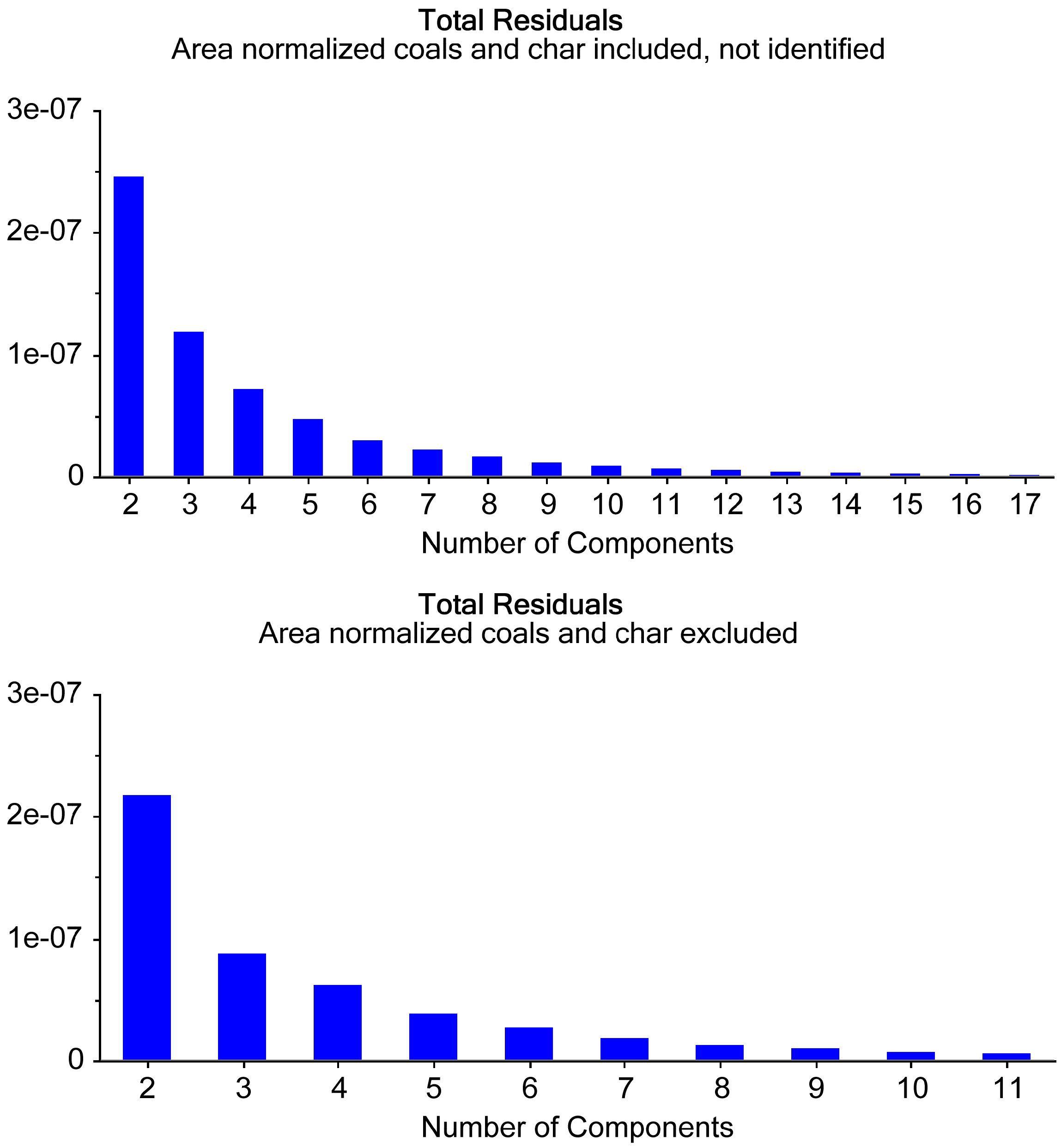

Figure 35 Total residual graphs of area normalized CO_2-EGA data with and without coals and char included. Area normalization of the data renders the y-axis unitless and should be considered only as intensity.

The decreases in total residuals with increasing number of components drops off at around 5-6 components indicating that using more components would effectively be modelling noise in the data.

Based on the peak temperatures and the shapes of the curves, the components were classed as green carbon, coal, char and inorganic carbon.

Discussion

The 5-component solution MCR-ALS component concentrations of a selection of soil samples using area normalization was selected for discussion below. Coals and char were included in the sample set, but not identified as pure components (see Figure 33).

There were several problems that arose with the use of MCR. These included the fact that the classes of materials (black carbon, coal and green carbon) encompass a range of materials with differing combustion profiles. There was also the issue of rotational ambiguity, where MCR determines there are multiple solutions (Abdollahi and Tauler, 2011). However, when different samples were included in MCR-ALS analyses (i.e. including coals and char in the data set with or without identifying them as pure components) the components had largely similar trends and the total residuals also remained similar.

To create the BC, Coal and Green Carbon values to input to a PLSR-DRIFT model, area normalized data MCR results were chosen as it was seen that proportional contributions were well correlated (See Chapter 6). As different coals have differing carbon levels and peak combustion temperature and are different again to the char (which itself is part of a continuum), to optimize the MCR solution, it would be beneficial to include samples of coal or BC that could reasonably be expected to be present in the samples. In the case of coal mine soils, locally mined coal could easily be included in the sample set.

Number of components

The rotational ambiguity, where there are multiple solutions to the MCR equation (Equation 4), present in this application of MCR-ALS may be promoted by the ambiguity in each of the carbon pools being modelled. Green carbon, BC and coal each contain a spectrum of different molecules.

To compare between six and seven components, the BC and coal curves were combined to create one class, as the additional curve in the seven component system is in the BC and coal temperature region. Seven-component systems tended to attribute more carbon to BC/coal than the six-component systems with only three samples decreasing in value, all of them from one pit (NP20_2). The average change in BC/coal values was a 32% increase from the mean value between the two cases. The increase in the BC/coal contributions resulted in a trade-off from the lower temperature green carbon component and both inorganic carbon components, since these have tails running through the same temperature ranges as BC and coal. The component concentrations are found in Appendix F and Figure 32.

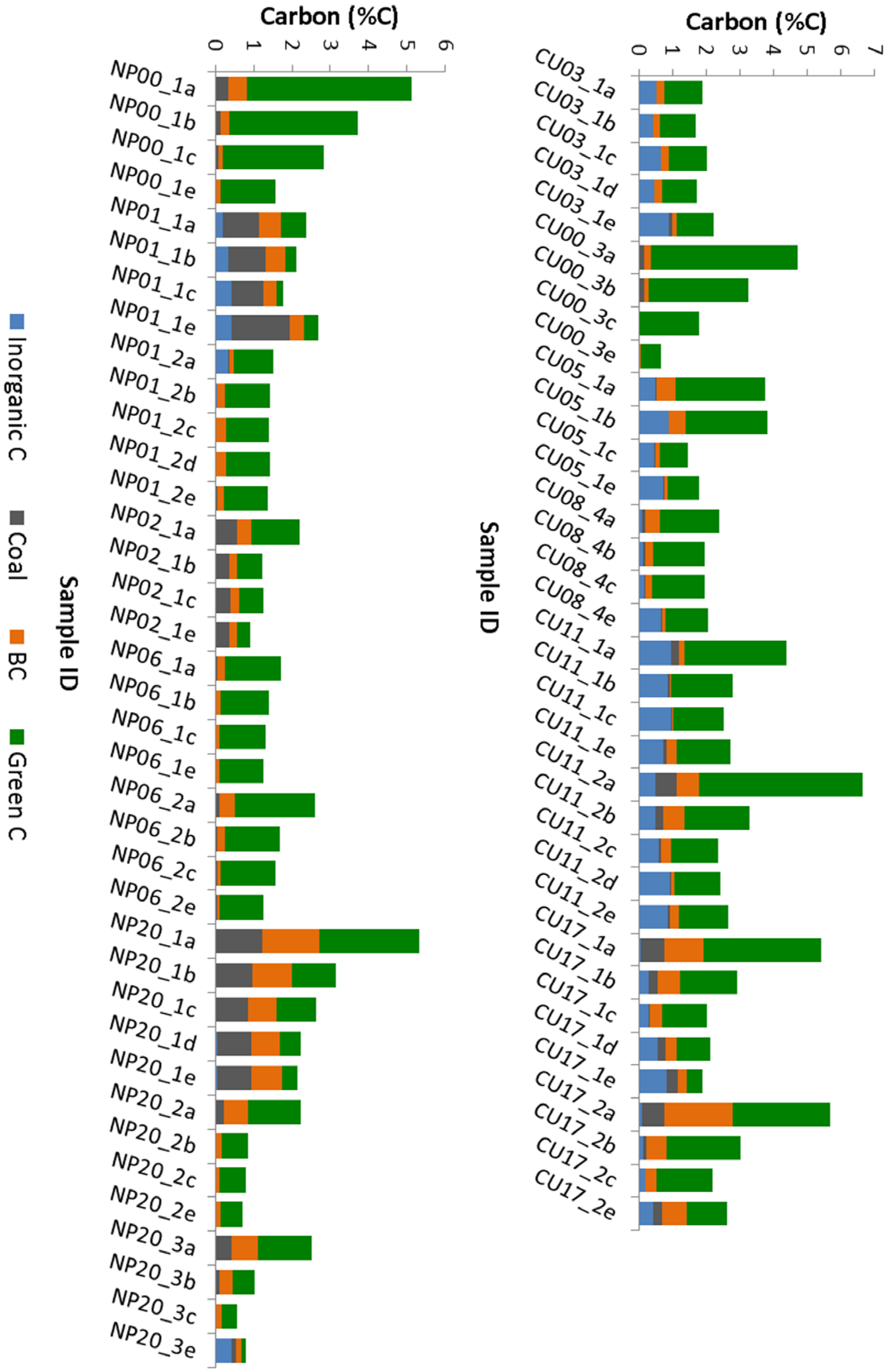

Figure 36 Carbon pools apportioned to soils from Curragh and Norwich Park mines

Sensitivity testing

To test the sensitivity of MCR-ALS, four samples of known mixtures of a minesoil (BW19_2d) with char and coal were added to the data set while the pure char and coal samples were removed. These mixtures are described in Chapter 6 and were the 2% carbon added 1:1, 3% carbon added 1:2, 1:1, 2:1 charcoal to coal. These four mixtures were chosen as to not outweigh the number of pure char and coal samples being removed. The new components concentrations were compared to the concentrations from the solution that included the pure char and coal samples. Calculated concentrations of coal and char for the mixtures were compared to the predicted amounts.

Based on the total residuals graph and selecting to separate coal and BC, a six-component solution was selected. The components were divided into two green carbons, and one of each BC and coal, and two inorganic carbons with peaks at ~ 350°C, 440°C, 550°C, 590°C, 710°C and 750°C respectively (Figure 37).

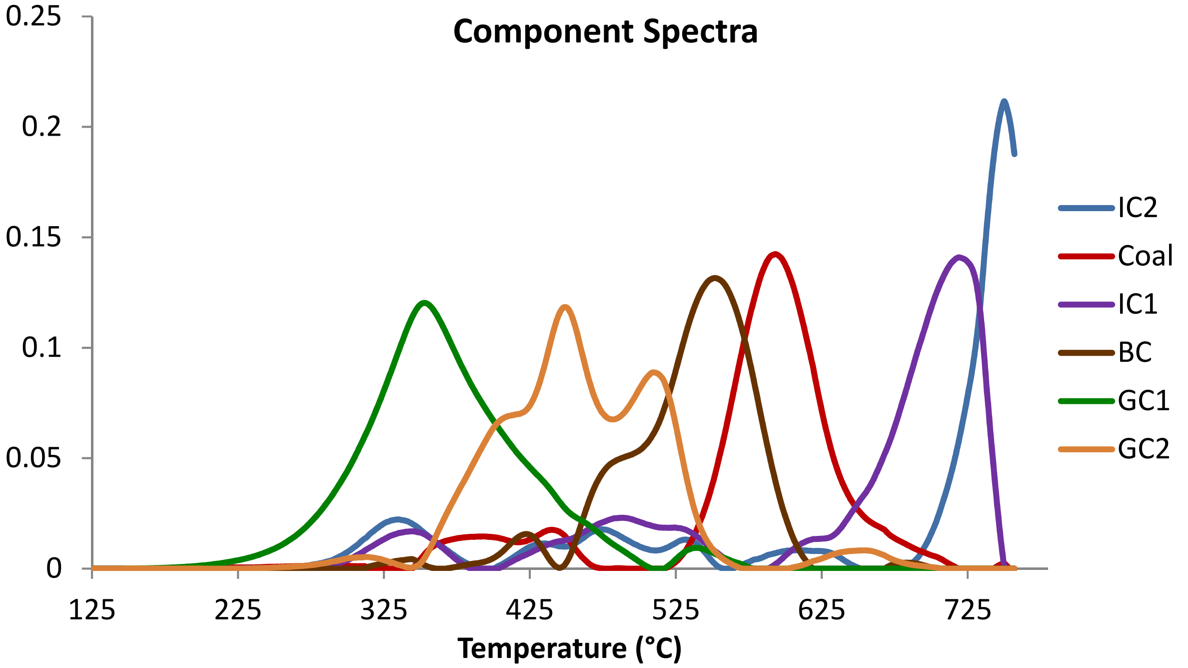

Figure 37 MCR-ALS components derived when pure coals and BC are replaced with minesoil mixtures with coal and BC

The changes in the values were generally an increase in green carbon and a decrease in coal and inorganic carbon values. The greatest absolute change was

0.6%C increase of green carbon in a surface sample (Figure 38). This amounts for a 22% increase from the model including pure coals and char.

The MCR-ALS component concentrations for the mixtures of minesoil with BC and coal were highly skewed to BC and green carbon, with the 2:1 BC to coal mixture reporting 0% coal while green carbon levels were also inflated (Table 11).

Table 11 MCR-ALS modeled carbon pools of mixtures of minesoil with BC and coal

Minesoil ID, target C level (BC:Coal)	Coal (%C)	BC (%C)	Green carbon (%C)	Sum total carbon (%C)
BW19_2d 3%C 1:1	0.039	1.360	1.653	3.052
BW19_2d 3%C 1:2	0.125	1.440	1.560	3.125
BW19_2d 3%C 2:1	0	1.285	1.775	3.06
BW19_2d 2%C 1:1	0.004	0.559	1.393	1.956

There was bias in this MCR-ALS model towards the less thermally stable pools. This change could be in response to the different source materials of the known mixtures that were used to replace the pure coals and BC. The mixtures were made from a soil from Blackwater mine combined with chestnut char and Goonyella coal. The PCA scores plot of DRIFT spectra in Chapter 7 indicated that samples from these minesoils were quite different from Curragh and Norwich Park samples. Regardless, this highlights the importance of having similar soil samples and pure coals/BC in the MCR-ALS analysis.

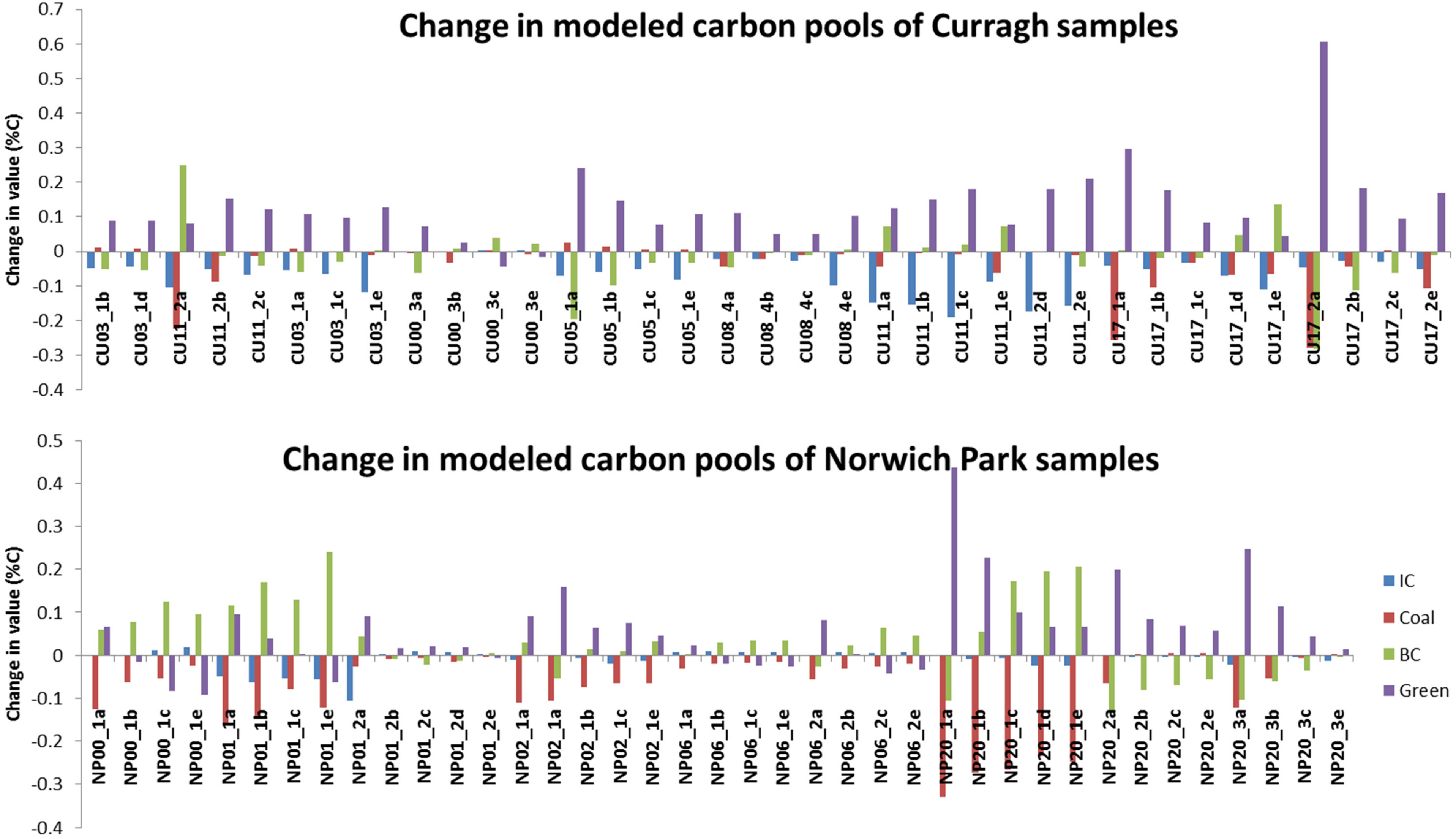

Figure 38 Changes in carbon levels of MCR-ALS models when pure coal and char samples are replaced with minesoil/coal/char mixtures

Recommended MCR-ALS Settings

In the tutorials accompanying the Unscrambler X software (2011), it recommended that initial guesses should only be used when all pure components are able to be identified. Furthermore, it warned that the results will be erroneous if only some of the pure components are identified as initial guesses.

Since it is impossible to have a pure component for soils containing SOM yet free of coal and BC, as BC is ubiquitous (Krull et al., 2008, Skjemstad et al., 1996), it is recommended that samples of BC and coal are included in the MCR-ALS analysis, but not identified as pure components. An alternative to this would be to create an artificial soil by adding pure organic matter to a mineral matrix. However, this may not produce CO_2-EGA curves that approximate naturally weathered and biologically transformed SOM as found in actual soils. Reducing the sensitivity to pure components does not compensate for the poorer fit of the produced components. However, if coals from the same locality as the soils used in the analysis or alternatively, a coal that is likely to be present in the soils is available, it should be included in the data set but not identified as a component.

Since the area normalized data shows the relative contributions of the different carbon fractions in a sample better than the mass normalized data it is the preferred normalization. It is because MCR-ALS is sensitive to the high carbon levels of the coal and black carbon relative to soils in mass normalized CO_2-EGA data that makes mass normalization inappropriate when carbon-rich pure samples are included (Tauler, 2016). Furthermore, using area normalization solves the problem of intensity ambiguity of the component solutions (Abdollahi and Tauler, 2011).

The chosen MCR-ALS Unscrambler settings for determining the different carbon fractions were as follows:

Samples of coals and BC were included in the data set but not identified as pure components. All soil samples were included, even outliers, as these did not change the components, since their numbers were few, but rather, had high residuals. CO_2-EGA data were area normalized. Sensitivity to pure components was reduced to 25 while iterations were increased to 150.

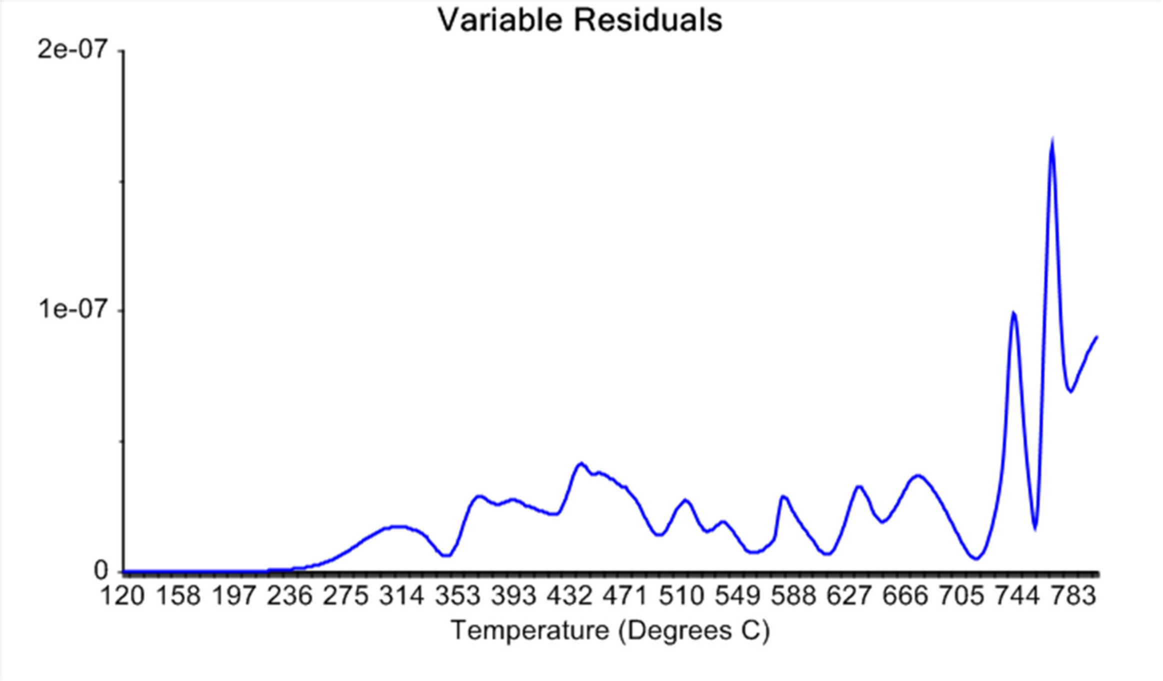

Figure 39 Residuals from 6-component solution, area normalized, reduced sensitivity to pure components

The selection of the number of components depends on the operator’s assessment of the residuals and individual component peak temperatures (Figure 40 and Figure 41). Figure 39 shows the temperature at which the residuals are accruing. In the system with pure coals and BC included, the residuals appeared to peak in the inorganic carbon temperature range (<700°C). There were also residuals in the green carbon temperature range. This may be reflective of the variety of different thermal stabilities of SOM.

