Ministry for Primary Industries
Manatū Ahu Matua

Review of soil carbon measurement methodologies and technologies, including nature and intensity of sampling, their uncertainties and costs

MPI Technical Paper No: 2012/36

Prepared for the Ministry for Primary Industries
by Landcare Research

ISBN No: 978-0-478-40450-0 (online)
ISSN No: 2253-3923 (online)

November 2012

New Zealand Government

Growing and Protecting New Zealand

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Landcare Research
Manaaki Whenua

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Landcare Research Contract Report: LC0910/083
MAF Contract No.: CONT-20165-SLMACC-LCR

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DATE: 11 February 2010

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Summary

Project and Client
Measurement methodologies and technologies, including nature and intensity of sampling, their uncertainties and costs were assessed by Landcare Research in collaboration with AgResearch, GNS Science, Massey University, Plant & Food Research, Scion and University of Waikato for the Ministry of Agriculture and Forestry in December 2009.

Main Findings
In a recent analysis of soil carbon concentration in a European monitoring network, Saby et al. (2008) showed that the minimum detection limit was 2 g C/kg soil. Tate et al. (2005) estimated the average carbon content for New Zealand pastoral soils to a depth of 0.3 m to be 35 g C/kg soil, so the minimum change in soil carbon likely to be detectable is 6%. Being able to verify this relatively small increase in carbon storage across New Zealand's pastoral soils could be extremely valuable. For New Zealand's 11 million hectares of pasture land (Meat & Wool 2009), an increase in soil carbon content of 2 g C/kg soil may be scaled (assuming 0.3 m depth of soil and bulk density of 1000 kg/m^3) up to 66 Tg C (66 × 10^{12} g C). If CO_2 is traded at NZ$ 20 per tonne, the value of 66 Tg C would be nearly NZ$ 5,000 million.

Methodologies for measuring carbon concentration in soil samples and their application at field scales were reviewed, based on scientific literature. The methodologies were classified into four groups consisting of

- conventional approaches using laboratory analysis of soil cores
- direct measurements of ecosystem carbon exchange
- emerging technologies
- developing technologies.

Distinctions were made on the basis of existing stage of development and adoption.

Conventional approaches of sampling employing soil cores and analysing for carbon concentration are used widely and the approach, coupled with a modelling framework formed the basis for the existing soil carbon inventory for New Zealand. Methods and procedures for sample collection and data analysis are outlined, addressing the needs specific to pastoral and forest systems. Although this proven approach is adopted widely, its principal disadvantage is the need to collect large numbers of samples (with associated costs) to account for spatial variability at the paddock scale or to determine temporal changes in soil carbon or differences following land use change. For one site using conventional approaches, the costs of establishing a plot, collecting soil samples and analysing for carbon concentration in soil cores to a depth of 0.3 m is estimated to be $5,000 to $6,000.

Two approaches to analysing statistical variability and uncertainty in estimates of soil carbon based on conventional approaches using laboratory analysis of soil cores are outlined and demonstrated. The first approach summarises methods to determine

errors associated with site selection, sampling and measurement, then provides algorithms to assess changes in soil carbon stocks and their standard errors.

The second approach uses power analysis together with example data sets to estimate the number of samples required to confirm a minimum statistically detectable change in carbon stocks either temporally at the same land use or with land-use change at the same site. The results for three case studies are shown: temporal change after 23 years in soil carbon for North Island dairy farms, land use change from dry stock pasture to arable cropping and land use change from pasture to plantation forestry. The numbers of samples needed to confirm a 2% change in soil carbon storage with a probability of 10% are 606, 2,449 and 741 for the three case studies, respectively. Sample requirements are much lower to detect a 10% change in soil carbon with the same probability of 10% (25, 102 and 30, respectively).

Direct measurements of carbon exchange at ecosystem scales are based on quantifying the components of the carbon balance for a site. While this approach is used widely in research to interpret the processes regulating carbon exchange, it is not likely to be adopted for compiling inventories. Uncertainty in estimates of annual sums of net ecosystem productivity can range from 0.3 to 1.0 Mg C/ha/y which is in the order of the carbon content of a sheet of computer printer paper! While this does not seem a great deal it approaches the rate of soil carbon loss reported for New Zealand pasture soils.

Emerging technology based on infra red sensing instrumentation (NIRS) is an alternative to conventional approaches with distinct benefits, despite the need for further development and testing. Instrumentation is available commercially and published work demonstrates the growing interest in successful application of the technologies. Measurement of soil samples involves less preparation, avoids the use of chemicals and is more rapid and thus cheaper than conventional laboratory soil carbon analytical methods. This technique has the further advantage that robust sensors have been developed that can be attached to trailers. When data from the sensors are coupled with GIS and geostatistical data, this allows rapid mapping of carbon at paddock scales in real time. Success of this technology has been demonstrated and is being developed further. This combined approach is very promising for rapid, real time spatial mapping of soil carbon concentration and to quantify changes in concentration with time or following management manipulations at paddock scales.

Developing technologies based on laser spectroscopy and nucleonic methods employing radioactive sources are classified as available only as prototype systems being tested. Laser-induced breakdown spectroscopy can be used for rapid measurements of soil carbon at high precision, but low penetration restricts its use to small samples. Inelastic neutron scattering (INS) is being developed as a rapid, non-disruptive method to measure soil carbon in profiles at field sites directly. However, investment costs to build the instrument are high and considerable further development and testing is required.

The principal benefits and disadvantages of each approach, in relation to purpose are listed as part of this summary in Table 1.

Table 1 Summary of methodologies for measuring soil carbon with indicative benefits and disadvantages

Methodology	Purpose	Benefits	Disadvantages
Conventional approaches			
Soil coring approaches using furnace technology for analysis	Analysis of individual core samples collected from plots to determine site spatial and/or temporal variability in soil carbon. With spatial data and models used as basis to build existing national soil carbon inventory	Proven analytical precision Standard protocols well established	Destructive sampling required High cost of sampling, preparation and laboratory analysis Large number of samples needed to account for spatial variability
Ecosystem carbon exchange	Determining biophysical drivers and processes regulating carbon exchange at paddock scales. Estimation of rates of carbon exchange and components of ecosystem carbon balance	Continuous measurements of net input and loss of carbon at high temporal resolution (typically 0.5 h) Account for diurnal and seasonal effects Excellent approach for flat land Large footprint for sample (10^3 m) Data well suited to interpretation using process-based models	High degree of technical expertise required Able to operate only at few sites Some problems with topography Some problems with low wind speeds, night-time exchange and sensor use during rain
Emerging technologies			
Near infrared reflectance spectroscopy (NIRS)	Alternative method for measuring core samples to determine spatial variability in soil carbon. Demonstrated non-disruptive extension using moving sensor to map spatial variability across paddock scale	Rapid collection of spectra Reduced sample preparation Low analytical cost Reduced sample size required compared with standard coring approaches High resolution of measurements (10^{-3} m) Possible *in situ*, non-destructive sampling Possible sensor attachment to moving tractor to collect spatial data.	Destructive sampling required for lab samples Large number of samples needed to account for spatial variability

		Measures organic and inorganic carbon pools (possibly fractions) simultaneously Possible to develop global library of spectra for monitoring and mapping soils	
Near infrared reflectance spectroscopy combined with geostatistics	Determination of spatial variability and mapping of soil carbon in real-time at paddock scales. Coupled with GIS and geostatistics to produce maps of soil carbon and other soil properties at regional scales	Robust field instrument able to be attached to trailer for ‘on-the-go’ measurements to 1 m depth Coupled with GIS, geostatistical interpretation allows rapid mapping of carbon and nitrogen at paddock scales in real time Deploy with electromagnetic sensor to map soil water content Possible remote use from satellites	Need to separate effects of roots, but possible Further testing with a wide range of soils needed Needs calibration for each soil type High degree of software expertise required
Developing technologies			
Laser-induced breakdown spectroscopy (LIBS)	Alternative technology for rapid, remote measurement of carbon in soil samples	Rapid determination (< 1 minute) Capable of being used remotely High detection limits and precision	Low penetration in profile (10^{-3} m) Very small sample volume (10^{-8} m^3) Interference from roots, stones, changes in soil texture, water content Calibration dependent on soil type
Inelastic neutron scattering (INS)	Alternative technology for rapid, remote point measurement of carbon in soil profiles	Rapid determination Non disruptive High penetration in profile (0.3 m) Large sample volume (up to 10^{-1} m^3) Analysis of multiple elements possible Able to measure litter, live carbon Possible simultaneous measurement of bulk density	Need to improve accuracy Interference from other elements Possible variability in depth measured On-going radiation certification costs Potential radiation hazard (gamma rays) High initial investment to build and licence equipment ($300,000, not including labour costs) Further development and testing required

1. Introduction

The development and evaluation of technologies for soil carbon measurement are mainly driven by the interest in quantifying soil carbon stocks, and rates of change over time, for national greenhouse gas emission inventories. The general feeling at present amongst scientists and policy analysts is that widespread soil sampling is unlikely to be the method by which soil carbon is measured and audited in an emissions trading scheme as this would simply be too costly in time and labour. Alternative technologies may provide more cost-effective opportunities with reduced need for sampling intensity, reduced analytical costs and on-site, real-time measurements at the paddock scale. This report provides a comparative review of the benefits and disadvantages of existing methods with new technologies that are emerging and those still under development. Emerging technologies are classified as those where instrumentation is available commercially and published work demonstrates the growing interest in successful application of the technologies. Developing technologies are classified as those where prototype systems are available but where considerable development is still required.

The objective of developing new technologies is to develop cost-effective approaches to measuring changes in soil carbon storage. Small changes in carbon storage are difficult to determine precisely. In a recent analysis of soil carbon concentration in a European monitoring network, Saby et al. (2008) showed that the minimum detection limit was 2 g C/kg soil. Tate et al. (2005) estimated the average carbon content for New Zealand pastoral soils to a depth of 0.3 m to be 35 g C/kg soil, so the minimum change in soil carbon likely to be detectable is 6%. Being able to discern and verify this relatively small increase in carbon storage across New Zealand's pastoral soils could be extremely valuable. For New Zealand's 11 million hectares of pasture land (Meat & Wool 2009), an increase in soil carbon content of 2 g C/kg soil may be scaled (assuming 0.3 m depth of soil and bulk density of 1000 kg/m^3) up to 66 Tg C (66 × 10^{12} g C). If CO_2 is traded at NZ$ 20 per tonne, the value of 66 Tg C would be nearly NZ$ 5,000 million. This suggests that there is a compelling reason to develop and test technologies to verify carbon storage changes accurately in pastoral agriculture soils across New Zealand.

Measurement technologies and technologies, including nature, intensity of sampling, their uncertainties and costs, were therefore assessed by Landcare Research in collaboration with AgResearch, GNS Science, Massey University, Plant & Food Research, Scion and University of Waikato for the Ministry of Agriculture and Forestry in December 2009.

The conventional approach to measuring soil carbon for inventory purposes and for measuring temporal changes in soil carbon or in response to land use change is to collect soil cores that are analysed for carbon concentration using standard laboratory instrumentation. Measurements of bulk density are also required to convert carbon concentration from a mass to volume basis. In this report, we provide a full description of this methodology, including estimates of uncertainty and costs. The high numbers of samples that are needed to account for spatial variability means that this approach is time consuming and expensive. Several new technologies are being developed to reduce these costs. Firstly, new proximal sensors are being developed for direct, rapid and instantaneous measurements of physical properties of soils that are associated with carbon concentration in cores collected from field sites, avoiding the need for chemical analysis. Secondly, these new sensors are being tested at field sites to measure soil carbon concentration directly without the need to remove soil cores. These sensors increase the ability to make many more measurements rapidly but issues of differences in calibration attributable to soil type and precision require further research. Thirdly, in combination with the use of proximal sensors for direct measurements of soil carbon at field sites, new methods are becoming available to extrapolate point measurements across a landscape, using spatial autocorrelation geostatistics. An entirely different approach to estimating temporal changes in soil carbon storage or differences with land use change at paddock scales is the estimation of components of carbon balance from measurements of carbon fluxes using micrometeorological methods. This approach is especially useful for interpreting the environmental and management drivers of changes in soil carbon.

This report is divided into four sections:

- conventional approaches using laboratory analysis of soil cores
- direct measurements of ecosystem carbon exchange
- emerging technologies
- developing technologies

For the conventional approaches using collection and analysis of soil cores, we have separated methodology specific to pastoral and forestry soils. While there is some overlap and repetition, these sections also recognise the differences in methodologies for the two land uses. Following description of the methodologies is a description of two complementary approaches applied to three data sets to estimate the statistical uncertainty in estimates of soil carbon, including calculation of the number of samples needed to provide estimates within set limits for uncertainty. Subsequent descriptions of methodologies for ecosystem exchange, emerging and developing technologies for direct measurement of soil carbon are also followed by discussion of uncertainty. Estimates of costs for each methodology are also included.

2. Conventional approaches using soil cores

2.1 Pastoral and cropping soils

2.1.1 Sample collection methods

Sample size, depth, placement and number

Measurement of a soil carbon stocks requires the collection of soil samples that adequately represent land units (e.g. paddock, slope position, experimental plot, etc) and represent all soil layers affected significantly by management or other factors (e.g. climate) that affect stock changes over time. Factors such as depth of tillage, plant root depth and horizon depth should be considered when selecting the maximum depth of sampling and the sectioning of soil into depth increments.

The size, number and length of cores sampled depend on the vertical and horizontal stratification or heterogeneity of soil organic matter across the land unit of interest (e.g. plot, paddock, catena, etc.) and the objectives of the research. In general, the greater the horizontal gradient, the greater the number of cores should be collected. Similarly, the greater the vertical gradient in soil carbon, the greater the number and the shorter the sample increments should be. Often the length of the sample increments increases with increasing depth because the soil carbon concentration tends to be more uniform with depth.

If the objective is to estimate the total carbon stock for an entire unit of land then the sample collection should roughly approximate the subunits of land by area. For example, if approximately one third of the land area is represented by shallow sandy soils and the other two thirds by deeper, silty soils, then the sampling of multiple cores should be distributed accordingly. Other subunits of interest may include paddock gateways, headlands, land shaded by hedgerows, poorly drained low lying areas and various positions along a slope.

Sampling relative to the position of annual or perennial plants is also important, particularly at the soil surface where plant carbon inputs are often distributed horizontally in relation to the root distribution. As a rule of thumb, soil samples are normally distributed across the soil surface in proportion to the approximate area represented by the plant row and inter-row. Where the plant distribution is not structured, care should be taken to collect samples from significant gaps in the plant canopy, where they occur, in addition to the areas under plant cover, in proportion to the areas they each represent.

Volumetric core sampling and corrections for bulk density

A simple approach for estimating soil carbon stocks is to press or carve a cylinder of known volume into the soil surface down to the depth of interest. The cylinder is removed and soil core extruded. Depending on the depth of sampling the extruded soil core may be divided into sections. The field moist sections of soil are weighed, homogenised and sub-sampled for analysis of total carbon and water content (Blakemore et al. 1987). Dry mass of the soil for each section is calculated using the water content and original field moist weight of the subsection. Bulk density is then determined by dividing the dry mass of the section by its volume.

The major error that can arise is when the insertion of the core causes compaction or shattering of the soil column. This can be tested for by comparing the depth of the hole in the soil profile to the length of the extruded core. Alternatively, where shorter, open-ended corers are used, it is often easier and more accurate to use a ruler to measure the distance from the top edge of the corer to the surface of the soil (usually at 3 to 4 locations), both inside and outside the corer, after it has been positioned to the correct depth for sampling. Soil compaction or shattering is only an issue where the soil is to be extruded and cut into sections representing different depth increments. There are no issues where the entire length of the soil core is to be used for bulk density and carbon analyses (i.e. for single depth samples). Where the core is extruded and cut into different depth increments, a relatively straightforward procedure can be used to correct for small amounts of top soil compaction or, in particular, where shattering has left the soil surface unstable and prone to collapsing when the soil core is extruded. In this case, a ruled cylinder can be used to determine the length of the soil core by measuring the distance from the soil core surface (inside the corer) to the top edge of the soil corer, in a core of known length. Once the core is extruded, this measurement can be used to measure from the bottom of the core to determine the correct depths for sectioning the core into various depth increments. Errors in bulk density resulting from compaction or shattering are usually largest when small diameter cylinders are used to collect cores and/or where the sampling depth is relatively shallow. Cultivated soils are particularly prone to the effects of compaction and shattering during sampling.

The following text and photographs describe a soil coring technique that applies many of the concepts outlined above and has been used successfully to measure soil carbon stocks to a fixed depth of 0.3 m or in equivalent masses of top soil (e.g. top 3,500 Mg/ha) in several significant field trials (e.g. the Millennium Tillage Trial) and on paddocks representing arable, vegetable and pastoral farming at various locations across New Zealand.

The technique employs a purpose built 0.45 m long steel cylindrical corer with a bevelled tip and a slightly recessed inside diameter of 50 mm (Fig. 1A). The corer is driven into the soil to a depth of approximately 0.35-0.45 m with repeated impacts from a slider hammer device attached to the top of the corer (Fig. 1B). The vibration from the impacts is reduced by the use of a Teflon washer fitted to the impact surface. Inside and outside measurements from the top of the soil surface can be used to confirm that the core has not been compacted. The corer is rotated and gently pulled from the soil with purpose built extraction tool. A ruled Perspex cylinder is placed in the top end of the corer to measure the length of the intact soil core, in a coring cylinder of known length (Fig. 1C). The soil is gently pushed from the top of the core on to a processing tray by applying a controlled force to the bottom of the core with a flat blunt ended probe (Figs. 1D-F). In this example a small ramp is used to support the soil core as it is pushed from the coring cylinder. The general aim is to produce an intact soil core with minimal disturbance to the soil surface. A half-cylinder cutting template made of Perspex is placed on top of the soil and positioned by measuring from the bottom of the soil core, based on the previous length of core measurements (Fig. 1G). A box knife is then used to cut the full-length core into increments of known depth, length and volume (Fig. 1H). The template is removed carefully and a thin, flat plastering knife is used to separate the core at each cut point and transfer the soil into an appropriate container (Fig. 1I). Normally the full length of the core exceeds the combined length of the samples to be collected, such that the bottom section of the core can be discarded. This is generally desirable because the bottom section (20-30 mm) of the core is often compacted by the force of the probe used to push out the core. Under most circumstances several soil cores would be collected from any particular land unit area (e.g. field trial plot, paddock etc.) using this method. The cores collected may be retained as separate and independent samples or combined by depth and/or sample location to form one or more composite samples.

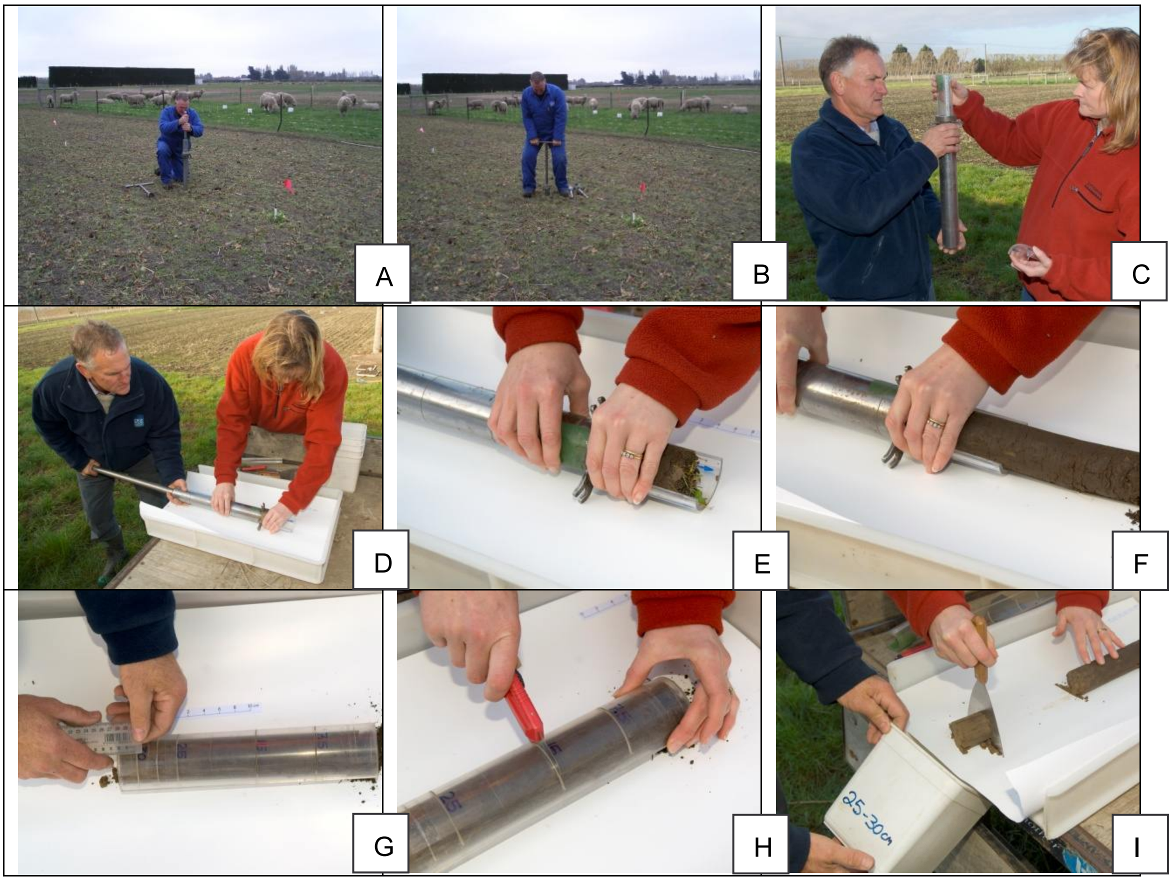

Fig. 1 A photographic sequence outlining the steps involved in the field collection and processing of soil cores for analysis of soil bulk density and soil carbon concentrations to be used in estimating soil carbon stocks to a depth of 0.3 m (see text for explanation).

There are several advantages of this particular coring method. The techniques allows collection of samples where: (1) compaction is evident and avoidable, (2) surface disturbance is minimised and corrected for in collecting samples of a known depth and volume, (3) bulk density and soil carbon (and other properties where required) can be measured from the same sample and 4) the results can be used to calculated soil carbon stocks to a defined depth (e.g. 0.3 m) or in equivalent masses of soil (e.g. the top 3,500 Mg of soil). An estimate of the cost associated with the method described above is given as follows. The estimate is based on a scenario where 10 soil cores are collected from a single paddock (e.g. 10 ha area) for estimating its soil carbon stock to 0.3 m depth. In this case the 10 soil cores are sectioned into 3 depth increments (e.g. 0-0.1, 0.1-0.2 and 0.2-0.3 m) and the samples composited by depth to form three composite samples for measurement of bulk density and soil carbon concentration.

The total cost for collecting and processing the samples, measuring the bulk density and soil carbon concentrations and calculating the soil carbon stock to 0.3 m is $450. This cost estimate does not include the costs associated with locating a suitable paddock, contacting the land owner and obtaining sampling approval, transport to and from the paddock and the addition of any supplementary measurements or calculations (e.g. equivalent mass). The addition of these factors depends very much on the specific research or measurement objectives and would add substantially to the per paddock cost estimate.

Sampling for equivalent mass calculations of carbon stocks

Soil carbon stocks are expressed commonly as the amount of carbon in a fixed-depth layer of soil per unit area of land (e.g. Mg C/ha to a specified depth). The fixed-depth approach is subject to bias when comparing carbon stocks temporally (or spatially) if bulk density changes (Ellert et al. 1998). For example, if the bulk density of the 0-0.3 m sampled layer of treatment A is 1.0 Mg/m^3 and that of treatment B is 1.10 Mg/m^3, the soil carbon stock in treatment B will be biased upward because it has 10% more soil in the sampled layer. Unless bulk density is very uniform, an "equivalent mass" sampling approach should be used to quantify temporal changes in soil carbon stocks or where there is interest in comparing soil carbon stocks under different land uses or management practices.

The objective of the equivalent mass approach is to enable estimation of carbon in a constant mass of soil during the assessment period (or spatial distribution). The approach involves sampling successive layers of soil and, using measured bulk density values, estimating the depth at which target soil mass is attained (the target mass will normally be the mass of soil to a specified depth at the beginning of the observation period, $t = 0$). The "equivalent mass" should include soil in all layers that are likely to be affected by the treatment or management practice of interest. Thus, if soil is ploughed to a depth of 0.2 m, the equivalent mass might be the mass of soil to a depth of 0.25 or, perhaps, 0.3 m. The essential requirement is that the soil mass remains consistent across treatments and time.

Soil sampling for the equivalent mass method is the same as for the conventional fixed depth method, except that an additional layer is sampled to ensure that the sampled soil mass equals or exceeds the target mass. The mass of soil per unit area, M, in each sampled layer is calculated as $M = D \times T \times 10{,}000$ where the units of M are Mg/ha, D is the bulk density (Mg/m^3), T is the thickness of the soil layer (m) and 10,000 is the conversion from square metres to hectares. The mass of soil in each layer is summed and adjustments are made if the total mass is less than, or exceeds, the target (equivalent) mass. If, for example, bulk density has decreased during the observation period, the target soil mass may be present in, say, the top 0.32 m layer, rather than in the 0-0.3 m layer. The additional depth increment to attain the target soil mass is calculated using the value of D measured for the layer below 0.3 m (e.g. the 0.3-0.35 m layer). In the above example, it is necessary to estimate the amount of carbon in the 0.3-0.32 m layer and add this to that in the 0-0.3 m layer. This estimate is made using the measured carbon concentration of the layer below 0.3 m (e.g. the 0.3-0.35 m layer). As carbon concentration usually declines with depth, the concentration in the 0.3-0.32 m layer may be somewhat higher than the value for the 0.3-0.35 m layer as a whole, and there may be a slight underestimation of carbon stocks. This error diminishes with smaller sampling increments.

Temporal changes in soil carbon stocks will usually be measured with greater sensitivity if successive samples are collected in the vicinity of previous cores (original sampling locations can be identified using a GPS recorder). Ellert et al. (2002) proposed that successive samples should be taken in a grid pattern within micro-plots to improve temporal resolution of changes in soil carbon. For efficient and cost-effective evaluation of these changes, the number of soil cores per experimental unit (micro-site, plot, paddock) should be adjusted for variability at each spatial scale.

Quantitative sampling from soil pits

The majority of soil profile data held in the New Zealand National Soils Database (NSD) were collected from soil pits as part of national and regional soil surveys. A subset of these soil profiles was sampled for both chemical and physical properties and can be used for calculation of soil carbon stocks. The approach used to collect these samples is described below.

Prior to sampling, the site is hand-augered to ensure that the specific location designated for sampling is representative of the surrounding area. A pit is dug to expose the soil profile down to the desired depth, often to 1 m. The horizons are identified and the soil profile is described. For each horizon, soil samples are taken for both chemical properties (in this case for carbon analysis) and physical properties (in this case for bulk density).

To collect a soil sample for chemical analysis, a slice of each horizon is scraped off the surface of the pit face over the appropriate depth increment (e.g. 0.1-0.2 m) and placed in a plastic bag. This sample is returned to the laboratory, passed through a 2 mm sieve to remove coarse roots and stones, then air-dried, and analysed for total carbon by Dumas combustion (see below).

Bulk density samples may be taken from the centre of each horizon by carving around a brass ring (68.8×10^{-6} m^3 volume) using a sharp knife to minimise disturbance of soil structure. Soil samples are dried at 105°C to a constant mass, weighed and bulk density calculated. In original sampling for the NSD, most bulk density samples were taken using a 200-core sampler (Soil Moisture Equipment Corp, Santa Barbara, California), which uses a small slide hammer to force a ring into the soil. A side-by-side comparison showed that the slide hammer approach underestimated bulk density in comparison with soil carving by about 5%, possibility due to soil shattering by the slide hammer (Schipper et al. 2007). Consequently, bulk densities from contemporary carving to calculate volumetric carbon stocks have been used.

Stocks of soil carbon are calculated as the product of the carbon concentration, bulk density of the horizon, and horizon depth. Soil carbon stocks to a depth of 0.3 m can be estimated by summing stocks of carbon above 0.3 m depth, and adding a linear proportion of the total carbon for the next horizon, depending on depth remaining to 0.3 m. It should be noted that bulk density measurements made from a subsection of a given horizon and applied to the whole horizon may introduce errors in estimates of soil carbon stocks, particularly where texture or organic matter content vary along the horizon.

In New Zealand, this pit-sampling approach has been used to resample soil profiles where previously soil samples have been taken using the same methodology to allow extent of change in soil carbon to be calculated (Schipper et al. 2007). In this case, archived soil samples are retrieved and analysed in the same run using a standard furnace (LECO CNS-2000) to minimise analytical errors. Sampling to date specifically for determining changes in soil carbon has not included profiles with significant stone content. These profiles would need to be treated differently by separating stone from the fine earth fraction and determining the volume of the stone fraction. Total carbon is measured on the fine earth fraction and profile carbon adjusted for volume of stones.

Sampling by depth or by horizon

As an alternative to sampling by horizon, soil samples can also be taken to a specified depth (e.g. 0.3 m). Bulk density cores would then be taken from the whole profile or sections within the profile or in the multiple cores collected at specified sample depths. Stocks of soil carbon are then calculated as the product of the bulk density, sample depth and carbon concentration. The major advantages of this approach are that bulk density can be measured from the entire length of the core or the depth increments of interest and that soil carbon concentration is measured on the same sample used for calculating the soil bulk density. The disadvantage of this approach is that the depth increments can overlap soil horizons. However, this is not a particular problem where the focus is on defining total soil carbon stocks and the depth of sampling consistently falls within one particular horizon. Expressing the results on an equivalent mass basis is helpful in ensuring that variable depth horizons do not confound the results.