The component spectra (Figure 40) is interpreted as having two green carbon components, a BC component as well as a coal and inorganic component. These can then be applied to the samples to assess carbon pool levels in those soils as seen in Figure 42.

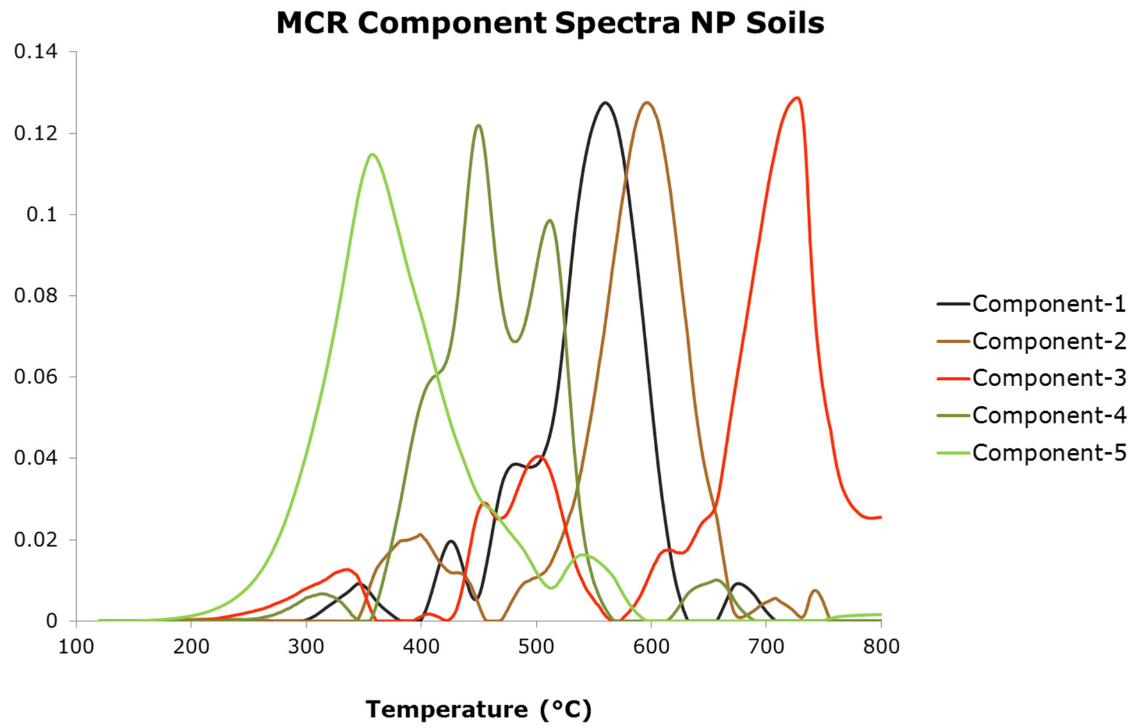

Figure 40 Pure components identified by MCR analysis of all Norwich Park TA-EGA thermograms without pure coal or BC thermograms included nor identified as component estimates. The general shape and peak temperatures of the components give the impression of inorganic carbonates, coal and charcoal curves.

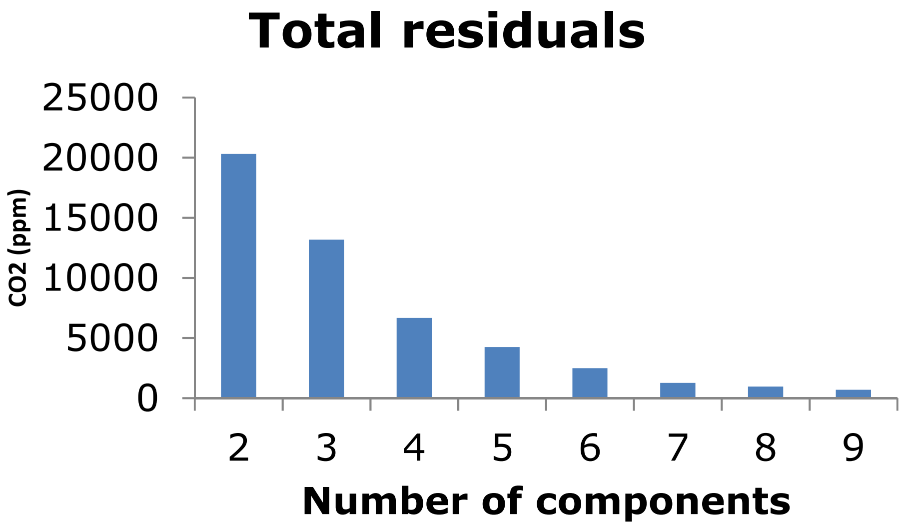

Figure 41 Total residuals from MCR analysis of Norwich Park soils with no pure coal or BC thermograms included nor identified.

Application of MCR-ALS to minesoils: an illustrative example

The high heterogeneity of minesoils makes it difficult to draw broad conclusions about the impact of land management decisions. However, it is possible to illustrate what MCR-ALS does reveal in a few pits for example.

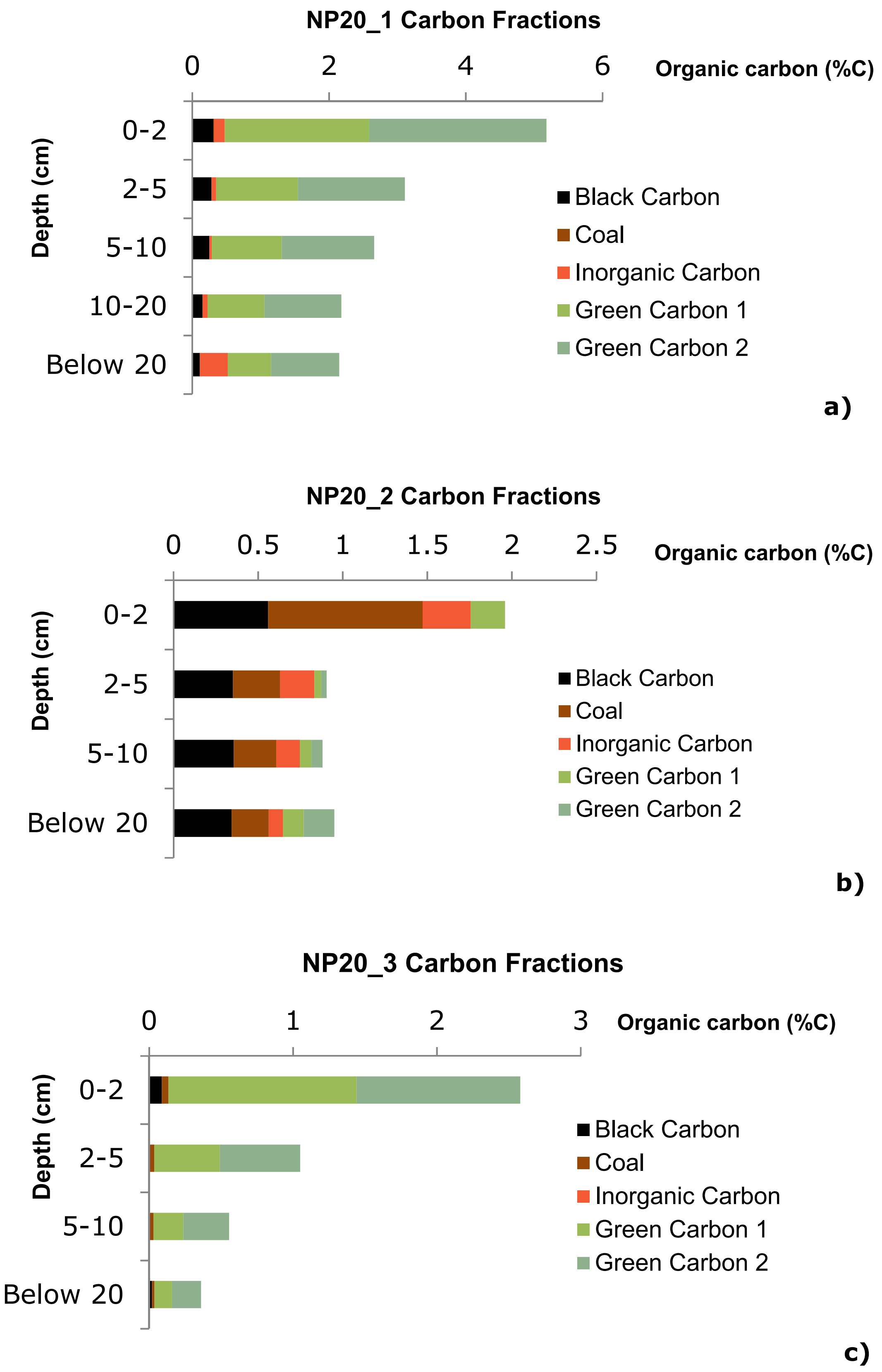

Figure 42 Three examples of the application of the MCR predictions of BC, coal, IC and green carbon contributions down a soil profile. All three sites are 20 years old rehabilitation at Norwich Park coal mine with buffel grass cover. a) southerly aspect, clay soil, topsoil not applied b) southerly aspect, topsoiled c) westerly aspect, topsoiled

Three pits from Norwich Park were chosen as having the same age of rehabilitation and same buffel grass cover (Figure 42, Appendix C). All three are expected to have undergone similar rehabilitation treatment. This does not mean that the sites are equivalent, since the topsoil cover layer used could have been from disparate collection sites and there is no documentation to trace the source nor application methods. However, along with other stochastic variables, such as slope position and aspect, this was the closest approximation to similar sites there was available. Collection notes stated site a) was a clay soil while site b) was expected to have high electrical conductivity due to observed piping. However, site b) had significantly lower electrical conductivity (23-51 µs/cm) than sites a) and c) which ranged from 66-393 µs/cm and 46-596 µs/cm, respectively. Sites a) and c) also had a more alkaline pH, all measuring above pH 7, with the highest being pH 9.57 in the spoil layer, while site b) ranged from pH 6.18-7.45. The colour of the topsoil in site c) was notably lighter in colour to a) and b) with spoil visibly mixed into the topsoil.

Despite the three example sites in Figure 42 having the same buffel grass cover and age, site b) is very different from the other two in having proportionally higher levels of coal and BC, lower pH and electrical conductivity. All three pits showed that coal and BC tend to be at higher levels near the surface. It would be expected at sites of greater rehabilitation age to have accumulated coal dust from aeolian deposition. The inconsistency between site observations and measured characteristics as well as the variability in carbon source compositions highlights the high heterogeneity in minesoils which complicate field-scale calculations requiring high numbers of samples.

Conclusion

Without any further information, MCR is able to produce pure component spectra. The number of components was reduced from the initial eight components produced by the software to five by toggling the component number setting. This increased the total residuals (unexplained signal) from 957 ppm CO_2 to 4252 ppm CO_2.

Applying the MCR predictions to the mine soils involves the multiplication of the acidified Dumas TOC results by the percentage contributions of each component. By doing this, an estimate of the BC, coal, and green carbon levels in each individual soil sample included in the MCR analysis is produced (see Figure 36 and Figure 42).

The presence of inorganic carbon complicates the analysis by introducing an additional carbon source with its resulting MCR components potentially contributing to uncertainty in the results; particularly if the shape of the tail for the IC component(s) includes peaks at temperatures associated with other carbon pools. MCR-ALS provides a purely mathematically driven solution and could conceivably include less thermally stable carbon in the IC component if it fits the data. The use of MCR-ALS on CO_2 EGA data requires further investigation and validation for use in calcareous soils.

The sensitivity test indicated that it was very beneficial to spike the sample set by including pure samples of BC and coal to give more weight to these carbon sources and avoid skewing the results towards the less thermally stable pools. An alternative way that may improve results is to restrict the samples in the MCR analysis to soils that are very similar. Further investigation into the effects of sample size and similarity is recommended.

8.2 Comparison of TA-EGA mine soil BC predictions with SCaRP MIR BC prediction (Validation)

Concurrent with the research for this PhD, the Commonwealth Scientific and Industrial Research Organisation (CSIRO) was developing an infrared spectroscopic model for predicting, amongst other things, several SOC fractions, including a measure named “resistant organic carbon” (ROC) (Sanderman et al., 2011). This fraction was intended to be used in Roth-C models for carbon cycling and represents the inert carbon pool. ROC was empirically determined using solid state ^{13}C NMR (Baldock et al., 2013b). ROC is considered to largely contain BC and potentially lignin as it contains aryl-carbon; the lignin contribution is corrected for by subtracting an averaged lignin signal from the NMR spectra (Baldock et al., 2013b, Skjemstad et al., 1999, Skjemstad et al., 1996). It was noted that cross-polarisation (CP) ^{13}C NMR had a weaker signal for the aryl-carbon than direct-polarisation (DP), which is a significantly more time intensive analysis. A correction factor was developed from 38 split size fractions, or 19 different samples, roughly 6% of the total number of NMR analysed soil fractions.

There are a few key points to consider when comparing a BC measurement with ROC. First, an ROC measurement might be greater than BC since it could include some portion of lignin-carbon. Second, the use of the CP/DP correction factor adds a source of error. Third, any infrared prediction model can only produce good results for new soils that fit the model set. 312 soils were used to build and test the ROC prediction model to be used for all Australian soils. These soils are natural soils, not the highly disturbed Anthroposol of mine soils.

Despite the large number of samples in the TOC calibration and the generally good levels of prediction, the Queensland calibration of SCaRP data has been seen to over-estimate TOC (Page et al., 2013).

Method

A set of ball milled mine soils were analysed at the Queensland State Government's Department of Science, Information Technology and Innovation Ecosciences Prescinct Boggo Road soil laboratory by MIR and predictions from the SCaRP calibrations were made. See Chapter 7 for a full description. The same set of soils were analysed at QUT with the BC prediction following the procedures set out in Chapter 7 and Chapter 1.6, respectively.

Soil mass correction factor

As SCaRP predictions are given in mg ROC/kg soil, and a number of samples sent for analysis were sieved to pass 0.2 mm prior to analysis, correction factors were calculated for the sieved samples. Individual correction factors were calculated using the equation below:

$$x = \frac{fines}{fines + coarse} \qquad \textbf{Equation 8}$$

Where, fines is the mass of the sieved soil, and coarse is the mass of the removed particles.

Results from the SCaRP calibration were multiplied by their individual correction factors. Where correction factors could not be derived due to lack of sample, a general correction factor was applied as the average of the correction factors calculated (average correction = 0.813, n = 13).

Results and Discussion

The paired t-test between the ROC values and the BC values from MCR could not reject that the two were from the same population ($n = 73$, two-tailed $p = 0.91$). Figure 43a) shows that there was not a strong correlation between BC and ROC. When coal was included with BC in Figure 43b), it is seen that in this suite of samples, those with low ROC values were more highly impacted than those with high ROC values, where some samples exhibited BC and coal values 10 times greater than the ROC value.

The samples that had the greatest deviation from the target 1:1 line all originated from one 20 year old rehabilitated pit. Similarly, all but one sample from the tree covertype with greater BC than ROC came from one 17 year old rehabilitated pit.

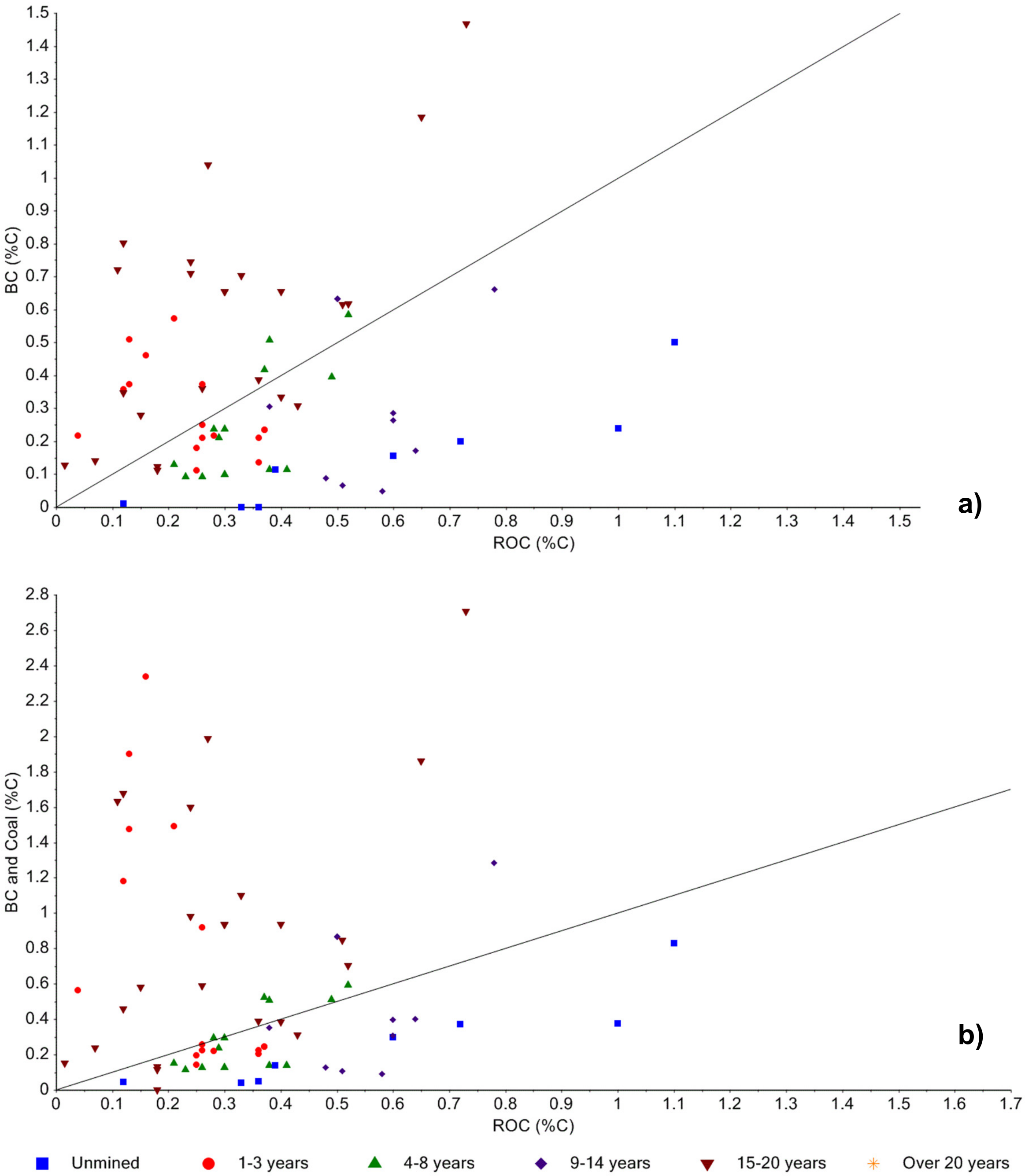

Figure 43 ROC from SCaRP MIR calibration compared with a)black carbon and b)sum of black carbon and coal as determined by TA-EGA with MCR-ALS with samples grouped by age of rehabilitation

When the area normalized thermograms were inspected, it was evident that the 20 year old site thermogram included a large peak above 500 °C, indicating a significant amount of thermally stable BC (Figure 44). The differences ranged from 0.5-0.8 %C accounting to 300-700% greater BC than ROC values. The 17 year old rehabilitated samples had a strong IC peak that may have contributed to the differences in the BC and ROC values.

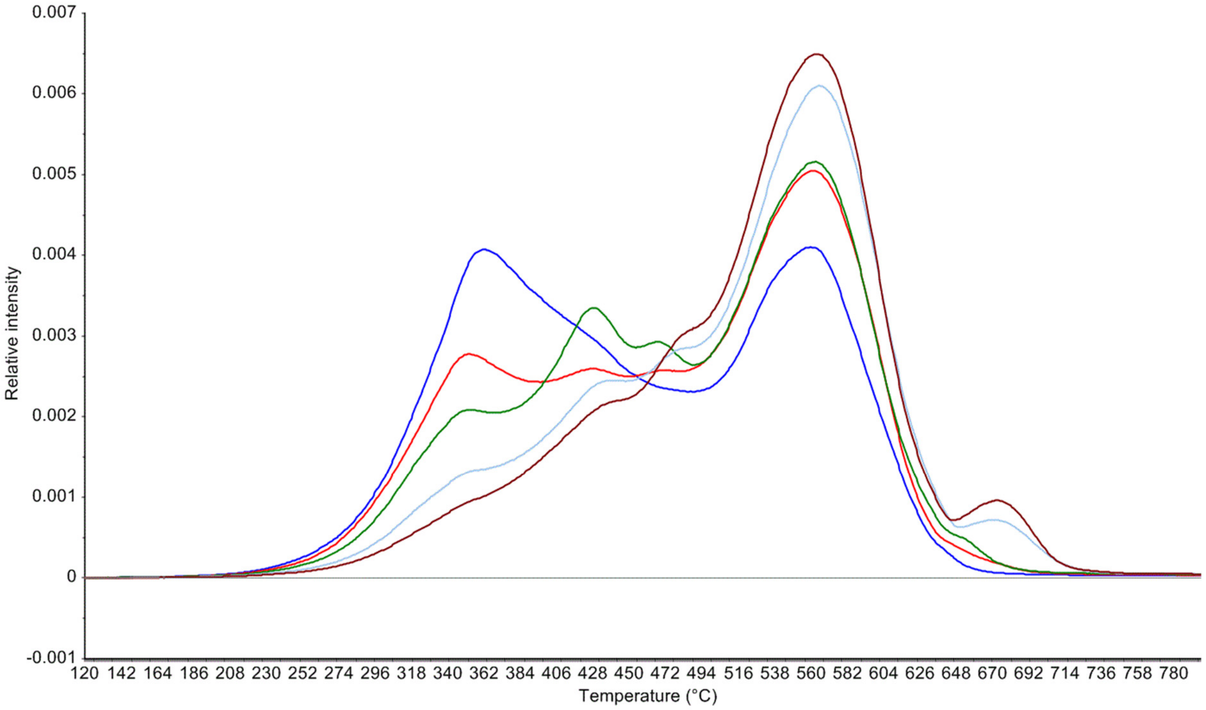

Figure 44 Area normalized CO_2-EGA thermograms of pit NP20_1 samples

While the dataset was too small to determine any significance, it was noted that unmined, tree and bush covertype samples tended to have higher ROC values than BC.

Conclusion

As there was not a strong correlation between BC and ROC it may be concluded that the two measurements are not similar enough to consider the two to be the same for this set of samples. There does remain the question of whether ROC, while well predicted by MIR (see Chapter 6.3) is a good predictor of BC and/or coal in minesoils. The thermograms of several high BC value/low ROC value samples (Figure 44) would indicate by the peak at ~570 °C, that there is significant levels of BC however their ROC values are low.

These results also raise the question of the molecular composition of the materials that are oxidizing at the BC peak temperature and how well these are modelled by MIR spectroscopy. It is possible that these more thermally stable materials are highly condensed carbon forms as these would not be detected using the NMR method that underpins the SCaRP ROC determination (Simpson and

Hatcher, 2004). Furthermore, this would agree with the theory of increasing thermal stability with increasing aromatic condensation (McBeath and Smernik, 2009).