Sample storage and handling

Field collected soil samples are normally held in air-tight plastic bags with most of the air removed and placed in an insulated, cool, dark container for transport to the laboratory. Samples should be held in a dark refrigerated (4-5^{o}C) container prior to processing for soil carbon analysis. Where large amounts of plant residues or root matter are present or where macro-fauna (e.g. earthworms) are abundant, processing the soils within one week of sample collection is recommended to ensure that these components don’t decompose significantly and, thereby, contribute to the measurements of soil carbon concentration.

2.1.2 Preparation and analysis of samples

For the analysis of soil carbon concentration there are broadly three approaches: wet oxidation and dry combustion followed either by measuring carbon loss by difference in mass (loss on ignition) or by measuring CO_2 evolved (Palmer 2003) – brief descriptions of these approaches follow. Several reviews and many comparative studies (both international and New Zealand-based) have been published on the analytical techniques for soil carbon measurement (Metson et al. 1979, Donkin 1991, Grewal et al. 1991, Soon & Abboud 1991, Ulmer et al. 1992, Kerven et al. 2000, Bhatti & Bauer 2002, Chacón et al. 2002, Jankauskas et al. 2006, Westman et al. 2006, Abella & Zimmer 2007, Sleutel et al. 2007, Chatterjee et al. 2009). In these studies, the dry combustion method is generally regarded as the standard or reference method against which other methods (e.g. loss on ignition and the Walkley-Black wet oxidation method) are compared and statistical relationships developed. Findings in terms of the performance of the various methods were variable. However, some studies (e.g. Grewal et al. 1991, Soon & Abboud 1991, Bhatti & Bauer 2002, Abella & Zimmer 2007) found that the loss on ignition method performed least well, was least well-correlated with those compared, or suffered from certain limitations. Moreover, Westman et al. (2006) found that the direct measurement of soil carbon (using dry combustion is preferable to using relationships with other measures such as loss on ignition. Overall, Kerven et al. (2000) described dry combustion as a rapid and reliable method and Chatterjee et al. (2009, p. 171) state that ‘In general, we conclude that automated dry combustion is the only reliable, comprehensive method for determining soil carbon concentration’. The following descriptions are consistent with laboratory current best practice with standard methods

Sample preparation

Soil organic matter and soil carbon are operationally defined fractions of the total organic matter that occurs in soil. Soils often contain varying amounts of ‘fresh or living organic matter’ such as above-ground (on the soil surface) and below-ground plant residues, including roots, and soil macro-fauna (e.g. earthworms, Carabid beetles, etc.) that occur variably both spatially and temporally. They are also ephemeral in nature and can contribute disproportionately to soil organic matter or soil carbon measurements under some circumstances. Consequently, standard procedures have been established to minimise the contributions of these components to the measurement of soil carbon concentration. The internationally accepted, operational definition of soil organic matter and soil carbon is the total soil organic matter or carbon found in air-dried soil that has passed through a 2-mm sieve. Where the purpose of soil carbon measurements is for inventory, determining the carbon concentration of the <2 mm soil fraction is probably adequate. However, where research is focussed on identifying management to sequester soil carbon or mitigate losses, measurements of carbon in fractions of organic matter that make up the <2 mm sieved soil (e.g. particulate organic matter, water soluble organic matter etc.) as well as those that are >2 mm in diameter (especially plant residues and roots) can be very informative.

Wherever possible, measurement of soil carbon concentration and bulk density on the same soil sample is recommended. In this case soil samples of a known volume and sample depth are first weighed field-moist, then crumbled and made to pass through a

2 mm sieve. Any plant residues, roots, macro-fauna (e.g. earthworms) or small stones retained on the sieve are normally discarded. Plant residues, roots and macro-fauna normally contribute very little to any error in estimates of bulk density. However, owing to their high density, stones can provide a significant source of error in estimates of bulk density and the resulting fixed-volume or equivalent mass based measurements of soil carbon stocks. Where significant quantities of stone are recovered, correcting the bulk density measurements for the mass of stones and using measurements of the carbon concentration in the fine-earth fraction (i.e. the stone-free soil) is recommended so that calculations of carbon concentration use the corrected values of bulk density.

Following sieving, a small subsample (e.g. 5-10 g) of the homogeneous field moist soil is removed and used to determine the moisture content by oven drying at 105^{o}C. This measurement of soil water content can then be used to calculate the dry mass of the entire soil sample and the bulk density where the sample was collected from a known volume of soil. The remaining sieved soil is then air-dried (normally for 7-10 days) and stored in sealed containers in a dry environment prior to carbon analysis.

The preparation and weighing of sieved soils for analysis depends very much on the specific techniques and instrumentation used to measure the carbon concentration.

Wet combustion

Wet combustion involving oxidation of organic matter in soil, generally using concentrated solutions of potassium dichromate and sulphuric acid, creates a reaction that generates heat which aids the reaction. Titration of remaining dichromate is used to calculate the amount of oxidised carbon.

Dry combustion - Loss on ignition

Loss on ignition involves taking an oven-dried soil sample of known mass and combusting the carbon in the soil by heating at high temperatures in a muffle furnace. After heating, the soil is reweighed and the decline in mass is attributed to combustion and loss of organic matter. A range of temperatures and heating times have been used but typically range from $300\text{-}500^{o}$C for between 2 and 6 hours. Excessively high temperatures can result in loss of non-organic compounds. The loss of mass needs to be adjusted for the percentage of organic matter as carbon (often set at 58%).

Dry combustion – measurement of CO_2 evolved

A soil sample is heated (950°C and greater) in a stream of oxygen, often in a tin cup to raise the temperature further. Soil organic matter is completely oxidised to CO_2, which can be directly measured using either infrared detection or a thermal conductivity detector following separation from other gases evolved. There are several commercial suppliers of equipment that use dry combustion to estimate soil carbon concentrations.

2.1.3 Special case for measuring changes in carbon for peat soils

This section focuses on measurement of carbon change in peat soils that have been converted to agriculture, which has generally involved removal of wetland vegetation, drainage, and application of nutrients and lime. Peats can extend several metres in depth and have very high carbon concentration. By definition, peats soil contain >16% carbon but often contain up to 45% carbon, essentially solely organic matter with very little inorganic material. These deposits can be quite deep extending to 8 or 9 m in some parts of the country.

For shallow peat soils (say < 0.1-0.2 m depth) the methods described for mineral soils can be applied, treating the peat as a high carbon content mineral soil. However, when peats are deeper, many of the traditional techniques do not apply because the surface of the peat soil retreats as the peat becomes degraded.

This loss in height of the peat is due to both decomposition (conversion to CO_2 and methane) and consolidation (as the peat is drained to allow land management the pore structure collapses). Although there is less total peat remaining, the surface peat soils can still contain very high amounts of carbon and traditional approaches for measuring carbon coupled to either equivalent mass sampling or correcting for bulk density do not apply. Instead the carbon concentration of the whole peat column would need to be measured (potentially to a depth of many metres).

The change in peat height to underlying mineral soil can be measured using peat probes. However, to estimate carbon loss requires partitioning the loss of height into decomposition and consolidation, which is very difficult to do. At one site in the Waikato, Schipper and Macleod (2002) demonstrated that about 63% of loss of peat height was due to consolidation the remainder being attributed to decomposition. This study compared the total carbon content (corrected for bulk density) of peat columns above a marker tephra layer in adjacent remnant peat bog and farm land. The authors reported losses of about 3.7 t C/ha/y on average subsequent to wetland clearance. Opportunities for these types of measurements are limited as there are few remaining remnant peat sites. Simply measuring changes in peat height without being able to partition losses into consolidation and decomposition is unlikely to be useful for determining losses of carbon.

A second approach has been to directly measure annual changes in CO_2 exchange of peat soils using eddy covariance approaches. Nieveen et al. (2005) used this approach at a site also in the Waikato and measured losses of carbon of about 1 Mg C/ha/y.

Losses of carbon from peat soils are expected to be greatest when land is initially cleared, then to decline with time.

2.2 Forest soils

2.2.1 Sample collection methods

Three main approaches to sample collection for mineral soil carbon stock assessments in forests and grasslands have been applied in New Zealand for both inventory and experimental (e.g. investigations of management impacts) purposes. These are: (1) volumetric core sampling, (2) small-diameter tube sampling (with bulk density assessment), and (3) quantitative soil pit sampling. Different approaches are used for the collection of samples from forest floor (L and FH) horizons. The issues of sampling by fixed-depth or by horizon, sampling for equivalent mass calculation, and sample size and bulking protocols are also discussed in this section.

Forest floor sampling

Fine woody debris (branches and other woody debris with a diameter of 25–100 mm), litter (leaf litter and branches < 25 mm in diameter, L horizon material), and fermented and humic materials (combined F and H horizons) are collected from within 0.1 m^2 collapsible PVC quadrats fixed to the ground surface. The quadrats may be made of collapsible PVC materials to facilitate transport into remote locations. However, where the FH horizon is of sufficient thickness, this material may by collected from within a stainless-steel ring of 98-mm internal diameter inserted through the FH horizon and (usually) into the surface mineral soil at an angle perpendicular to the ground surface. The thickness of the FH horizon sampled from within the ring is calculated by taking depth measurements from the top of the ring before and after collection of the material. Volumes of L and FH material collected within quadrats are estimated in the field (Davis et al. 2004).

Volumetric core sampling

The volumetric core sampling approach used for forest soil sampling (Davis et al. 2004) is similar to that described for grassland soils. Stainless-steel rings of 98 mm internal diameter and 100 mm in length (i.e. known volume) are inserted into the mineral soil perpendicular to the ground surface and cores are taken at 0.1 m depth increments to a total depth of 0.3 m. The extraction of each core involves careful excavation of a small pit adjacent to the ring that extends just beyond the lower depth of the ring, while ensuring that the soil directly below the ring is not disturbed, and the insertion of a thin, flat trowel at the base of the ring to lift it and the core out. The core is then removed from the ring and placed in a labelled plastic sample bag. Regular depth-checking is performed using a tape-measure during ring insertion, particularly beyond 0.1 m depth, to ensure the correct depth range is being sampled and that compaction of the soil core is not occurring (Davis et al. 2004). The soil data collection manual of Davis et al. (2004) also outlines detailed procedures for core measurement and extraction in the case of striking obstructions during ring insertion such as tree roots such that a viable sample may still be collected.

The volumetric core sampling approach described by Davis et al. (2004) was used for the soil sampling of the Carbon Measurement System (CMS) plots in natural forest and shrubland sites (providing data for the Soil CMS dataset) and has also been applied to some experimental work investigating the impacts of various forest management practices on soil carbon stocks (Jones 2007, Jones et al. 2008).

An advantage of the volumetric core sampling approach is that bulk density and soil carbon concentration can be measured on the same sample. If sub-samples from a set of cores (e.g. taken within a plot) are bulked for carbon and nitrogen analysis (see below), the individual bulk density data for each core can be combined (i.e. total mass per unit volume for the plot) to give a plot-averaged bulk density that is assumed to be a better estimate of the bulk density of the soil in the plot than the estimate that would be obtained if a separate, single core for bulk density assessment was taken to represent the plot. Volumetric core samples are commonly split (using a sample splitter) after air-drying to provide two sub-samples — one for measurement of carbon and nitrogen concentrations, the other for determination of the water content which is required for the bulk density calculation.

Sampling at depths below 0.3 m using the standard volumetric core approach is difficult and time consuming for most soils because core extraction becomes more difficult without the excavation of a much larger pit around the ring to allow access. However, an approach for using a motorised auger to insert a PVC tube into the soil and extract cores to depth (up to 1 m) was developed for soil carbon stock assessment and its use in an experimental study in the Puruki catchment near Rotorua has been described by Oliver et al. (2004). Fig. 2 shows soil cores (split in half and placed side-by-side to reveal the profile) collected using the motorised auger.

The volumetric core approach is suitable for soils with either no gravel or limited gravel content. Where the soil gravel content is more than moderate, the quantitative pit approach is likely to be more appropriate. Conversely, gravel-free soils, depending on other factors such as cohesiveness and density, may be sampled more efficiently using the small-diameter tube sampling approach.

Small-diameter tube sampling with bulk density assessment

Small-diameter tube sampling, which involves manually pushing a stainless-steel tube (usually configured like a ‘pogo-stick’, Fig. 3) into the soil to the desired depth and at an angle that is perpendicular to the ground surface, is an efficient means of collecting soil samples to fixed depths for the purposes of chemical analysis. However, the approach is generally only suitable for gravel-free soils that are sufficiently cohesive and are not excessively dense or hard. The main disadvantages of the approach are the potential for soil core compaction during tube insertion and the need to measure and separate cores by the depth ranges of interest. The main advantage is that relatively large numbers of cores can be collected rapidly across the land area of interest (e.g. a plot) and bulked by depth range to provide a single sample (to be sub-sampled) per plot for analysis.

The diameter of tube samplers may vary but is commonly about 25 mm. Most small-diameter tube samplers will have depth markings on the outer surface of the tube to guide the operator in inserting the tube to the correct depth in the soil.

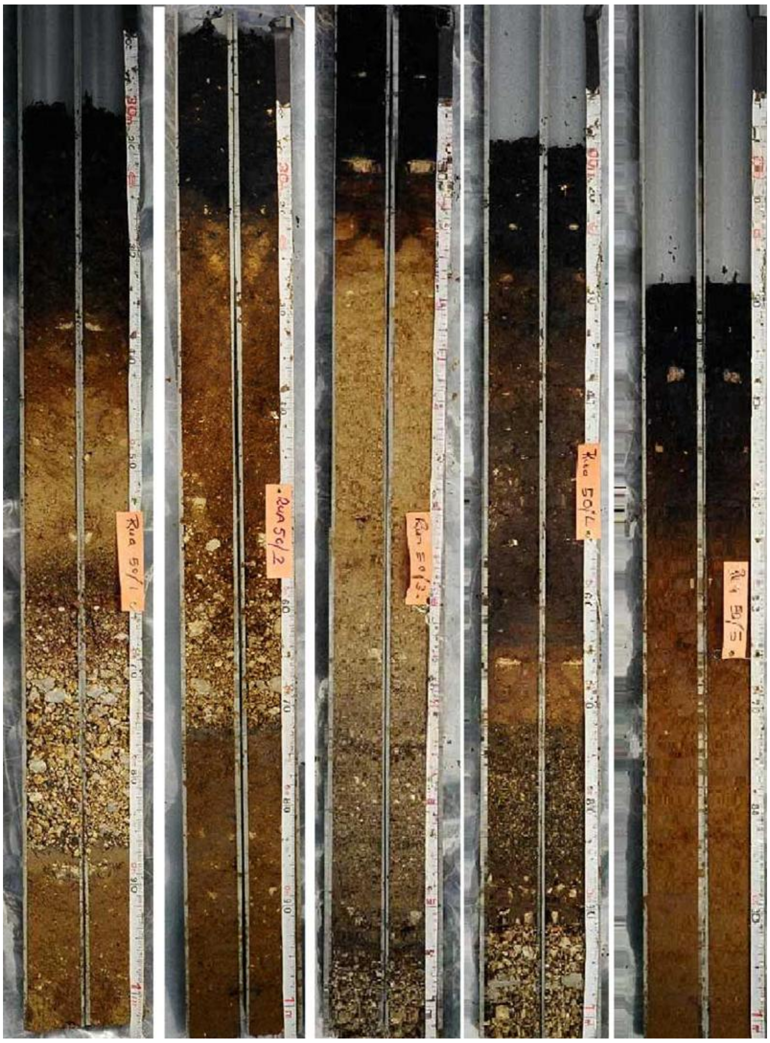

Fig. 2 Soil cores collected from the Puruki experimental catchment using a motorised auger (after Oliver et al. 2004).

Unlike the volumetric core and quantitative pit approaches, samples collected using the small diameter tube sampling approach are not collected on a volumetric basis (i.e. the volume from which the soil material was collected is not known precisely). Therefore, this approach must be accompanied by the collection of a sufficient number of bulk density samples (usually collected using the volumetric core sampling approach) to represent the area being sampled in order to calculate soil carbon stocks. It is usually expected that mineral soil bulk density will be less variable than soil carbon concentration and so the number of samples required to assess the bulk density of a given area adequately is likely to be less than the number required to assess the soil carbon concentration adequately. This means that fewer volumetric core samples are likely to be required with this approach than would be the case if volumetric core sampling were being used for the measurement of both soil carbon concentration and bulk density.

Fig.3 An example of the collection and bulking of topsoil samples for soil chemical analysis using a small-diameter tube sampler within an experimental plot (after Jones, 2004).

Quantitative soil pit sampling

Where rocks or coarse roots preclude volumetric core and small-diameter tube sampling, volumetric sampling can be undertaken using the quantitative pit approach which involves excavating 0.1 m^2 pits and sampling the soil materials in increments of 0.1 m depth. Pit dimensions are guided by placing and securing a 0.1 m^2 quadrat on the ground at the selected sample point (Fig. 4). Accurate measurement of the pit dimensions (to calculate volume) is essential in this approach, hence the term ‘quantitative pit’. Considerable care is required in dealing with coarse gravel or boulders that span pit or sample depth range boundaries. The volume that these materials occupied within the pit and depth range boundaries must be noted and that volume replaced in the sample by smaller stones of equivalent volume (Davis et al. 2004).

If the sampling is being undertaken at a remote location so that the samples must be carried over a considerable distance, sub-sampling in the field will most likely be necessary (including sub-sampling of organic materials) given the volume of material being excavated. Where sub-sampling is required, the fresh mass of both the complete sample after homogenising and the sub-sample are recorded in the field to allow correction factors to be subsequently applied. If stones are to be discarded, these are also weighed prior to discarding (Fig. 5). However, the entire sample from each depth range should be retained for sub-sampling in the laboratory where ever possible (Davis et al. 2004).

Fig. 4 An example of the excavation of a quantitative pit to 0.1 m depth in a soil containing coarse gravel (after Davis et al. 2004).

Fig. 5 An example of weighing gravel (left) and sub-sampling during quantitative pit excavation (right) (after Davis et al. 2004).

The quantitative pit sampling approach is probably the most time-consuming and, as a consequence, costly approach but is considered to be without obvious bias when volume is assessed by back-filling with an appropriate material (e.g. sand, Harrison et al. 2003).

Sampling by fixed-depth or by horizon

Current standard practice to sample carbon stocks in mineral New Zealand forest soils is by using fixed-depths for soil carbon stock assessment (and most other purposes) rather than by soil horizon. Samples are collected commonly from the 0-0.1, 0.1-0.2, and 0.2-0.3 m depth ranges for inventory purposes and some experimental studies of management effects (e.g. Jones et al. 2008). Some studies have examined soil carbon stocks at various depth intervals below 0.3 m depth (e.g. Beets et al. 2002, Oliver et al. 2004). The main reasons for sampling by fixed depths are that sampling by soil horizon is fraught with difficulties and that the New Zealand Soil CMS requires that soil carbon stock data be collected by fixed-depth. The variability of horizon thicknesses, particularly in previously disturbed forest soils, and the lack of continuity of horizons across soil types and landscapes mean systematic sampling for inventory purposes is extremely difficult because there is no consistent frame of reference. Moreover, sampling by horizon complicates sample collection and requires a higher level of interpretive skill on the part of the sampler due to the necessity to identify horizon boundaries correctly. The corollary of this is that the cost of sampling is likely to be greater if sampling is by horizon. Nevertheless, it is important that information on the differentiation of profiles in the soil horizon is collected while undertaking systematic sampling by depth to assist with the subsequent interpretation of the data. To this end, at least one full soil profile description is undertaken to represent Soil CMS plots (Davis et al. 2004) or the experimental site being sampled.

In contrast to mineral soils, forest floor materials are sampled by horizon with the less decomposed leaf litter material of the L horizon collected separately from the fermented and humic material of the F/H horizon. Where forest floor materials have been buried by the deposition of mineral soil material or where soil disturbance and mixing has occurred at a selected sampling site, the recommendation of Davis et al. (2004) is that the sampling of fixed depths be undertaken, as per undisturbed mineral soils, from the present ground surface.

The same issues concerning fixed volume and equivalent mass methodologies apply as those described above.

Sample size, sub-sampling, and bulking

The current standard methods of measuring soil total carbon and nitrogen (e.g. dry combustion) do not require a large sample sizes (by mass or volume), usually only about a ‘spoon-full’ of soil is sufficient. However, there are several reasons why it is both necessary and vitally important that much more than a ‘spoon-full’ of soil is collected: (1) the area and depth ranges being sampled must be represented adequately to account for the variability in soil carbon concentration and bulk density, (2) to provide an adequate amount of material to allow for the measurement of both soil carbon concentration and water content, and (3) the need to archive the remaining soil material for future reference. Ultimately, the amount of soil material collected from a given depth range (e.g. 0-0.1 m) within a plot, paddock, or farm will depend on the sample collection approach used and the number of points spatially at which individual or composite (bulked) samples are collected. The latter will be determined by the sampling design adopted and the former influenced by the nature of the soils to be sampled.

Davis et al. (2004) estimated that approximately 46 kg of soil would be collected for each CMS plot if the soil was sampled to 1 m depth using the combination of small-diameter tube and volumetric core sampling approaches recommended for those plots. A total mass of 18 kg of soil per plot was estimated if samples were collected only to a depth of 0.3 m. Clearly, bulking by depth and sub-sampling in the field may be necessary for logistical reasons if sampling to 1 m depth and where an assessment of within-plot variability is not required. In this case, Davis et al. (2004) suggest that is preferable to bulk and sub-sample to reduce the sample size to be carried rather than attempt to reduce the sample size collected by using smaller diameter sampling rings or tubes as this may reduce the precision of the mean estimates. However, the soil must be adequately dry and friable to enable the bulked samples to be thoroughly mixed prior to sub-sampling and it is essential that both the total and sub-sample weights are recorded. The benefits of bulking and sub-sampling are not just restricted to solving logistical problems as bulking can significantly reduce the number of samples to be analysed (and reduce the associated costs) without a reduction in the precision of mean estimates. For this reason, some researchers (Ruark and Zarnoch 1992, Blumfield et al. 2007) view sample bulking as a solution to the problem of excessively large sample numbers that may be required to account for soil carbon variability.

2.2.2 Preparation, analysis of samples and laboratory current best practice

This section outlines the current best practice in terms of the sample preparation and analytical procedures used for the assessment of carbon stocks in forest soils. Some methodological issues are also raised for consideration.

Procedures for the preparation of forest floor samples differ somewhat from those for mineral soils and so these are addressed separately below. The procedures described here are generally consistent with those given in Davis et al. (2004).

Forest floor sample preparation

Forest floor samples, which usually represent fine woody debris and L and FH horizons, are sorted to remove any live roots (if present). The dead organic materials are oven-dried (at 70°C) to constant mass and weighed. The samples are then chipped (if necessary) and ground and a sub-sample is taken for carbon and nitrogen analysis. The remaining sample is archived.

Mineral soil sample preparation

Mineral soil samples collected non-volumetrically for total carbon and nitrogen analysis are air-dried (at ≤ 40°C) to constant mass, passed through a 2 mm sieve, and a representative sub-sample of the fine (< 2 mm) fraction material is removed and fine-ground for total carbon and nitrogen determination. A further sub-sample (or the remainder of the sample) is archived. The coarse (> 2-mm) fraction is sorted into its gravel, live roots, and dead organic material components. A sub-sample of the dead organic materials may be taken for determination of carbon and nitrogen concentration after being oven-dried (at 70°C) to constant mass and fine-ground. If required (for an assessment of coarse fraction carbon stocks in, for example, vesicular gravels), the gravel component may be also be fine-ground and a representative sub-sample taken for carbon and nitrogen analysis (and the remainder archived).

Where volumetric core or quantitative pit sampling alone has been used for the collection of mineral soil samples, it is necessary to measure both total carbon and water content (for bulk density assessment) on the same sample. In which case, the sample preparation procedure is slightly different. Air-dried samples are passed through a 2 mm sieve and the fine fraction is then weighed, homogenised, and split in half with one half used for total carbon and nitrogen analysis and the other half weighed and oven-dried (at 105°C) to constant mass for the measurement of moisture content (by mass difference). The water content factor (air dried mass/oven dried mass, Blakemore et al. 1987) can then be applied to the air dried mass of the whole sample to give the total oven dried mass. Total oven dried mass divided by the original volume of the sample gives the dry bulk density. As described above, the coarse fraction is sorted into its gravel, live roots, and dead organic material components. The air dried mass of the gravel is recorded, and the dead organic materials are oven-dried (at 70°C) to constant mass and the weight recorded. A sub-sample of the dead organic materials may be taken for determination of carbon and nitrogen concentration. If a full assessment of coarse fraction carbon stocks is required, the gravel component may be also split with half fine-ground and used for carbon and nitrogen determination, and the other half weighed prior to being oven-dried (at 105°C) for the assessment of water content.

If small-diameter tube sampling has been used, separate volumetric samples for bulk density assessment would have been collected and so the full fine fraction of these samples can be oven-dried after the air-dry mass has been recorded. Sorting and treatment of the coarse fraction components would need to proceed as described above.

2.2.3 Analysis of carbon and nitrogen concentrations

Methods for measuring carbon concentration in soils have been discussed earlier. For soils with no inorganic carbon, total carbon is equivalent to organic carbon. The loss on ignition technique provides a measure of organic matter content rather than carbon. Therefore, an adjustment factor appropriate for the soil in question (usually about 0.5) must be applied to calculate carbon concentration (Bhatti & Bauer 2002, Palmer 2003).

Current practice for New Zealand forest soils is to analyse total carbon and nitrogen concentration using the dry combustion method using a thermal combustion furnace (LECO CNS-2000, modified Dumas method) for inventory and experimental purposes. Kowalenko (2001) concluded that the LECO CNS-2000 instrument provided a good to excellent measure of soil total carbon.

2.2.4 Methodological issues to be considered

In a recent report, Jones et al. (2009) listed the development of consistent methods and protocols for the measurement of soil carbon stocks across all land uses as a key research priority because the investigation of land use change effects may be hampered if some potential differences in the nature of soil samples collected under different land uses are not considered and consistency ensured.

Analysis of the mineral soil coarse fraction

It is standard practice in New Zealand to determine mineral soil carbon stocks on the fine (< 2 mm) fraction only, with the coarse (> 2 mm) fraction discarded. However, there is some evidence in the forest soil literature (both international and local) to suggest that the coarse fraction of some forest soils can contain a substantial proportion of the whole-soil carbon stock (Harrison et al. 2003, Homann et al. 2004, Jones et al. 2008). In a New Zealand forest study, Jones et al. (2008) found that 25% of the total mineral soil carbon stock was contained in the coarse fraction of a plantation forest soil formed in a highly vesicular parent material (Tarawera scoria). It appears that much of the coarse fraction carbon stock found in this soil can be attributed to the fine fraction material coating the vesicles of the scoria gravel. Nevertheless, it could be argued that ignoring the carbon stock contained in the coarse fraction of this soil would lead to the underestimation of the carbon it actually contains. Furthermore, other forest soils that do not contain particularly vesicular parent materials but which have been disturbed by management activity (or conversion to grassland) may have coarse (and fine) organic fragments incorporated into the surface mineral soil. If these soils are sampled soon after the incorporation of the organic fragments occurred then, according to standard practice, those fragments that are > 2 mm in size would be sieved out and discarded (i.e. excluded from the analysis) but if sampled some years following incorporation, the decomposing fragments are likely to pass through the sieve and be measured as part of the fine-fraction soil carbon stock. It is suggested that consideration be given to the development of consistent protocols for the treatment of the mineral soil coarse fraction with respect to the assessment of soil carbon stocks.

Other potential issues

Other potential methodological issues that may require some consideration in terms of achieving consistency across land uses include: (1) the influence of very fine, formerly live, pasture roots or root fragments passing through 2 mm (or coarser) sieves and being incorporated into samples for carbon analysis on carbon stocks. Given that soils under grassland are likely to contain many more very fine roots per unit volume than soils under forest, this may be an issue when investigating the effects of afforestation on soil carbon stocks and (2) the effect of, and need for, fine-grinding of samples prior to analysis using dry combustion.

2.3 Calculations of carbon stocks

2.3.1 Current best practice

Some international, regional scale studies have estimated bulk density from regression relationships between total carbon content and a small set of bulk density measurements (Bellamy et al. 2005). While these regressions are possible, they have been strongly criticised (Smith et al. 2007) and they can be particularly weak for soils with high organic matter content. Direct measurement of bulk density are essential to determine soil carbon stocks for national accounting purposes until such a time that a pedo-transfer function(s) can be shown to be robust across a wide range of soils and land uses.

The calculation of carbon stocks on a mass per unit area basis in forest floor horizons is straightforward and simply involves multiplying the mass of the material collected from within a known ground area by the carbon concentration of that material, then scaled spatially. Calculation of fine fraction carbon stocks of fixed mineral soil depth ranges should also be straightforward in most cases. For volumetric core or quantitative pit sampling where the volume from which the sample is taken is well-defined, the fine fraction carbon stock can simply be calculated from the mass of the fine fraction collected from within a known area and a known depth range multiplied by the carbon concentration of the fine fraction, then scaled spatially. This simple calculation would also apply in the case of non-volumetric sampling (e.g. small-diameter tube sampling) provided dedicated volumetric samples are also taken to determine the density of the fine fraction for the corresponding depth ranges.

Equations for estimating fine-fraction soil carbon stock calculation are available in the literature (Huntington et al. 1989, Palmer 2003) but these seem unnecessarily complex in that they tend to include an adjustment for the volume of gravel. This correction should not be necessary provided the volumetric sample collected represents the bulk soil and the mass of the fine-fraction contained within the known sample volume is measured. The use of volume estimates or rock density assumptions, or both, is likely to introduce unnecessary error in to the carbon stock assessment. Therefore, it is suggested that this approach only be used where there is no alternative (i.e. soil density was not sampled or measured adequately). Adequate numbers of volumetric samples should be taken to determine the density of the fine fraction (or coarse fraction if required) in all new sampling programmes for soil carbon stock assessment. If the gravel content of the soil is too great for volumetric core sampling then the quantitative pit approach should be used.

It is important to note that slope steepness should also be factored into the calculation of soil carbon stocks (Jones 2007). The expression of soil carbon stocks on a mass per unit area basis assumes that the land surface is flat (i.e. the area of a planar surface is represented) whereas soil samples are taken perpendicular to the ground surface. Where samples are collected on sloping land, the horizontal projection of the sample collection area to a planar surface would result in an effective reduction in the size of the surface area sampled. Basic geometry can be used to adjust the surface area of volumetric samples by the steepness slope to give the true (smaller) planar sampling area. This correction has the effect of slightly increasing the calculated soil carbon stock. The steeper the slope, the greater the correction required.

2.3.2 Fixed volume and equivalent mass methodologies

Most measurements of soil carbon are expressed on a % dry mass basis (mass of carbon/mass of oven-dry soil × 100) and converted to an area basis for a fixed-depth of sampling (i.e. fixed-volume of soil) or for equivalent mass of soil. Measurements of bulk density are essential for determining soil carbon stock on an aerial basis, regardless of whether stocks are expressed on volumetric basis to a fixed depth (e.g. Mg C/ha in the upper 0.3 m depth) or on an equivalent mass basis (e.g. Mg C/ha in the upper 3,500 Mg of dry soil).

Comparisons of soil carbon stocks for purposes of measuring changes or quantifying the efficacy of mitigation options assume that the carbon stock measurements are based on the same mass of soil. This assumption is generally valid where bulk density has remained constant with time or across various mitigation practices. Where the constant bulk density assumption holds, fixed-depth sampling provides a convenient and practical means of measuring soil carbon stocks. However, where bulk density has changed over time or under different management practices owing to the effects of soil disturbance (e.g. soil tillage, sub-soiling, stock treading, wheel traffic, etc.) or consolidation (e.g. loss of structure) it is important to appraise any differences in soil carbon stocks on the basis of the same mass of soil. It is important to note that relatively small differences in bulk density can result in relatively large differences in estimates of soil carbon stocks. In both cases, it is important to ensure that the depth of soil sampling exceeds the depth of soil disturbance and includes the zone of dominant plant or management influence on soil carbon stocks. Current international standard protocols focus on sampling to a depth of 0.3 m.

Areal estimates of soil carbon stocks using bulk density corrections or equivalent soil mass sampling become more consistent as the sampling depth become greater. This is because soil carbon concentration declines with depth and changes in soil mass per unit depth are greatest at the surface.

In cases where significant soil disturbance is known to have occurred and sampling is relatively shallow (i.e. within the disturbed zone) equivalent mass sampling is recommended.

When sites are re-sampled, changes in soil bulk density should be checked wherever possible.

2.3.3 Issues with disturbed or cultivated soils

Forest soil cultivation practices generally only disturb a proportion (about 30% in some cases) of the total area of land under cultivation (Jones 2007). The disturbed areas are usually comprised of discrete and well-defined disturbance features that conform to regular patterns (e.g. spot-mounds and associated hollows aligned in rows). The fact that only a proportion of the land area under this type of management is actually disturbed must be taken into account in the assessment of soil carbon stock change. Therefore, an area-adjusted approach that compares pre-cultivation stocks with post-cultivation stocks over the entire site is required.

The area-adjusted approach requires quantitative information relating to the proportion of a given land area (on the horizontal plane) occupied by each identified disturbance feature. The area of undisturbed soil can be obtained by difference. It must be assumed that stocks measured in undisturbed soil are representative of and equivalent to the pre-cultivation stocks across the whole area in question. The stocks of each disturbance feature and undisturbed soil can then scaled by the relative proportion of the total area each occupied and the sum of these ‘area-adjusted’ stocks is taken as the total post-cultivation stock for the area in question. The difference between the pre- and post-cultivation stocks gives the magnitude and direction of change (Jones 2007).

2.4 Uncertainty in detecting changes in soil carbon using soil cores

In this section we present two complementary approaches to estimating uncertainty. The first approach summarises methods to determine errors associated with site selection, sampling and measurement and then provides algorithms to assess changes in soil carbon stocks and their standard errors. The second approach uses example data sets to estimate the number of samples required to confirm a minimum statistically detectable change in soil carbon stocks.

2.4.1 Source and size of uncertainty in measuring changes in soil carbon stocks

This section identifies the errors associated with the estimation of changes in soil carbon stocks. The first part provides a method for determining a compound error term associated with (i) site selection, (ii) sampling and (iii) measurement. The last part provides a series of algorithms for assessing change in the soil carbon stock and the standard error of the change. This provides an assessment of uncertainty and reproducibility of the soil carbon stock change, following the procedure of Stolbovoy et al. (2007).

Goidts et al. (2009) conclude that true uncertainties in soil organic carbon stock assessments are quantified rarely even though they are critical in determining the result and reliability of carbon monitoring schemes. The authors describe a method to identify and quantify the uncertainty in soil organic carbon stock assessments for different scales and spatial landscape units (LSU) under agriculture. They consider the relative error and interactions between each variable in the calculation of a soil carbon stock (sampling depth, bulk density, rock fragment content, soil organic carbon concentration), as well as interactions with errors as the stock is calculated at different scales, from sample scale (soil sample), to microsite scale (3 to 5 samples within a circle of 4 m radius), field scale (samples from the re-sampling within the same field), landscape scale (samples from all soil profiles belonging to one LSU), and finally the most aggregated level, regional scale (samples from all LSU in the carbon monitoring scheme). The authors use data from 28 geo-referenced soil profiles re-sampled 50 years after an initial sampling in 15 LSUs characterised by land use, region and soil type, in Belgium. The mean and error in each variable was calculated. The interaction of the errors in the calculation that create uncertainty in soil organic carbon stocks was able to be propagated by two different methods: i) the Monte Carlo simulation method (MC), which generated numerous soil organic carbon stocks using random values for each individual variable (stochastic approach) and ii) 'the statistical differentials method' (or the ''δ method'), which gave a general equation for the error propagation (deterministic approach).

Both methods produced similar results for the variation in estimates of soil organic carbon stocks. The coefficient of variation of the soil organic carbon increased from 5% to 12% at the sample analysis scale, and from 15% to 35% at the landscape scale. This uncertainty analysis identified measurement errors that could be reduced by changes in practice or simply by reworking the data. For example there was a large error associated with re-sampling of the sites (> 4 m apart). This re-sampling, which is equivalent to creating a new sampling plot in the New Zealand Carbon Monitoring Scheme, had a root mean standard error of 30% for cropland, and 54% for grassland, when the first and second samplings were compared. The authors were able to show that if the soil organic carbon stock was re-calculated on the equivalent mass of soil in each profile rather than soil depth, then the root mean standard error for predicting soil organic carbon at a new site could be reduced by 50%.

Goidts et al. (2009) provide examples of how errors can be reduced in the soil organic carbon analysis step, and in the bulk density measurement step. Different methods for soil organic carbon analysis have different precision. Goidts et al. (2009) report that precision (coefficient of variation, CV) of such analytical methods could range from 1.2 to 15.8% for the loss-on-ignition method (LOI), from 1.6 to 4.2% for the Walkley–Black method (WB), and from 1.3 to 7.1% for dry combustion (Goidts et al. 2009). It is obviously preferable to use the method with the lowest CV for sample analysis. The Landcare Research Environmental Chemistry Laboratory reports a CV of 1.9% for the 'LECO' dry combustion determination for carbon content (L. Hill, pers. comm.), which is consistent with high precision.

Spatial errors in bulk density measurement are often not considered in sampling strategies although it is important to measure bulk density (D) with each soil organic carbon determination. Goidts et al. (2009) found negligible error (CV of 1-2%) in D at the replicated sample scale but the CV increased to 10% at site and field scales, and to 15% if the soils were stony. Boucneau et al. (1998) and De Vos et al. (2005) showed that indirect estimation of D based on pedotransfer functions can lead to errors from 9% up to 36% of the soil organic carbon stock.

The stone content or coarse fragment (f in Eq. 1) also contributes a small error at the sample scale (3% to 4%). At the site scale the error increases to between 22% for cropland and 62% for pasture (Goidts et al. 2009). This was presumably due to less anthropogenic mixing in the pasture profile.

Intensive measurement of D and the coarse fragment is possible in paired site comparisons designed to estimate changes in soil organic carbon stock with land use. Intensive measurement, however, is not possible with regional or national soil organic carbon stock inventories. A combination of other more easily measured (e.g. proximally sensed) co-variates such as penetrometer readings, electrical conductivity and soil reflectance could be used to improve the accuracy of prediction of *D* and *f* by pedotransfer functions.

The calculation methods shown below are consistent with soil carbon monitoring schemes for field sampling campaigns (e.g. New Zealand Soil Carbon Monitoring Scheme, Davis et al. 2004, Goidts et al. 2009), compliant with the sampling strategies recommended by IPCC (see http://www.ipcc-nggip.iges.or.jp/public/gpglulucf/gpglulucf_files/Chp4/Chp4_3_Projects.pdf).

The algorithms can be used to assess (i) soil carbon stocks, (ii) changes in soil carbon stocks, (iii) uncertainty and (iv) reproducibility of the change in organic carbon stock and the standard error of the change (Stolbovoy et al., 2007):

Step 1: Calculation of soil organic carbon density (*SCD*) for the sampling site (SCD_{site})

$$SCD_{site} = \sum_{layer=1}^{j} (SOC_{content} * bulk\ density * depth * (1 - frag)) \tag{1}$$

where

$SOC_{content}$ is the soil organic carbon content, % mass or $(100 * kgC/kgsoil)$

bulk density is a soil bulk density $\left(\frac{kgsoil}{dm^3}\right)$

depth is a thickness of the sampled layer (dm)

frag is volume of coarse fragments as percentage of mass, or $\left(\frac{stone\ m^3}{soil\ m^3}\right)$

The SCD_{site} provides an average value for the sampling site, which is derived from taking a composite sample combining a number of sub-samples.

Step 2: Calculation of mean soil carbon density for the plot $(S\bar{C}D_p)$

$$S\bar{C}D_p = \frac{1}{n} \sum_{site=1}^{n} SCD_{site} \tag{2}$$

where

SCD_{site} is as indicated in Equation 1

n is a number of sampled sites within the plot.

Step 3: Calculation of reference soil organic carbon stock for the plot ($SOC_{refstock}$)

$$SOC_{reference} = S\bar{C}D_p * A_p \tag{3}$$

where

$S\bar{C}D_p$ is as indicated in Equation 2

A_p is an area of the plot

Step 4: Calculation of changes in soil organic carbon stock for plot (ΔSOC_{stock})

$$\Delta SOC_{stock} = SOC_{new} - SOC_{refstock} - f_{org} - f_{lim} \tag{4}$$

where

$SOC_{refstock}$ is a reference organic carbon stock as indicated in Equation 3

SOC_{new} is a new soil organic carbon stock (second sampling), which is computed similarly to $SOC_{reference}$

f_{org} is the carbon applied with organic fertilizers

f_{lim} is the carbon applied with lime.

Uncertainty

The uncertainty of the changes in soil organic carbon stock can be characterised by the standard error of the change value, calculated as follows:

Step 5: Calculation of standard error for mean soil carbon density $s(\Delta S\bar{C}D_p)$

$$s(\Delta S\bar{C}D_p) = \sqrt{\frac{1}{n(n-1)}\sum_{site=1}^{n}(\Delta SOC_{site} - \Delta S\bar{O}C_p)^2} \tag{5}$$

Where

$\Delta SOC_{site} = SCD_{new} - SCD_{reference}$ is a change in soil organic carbon stock for the sampling site

$\Delta S\bar{O}C_p$ is the average of ΔSOC_{site} for the plot

n is a number of sampling sites within the plot

Step 6: Calculation of standard error of the changes of soil organic carbon stock in the plot $s(\Delta SOC_{stock})$

$$s(\Delta SOC_{stock}) = s(\Delta S\bar{C}D_p) * A_p \tag{6}$$

where

$s(\Delta S\bar{C}D_p)$ is as indicated in Equation 5

A_p is the area of the plot

Step 7: The soil organic carbon stock and its standard error is

$$\Delta SOC_{stock} \pm s(\Delta SOC_{stock}) \tag{7}$$

Expressing the inaccuracy of the result in terms of standard error does not require normality assumptions but does not give a specific level of confidence.

Reproducibility

Reproducibility (*RP*) is assessed by two parallel samplings using a shift in the positioning of the sampling sites. Parallel sampling simulates an error of the average $S\bar{O}C_{stock}$ coming from the mistake of the sampling site positioning, and assesses any short distance variation of the soil characteristics (Stolbovoy et al. 2007). The variation in question is soil-specific and therefore is unique for each experimental plot. Stolbovoy et al. (2007) also suggest that this variation is attributed to certain agricultural regions for which soil/land cover combination is common. Technically, the data for *RP* can be defined as follows. The first sampling is described above. The second sampling site is within a few metres. The procedure of the second time estimate is similar to that of the first one. Additional computational steps to define the *RP* will be (Stolbovoy et al. 2007):

Step 8: Calculation of the difference (absolute) in the averages between first and second estimates of the $S\bar{O}C_{stock}$

$$\Delta SOC_{plot} = |S\bar{O}C_{stock1} - S\bar{O}C_{stock2}| \tag{8}$$

Where $S\bar{O}C_{stock1}$ and $S\bar{O}C_{stock2}$ are average SOC stocks for the first and second samplings within given plot.

Step 9: Calculation of the reproducibility (RP) of the sampling results for the plot *i*:

$$RP_{plot\,i} = \frac{\Delta SOC_{plot\,i}}{S\bar{O}C_{stock1}} * 100 \tag{9}$$

Where $RP_{plot\,i}$ is given in percent.

In summary, to report regional or national inventories or to detect and report land use change effects, soil carbon monitoring systems require similar information but different approaches for improving their precision and accuracy. Both approaches require the same detailed investigation into the level of uncertainty that exists in all variables that are used in the calculation of soil carbon stocks at a range of scales. Recent European research (Goidts et al.

2009, Stolbovoy et al. 2007) indicates relevant methodologies that should be investigated for use in New Zealand for improving the precision and accuracy of soil carbon monitoring.

Reduction of sampling error

The uncertainty analysis of Goidts et al. (2009) indicates that errors of soil organic carbon measurement at the sample scale (laboratory determinations) and bulk density are small but require very precise reproducible methodology to minimise error. Larger errors are encountered with re-sampling (when field sites with similar properties are sought) and these relate to changes in soil bulk density, % coarse fragments and horizon changes in the soil depth to be re-sampled. They also relate to the ability to describe, interpret and map the impact of pedogenesis, land use history and intensity of management at the site, field and regional scales. Within New Zealand, accurate maps showing records for example of climate, pedological description, erosion, flooding, volcanic activity and accurate long term records of land use, management and productivity are essential for this purpose.

Reduction of error in paired site comparisons

It is possible to conclude from the work of Goidts et al. (2009) and Stolbovoy et al. (2007) that to improve the precision and accuracy of detecting land use change effects attention to detail has to be given to selection of paired sites. Initial research should invest heavily in showing that re-sampling at the plot or field scale leads to low errors in the determination of soil carbon stocks. This involves ensuring that within-site sampling strategies (sampling grid system) encompass all within-site variability at each sampling (Stolbovoy et al. 2007). Initial sampling should allow for geostatistical analysis to be used to determine appropriate spacing for sampling of all measured variables at all scales. Across sites, paired for land use change, it is recommended that the site physical and historic data are entered into and tested against a geospatial database that is populated with the appropriate information. Field scale mapping of co-variates that can be proximally and remotely sensed rapidly (such as penetrometer readings, electrical conductivity and soil reflectance) should be investigated as a method for expediting the selection of landscape units with similar (for use as paired sites) and different attributes (to avoid inclusion in paired site comparisons).

Understanding uncertainty in national inventory models

The levels of uncertainty that exist in the current model for estimating national carbon stocks need to be known in order to improve the system for reporting New Zealand soil carbon inventories. An uncertainty analysis should be undertaken to identify and quantify the uncertainty in soil organic stock assessments at all scales. Geospatial data used in the paired site comparisons needs to be expanded as part of the national land cover data layers. An error propagation method similar to that used by Goidts et al. (2009) should be used to assess and direct activity into improving the national inventory model. Levels of uncertainty generated by the error propagation model will identify its limitations and at what scales it should be tested for validation.

In conclusion, the compound error term is rarely fully determined, with the information required to do the analysis being largely unavailable. Section 2.4.2 provides a method that is used more frequently to assess the number of samples required to confirm a minimum detectable change statistically. However it is important to emphasise that this method is handling the error term encapsulated within the soil carbon stock change estimate. Fewer samples would be required if the compound error term could be minimised as a first step in this 'estimation of uncertainty' procedure.

2.4.2 Determination of sample number for assessment of minimum detectable change

Minimum detectable change in the carbon stocks of forest soils has been investigated in several published studies. Homann et al. (2001) and Homann et al. (2008) have investigated minimum detectable change or differences associated with forest management treatments in field experiments. Yanai et al. (2003) undertook power analyses of previous studies of forest floor carbon stock change over time and found that the studies reviewed could not detect significant changes less than 15 to 20%, concluding that the re-measurement of plots or sites across time periods provides greater statistical power in terms of the detection of changes than the measurement of spatially un-related sites across time periods.

Using case study data from New Zealand sites, the objective of the analysis in this report is to estimate the number of samples needed to detect a true difference in a change in soil carbon storage. The probability of obtaining a significant result (detection of a change) depends on variability of the data (quantified by the standard deviations), size of the change and the number of samples (the number of sites at which soil carbon storage has been determined). Thus, for a given standard deviation and number of sites, as the change in soil carbon storage increases, so does its detection probability (Fig. 6). Consequently, estimates of the standard deviation, number of sites and probability may be combined to estimate a minimum detectable change in soil carbon storage according to what's called power analysis. Estimates of uncertainty for soil carbon storage using power analysis were developed by the late Greg Arnold.

The power of a statistical test is the probability of correctly rejecting the null hypothesis when it is false. Here, the null hypothesis is that soil carbon storage had not changed from the first to the second sampling period. The probability of rejecting the null hypothesis when it is true is indicated by a specified significance level, commonly 5%. Thus, 5% of the time, the test is expected to erroneously lead us to conclude the null hypothesis is false when it is actually true. There is only a 5% chance of committing this type of error, sometimes called a false positive. Thus, this error means there was actually no change in soil carbon storage over time but it is possible to conclude wrongly that soil carbon storage changed over time according to a statistical test of the data from repeated sampling. The error may be reduced by increasing the sample size.

The power of a statistical test may also be considered the probability of obtaining a statistically significant result (detection of a change) from the data generated by a comparative experiment, performed on random samples from the population(s) of interest. Power analysis begins by specifying a difference that needs to be detected by repeated sampling. With this, there needs to be an associated estimate of the standard deviation and the significance level and power specified. With these data, the required number of sampling sites may be estimated. A two-sided hypothesis test is appropriate because soil carbon storage from the second sampling may be greater or less than that of the first sampling as well as unchanged, the null hypothesis.

An initial analysis by Greg Arnold was undertaken to estimate uncertainty in data on changes in carbon stocks in grazed dairy farm at 31 sites in the North Island as published by Schipper et al. (2007). A power analysis was performed to determine sample numbers needed to have 80% confidence of detecting a real difference in carbon storage over a period of 21 ± 3 years (mean ± standard deviation) at the 5% level of significance. In this study, the average loss of carbon between two samplings was 2.1 kg C/m^2, calculated from 31 sites. The standard deviation of these 31 changes was 4.8 kg C/m^2. The sample sizes required to detect a range of differences using standards deviations of between 3 and 5 kg C/m^2 is shown in Fig. 6. With a standard deviation of 5, a sample of 50 is required for 80% certainty of showing a difference of 2 kg C/m^2 to be significant. For an 80% chance of a true difference of 2 kg C/m^2 being significant the calculation must allow some leeway for the particular sample selected to have a difference smaller than 2, or standard deviation larger than 5. In fact a difference of 2.1 kg/m^2 was significant with a sample of 31. However, the 2.1 kg/m^2 could have been a low estimate when the true decrease was 2.5 kg/m^2 or a high estimate when the true decrease was 1.5 kg/m^2. A sample of 50 would have ensured a significant difference even if the sample of 31 had given an estimate of less than 2 kg/m^2.

As more detailed analyses are performed (e.g. within a land use, soil order or land form combination) the standard deviation of the amount of change is likely to be lower. Consequently, the number of profiles that need to be sampled will decline to correctly identify a true change (loss or gain) in soil carbon.

For a more detailed analysis, the use of power analysis has been revisited using three case studies presenting data from:

- North Island dairy farms (published by Schipper et al. 2007)
- land use change from dry stock pasture to arable cropping (data from Plant & Food Research)
- land use change from pasture to plantation forestry (data collated by Scion).

North Island dairy farms

A subset of the data from North Island dairy farms (Schipper et al. 2007) consisted of soil that was sampled repeatedly at 23 farms or sites over a period of 21 ± 3 years (mean ± standard deviation, Table 2). The sites were virtually identical for each sampling because the two excavation pits had been literally side by side at each site. The pits were generally sampled to a depth of about 1 m.

Two determinations of soil carbon storage, the change in soil carbon storage and time elapsed between the repeated samples are listed in Table 3. From these data, the mean change in soil carbon storage was -1.4 ± 3.7 kg C/m^2 (mean ± standard deviation). The negative sign indicates that here was a net loss of soil carbon over the time period. Starting with the null hypothesis that the change in soil carbon storage was zero, a two-tailed test for significant difference between the hypothesised mean of zero and the mean loss in soil carbon storage of 1.4 kg C/m^2 was undertaken. A t value from this mean and the standard error is 1.79. For a probability of 5%, the critical t value for a two-tailed test is 2.07. The computed absolute value of t is less than the critical value, so the null hypothesis is not rejected because the probability is >5%. For a probability of 10%, the critical t value for a two-tailed test is 1.72. The computed absolute value of t is greater than the critical value, so the null hypothesis is rejected because the probability is >10%. This means we can be 90% certain the soil carbon storage declined significantly over the 21 ± 3 year period between samplings.

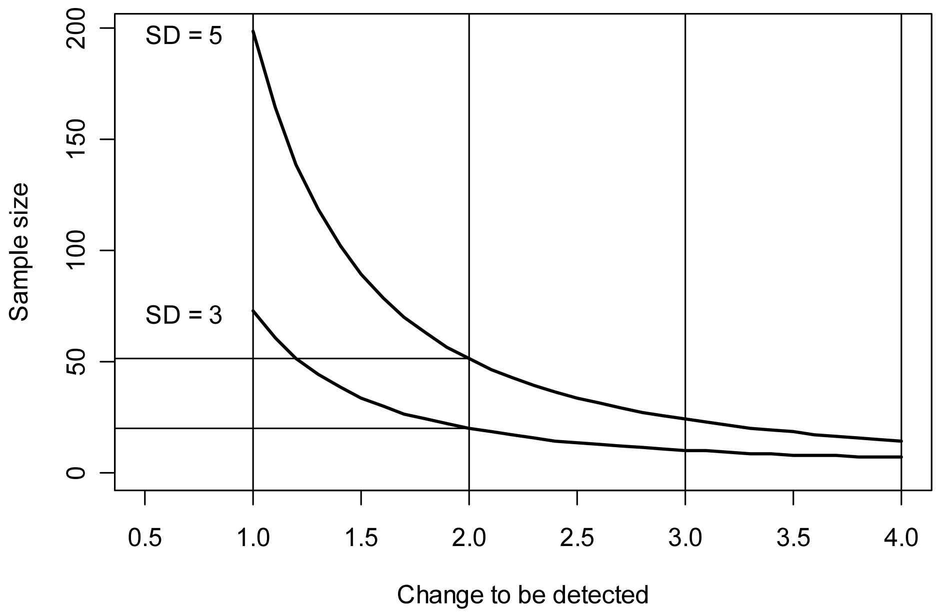

Fig. 6 Sample sizes needed to be able to detect a given change in soil carbon stock. The horizontal axis refers to a change in soil carbon stock (kg/m^2) and SD refers to standard deviation.

From the earlier analysis undertaken by Greg Arnold using data published by Schipper et al. (2007) reporting the results of repeatedly sampling soils from 31 dairy cattle farm and dry stock (beef cattle) farm sites, the mean loss in soil carbon storage was 2.1 kg C/m^2 (see above). Schipper et al. (2007) reported 95% confidence limits that were losses of 3.84 and 0.25 kg C/ m^2 (probability 3%), respectively. One of the sites (SB9633) showed an extreme carbon loss of 21 kg C/m^2. Omitting this site from the data set, the mean loss in soil carbon storage was 1.4 kg C/m^2 and the 95% confidence limits were losses of 2.69 and 0.13 kg C/m^2, respectively. Data used in the analysis in Tables 2 and 3 showed a mean (± standard deviation) loss in soil carbon storage of 1.4 ± 3.7 kg C/m^2.

Using power analysis, the number of sites required to detect a decrease of 1.4 kg C/m^2 at significance and power levels of a probability of 10% and 90%, respectively, is 33 sites. Thus, to have a 90% chance of detecting a statistically significant decrease in mean soil carbon storage of 1.4 kg C/m^2, 60 sites need to be sampled repeatedly over 23 ± 3 years. A decrease of-1.4 kg C/m^2 was significantly different from zero with a sample of 23 sites (probability < 10%). A further point discussed by Greg Arnold is that, by being 90% certain that a 'true' decrease in soil carbon storage of 1.4 kg C/m^2 will be statistically significant, the power analysis calculation includes some tolerance for the sample to yield a change smaller than 1.4 kg C/m^2. Put another way, based on the repeated sampling, the change in soil carbon storage of 1.4 kg C/m^2 could have been a high estimate of the lower 'true' value. Finally, if the standard deviation was 4.4 kg C/m^2, to detect a decrease of 1.4 kg C/m^2 at significant and power levels of 10 and 90%, respectively, the requirement for measurements is estimated to be 85 sites.

Table 2 Characteristics of 23 dairy farm sites where soil was sampled repeatedly for determination of carbon storage, a subset of data reported by Schipper et al. (2007).

Site code	Elevation m	Annual rainfall mm	Average air temperature °C	Sampling depth mm	Year of first Sampling	Year of second Sampling
9952	40	1200	13	1050	1984	2003
9557	60	1010	13	1150	1980	2003
10027	25	1200	13	1200	1986	2004
9909	92	2000	13	850	1984	2005
10029	6	1150	13	1050	1986	2004
9635	3	1200	13	1060	1980	2004
9634	3	1200	13	770	1980	2004
9801	30	1300	13	1080	1982	2004
10039	8	1000	13	1000	1986	2004
9938	18	1100	13	1000	1984	2004
9903	55	1529	13	1180	1984	2005
9907	82	1900	13	1020	1984	2005
9908	76	1900	13	1000	1984	2005
9949	80	1257	13	970	1984	2003
10094	140	650	12	1100	1987	2005
10041	60	1100	13	1000	1986	2004
9950	40	1200	13	1100	1984	2004
9945	40	1200	13	1280	1984	2004
9314	76	1520	13	1050	1976	2005
9800	30	1300	13	1040	1982	2004
9538	213	1600	15	910	1979	2004
9317	76	1520	13	1070	1976	2005
10042	25	1000	13	1100	1986	2004

Another important point raised by Greg Arnold is related to the efficiency of repeatedly sampling at sites compared with selecting a set of sites for the second sampling without reference to the first set (i.e. randomly). For comparative power analysis of the latter case, the standard deviation associated with each sampling from the data in Table 3 was estimated at 10 kg/m^2. Using this as the standard deviation in the power analysis to determine the number of sites required to detect a change of 1.4 kg C/m^2 at significant and power levels of 10% and 90%, respectively the estimate of the number of sites needed to be measured is 875, recognising the need to detect the change between two, separate means, each from sets of sites where the standard deviation was 10 kg/m^2. This shows clearly the considerable merit in purposeful sampling.

Table 3 Soil carbon storage for repeated samples, the change in soil carbon storage and time elapsed between the repeated samples at 23 dairy farm sites, a subset of data reported by Schipper et al. (2007). Negative signs indicate losses of soil carbon.

Site code	Soil carbon storage at first sampling kg C/m^2	Soil carbon storage at second sampling kg C/m^2	Change in soil carbon storage kg C/m^2	Elapsed time years
9952	21.7	16.8	-4.9	19
9557	34.2	32.7	-1.5	23
10027	16.8	9.6	-7.2	18
9909	38.8	47.0	8.2	21
10029	21.9	16.6	-5.3	18
9635	16.9	16.4	-0.5	24
9634	15.0	15.9	0.9	24
9801	11.9	12.6	0.7	22
10039	22.5	21.2	-1.3	18
9938	16.3	13.5	-2.8	20
9903	37.6	33.7	-3.9	21
9907	34.3	31.9	-2.4	21
9908	38.8	38.2	-0.6	21
9949	21.3	19.6	-1.7	19
10094	13.2	13.3	0.1	18
10041	16.5	11.1	-5.4	18
9950	12.2	9.6	-2.6	20
9945	13.5	13.9	0.4	20
9314	30.6	30.3	-0.3	29
9800	19.4	16.9	-2.5	22
9538	27.8	24.2	-3.6	25
9317	33.9	41.8	7.9	29
10042	19.4	16.3	-3.1	18

Changing the values of parameters adopted in the power analysis model adds further perspective to estimates of uncertainty. For example, using the same data set from Tables 1 and 2, the same mean (± standard deviation) loss in soil carbon storage of 1.4 ± 3.7 kg C/m^2 over 21 ± 3 years, with a probability of 90% (power level 10%), the detectable changes in carbon storage if 100 and 500 sites were sampled are 1.1 and 0.5 kg C/m^2, respectively. If the probability were changed to 20 and 50% (power level reduced to 80 and 50%), the corresponding detectable changes in soil carbon would be 0.9 and 0.4 kg/m^2, for 100 sites sampled and 0.6 and 0.3 kg C m^{-2} for 500 sites sampled. From the data in Table 3, the mean value of soil carbon storage was around 22 kg C/m^2. For 500 sites, with a probability of 10% (power level of 90%), the minimum detectable change in soil carbon storage was

0.5 kg C/m^2. Thus, an estimate of a 2% change in soil carbon storage is the minimum detectable value over 23 ± 3 years.