It is possible that some minesoils may not be well modelled by the SCaRP calibration. Further examination of high BC value/low ROC value minesoils with NMR spectroscopy would clarify the disparity between the two values.

9 Conclusions and Further work

The aim of this research was to develop a method to determine the quantity of green carbon, the soil carbon attributable to rehabilitation in minesoils, indirectly from the difference between TOC and the sum of BC and coal (see Equation 2) as a means to assess the effect of land management on SOM levels. Additional hypotheses of whether green carbon could be predicted using DRIFTs and if there is a difference in GC levels between different ages of rehabilitation and depth were also investigated. Towards these ends, a novel thermal definition of BC was created through the integration of CO_2 evolution data and the chemometric technique multivariate curve resolution. It was shown that this method, thermal analysis with MCR-ALS, could differentiate between coal and BC, two materials with significant overlap in their combustion signatures (see Figure 13). This development is an improvement over other BC measurement techniques that cannot separate these two carbon-rich materials (e.g. UV photo-oxidation, TG-DSC) and is able to separate “recent” inputs into GC and BC, unlike radiocarbon analysis (Rumpel et al., 2000, Ussiri and Lal, 2008b). Attempts to predict GC as defined by the thermal analysis/chemometric method using mid-infrared DRIFT spectroscopy produced models with relatively high prediction error, ranging from 0.12-0.43 %C.

Characterization of the collected minesoils showed that minesoils from Bowen Basin coal mines can vary in carbon content, texture and bulk density on small scales. This is most likely due to the method of the creation of the landforms from which the samples were collected and agrees with the findings of high variability of Shukla et al. (2007) and Sencindiver and Ammons (2000). Most minesoils included in this study were classed as clay or contained >25% clay (Figure 10). The high levels of clay would suggest the potential to store high levels of organic matter in these minesoils. However, there was not a strong correlation between carbon content and clay content (Chapter 5). It was also demonstrated that there is variability in the carbon pool contributions within pits and between pits from the same mine and of the same rehabilitation age in by comparing three 20-year old rehabilitated pits (Figure 42). Despite the known high levels of variability samples could be differentiated by minesite by PCA of DRIFT spectra (Figure 21). This would indicate that while minesoils have high local heterogeneity, they are not so heterogeneous as to be indistinguishable from each other. However, the source of this differentiation was not investigated and there were an insufficient number of independent samples from different covertypes and/or age groupings to examine trends; furthermore, it could arise from the different topsoils applied during rehabilitation.

Also demonstrated was the use of different thermal combustion signatures of separate carbon fractions can be used to differentiate them in minesoils. MCR can separate fractions with greatly overlapping combustion signatures. However, this technique requires interpretation of the solutions resolved by the algorithm, and thus, some prior knowledge of what might be expected is required and may be open to operator error.

Ussiri and Lal (2008b) reported a trend of increasing coal and older carbon with depth. This trend, however, was not evident in the soils tested from Curragh and Norwich Park (see Figure 32, Figure 42). Older rehabilitated samples did, however, have higher levels of green carbon nearer the surface, and decreasing with depth. This is consistent with the view of carbon inputs entering mainly from the surface and was also exhibited in unmined sites (Figure 36). If using 1.6%C as an average GC concentration for Curragh mine soils at the 5-10cm depth, and 1.04 g/cm^3 as the average bulk density for that depth, there would be 35.4 tonnes/ha to a depth of 20cm of GC.

In Chapter 7 the best MCR analysis included all coal samples (multiple mines) and charcoal along with all of the soils without identifying any initial guesses. This allowed more components to be identified as the Unscrambler sets the number of components based on the number of initial guesses if used. Constraints applied included non-negativity in component concentrations and spectra. The maximum number of alternating least squares iterations was 150 and sensitivity was reduced to 25. Thermograms were normalised by area (CO_2 detected). Amounts of BC and coal were calculated by multiplying their component percentage contribution by TC.

Further testing of MCR-ALS with soils containing inorganic carbon, varying sample set size and similarity, spiking with different carbonaceous materials and the effect of acid treatments to remove inorganic carbon is recommended.

DRIFT

The potential for quick analyses with relatively low sample preparation requirements have prompted the investigation into whether GC can be determined using MIR DRIFTs. The contributions for the three carbon fractions, (coal, BC and GC) were used in building a PLSR model with minesoils. The model was cross validated using a set of samples that were excluded from the prediction set as well as compared to the prediction of ROC from SCaRP as a form of validation. That the fractions modelled by MCR-ALS were not well predicted by infrared spectroscopy, when using SCaRP ROC values as comparison, may indicate that the spectral library upon which the PLSR model is built is not sufficiently large enough to overcome the large variability in minesoils. Better results might yet be achieved with different spectral pre-processing. Additionally, it may be that the relative immaturity of the soils have not allowed the physicochemical interactions of SOM with the mineral matrix to come to equilibrium, further differentiating minesoils from natural soils and decoupling the linkage and correlation between the stability of SOM fractions and other characteristics of the soil, i.e. clay content. This would call into question whether ROC gives a satisfactory prediction for coal and BC in minesoils if they do not follow trends seen in natural soils. This is further strengthened by the sometimes large differences in BC/ROC quantities where the thermograms show highly thermally resistant materials are present in the minesoils.

The poor prediction of the MCR-ALS identified pools by DRIFTs modelling indicates that the pools are not tightly linked to the molecular structure of different SOM as can be detected by DRIFTs. This is supported by the various curves, shoulders, and tails of the different MCR components indicating that those pools are comprised of a variety of molecules with different temperatures of combustion. Further examination of the molecular moieties comprising the different pools may be beneficial in further defining the carbon pools.

A cost benefit analysis is recommended to determine the importance of fast analytical method (DRIFT) over the uncertainty in accuracy of using a spectral definition of BC for the intention of quantifying green carbon in mine soils. While large numbers of samples (~20 000) would be required to detect changes of 0.2-0.3%C, if the accuracy of the prediction is questionable it may be more advisable to increase the minimum detection limit and reduce the sample numbers. However, with the large volumes of mine soils under rehabilitation and the lack of research into methods to increase GC by large amounts, coarse minimum detection limits would be undesirable.

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Appendix A

BC Standard Soil Data Sheet

Wiesenboden (Vertisol) Australia

This soil is intended for use by scientists interested in developing and comparing methods for BC estimation in soils. Soil sample collected under the auspices of the "International Steering Committee for Black Carbon Reference Materials" (http//www.du.edu/~dwismith/bcsteer.htm). Soil collected and analyzed by CSIRO Land & Water, Adelaide, Australia. Samples treated with 50 KGy gamma radiation. Sterilization and analyses funded by Australian Greenhouse Office. CSIRO Land & Water cannot guarantee the accuracy or otherwise of the data presented on this sheet.

Chemical Analyses

pH$_{(water)}$ 1/5	pH$_{(CaCl2)}$ 1/5	EC (dS/m) 1/5	**OC[1] (gC/kg)**	TN[1] (gN/kg)	**BC[2] (gC/kg)**	IC[3] (gC/kg)
7.7	7.1	0.16	**32.7**	2.4	**10.4**	0.5

Exchangeable Cations (pH 8.5, cmol(+)/kg)

Ca	Mg	Na	K	Total
24.5	4.4	0.32	2.14	34.2

Particle Size Analyses (%)

Clay	Silt	Fine Sand	Coarse Sand
37	24	30	7

NMR Data (proportion of OC(%) in six regions)[4]

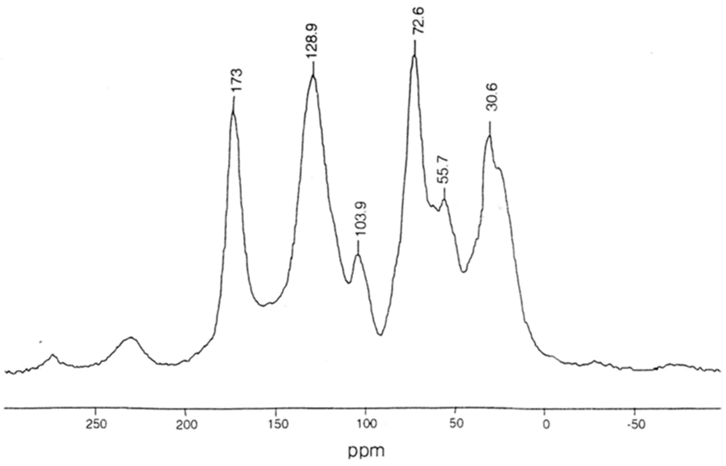
190-220 ppm (ald/ketone)	165-190 ppm (carbonyl)	145-165 ppm (O-aryl)	110-145 ppm (aryl)	45-110 ppm (O-alkyl)	0-45 ppm (alkyl)
0.8	13.9	3.3	30.3	32.5	19.2

[1] Leco CNS-2000 (Matejovic, I. (1997) Determination of carbon and nitrogen in samples of various soils by the dry combustion. *Communications in Soil Science and Plant Analysis* **28(17&18),** 1499-1511.)

[2] Photo-oxidation/NMR. (Skjemstad, J.O., Taylor, J.A., and Smernik, R.J. (1999) Estimation of charcoal (char) in soils. *Communications in Soil Science and Plant Analysis* **30(15&16),** 2283-2298.)

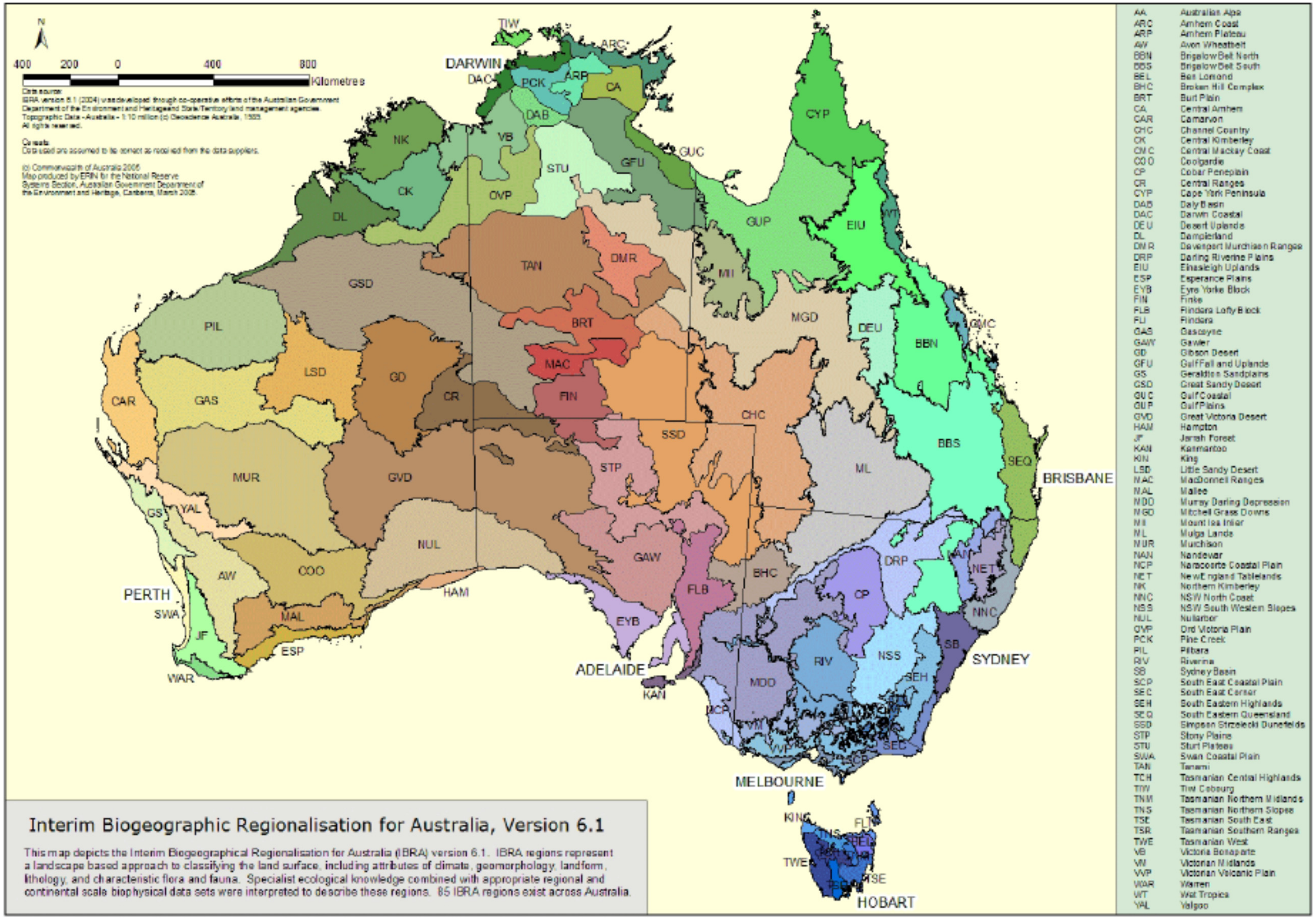
[3] Volumetric (Collins Calcimeter).

[4] HF treated soil. (Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., and Newman, R.H. (1994) The removal of magnetic materials from surface soils. A solid state ^{13}C CP/MAS n.m.r. study. *Australian Journal of Soil Research* **32,** 1215-1229).



Solid state ^{13}C NMR spectrum of HF treated Australian soil.

APPENDIX B



Interim Biogeographic Regionalisation for Australia, Version 6.1

This map depicts the Interim Biogeographical Regionalisation for Australia (IBRA) version 6.1. IBRA regions represent a landscape based approach to classifying the land surface, including attributes of climate, geomorphology, landform, lithology, and characteristic flora and fauna. Specialist ecological knowledge combined with appropriate regional and continental scale biophysical data sets were interpreted to describe these regions. 85 IBRA regions exist across Australia.

Data source:
IBRA version 6.1 (2004) was developed through co-operative efforts of the Australian Government Department of the Environment and Heritage and State/Territory land management agencies.
Topographic Data - Australia - 1:10 million (c) Geoscience Australia, 1998.
All rights reserved.

Caveats
Data used are assumed to be correct as received from the data suppliers.

(c) Commonwealth of Australia 2005
Map produced by ERIN for the National Reserve Systems Section, Australian Government Department of the Environment and Heritage, Canberra, March 2005.

AA	Australian Alps
ARC	Arnhem Coast
ARP	Arnhem Plateau
AW	Avon Wheatbelt
BBN	Brigalow Belt North
BBS	Brigalow Belt South
BEL	Ben Lomond
BHC	Broken Hill Complex
BRT	Burt Plain
CA	Central Arnhem
CAR	Carnarvon
CHC	Channel Country
CK	Central Kimberley
CMC	Central Mackay Coast
COO	Coolgardie
CP	Cobar Peneplain
CR	Central Ranges
CYP	Cape York Peninsula
DAB	Daly Basin
DAC	Darwin Coastal
DEU	Desert Uplands
DL	Dampierland
DMR	Davenport Murchison Ranges
DRP	Darling Riverine Plains
EIU	Einasleigh Uplands
ESP	Esperance Plains
EYB	Eyre Yorke Block
FIN	Finke
FLB	Flinders Lofty Block
FLI	Flinders
GAS	Gascoyne
GAW	Gawler
GD	Gibson Desert
GFU	Gulf Fall and Uplands
GS	Geraldton Sandplains
GSD	Great Sandy Desert
GUC	Gulf Coastal
GUP	Gulf Plains
GVD	Great Victoria Desert
HAM	Hampton
JF	Jarrah Forest
KAN	Kanmantoo
KIN	King
LSD	Little Sandy Desert
MAC	MacDonnell Ranges
MAL	Mallee
MDD	Murray Darling Depression
MGD	Mitchell Grass Downs
MII	Mount Isa Inlier
ML	Mulga Lands
MUR	Murchison
NAN	Nandewar
NCP	Naracoorte Coastal Plain
NET	New England Tablelands
NK	Northern Kimberley
NNC	NSW North Coast
NSS	NSW South Western Slopes
NUL	Nullarbor
OVP	Ord Victoria Plain
PCK	Pine Creek
PIL	Pilbara
RIV	Riverina
SB	Sydney Basin
SCP	South East Coastal Plain
SEC	South East Corner
SEH	South Eastern Highlands
SEQ	South Eastern Queensland
SSD	Simpson Strzelecki Dunefields
STP	Stony Plains
STU	Sturt Plateau
SWA	Swan Coastal Plain
TAN	Tanami
TCH	Tasmanian Central Highlands
TIW	Tiwi Cobourg
TNM	Tasmanian Northern Midlands
TNS	Tasmanian Northern Slopes
TSE	Tasmanian South East
TSR	Tasmanian Southern Ranges
TWE	Tasmanian West
VB	Victoria Bonaparte
VM	Victorian Midlands
VVP	Victorian Volcanic Plain
WAR	Warren
WT	Wet Tropics
YAL	Yalgoo

APPENDIX B

Taken from Chan, J., Baumgartl, T., Erskine, P., Glenn, V., 2015. ACARP Report C19029 Soil Organic Matter and Green Carbon in Rehabilitation: Their Role in the Carbon Balance

Sampling location coordinates

Blackwater Mine sampling locations, 23 -24 August, 2010.

	AGD_1984_AMG_Zone_55	
Site ID	**Easting**	**Northing**
BW00_1	690835	7360750
BW12_1	683873	7381255
BW14_1	686195	7349927
BW14_2	686174	7349911
BW18_1	686074	7356692
BW18_2	686073	7356691
BW18_3	686072	7356691
BW19_1	685670	7355848
BW19_2	685669	7355847
BW19_3	685667	7355846
BW31_1	684584	7371342

Curragh Mine sampling locations, 24 - 25 August, 2010 and 13 to 15 May, 2013.

	AGD_1984_AMG_Zone_55	
Site ID	**Easting**	**Northing**
CU00_1	688351	7403331
CU00_2	693154	7410450
CU00_3	693935	7405604
CU02_1	690533	7404375
CU02_2	690712	7403952
CU03_1	690192	7396786
CU05_1	690510	7404359
CU07_1	691746	7407167
CU08_1	690553	7398560
CU08_2	690552	7398558
CU08_3	690386	7400454
CU08_4	690325	7400558
CU10_1	689909	7398096
CU10_2	689910	7398103
CU10_3	692736	7408917
CU10_4	692696	7408860
CU11_1	690607	7398699
CU11_2	690605	7398660
CU13_1	690917	7398950
CU17_1	691533	7406280
CU17_2	691527	7406212
CU21_1	689314	7402745

German Creek mine sampling locations, 26 - 27 August, 2010.

APPENDIX B

Site ID	AGD_1984_AMG_Zone_55	
	Easting	**Northing**
GC00_1	661860	7463010
GC08_1	660359	7466681
GC08_2	657522	7455898
GC24_1	656916	7456494
GC26_1	660076	7463846
GC26_2	660076	7463841

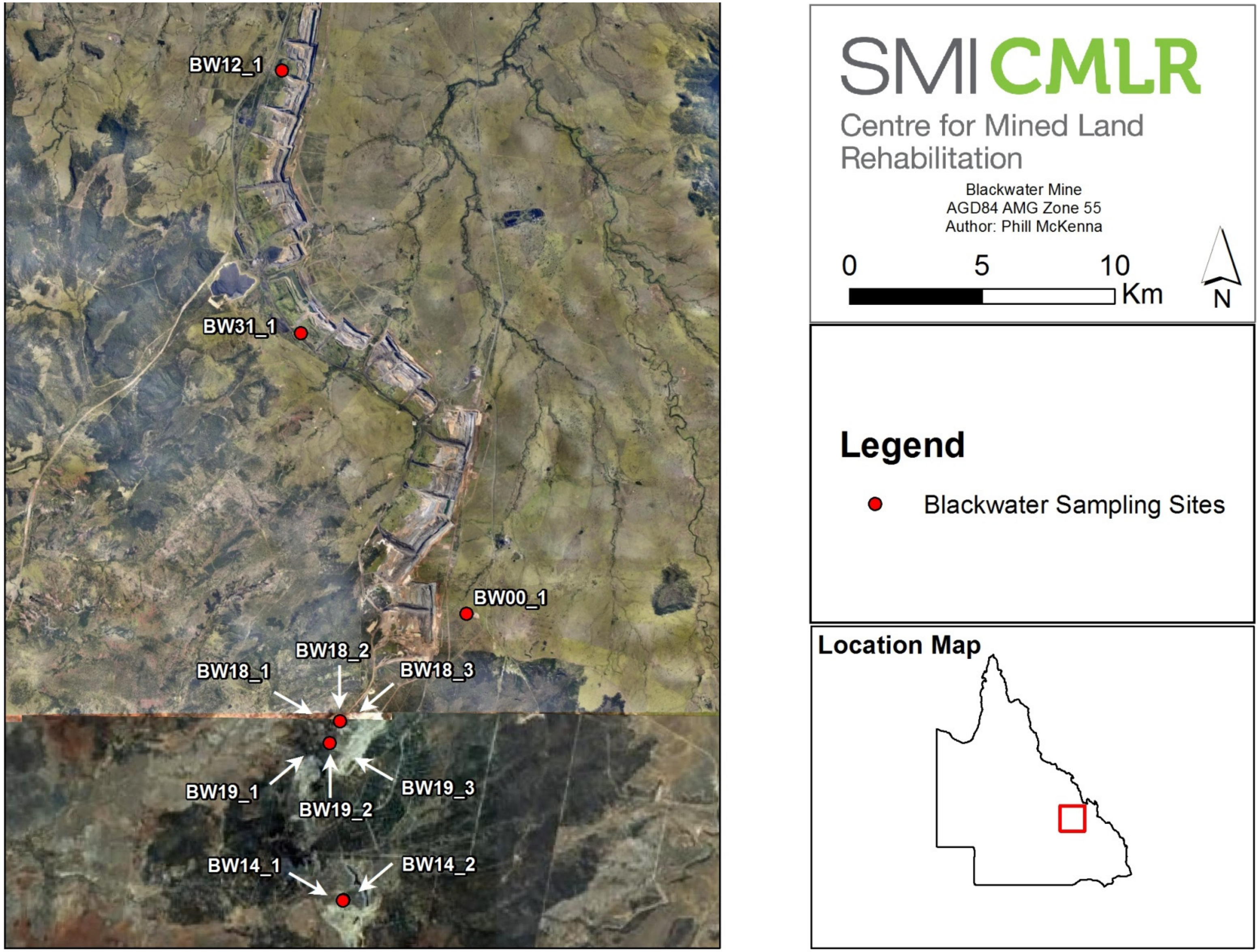
Norwich Park Mine sampling locations, 16 and 17 April, 2013.

Site ID	AGD_1984_AMG_Zone_55	
	Easting	**Northing**
NP00_1	644690	7497378
NP01_1	654128	7478638
NP01_2	644540	7499344
NP02_1	654017	7478542
NP06_1	651110	7489599
NP06_2	651128	7489628
NP10_1	643580	7498738
NP10_2	646822	7496567
NP10_3	644267	7498170
NP20_1	652582	7477964
NP20_2	652941	7478239
NP20_3	650562	7480094
NP27_1	651466	7482364

Appendix C - From Chan, J., Baumgartl, T., Erskine, P., Glenn, V., 2016. ACARP report C19029: Soil organic matter and green carbon in rehabilitation: their role in the carbon balance

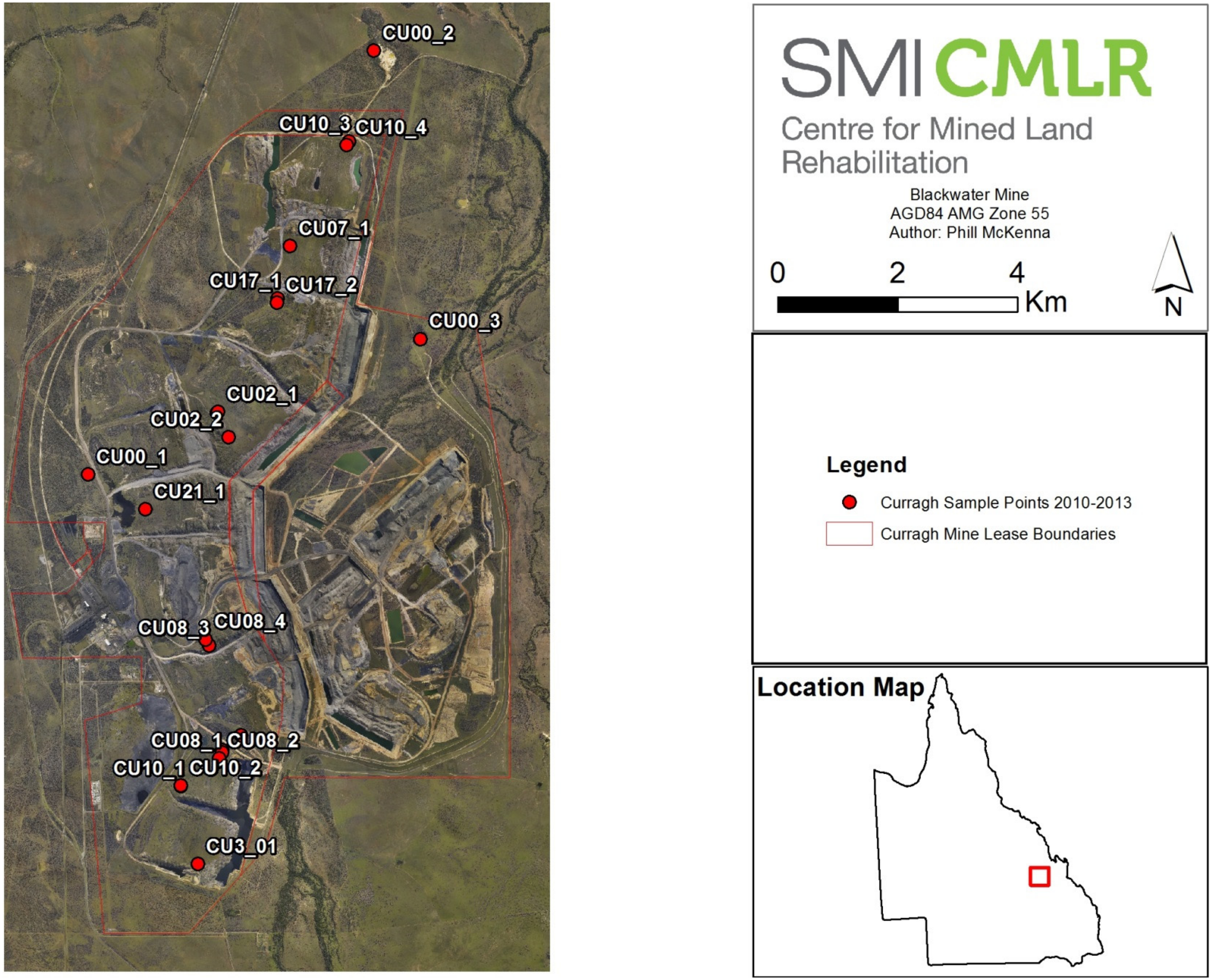
Sample location maps

Blackwater Mine



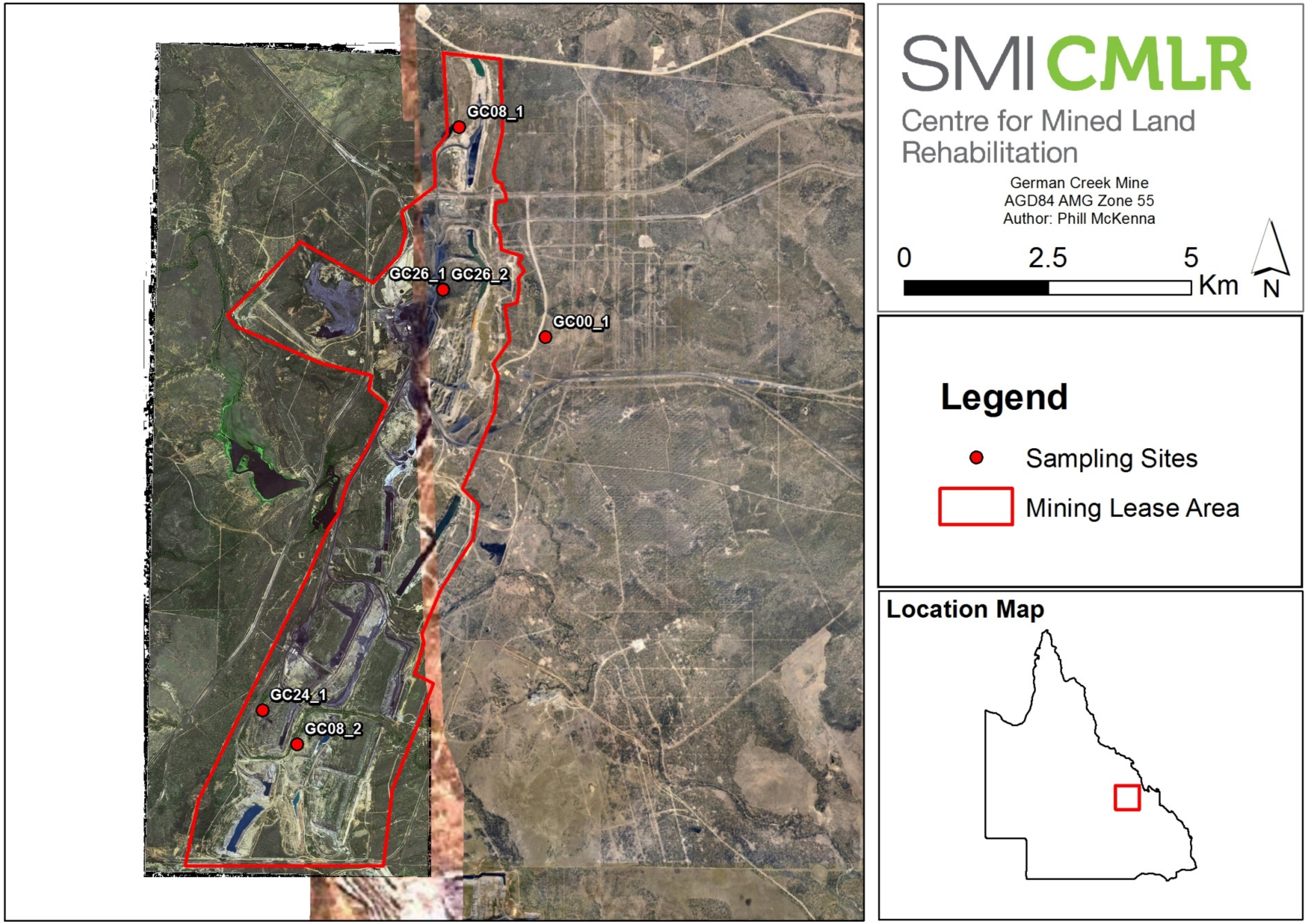
Appendix C - From Chan, J., Baumgartl, T., Erskine, P., Glenn, V., 2016. ACARP report C19029: Soil organic matter and green carbon in rehabilitation: their role in the carbon balance

Curragh Mine



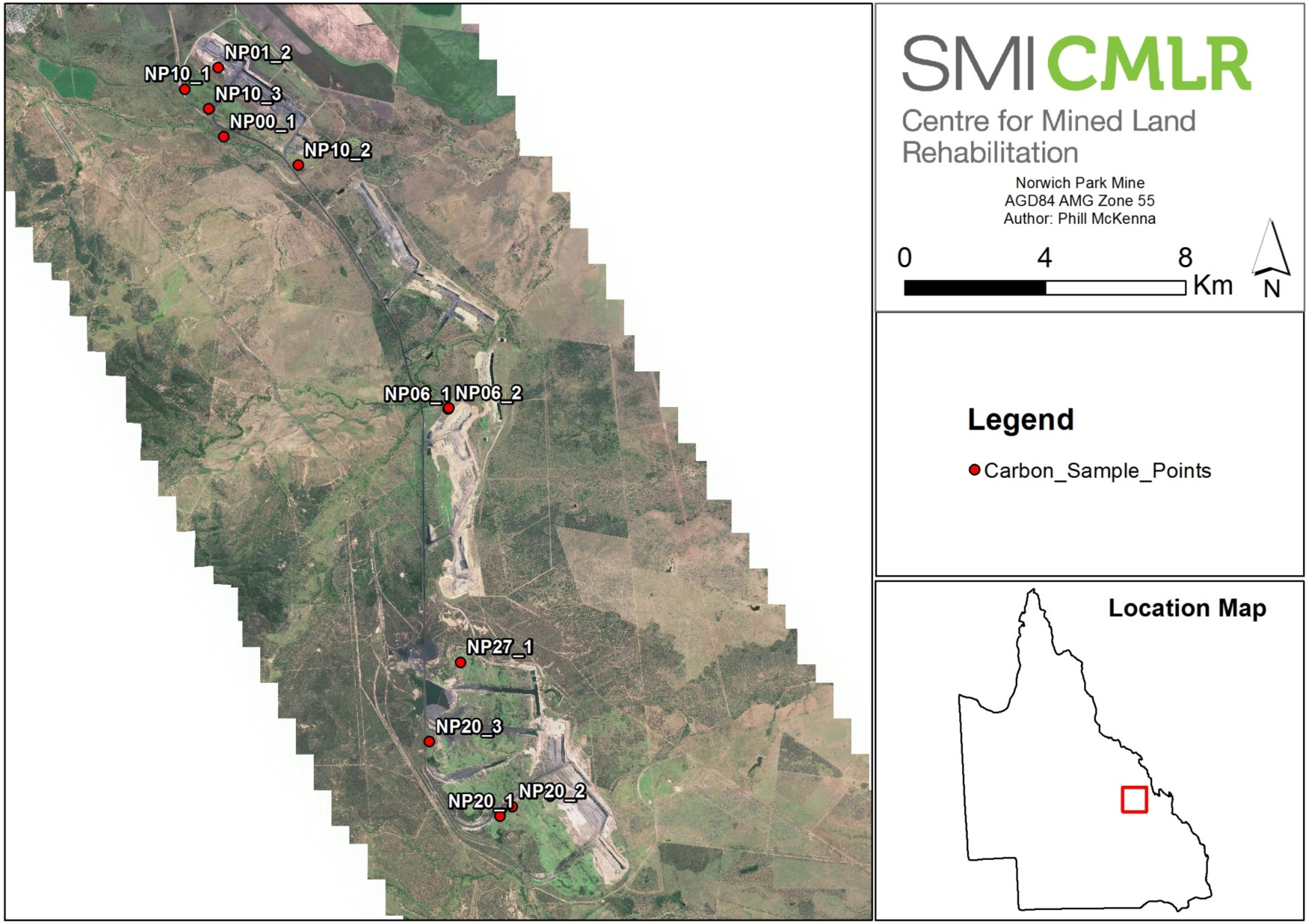
Appendix C - From Chan, J., Baumgartl, T., Erskine, P., Glenn, V., 2016. ACARP report C19029: Soil organic matter and green carbon in rehabilitation: their role in the carbon balance

German Creek Mine



Appendix C - From Chan, J., Baumgartl, T., Erskine, P., Glenn, V., 2016. ACARP report C19029: Soil organic matter and green carbon in rehabilitation: their role in the carbon balance

Norwich Park Mine



APPENDIX C

Soil profile descriptions

Blackwater Mine

Profile BW00_1	
	
Age (Rehab year)	Unmined site
Date sampled	23 August 2010
Slope	
Aspect	
Vegetation cover	Dense *Cenchrus ciliaris*
Vegetation composition	Canopy: *Acacia harpophylla* Midstorey: *Carissa* sp. Groundstorey: *Cenchrus ciliaris*
Soil surface description	
Topsoil applied?	N/A
Topsoil depth / stratification	
Other features	*Acacia harpophylla* pulled (cleared) sometime since 2000; Light grazing land use; Roots (1 – 3 mm diameter) most abundant at a depth of 0 – 15 cm; Soil dark and not easily friable

Profile BW12_1

Age (Rehab year)	12 years (1998)
Date sampled	23 August 2010
Slope	4 - 5%
Aspect	W
Vegetation cover	Dense *Cenchrus ciliaris*
Vegetation composition	Canopy: Sparse *Acacia salicina, moderate cover of Leucaena* sp. Groundstorey: dense *Cenchrus ciliaris* with *Senecio* sp.
Soil surface description	
Topsoil applied?	Topsoiled (Brigalow clay topsoil)
Topsoil depth / stratification	
Other features	Dense root mat present

Profile BW14_1

Age (Rehab	14 years (1996)

year)	
Date sampled	23 August 2010
Slope	8%
Aspect	NNE
Vegetation cover	Dense *Cenchrus ciliaris*
Vegetation composition	Canopy: *Corymbia citriodora, Eucalyptus populnea* Midstorey: *Enchylaena tomentosa* Groundstorey: *Cenchrus ciliaris*
Soil surface description	Deep litter layer present
Topsoil applied?	Yes
Topsoil depth / stratification	Topsoil to a depth of 28 cm; Spoil below; Sharp delineation between accumulated soil and spoil horizon
Other features	Few roots present; Many dead acacias

Profile BW14_2

Age (Rehab year)	14 years (1996)
Date sampled	23 August 2010
Slope	8%
Aspect	
Vegetation cover	Dense *Cenchrus ciliaris*
Vegetation composition	Midstorey: *Dodonaea sp.* Groundstorey: *Cenchrus ciliaris,* Bryophyta
Soil surface description	Deep litter layer present
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Deep topsoil (spoil not observed)
Other features	

Profile BW18_1

Age (Rehab year)	18 years (1992)
Date sampled	23 August 2010
Slope	17%
Aspect	
Vegetation cover	
Vegetation composition	Saltbush
Soil surface description	
Topsoil applied?	Unknown
Topsoil depth / stratification	Accumulated topsoil to a depth of 20 cm; Spoil below; Sharp delineation between accumulated soil and spoil horizon
Other features	Area of soil accumulation; Roots present throughout profile

Profile BW18_2

Age (Rehab year)	18 years (1992)
Date sampled	23 August 2010
Slope	Low slope on ridge
Aspect	NW
Vegetation cover	
Vegetation composition	*Acacia shirleyi*
Soil surface description	Litter present
Topsoil applied?	Unknown
Topsoil depth / stratification	
Other features	Roots present throughout profile

Profile BW18_3

Age (Rehab year)	18 years(1992)
Date sampled	23 August 2010
Slope	
Aspect	
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	
Soil surface description	Rocky surface
Topsoil applied?	Unknown
Topsoil depth / stratification	Topsoil to a depth of 25 cm; Spoil below
Other features	Very dense *Cenchrus ciliaris* roots present to a depth of 25 cm; Some roots extend into spoil; Beside an ant nest

Profile BW19_1

Age (Rehab year)	19 years (1991)
Date sampled	23 August 2010
Slope	17%
Aspect	
Vegetation cover	Dense *Cenchrus ciliaris*
Vegetation composition	Canopy: *Corymbia citridora, Acacia* spp. Groundstorey: *Cenchrus ciliaris*
Soil surface description	High litter cover
Topsoil applied?	Topsoiled (hardsetting sandy topsoil)
Topsoil depth / stratification	
Other features	Roots (1 - 3 mm diameter) present to a depth of 20 cm; Many dead acacias

Profile BW19_2

Age (Rehab year)	19 years (1991)
Date sampled	23 August 2010
Slope	17%
Aspect	W
Vegetation cover	Poaceae sp.
Vegetation composition	
Soil surface description	
Topsoil applied?	Topsoiled (hardsetting sandy topsoil)
Topsoil depth / stratification	Topsoil to a depth of 16 cm; Stratification indicates downward movement of water
Other features	Roots present throughout profile (including spoil); High litter content to a depth of 0.5 cm

Profile BW19_3

Age (Rehab year)	19 years (1991)
Date sampled	23 August 2010

Slope	17%
Aspect	SW
Vegetation cover	Dense *Cenchrus ciliaris*
Vegetation composition	
Soil surface description	
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Topsoil to a depth of 26 cm; Spoil below
Other features	Dark, moist, clay soil; Roots present throughout profile (particularly near surface and at a depth of 14 – 24 cm; Roots present in spoil); Soil at a depth of 20 – 26 cm is influenced by char or coal

Profile BW31_1

Age (Rehab year)	31 years (1979)
Date sampled	23 August 2010
Slope	20%
Aspect	ENE
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	*Cenchrus ciliaris*, forbs
Soil surface description	
Topsoil applied?	Topsoiled (1981)
Topsoil depth / stratification	
Other features	Grazing land use; Roots up to 10 mm diameter present; Roots (1 – 3 mm diameter) abundant at a depth of 0 – 20 cm; Erosion observed

Curragh Mine

Profile CU00_1	
	
Age (Rehab year)	Unmined site
Date sampled	25 August 2010
Slope	Flat
Aspect	Flat
Vegetation cover	
Vegetation composition	Brigalow regrowth vegetation community: Canopy: *Acacia harpophylla* Midstorey: *Enchylaena tomentosa* Groundstorey: *Cenchrus ciliaris,* Poaceae spp., *Harrisia* spp.
Soil surface description	
Topsoil applied?	N/A
Topsoil depth / stratification	
Other features	Cracking clay; Roots (1 – 3 mm diameter) present throughout profile; Increasing aggregate size with depth

Profile CU00_2

Age (Rehab year)	Unmined site
Date sampled	14 May 2013
Slope	7%
Aspect	SW (242º)
Vegetation cover	*Eucalyptus thozetiana*
Vegetation composition	Canopy: Moderate cover of *Eucalyptus thozetiana, Acacia harpophylla* Midstorey: Sparse to moderate cover of *Croton phebalioides*, *Carissa ovata* with mixed shrub species Groundstorey: Moderate to dense *Paspalidium* spp., *Aristida* spp., mixed Poaceae spp. and forb species
Soil surface description	
Topsoil applied?	N/A
Topsoil depth / stratification	
Other features	Fallen branch and grasses adjacent to pit; Light grazing land use with previous logging

Profile CU00_3

Age (Rehab year)	Unmined site
Date sampled	15 May 2013
Slope	1%
Aspect	E (78^{o})
Vegetation cover	*Eucalyptus cambageana* and *Acacia harpophylla*
Vegetation composition	Canopy: Moderate cover of *Eucalyptus cambageana, Acacia harpophylla* with mixed tree species Midstorey: Sparse to moderate cover of *Alectryon diversifolius*, *Carissa ovata*, with mixed shrub species Groundstorey: Moderate to dense *Cenchrus ciliaris, Enteropogon unispiceus*, mixed Poaceae spp. and vine species
Soil surface description	
Topsoil applied?	N/A
Topsoil depth / stratification	
Other features	Red-brown soil; Dry, hard soil; Heavy grazing land use

Profile CU02_1	
	
Age (Rehab year)	2 years (2008)
Date sampled	24 August 2010
Slope	
Aspect	N
Vegetation cover	Grass
Vegetation composition	*Cenchrus ciliaris*, Poaceae sp.
Soil surface description	Loose, crumbly surface soil
Topsoil applied?	Topsoiled
Topsoil depth / stratification	
Other features	

Profile CU02_2	
	
Age (Rehab year)	2 years (2008)

Date sampled	24 August 2010
Slope	Near-flat
Aspect	NE
Vegetation cover	Fabaceae sp.
Vegetation composition	
Soil surface description	Old leaf litter present
Topsoil applied?	Topsoiled
Topsoil depth / stratification	
Other features	Topsoil to a depth > 25 cm; Spoil not observed; High clay content below 5 cm depth; Soil macrofauna (insects) observed; Fungal hyphae associated with plant roots

Profile CU03_1

Age (Rehab year)	3 years (2010)
Date sampled	13 May 2013
Slope	7%
Aspect	NE (38°)
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	Canopy: Very sparse *Acacia* spp., *Parkinsonia aculeata* Midstorey: Sparse *Enchylaena tomentosa* Groundstorey: Dense *Cenchrus ciliaris*
Soil surface description	Ripped surface

Topsoil applied?	Yes
Topsoil depth / stratification	Topsoil to a depth of 40 cm; Spoil below
Other features	Brown clay soil with high clay content at depth; Soil crumbly to a depth of 20 cm; White hyphae observed at a depth of 10 to 20 cm

Profile CU05_1

	
Age (Rehab year)	5 years (2008)
Date sampled	13 May 2013
Slope	17%
Aspect	NE (32^{o})
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	Canopy: Very sparse *Acacia salicina*, *Senna artemisioides* ssp. *artemisioides* Groundstorey: Dense *Cenchrus ciliaris* with *Panicum coloratum, Melinis repens, Sesbania cannabina, Macroptilium lathyroides, Clitoria ternatea, Ipomoea* sp.
Soil surface description	
Topsoil applied?	Yes
Topsoil depth / stratification	
Other features	Midslope; Cracking clay soil; Roots present throughout profile (including spoil)

Profile CU07_1	
	
Age (Rehab year)	7 years (2006)
Date sampled	13 May 2013
Slope	12%
Aspect	W (264°)
Vegetation cover	*Senna artemisioides* ssp. *oligophylla*
Vegetation composition	Canopy: Sparse *Eucalyptus* spp., *Acacia* spp. Midstorey: Sparse *Senna artemisioides* ssp. *oligophylla* Groundstorey: Dense *Cenchrus ciliaris* with *Clitoria ternatea*
Soil surface description	Litter present
Topsoil applied?	Yes
Topsoil depth / stratification	Topsoil to a depth of 30 cm; Spoil below
Other features	Dark clay soil; *C. ternatea* roots near pit; Larger roots (10 mm diameter) in pit; White hyphae observed in litter to a depth of 10 cm

Profile CU08_1

Age (Rehab year)	8 years (2002)
Date sampled	25 August 2010
Slope	5%
Aspect	
Vegetation cover	Dense *Cenchrus ciliaris* (98% cover)
Vegetation composition	<u>Canopy</u>: *Eucalyptus* spp., *Acacia salicina* <u>Midstorey</u>: *Senna artemisioides* <u>Groundstorey</u>: *Cenchrus ciliaris,* Chenopodiaceae sp.
Soil surface description	
Topsoil applied?	Topsoiled
Topsoil depth / stratification	
Other features	Lower slope; Between two contour banks

Profile CU08_2

Age (Rehab year)	8 years (2002)
Date sampled	25 August 2010
Slope	
Aspect	
Vegetation cover	*Senna artemisioides*
Vegetation composition	Midstorey: *Senna artemisioides* Groundstorey: *Cenchrus ciliaris*
Soil surface description	
Topsoil applied?	Topsoiled
Topsoil depth / stratification	
Other features	Fine roots present to a depth of 18 cm; Thick roots present at a depth of 5 – 10 cm; Dense clay material below 18 cm