A recent meta-analysis was undertaken of data from 25 European countries providing information about their carbon monitoring network for agricultural soils (Saby et al. 2008). Based on 996 pasture sites across England and Wales that were repeatedly sampled over about 20 years (first during 1978-1983 and again during 1995-2003), the minimum detectable change in soil carbon content was 3.3 g C/kg soil. In New Zealand, the mean carbon content of pastoral soils is 35 g C/kg to a depth of 0.3 m according to Tate et al. (2005). Combining these data from England and Wales, they were transformed to estimate a 9% ([3.3/35] ×100) change in soil carbon storage as a minimum detectable value. For comparison, for the 23 dairy farm sites in New Zealand (Schipper et al. 2007), the mean decrease in soil carbon storage was 1.4 kg C/m^2 and the mean soil carbon storage at first sampling time was 23.2 kg C/m^2, so the detectable change ([1.4/23.2] ×100) was 6%. This larger percentage in the European farms compared with the sites in New Zealand represented a much greater variety of farm types and soils.

These estimates are based on the assumption of a constant rate of decrease in soil carbon storage at the sites in New Zealand and that the period between the two sampling times (mid 1980s to mid 2000s) was representative. This seems unlikely because during this period, there were unprecedented changes on dairy farms including significant increases in density of the grazing cattle and urea fertiliser application rate. However, this is not meant to diminish the obvious value of using repeated samples and the change of conditions might be helpful for interpreting the detected change in soil carbon storage over the period.

Land use change from dry stock pasture to arable cropping

The data used are a subset from the Land Management Index dataset selected for land use change from dry stock (sheep and beef) grazed pasture to arable cropping on flat land for three representative soil types in Canterbury, Auckland and Hawkes Bay (Table 4). The data do not represent paired plots per se, but within a region, soils were similar for the two land uses. Power analysis was used to estimate minimum detectable changes in soil carbon storage for different numbers of sampling sites.

The mean (± standard deviation, $n = 24$) change in soil carbon storage was a loss of 35.6 ± 37.2 Mg C/ha. The mean soil carbon storage in the pasture plots was 108.1Mg C/ha, so on average, there was a 33% change in carbon storage ([35.6/108.1]×100). Thus, we detected a mean 33 ± 34 % reduction in carbon storage over the upper 0.3 m depth of mineral soil.

For a 90% chance of detecting a statistically significant (probability < 10%) change in the mean soil carbon storage of 20% ([21.6/108.1] ×100), 10%, 5% and 2%, the number of sites that would have to be sampled repeatedly were estimated to be 26, 102, 407 and 2,449, respectively.

Land use change from pasture to plantation forestry

The data are a compilation of published estimates of the change in soil, carbon storage following conversion of pasture to *Pinus radiata* plantation forestry at 23 paired sites (Table 5). Power analysis was used to estimate minimum detectable changes in soil carbon storage for different numbers of sampling sites.

Table 4 Soil carbon storage from the surface to a depth of 0.3 m in pasture and changes in carbon storage based on comparison with an arable plot. These data came from 24 sites (A Auckland, C Canterbury, H Hawkes Bay). Negative signs indicate losses of soil carbon.

Site code	Soil carbon storage in pasture Mg C/ha	Change in soil carbon storage compare with cropping Mg C/ha
2C 39	98.5	-15.4
2C 40	98.1	-22.9
2C 41	91.6	-19.6
2C 46	84.3	-9.6
3C 56	87.7	2.0
3C 62	78.5	12.2
3C 66	91.8	-10.7
2A 55	130.8	-78.3
2A 56	114.9	-58.2
2A 60	136.9	-62.4
2A 61	168.4	-107.0
2A 62	178.1	-114.5
2A 65	132.1	-81.9
2A 66	129.7	-72.8
3A 42	130.5	-38.7
3A 43	111.2	-39.9
2H 10	126.0	-71.0
3H 7	97.8	-38.8
3H 8	90.6	-26.1
3H 9	85.2	-15.5
3H 35	77.3	6.0
3H 36	73.0	16.5
3H 37	87.0	-0.1
3H 59	94.9	-8.0

The mean (± standard deviation, n = 23) change in soil carbon storage to a depth of 0.1 m in the mineral soil with land use change was a loss of 4.8 ± 9.3 Mg C/ha. The mean soil carbon storage in the pasture plots was 49.5 Mg C/ha, so on average, there was a 10% change in carbon storage ([4.8/49.5] ×100). In the plantation plots, the mean tree age was 21 ± 5 years. The mean (± standard deviation) percentage reduction in carbon storage was10 ± 19%.
For a 90% chance of detecting a statistically significant (probability< 10%) change in the mean soil carbon storage of 5 and 2% ([2.7/49.5] ×100 and ([1.2/49.5] ×100, respectively), the numbers of sites that would have to be sampled repeatedly (assuming 21 years between re-sampling) were estimated to be 100 and 500.

Table 5 Soil carbon storage from the surface to a depth of 0.1 m in 23 pasture plots, the change in soil carbon storage based on comparison between paired plantation forest plots and tree age indicating the time elapsed for the land use change from pasture to plantation. These data came from 23 sites. Negative signs indicate losses of soil carbon.

Source	Soil carbon storage in pasture plot	Change in soil carbon storage following conversion to forestry	Tree age
	Mg C/ha	Mg C/ha	years
Scott et al. (1999)	47.3	-10.3	23
Scott et al. (1999)	47.3	-12.8	23
Ross et al. (2002)	24.4	-5.2	25
Beets et al. (2002)	54.3	-11.5	20
Ross et al. (2002)	51.0	-2.9	28
Davis (2001)	38.3	-3.4	25
Davis (1994)	51.7	1.3	10
Giddens et al. (1997)	42.2	-2.4	19
Giddens et al. (1997)	44.1	-8.3	20
Giddens et al. (1997)	82.5	-4.8	20
Giddens et al. (1997)	53.9	0.1	18
Giddens et al. (1997)	43.3	7.8	30
Giddens et al. (1997)	40.0	-17.5	19
Giddens et al. (1997)	28.4	6.1	17
Giddens et al. (1997)	35.5	-10.5	13
Giddens et al. (1997)	59.9	5.6	24
Schipper & Sparling (2000)	57.1	11.8	25
Sparling et al. (2000)	64.5	12.2	18
Sparling et al. (2000)	61.0	-8.2	22
Parfitt et al. (1997)	43.3	-8.2	20
Ross et al. (1999)	63.0	-20.0	23
Ross et al. (2002)	52.3	-8.0	20
Ross et al. (2002)	52.5	-20.8	30

In summary, calculated estimates of the numbers of sites needed to be sampled to give a range of detectable changes in soil carbon ranging from 2 to 10% are shown in Table 6.

Table 6 Summary of sampling strategies and power analyses to estimate minimum detectable changes in soil carbon storage with significance and probability of 10% and 90%, respectively, based on statistics given earlier. Repeated sampling within a land use is used to estimate changes over time (average soil carbon storage was 22 kg C/m^2), while matched and paired sites are used to estimate changes corresponding with changes in land use (average soil carbon storages were 108 and 50 kg C/m^2, respectively).

Soil sampling strategy	Detectable change in soil carbon storage %	Number of sites needed to be sampled
Repeated sampling at the same sites		
Repeated sampling over 23 years in dairy farm paddocks	10	25
Repeated sampling over 23 years in dairy farm paddocks	5	98
Repeated sampling over 23 years in dairy farm paddocks	2	606
Matched sites across two land uses		
Matched sites across two land uses (pasture grazed by sheep and beef cattle versus arable cropping)	10	102
Matched sites across two land uses (pasture grazed by sheep and beef cattle versus arable cropping)	5	207
Matched sites across two land uses (pasture grazed by sheep and beef cattle versus arable cropping)	2	2,449
Paired sites across two land uses		
Paired sites across two land uses (pasture grazed by sheep and beef cattle versus 21 year old plantation forest)	10	30
Paired sites across two land uses (pasture grazed by sheep and beef cattle versus 21 year old plantation forest)	5	119
Paired sites across two land uses (pasture grazed by sheep and beef cattle versus 21 year old plantation forest)	2	741

2.5 Estimated costs of detecting changes in soil carbon using conventional soil cores

An attempt to summarise costs for establishing plots, collecting and analysing soil core samples for measurements of carbon concentration was prepared for MfE by Jones et al. (2009) and is reproduced in Table 7.

Table 7 Estimated costs for establishing plots, collecting soil samples and analysing for carbon concentration in soil cores.

Activity	Estimated cost $
Per plot sampling	
Plot establishment	1,000
Plot sampling and measurement	2,000
Consumables	50
Travel & accommodation expenses	1,950
Sub-total	5,000
Per plot sample preparation and analysis	
Analysis of all samples collected	
Sample preparation (4 points by 3 depths = 12 samples[1])	780
Sample analysis (4 points by 3 depths = 12 samples†)	360
Sub-total	1,140
Analysis of bulked samples (by plot)	
Sample preparation (3 depths = 3 bulked samples†)	225
Sample analysis (3 depths = 3 bulked samples†)	90
Sub-total	315
L & FH bulked samples (by plot for forest plots only)	
Sample preparation (2 horizons = 2 bulked samples)	150
Sample analysis (2 horizons = 2 bulked samples)	60
Sub-total	210
Per site (un-bulked samples, 1 plot) [forest plots]	6,140 [6,350]
Per site total (bulked samples, 1 plot) [forest plots]	5,315 [5,525]

[1] Sampling of annual cropland or land subject to mass-movement erosion may require sampling of an additional depth range below 0.3 m depth (e.g. 0.3-0.6 m).

3. Direct measurement of ecosystem carbon exchange

3.1 Estimating changes in soil carbon from measurements of ecosystem CO_2 exchange

An alternative to measuring changes in soil carbon stocks is to measure all the inputs and output of carbon at an enterprise sale. In mass terms, the exchange of carbon between ecosystems and the atmosphere is dominated by CO_2 exchange, resulting from the balance between photosynthesis and respiration. Both of these processes are biological but are constrained by physical and climatic factors. Other carbon exchanges that may affect soil carbon stocks include loss of dissolved carbon in drainage water or erosion (Ghani et al. 2007), biomass imports and exports, and methane emissions from livestock. In agricultural systems with well-drained soils, methane emissions from soil are generally very low, and are normally not included in the carbon budget. Recent work has shown that non-biological processes can also contribute to CO_2 fluxes from the surface to the atmosphere, especially under very dry conditions where microbial respiration is limited by lack of water (Rutledge et al. 2010). However, the significance of this process to New Zealand ecosystems is not known.

Measurements of carbon exchange are typically used to compile carbon budgets at spatial scales ranging from paddock to farm (Nieveen et al. 2005) and temporal scales from half-hourly to annually. Measurements allow the development and testing of process-based functional relationships between CO_2 exchange and vegetation characteristics, and environmental variables including irradiance, temperature, humidity and soil water content. Carbon exchange measurements also allow interpretation of ecosystem response to normal and extreme variations in climate variables such as drought, as well as land management practices such as cultivation and animal grazing intensity. They also provide data that can be used to ground truth predictive models of carbon exchange.

Worldwide, the eddy covariance technique is used to measure the net exchange (or flux) of CO_2 between the Earth's surface and the atmosphere, for ecosystems ranging from forests to grasslands and from tropical forests to sub-arctic tundra (Baldocchi 2008). These measurements can be coupled to other flows of carbon (biomass transfer and dissolved carbon and methane losses) to calculate annual budgets of carbon at an enterprise scale. Furthermore, the spatial and temporal scales of these measurements allow detailed analysis of the drivers that regulate carbon gains or losses, from half-hourly to seasonal timescales. Technical developments during the past two decades have enabled continuous and routine measurements of net ecosystem exchange of CO_2 (NEE) to be made, typically at 30-minute averaging time steps, which are then summed over daily, seasonal and annual periods. Time-series of NEE are commonly partitioned into its gross components, ecosystem respiration (RE) and gross ecosystem production (GEP) that are then used to develop functional relationships (Reichstein et al. 2005).

There are four main reasons why the eddy covariance technique has been widely adopted in studies of ecosystem carbon exchange (Baldocchi 2003): (1) the spatial scale of the so-called 'flux footprint', or the area of land contributing the majority of the carbon flux signal, is appropriate to integrating across the scale of ecosystems, ranging from paddocks to several hectares, (2) the approach provides a direct measure of net CO_2 exchange across the soil/vegetation-atmosphere interface, (3) carbon exchange is measured across a range of temporal scales from sub-hour to annual and inter-annual and (4) the measurement does not disturb the surface, unlike chamber methods, so normal ecosystem processes or land management processes can continue uninterrupted.

3.2 Eddy covariance and chamber measurements

Eddy covariance and chamber techniques provide complementary data at common temporal but vastly different spatial scales that can be jointly used to determine the role of specific management practices on carbon budgets (e.g. tillage, pugging, and urine patch dynamics). Eddy covariance measures the net vertical exchange of CO_2 passing a fixed measurement location, commonly on a tower several metres above the surface up to a spatial scale of hectares. The estimates include the net effects of photosynthesis (uptake by vegetation) and respiration (return of CO_2 to the atmosphere from soil and vegetation), and is non-disruptive to the land surface. A wide range of other environmental variables are also measured, especially those known to be important for regulating CO_2 exchange, including irradiance, temperature and soil water status). Soil respiration chambers typically cover a few hundredths of a square metre of soil that may also contain plants, and usually require plastic collars to be emplaced in the soil for the duration of a study. Often opaque chambers are used which eliminate sunlight so that only surface respiration is measured.

3.2.1 Eddy covariance methodology

Eddy covariance measurements of CO_2 exchange require fast (usually either 10 or 20 Hz) measurements of vertical wind velocity, using a sonic anemometer, and fluctuations of the mixing ratio of CO_2 with either an open- or closed-path gas analyser. In practice the three-dimensional wind field is normally measured, along with fluctuations in air temperature and humidity, so that fluxes of energy and water vapour (evaporation rates) are also measured. Combining measured CO_2 and water vapour fluxes allows calculation of water use efficiency. High frequency raw data, as well as lower frequency (typically 30-minute) fluxes and averaged ancillary data are usually captured by a data logger or computer. Details of calculations used in the eddy covariance method are provided elsewhere (Baldocchi, 2003). Ancillary environmental measurements are required for quality assurance and gap-filling as well as interpretation of flux data. Modern eddy covariance systems can normally operate at remote sites using solar panels and batteries and with communication systems for data transfer ranging from cell phone to satellite. CO_2 and water vapour mixing ratios are measured using either 'closed-path' or 'open-path' instruments. Closed path gas analysers allow a more controlled environment for precision measurement and fluxes require less correction for issues such as air density fluctuations. In recent years there has been a move towards the use of open path gas analysers because the modern instruments have generally very stable responses and low power demands, requiring little maintenance and less correction for frequency loss down the often long sampling tubes used for closed path systems. Open path methane sensors are also becoming more reliable, which may mean that methane flux measurement may soon become routine.

Site requirements and footprint

Instruments are usually mounted on a tower or other structure several metres above the surface. A general rule of thumb is that flux measurements are affected by the type of surface up to 100 times as far upwind as the instruments are mounted vertically above the surface. A number of ‘footprint’ modelling techniques exist that allow this to be determined with more statistical certainty. For example, instruments mounted on a tower 3 m above grazed pasture will, on average, be measuring the integrated CO_2 exchange derived from paddocks up to 300 m distant in the upwind direction. Cross-wind turbulence means that this footprint also has a cross-wind dimension. Eddy covariance measurements of CO_2 exchange should therefore be considered as area averages. However the exact footprint has dimensions that change continuously with wind direction, wind speed and atmospheric stability. Eddy covariance measurements are less well suited for cluttered or highly variable land management situations, although very tall towers allow ‘landscape’ fluxes to be measured, for example in urban environments. For example, an eddy covariance system sited in a small maize field surrounded by pasture would produce measurements variably affected by both surfaces. Eddy covariance measurements are best located on flat, non-sloping terrain, although some degree of sloping is acceptable given sufficient care.

Corrections and deficiencies

Raw eddy covariance measurements require a number of corrections, usually applied via post-processing and these are well documented (Baldocchi 2003) and applied widely. Measurements are often interrupted by rain or mist wetting the sensors, occasionally by maintenance or instrument calibration, and more rarely by instrument or power system malfunction.

A major problem is that when atmospheric turbulence is not fully developed under low wind speed conditions, frequently the situation at night, atmospheric transport processes close to or within the plant canopy may become decoupled from the overlying atmosphere where eddy covariance measurements are made. This may lead to CO_2 ‘draining’ down slope, or building up close to the surface without being detected at measurement height. Affected measurements are usually eliminated from the flux time series using the so-called ‘friction velocity correction’ (Papale et al. 2006). In practice this means that measurements made during light or calm wind conditions are assumed invalid.

Gaps in the measured flux time-series must be ‘gap-filled’ in order to calculate daily, seasonal and annual totals of CO_2 (and water vapour) exchange. A range of techniques are used ranging from replacing missing data with the mean of valid data measured at the same time on surrounding days, using functional relationships between respiration or photosynthesis and environmental variables, to sophisticated neural network algorithms. Comprehensive comparisons between various approaches have been described by Falge et al. (2001) and Moffat et al. (2007). Gap filling increases the uncertainty in accumulated fluxes, especially at short time scales (see discussion on errors below).

A remaining challenge for the eddy covariance community of researchers is the so called ‘energy balance closure problem’. In theory, if independent measurements are made of all components of the surface energy balance (main terms are net radiation, soil heat flux, sensible heat flux, latent heat flux), the surface energy balance should be able to be closed. In practice this is unlikely on a half-hour basis because of random measurement errors. However a bias also usually exists so that the sum of sensible and latent heat fluxes is usually less than the sum of net radiation and the soil heat flux. Published reviews include that by Wilson et al. (2002) who found that, for 50 site-years of data from 22 eddy covariance sites, energy balance closure was deficient by an average of 20%. There are several potential reasons for this that are not reviewed here (Oncley et al. 2007) although it appears that the accuracy of the instrumental methods and calculations used in the eddy covariance technique are not the cause (Foken et al. 2009). There is neither independent measurement nor clear consensus on the full implication for CO_2 fluxes, for which no analogous ‘closure’ check is available at a timescale relevant to the measurements. In contrast, many researchers are currently adjusting measured energy fluxes to ‘force’ closure.

Errors and uncertainty

There are several sources of uncertainty in eddy covariance data. At the short timescales over which fluxes are measured (typically a half-hour), there is a substantial random error component because of the nature of turbulent transport processes and spatial variations present within the flux footprint. At this timescale systematic errors are also common, associated with instrument system design and placement, calibration, and data processing constraints. Many of these are known and corrected for (e.g. the effect of physical separation between sonic anemometer and gas analysers). Random errors typically are not normally distributed, rather they are heteroscedastic (uncertainties increase with the absolute magnitude of the flux). Additionally uncertainties in night time estimates of NEE are higher than those for day time estimates (Hollinger & Richardson 2005). These random errors become less important at longer timescales over which sums of NEE are compiled. Instead, the uncertainties due to data filtering (especially under low wind speed conditions) and gap filling become more important (Hagen et al. 2006). Comprehensive comparisons of the uncertainties arising from choice of filtering and gap filling methods have been carried out by Falge et al. (2001), Papale et al. (2006) and Moffat et al. (2007), van Gorsel et al. (2009). Hagen et al. (2006) carried out an uncertainty analysis of seven years of eddy covariance data for a forest site in Maine, USA. At the half-hour timescale uncertainties in eddy covariance fluxes approached 100% of the magnitude of the flux observations, but as the time interval increased over which NEE was summed, uncertainty dropped dramatically until it was less than 10% at the annual scale. Half hourly flux datasets are consequently very noisy. This is counterbalanced by the very large number of observations that are made at this timescale so that biophysical models developed using these data are usually robust, and measured seasonal and inter-annual variations in NEE are statistically sound (Hollinger et al. 2004).

Annual sums of NEE and its component fluxes GEP and RE are often required. Annual NEE is obtained by summing half hourly observations. Gaps are filled using a variety of techniques including using models of RE and NEE derived from valid observations. RE is typically modelled from air temperature and soil temperature and water content and NEE using light-response relationships. Gap filling errors typically total around 0.5 Mg C/ha/y, even with approximately 65% of a dataset missing (Falge et al. 2001). To partition NEE requires the use of models (Desai et al. 2008, Reichstein et al. 2005) except at night time when RE=NEE. Calculating GEP requires the additional assumption that daytime respiration can be approximated by models derived from night time observations, which might not always be the case (Desai et al. 2008, Rutledge et al. 2010), and the timescales over which models are developed need to be appropriate (Reichstein et al. 2005).

Uncertainty estimates of annual sums of NEE generally range from 0.3–1.0 Mg C/ha/y which is in the order of the carbon content of a sheet of computer printer paper (Baldocchi 2008)! While this does not seem a great deal it approaches the rate of soil carbon loss reported by Schipper et al. (2007) for New Zealand pasture soils. Also, NEE is the often small difference between its large components GEP and RE, so at times the uncertainty in NEE includes zero. For example, Nieveen et al. (2005) estimated mean (± standard deviation) NEE from eddy covariance measurements over a grazed pasture for a New Zealand peat soil to be 0.045 ± 0.5 Mg C/ha/y where both GEP and RE were approximately 13.5 Mg C/ha/y.

3.2.2 Soil respiration chambers

Soil respiration is usually the largest component of return of CO_2 to the atmosphere in the terrestrial carbon budget, typically accounting for 50–70% of RE (Loescher et al. 2006). Chambers connected to gas analysers are usually deployed to measure soil respiration, although within-soil CO_2 sensors are also used to estimate soil surface CO_2 flux (Tang et al. 2003). Chambers that enclose plants and soil measure both heterotrophic (soil organisms) and autotrophic (plant) components of respiration. Transparent chambers placed at the soil surface are used to measure photosynthesis, and chambers are also commonly used to measure fluxes of other trace gases such as methane and nitrous oxide that are still challenging to measure with the eddy covariance technique.

Several reviews of soil respiration chamber designs and flux calculations have been published (Livingston & Hutchinson 1995) along with a careful consideration of potential biases (Davidson et al. 2002).

A characteristic of most chambers is their small size, typically enclosing just a few hundredths of a square metre of the soil surface. Plastic collars are usually inserted in the soil to provide a reliable seal for the chambers and also to minimise disturbance from multiple measurements at the same location. Multiple spatial measurements of soil CO_2 flux are required to fully characterise spatial variation, and it is often challenging to directly compare eddy covariance and chamber measurements of RE for this reason (Davidson et al. 2002). The coefficient of variation of spatial measurements of soil respiration can be used to estimate the number of chambers needed to measure the spatial mean soil respiration to a known level of confidence (Loescher et al. 2006). Spatial variability of soil respiration determines the precision of the mean flux, while biases in measured soil respiration due to chamber design affect accuracy.

Most soil respiration chambers are of the ‘non-steady state’ type, where the flux of CO_2 from the soil is calculated from the rate of increase of CO_2 in the headspace of the chamber, typically over the course of 1–2 minutes after the chamber is closed. Chambers are usually open between measurements to minimise the disturbance of normal soil–atmosphere exchange processes and to prevent the development of artificial soil temperature and water content regimes. There are several designs of commercially available soil respiration chamber systems, including those that allow multiple automatic ‘long-term’ chambers to be deployed. Sources of bias errors due to chamber design and operation are well known (Davidson et al. 2002), and modern commercially available instruments such as the LI-COR 8100 system are designed to minimise these, or account for biases in processing software. Briefly, bias errors can be caused by the alteration in gas diffusion gradients from soil to atmosphere that lead to underestimates of soil respiration flux of 0–15% depending on soil texture and water content. Correct venting of chambers so that the chamber is at atmospheric pressure is also important.

3.2.3 Brief review of studies using eddy covariance to determine changes in soil carbon

Compared with the number of studies that have used the eddy covariance technique to investigate ecosystem carbon exchanges for forests, there have been relatively few studies carried out on grassland ecosystems, and even fewer on intensively managed pasture-based grazing systems similar to those used in New Zealand. In recent reviews by Mudge (2009) and Wallace (University of Waikato, in prep.), a compilation of published studies has led to the following conclusions.

Of most relevance to studies of potential changes to soil carbon stocks in agricultural systems is the net ecosystem carbon balance (NECB), which accounts for the annual flows of carbon in all forms, including CO_2, CH_4, dry matter imports and exports (including meat and milk products), dissolved carbon in drainage or runoff, and erosion. The fluxes of CO_2, RE and GPP, are usually far larger than all other terms in the carbon budget, but they are often close to being in balance so that NEE is normally a net uptake of carbon in the range 3,000 to 0 kg C/ha/y for pastures with mineral soils (i.e. a net carbon sink). NEE is highly variable between different land management practices and soils, and the level of inter-annual variability is typically large because climatic variability between years strongly affects GPP and RE.

Managed pastures with mineral soils are generally carbon sinks, whereas managed pastures on peat soils are usually sources of carbon. Drought conditions reduce both GPP and RE, and NECB in years with drought often indicate losses of soil carbon.

There has only been one published study of NECB for a New Zealand farm. Nieveen et al. (2005) reported values of NEE close to zero for a dairy farm with shallow drains on deep peat near Hamilton. However calculation of the NECB indicated a carbon loss of 1,061 kg C/ha/y for the single year studied, because of methane emitted by cows and milk exports. Mudge (2009) reported NECB as a net uptake of 880 kg C/ha/y during a year with a severe drought on a Waikato dairy farm with mineral soils. Hunt et al.(2004) reported NEE for a sparse tussock grassland near Twizel in the central South Island during two years with contrasting rainfall. The ecosystem was a carbon source in the dry year and a net carbon sink in a wetter than average year. Eddy covariance data were combined with soil respiration chamber measurements and led to the conclusion that 85% of RE emanated from the soil surface.

Brown et al. (2009) used a combination of soil respiration chambers and eddy covariance to investigate temperature and soil water content controls on soil respiration in a grazed pasture in Canterbury, with observed seasonal changes driven mainly by temperature due to the well-watered conditions experienced during the study.

3.2.4 Estimated costs to set up measurement systems

Eddy covariance systems

One of the most frequently used configurations of eddy covariance systems presently widely in use is based around an open path CO_2/H_2O gas analyser (Li-Cor Inc., Model LI-7500) and the sonic anemometer/thermometer (Campbell Scientific Inc., Model CSAT3). Recent developments in data logging and flash memory technology mean that high-frequency eddy covariance calculations and data storage are very straight-forward to manage in the field. Data loggers such as the Campbell Scientific Inc. CR3000 are suitable for this purpose.

A recent development by Li-Cor Inc. is a new ‘enclosed-path’ gas analyser, built around the proven LI-7500 platform. Advantages include less data lost due to rain & other interference with the optical path, reduced temperature fluctuations in the optical path minimise the size of density corrections, and potential for on-board data logging of all sensors so data logger costs can be reduced. The cost of an eddy covariance system based on this instrument is likely to be similar to the open-path system quoted in Table 8.

Table 8 Approximate costs of open path eddy covariance system components (December 2009).

Eddy covariance system major components	Estimated cost $
LI-7500 open path CO_2/H_2O gas analyser	25,500
CSAT3 sonic anemometer/thermometer	12,000
CR3000 data logger/control module (including flash memory add-on)	6,100
Ancillary instrumentation (radiation balance components, photosynthetically active radiation, air temperature & humidity, soil temperature & heat flux, soil moisture, wind speed & direction, rainfall)	16,000
Solar power system (panels, controller, batteries)	4,000
Tower system (cost depends on height) & other hardware, plus data logger enclosure	2,500
Telecommunications (cell phone modem, aerial)	650
Total cost	**66,750**

While eddy covariance systems are relatively affordable and straight-forward to set up, specialised knowledge is required in order to ensure high data quality. Some of the post-field data processing and analyses remain very challenging, meaning the eddy covariance technique is still not entirely routine. Modern gas analysers such as the LI-7500 are exceptionally stable, but still require calibration checks at regular intervals. The most reliable way to achieve this is by using reference gases in a laboratory situation rather than in the field. To minimise data gaps, some groups now use a ‘floating’ instrument that is calibrated in the laboratory and then swapped for a field-deployed instrument that is then calibrated and moved on to another deployment. This requires an additional sensor.

Soil respiration chamber systems

For soil respiration measurements, the automated system (Model 8100) manufactured by Li-Cor Inc. has become an industry standard in recent years. Soil respiration is highly variable spatially, and estimates at field plot scales require the use of either multiple spot measurements or multiple automated chambers (Table 9).

Table 9 Approximate costs of four chamber LI-COR 8100 soil respiration chamber system (December 2009).

Chamber system major components	Estimated cost $
LI-8100 gas analyser and control system	36,000
LI-8100 automated 4-chamber multiplexed system	57,000
Solar power system for automated chambers	2,000
Total cost	95,000

4. Emerging technologies

Recent developments in reflectance spectroscopy have led to its emergence as a method to improve the efficiency of soil carbon analysis and stock estimation (Wetterlind et al. 2008). Reflectance spectroscopy techniques requires calibration of soil organic carbon concentration against standard laboratory measurements using furnace-based analysers but the methodology is a promising because it can be used successfully with a marked reduction in the number of samples that are needed to be analysed by standard methods.

4.1 Near infrared spectroscopy (NIRS)

Visible and near infrared diffuse reflectance spectroscopy (Vis-NIR DRS) has been extensively researched as a rapid and non-destructive laboratory and field method for determination of soil organic carbon (e.g. Ben-Dor et al. 1999a). Vis-NIR DRS is now being used for routine laboratory estimation of soil carbon (Malley et al. 2004) and promises to be a versatile tool which can be used *in situ* in field conditions for soil carbon analysis.