Profile CU08_3	
	
Age (Rehab year)	8 years (2005)
Date sampled	14 May 2013
Slope	9%
Aspect	WSW (242°)
Vegetation cover	*Senna artemisioides* ssp*. oligophylla*
Vegetation composition	Canopy: Sparse to moderate cover of *Acacia spp.* Midstorey: Sparse *Senna* spp.*, Acacia macradenia* Groundstorey: Moderate to dense *Cenchrus ciliaris* and *Chloris gayana* with *Stylosanthes sp., Macroptilium lathyroides, Megathyrsus maximus, Urochloa* sp.*, Cullen tenax*
Soil surface description	
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Mixed soil and spoil without clear stratification.
Other features	Brown and tan substrate; Many rocks

Profile CU08_4

Age (Rehab year)	8 years (2005)
Date sampled	14 May 2013
Slope	9%
Aspect	W (262°)
Vegetation cover	*Eucalyptus camaldulensis*
Vegetation composition	Canopy: Moderate cover of *Eucalyptus camaldulensis*, *Acacia macradenia*, *A. stenophylla, A. salicina, Corymbia citriodora.* Midstorey: Moderate cover of *Senna* spp.*, Acacia podalyriifolia* Groundstorey: Moderate to dense *Cenchrus ciliaris* with *Stylosanthes scabra, Megathyrsus maximus, Macroptilium lathyroides, Sesbania cannabina, Chloris gayana*
Soil surface description	Loose, crumbly surface soil
Topsoil applied?	
Topsoil depth / stratification	
Other features	Fungal hyphae observed near soil surface

Profile CU10_1

Age (Rehab year)	10 years (2000)
Date sampled	25 August 2010
Slope	
Aspect	NW
Vegetation cover	Dense *Cenchrus ciliaris*
Vegetation composition	
Soil surface description	
Topsoil applied?	Topsoiled
Topsoil depth / stratification	
Other features	High clay content; Roots present in profile below a depth of 20 cm

Profile CU10_2

Age (Rehab year)	10 years (2000)
Date sampled	25 August 2010

Slope	
Aspect	
Vegetation cover	Dense *Cenchrus ciliaris*
Vegetation composition	Canopy: *Acacia salicina, Acacia* spp. Groundstorey: *Cenchrus ciliaris,* Chenopodiaceae sp.
Soil surface description	
Topsoil applied?	Not topsoiled
Topsoil depth / stratification	
Other features	Uppermost 2 – 3 cm of soil profile comprises topsoil alluvium from upper slopes; Coal present (particularly abundant below a depth of 10 cm); Soil macrofauna (Myriapoda) observed

Profile CU10_3

Age (Rehab year)	10 years (2003)
Date sampled	15 May 2013
Slope	5%
Aspect	N (12°)
Vegetation cover	*Senna artemisioides* ssp. *oligophylla*
Vegetation composition	Canopy: Sparse to moderate cover of *Acacia salicina, A. stenophylla, Eucalyptus cambageana* Midstorey: Sparse *Senna artemisioides* spp. *oligophylla, S. artemisioides* ssp. *coriacea, Acacia holosericea, Enchylaena tomentosa* Groundstorey: Dense *Cenchrus ciliaris*

Soil surface description	
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Spoil present
Other features	*Acacia* sp. near pit; Dense clay material towards bottom of pit

Profile CU10_4

Age (Rehab year)	10 years (2003)
Date sampled	15 May 2013
Slope	9%
Aspect	NE (50°)
Vegetation cover	*Acacia stenophylla*
Vegetation composition	Canopy: Sparse *Acacia stenophylla, A. salicina* Midstorey: Sparse *Enchylaena tomentosa, Senna artemisioides* spp. *coriacea* Groundstorey: Dense *Cenchrus ciliaris* with *Rhynchosia minima, Phyllanthus maderaspatensis, Abutilon oxycarpum, Ipomoea plebeia, Corchorus trilocularis, Megathyrsus maximus*
Soil surface description	
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Topsoil to a depth of 25 cm; Spoil below
Other features	Dense clay material towards bottom of pit; Pit within dripline of *Acacia stenophylla* with *Cenchrus ciliaris* groundcover

Profile CU11_1	
	
Age (Rehab year)	11 years (2002)
Date sampled	14 May 2013
Slope	9%
Aspect	N (8°)
Vegetation cover	*Senna artemisioides* ssp. *oligophylla*
Vegetation composition	Canopy: Moderate cover of *Acacia salicina*, *A. holosericea, Corymbia citriodora* Midstorey: Moderate cover of *Senna artemisioides* ssp. *oligophylla* Groundstorey: Dense *Cenchrus ciliaris* with *Chloris gayana*
Soil surface description	
Topsoil applied?	
Topsoil depth / stratification	
Other features	Dark brown, rocky soil; Pit within dripline of *Senna artemisioides* spp. *oligophylla*

Profile CU11_2

Age (Rehab year)	11 years (2002)
Date sampled	14 May 2013
Slope	4%
Aspect	NE (44°)
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	Canopy: Sparse to moderate cover of *Acacia salicina* Midstorey: Sparse *Senna artemisioides* ssp. *oligophylla* Groundstorey: Dense *Cenchrus ciliaris* with *Macroptilium lathyroides, Rhynchosia minima, Sesbania cannabina*
Soil surface description	
Topsoil applied?	
Topsoil depth / stratification	
Other features	

Profile CU13_1

Age (Rehab year)	13 years (1997)
Date sampled	25 August 2010
Slope	
Aspect	NNE
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	
Soil surface description	Loose topsoil
Topsoil applied?	Topsoiled
Topsoil depth / stratification	
Other features	Roots and termites present below a depth of 25 cm

Profile CU17_1	
	
Age (Rehab year)	17 years (1996)
Date sampled	14 May 2013
Slope	13%
Aspect	WNW (280^{o})
Vegetation cover	*Eucalyptus populnea* and *Corymbia citriodora*
Vegetation composition	Canopy: Sparse to moderate cover of *Eucalyptus populnea, Corymbia citriodora, Acacia salicina, A. harpophylla, A. stenophylla, E. crebra, E. camaldulensis* Midstorey: Very sparse *Acacia salicina, Leucaena sp., Enchylaena tomentosa* Groundstorey: Dense *Cenchrus ciliaris* with *Stylosanthes scabra, S. hamata, Bothriochloa decipiens*
Soil surface description	Loose, crumbly surface soil
Topsoil applied?	
Topsoil depth / stratification	Topsoil to a depth of 16 cm; Spoil below
Other features	Root (2 cm diameter) near surface

Profile CU17_2

Age (Rehab year)	17 years (1996)
Date sampled	14 May 2013
Slope	15%
Aspect	WNW (288^{o})
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	Canopy: Sparse *Acacia salicina, Eucalyptus populnea, E. crebra, A. stenophylla, Corymbia citriodora* Groundstorey: Dense *Cenchrus ciliaris* with *Macroptilium lathyroides, Rhynchosia minima, Sesbania cannabina, Stylosanthes scabra, Indigofera brevidens*
Soil surface description	
Topsoil applied?	
Topsoil depth / stratification	
Other features	Dense *Cenchrus ciliaris* roots in the top 30 cm; Woody material present at a depth of 2 to 5 cm.

Profile CU21_1	
	
Age (Rehab year)	21 years (1989)
Date sampled	25 August 2010
Slope	
Aspect	WSW
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	Canopy: *Eucalyptus populnea, Acacia salicina*, *Acacia* spp. Groundstorey: *Cenchrus ciliaris*, Indeterminable shrub, *Heteropogon contortus,* Poaceae spp.
Soil surface description	
Topsoil applied?	
Topsoil depth / stratification	Topsoil to a depth of 30 cm; Spoil below
Other features	Cracking clay; Roots (1 – 3 mm diameter) present throughout profile; Increasing aggregate size with depth; Soil macrofauna (termites) observed

APPENDIX C

German Creek Mine

Profile GC00_1	
	
Age (Rehab year)	Undermined site
Date sampled	26 August 2010
Slope	Flat
Aspect	Flat
Vegetation cover	Dense *Cenchrus ciliaris*; Adjacent to *Eucalyptus* sp.
Vegetation composition	*Eucalyptus* spp., *Acacia* spp., *Cenchrus ciliaris.*
Soil surface description	
Topsoil applied?	N/A
Topsoil depth / stratification	
Other features	Duplex soil profile; Sandy A horizon to a depth of 15 cm; Mottled cracking clay B horizon below 15 cm; Roots (1 – 3 cm diameter) present at low abundance

Profile GC08_1	
	

Age (Rehab year)	8 years (2002)
Date sampled	26 August 2010
Slope	Flat ridge top
Aspect	
Vegetation cover	
Vegetation composition	Canopy: *Eucalyptus* spp., *Acacia flavescens* Groundstory: Poaceae spp., Asteraceae spp.
Soil surface description	Deeply ripped; Woody debris present.
Topsoil applied?	Topsoiled
Topsoil depth / stratification	
Other features	Horizon boundary at 15 cm depth; Sandy clay soil; Fine roots present below a depth of 5 cm.

Profile GC08_2

Age (Rehab year)	8 years (2002)
Date sampled	27 August 2010
Slope	Steep slope
Aspect	W
Vegetation cover	*Cenchrus ciliaris* (15% cover)
Vegetation composition	Canopy: *Eucalyptus spp.* Groundstorey: *Cenchrus ciliaris*
Soil surface description	Alluvium from upper slopes present; Organic matter is incorporated in upper soil horizon
Topsoil applied?	
Topsoil depth / stratification	
Other features	Dispersive soils in vicinity (piping erosion present); Soil crumbly; Aggregates to 3 cm diameter present; Sandy and clayey components present

Profile GC24_1	
	
Age (Rehab year)	24 years (1986)
Date sampled	27 August 2010
Slope	Steep slope
Aspect	
Vegetation cover	*Chloris gayana* (99% cover)
Vegetation composition	Canopy: *Eucalyptus spp.* Groundstorey: *Chloris gayana*
Soil surface description	
Topsoil applied?	
Topsoil depth / stratification	
Other features	

Profile GC26_1	
	
Age (Rehab year)	26 years (1984)

Date sampled	26 August 2010
Slope	16%
Aspect	WNW
Vegetation cover	Bare soil
Vegetation composition	
Soil surface description	Alluvium from upper slopes present
Topsoil applied?	Topsoiled (Sandy topsoil)
Topsoil depth / stratification	
Other features	Horizon boundary at 16 cm depth; Roots (3 – 5 mm diameter) present in topsoil

Profile GC26_2

Age (Rehab year)	26 years (1984)
Date sampled	26 August 2010
Slope	16%
Aspect	WNW
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	Canopy: *Acacia* spp. Standing dead stems (*Acacia* spp.) present. Groundstorey: *Cenchrus ciliaris*
Soil surface description	
Topsoil applied?	Topsoiled
Topsoil depth / stratification	
Other features	Distinct uppermost horizon (0 – 2 cm) with a high level of organic matter

Norwich Park Mine

Profile NP00_1	
	
Age (Rehab year)	Unmined site
Date sampled	16 April 2013
Slope	Near-flat
Aspect	S
Vegetation cover	Dense *Cenchrus ciliaris* (85% cover)
Vegetation composition	Canopy: *Atalaya hemiglauca*, *Acacia* spp., *Eucalyptus* spp., *Corymbia tessellaris* Midstorey: *Grewia ?latifolia* Groundstorey: *Cenchrus ciliaris* with *Sida cordifolia, Ipomoea* sp.
Soil surface description	
Topsoil applied?	N/A
Topsoil depth / stratification	
Other features	Very dark brown soil; Near creek; Pit located between *Cenchrus ciliaris* tussocks; Soil may have been previously disturbed (broken root present); Invertebrates present (including Araneae (spider), Annelid (worm))

Profile NP01_1

Age (Rehab year)	1 year (reworked in 2012; established in 2009)
Date sampled	16 April 2013
Slope	4%
Aspect	NE (45°)
Vegetation cover	*Melinis repens* with mixed forbs and Poaceae spp.
Vegetation composition	Canopy: very sparse *Eucalyptus* spp., *Corymbia citriodora, Acacia salicina* Groundstorey: *Melinis repens, Emilia sonchifolia, Crotalaria* spp.*, Sesbania* spp.*, Solanum nigrum, Cenchrus ciliaris, Chloris gayana*
Soil surface description	
Topsoil applied?	Very little topsoil present; Dragline spoil present
Topsoil depth / stratification	
Other features	Dark brown and mottled substrate; Many rocks present; Site recontoured due to erosion but trees retained during reworking

Profile NP01_2

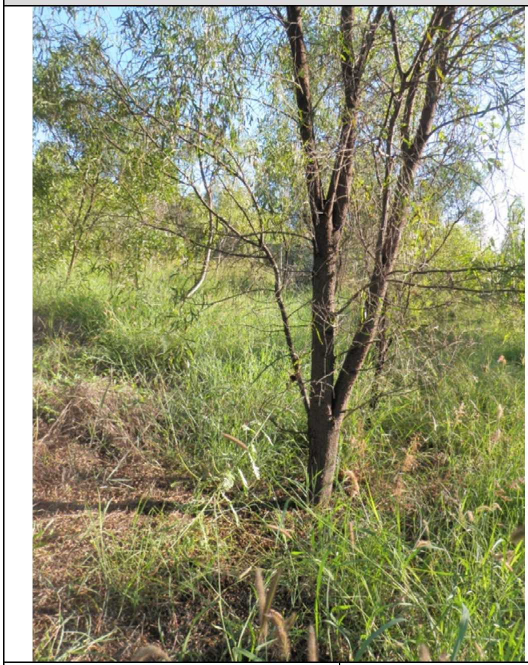
Age (Rehab year)	1 year (2012) (site contouring completed by 2011)
Date sampled	17 April 2013
Slope	11%
Aspect	SW (216°)
Vegetation cover	Mixed grass and graminoids
Vegetation composition	Canopy: *Acacia* sp. seedlings Groundcover: *Panicum effusum, Panicum decompositum, Iseilema vaginiflorum, Eriochloa* sp., *Cyperus* sp., *Dichanthium* sp. with *Macroptilium* sp., *Alysicarpus muelleri, Rhynchosia minima, Clitoria ternatea*
Soil surface description	Deeply ripped surface
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Deep topsoil (spoil not observed)
Other features	Dark brown to black clay soil

Profile NP02_1

Age (Rehab year)	2 years (reworked in 2011; established c.2005)
Date sampled	16 April 2013
Slope	5%
Aspect	NNW (346°)
Vegetation cover	Dense *Cenchrus ciliaris* (98% cover)
Vegetation composition	
Soil surface description	Soil surface crusted
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Topsoil to a depth > 1 m
Other features	Clayey; Roots present throughout profile; Soil macrofauna observed; Coal reject observed at 2-5 cm increment.

Profile NP06_1

Age (Rehab year)	5 years (2007)
Date sampled	16 April 2013
Slope	16%
Aspect	NW (310º)
Vegetation cover	*Eucalyptus tereticornis* with *Cenchrus ciliaris*
Vegetation composition	Canopy: *Eucalyptus tereticornis, Eucalyptus* spp., *Acacia macradenia, Acacia* spp. (2% cover) Groundstorey: *Cenchrus ciliaris, Chloris gayana* with *Melinis repens, Heteropogon contortus, Sesbania* sp., *Parthenium hysterophorus* (95% plant cover)
Soil surface description	
Topsoil applied?	Topsoiled
Topsoil depth / stratification	
Other features	Dark brown soil

Profile NP06_2	
	
Age (Rehab year)	5 years (2007)
Date sampled	16 April 2013
Slope	16%
Aspect	NW (310°)
Vegetation cover	*Acacia macradenia*
Vegetation composition	Canopy: *Acacia macradenia* with mixed tree species (40% cover) *Groundstorey: Cenchrus ciliaris* (60% cover) with *Chloris gayana*, *Sesbania* sp., *Glycine* sp., *Heteropogon contortus, Parthenium hysterophorus*
Soil surface description	Litter present (20% cover)
Topsoil applied?	
Topsoil depth / stratification	
Other features	Dark brown soil

Profile NP10_1


Age (Rehab year)	10 years (2003)
Date sampled	16 April 2013
Slope	7%
Aspect	W (260^{o})
Vegetation cover	Dense *Cenchrus ciliaris* (80% cover)
Vegetation composition	Midstorey: Very sparse *Leucaena* sp., *Acacia* sp. Groundstorey: Dense *Cenchrus ciliaris* with *Neptunia* sp., *Sorghum* sp., *Macroptilium* sp., *Crotalaria* sp., *Desmodium* sp., *Oxalis* sp.
Soil surface description	Litter present
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Topsoil to a depth of 30 cm; Spoil below
Other features	Dark brown, moist, soft surface soil; Slight mottling; Annelid (worm) present at a depth of 0 – 2 cm

Profile NP10_2


Age (Rehab year)	10 years (2003)
Date sampled	16 April 2013
Slope	11%
Aspect	SSW (230^{o})
Vegetation cover	Dense *Cenchrus ciliaris* (98% cover)
Vegetation composition	*Cenchrus ciliaris* with *Crotalaria* sp., *Alysicarpus muelleri, Hibiscus* sp., *Sorghum* sp.
Soil surface description	Litter present
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Deep topsoil (spoil not observed)
Other features	Dark brown, moist upper horizon; May be a self-mulching clay

Profile NP10_3	
	
Age (Rehab year)	10 years (2003)
Date sampled	17 April 2013
Slope	6%
Aspect	SSE (156^{o})
Vegetation cover	Dense *Cenchrus ciliaris* (90% cover)
Vegetation composition	Canopy: *Acacia* sp. Groundcover: *Cenchrus ciliaris* with *Urochloa ?mosambicensis*, *Clitoria ternatea, Sorghum* sp., *Parthenium hysterophorus*

Soil surface description	Thick litter layer present
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Deep topsoil (spoil not observed); Site recorded to have dragline spoil at depth
Other features	Dark brown soil

Profile NP20_1

Age (Rehab year)	20 years (1993)
Date sampled	16 April 2013
Slope	6%
Aspect	S (196°)
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	Canopy: Very sparse *Acacia salicina* Midstorey: Sparse *Leucaena* sp. Groundstorey: Dense *Cenchrus ciliaris* (>80% cover), *Chloris gayana* (2% cover), *Macroptilium* sp. (80% cover)
Soil surface description	Uneven surface
Topsoil applied?	Not topsoiled
Topsoil depth / stratification	
Other features	Dark brown, clayey substrate; Mottling present at a depth of 10 to 20 cm

Profile NP20_2

Age (Rehab year)	20 years (1993)
Date sampled	16 April 2013
Slope	12%
Aspect	S (190°)
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	Dense *Cenchrus ciliaris* and *Macroptilium* sp. with *Chloris gayana*, *Leucaena* sp. seedlings (100% plant cover)
Soil surface description	Pipe erosion
Topsoil applied?	Topsoiled
Topsoil depth / stratification	
Other features	Brown, moist soil

Profile NP20_3

Age (Rehab year)	20 years (1993)
Date sampled	16 April 2013

APPENDIX C

Slope	15%
Aspect	W (272º)
Vegetation cover	*Cenchrus ciliaris*
Vegetation composition	Dense *Cenchrus ciliaris* with *Macroptilium* sp., *Chloris gayana*
Soil surface description	
Topsoil applied?	Topsoiled
Topsoil depth / stratification	Soil-spoil mixture throughout profile
Other features	Pale brown

Profile NP27_1

Age (Rehab year)	27 years (1986)
Date sampled	17 April 2013
Slope	14%
Aspect	SE (124°)
Vegetation cover	Dense *Cenchrus ciliaris* (98% cover)
Vegetation composition	*Cenchrus ciliaris* with *Macroptilium* sp., *Panicum decompositum, Stylosanthes* sp., *Pterocaulon serrulatum*
Soil surface description	Rocks present
Topsoil applied?	Not topsoiled
Topsoil depth / stratification	
Other features	Rocks present; Most roots present in profile at a depth of 0 – 15 cm, with a smaller density of roots at a depth of 20+ cm.

APPENDIX D

Sample ID	Mine name	Year collected	Rehabilitation age (years)	Covertype	Total C (%C)	Total Organic C (%C)	Total N (%N)	Walkley Black C	EC (µs/cm)	pH	Bulk Density (g/cm^3)
NP02_1a	Norwich Park	2013	2	Grass	2.21	1.99	0.15	NA	68.3	7.77	1.16
NP02_1b	Norwich Park	2013			1.23	1.28	0.07	NA	53.2	6.49	1.16
NP02_1c	Norwich Park	2013			1.26	1.19	0.07	NA	53.2	7.1	1.26
NP02_1d	Norwich Park	2013			1.16	1.1	0.06	NA	76.9	8.25	1.37
NP02_1e	Norwich Park	2013			0.9	0.811	0.05	NA	48.6	7.36	1.58
NP01_1a	Norwich Park	2013	1	Grass	2.36	2.25	0.15	NA	47.4	7.96	1.15
NP01_1b	Norwich Park	2013			2.12	2.1	0.11	NA	54.5	8.84	1.15
NP01_1c	Norwich Park	2013			1.76	1.37	0.09	NA	88.3	9.44	1.20
NP01_1d	Norwich Park	2013			1.51	1.22	0.08	NA	97	9.67	1.25
NP01_1e	Norwich Park	2013			2.69	1.96	0.11	NA	99.5	9.2	1.35
NP20_1a	Norwich Park	2013	20	Grass	5.31	5.18	0.33	NA	76.4	7.12	0.51
NP20_1b	Norwich Park	2013			3.14	3.11	0.2	NA	66.2	7.41	0.51
NP20_1c	Norwich Park	2013			2.63	2.66	0.15	NA	73.5	8.4	0.76
NP20_1d	Norwich Park	2013			2.24	2.18	0.11	NA	162.7	9.12	1.00
NP20_1e	Norwich Park	2013			2.15	2.15	0.09	NA	393	9.57	1.48
NP20_2a	Norwich Park	2013	20	Grass	2.24	1.96	0.16	NA	46.1	6.67	1.41
NP20_2b	Norwich Park	2013			0.86	0.905	0.07	NA	23.8	6.18	1.41
NP20_2c	Norwich Park	2013			0.79	0.881	0.06	NA	23.3	6.3	1.41
NP20_2e	Norwich Park	2013			1	0.951	0.07	NA	25.6	6.67	1.42
NP20_2d	Norwich Park	2013			0.7	0.794	<0.05	NA	51	7.45	1.42
NP20_3a	Norwich Park	2013	20	Grass	2.5	2.58	0.17	NA	84.5	8.1	1.17
NP20_3b	Norwich Park	2013			1.02	1.05	0.07	NA	46	8.25	1.17
NP20_3c	Norwich Park	2013			0.58	0.556	<0.05	NA	53.7	8.41	1.22
NP20_3d	Norwich Park	2013			0.83	0.411	<0.05	NA	149.6	9.03	1.28
NP20_3e	Norwich Park	2013			0.81	0.361	<0.05	NA	596	9.31	1.38
NP10_1a	Norwich Park	2013	10	Grass	1.8	1.66	0.11	NA	62.6	7.75	1.00
NP10_1b	Norwich Park	2013			1.5	1.47	0.08	NA	68	8.66	1.00
NP10_1c	Norwich Park	2013			1.45	1.31	0.08	NA	67.8	8.14	1.07
NP10_1d	Norwich Park	2013			1.34	1.26	0.08	NA	85.8	8.81	1.13
NP10_1e	Norwich Park	2013			1.44	1.23	0.07	NA	127	8.98	1.26
NP00_1a	Norwich Park	2013	Not mined	Grass	5.12	5.18	0.28	NA	66.5	6.84	1.13
NP00_1b	Norwich Park	2013			3.72	3.8	0.22	NA	46.3	6.46	1.13
NP00_1c	Norwich Park	2013			2.83	2.71	0.17	NA	39.5	6.88	1.15
NP00_1d	Norwich Park	2013			1.96	1.91	0.12	NA	39.5	6.79	1.18
NP00_1e	Norwich Park	2013			1.56	1.56	0.1	NA	59	7.39	1.24
NP10_2a	Norwich Park	2013	10	Grass	1.67	1.51	0.1	NA	68.8	7.54	0.94
NP10_2b	Norwich Park	2013			1.66	1.3	0.08	NA	77.9	7.54	0.94
NP10_2c	Norwich Park	2013			1.23	1.17	0.07	NA	82.8	7.7	0.97
NP10_2d	Norwich Park	2013			1.3	1.19	0.07	NA	91	7.77	1.01
NP10_2e	Norwich Park	2013			1.22	1.1	0.07	NA	102.3	8.69	1.07
NP06_1a	Norwich Park	2013	6	Tree	1.7	1.7	0.11	NA	45.4	7.95	1.02

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NP06_1b	Norwich Park	2013			1.41	1.37	0.09	NA	56.1	7.91	1.02
NP06_1c	Norwich Park	2013			1.32	1.25	0.08	NA	52.6	8.28	1.09
NP06_1d	Norwich Park	2013			1.31	1.3	0.08	NA	60.3	8.3	1.15
NP06_1e	Norwich Park	2013			1.26	1.23	0.08	NA	54.5	8.35	1.27
NP06_2a	Norwich Park	2013	6	Tree	2.6	2.54	0.18	NA	74.5	6.19	1.08
NP06_2b	Norwich Park	2013			1.67	1.62	0.11	NA	53.4	7.56	1.08
NP06_2c	Norwich Park	2013			1.58	1.47	0.1	NA	61.3	8.05	1.08
NP06_2d	Norwich Park	2013			1.2	1.23	0.08	NA	52	7.97	1.08
NP06_2e	Norwich Park	2013			1.26	1.16	0.08	NA	64.6	8.05	1.08
NP27_1a	Norwich Park	2013	27	Grass	4.33	1.29	0.28	NA	70.1	7.22	1.58
NP27_1b	Norwich Park	2013			4.57	4.42	0.29	NA	57.9	6.48	1.58
NP27_1c	Norwich Park	2013			0.93	0.942	0.08	NA	61.5	6.4	1.57
NP27_1d	Norwich Park	2013			0.76	0.743	0.06	NA	86.6	6	1.56
NP27_1e	Norwich Park	2013			0.22	0.234	<0.05	NA	124.1	5.97	1.54
NP10_3a	Norwich Park	2013	10	Grass	5.26	5.19	0.36	NA	136.2	7.56	0.73
NP10_3b	Norwich Park	2013			2.04	2.03	0.14	NA	72.9	7.75	0.73
NP10_3c	Norwich Park	2013			1.37	1.38	0.09	NA	53.3	7.77	0.88
NP10_3d	Norwich Park	2013			1.19	1.16	0.08	NA	58.8	8.13	1.03
NP10_3e	Norwich Park	2013			1.1	1.04	0.07	NA	67	8.31	1.32
NP01_2a	Norwich Park	2013	1	Grass	1.5	1.45	0.09	NA	36.9	8.14	0.84
NP01_2b	Norwich Park	2013			1.43	1.38	0.09	NA	46.1	8.26	0.84
NP01_2c	Norwich Park	2013			1.41	1.36	0.08	NA	44	8.02	0.88
NP01_2d	Norwich Park	2013			1.43	1.41	0.08	NA	57.1	8.28	0.92
NP01_2e	Norwich Park	2013			1.36	1.29	0.08	NA	58.5	8.46	1.00
CU05_1a	Curragh	2013	5	Grass	3.75	3.26	0.26	NA	117.7	8.04	1.10
CU05_1b	Curragh	2013			3.81	1.8	0.26	NA	95.5	8.11	1.10
CU05_1c	Curragh	2013			1.46	1.15	0.09	NA	91.9	8.32	1.16
CU05_1d	Curragh	2013			2.07	1.13	0.11	NA	117.3	8.35	1.23
CU05_1e	Curragh	2013			1.8	1.24	0.11	NA	155.9	8.64	1.36
CU07_1a	Curragh	2013	7	Bush	3.78	3.76	0.26	NA	139.5	7.52	1.07
CU07_1b	Curragh	2013			2.35	2.32	0.17	NA	108	7.02	1.07
CU07_1c	Curragh	2013			1.81	1.71	0.13	NA	101.7	7.67	1.11
CU07_1d	Curragh	2013			1.75	1.65	0.12	NA	112.5	7.89	1.15
CU07_1e	Curragh	2013			1.71	1.55	0.12	NA	155.1	8.2	1.23
CU03_1a	Curragh	2013	3	Grass	1.9	1.54	0.12	NA	85.3	7.82	1.02
CU03_1b	Curragh	2013			1.68	1.41	0.11	NA	88.3	8.23	1.02
CU03_1c	Curragh	2013			2.02	1.36	0.11	NA	97.8	8.34	1.06
CU03_1d	Curragh	2013			1.71	1.31	0.1	NA	121.2	7.45	1.10
CU03_1e	Curragh	2013			2.21	1.53	0.12	NA	211.7	8.89	1.17
CU11_1a	Curragh	2013	11	Bush	4.39	3.74	0.25	NA	116.3	7.79	1.11
CU11_1b	Curragh	2013			2.77	2.22	0.18	NA	97.4	7.79	1.11
CU11_1c	Curragh	2013			2.52	1.82	0.16	NA	93.4	8.14	1.12
CU11_1d	Curragh	2013			2.5	1.82	0.15	NA	111.3	7.99	1.14
CU11_1e	Curragh	2013			2.72	2.19	0.15	NA	120.7	8.11	1.18
CU11_2a	Curragh	2013	11	Grass	6.65	6.29	0.37	NA	333	7.85	1.10
CU11_2b	Curragh	2013			3.27	2.85	0.18	NA	186.7	7.84	1.10

CU11_2c	Curragh	2013			2.36	1.88	0.14	NA	187.6	7.21	1.12
CU11_2d	Curragh	2013			2.41	1.72	0.15	NA	150.4	7.51	1.13
CU11_2e	Curragh	2013			2.66	2.04	0.17	NA	147.5	7.81	1.17
CU08_3a	Curragh	2013	8	Senna	3.2	3	0.17	NA	94.4	7.65	1.19
CU08_3b	Curragh	2013			3.03	2.76	0.15	NA	100.9	8.14	1.19
CU08_3c	Curragh	2013			3.64	3.28	0.16	NA	128.5	8.25	1.22
CU08_3d	Curragh	2013			5.41	5.04	0.2	NA	367	8.75	1.24
CU08_3e	Curragh	2013			7.13	6.74	0.24	NA	436	8.99	1.29
CU08_4a	Curragh	2013	8	Tree	2.38	2.22	0.16	NA	88.5	8.1	0.95
CU08_4b	Curragh	2013			1.96	1.86	0.13	NA	92.8	7.42	0.95
CU08_4c	Curragh	2013			1.94	1.85	0.13	NA	95.5	8.02	1.00
CU08_4d	Curragh	2013			1.91	1.83	0.13	NA	114.7	8.47	1.06
CU08_4e	Curragh	2013			2.05	1.66	0.12	NA	151.6	8.7	1.17
CU17_1a	Curragh	2013	17	Tree	5.42	5.22	0.31	NA	112.8	8.1	0.95
CU17_1b	Curragh	2013			2.91	2.77	0.18	NA	93.6	8.1	0.95
CU17_1c	Curragh	2013			2.03	1.85	0.13	NA	102.5	7.4	1.07
CU17_1d	Curragh	2013			2.11	1.74	0.12	NA	104.1	7.2	1.18
CU17_1e	Curragh	2013			1.88	1.24	0.11	NA	123.2	8.73	1.41
CU17_2a	Curragh	2013	17	Grass	5.66	5.35	0.31	NA	113.6	7.5	0.83
CU17_2b	Curragh	2013			3	2.84	0.19	NA	93.8	8.12	0.83
CU17_2c	Curragh	2013			2.19	2.09	0.14	NA	98.8	8.14	0.94
CU17_2d	Curragh	2013			2.14	1.81	0.14	NA	109	8.19	1.04
CU17_2e	Curragh	2013			2.63	2.29	0.15	NA	105.1	8.38	1.25
CU00_2a	Curragh	2013	Not mined	Tree	7.93	7.8	0.43	NA	79	5.45	1.14
CU00_2b	Curragh	2013			5.77	5.68	0.32	NA	73.4	5.55	1.14
CU00_2c	Curragh	2013			2.81	2.79	0.18	NA	75.6	6.94	1.23
CU00_2d	Curragh	2013			2.06	2.09	0.15	NA	183.5	6.34	1.32
CU00_2e	Curragh	2013			0.9	0.892	0.09	NA	736	4.54	1.50
CU00_3a	Curragh	2013	Not mined	Tree	4.71	4.68	0.28	NA	91.5	7.05	1.29
CU00_3b	Curragh	2013			3.25	3.32	0.21	NA	63.8	6.26	1.29
CU00_3c	Curragh	2013			1.8	1.78	0.11	NA	47.7	6.6	1.31
CU00_3d	Curragh	2013			0.94	1.02	0.07	NA	52.4	7.67	1.33
CU00_3e	Curragh	2013			0.65	0.642	0.06	NA	68.8	7.35	1.37
CU10_3a	Curragh	2013	10	Bush	3.12	3.05	0.21	NA	98.2	8.19	1.18
CU10_3b	Curragh	2013			2.3	2.17	0.17	NA	98.6	7.12	1.18
CU10_3c	Curragh	2013			2.03	1.82	0.14	NA	92.2	7.59	1.19
CU10_3d	Curragh	2013			2.24	2.09	0.16	NA	132.4	7.32	1.20
CU10_3e	Curragh	2013			2.2	2.04	0.16	NA	163.2	7.8	1.23
CU10_4a	Curragh	2013	10	Tree	3.5	3.46	0.25	NA	373	7.3	1.10
CU10_4b	Curragh	2013			1.96	1.96	0.15	NA	190.6	7.54	1.10
CU10_4c	Curragh	2013			1.82	1.78	0.14	NA	178.7	7.85	1.16
CU10_4d	Curragh	2013			2.3	2.18	0.15	NA	176.7	8.03	1.22
CU10_4e	Curragh	2013			1.86	1.65	0.13	NA	210.5	8.7	1.33
BW18_3a1	Blackwater	2010	18	Grass	2.24	2.49	0.08	1.8	NA	NA	1.26
BW18_3a2	Blackwater	2010	18		1.94	1.93	0.105	1.51	NA	NA	
BW18_3b	Blackwater	2010	18		1.32	1.46	0.07	1	NA	NA	

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BW18_3c	Blackwater	2010	18		1.46	1.34	0.11	1.09	NA	NA	
BW18_3e	Blackwater	2010	18		1.18	1.21	0.08	0.73	NA	NA	
BW19_1a1	Blackwater	2010	19	Tree	4.03	3.63	0.22	3.03	NA	NA	1.32
BW19_1a3	Blackwater	2010	19		2.59	2.42	0.14	1.76	NA	NA	
BW19_1b	Blackwater	2010	19		0.78	0.84	0.08	0.58	NA	NA	
BW19_1c	Blackwater	2010	19		0.56	0.65	0.08	0.65	NA	NA	
BW19_1e	Blackwater	2010	19		0.18	0.25	0.05	0.44	NA	NA	
BW19_2a1	Blackwater	2010	19	Grass	2.39	2.35	0.17	1.95	NA	NA	1.44
BW19_2a2	Blackwater	2010	19		2.2	2.04	0.16	1.71	NA	NA	
BW19_2a3	Blackwater	2010	19		1.58	1.59	0.1	1.11	NA	NA	
BW19_2b	Blackwater	2010	19		0.91	0.98	0.09	0.96	NA	NA	
BW19_2c	Blackwater	2010	19		0.66	0.83	0.08	0.7	NA	NA	
BW19_2d	Blackwater	2010	19		1.19	1.35	0.11	1.12	NA	NA	
BW00_1a3	Blackwater	2010	Not mined	Grass	2.12	1.95	0.2	1.68	NA	NA	1.43
BW00_1b	Blackwater	2010			2.13	2.18	0.17	1.8	NA	NA	
BW31_1a1	Blackwater	2010	31	Grass	3.35	3.13	0.2	2.22	NA	NA	1.06
BW31_1a2	Blackwater	2010	31		3.14	2.77	0.19	2.13	NA	NA	
BW31_1a3	Blackwater	2010	31		2.65	2.52	0.14	1.93	NA	NA	
BW31_1b	Blackwater	2010	31		3.43	3.02	0.19	2.51	NA	NA	
BW31_1c	Blackwater	2010	31		3.05	2.45	0.17	1.99	NA	NA	
BW31_1d	Blackwater	2010	31		2.47	2.2	0.11	1.61	NA	NA	
BW31_1e	Blackwater	2010	31		2.75	2.03	0.13	1.78	NA	NA	
CU02_2a2	Curragh	2010	2	Grass	1.29	1.08	0.09	0.87	NA	NA	1.08
CU02_2d	Curragh	2010	2		1.32	1.19	0.12	0.95	NA	NA	
CU10_1a1	Curragh	2010	10	Grass	3.03	2.45	0.23	1.85	NA	NA	0.93
CU10_1a2	Curragh	2010	10		2.49	2.22	0.14	1.6	NA	NA	
CU10_1a3	Curragh	2010	10		2.15	1.81	0.12	1.42	NA	NA	
CU10_1b	Curragh	2010	10		1.86	1.56	0.11	1.28	NA	NA	
CU10_1c	Curragh	2010	10		1.86	1.45	0.09	1.27	NA	NA	
CU10_1d	Curragh	2010	10		1.775	1.4	0.135	1.22	NA	NA	
CU10_1e	Curragh	2010	10		1.82	1.62	0.12	1.16	NA	NA	
CU10_2a2	Curragh	2010	10	Grass	2.81	2.56	0.16	1.79	NA	NA	1.22
CU10_2a3	Curragh	2010	10		2.9	2.46	0.15	1.88	NA	NA	
CU10_2b	Curragh	2010	10		3.17	2.75	0.14	2.02	NA	NA	
CU10_2d	Curragh	2010	10		4.8	4.31	0.19	3.48	NA	NA	
CU08_1a1	Curragh	2010	8	Grass	2.82	2.43	0.17	1.9	NA	NA	0.93
CU08_1a2	Curragh	2010	8		2.86	2.37	0.16	1.9	NA	NA	
CU08_1a3	Curragh	2010	8		2.6	2.03	0.13	1.72	NA	NA	
CU08_1c	Curragh	2010	8		2.39	1.69	0.12	1.58	NA	NA	
CU08_1d	Curragh	2010	8		2.21	1.81	0.11	1.63	NA	NA	
CU08_1e	Curragh	2010	8		2.09	1.54	0.11	1.47	NA	NA	
CU08_2a1	Curragh	2010	8	Bush	5.71	5.56	0.34	4.44	NA	NA	1.06
CU08_2a2	Curragh	2010	8		4.67	3.59	0.26	3.04	NA	NA	
CU08_2a3	Curragh	2010	8		2.98	2.39	0.17	1.88	NA	NA	
CU08_2b	Curragh	2010	8		2.07	1.58	0.11	1.4	NA	NA	
CU08_2c	Curragh	2010	8		2.08	1.59	0.11	1.5	NA	NA	

APPENDIX D

CU08_2d	Curragh	2010	8		2.18	1.77	0.12	1.55	NA	NA	
CU08_2e	Curragh	2010	8		1.07	1.1	0.03	0.97	NA	NA	
CU13_1b	Curragh	2010	13	Grass	1.38	1.34	0.07	1.01	NA	NA	0.97
CU13_1c	Curragh	2010	13		1.36	1.26	0.08	1.02	NA	NA	
CU13_1d	Curragh	2010	13		1.25	1.08	0.07	0.92	NA	NA	
CU13_1e	Curragh	2010	13		1.68	1.33	0.08	1.16	NA	NA	
GC08_1a1	German Creek	2010	8	Tree	3	2.93	0.23	2.45	NA	NA	1.49
GC08_1a3	German Creek	2010	8		0.71	0.78	0.04	0.73	NA	NA	
GC08_1b	German Creek	2010	8		0.65	0.69	0.04	0.62	NA	NA	
GC08_1c	German Creek	2010	8		0.6	0.68	0.05	0.61	NA	NA	
GC08_1d	German Creek	2010	8		0.77	0.92	0.04	0.69	NA	NA	
GC08_1e	German Creek	2010	8		0.29	0.42	0.07	0.5	NA	NA	
GC26_1a1	German Creek	2010	26	Tree	1.8	2.02	0.09	1.19	NA	NA	1.48
GC26_1a2	German Creek	2010	26		1.64	1.64	0.08	1.1	NA	NA	
GC26_1a3	German Creek	2010	26		1.98	2.07	0.08	1.33	NA	NA	
GC26_1b	German Creek	2010	26		2.04	2.11	0.1	1.39	NA	NA	
GC26_1c	German Creek	2010	26		1	1.08	0.05	0.84	NA	NA	
GC26_1d	German Creek	2010	26		1.9	1.89	0.12	1.2	NA	NA	
GC26_1e	German Creek	2010	26		1.2	1.16	0.09	0.86	NA	NA	
GC26_2a1	German Creek	2010	26	Tree	3.93	4.45	0.18	2.22	NA	NA	1.32
GC26_2a2	German Creek	2010	26		3.36	3.26	0.14	2.07	NA	NA	
GC26_2a3	German Creek	2010	26		2.12	2.24	0.09	1.49	NA	NA	
GC26_2b	German Creek	2010	26		1.42	1.68	0.06	1.1	NA	NA	
GC26_2c	German Creek	2010	26		0.88	0.99	0.05	0.78	NA	NA	
GC26_2d	German Creek	2010	26		0.77	0.93	0.07	0.74	NA	NA	
GC26_2e	German Creek	2010	26		1.1	1.26	0.11	0.92	NA	NA	
GC24_1a1	German Creek	2010	24	Grass	1.66	1.61	0.16	1.24	NA	NA	1.30
GC24_1a3	German Creek	2010	24		1.06	1.01	0.11	0.89	NA	NA	
GC24_1b	German Creek	2010	24		0.98	1.04	0.11	0.97	NA	NA	
GC24_1c	German Creek	2010	24		1	1.02	0.15	0.93	NA	NA	
G38	German Creek	2010	NA	NA	0.995	1.2	0.11	0.98	NA	NA	NA

APPENDIX D

APPENDIX E

Analytical Services
27 July 2006
File: ProceduresoilOCcalcareous1.doc

Procedures for the Preparation of Calcareous Soils for Organic Carbon Analysis

The analysis of calcareous soils for Organic Carbon on a Combustion Analyser requires the removal of the inorganic carbonates prior to analysis as some of this will be measured by the combustion process. The addition of acid destroys the carbonates but excess acid must be removed prior to analysis to prevent corrosion problems in the system.

Soil treatment

Reagents

1. 4 N H_2SO_4 Add 11 mL of concentrated sulphuric acid to 90 mL of deionised water.
2. Saturated $Ba(OH)_2$ Sparge 100 mL of deionised water in a 250 mL Buchner flask with nitrogen for 15 min. Add 6.5 g of $Ba(OH)_2.8H_2O$ (AR) to the flask and stir on a magnetic stirrer for 30 min. Leave to stand for 24 h and then filter through a GF/A filter paper. Return the solution to the flask and fit a CO2 trap to prevent atmospheric CO2 from dissolving and reacting.

Procedure

1. Weigh 500 – 600 mg of oven dried soil sample into a watchglass or heat-resistant weighing boat.
2. Add 0.5 mL of acid evenly to the sample to react with the carbonates. If the sample is not completely wet then add a few drops of deionised water with a Pastuer pipette. Note any effervescence of carbon dioxide.
3. Add 0.5 mL of saturated barium hydroxide solution to neutralise the excess acid.
4. Place in order on a Hotplate set at 110 °C and take the samples to dryness.
5. Combust the dried samples at 950 °C along with EDTA calibrations, blanks and ASPAC QC check samples.

Safety Precautions:

1. Wear plastic gloves and safety glasses.
2. Perform all operations in the Fume Cupboard.
3. Wash your hands after working with the samples.