In New Zealand, Hill Laboratories use NIRS for routine soil carbon, soil nitrogen and available nitrogen analyses (R Hill personal communication 2009). Vis-NIR DRS, using either all or part of the 350–2500 nm range of the electromagnetic spectrum, is becoming the preferred reflectance spectroscopy method for rapid, non-destructive simultaneous assessment of a suite of soil properties (Shepherd & Walsh 2002, Brown et al. 2006, McBratney et al. 2006, Brown 2007, Awiti et al. 2008) by scanning air-dried, sieved samples, normally placed in a flat cell or petri dish. This is despite research showing that mid-infrared (MIR) spectroscopy is perhaps more accurate than Vis-NIR DRS (McCarty et al. 2002, Pirie et al. 2005, Viscarra Rossel et al. 2006, Reeves et al. 2008). However, variability in soil water content prevents effective use of MIR spectroscopy because absorbance of MIR wavelengths by water obscures the absorbance features of important chromophores (Lund et al. 2008).

The advantage of Vis-NIR DRS is that it requires less sample preparation and allows measurement on field-moist soils. This simplicity has allowed the development of a number of proximal sensing technologies for *in situ* field measurement of soil properties that are now being evaluated for reconnaissance mapping of soil carbon and nitrogen concentrations (Lund et al. 2008, Mouazen et al. 2005, 2007, Sudduth et al. 2008), as well as more precise measurement of soil organic carbon stocks (Kusumo et al. 2008).

4.1.1 Theory

Most organic molecules have well defined reflectance or transmittance features at visible (<750 nm) and NIR (750-3000 nm) wavelengths. These occur due to vibration of a molecule (Fig. 7) at a fundamental frequency, or wavelength, with a series of overtones, similar to the vibrating string of a musical instrument (Analytical Spectral Devices 2005). The absorbance of NIR by molecules is due to overtone and combination bands primarily of O-H, C-H, N-H and C=O groups whose fundamental molecular stretching and bending absorb in the MIR region.

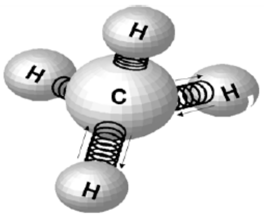

Fig. 7 Vis-NIR spectral energy is reflected and absorbed primarily by the molecular O-H, C-H, N-H and C=O bonds, as in this vibrating methane molecule (Analytical Spectral Devices 2005).

The overtone and combination band NIR absorbances give complex spectra of the complex organic molecules, not directly interpretable as in other spectral regions. Their analysis relies on chemometric software for (i) spectral pre-processing and processing and (ii) statistical analysis of derived components of the processed spectra. A ‘calibration’ set of analyses is used to calibrate the spectra. The biggest advantage of such a method is little or no sample preparation time with real-time data. Vis-NIR DRS relies on the accuracy of analysis of the reference samples used for the calibration set.

When Vis-NIR energy is projected onto a sample surface some of it is directly reflected, some is scattered and some is transmitted through the sample. Only the part of the beam that is transmitted within the sample and then back-scattered to the surface is considered as diffuse reflection, and it is this part of the spectrum that can be interpreted to assess soil properties such as carbon concentration. The six most common chromophores influencing soil reflectance in the visible (Vis) and near infrared (NIR) wavelength ranges (350-2500 nm) are clay minerals, carbonates, organic matter, water, iron oxides and soil salinity (Ben-Dor 2002). Soil organic matter concentration can be predicted successfully from measurements of diffuse reflectance in the Vis-NIR range.

4.1.2 Laboratory techniques

There is a significant history of development of laboratory methods using near infrared reflectance spectroscopy (NIRS) to observe change in soil organic matter (Bowers & Hanks 1965). NIRS has since been extended to predict other soil chemical and physical properties such as total carbon, organic carbon, total nitrogen, NH_4-N, NO_3-N, CEC, P, K, Ca, Mg, pH, water content, and soil particle size (Ben-Dor & Banin 1995, Chang et al. 2001, Cozzolino & Moron 2006, Islam et al. 2003, Reeves & McCarty 2001, Shepherd & Walsh 2002). Despite prediction accuracies for a wide range of soil properties ranging from poor to excellent (Viscarra Rossel et al. 2006), Malley & Martin (2003) conclude that NIRS is most successful for predicting total carbon, organic carbon, total nitrogen, cation exchange capacity and water content. Accuracy of prediction depends on sample preparation and suitable spectral pre-treatment before undertaking a multivariate statistical analysis (Chang & Laird 2002).

Sample preparation

Standard soil coring or profile wall sampling techniques are used to collect samples. Most published reports of estimates of soil carbon and nitrogen concentrations using NIRS are from laboratory methods using homogenous samples prepared by air-drying, grinding and sieving soils to eliminate the effect of differences in water content and heterogeneous surface structure on sample reflectance (Malley et al. 2004). It is very important that the process of

Fig. 8 A benchtop Vis-NIR DRS scanning reflectance spectrometer.

sample preparation is highly reproducible and presents the sample with the same particle size range each time. There is however no standard particle size that is recommended. The positive effect of fine grinding on the accuracy of determinations of total carbon and nitrogen has been reported by a number of workers in clay soils and several other soil types (Dalal & Henry 1986, Reeves et al. 2002, Russel 2003, Barthes et al. 2006). In contrast, Fystro (2002) reported lower accuracy with finer samples (0.5 mm ground) than with coarser samples (4 mm sieved) in coarse-textured soils. These apparently contradictory results might be explained by different light transmission in clay and coarse-textured soils due to the different size and arrangement of soil particles (Chang et al. 2001). Barthes et al. (2006) stated that aggregate destruction upon grinding might increase the prediction accuracy, because the wide range of well developed heterogeneous aggregates in many clay soils might affect reflectance adversely. In contrast, in coarse-textured soils with little aggregate development, grinding might break up quartz (or other primary minerals) which could alter sample composition and lead to the peeling of coatings, creating a more heterogeneous particle size distribution (Barthes et al. 2006). Whist drying the soil for analysis of carbon and nitrogen concentration is recommended, Fystro (2002) found this was not necessary.

Acquisition of spectra

Soil samples are placed in a benchtop, scanning reflectance spectrometer in sample cups that normally present a flat surface area of approximately 2000 mm^2 (Fig. 8).The cup is rotated while multiple scans are recorded and averaged. The spectrometer typically records spectra with a sampling interval of 1.4–2.0 nm for a Vis-NIR wavelength range such as 350 - 2500 nm (Fig. 9, upper). It is necessary to calibrate the spectrometer with a white reference at regular intervals during sample recording unless the spectrometer has an internal reflectance standard (double beam).

Spectral processing

Wavebands exhibiting obvious noise (often at the extremes of the measurement range) are excluded. To remove noise across the spectral range of interest a technique such as Savitzky-Golay filtering (Brereton 2003) is employed to smooth the spectra. To facilitate the regression analysis required to establish a calibration algorithm the data are normally reduced (perhaps tenfold) to a smaller number of wider wavelength bands. However, this may not be necessary with modern chemometric software packages such as Parles (Viscarra Rossel 2008) and Unscrambler (Esbensen 2002).

To remove baseline variations and overlapping peaks (Hruschka 2001) the data are usually transformed to the first derivative (Fig. 9, lower). This commonly uses the Savitzky-Golay algorithm to fit simple polynomials to small sections of the reflectance spectra and calculates their slope between finite bands. These derivatives may then be averaged for the replicate spectra acquired from every soil sample.

Calibration of spectral data with reference measurements (the 'standard curve')

A sample of the transformed spectral data (calibration set) is calibrated against paired data where carbon concentration has been measured independently with standard laboratory techniques using a multivariate analysis technique such as partial least square regression. The regression model is then used to predict the carbon concentration in other samples that have similar spectral attributes. In practice, samples that have spectral attributes that lie outside the calibration range should be analysed to provide their reference value. Once analysed the paired spectral and reference data can be used to extend the current calibration set or create a new calibration cluster. Principal component analysis of the spectral data is one method that can be used to test whether new samples have spectral attributes similar to the range covered by the calibration set. An example of this application (Fig. 9) is described by Kusumo et al. (2008).

The ability of multivariate regression analysis to predict the chemical properties of unknown soils (validation sets) to accurately relies heavily on whether the spectral and chemical properties of the unknown soil fall within the range of the calibration set (Brimmer et al. 2001, Williams 2001). In the development of calibration models, it is common that the chemical properties of soils used for validation are known. In this case soils with the same range of chemical properties are allocated to the same soils with the same properties in the calibration and validation sets (Martin et al. 2002). In practice, however, only spectral data and the location of a soil sample may be known, so principle component analysis of the spectral data will be required to select appropriate calibration data for the unknown sample.

Application of laboratory techniques -- Global spectral libraries

International researchers are collaborating to progress the development of a *global spectral library* to progress soil spectroscopy into a powerful diagnostic tool for soil monitoring, mapping and management (Viscarra Rossel 2009). For example, a diverse collection of over 1000 archived eastern and southern African topsoil samples was used to test a spectral library for rapid non-destructive estimation of soil properties based on analysis of diffuse reflectance spectroscopy (Shepherd & Walsh 2002). Soil properties were calibrated to soil reflectance data using multivariate adaptive regression splines. The validation r^2 values for regressions was 0.80 for organic carbon. Simultaneous determinations of exchangeable Ca (r^2= 0.88), exchangeable Mg (r^2=0.81), effective cation exchange capacity (r^2=0.88), clay content (r^2=0.80), sand content (r^2=0.76), and soil pH (r^2=0.70) were also achieved. The predictive value of the spectral libraries can be increased iteratively through detection of spectral outliers among new samples. Such an approach opens up new possibilities for modelling, assessment and management of risk in soil evaluations (Shepherd & Walsh 2002). The Soil Spectroscopy Group (more than 45 collaborators from 23 countries) has more recently used

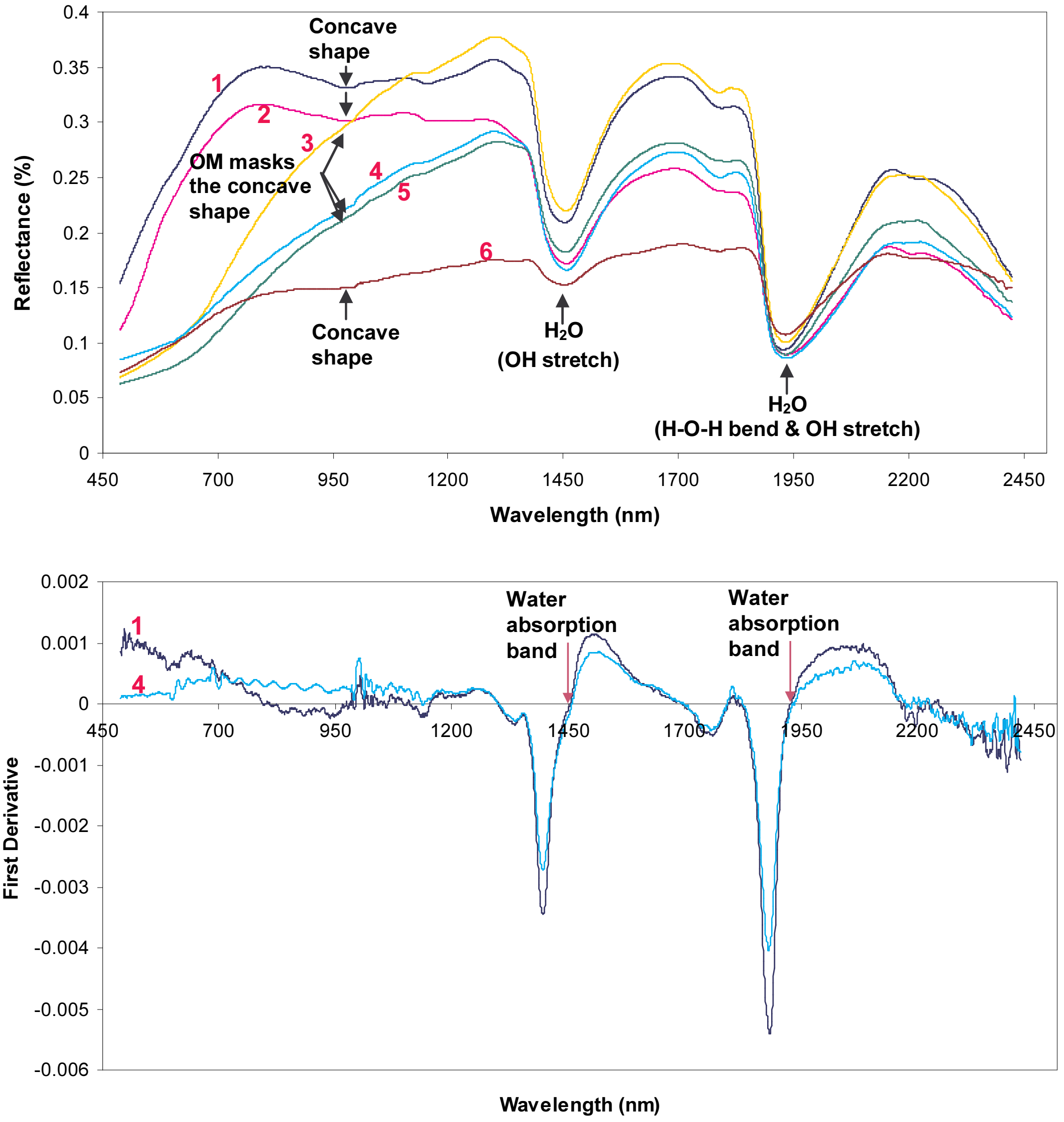

Fig.9 Reflectance spectra (upper) and first derivative (lower) from selected soil samples with different carbon concentrations and water contents, (1) carbon 0.26%, water 38%, (2) 1.41%, 68%, (3) 10.12%, 56%, (4) 11.21%, 78%, (5) 7.31%, 36%, (6) 0.82%, 11%. Taken from (Kusumo et al. 2008).

4,444 soil spectra, with chemometrics (partial least square regression and clustering) to predict soil organic carbon concentration (r^2=0.64) and clay content (r^2=0.70) in soils collected from each continent, including a set of spectra from New Zealand (Viscarra Rossel et al. 2008). Another example (Brown et al. 2006) examined the precision and accuracy of empirical Vis-NIR soil characterisation modelling when applied to a diverse, ‘global’ set of independent soil samples from five continents and a wide range of climatic regions (3,768 soil samples from Africa, Asia, the Americas, and Europe). Best predictions were for clay content, mineralogy (smectite, kaolinite), organic carbon, inorganic carbon, extractable iron, and cation exchange capacity. Brown et al. (2006) concluded that Vis-NIR DRS soil characterisation has the potential to replace or augment standard soil characterisation techniques where rapid and inexpensive analysis is required. Although Brown (2007) applied the global calibration to a watershed in Uganda and was able to predict clay mineralogy (smectite) remarkably well without including any local soil samples the analysis lacked sufficient accuracy for soil organic matter estimation.

These examples demonstrate the powerful use of chemometrics to analyse large data sets of soil spectra obtained from routine laboratory estimation of soil carbon by VIS-NIR DRS, for global soil carbon predictions.

4.1.3 Field techniques

The largest component in the uncertainty of estimating soil carbon stocks is the spatial variability of soil carbon within and across soil units (Wu et al. 2009). Acquisition of positional data with sufficient field measurements provides opportunity to assess and quantify spatial variability of soil properties. Pedometricians use geostatistics to interrogate large spatially located datasets acquired with GPS and remote and proximal sensing methods and have applied landscape models to develop soil attribute maps (McBratney et al. 2006). With the advent of robust and portable Vis-NIR DRS spectrometers, there is an emerging opportunity to develop rapid, high density, field determinations *in situ* of soil carbon that speed the process of mapping soil carbon stocks, (Wetterlind et al. 2008), and reduce the large numbers of soil samples that have to be analysed chemically analysed. Wetterlind et al. (2008) were able to predict soil carbon concentration at 150 positions with spectral reflectance, using a calibration set of only 25 samples in which carbon concentration had been measured by furnace technology. Field Vis-NIR DRS has the potential to directly measure soil carbon content *in situ*, for a known volume of soil. These techniques have the ability to include root carbon (Kusumo et al. 2009b), often removed in laboratory sieving and ignored

The various methods proposed for utilising field Vis-NIR DRS spectrometers to measure soil organic carbon *in situ* have a common set of high level protocols:

- Acquire a large number of spectral reflectance data samples from geo-referenced locations
- Collect soil samples from a smaller selection (calibration set) of the geo-referenced locations. It is preferable that the soil samples collected represent the soil surface from which the spectral reflectance was acquired. In addition, the soils selected for the calibration set should have spectral data that cover the range of spectral attributes observed in the larger population of samples
- Analyse the calibration set of soil samples to provide the reference set of soil measurements (in this case soil organic carbon)
- Use chemometric software to calibrate the spectral data to the reference data
- Predict the soil organic content at the remaining geo-referenced locations using their spectral data and the calibration model.

Soil sampling, preparation and acquisition of spectra

Direct estimation of soil carbon at field sites reduces or eliminates soil preparation. On-the-go mapping systems employing shanks (Mouazen et al. 2005) pulled through the soil (Fig. 10) prepare a smooth flat shear-surface for spectral acquisition automatically. The Veris probe (Fig. 11, Lund et al. 2008) creates a smooth vertical shear surface for this purpose and therefore also eliminates the need for soil preparation. As the smooth shear-surface is created, spectra are acquired through sapphire windows in the shank or soil probe. The field method of Kusumo et al. (2009a) uses a soil coring technique. Spectra are collected from the intact circumference, or a cross-sectioned surface of the soil core. To develop robust calibrations, a subset of the scanned soil samples is required for reference measurement by laboratory analysis.

The methodologies employed to acquire spectra by the various field techniques are sufficiently different that they will be discussed separately. Most field spectrometers are single beam and therefore require calibration with a white spectral reflectance standard before sample spectra can be acquired. The spectral data processing and calibration, however, are the same as those described for laboratory techniques as described above.

Reconnaissance soil carbon mapping using shank technology

Development of shank-type VIS-NIR tools shows promise for reconnaissance soil carbon mapping (Lund et al. 2008, Mouazen et al. 2005, 2007, Sudduth et al. 2008). Mouazen et al. developed a system attached to a subsoiler, mounted to a 3-point tractor hitch (Fig. 10). Fibre optic cables connect a light source (mounted in a protective case attached to the base of the subsoiler) to a GaAs diode-array for measurement in the NIR region (944.5-1710.0 nm), and a Si array for the visible and short wave infra red region (306.5-1135.5 nm). As the tractor moves, light from the light source is reflected from the soil, along the cable to the detectors.

Fig. 10 Subsoiler-optical unit for on-line Vis-NIR DRS field measurement (Mouazen et al. 2005).

Soil water content, soil carbon, pH and phosphorus were estimated simultaneously (Mouazen et al. 2007), demonstrating the success of the on-line shank method for reconnaissance-style soil mapping. The system has also been used with a single beam load cell and transducer to estimate bulk density and draught (Mouazen et al. 2005). Draught, or soil mechanical resistance, is a measure of soil compaction.

Lund et al. (2008) have led research and development internationally in developing a field shank (Fig. 11, left) and probe (Fig. 11, right) based Vis-NIR DRS tools for field estimation of soil carbon, and the equipment is available commercially (Veris Technologies). The shank module, of similar concept to that of Mouazen et al. (2005) and Shonk et al. (1991) can be pulled through the soil, and when accurate RTK-DGPS positional data are collected simultaneously, these data can be used for soil carbon mapping at the paddock scale. A survey of multiple fields in four USA states using the Veris Vis-NIR DRS shank module showed that results correlated well with independent measurements of soil carbon in three of the four states, with RPD (standard deviation/root mean square error) scores of 2 or better (Table 10).

When maps are generated from the calibration estimations and lab samples overlaid, the spatial structure of measurements of carbon at paddock scales and the correlation between the Vis-NIR DRS system and laboratory analysed samples are encouraging (Fig. 12, Lund et al. 2008).

Fig. 11 Vis-NIR DRS shank module (left) and the Vis-NIR DRS probe module (right) (Lund et al. 2008).

Table 10 Results of VIS-NIR shank module carbon calibrations from 24 fields in 4 states (Lund et al. 2008).

Site	RPD	R2	RMSE (% carbon)	Std Dev (% carbon)
6 Maryland fields	1.26	0.43	0.190	0.240
6 Illinois fields	3.26	0.90	0.230	0.750
6 Iowa fields	2.06	0.74	0.520	1.070
6 Kansas fields	2.00	0.76	0.136	0.272

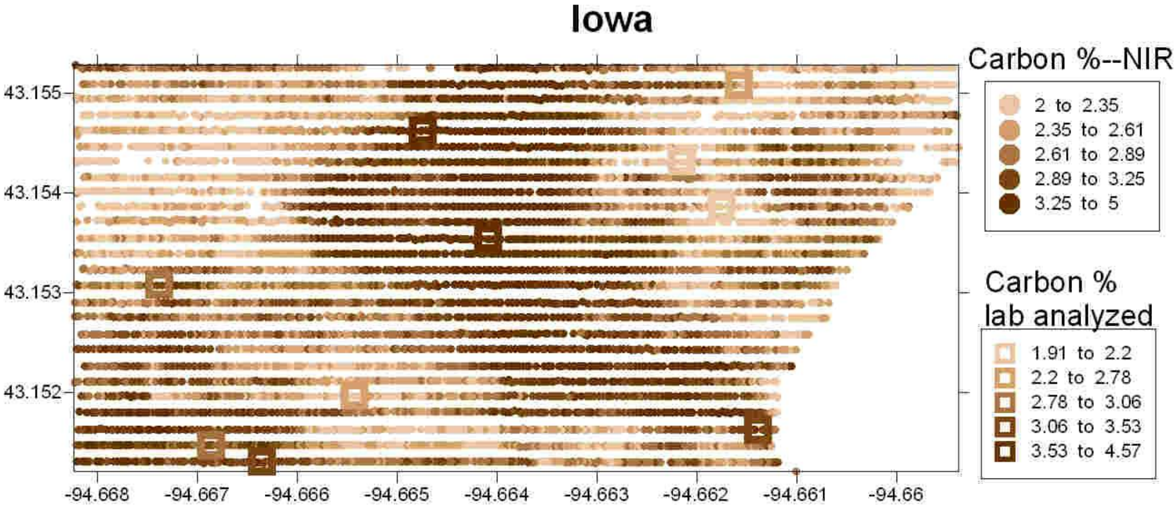

Fig. 12 Carbon estimation from VIS-NIR shank module with lab samples overlaid.

Accurate field estimation of volumetric soil carbon to a fixed depth

A limitation of the single shank technology is the fixed soil depth it is designed to view. The shank is not designed to quantitatively assess volumetric soil carbon content to a fixed depth. Probing (Lund et al. 2008) and coring techniques (Kusumo et al. 2008) are more suited for this purpose. The VIS-NIR probe (Fig. 11, right) was developed to specifically sample a column to a fixed depth (e.g. 0.3 m) for soil carbon accounting purposes. Results from an initial trial by Lund et al. (2008) are shown in Table 11. The probe module consisted of an array of Vis-NIR, electrical conductivity and force sensors and it collects Vis-NIR measurements to a depth of 1 m via a sapphire window pressed directly against the soils, at a rate of 20 spectra per second with a resolution of 8 nm. The data show that measurements using an array of sensors may allow simultaneous estimation of bulk density, a necessary requirement for any assessment of changes in soil carbon (Table 11).

Table 11 Results from the sensor probe on six Kansas field sites (Lund et al. 2008).

		% carbon				Bulk density (g/cm^3)			
Site	n	RPD	R²	RMSE	Std Dev	RPD	R²	RMSE	Std Dev
Drummond	42	1.81	0.69	0.22	0.40	1.11	0.21	0.12	0.14
Kejr	51	3.06	0.89	0.17	0.51	1.28	0.40	0.13	0.17
Lund_CT	33	2.89	0.88	0.08	0.22	2.09	0.76	0.07	0.14
Lund_NT	38	2.09	0.77	0.20	0.42	2.16	0.78	0.08	0.18
Markley	45	2.52	0.84	0.14	0.35	1.95	0.73	0.10	0.19
Tarn	52	1.97	0.74	0.16	0.31	1.59	0.61	0.11	0.17

A manual coring technique employing a back-pack Vis-NIR DRS method has been developed by Kusumo et al. (2008, 2009a, 2009b) (Fig. 13). Spectra are collected in the field, from a stationary surface of an intact soil core, for estimation of soil carbon, soil nitrogen and root density. Increasing the spectrometer's field of view by acquiring spectra from the curved vertical wall of the soil core instead of the flat surface, (with soil samples taken from the same section for reference analysis in the laboratory) markedly improved the prediction accuracy (carbon prediction r^2=0.97, RMSECV = 0.21%, RPD = 5.80, nitrogen prediction r^2 = 0.96, RMSECV = 0.02%, RPD = 5.17).

A set of results obtained from 18 cores evenly distributed over 1 ha of permanent pasture on a recent orthic gley soil (Kairanga fine sandy loam) show the high level of accuracy that is obtainable in predicting soil organic carbon and nitrogen to a depth of 0.3 m (Fig. 14).

4.1.4 Use of geostatistics to improve soil carbon estimations

The high spatial variability in soil carbon is challenging. At what scale should the landscape, or the soil series, or the paddock, be sampled for carbon accounting? What representative sites should be chosen and at what scale should samples be taken to define the appropriate units (Conant & Paustian 2002, Hedley et al. 2009)? Once a unit is defined, a further question is are the statistics describing the mean and variance of the amount of carbon in that unit able to be extrapolated to other apparently similar units?

Fig.13 Backpack Vis-NIR DRS apparatus for field collection of soil spectra. The backpack contains three spectrophotometers which receive hyperspectral reflective energy via a fibre optic cable from the soil surface. Note the prototype soil probe developed to collect soil spectra (being held by B. Kusumo), and the soil corer used to extract soil cores.

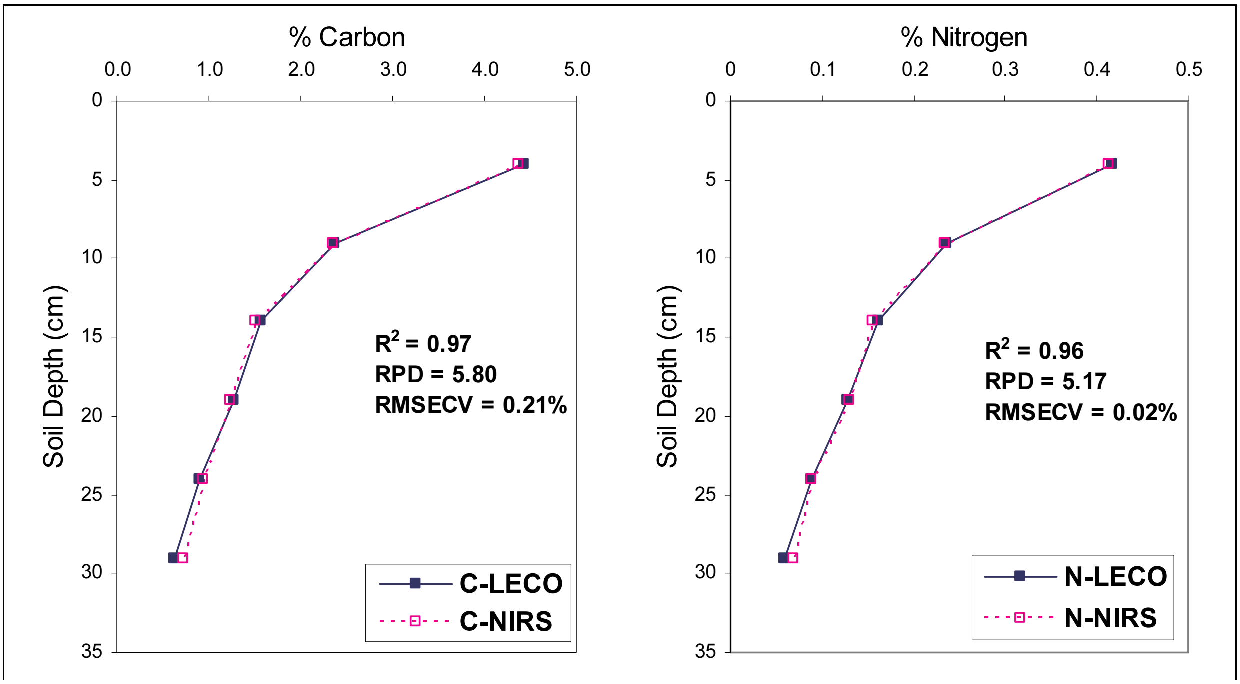

Fig. 14 The average laboratory measured (LECO) total C and N concentrations at different soil depths and those predicted from soil spectral reflectance (NIRS) under permanent pasture on Kairanga fine sandy loam. Values are predicted using leave-one-out cross-validation procedure (Kusumo et al. 2010).

At the regional and farm scale, digital information on topography (digital elevation maps), climate, vegetation cover, land use and time since land use change can be used in association with geographic information system (GIS) software to assist in defining the appropriate sites for sampling and measurement. At the soil unit and land use scale (paddock scale) some thought needs to be given to the soil sampling density that will be evaluated for the purpose of capturing the true mean and variance of carbon within the functional unit of soil type/land use/land use change.

In this section the use of geostatistics to improve the sampling procedures for measuring soil carbon, and the use of remote or proximally sensed ancillary data to reduce the numbers of soil samples to identify similar (repeating) units in the landscape are considered.

Introduction to geostastistics

Soil sampling and analysis has focussed traditionally on predicting a mean value with an associated error term (e.g. standard deviation, coefficient of variation). The mean value is then used to represent a designated soil area. In this approach, the spatial relationship of point values is ignored. Geostatistics accepts the existence of spatial autocorrelation, in contrast to classical statistics which assumes that point data are independent and spatially uncorrelated (Webster & Oliver 2007).

Investigation of issues of autocorrelation started in the 1980s with the advent and accessibility of powerful statistical and GIS software, together with GPS systems and proximal sensing methods, such as EM mapping.

The spatial structure of point data is explored using a variogram which expresses the way in which the variance of a property changes as the distance and direction separating any two points varies (Oliver & Webster 1991), (Fig. 14), described mathematically as

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left[A_i(x_i) - A_i(x_i + h)^2\right] \tag{10}$$

where $\gamma(h)$ is the semivariance between a pair of points N, A_i is the value of a given property at location x_i and h is the lag distance (Oliver & Webster 2007).