MCR-ALS Component Concentrations

	IC (%C)	Coal (%C)	BC (%C)	Green (%C)
CU03_1b	0.42	0.02	0.18	1.07
CU03_1d	0.45	0.01	0.21	1.03
CU11_2a	0.50	0.62	0.66	4.87
CU11_2b	0.49	0.24	0.63	1.91
CU11_2c	0.60	0.05	0.31	1.41
CU03_1a	0.52	0.01	0.23	1.14
CU03_1c	0.65	0.02	0.21	1.15
CU03_1e	0.90	0.07	0.14	1.10
CU00_3a	0.00	0.17	0.20	4.34
CU00_3b	0.00	0.14	0.16	2.95
CU00_3c	0.00	0.04	0.00	1.76
CU00_3e	0.01	0.03	0.01	0.60
CU05_1a	0.51	0.01	0.58	2.65
CU05_1b	0.88	0.00	0.51	2.42
CU05_1c	0.46	0.02	0.13	0.85
CU05_1e	0.73	0.03	0.10	0.94
CU08_4a	0.10	0.11	0.42	1.76
CU08_4b	0.12	0.06	0.24	1.54
CU08_4c	0.17	0.03	0.21	1.54
CU08_4e	0.65	0.02	0.11	1.26
CU11_1a	0.95	0.23	0.17	3.04
CU11_1b	0.86	0.04	0.07	1.80
CU11_1c	0.95	0.04	0.05	1.48
CU11_1e	0.71	0.11	0.29	1.61
CU11_2d	0.93	0.04	0.09	1.35
CU11_2e	0.87	0.04	0.26	1.49
CU17_1a	0.07	0.68	1.18	3.49
CU17_1b	0.29	0.28	0.65	1.68
CU17_1c	0.29	0.05	0.33	1.36
CU17_1d	0.54	0.23	0.36	0.98
CU17_1e	0.84	0.30	0.28	0.46
CU17_2a	0.10	0.64	2.05	2.87
CU17_2b	0.13	0.09	0.62	2.17
CU17_2c	0.20	0.00	0.31	1.68
CU17_2e	0.43	0.27	0.71	1.22
NP00_1a	0.00	0.33	0.50	4.29
NP00_1b	0.00	0.14	0.24	3.34
NP00_1c	0.00	0.07	0.12	2.64
NP00_1e	0.00	0.02	0.11	1.42
NP01_1a	0.21	0.92	0.57	0.66
NP01_1b	0.35	0.97	0.51	0.29
NP01_1c	0.43	0.82	0.36	0.15

NP01_1e	0.43	1.52	0.37	0.36
NP01_2a	0.34	0.03	0.11	1.01
NP01_2b	0.05	0.01	0.20	1.17
NP01_2c	0.01	0.01	0.25	1.14
NP01_2d	0.02	0.01	0.24	1.15
NP01_2e	0.04	0.00	0.18	1.14
NP02_1a	0.01	0.55	0.37	1.28
NP02_1b	0.01	0.35	0.21	0.67
NP02_1c	0.03	0.36	0.24	0.63
NP02_1e	0.02	0.35	0.22	0.32
NP06_1a	0.00	0.05	0.21	1.43
NP06_1b	0.00	0.03	0.10	1.28
NP06_1c	0.00	0.03	0.08	1.21
NP06_1e	0.01	0.02	0.08	1.16
NP06_2a	0.00	0.12	0.40	2.09
NP06_2b	0.02	0.03	0.19	1.42
NP06_2c	0.03	0.03	0.09	1.43
NP06_2e	0.02	0.02	0.07	1.15
NP20_1a	0.00	1.24	1.47	2.60
NP20_1b	0.01	0.95	1.04	1.15
NP20_1c	0.01	0.85	0.74	1.02
NP20_1d	0.04	0.91	0.72	0.57
NP20_1e	0.06	0.88	0.80	0.42
NP20_2a	0.00	0.23	0.61	1.39
NP20_2b	0.00	0.00	0.18	0.68
NP20_2c	0.00	0.00	0.11	0.67
NP20_2e	0.02	0.01	0.12	0.55
NP20_3a	0.02	0.40	0.70	1.38
NP20_3b	0.00	0.11	0.35	0.56
NP20_3c	0.01	0.02	0.13	0.42
NP20_3e	0.43	0.10	0.14	0.14
German Creek Coal	0.19	32.12	19.25	8.80
Goonyella Coal	0.00	14.31	37.38	13.87
Curragh Coal	0.08	22.55	17.55	8.96
Chestnut Char	0.00	0.00	42.92	25.28

APPENDIX F

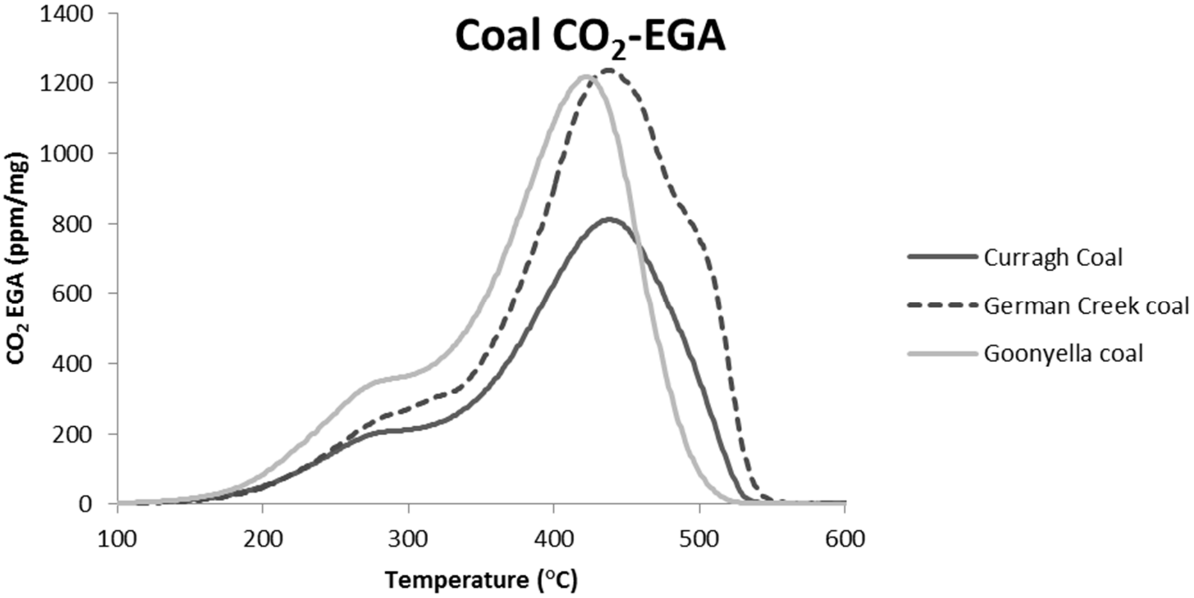

Figure F 1 CO_2-EGA thermograms for coals from Curragh, German Creek and Goonyella coal mines. The peak combustion temperatures for the coals centre around 430 °C. The carbon richness of the Goonyella and German Creek coals are greater than that of the Curragh coal and they both exhibit greater volatilization at their peak combustion temperatures than the Curragh coal.

APPENDIX G

Evaluation of Sample Analysis Methodologies

Standard methods of soil preparation involve the drying and sieving of the samples prior to cold storage. The purpose of this processing is to separate the fine soil from coarser material and slow down changes due to microbial degradation. It is recommended by the US EPA to analyse samples within 28 days of sampling or risk the sample having changed significantly from the time of sampling (Schumacher, 2002).

Within the collected soil there can exist non-soil components, such as rocks, living roots, and litter. While sieving removes the majority of these non-soil components, thin roots and pieces of litter often still remain in the sample. As organic matter is the source of organic carbon, the presence of organic, non-soil components may artificially inflate the measured organic carbon content. Few papers in the literature mentioned removing non-soil organic matter from samples (Czimczik et al., 2005).

The effect of the removal of organic matter

The presence of contaminants in a soil sample has the potential to alter the analytical results. Contaminants include anything which is not soil, including organic matter. In coal mine soils there is a greater likelihood of coal fines and dusts contaminating soil samples. To remove organic matter and coarse coal contaminants in a soil sample involves the intense visual inspection and manual extraction. This process is time consuming and has the potential to greatly inflate the time required for analysis. It was decided to test whether meticulous removal of contaminating organic matter and coal was required to ensure reliable results.

Methods

Following sieving, samples of mine soils BW18_3a1, BW18_3a2, BW19_2a1, BW19_2a3, BW19_2b, BW19_2d, CU10_2d, the two natural soils and BW38 were divided in two using a riffle splitter. Both treatments had all litter and non-soil organic matter observable by the naked eye removed within 30 minutes, while one treatment had the removed organic matter returned and mixed back in. Both treatments were ground with a mortar and pestle to pass through a 0.5 mm sieve and tested for total organic carbon by Heanes chemical oxidation (BW18_3, BW19_2, CU10_2) (28.3, 29.2, 2000 T1.2) or Dumas elemental analysis (Brigalow, buffel grass, G38)

(Rayment and Lyons, 2011). Acidification of samples was not required as the presence of inorganic carbon was not detected, evidenced by the lack of effervescence upon the addition of 4M HCl (Rayment and Lyons, 2011).

Results and Discussion

The results for the Heanes TOC mine soils was inconsistent between samples and confounding, as some samples showed significant increase in TOC levels where the litter and roots were removed. This runs contrary to the belief that the presence of litter and roots would result in a higher TOC content. The analyses were run singularly for each soil sample, however, each was tested using three separate methods of carbon analysis at the Department of Environment and Resource Management laboratory, Heanes (1984) TOC, Dumas TC and Walkley-Black (1934) OC and each method showed higher mean values after organic matter removal (Rayment and Lyons, 2011).

The Dumas TC tested set using one rehabilitated mine soil from Blackwater coal mine and two natural soils from the Brigalow belt, one remnant Brigalow site and one buffel grass dominated site were tested in triplicate. When outliers were removed, these showed that the removal of organic matter decreased the TC readings significantly for both buffel grass dominated soil and Brigalow groundcover soil (p = 0.047 and p = 0.043, respectively) (**Figure G 45**).

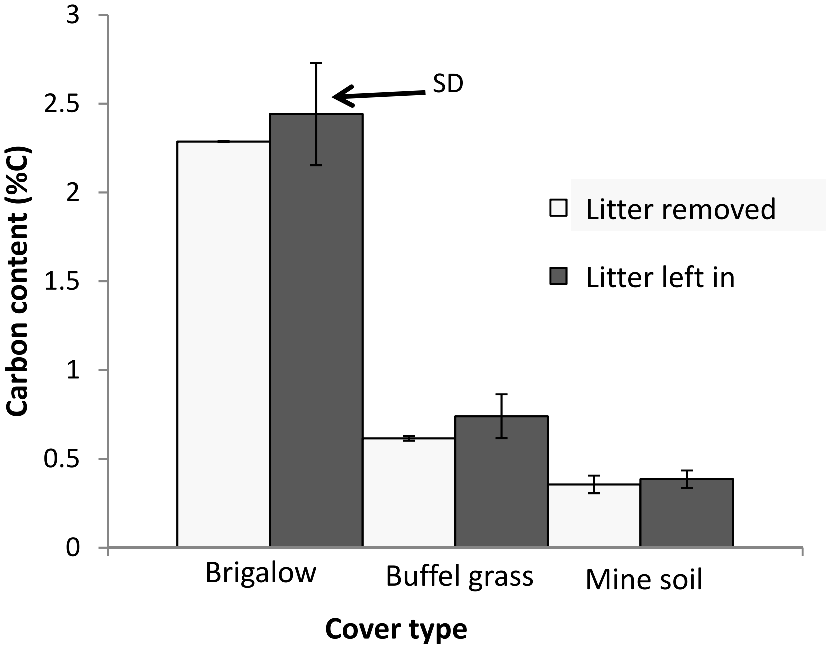

Figure G 45 Effect of removal of organic matter

The reason behind the initial confounding results from the first run of mine soils tested with Heanes (1984) that differ from the second run including natural soils is not understood.

It was also found that although removing organic matter increases carbon content, it was not significant (one-tailed paired t-test for TC p=0.14, n=7 mean TC_{picked} = 2.15%C, mean $TC_{unpicked}$ = 1.66%C), probably due to the small sample size. Furthermore, when one outlier was removed, the difference in the mean carbon values was >0.03%C and deemed not a large enough difference to merit continuing with organic matter removal.

By not having to remove all traces of non-soil organic matter, soil processing will be quicker, larger sample numbers can be processed and analysed in a more timely manner.

Time to analysis (Loss of carbon during storage)

Soil carbon resides in different fractions with different residence times, from labile to recalcitrant or inert. Carbon loss is due to microbial respiration and degradation of organic matter. Due to the length of time between sampling trips, there was some interest in whether soils from the first trip would retain their original carbon contents after more than 12 months in cold storage. If they did, they could be further used for analysis.

Other questions arise as the US EPA recommends analyzing samples within 28 days of sampling (Schumacher, 2002). This leads to questions such as, how much time can pass between measuring TOC and scanning on a DRIFT spectrometer before the sample is changed due to carbon loss? If samples cannot be analyzed within the EPA recommended 28 days, do the samples degrade further?

Methods

Study site

The two natural soils from the Brigalow Research Station were used: one remnant Brigalow stand and one buffel grass dominated paddock. One sample of rehabilitated mine soil from Goonyella coal mine in Queensland’s Bowen Basin was also included in this study.

Sample collection and processing

Following processing, aliquots of all of the soils underwent Dumas TOC analysis on a LECO TruSpec CHN analyser in triplicate (Rayment and Lyons, 2011). Samples were repeatedly analyzed over five months at roughly once-weekly intervals. Acidification of samples was not required as the presence of inorganic carbon was not detected by HCl drop test (Rayment and Lyons, 2011). Samples were stored in a cold room at 4°C between analyses.

Results and Discussion

Little change was observed in the carbon content of the soils over the five months of testing (Figure G 46). However, the baseline started beyond the recommended 28 days following sampling. The mine soil tested did not exhibit a trend of carbon loss.

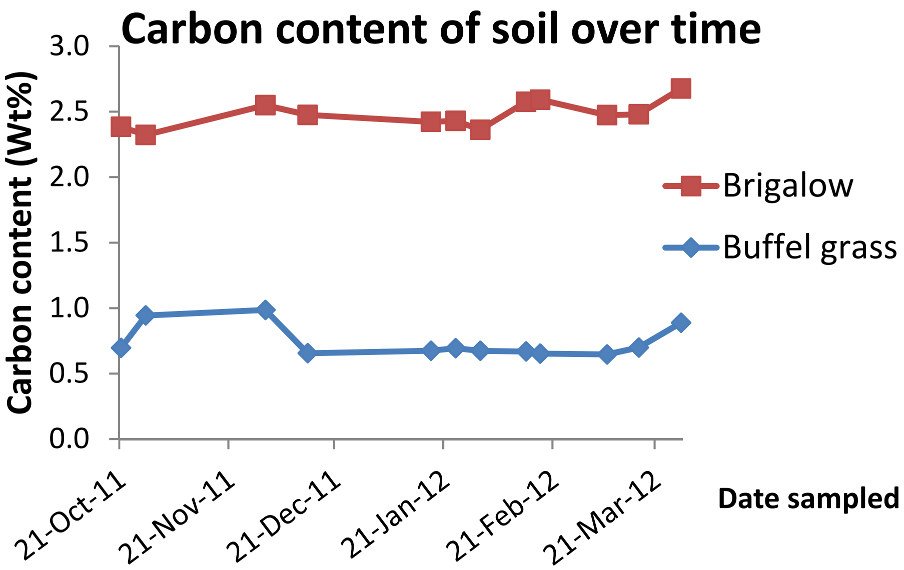

Figure G 46 Carbon content in natural soils during five months in cold storage

This experiment was repeated to establish a baseline within 28 days from sampling on natural soils. Samples of soil under Brigalow and buffel grass cover were analyzed, in duplicate, 15, 19, 22, 29, and 54 days from sampling to establish whether soils analyzed more than 28 days following collection can be used for green carbon determination (Figure G 47).

APPENDIX G

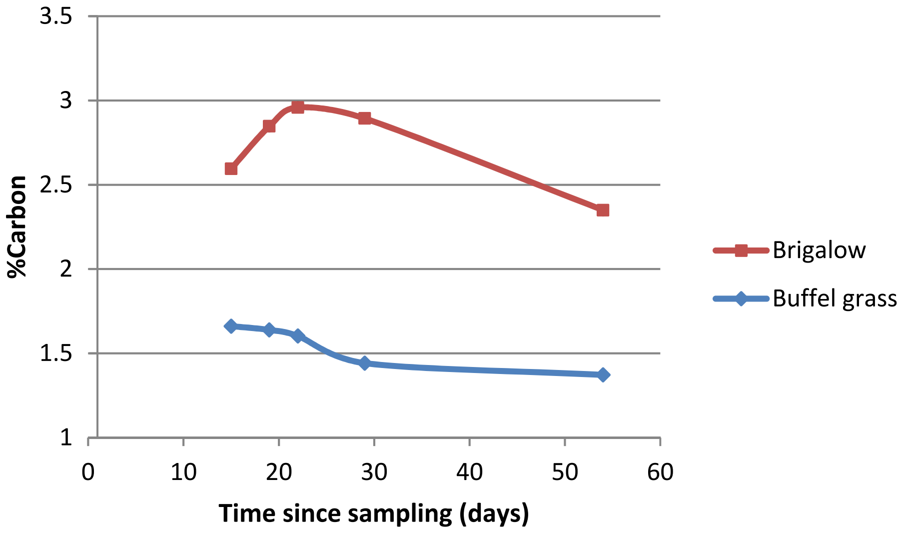

Figure G 47 Carbon content in natural soils during 2 months in cold storage

ANOVA analysis showed there was no significant difference between the means of the TOC values within 29 days from sampling for the Brigalow soil (p=0.217) and a significant difference when 54 days from sampling was added to the data set (p=0.026). Soil under buffel grass had a significant difference when 29 days from sampling was added (p=0.003) to the data set of 22 days from sampling (p=0.256).

To attain a true TOC result, samples of soil must be processed and analyzed within 28 days from sampling. After 28 days the OC levels have changed significantly from what they were and TOC readings will not be representative of the samples taken from the field.

Schumacher (2002) attributed this carbon loss to microbial degradation and/or volatilization of organic compounds. The carbon loss was described as “generally small” (i.e. <1.0%C) and its importance was minimized in the US government document. Furthermore, most published research does not specify whether TOC measurements were taken within 28 days of sampling, meaning either this is a given or not considered a very important factor in the analysis. Also, since the loss seems to taper off over time, it would appear that the most readily lost carbon is not being replenished over time in storage. As such, the time sensitivity of TOC measurement was not made into a defining feature of this research, however, all samples collected in 2013 were analysed for TOC within 28 days from sampling.

This leads to questions on whether it is feasible to analyse all samples within 28 days or whether it is simpler to base measurements on shelf stable carbon levels.

Also, it should be noted that adhering to the 28 day time limit for reliable TOC measurements can increase the cost of sample collection if sample processing and laboratory running time are limiting factors, resulting in greater numbers of trips for fewer samples.

Whether the change in TOC over time is appreciable in DRIFTs should be further investigated. Other questions that can be tested are whether the length of time post sampling can be determined with DRIFTs.

Total Organic Carbon Methods Comparison

There are multiple soil carbon measurement methods. The leading Australian soil methods manual lists 14 different methods of measuring different fractions of soil carbon (Rayment and Lyons, 2011). Total organic carbon (TOC) is an essential measurement for determining the green carbon fraction by deduction of the black carbon and coal carbon fractions. Since TOC analysis was carried out by different laboratories a comparison of their measurement methods was run to determine whether they produced similar results.

One laboratory used Heanes (1984) chemical oxidation (method 6B1 in Rayment and Lyons, 2011), while the other relied on acidified Dumas thermal oxidation (method 6B3)(Rayment and Lyons, 2011). Heanes method (1984) is not used frequently outside of Australia and acidified Dumas method is usually cited in the literature, making acidified Dumas more attractive as TOC measurement method.

When using acidified Dumas there is a choice of what acid to use to oxidize the inorganic carbon into CO_2 while preserving the organic carbon species. HCl is often the acid of choice; however, H_2SO_3 is also recommended (Caria et al., 2011, Fernandes and Krull, 2008, Rayment and Lyons, 2011). The choice of acidification method may ultimately be decided by the analytical laboratory as there are risks of damaging the elemental analyzer (Appleton, 2011, pers. comm., Appendix E).

Methods

Following processing, 15 samples of mine soils from Blackwater and Curragh coal mine rehabilitation were sent for Heanes (1984) TOC analysis at the Department of Environment and Resource Management laboratories. Another set of the same samples were ground and sieved to 1 mm fineness. Small aliquots were placed on watchglasses and treated with 2M H_2SO_4 added drop-wise until effervescence was not observed. Concentrated $Ba(OH)_2$ solution was added drop-wise, to a maximum two drops to neutralize any excess acid and the samples were dried on a hotplate. There is a risk of adding carbonates to the sample if $Ba(OH)_2$ is in excess as it will react with atmospheric CO_2 to form $BaCO_3$ precipitate. These acid-treated samples were sent for Dumas TOC analysis at the Analytical Services unit of the School of Agriculture and Food Sciences at the University of Queensland St Lucia campus (Rayment and Lyons, 2011).

Results and discussion

Results from both labs were analyzed using a paired t-test. The statistical analysis revealed that the results from the different labs were significantly different ($p = 0.03$, two-tailed, $n=15$). The cause for the difference, however, was not identified but is most likely due to laboratory differences or differences in their methods (see Table G 12 in the appendices for values). However, when the uncertainty in the measurements was set at 10% for Heanes, as stated in the reported results, and assumed 5% for Dumas, only two of the samples were significantly different. As the majority of the samples were not significantly different between the two methods when uncertainty is included, the results may be considered sufficiently similar.

The use of one method/lab is the ideal protocol for the determination of TOC. However, this may not be possible due to machinery breaking down, laboratory upgrades, or large sample backlogs when time dependence is considered (see Time to analysis (Loss of carbon during storage)).

The method to determine TOC for the samples collected in 2010 have been a mixture of Heanes (1984) and H_2SO_4 acidified Dumas. Following the results from this and the loss of carbon during storage experiments, all samples collected in 2013 were analyzed within 28 days from sampling at the same laboratory using H_2SO_3 acidified Dumas.

Table G 12 Heanes and Dumas TOC results

Sample ID	Heanes TOC (%C)	Dumas TOC (%C)
28.3 0-0.5	2.49	2.37
28.3 0.5-1	1.93	2.19
29.2 0-0.5	2.35	2.13
29.2 1-2	1.59	1.74
29.2 2-5	0.98	1.42

29.2 10-20	1.20	1.35
7.1 0-0.5	3.13	3.11
7.1 0.5-1	2.77	2.87
7.1 1-2	2.52	2.83
7.1 2-5	3.02	3.31
7.1 5-10	2.45	2.76
7.1 10-20	2.20	1.93
7.1 20+	2.03	2.25
2000 T1.1 10-20	1.41	1.72
G38	1.13	1.20

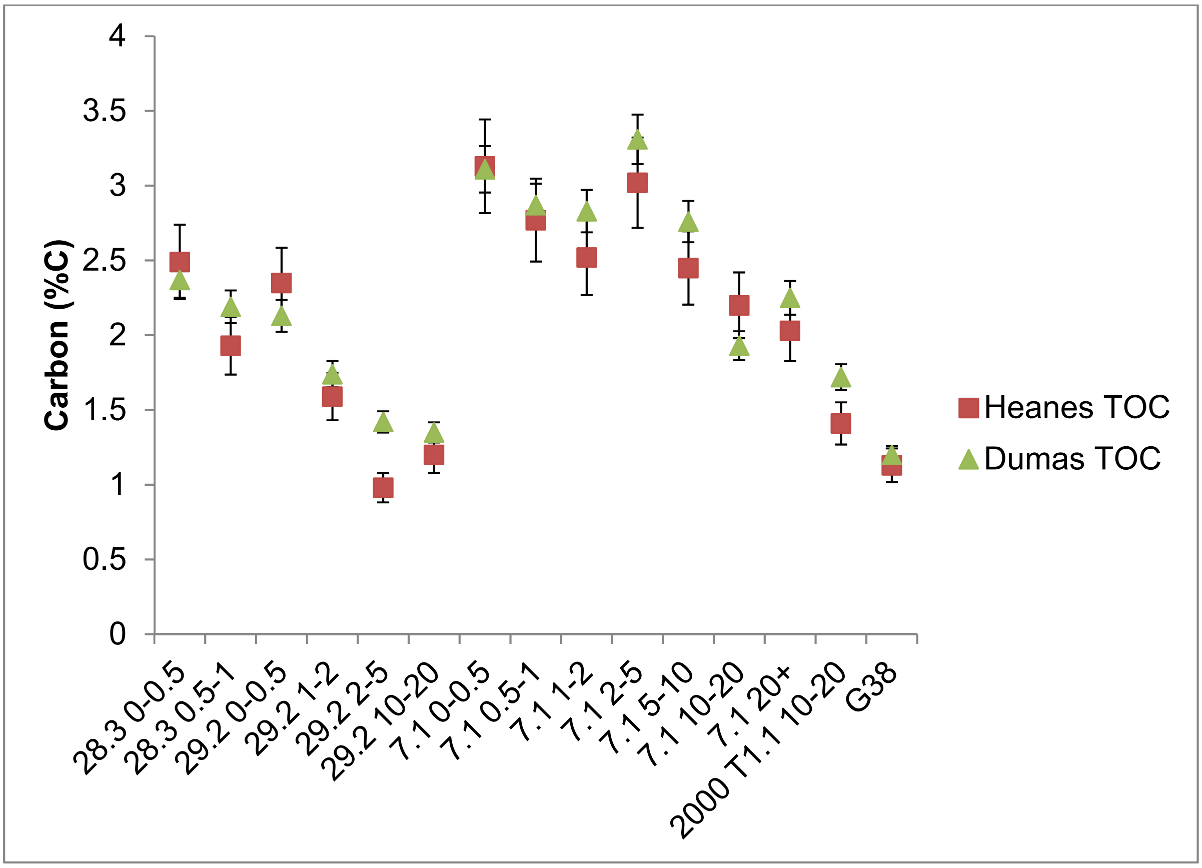

Figure G 48 A comparison of Heanes and Acidified Dumas TOC results on a suite of minesoils. When measurement error is included, TOC results from samples 29.2 2-5cm and 2000 T1.1 10-20 cm remain significantly different.

Verification of black carbon detection by elemental analysis

Black carbon is thermally stable and combusts at temperatures higher than green carbon. To verify that elemental analysis measures relevant sections of the BC continuum mixtures of clean sand and wood char of known proportion were analyzed.

APPENDIX G

Materials

Reference materials from the international black carbon ring trial, Vertosol and chestnut charcoal, were used as they are well characterized by multiple black carbon measurement methods (Hammes et al., 2007). Laboratory grade, acid washed sand was thermally treated to remove carbon impurities.

Method

Using the reference soil and the carbon-free sand as the matrices, charcoal was added by weight to create three mixtures of known BC percentages from ~0.5% - 3%. The vials of matrix and charcoal were placed in an end-over-end shaker for 30 minutes to homogenize the mixtures.

Subsamples of the mixtures and a blank matrix were analyzed by Dumas elemental analysis in duplicate and compared to the known BC content by paired t-test. Aliquots were also analysed by Rock-Eval pyrolysis on a Rock-Eval 6 (Vinci Technologies, Nanterre, France).

Results and discussion

The paired t-test of all eight sand mixture subsamples (0, 1, 2, and 3% charcoal) indicated the Dumas method gives results similar to the calculated carbon content ($p = 0.5$). There was no obvious bias in measured carbon content compared to calculated carbon content (Figure G 49).

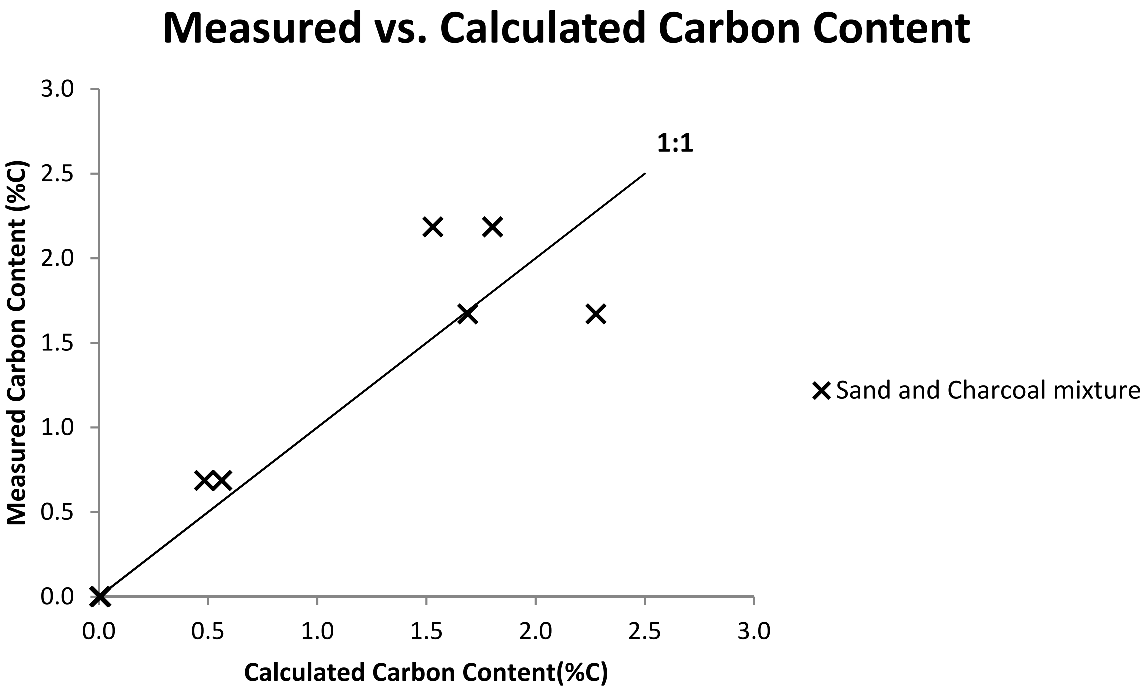

Figure G 49 Black carbon detection by Dumas method of mixed sand and charcoal

The reason for the discrepancy between measured and calculated BC may be due to human error. The fine charcoal powder has the propensity to cling to the sides of vials, is light weight and is easily influenced by static electricity. As such, it was difficult to avoid loss of material and maintain homogeneity during transference between containers and weigh boat. Variance within duplicates was highest for the 2% added charcoal mixture with a variance of 0.172% from an expected 1.67% C value and lowest for 1% added charcoal, 0.003% from an expected 0.04% C value. The values for the blank sand were 0.01 %C, as expected.

Spatial distribution of organic carbon in the soil profile

Mine soils are, essentially, new soils and are highly heterogeneous across distance and depth. They are poor in organic carbon due to the weathering during stockpiling and it may be possible to discern the accumulation of soil organic matter, as soil organic carbon along its depth (Ussiri and Lal, 2008a, Ghose and Kundu, 2003). It is assumed that the main source of organic matter in mine soils is from the litter layer on the surface of the soil. This may be supported by the fact that forested soils contain higher proportions of total SOC in one meter depth in the top 20 cm than grassland in similar climatic range (Jobbágy and Jackson, 2000). The integration of this organic matter into the soil would be in a downward migration pattern. In order to detect this pattern a specialized sampling protocol was used, with small depth increments being sampled near the surface and increasing with depth. The understanding that pollutants may migrate in soil has led to the sampling along depth as well as across lateral distance; however, these studies used coarser increments of 5cm and horizons (>>1cm) (Sielaff and Einax, 2007, Ping et al., 2007) The separate increments were tested for total organic carbon by Heanes wet chemical oxidation (Rayment and Lyons, 2011).

Methods

Study sites

Areas of rehabilitation at three Bowen Basin coal mines, Blackwater, Curragh and German Creek, were visited and sampled in August 2010. The ages of rehabilitation ranged from 8-19 years of rehabilitation. Sites were selected based on site characteristics, such as slope placement and groundcover type (cover type). Areas where vegetation had not been established were excluded from the study as they are not considered successful rehabilitation and would not have organic matter accretion and subsequently, no green carbon (Ussiri and Lal, 2008a).

Sample collection and processing

Surface vegetation and litter were removed before holes were dug until 30 cm depth or the spoil layer was reached. Using a paint scrapper and trowel, seven depth increments were sampled according to distance from the surface: 0-0.5cm; 0.5-1 cm; 1-2 cm; 2-5 cm; 5-10 cm; 10-20 cm; below 20 cm. If the applied topsoil layer was less than 20 cm deep, the 10-20 cm increment was where in most cases the spoil layer was reached and below this depth was only spoil. The spoil layer was not sampled as the presence of green carbon was not expected since roots often could not penetrate the material, which was hard, rocky, and difficult to dig in.

Samples were labeled, placed in plastic bags and stored in plastic tubs until they could be transferred to a refrigerator at the end of a day. Samples were transported to Brisbane by courier in a non-refrigerated vehicle.

Upon receipt at the laboratory, samples were placed into a cold room set at 4°C. Samples were later dried in an oven set at 40°C for 7 days. Dry samples were gently crushed with a mortar and pestle to break up clods and sieved on a 2mm sized screen. During crushing and sieving, large rocks and pieces of organic matter were manually removed.

Results and Discussion

There was little change in organic carbon levels seen in the few whole depth profiles tested. One site that had been rehabilitated for a longer period than the rest at 19 years, roughly 10 years more than the rest, exhibited less difference between depth increments nearest the surface than some newly rehabilitated sites (Figure G 50).

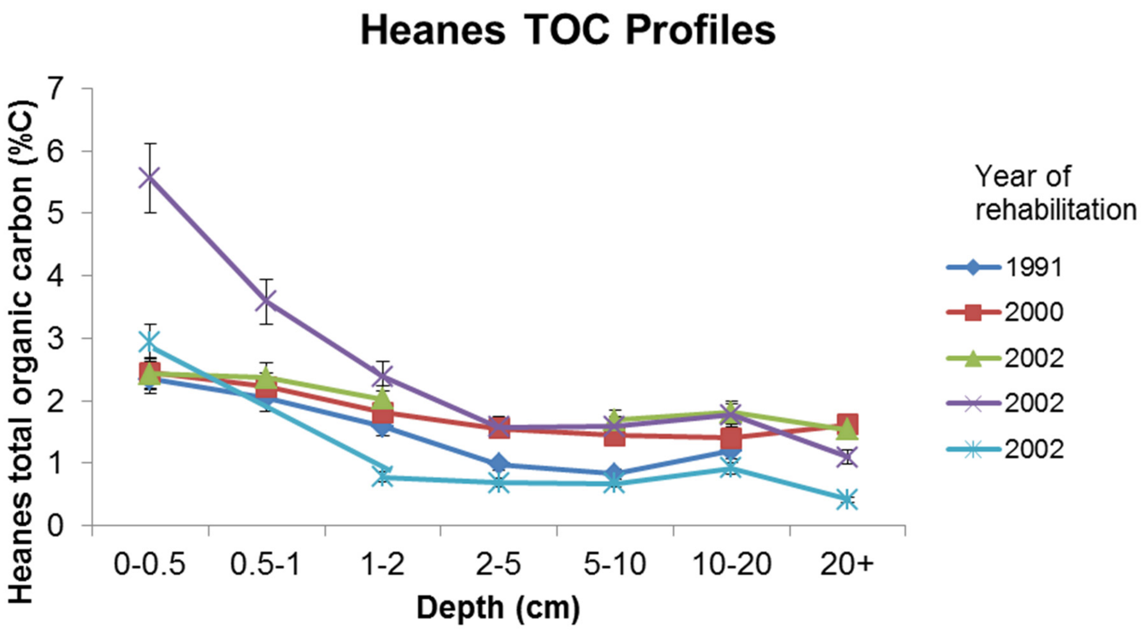

Figure G 50 Total organic carbon content along depth

The reason why the concentration gradient is less steep with depth for the longer rehabilitated site than two of the newer rehabilitated sites cannot be drawn from such a small dataset. These measurements are somewhat unexpected since the longer a rehabilitated site has vegetation i.e. the older the rehabilitation, the more opportunity there is for fresh organic matter to enter and accumulate in the soil. Since the litter layer was assumed to be the predominant way for organic matter to enter the soil the highest concentration of carbon would be nearest the surface and litter layer.

It can be noted that the site with the greatest TOC difference along depth was inside the drip zone of a senna bush where the soil was noticeably richer brown-looking. The difference between the two sites within one field (sites CU08_1 and

CU08_2) may indicate that kind of carbon content difference groundcover type may have as site CU08_1 was adjacent to a buffel grass tussock.

Conclusion

As no significant difference in carbon content between the top two 0.5 cm depth increments was found in the majority of samples tested, sampling to monitor carbon accretion should have depth increments no finer than 1cm. Sampling small increments finer than 1 cm in partly very hardened top soil is difficult and is reliant on the skill of the sampler. The high likelihood of sampling error when increments are very fine further decreases its usefulness. As there is doubt on the truthfulness of results when reporting on such difficult to sample increments, it lends weight to increasing increment size.

Accordingly, the second sampling campaign collected fewer depth increments and focussed on targeting different cover types (buffel grass, senna bush, trees) to investigate the effect of cover type. The following depth increments were collected: 0-2 cm, 2-5 cm, 5-10 cm, 10-20 cm, and below 20 cm. Such sampling will abate issues regarding sampler precision and increase collection and analysis economy. Sampling also targeted areas with the different types of cover over a range of ages to investigate the effect of time.

Appendix H

PCA Overview Graphs

The Unscrambler (CAMO Software AS, 2011) automatically produces graphs when a PCA is run.

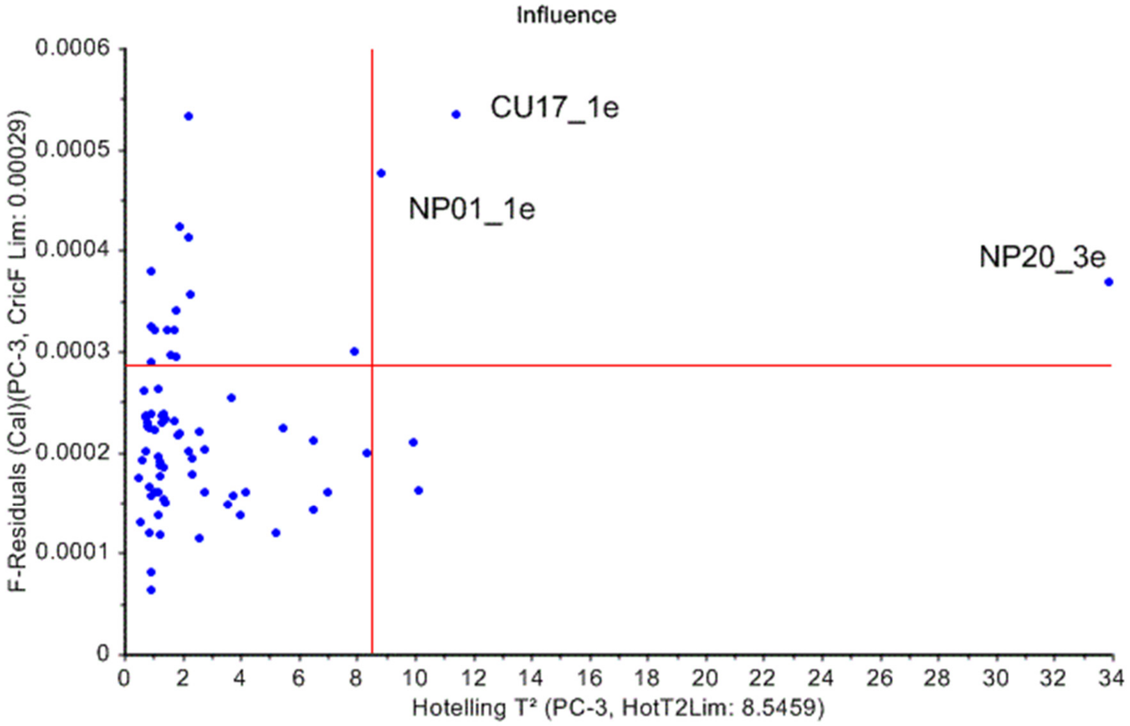

Figure H 1 PCA influence plot showing potential outliers in upper right quadrant. This PCA model is using three principal components. NP20_3e shows high influence with high residuals whereas CU17_1e is showing higher residuals but falling somewhat closer outside of the Hotelling T^2 ellipse than NP20_3e.

Appendix H

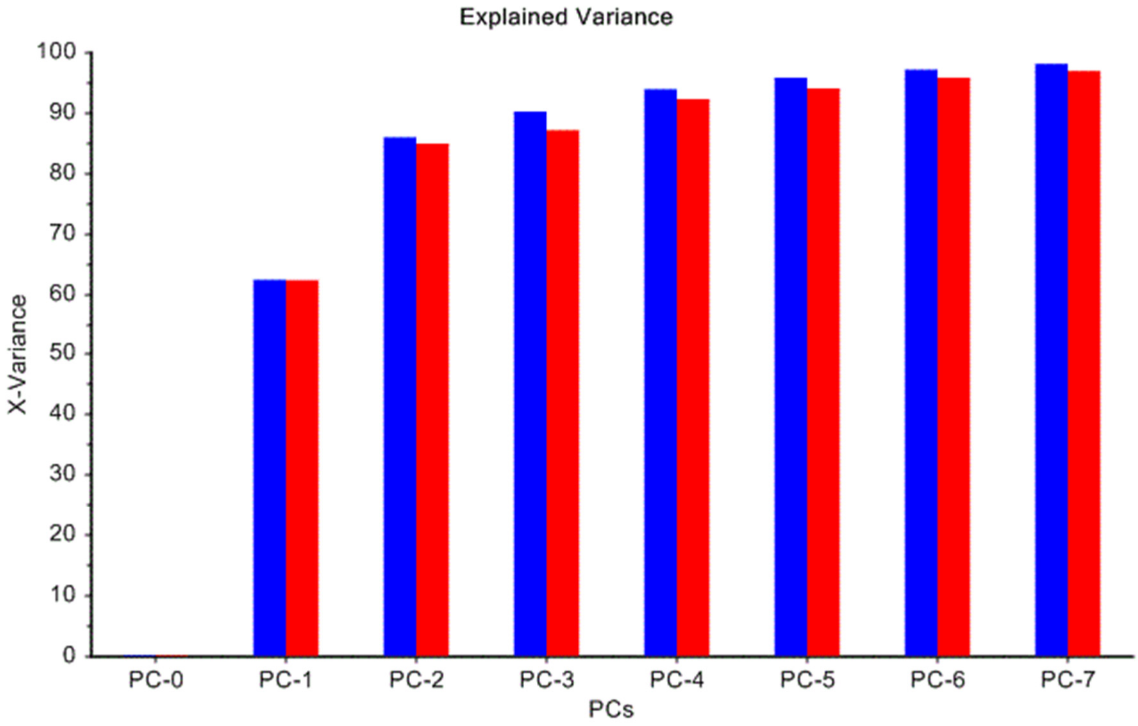

Figure H 2 PCA explained variance plot shows the amount of variance in the data that is explained based on the number of principal components used. This graph is used to determine the number of principal components to use.

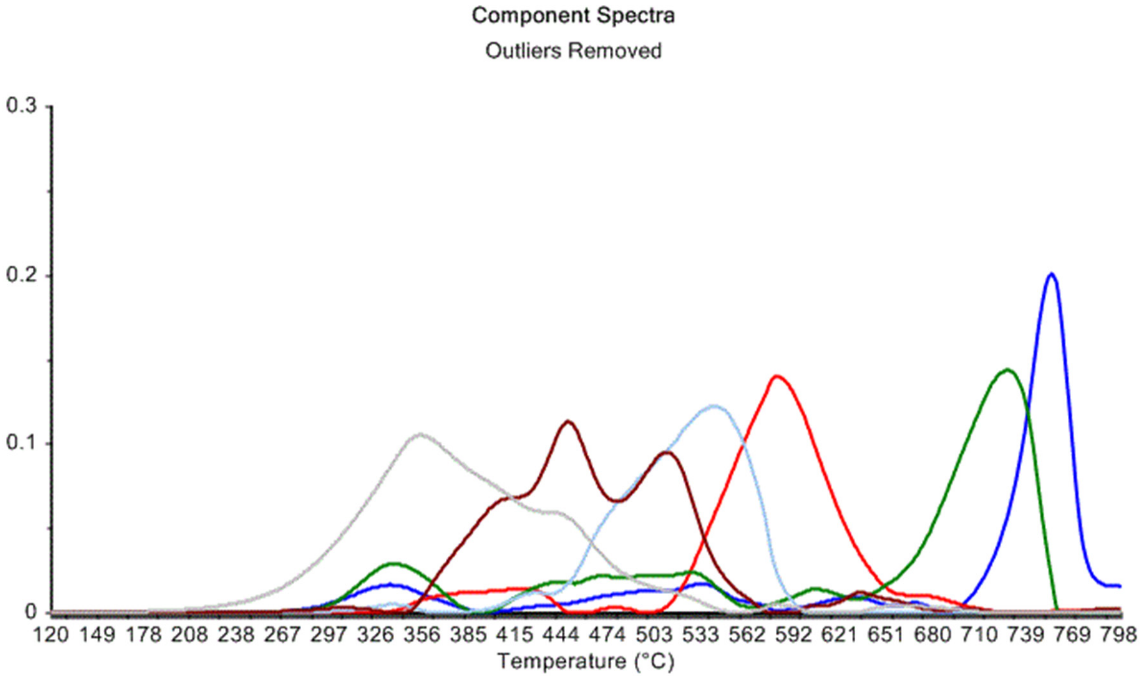

Figure H 3 Pure components of the six component MCR solution when outliers have been removed. While the peak temperatures have remained the same, the tails of the components have changed and the shape of the BC component (in light blue) has a broader shoulder.

Appendix I

Table I - 1 Sample types and the analyses they underwent. Sand refers to the carbon-free sand, Brigalow refers to the samples from the Brigalow Research Station, Vertosol refers to the reference Vertosol.

Sample ID	Sample name	TC, TOC	WBOC	TA-EGA	DRIFT	PSA
Sand		Y	N	Y	N	N
Brigalow		Y	N	N	N	N
Vertosol		Y	N	Y	Y	N
NP02_1a	R2.1 2011	Y	N	Y	Y	Y
NP01_1a	R2.1 2012	Y	N	Y	Y	Y
NP20_1a	NP2.1	Y	N	Y	Y	Y
NP20_2a	NP2.2	Y	N	Y	Y	Y
NP20_3a	NP4.1	Y	N	Y	Y	Y
NP10_1a	NP13.1	Y	N	N	Y	Y
NP00_1a	NP15.1	Y	N	Y	Y	Y
NP10_2a	NP 14.1	Y	N	N	Y	Y
NP06_1a	NP17.1	Y	N	Y	Y	Y
GC08_1a3	43.1 1-2	Y	Y	Y	Y	N
CU10_1a1	2000 T1.1	Y	Y	Y	Y	Y
BW31_1a2	7.1 0.5-1	Y	Y	Y	Y	Y
NP06_2a	NP17.2	Y	N	Y	Y	Y
NP27_1a	NP9.1	Y	N	N	Y	Y
NP10_3a	R10.1	Y	N	N	Y	Y
NP01_2a	NPR12.1 2012	Y	N	Y	Y	Y
CU05_1a	R9.1 2008	Y	N	Y	Y	Y
CU07_1a	R12.1 2006 T1	Y	N	N	Y	Y
CU03_1a	R2.1 2010	Y	N	Y	Y	Y
CU11_1a	R2.1 2002 (2013)	Y	N	Y	Y	Y
CU11_2a	R2.2 2002 (2013)	Y	N	Y	Y	y
CU08_2a1	2002 T1.2	Y	Y	Y	Y	Y
BW19_2a2	29.2 0.5-1	Y	Y	Y	Y	Y
CU08_3a	R4N.1 2005	Y	N	N	Y	Y
CU08_4a	R4N.2 2005	Y	N	Y	Y	Y
CU17_1a	R11S.1 1996	Y	N	Y	Y	Y
CU17_2a	R11S.2 1996	Y	N	Y	Y	Y
CU00_2a	Ref GPT	Y	N	N	Y	Y
CU00_3a	Ref EC	Y	N	Y	Y	Y
CU10_3a	R12N T1.1 2003	Y	N	N	Y	Y
CU10_4a	R12N T1.2 2003	Y	N	N	Y	Y
GC26_1a1	2.1 0-0.5	Y	Y	Y	Y	Y
GC26_2a1	2.2 0-0.5	Y	Y	Y	Y	Y
CU10_2b	2000 T1.2 2-5	Y	Y	Y	Y	Y