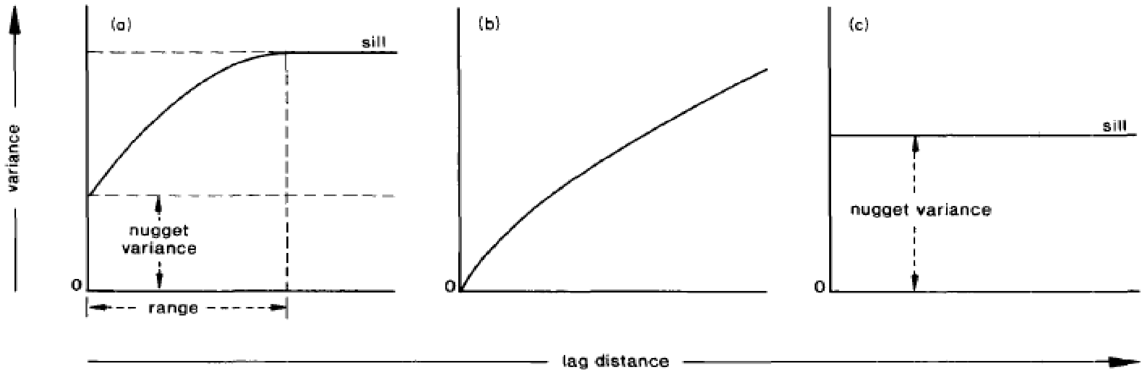

Fig. 15 Three theoretical functions for spatial correlation: (a) bounded variogram, (b) unbounded variogram, and (c) pure nugget variogram (Oliver & Webster 1991).

The importance of correct selection of the variogram model is vital before the next step when the variogram model parameters are used to interpolate a prediction surface (i.e. map), a process known as kriging. Fig. 15 shows three variogram models. In most cases variance will increase with increasing lag distance, as shown in Figs 15a and b. These variograms are interpreted as showing strong correlation or spatial dependence (low variance) at the shortest distances, which weakens as the separation increases. This intuitively expresses what we should expect: places near each other are more similar than places further apart. The variogram increases and then flattens when it reaches a maximum variance known as the sill variance and it is described as bounded (Fig. 15a). The lag distance at which the sill is reached is the range, which marks the limit of spatial dependence. Alternatively the variogram might increase indefinitely as in Fig. 15b, which is termed unbounded. Frequently the variogram has a positive intercept on the ordinate, the nugget, which corresponds to random variation at a point and method error. A completely flat variogram, termed pure nugget (Fig. 15c) shows that there is no spatial dependence in the data, the classical solution, but frequently not observed in practice. A pure nugget variogram from survey data suggests that the scale of variability has not been captured and defined by the sampling strategy, because soil scientists know that soil is a continuum where there is spatial dependence at some scale (Webster & Oliver 2007, McBratney & Webster 1986).

A minimum of 100 sampling positions is required to obtain a stable variogram (Kerry and Oliver 2008) and so this type of analysis is particularly well suited to large regional and national soil carbon datasets (e.g. New Zealand: McNeill et al. 2009, UK: Frogbrook et al. 2009, Australia: Minasny et al. 2006) to define the spatial structure and improve predicted soil carbon map layers.

Once the variogram is obtained, the model parameters are used to krige the prediction surface. For any cell size the variance is calculated based on the average variance of all the point pairs within the cell. As cell size increases the number of point pairs increases and a second variogram is estimated. Once this variogram is estimated a smaller cell size can be used to create the actual output grid. The kriging equation predicts a value at a specific location from the weighted sum of variances of all other values. The development of spatial soil statistics was heralded as a breakthrough for soil science in the 1980s (Webster 1985), and the development of sophisticated GIS software since then has enabled great advances in the quantification of soil spatial variability and spatial interpolation of soil properties, such as soil carbon. The kriging process predicts a map of mean values and standard deviations.
If less than 100 sample points are available, ancillary data such as satellite imagery or on-the-go proximal sensing data can be used to (i) co-krige with the sparse soil carbon data or (ii) explore and define spatial structure of the area for targeted soil sampling. Without some knowledge of spatial scale there is no certainty that the sampling interval selected will provide data to fully include spatial variability. As a rule of thumb, the sampling interval should be less than one half the range of spatial variation (Kerry & Oliver 2008). This provides a method to ensure that the spatial soil variability at that site is sampled adequately.

Using geostatistics and ancillary data to improve soil carbon estimations

Frequently the cost of sampling and analysis prohibits the number of soil samples taken for soil carbon analysis to less than 100. In this case, variogram analysis is inadvisable and the possibility of co-kriging a related, more easily acquired, soil property should be investigated. The development of field deployed ‘on-the-go’ proximal sensing systems and scanners has led to great advances during the last decade to provide a range of sensors for rapid sensing and logging of soil properties (Viscarra Rossel & McBratney 1998, Adamchuk et al. 2004). One such sensor is the electromagnetic sensor which measures the apparent electrical conductivity of a volume of soil over which it passes. The electrical conductivity of a soil is largely determined by soil texture and water content in non-saline soils (Hedley et al. 2004, Sudduth et al. 2005) and thousands of spatially defined data points can be acquired within a few hours.

The Geonics EM38 is the most commonly used electromagnetic sensor (Fig. 16). The more recent EM38-DD records soil electrical conductivity to two depths (0.75 and 1.5 m) simultaneously. The high sampling frequency greatly enhances the ability of the sensor data to estimate soil texture and water content, and because these two soil properties are often related to soil carbon, provides a potential opportunity to improve estimates of soil carbon concentration from sparse soil carbon data using co-kriging or some other form of geostatistics. Very little research is reported in the literature investigating the potential of this concept. Martinez et al. (2009) used a normalised electrical conductivity difference from the two values acquired with an EM38-DD system to improve soil carbon predictions and concluded that this was useful for spatial estimation of soil organic carbon. However co-kriging of soil carbon and soil electrical conductivity was unsuccessful because there was little to no relationship between them at the study site. This is attributed to (i) differences in soil volume explored by the EM38-DD and manual augering, (ii) small range in soil organic matter concentration, (iii) weight based soil organic carbon observations against volumetric electrical conductivity measurements, and (iv) bulk influence of other soil properties on

Fig. 16 On-the-go EM mapping system, employing a Geonics EM38, RTK-GPS, datalogger, on-board field computer and ATV

electrical conductivity. However, electrical conductivity was a good predictor of soil organic carbon between direct drill and conventional plots, so that electrical conductivity was used as secondary information during simple kriging with varying local means, to improve predictions of soil organic carbon, and the root mean square error was reduced by 8%.

Other researchers have used other forms of ancillary data more that are more easily acquired to improve predictions of soil carbon concentration, such as DEMs or satellite imagery co-kriged with soil organic matter data (Wu et al. 2009). Broge et al. (2004) used spectral reflectance and electrical conductivity measurements to predict topsoil organic matter and found that electrical conductivity did not improve predictions of soil carbon. However they used point data with no geostatistical analysis.

Gomez et al. (2008) compared remote and proximal Vis-NIR hyperspectral sensing data for predicting soil organic carbon and found that the proximal sensing data (n=146) were more accurate than Hyperion spectra of a similar resolution (30 m), which they attribute to greater spectral noise in the remote data.

Soil electrical conductivity data are now used routinely in several countries (North America, Australia, Europe) to quantify soil variability, develop zones for targeted soil sampling (Lund et al. 2008) and to improve and define soil mapping units (Anderson-Cook et al. 2002, James et al. 2003).

4.1.5 Applicability of the Vis-NIR DRS techniques for estimating soil carbon

Alternative laboratory methodology

Laboratory analysis of soil carbon for samples using Vis-NIR DRS is ready for use as a lower cost companion to furnace-technology soil carbon analysers. Providing the analyst (a) establishes reproducible sample preparation procedures that present consistently uniform soil reflectance surfaces to the scanning spectrometer and (b) operates chemometric software that is capable of (i) allocating the sample spectral data to the most appropriate calibration library and (ii) identifying spectral outliers that require analysis by furnace technologies. Such systems are already working well with a measurement accuracy very similar to the furnace technologies that were used to derive the reference data (R Hill personal communication).

Field reconnaissance mapping with portable Vis-NIR DRS spectrometers

Rapid surveys of surface soils using either manual coring or shank techniques can provide a reconnaissance map of soil organic carbon and other soil properties) Such maps (Fig. 12) can be used to zone soils for more detailed sampling with increased depth. Zoning will reduce the numbers of deep cores that need to be taken and analysed for soil carbon. Lund et al. (2008) has already shown that soil zones with a range of soil carbon concentrations from 2% to 4.6% can be measured to an average accuracy (root mean square error) of 0.2%. Kusumo et al. (2010) employing a manual coring technique with a back pack spectrometer were able to measure soil organic carbon concentrations from 0.27% to 5.2% with an accuracy (root mean square error) of 0.21%. This degree of accuracy is appropriate for reconnaissance mapping.

It is likely that further developments in the chemometric analysis of field acquired spectra will lead to improvements in measurement accuracy. In particular, adopting on-the-go calibration with a choice of separate spectral calibration libraries for samples of high and low carbon concentrations and different mineralogy. In addition, incorporation of ancillary soil measurements (such as digital elevation mapping and electromagnetic data) into the geostatistical analysis of the spectral data will assist in the delineation of soil units.

Accuracy in field estimation of volumetric soil carbon to a fixed depth

The soil probing technique (Fig.11) and the manual soil coring technique (Figs. 14 and 15) are developments that are most likely to provide on-the-go techniques for estimation of soil carbon in a fixed soil depth or volume. The small number of surveys that have been completed with the probe indicate that it currently operates with the same level of accuracy as the shank. In six field studies (Table 11), where the average soil organic carbon concentration to depth ranged from 2% to 3.7%, the accuracy of measurement ranges from 0.08% to 0.22%. The coring technique used by Kusumo et al. (2010) currently has a similar level of accuracy when the root mean square error is calculated for the full calibration range of 0.2% to 5.2%. As discussed above there are several of ways in which calibration and prediction of carbon concentration could be achieved with greater accuracy.

Vis-NIR DRS techniques have an advantage in that they allow direct assessment of the volumetric quantity of soil carbon and directly accommodate its spatial variation. The disadvantage may be that the spectral attributes of the soil change with time, influencing the predictive ability of calibration sets for soil carbon at another time. Other soil chromophores such as water content, redox state of metal oxides and root distribution may change seasonally. Recent research by Kusumo et al. (2009a) has shown that, in a Recent Orthic Gley Soil, core samples taken in May and November with different mean volumetric water contents of 0.20 and 0.30 m^3/m^3 gave virtually identical calibration results (Fig. 17). Calibration models, using partial least squares regression produced in either month were equally accurate in predicting the reference soil carbon and nitrogen concentrations. Similar studies would need to be carried out on a wide range of soils to establish whether seasonal changes influence the temporal robustness of spectral calibrations.

4.1.6 Estimated cost for sample analysis

Costs of sampling and analysis for soil organic carbon including a comparison of a field sampling campaign followed (i) by organic carbon determination by dry combustion and (ii) by combination of dry combustion and Vis-NIR field reflectance spectroscopy (Table 12). The cost model is based on the current sampling protocol that is recommended by the New Zealand Soil Carbon Monitoring System (NZSCMS) for field sampling campaigns (Davis et al. 2004). The NZSCMS is compliant with the sampling strategies recommended by IPCC (http://www.ipcc-nggip.iges.or.jp/public/gpglulucf/gpglulucf_ files/Chp4/Chp4_ 3_ Projects.pdf) and consistent with similar land use unit sampling procedures described by Goidts et al. (2009). Cost comparisons of soil carbon determination for national monitoring schemes often consider only the comparative cost of laboratory soil organic carbon methods. When the field sampling campaign is considered the analytical cost may be less than 40% of the total cost. For this reason, and for the reason that the nature of the field campaign will change slightly if Vis-NIR field reflectance spectroscopy is used, we have considered a cost model that covers all aspects of the field sampling campaign. The costings in Table 11 are based on a field campaign, using coring techniques in stone free soils, at 20 sites that represent cells in the NZSCMS. Estimates represent a 7 day field campaign that involves two field staff either working remotely from their home based or working within a 90 minutes' car journey from their home base.

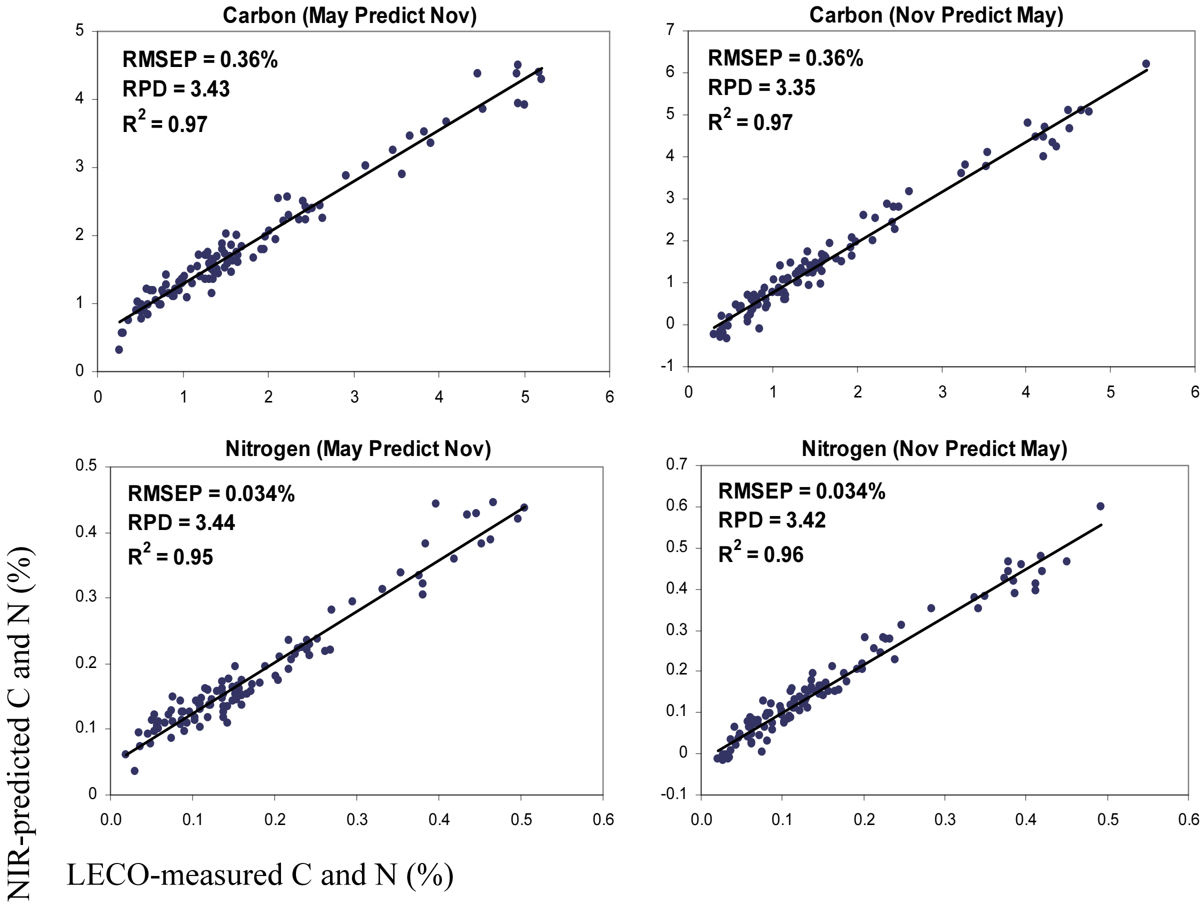

Fig. 17 The May calibration model based on partial least squares regression is shown predicting soil carbon and nitrogen concentrations from spectra acquired in November (and vice versa).

These costs assume that at each of the 20 sites, eight cores are taken in each of four quadrants of a square centred around a soil profile. The cores are sectioned into three depths and each depth is bulked for a quadrant (20 × 4 × 3 = 240 samples) and sent for determination of soil organic carbon by dry combustion in the laboratory (dry combustion) and bulk density. Alternatively only 30% of the samples are sent for soil organic carbon determination by dry combustion but the reflectance spectra of all samples are acquired in the field (using the manual coring method described by Kusumo et al. (2008). Partial least square regression analysis is used to develop a calibration model from the 30% of samples that have both spectral and soil organic data (the calibration set). The calibration model is used to predict the soil organic carbon concentrations for the remaining 70% of samples (dry combustion plus field Vis-NIR). The costs include reporting the current soil organic carbon stocks to 0.3 m depth at each site. The costs do not include site establishment or verification costs or the cost of preparing a detailed report.

The calculations illustrate that for a field campaign as specified there is a potential cost reduction of between 13% and 14% (depending upon field accommodation, food and fuel costs) if field reflectance spectroscopy can be used to predict soil organic carbon for 70% of the samples. This margin increases as sample number increases because the calibration set can become a smaller percentage of the total sample number reducing further the proportion of laboratory costs. Current research which aims to develop more automated methods of acquiring reflectance spectra in the field would also reduce field labour costs.

Table 12 A comparison of costs for a field sampling campaign (with and without motel accommodation and airfares) followed by soil organic carbon determination by (i) dry combustion or (ii) by combination of dry combustion and field reflectance spectroscopy.

Item	Field campaign away from home base involving airfare and motel accommodation Estimated cost $		Field campaign within 90 minutes from home base Estimated cost $	
	Dry combustion	Dry Combustion plus field Vis-NIR	Dry combustion	Dry Combustion plus Vis-NIR
Total Personnel Cost	7,265	8,309	7,265	8,309
Analytical costs	11,766	5,149	11,766	5,149
Office	550	550	550	550
Travel, food, fuel, accommodation	7,100	7,100	2,000	2,000
Overheads	8,500	9,722	8,500	9,722
Total	35,180	30,829	30,080	25,729
Cost per site	1,759	1,541	1,504	1,286
Cost per sample	147	128	125	107
Cost per core	440	385	376	322

4.1.7 Advantages and disadvantages

In summary, the main advantages of Vis-NIR DRS spectroscopy for estimating soil carbon concentrations is the method can reduce markedly the number of samples that need to be analysed by standard methodology and that the method allows *in sit*, non-disruptive measurements on field-moist soils (Table 13). These lead to opportunities such as reconnaissance mapping and direct volumetric determination of soil organic carbon in the field.

Table 13 Advantages and disadvantages of determining soil organic carbon by Vis-NIR DRS spectroscopy compared to conventional methodologies using core samples.

Advantages	Disadvantages
Can be applied as a laboratory or field method	Instrumentation is as expensive as furnace technology
More rapid, timely, cheaper, and hence more efficient at obtaining data when a large number of samples and analyses are required, than conventional laboratory soil carbon analytical methods. This is mostly because the method involves little to no sample preparation, does not use chemicals, so no chemical wastes	Sophisticated spectral processing and statistical software are required to interpret the complex spectra and develop calibration factors
A single spectrum can be used to assess multiple physical, chemical and biological properties (e.g. possibility exists to analyse for total organic carbon, mineralisable nitrogen and root density, simultaneously)	Vis-NIR is not a stand-alone technology. Furnace technology has to retained for calibration
Reconnaissance 'on-the-go shank' method acquires sufficient spatially located soil organic carbon values rapidly to interpolate across a landscape and produces real-time data	Calibrations need to be updated constantly, to include 'outlying' samples until the calibration is acceptable. Calibrations need to be validated, either by leave-one-out cross validation or by using a subset of the data
Accurate field analysis is possible by collected static spectra from an intact core surface, or probe, for direct volumetric determination of soil organic carbon in the field	
Potential and international effort to develop local and global calibrations for real-time soil carbon spectral analysis (field and lab)	
Potential to use spectral processing to identify different organic fractions and pools in the soil, to assist soil carbon modelling. An added advantage is that the low energy wavelengths make it a non-destructive method	

5. Developing technologies

5.1 Laser-induced breakdown spectroscopy (LIBS)

LIBS followed the development of the laser in the 1960s as a method that utilises the atomic emission spectra generated when a pulsed laser is focussed at a specific site (a few millimetres in size) without any sample preparation. The approach can be used on solids, liquids and gases. The development of LIBS prior to 1995 was mostly conducted for the US military (Harmon et al. 2005) and space exploration purposes (NASA), but the method was not available for commercial and research applications. Since about 1995, research development of LIBS has focussed on its capability of analysing materials outside analytical laboratories. There has been particular interest in its use for quality and safety assessment of industrial materials. During this period there have been significant technological advances facilitating the development of compact and rugged instruments for applications outside the laboratory (Harmon et al. 2005). Currently there are over 65 LIBS-related patents world-wide (Cremers & Radziemski, 2006), for a wide range of applications.

The evaluation of LIBS for soil diagnostics (Bublitz et al. 2001) and more recently for total soil carbon measurement (Ebinger et al. 2003) has been technically challenging and will be discussed in more detail below.

5.1.1 Theory

A pulsed laser beam is directed at a sample to create high temperature microplasma (Fig. 18). A short-pulsed solid-state laser is focused optically to heat the surface of a target sample material rapidly to the point of volatilisation and material ablation, which results in the generation of high temperature plasma on the surface of the sample (Fig. 19). Upon cooling, the excited atomic, ionic, and molecular fragments produced within the plasma emit radiation that is characteristic of the elemental composition of the volatilized material. Fibre optic technology, offering the potential for instrument portability, can be used to collect the light signal and deliver it to a spectrometer that is capable of resolving part or all of the 200 to 980 nm spectral region (Fig. 20). All elements emit within this region, so that both the detection of elemental, ionic and molecular species on the basis of spectral line presence and the quantitative analysis based on differences in spectral line intensity can be achieved (Harmon et al. 2005).

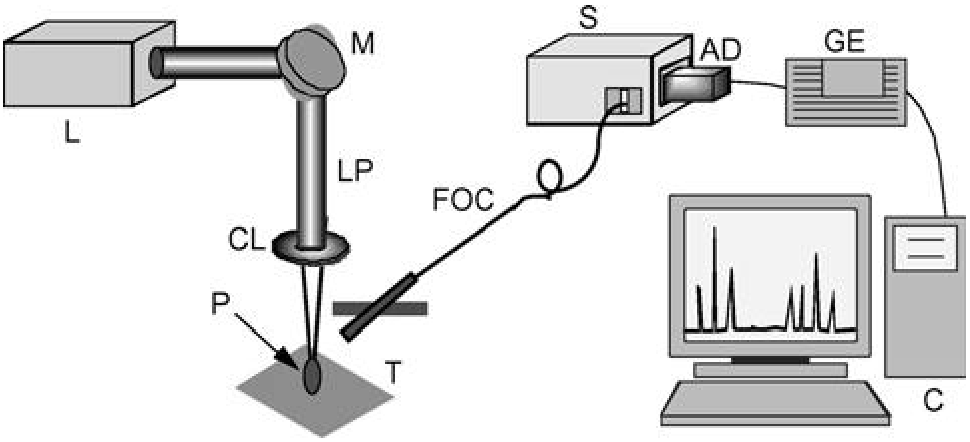

Fig. 18 Diagram of a typical laboratory LIBS apparatus. L = short-pulsed Q-switched solid-state laser, M = mirror, LP = laser pulse, CL = lens, P = plasma, T = target, FOC = fibre optic cable, S = spectrograph, AD = array detector, GE = gating electronics, C = computer (Cremers and Radziemski, 2006).

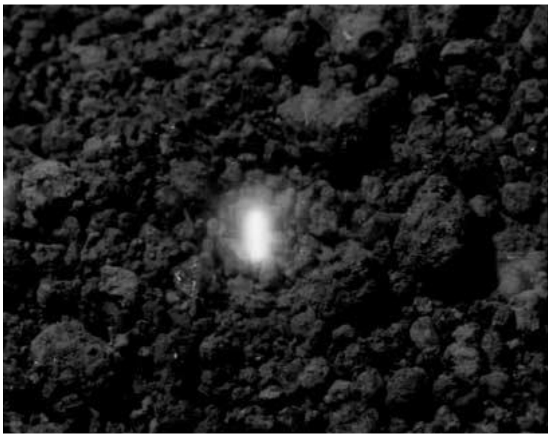

Fig. 19 Laser plasma (4-5 mm in height) formed on soil by a spherical lens (Cremers & Radziemski 2006).

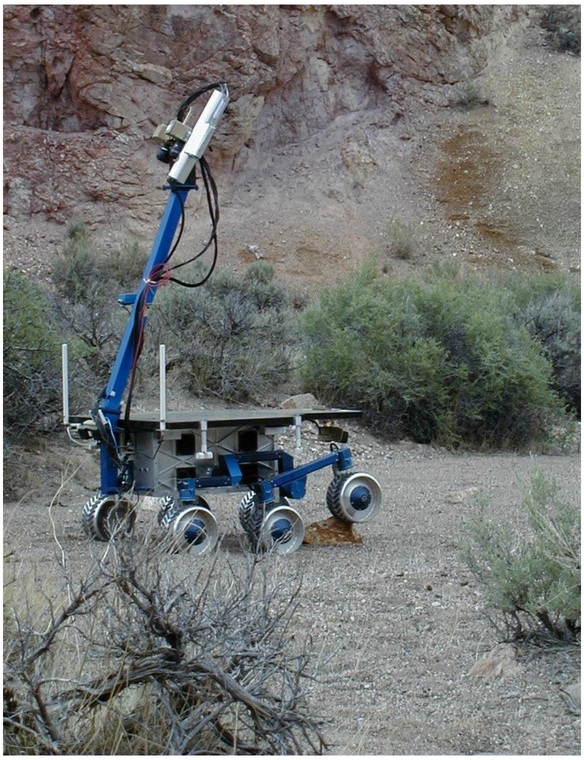

Fig. 20 NASA AMES K-9 rover fitted with prototype LIBS instrument, with the laser and telescope on the mast and spectrograph, detector and electronics in the body (Image from NASA Ames Research Centre).

5.1.2 Current progress and future development

NASA continues to develop LIBS for space exploration, which is beyond the scope of this review. However, recently there has been more affordable development of LIBS for industrial (Miziolek et al. 2006) and research purposes which provides a potentially new instrument for field soil analysis (Gehl & Rice 2007, Johnston et al. 2004). Its advantages are simultaneous multi-component analysis without any sample preparation. Disadvantages include a very small area of exploration (sample volume is about 1 to 5 mm^3 per pulse), so that spatial variability of carbon in soil profiles has to be accounted for by a very large number of multiple spot analyses (Bublitz et al. 2001). LIBS is an appropriate technology for remote elemental analysis, and is particularly appropriate for detection of heavy metals such as Cd, Cu, Cr, Ni, Pb and Zn (Wisbrun et al. 1994), although there is now some interest in its possible ability to assess soil carbon concentration. The complexity of the heterogeneous soil medium (e.g. texture, water content) has complicated analysis of LIBS plasma for elemental detection in soils (Bublitz et al. 2001, Chatterjee et al. 2009). Varying soil water content influences spectral line intensity during plasma relaxation, and this effect on quantitative LIBS analysis (Bublitz et al. 2001) requires further research. Soil carbon concentration is determined by analysing the unique spectral carbon signature at 247.8 or 193 nm or both.

Ebinger et al. (2003) extended LIBS to measure total soil carbon in laboratory samples, with the advantage of being able to acquire data in seconds from soils with little preparation. Iron (Fe) interference with the soil carbon line at 248 nm was discovered, but this can be resolved used the 193 nm line. In this study, calibration of carbon measurements by LIBS against measurements from dry combustion for three Colorado soils indicated that the results of the two methods were highly correlated ($r^2 = 0.99$) and repeated calibration curves indicated that use of the LIBS method gave reproducible results.

Bricklemyer et al. (2008) explain that LIBS is unable to distinguish between organic and inorganic carbon and also discuss the limitations of the very small sample size. These authors compared Vis-NIR with LIBS on 81 intact soil cores and found that Vis-NIR was a better predictor of soil organic carbon concentration. They also tried combining the Vis-NIR and LIBS data to improve predictions which slightly improved the prediction of total carbon but did not improve predictions of inorganic carbon or total organic carbon compared to results using individual sensors. They concluded that additional research is required, specifically sensor interaction, LIBS data reduction, and improved statistical and data mining algorithms before possible integration of these sensors for soil mapping.

5.1.3 Sampling requirements and protocols

Soils can be sampled *in situ* by the laser pulse, so that little to no sample preparation is required. Alternatively the method can be used in the laboratory on prepared soil, e.g. soil sieved to < 2 mm (Ebinger et al. 2006), pressed soils (Chatterjee et al. 2009) or soil cores (Bricklemyer et al. 2009). Ebinger et al. (2006) describe a method where a laser beam, at a specific wavelength, with a lens of 50 mm focal length is focused on each sample to form microplasma that emits light that is characteristic of the sample's elemental composition. The emitted light is spectrally resolved using a grated-intensified photo-diode array detector.
So far there is no reported research on the effects of fine roots and other biological material at varying degrees of decomposition on soil carbon analysis by LIBS. Also, the effects of carbonates and soil water content on spectral line intensity require further evaluation (Gehl & Rice 2007).

LIBS analysis is rapid, and Bricklemyer et al. (2008) report analysis times of approximately 5 seconds to obtain 5 spectra with 10 laser shots per spectrum. Numerous calibrations are required to account for varying soil properties (e.g. texture, carbonate, water content), although Chatterjee et al. (2009) comment that this is impractical for a field deployed instrument. Multivariate statistical analysis helps control the variability in carbon concentrations due to influence of the soil's matrix. Reproducibility of LIBS analyses can be improved by (i) increasing the number of shots and averaging the spectra over more shots, (ii) applying the method of intensity ratios of carbon with Si and Al (Ebinger et al. 2003), and (iii) using MVA techniques (Chatterjee et al. 2009).

5.1.4 Applicability of the approach

LIBS has been developed for multi elemental analysis of materials, and is best suited to analysis of species with higher atomic weights than that for carbon (=12). Significantly more research and development is required before its suitability for soil carbon analysis can be assessed fully. The method is being developed to account for soil matrix effects on the carbon line intensity, for example by adopting multivariate statistical analysis. The inability of the very small sample size to assess spatial variability is a disadvantage. Despite these drawbacks, portable instruments are becoming available commercially and methods will no doubt continue to be investigated and refined for field soil carbon analysis, due to the need to develop improved portable rapid methods for soil carbon analysis for accounting purposes.

5.1.5 Advantages and disadvantages

Commercialisation of a portable LIBS system provides opportunity for further research and development of this technique for soil carbon analysis (Table 14). The approximate cost of a unit that can detect soil carbon with high detection limits as well as collect other spectral features for multivariate analysis is $200,000. Future research is needed to reduce the variability of the LIBS signal caused by the presence of rock fragments, roots, and other materials.

Table 14 Advantages and disadvantages of measuring soil carbon using LIBS.

Advantages	Disadvantages
Fast analysis time (< 1 minute), portable	Instrument development is focused on remote elemental analysis for space exploration, industrial monitoring, and military applications.
Excellent instrument detection limit and precision	Very small sample size (1-5 mm^3)
Capable of remote surface chemical analysis	Utility for soil carbon analysis is still to be fully demonstrated

5.2 Inelastic neutron scattering (INS) and related nucleonic methods

5.2.1 Current progress and future developments

An inelastic neutron scattering (INS) device can measure soil carbon by bombarding soil with high energy neutrons. Neutrons with a high energy are required in order to generate 4.43 MeV (million electron volts) gamma rays from collisions with carbon atoms. In principle, the quantity of 4.43 MeV gamma rays recorded by a detector should be proportional to the number of carbon atoms in a sample. An advantage of the technique is that both neutrons and gamma rays are extremely effective at penetrating matter, since they are particles with neutral charge and the highest energy photons, respectively.

Over the last ~9 years, a group at Brookhaven National Laboratory in the United States has been developing a device that uses INS to attempt practical measurement of soil carbon. This group has published results from a device that has undergone laboratory and field testing. The current version of the Brookhaven INS device has been described as an 'alpha' prototype, and a 'beta' prototype has been proposed. The performance of INS for carbon measurement can also be inferred from studies of other carbon bearing materials, such as coal, petroleum-bearing rocks, cargo and contraband.

5.2.2 Theory

The collision of high energy neutrons (also termed 'fast' neutrons) with atoms such as carbon is termed inelastic neutron scattering (INS) when a nuclear reaction occurs, but the neutron still rebounds. When a nuclear reaction occurs, a gamma ray may be emitted immediately ('prompt' gamma emission), or radioactive decay may occur after some time. In contrast, elastic scattering is the more common result of the collisions of neutrons with atomic nuclei, and implies no energy loss due to reactions. That is, in elastic neutron scattering, the neutron and atom rebound off one another with no energy loss – essentially like billiard balls.

When an INS reaction occurs between a fast neutron and a carbon atom, a 4.43 MeV gamma ray is emitted immediately. This gamma ray has a very high energy -4.43 MeV, where an electron volt is the energy of one electron (e) moving across a potential gradient of one volt (V). For comparison, the energy associated with a photon of visible light is roughly 2 eV, 2 million times less than the gamma rays emitted by INS involving carbon atoms.

INS has been proposed as a potential technology for non-invasive scanning of materials because: (1) fast neutrons are very effective at penetrating materials as a result of both their high energy and neutral charge, and (2) the gamma rays produced are a very high energy form of light that also penetrates materials very effectively. In addition, the gamma rays tend to have unique energies associated with each element, allowing elemental compositions to be measured. INS has been developed or is being explored for the estimation of carbon concentration in a range of materials including soil. Although neutrons and gamma rays penetrate materials including soil, intensity is still lost during transmission due to absorption and scattering. This loss of intensity is termed attenuation, and represents a critical concern for quantitative estimation of elemental abundance using non-invasive scanning techniques in soil (Gardner 1986), including INS.

5.2.3 Brookhaven INS Device

The United States Brookhaven National Laboratory has been developing an INS device intended to achieve practical measurement of soil carbon (Wielopolski et al. 2008a, Chatterjee et al. 2009). The initial development of the INS device (Fig. 21) was reported in Wielopolski et al. (2000) and a patent was granted in 2002 (Wielopolski & Hendry 2002). The basis of the instrument is that the counts recorded in a peak of 4.43 MeV gamma rays are proportional to the number of carbon atoms in a soil volume beneath the detector.

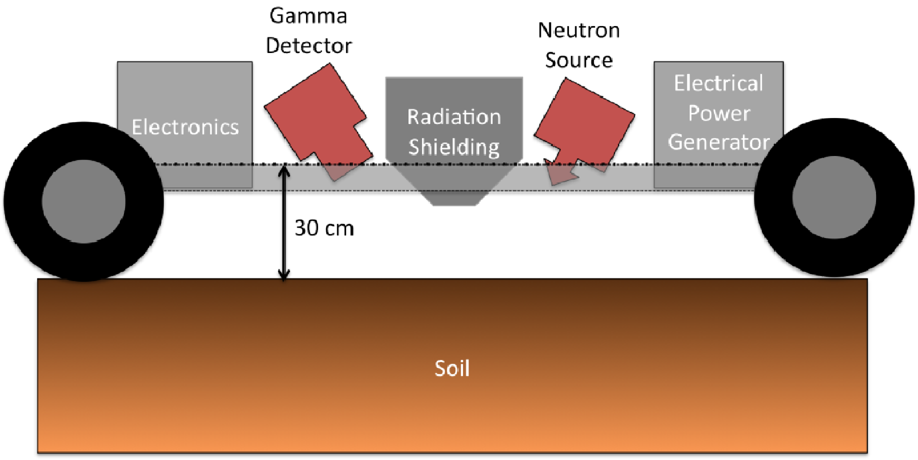

Fig. 21 A simplified depiction of the Brookhaven INS device based on Wielopolski et al. (2008a). The principal components of the device are a 14 MeV neutron source and multiple gamma ray detectors, mounted 30 cm above soil. Radiation shielding between the neutron source and the detector improves performance (Wielopolski et al. 2008b). The neutron source and electronics require electrical power, which is provided by an onboard generator. The device is mounted on a four wheeled cart, which would be capable of traversing arable land, paddocks and some forests, but not rugged forest or mountain land.

An important characteristic of this system has been the development of a pulse sequence for the neutron generator, based on extensive calculations and electronics development. High energy (14 MeV) neutrons are generated for 25 microseconds, and then the neutron generator is switched off for 75 microseconds. During the time when no high energy neutrons are produced, there should be no neutrons present in the soil with the energy required to produce 4.43 MeV gamma rays from INS involving carbon atoms. During these 75 microseconds, a background spectrum of gamma emissions from lower energy (thermal) neutrons can be measured. In principle, this design allows the thermal neutron capture (TNC) background to be subtracted from the spectrum obtained during the 25 microsecond pulses of high energy neutrons, yielding an INS spectrum free of TNC background.

The full function of the Brookhaven INS device is reported in Wielopolski et al. (2008a) and several publications outline calculations of the behaviour of the fast neutrons in soil (Wielopolski et al. 2005, Biegalski et al. 2008, Doron et al. 2008). Additional publications such as Mitra et al. (2007) outline the development of electronic or physical systems, and are not reviewed extensively here.

Overall, Wielopolski et al. (2008a, b) describe the INS device as an ‘alpha’ prototype, and have proposed the construction of a ‘beta’ prototype with minor changes – mainly additional detectors to improve signal to noise ratio and changes in the shielding (Wielopolski et al. 2008b).

5.2.4 INS for the estimation of carbon in other materials

Coal

The most progress on accurate measurements of carbon using INS is on coal (Sowerby 2009), providing evidence that the approach appears more promising than for soil carbon measurement to date. The long running studies have primarily focussed on the need to measure the carbon content of coal on conveyor belts feeding coal-fired power plants. The studies were originally motivated by efficiency optimisation, but additional benefits are now realised in the ability for more accurate accounting of fossil carbon use. The best available accuracy for INS measurement of carbon in coal is 0.5% for coals ranging from 50 to nearly 100% carbon (Sowerby 2009).

The main implication of studies using INS with coal is the realisation that the ability to estimate soil carbon with accuracies greater than 0.5% may be difficult to achieve. The application of INS to material such as coal conveyor belts appears better suited to reliable INS measurement than the geometry of the Brookhaven device, because it avoids issues related to an unknown penetration depth. This in turn suggests that INS studies of intact soil cores may be viable with INS, and it should be noted that large diameter soil cores could potentially be scanned and then replaced in their original location. With such an approach it might be possible to scan for bulk density using gamma rays or x-rays, enabling precise equivalent-mass calculations of soil carbon density.

Petroleum Drill Holes

It has been known for many years that INS is a practical method for detecting carbon in boreholes drilled for oil and gas exploration (Gorov et al. 1971, Underwood and Dyos 1986). The detection of high carbon levels in rock formations is of strong interest for this industry as it signals evidence of oil, gas or the source rocks for oil and gas which may be in the process of migrating to another location. INS devices have seen considerable use, but yield what can only be considered qualitative estimates of carbon abundance, which would appear not to provide the accuracy required for measurements of soil carbon.

The main implication of 'down-core' INS studies in the petroleum industry for efforts to estimate soil carbon is that considerable experience exists with lowering INS devices down boreholes, but has not typically yielded estimates with a high degree of accuracy. However, this situation is improving with ongoing development (Jacobi and Longo 2009), driven largely by the potential for INS and related nucleonic techniques to simultaneously estimate the concentrations of multiple elements in addition to carbon.

Cargo and Contraband

INS has been explored as a technology for scanning cargo and airport luggage for materials such as illicit drugs and explosives (Buffler 2004, Sowerby & Tickner 2007). This application of INS is leading to technological development, particularly for using multiple scanning technologies simultaneously, but holds less immediate relevance to the measurement of carbon dispersed throughout a medium such as soil.

5.2.5 Sampling requirements and protocols

The design of the Brookhaven INS device is focused on using a neutron source and detectors mounted on a cart to undertake a measurement of soil carbon at a single location. Currently, a single measurement is estimated to take 30 minutes. The cart and neutron source are designed so that the radiation hazard is minimised. The main issue with the device is that few field measurements have been reported in the literature. As a result, the accuracy and depths sampled are judged to remain uncertain. It is likely that considerable redesign and assessment would be required prior to recommending detailed sampling requirements and protocols appropriate for estimating the accuracy and costs of carbon inventory developed using an INS device.

INS measurements to date

Published reports of measurements from the Brookhaven INS device published in Wielopolski et al. (2008a) consist of:

- Measurements obtained on ‘sandpits’ with different uniform carbon concentrations
- Three sites at Brookhaven National Laboratory, New York, USA
- Three sites at Duke Forest, North Carolina, USA

These measurements suggest that the device can detect soil carbon concentration on a mass basis of approximately 0.5-1%. Such a detection limit implies a reproducibility (standard error) of <0.3%. While the Brookhaven team suggests that increased accuracy can be obtained by counting longer or adding additional detectors (Wielopolski et al. 2008a, b), a number of sources of error and bias remain unaddressed.

Field protocols

The current design of the INS device incorporates safety features, including a neutron source that can be switched off, allowing radiation safety to be relatively straightforward, even when the device is deployed in the field. As a result, the main limitation of where the device can be deployed will be the ability of the four-wheel cart to access a site.

Applicability of the approach

Several key questions and concerns potentially limit the application of the Brookhaven INS device to soil carbon measurement. Several factors conspire to make deeper soil carbon less visible than soil carbon near the surface. These factors include neutron attenuation with depth, the attenuation of the 4.43 MeV gamma rays in soil, and the distance to the detector. In addition, gamma emissions from the thermal neutron capture of Fe and Si may interfere with the 4.43 MeV gamma ray peak obtained from carbon. An additional concern is that any INS device will observe total carbon, including live vegetation, surface litter and organic layers, as well as inorganic carbon. These carbon stocks, where present, would need to be subtracted from the INS soil carbon estimate. Overall, a number of concerns exist and measurements remain unverified with respect to these concerns, leading to the potential for unexpected variability and/or bias.

5.2.6 Depth of detection with the Brookhaven device

Several factors conspire to make deeper soil carbon less visible that soil carbon near the surface as demonstrated in Fig. 21.

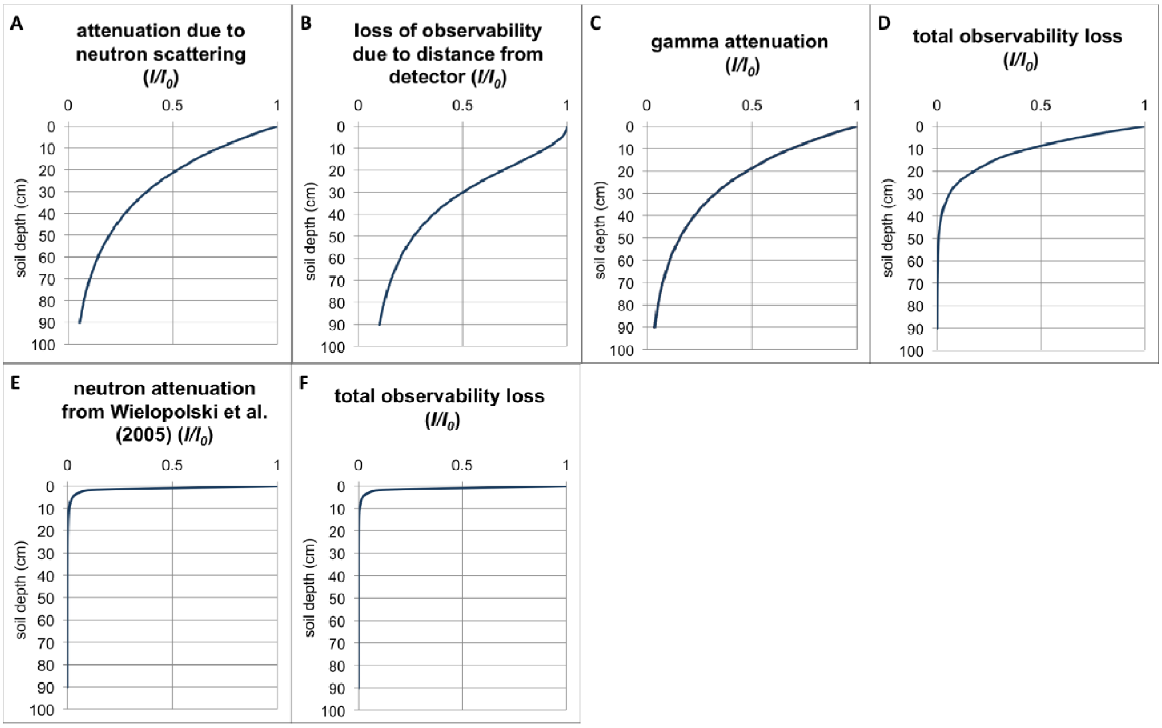

Fig. 21 Ability to observe soil carbon using the Brookhaven INS device, with each panel showing the intensity of signal derived from soil depth, relative to the intensity of signal from the soil surface. A) Loss of 14 MeV neutron flux due to scattering, B) loss of ability to observe carbon due to inverse square of distance from gamma emission to the detector, C) attenuation of the 4.43 MeV gamma rays by the soil mass, D) total loss of ability to observe carbon as a function of depth based on A, B and C. Panel E shows the equivalent of panel A, as reported in Fig. 9 of Wielopolski et al. (2005) for a soil with bulk density 1.2 g/cm^3, and panel F shows the total loss in observation ability by combining results from panels E, B and C.

Neutron attenuation with depth

Neutron penetration into soil is governed by collisions with the nuclei of atoms. Calculating the likelihood of a collision with atoms likely to be in the path of a neutron is relatively straightforward for the first collision, but becomes exceedingly complex as the neutron subsequently undergoes numerous additional collisions. Along the path a neutron follows, the likelihood of a collision can be calculated based on the cross section of the atoms encountered and number of atoms. Cross sections for all common atoms, representing nearly all possible reactions, have been tabulated into comprehensive databases. Cross sections are measured in barns (a unit equal to 10^{-24} cm^2) and are typically highly dependent on neutron energy. The relevant databases are now widely available on the Internet at http://www.nndc.bnl.gov/sigma/

For the 14 MeV neutrons entering soil from the neutron generator in the Brookhaven INS device, the three main steps of attenuation are: scattering, thermalisation and capture. The first step, scattering, involves any collision with a nuclei. After this collision, the neutrons are effectively scattering in all directions, and not on average penetrating deeper into soil. In most collisions, the neutrons will retain their energy (e.g. 14 MeV) and be scattered elastically, because their mass is small relative to the mass of most atoms. The neutrons primarily lose energy when they impact hydrogen atoms, which have a mass nearly equal to the neutron. This process is called thermalisation, because it continues until the energy of the neutrons reaches equilibrium with the thermal velocities of surrounding atoms governed by temperature. For the purposes of understanding 4.43 MeV emissions from carbon atoms, only the first few collisions with hydrogen atoms are relevant, because the neutrons need to retain an energy in excess of about 5 MeV to undertake reactions producing the 4.43 MeV emissions. It is relevant to note that the neutrons will also lose energy when inelastic scattering reactions (such as the 4.43 MeV emissions from carbon atoms) occur, but these reactions are less common than elastic scattering reactions. Over the course of a second or less, neutrons will either escape the boundaries of the experiment or be consumed by neutron capture reactions which become considerably more likely as neutrons reach thermal velocities. In neutron capture reactions, the neutrons become incorporated in atomic nuclei, in many cases causing radiation to be emitted.

Two approaches can be examined for considering the attenuation of neutrons, and their availability to undertake INS reactions with carbon atoms producing 4.43 MeV gamma rays as a function of soil depth. First, the behaviour of a vast number of individual neutrons can be simulated, using Monte Carlo techniques. Such an approach has been undertaken by the Brookhaven group in development of the INS device (Fig. 21E) and confirms the relevance of processes described above (Wielopolski et al. 2005, Doron et al. 2008, Biegalski et al. 2008). The main drawback of this approach is that the high level of complexity makes it difficult to fully describe or check all the calculations. As a result, a second approach involving calculating the initial attenuation due to scattering can be undertaken using simple calculus. This approach cannot yield an exact answer, but along with experimental data, provides some background against which complex simulations can be compared (Fig. 21A).

Monte Carlo simulations of individual neutrons have been undertaken by the Brookhaven group. Broadly, the elemental composition of soil has been considered, although the specific elemental abundances used in models are not clearly described (Wielopolski et al. 2005, Doron et al. 2008, Biegalski et al. 2008). A major concern is the lack of specific consideration of hydrogen in soil, appearing to be absent from the list of elements for average global soils included in the neutron simulations (Wielopolski et al. 2005, Doron et al. 2008). Hydrogen exists not only in soil water, but also in some minerals and organic matter. A broadly applicable chemical formula for organic matter is CH_2O, and a more specific formula for the Redfield ratio is $C_{106}H_{263}O_{110}N_{16}P_1$, emphasing that hydrogen is likely to be associated with carbon (Sterner & Elser 2002, p30). Care must be taken since hydrogen is commonly excluded from tables of soil composition, both because it is difficult to analyse, and soil composition is usually expressed per unit dry mass as soil water varies markedly over time. Furthermore, hydrogen is a small component by mass, but can be the most abundant element by number of atoms in wet soil. It is the abundance by number of atoms that matters for interactions with neutrons. For three soils listed in Wielopolski et al. (2005), hydrogen abundance by mass is listed as varying from 0.21% to 2.81%, with no value reported for an approximate mean global soil composition.

Under field conditions in New Zealand, few situations exist where soil water content is less than 1% on a soil mass basis except in the most extreme drought conditions. It is therefore recommended that more careful consideration of hydrogen abundance in soil, and particularly in soil water be considered. Variable soil water content has been modelled, but yields a result that may be considered unintuitive – with variation in water content between 0 and 50% causing no observable effect, but a simulation with 100% water content producing a decrease in neutron penetration by several orders of magnitude (Wielopolski et al. 2005). It is plausible that the simulation results presented in Wielopolski et al. (2005) could have been obtained by modelling a soil where water content replaced mineral content. Given the details presented in the published work, the simulations cannot be reconstructed. It would be desirable for experimentation to be undertaken in soils with varying water content. At present, relevant and reliable information can be related from the extensive experience of soil scientists using neutrons with a similar energy (5 MeV) to estimate soil water content using the rate of thermalisation (Jury et al. 1991, Gardner 1986). The effective penetration depth of measurements is known to vary from ~150 mm in wet soil to ~700 mm in dry soil.

Regardless of possible issues with the neutron attenuation calculations, clear information suggests that a strong measurement bias will exist for surface soil carbon relative to deeper soil carbon. The axes in the Figures are logarithmic in the publications by Wieloposki et al. (2005) and Biegalski et al. (2008), implying that the flux of fast neutrons capable of producing 4.43 MeV gamma rays through INS with carbon atoms decreases by a factor of ~100 in the upper 100 mm of soil. The information for a soil with a bulk density of 1.2 g/cm^3 has been redrawn from fig. 9 in Wielopolski et al. (2005) on a linear scale in Fig. 21E.

As mentioned above, it is also possible to undertake a simple direct calculation of attenuation due to the initial scattering of fast (14 MeV) neutrons. The attenuation calculation takes the form

$$I/I_0 = e^{-\sigma N_A n_M \rho x} \qquad (11)$$

where s is the cross section, N_A is Avogadro's number for the number of atoms (6.02×10^{23}) in one mole, n_M is the number of atoms per unit mass, r is the density, and x is the depth in soil. The calculation yield a result for the intensity of the neutron flux, I, at depth x, relative the flux at the surface, I_0.

To evaluate a simple form that gives a relevant result, the exponent taken as the base *e* can be evaluated once for hydrogen and once for heavier elements. For hydrogen, $n_M = 2/18$ when present in water and σ is approximately 0.6×10^{-18} m^2 for 14 MeV neutrons. For heavier elements common in soil, it is possible to roughly consider the three main elements, O, Si and Al by taking n_M as approximately 1/22 and σ as approximately 0.9×10^{-18} m^2 for 14 MeV neutrons. For a water content of 0.2 g/cm^3 and dry soil bulk density of 1 g/cm^3, this calculation suggests that that the attenuation due to scattering will be approximately half within 0.2 m (Fig. 21). This is considerably less than found by the complex Monte Carlo simulations.

Overall, published calculations (Wieloposki et al. 2005, Biegalski et al. 2008) and the simple calculation presented above suggest that the depth seen by the Brookhaven INS device is likely to be less than the 0.3 m reported by Wieloposki et al. (2008a). However, the calculations produce differing results. The complex Monte Carlo simulations suggesting that attenuation through ~0.1 m of soil may be up to the order of a factor of 100. In contrast, the simple calculation above suggests a higher level of penetration that is more consistent with the assertion that the device measures to a depth of approximately 0.3 m. If these calculations are correct, two additional sources of bias toward more shallow depths merit consideration.

Attenuation of 4.43 MeV gamma rays

A major difficulty that appears to be unaddressed in publications related to the Brookhaven device is the attenuation of 4.43 MeV gamma rays by soil. Although gamma rays are effective at penetrating soil, this attenuation is very significant and has been known for many years as having the capacity to measure soil bulk density precisely (Gardner & Calissendorf 1967). The attenuation of gamma rays by soil and other materials is well known, and interestingly is very closely related to material density (Gardner 1986). As a result, this effect can be estimated accurately and with reasonable precision.

Gamma ray attenuation, estimated as the reduction in the intensity (I) relative to the initial intensity (I_0) can be estimated from

$$I/I_0 = e^{-\mu\rho x} \tag{12}$$

where x is distance (m), ρ is the material density and μ is the attenuation coefficient. A range of soil materials from pure Si oxides, to pure Fe oxides to pure water will have attenuation coefficients, μ, between 0.030 and 0.032 cm^2/g which can readily be obtained. Within this range for μ, and assuming a soil bulk density (including water) of 1.2 g/cm^3, gamma rays emitted at 0.3 m depth will have a probability of being observed that is only one third of gamma rays emitted from the soil surface (Fig. 21B).

Distance to detector(s)

An additional difficulty that also appears to be unaddressed in publications related to the Brookhaven device is the fact the relative intensity of the gamma rays at the detector will decrease as the distance between the detector and point of emission increases. Taking an ideal system approach to the geometry, the rate of decrease will follow the inverse square law, applied typically to radiation observations. Therefore, in the absence of attenuation due to soil, a detector 0.3 m above the soil surface will observe a factor of 4 decrease in a gamma emission produced at the soil surface versus the signal 0.3 m below the soil surface. In practice, some factors involving the geometry of the neutron source and detector could cause deviation from the ideal inverse square relationship, but the basic principle should hold that geometry dictates that emissions from deep soil will be less effectively measured than emission from surface soil.

Applied in a similar formulation to the equation above for gamma attenuation, the inverse squared relationship relates the observed intensity of an emission at soil surface to an emission at depth x in soil, where h is the height of the detector above soil, such that

$$I/I_0 = h^2/(h+x)^2 \tag{13}$$

The result (Fig. 21C) suggests that an additional signal loss of approximately half occurs over the first 0.2 m of soil due to the distance to the detector. It is noted that this calculation assumes the detector is located vertically directly over soil, and this calculation produces an overestimate if the configuration is oblique.

Combined calculation of depth observed by INS

Each of the calculations presented above can be combined by multiplication to estimate a combined I/I_0, which represents the total ability to observe carbon at any depth, relative to carbon at the soil surface (I_0). Combined calculations are presented in Fig. 21C using the simplified estimate of attenuation due to neutron scattering and in Fig. 21F using the estimate obtained from Wielopolski et al. (2005).

The estimates of the total ability to observe show that the multiplicative effect of the three different calculations may lead to greater bias toward surface soil from that reported by Wielopolski et al. (2008a, b). Overall, Fig. 21C implies that the ability to observe carbon is halved by 0.1 m soil depth, and the situation is considerable worse in Fig. 21F. Although some calculations performed by Wielopolski et al. (2005) have been described as indicating that the device is not sensitive to soil water content, the application of Eqs. 12 and 13 to soil water imply a strong sensitivity that should be further investigated. Variation in soil bulk density will also cause variation in the depth observed. Overall, it appears that there will be considerable variability in the depth observed by INS, and careful experimental verification is required before the device can be applied to soil carbon measurement with confidence.

5.2.7 Accuracy and sensitivity

Signal to noise ratio

In any device measuring counts, signal to noise ratio is critical. Detectability reported by the Brookhaven group is approximately 0.5-1% carbon on a mass basis. Such a detection limit implies reproducibility (standard error) of ≤0.3%, which is similar to the accuracies of ~0.3% obtained by various INS devices applied to measure carbon in coal (Sowerby 2009). This level of accuracy may be of some utility for estimating soil carbon stocks, but is unlikely to meet the requirements of soil carbon inventory focusing on changes in stocks over time or between sites in an experiment. Increasing the number of detectors (or the neutron flux) would enhance this signal to noise ratio, and has been proposed. However, achieving a higher level of detection assumes no interferences from elements with a variable concentration in soil will have to be overcome.

Possible interferences generating bias

If the baseline underneath the 4.43 MeV gamma peak derived from INS on carbon atoms is entirely random, then efforts to improve the signal to noise ratio ratio (e.g. by longer counting or adding detectors) will result in improved carbon detection and accuracy. If the baseline includes interferences, then this will not be the case and the measured size of the carbon peak will include bias. Furthermore, the amount of bias will vary if the sources of interference vary between or within soils. Likely interferences that will affect baseline include interferences on neutron or gamma attenuation in soil, and specific peaks underlying the 4.43 MeV carbon peak.

Wielopolski et al. (2008a) describe the need to monitor and correct for two gamma emissions derived from Si, which is a dominant element in many soils. The correction can be accomplished without great difficulty because the abundance of Si can be estimated from a distinct Si peak at 1.78 MeV. Such interference is unlikely to be a source of major variability or bias because the abundance of Si in soil is unlikely to vary as much as other elements such as Fe.

Unfortunately, it has also been observed in studies of carbon in coal that Fe does produce significant TNC gamma emissions underneath the 4.43 MeV peak used to estimate carbon abundance (Cywicka-Jakiel et al. 1999). Although the authors of the INS study on coal show that the Fe interference can also be corrected for, this interference may be of greater concern because the Fe content of soil is likely to vary more than Si between soils and as a function of soil depth. The presence of an Fe interference is not discussed by Wielopolski et al. (2008a) but appears likely based on spectra presented in that work, and also in the patent for the INS device (Wielopolski & Hendry 2002).

The magnitude of the Si and/or Fe interference is clearly very significant compared with the size of the 4.43 carbon peak. Further, it must be noted that both the Fe and Si interferences result from TNC rather than INS, and therefore the magnitude of the required correction may vary depending on the relative abundance of thermal versus high energy neutrons. Thus, there would appear to remain a potential for bias in measurements from some soils or experimental conditions.

Measuring total carbon rather than soil organic carbon

Any INS device will measure total carbon, including live roots and inorganic carbon (carbonate). This means that where live roots and or inorganic carbon represent significant soil carbon stocks, the INS device will not provide an estimate of the required quantity. In addition, carbon measured by INS will include surface litter or organic horizons, as well as aboveground vegetation such as grass. Given the issues described above, rates of attenuation in soil, litter and grass could have pronounced effects on measurements.

5.2.8 Experimental verification

Experimental verification has been undertaken (Wielopolski et al. 2008a), but not at a level sufficient to allay concerns about interferences that may generate bias. In addition to the experiments recommended in the section above, it is recommended that the performance of the INS device be examined in synthetic mixtures with a varying content of elements proposed to interfere with the 4.43 MeV gamma rays associated with carbon. Since the interfering peaks are derived from TNC rather than INS, it is also recommended that the soil water content be varied during these experiments to test for varying rates of neutron thermalisation. It would also be desirable to undertake both experimental and numerical efforts to verify that unbiased measurements can be obtained with grass or litter at the soil surface.

5.2.9 Costs associated with a deployable INS system

Chatterjee et al. (2009) estimate the cost of the Brookhaven INS device at approximately US$150,000. An attempt was made to verify these costs by estimating the costs of components. The most expensive component will be a pulsed 14 MeV neutron source, and a quote of €115,000 was obtained for such a device. The costs of large NI detectors with gated electronics will be approximately $5,000 each, with a requirement to install a large number of these detectors. Wielopolski et al. (2008a) recommend 15 detectors. One-off radiation licensing costs are likely to be in the range of NZ$50,000, with annual operating costs in the range of NZ$5,000 or less for radiation badges etc. A potentially variable but significant cost is the replenishment of the tritium in the neutron source. Thus, a total development cost to build and license a device in New Zealand is likely to be in excess of NZ$300,000.

5.2.10 Conclusions and Recommendations

The Brookhaven INS device has been developed to an 'alpha' prototype stage, and further 'beta' prototype development has been recommended (Wielopolski et al. 2008a). Measurements to date confirm the basic principle of carbon measurement using INS, but have not verified the measurement capabilities of the INS system systematically. The likely accuracy carbon measurement using INS based both on experience with the Brookhaven device (Wielopolski et al. 2008a) and with equipment for estimating the carbon content of coal (Sowerby 2009) is approximately 0.3-0.5% (standard error). This accuracy implies limited potential for soil carbon inventory, where rates of change between two points in time require measurements with high accuracy and reproducibility.

Several key questions and concerns potentially limit the application of the Brookhaven INS device to soil carbon measurement. Factors conspiring to make deeper soil carbon less visible to INS than carbon near the soil surface include neutron attenuation with depth, the attenuation of the 4.43 MeV gamma rays in soil, and the distance to the detector. In addition, gamma emissions from the thermal neutron capture of Fe and Si may interfere with the 4.43 MeV gamma ray peak obtained from carbon. An additional concern is that any INS device will observe total carbon, including live vegetation, surface litter and organic layers, as well as inorganic carbon.

Calculations above indicate that the ability to observe carbon at depths below 0.1-0.2 m will be limited with INS, and that the ability to observe soil carbon deeper in the soil profile may vary depending on conditions. If INS measurement is largely confined to this depth range, then it does not appear to be competitive with approaches involving the collection of many small diameter soil cores. On the other hand, confirmation of a narrower observation window for INS would imply that the instrument could be lowered down a borehole into soil, or used to scan cores ≥50 mm in diameter, which could be returned into soil following measurement. The remaining challenge would be overcoming the relatively high detection limit of soil carbon. Nevertheless, a chief advantage of these alternative measurement approaches is that they might allow measurement of soil bulk density using simultaneous gamma or x-ray scanning.

Given uncertainty regarding the scope of work required to develop a robust INS soil carbon measurement approach, it is recommended that the probable scope of a development programme (~NZ$10 million) is beyond the benefits of the technology in New Zealand. Only involvement in a global or multinational project to develop INS and related nucleonic techniques as a practical tool for soil carbon measurement is likely to have potential benefit to New Zealand.

6. Acknowledgements

The authors acknowledges assistance from those contributed to the sections on developing technologies in this report through workshops, discussion and review, including Chris Kroger, Gavin Wallace, Murray Bartle and Bernard Barry. The authors are grateful to Surinder Saggar for his review and Christine Bezar for her editorial improvement of the report.

7. References

Abella SR, Zimmer BW 2007. Estimating organic carbon from loss-on-ignition in northern Arizona forest soils. Soil Science Society of America Journal 71:545–550

Adamchuk VI, Hummel JW, Morgan MT, Upadhyaya SK 2004. On-the-go soil sensors for precision agriculture. Computers and Electronics in Agriculture 44:71–91.

Analytical Spectral Devices 2005. Introduction to NIR Technology, ASD Inc., Boulder Colorado, USA, ASD Document 600510 Rev. 2.

Anderson-Cook CM, Alley MM, Roygard JKF, Khosla R, Noble RB, Doolittle JA 2002. Differentiating soil types using electromagnetic conductivity and crop yield maps. Soil Science Society of America Journal 66:1562–1570.

Awiti AO, Walsh MG, Shepherd KD, Kinyamario J 2008. Soil condition classification using infrared spectroscopy: A proposition for assessment of soil condition along a tropical forest-cropland chronosequence. Geoderma 143:73–84.

Blakemore LC, Searle L, Daly BK 1987. Methods for chemical analysis of soils. Scientific Report. 80. New Zealand Soil Bureau, Lower Hutt, New Zealand.

Baldocchi DD 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future. Global Change Biology 9:479–492.

Baldocchi DD 2008. 'Breathing' of the terrestrial biosphere: lessons learnt from a global network of carbon dioxide flux measurement systems. Australian Journal of Botany 56:1–26.

Barthes BG, Brunet D, Ferrer H, Chotte JL, Feller C 2006. Determination of total carbon and nitrogen content in a range of tropical soils using near infrared spectroscopy: influence of replication and sample grinding and drying. Journal of Near Infrared Spectroscopy 14:341–348.

Beets PN, Oliver GR, Clinton PW 2002. Soil carbon protection in podocarp/hardwood forest and effects of conversion to pasture and exotic pine forest. Environmental Pollution 116: S63 – S73.

Bellamy PH, Loveland PJ, Bradley RI, Lark RM, Kirk GJD 2005. Carbon losses from all soils across England and Wales. Nature 437:245–248.

Ben-Dor E 2002. Quantitative remote sensing of soil properties. Advances in Agronomy 75:173–243.

Ben-Dor E, Banin A 1995. Near-infrared analysis as a rapid method to simultaneously evaluate several soil properties. Soil Science Society of America Journal 59: 364–372.

Ben-Dor E, Irons JR, Epema G 1999. Soil reflectance. In Remote sensing for the earth science: Manual of remote sensing. (Ed. AN Rench). (John Wiley & Sons: New York).

Bhatti JS Bauer IE 2002. Comparing loss-on-ignition with dry combustion as a method for determining carbon content in upland and lowland forest ecosystems. Communications in Soil Science & Plant Analysis 33 (15-18):3419–3430.

Biegalski S, Doron O, Wielopolski L. 2008. Time and depth dependent fluxes due to 14 MeV neutrons impinging soil. Journal of Radioanalytical and Nuclear Chemistry 277:193–198.

Blakemore LC, Searle PL, Daly BK 1987. Methods for chemical analysis of soils. New Zealand Soil Bureau Scientific Report 80. New Zealand Soil Bureau, Department of Scientific and Industrial Research, Lower Hutt.

Blumfield TJ, Xu ZH, Prasolova NV 2007. Sampling size required for determining soil carbon and nitrogen properties at early establishment of second rotation hoop pine plantations in subtropical Australia. Pedosphere 17:706–711.

Boucneau G, Van Meirvenne M, Hofman G 1998. Comparing pedotransfer functions to estimate soil bulk density in northern Belgium. Pedologie – Themata 5:67–70.

Bowers S, Hanks RJ 1965. Reflectance of radiant energy from soils. Soil Science 100:130–138.

Brereton RG 2003. 'Chemometrics: Data analysis for the laboratory and chemical plant.' (John Wiley & Sons: Chichester, UK).

Bricklemyer RS, Brown DJ, Clegg SM, Barefield J 2008. Simulated in situ soil carbon measurements using combined Vis-NIR and LIBS sensors. In Proceedings of the 1st Global Workshop on High Resolution Digital Soil Sensing and Mapping, held under the auspices of the International Union of Soil Sciences (IUSS), Working Group on Digital Soil Mapping, Sydney, Australia, 5-8 February 2008. CDROM.

Brimmer PJ, DeThomas FA, Hall JW 2001. Method development and implementation of near-infrared spectroscopy in industrial manufacturing support laboratories. In 'Near-infrared technology in the agriculture and food industries'. (Eds. P Williams, K Norris) pp. 199–214. American Association of Cereal Chemist, Inc.: Minnesota, USA.

Broge NH, Thomsen AG, Greve MH 2004. Prediction of topsoil organic matter and clay content from measurements of spectral reflectance and electrical conductivity. Acta Agriculture Scandinavia B, Soil and Plant Science 54:232–240.

Brown DJ 2007. Using a global Vis-NIR soil-spectral library for local soil characterization and landscape modeling in a 2nd-order Uganda watershed. Geoderma 140:444–453.

Brown DJ, Shepherd KD, Walsh MG, Mays MD, Reinsch TG 2006. Global soil characterization with VNIR diffuse reflectance spectroscopy. Geoderma 132:273–290.

Brown M, Whitehead D, Hunt JE, Clough TJ, Arnold GC, Baisden WT, Sherlock RR 2009. Regulation of soil-surface respiration in a grazed pasture in New Zealand. Agricultural and Forest Meteorology 149:205–213.

Bublitz J, Dŏlle C, Schade W, Hartmann A, Horn R 2001. Laser-induced breakdown spectroscopy for soil diagnostics. European Journal of Soil Science 52, 305-312.

Buffler A 2004. Contraband detection with fast neutrons. Radiation Physics and Chemistry 71:853–861.

Chacón N, Dezzeo N, lster H, Mogollón P 2002. Comparison between colorimetric and titration methods for organic carbon determination in acidic soils. Communications in Soil Science & Plant Analysis 33:203–211.

Chang CW, Laird DA 2002. Near-infrared reflectance spectroscopic analysis of soil C and N. Soil Science 167:110–116.

Chang CW, Laird DA, Mausbach MJ, Hurburg Jr CR 2001. Near-infrared reflectance spectroscopy - Principal component regression analysis of soil properties. Soil Science Society of America Journal 65:480–490.

Chatterjee A, Lal R, Wielopolski L, Martin MZ, Ebinger MH 2009. Evaluation of different carbon determination methods. Critical Reviews in Plant Science 28:164–178.

Conant RT, Paustain K 2009. Spatial variability of soil organic carbon in grasslands: implications for detecting change at different scales. Environmental Pollution 116:S127–S135.

Cozzolino D, Moron A 2006. Potential of near-infrared reflectance spectroscopy and chemometrics to predict soil carbon fractions. Soil & Tillage Research 85:78–85.

Cremers DA, Radziemski LJ 2006. History and fundamentals of LIBS. In Miziolek AW, Palleschi V, Schechter I (Eds.) Laser-Induced Breakdown Spectroscopy: Fundamentals and Applications. Cambridge University Press.

Cywicka-Jakiel T, Loskiewicz J, Nezamzadeh M, Tracz G 1999. The influence of high iron content in coal ash on measurement of 4.43 MeV carbon [gamma]-rays. Applied Radiation and Isotopes 51:419–427.

Dalal RC, Henry RJ 1986. Simultaneous determination of moisture, organic carbon, and total nitrogen by near infrared reflectance. Soil Science Society of America Journal 50:120–123.

Davidson EA, Savage K, Verchot LV, Navarro R 2002. Minimizing artifacts and biases in chamber-based measurements of soil respiration. Agricultural and Forest Meteorology, 113: 21–37.

Davis MR 1994. Topsoil properties under tussock grassland and adjoining pine forest in Otago, New Zealand. New Zealand Journal of Agricultural Research 37:465–469.

Davis MR 2001. Soil properties under pine forest and pasture at two hill country sites in Canterbury. New Zealand Journal of Forestry Science 31:3–17.

Davis M, Wilde H, Garrett L, Oliver G 2004. New Zealand Carbon Monitoring System. Soil Data Collection Manual. Caxton Press, Christchurch.

De Vos B, Van Meirvenne M, Quartaert P, Deckers J, Muys B 2005. Predictive quality of pedotransfer functions for estimating bulk density of forest soils. Soil Science Society of America Journal 69, 500–510.

Desai AR, Richardson AD, Moffat AM, Kattge J, Hollinger DY, Barr A, Falge E, Noomets A, Papale D, Reichstein M, Stauch VJ. 2008. Cross-site evaluation of eddy covariance GPP and RE decomposition techniques. Agricultural and Forest Meteorology 148:821–838.

Donkin MJ 1991. Loss-on-ignition as an estimator of soil organic carbon in A-horizon forestry soils. Communications in Soil Science & Plant Analysis 22:233–241.

Doron O, Wielopolski L, Biegalski S 2008. Advantages of mesh tallying in MCNP5 for soil analysis calculations. Journal of Radioanalytical and Nuclear Chemistry 276:183–186.

Ebinger MH, Norfleet ML, Breshears DD, Cremers, DA, Ferris MJ, Unkefer PJ, Lamb MS, Goddard KL, Meyer CW 2003. Extending the applicability of laser-induced breakdown spectroscopy for total soil carbon measurement. Soil Science Society of America Journal 67:1616–1619.

Ellert BH, Janzen HH, Entz T 2002. Assessment of a method to measure temporal changes in soil carbon storage. Soil Science Society of America Journal 66:1687–1695.

Ellert BH, Janzen HH, McConkey BG 1998. Measuring and comparing soil carbon storage. In Assessment Methods for Soil Carbon. R Lal, JM Kimble, RF Follett, BA Stewart Eds. p. 131–146.Lewis Publishers, Boca Raton, Florida , USA.

Esbensen K 2002. Multivariate Data Analysis in Practice. 5th Ed. ISBN 82-993330-3-2.

Falge E, Baldocchi D, Olson R, Anthoni P, Aubinet M, Bernhofer C, Burba G, Ceulemans R, Clement R, Dolman H, Granier A, Gross P, Grünwald T, Hollinger D, Jensen N-O, Katul G, Keronen P, Kowalski A, Ta Lai C, Law BE, Meyers T, Moncrieff J, Moors E, Munger JW, Pilegaard K, Rannik Ü, Rebmann C, Suyker A, Tenhunen J, Tu K, Verma S, Vesala T, Wilson K, Wofsy S. 2001. Gap filling strategies for defensible annual sums of net ecosystem exchange. Agricultural and Forest Meteorology 107:43–69.

Foken T, Mauder M, Liebethal C, Wimmer F, Beyrich F, Leps J-P, Raasch S, DeBruin H, Meijninger W, Bange J 2009. Energy balance closure for the LITFASS-2003 experiment. Theoretical and Applied Climatology doi 10.1007/s00704-009-0216-8.

Frogbrook ZL, Bell J, Bradley RI, Evans C, Lark RM, Reynolds B, Smith, Towers W 2009. Quantifying terrestrial carbon stocks: examining the spatial variation in two upland areas in the UK and a comparison to mapped estimates of soil carbon. Soil Use and Management 25:320–332.

Fystro G 2002. The prediction of C and N content and their potential mineralisation in heterogeneous soil samples using Vis-NIR spectroscopy and comparative methods. Plant and Soil 246:139–149.

Gardner WH. 1986. Water Content. Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods. Madison, USA: Soil Science Society of America. p 493-544.

Gardner WH, Calissendorff C. 1967. Gamma ray and neutron attenuation measurement of soil bulk density and water content. Isotope and Radiation Techniques. Proc. Symp. Techniques in Soil Physics and Irrigation Studies. Istanbul: IAEA Vienna. p 101–113.

Giddens KL, Parfitt RL, Percival HJ 1997. Comparison of some soil properties under *Pinus radiata* and improved pasture. New Zealand Journal of Agricultural Research 40:409–416.

Ghani A, Dexter M, Carran R, Theobald P 2007. Dissolved organic nitrogen and carbon in pastoral soils: the New Zealand experience. Eurasian Journal of Soil Science 58:832–843.

Gehl RJ, Rice CW 2007. Emerging technologies for in situ measurement of soil carbon. Climatic Change 80: 43–54.

Goidts E, Wesemael B van, Crucifix, M 2009. Magnitude and sources of uncertainties in soil organic carbon (SOC) stock assessments at various scales. European Journal of Soil Science 60: 723–739.

Gomez C, Viscarra Rossel, RA, McBratney AB 2008. Soil organic carbon prediction by hyperspectral remote sensing and field Vis-NIR spectroscopy: An Australian case study. Geoderma 146:403–411.

Gorov LI, Demidov AM, Ivanov VA 1971. Possibilities of oil-well logging with a Ge(Li) γ-detector and Po–Be neutron source. Atomic Energy 30:79–82.

Grewal KS, Buchan GD, Sherlock RR, 1991. A comparison of three methods of organic carbon determination in some New Zealand soils. Journal of Soil Science 42:251–257.

Hagen SC, Braswell BH, Linder E, Frolking S, Richardson AD, Hollinger DY 2006. Statistical uncertainty of eddy flux–based estimates of gross ecosystem carbon exchange at Howland Forest, Maine. Journal of Geophysical Research, 111: D08S03, doi:10.1029/2005JD006154.

Harmon RS, De Lucia FC, Miziolek AW, McNesby KL, Walters RA, French PD 2005. Laser-induced breakdown spectroscopy (LIBS) – an emerging field-portable sensor technology for real-time, in-situ geochemical and environmental analysis.

Harrison RB, Adams AB, Licata C, Flaming B, Wagoner GL, Carpenter P, Vance ED 2003. Quantifying deep-soil and coarse-soil fractions: Avoiding sampling bias. Soil Science Society of America Journal 67:1602–1606.

Hedley CB, Kusumo H, Hedley, MJ, Tuohy MP, Hawke M 2009. Soil C and N sequestration and fertility development under land recently converted from plantation forest to pastoral farming. New Zealand Journal of Agricultural Research 52 443–453.

Hedley CB, Yule IY, Eastwood CR, Shepherd TG, Arnold G 2004. Rapid identification of soil textural and management zones using electromagnetic induction sensing of soils. Australian Journal of Soil Research 42:389–400.

Hollinger DY, Aber J, Dail B, Davidson EA, Goltz SM, Hughes H, Leclerc MY, Lee JT, Richardson AD, Rodrigues C, Scott NA, Achuatavarier D, Walsh J 2004. Spatial and temporal variability in forest and atmosphere CO_2 exchange. Global Change Biology 10:1689–1706.

Hollinger DY, Richardson AD 2005. Uncertainty in eddy covariance measurements and its application to physiological models. Tree Physiology 25:873–885.

Homann PS, Bormann BT, Boyle JR 2001. Detecting treatment differences in soil carbon and nitrogen resulting from forest manipulations. Soil Science Society of America Journal, 65:463–469.

Homann PS, Bormann BT, Boyle JR, Darbyshire RL, Bigley R 2008. Soil C and N minimum detectable changes and treatment differences in a multi-treatment forest experiment. Forest Ecology and Management 255:1724–1734.

Homann PS, Remillard SM, Harmon ME, Bormann BT 2004. Carbon storage in coarse and fine fractions of pacific northwest old-growth forest soils. Soil Science Society of America Journal 68:2023–2030.

Hruschka WR 2001. Data analysis: wavelength selection methods. In Near-Infrared Technology in Agriculture and Food Industries. (P Williams, K Norris, Eds.) p. 39–58. American Society of Cereal Chemists, Inc. St Paul, Minnesota, USA.

Hunt JE, Kelliher FM, McSeveny TM, Ross DJ, Whitehead D 2004. Long-term carbon exchange in a sparse, seasonally dry tussock grassland. Global Change Biology 10:1785–1800.

Huntington TG, Johnson CE, Johnson AH, Siccama TG, Ryan DF 1989. Carbon, organic matter, and bulk density relationships in a forested spodosol. Soil Science 148:380–386.

Islam K, Singh B, McBratney A 2003. Simultaneous estimation of several soil properties by ultra-violet, visible, and near-infrared reflectance spectroscopy. Australian Journal of Soil Research 41:1101–1114.

Jacobi DJ, Longo JM 2009. US Patent 7615741 - Determining organic carbon downhole from nuclear spectroscopy. USA.

James IT, Waine TW, Bradley RI, Taylor JC, Godwin RJ 2003. Determination of soil type boundaries using electromagnetic induction scanning techniques. Biosystems Engineering 86:421–430.

Jankauskas B, Slepetiene A, Jankauskiene G, Fullen MA, Booth CA 2006. A comparative study of analytical methodologies to determine the soil organic matter content of Lithuanian Eutric Albeluvisols. Geoderma 136:763–773.

Johnston CA, Groffman P, Breshears DD, Cardon ZG, Currie W, Emanuel W, Gaudinski J, Jackson RB, Lajtha K, Nadelhoffer K, Nelson D, Post WM, Retallack, G, Wielopolski L 2004. Carbon cycling in soil. Frontiers in Ecological Environments 2:522–528.

Jones HS, 2004. Impacts of forest harvesting on the performance of soil-landscape modelling in a radiata pine forest, northern New Zealand. Unpublished PhD. thesis, lodged in the Library, University of Waikato, Hamilton.

Jones HS 2007. Effects of forest soil cultivation on the carbon stocks and other properties of contrasting volcanic soils, Ensis Contract Report for Ministry for the Environment. New Zealand Forest Research Institute Ltd, Rotorua.

Jones HS, Davis M, Wang H 2009. Effects of Forest Management Practices on Soil Carbon. In Kirschbaum M, Trotter C, Wakelin S, Baisden T, Curtin D, Dymond J, Ghani A, Jones H, Deurer M, Arnold G, Beets P, Davis M, Hedley C, Peltzer D, Ross C, Schipper L, Sutherland A, Wang H, Beare M, Clothier B, Mason N, Ward M. Carbon Stocks and Changes in New Zealand's Soils and Forests, and Implications of Post-2012 Accounting Options for Land-Based Emissions Offsets and Mitigation Opportunities. Landcare Research Contract Report: LC0708/174, 1-457. Landcare Research New Zealand Ltd., Lincoln.

Jones HS, Garrett LG, Beets PN, Kimberley MO, Oliver GR 2008. Impacts of harvest residue management on soil carbon stocks in a plantation forest. Soil Science Society of America Journal 72:1621–1627.

Jury W, Gardner WR, Gardner WH. 1991. Soil Physics: Wiley.

Kerry R, Oliver MA 2008. Determining nugget:sill ratios of standardized variograms from aerial photographs to krige sparse soil data. Precision Agriculture 9:33–56.

Kerven G., Menzies NW, Geyer MD 2000. Soil carbon determination by high temperature combustion - A comparison with dichromate oxidation procedures and the influence of charcoal and carbonate carbon on the measured value. Communications in Soil Science & Plant Analysis 31:1935–1939.

Kowalenko CG 2001. Assessment of Leco CNS-2000 analyzer for simultaneously measuring total carbon, nitrogen, and sulphur in soil. Communications in Soil Science & Plant Analysis 32: 2065–2078.

Kusumo BH, Hedley MJ, Hedley CB, Arnold GC, Tuohy MP 2009a. Predicting pasture root density from soil spectral reflectance: field measurement. European Journal of Soil Science doi: 10.1111/j.1365-2389.2009.01199.x

Kusumo BH, Hedley MJ, Hedley CB, Hueni A, Arnold GC, Tuohy MP 2009b. The use of Vis-NIR spectral reflectance for determining root density: evaluation of ryegrass roots in a glasshouse trial. European Journal of Soil Science 60:22–32.

Kusumo BK, Hedley CB, Hedley MH, Hueni A Touhy M, Arnold G 2008. The use of diffuse reflectance spectroscopy for in situ carbon and nitrogen analysis of pastoral soils. Australian Journal of Soil Research 46:623–635.

Kusumo BH, Hedley MJ, Tuohy MP, Hedley CB, Arnold GC 2010. Predicting soil carbon and nitrogen concentrations and pasture root densities from proximally sensed soil spectral reflectance. In Proximal sensing for high resolution mapping Eds. RA Viscarra-Rossel, AB McBratney, B Minasny. Springer Publications. In Press.

Livingston GP, Hutchinson GL 1995. Enclosure-based measurement of trace gas exchange: applications and sources of error. In PA Matson, RC Harriss (Eds.), Biogenic Trace Gases: Measuring Emissions from Soil and Water. Blackwell Scientific Publications, Oxford, pp. 14–51.

Loescher HW, Law BE, Mahrt L, Hollinger DY, Campbell J, Wofsy SC. 2006. Uncertainties in, and interpretation of, carbon flux estimates using the eddy covariance technique. Journal of Geophysical Research. 111: doi:10.1029/2005JD006932.

Lund E, Giyoung K, Maxton C, Drummond P, Jensen K 2008. Near-infrared soil spectroscopy: results from field trials using a commercially available spectrophotometer. Proceedings of the 1st Global Workshop on High Resolution Digital Soil Sensing and Mapping, held under the auspices of the International Union of Soil Sciences (IUSS), Working Group on Digital Soil Mapping, Sydney, Australia, 5–8 February 2008. CDROM.

Malley DF, Martin PD 2003. The use of near-infrared spectroscopy for soil analysis. In Tools for nutrient and pollutant management: Application to agriculture and environmental quality. LD Currie, JA Hanly, Eds.Massey University, Palmerston North, New Zealand. p. 371–404.

Malley DF, Martin PD, Ben-Dor E 2004. Application in analysis of soils. In Near-infrared Spectroscopy in Agriculture. Agronomy Monograph 44. KA Barbarick, CA Roberts, WA Dick, JJ Workman, JB Reeves III, L Al-Amoodi, Eds. p. 729–784. American Society of Agronomy, Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc.: Madison, Wisconsin, USA.

Martin PD, Malley DF, Manning G, Fuller L 2002. Determination of soil organic carbon and nitrogen at the field level using near-infrared spectroscopy. Canadian Journal of Soil Science 82: 413–422.

Martinez G, Vanderlinden K, Ordonez R, Muriel JL 2009. Can apparent electrical conductivity improve the spatial characterization of soil organic carbon? Vadose Zone Journal 8:586–593.

McBratney AB, Minasny B, Viscarra Rossel, R 2006. Spectral soil analysis and inference systems: A powerful combination for solving the soil data crisis. Geoderma 136:272–278.

McBratney AB, Webster R 1986. Choosing functions for semi-variograms and fitting them to sampling estimates. Journal of Soil Science 37:617–639.

McCarty GW, Reeves JB, Reeves VB, Follett RF, Kimble JM 2002. Mid-infrared and near-infrared diffuse reflectance spectroscopy for soil carbon measurement. Soil Science Society of America Journal 66:640–646.

McNeill SJ, Forester G, Giltrap D 2009. Spatial autocorrelation analysis of data for the soils CMS model. Landcare Research Contract Report: LC0910/003, 34p.

Meat & Wool 2009. Compendium of New Zealand Farm Facts. Meat & Wool New Zealand Economic Services, Wellington, 24p.

Metson AJ, Blakemore LC, Rhoades DA 1979. Methods for the determination of soil organic carbon: a review, and application to New Zealand soils. New Zealand Journal of Science 22: 205–228.

Minasny B, McBratney AB, Mendonca-Santos, ML, Odeh IOA, Guyon B 2006. Prediction and digital mapping of soil carbon storage in the Lower Namoi Valley. Australian Journal of Soil Research 44:233–244.

Mitra S, Wielopolski L, Tan H, Fallu-Labruyere A, Hennig W, Warburton WK. 2007. Concurrent measurement of individual gamma-ray spectra during and between fast neutron pulses. IEEE Transactions on Nuclear Science 54:192–196.

Miziolek AW, Palleschi V, Schechter I (Eds.) 2006. Laser-induced breakdown spectroscopy: fundamentals and applications. Cambridge University Press, UK.

Moffat AM, Papale D, Reichstein M, Hollinger DY, Richardson AD, Barr AG, Beckstein C, Braswell BH, Churkina G, Desai AR, Falge E, Gove JH, Heimann M, Hui D, Jarvis AJ, Kattge J, Noormets A, Stauch VJ. 2007. Comprehensive comparison of gap-filling techniques for eddy covariance net carbon fluxes. Agricultural and Forest Meteorology 147:209–232.

Mouazen AM, De Baerdemaeker J, Ramon H 2005. Towards development of on-line soil moisture content sensor using a fibre-type NIR spectrophotometer. Soil and Tillage Research 80:171–183.

Mouazen AM, Maleki MR, de Baerdemaeker J, Ramon H 2007. On-line measurement of some selected soil properties using a VIS-NIR sensor. Soil and Tillage Research 93:13–27.

Mudge P 2009. Annual carbon balance of an intensively grazed pasture: magnitude and controls, Unpublished MSc Thesis, lodged in the Library, University of Waikato, Hamilton.

Nieveen JP, Campbell DI;, Schipper LA, Blair I 2005. Carbon exchange of grazed pasture on a drained peat soil. Global Change Biology 11:607–618.

Oliver GR, Beets PN, Garrett LG, Pearce SH, Kimberly MO, Ford-Robertson JB, Robertson KA 2004. Variation in soil carbon in pine plantations and implications for monitoring soil carbon stocks in relation to land-use change and forest site management in New Zealand. Forest Ecology and Management 203:283–295.

Oliver MA, Webster R 1991. How geostatistics can help you. Soil Use and Management 7:206–217.

Oncley S, Foken T, Vogt R, Kohsiek W, DeBruin H, Bernhofer C, Christen A, Gorsel E, Grantz D, Feigenwinter C, Lehner I, Liebethal C, Liu H, Mauder M, Pitacco A, Ribeiro L, Weidinger T 2007. The Energy Balance Experiment EBEX-2000. Part I: overview and energy balance. Boundary-Layer Meteorology 123: 1–28.

Palmer CJ 2003. Techniques to measure and strategies to monitor forest soil carbon. In Kimble JM, Heath LS, Birdsey RA, Lal R, Eds., The Potential of U.S. Forest Soils to Sequester Carbon and Mitigate the Greenhouse Effect. CRC Press, Boca Raton, p. 73–90.

Papale D, Reichstein M, Aubinet M, Canfora E, Bernhofer C, Kutsch W, Longdoz B, Rambal S, Valentini R, Vesala T, Yakir,D. 2006. Towards a standardized processing of net ecosystem exchange measured with eddy covariance technique: algorithms and uncertainty estimation. Biogeosciences, 3:571–583.

Parfitt RL, Percival HJ, Dahlgren HA, Hill LF. 1997. Soil solution chemistry under pasture and radiate pine in New Zealand. Plant and Soil 191:279–290.

Pirie A, Singh B, Islam K 2005. Ultra-violet, visible, near-infrared, and mid-infrared diffuse reflectance spectroscopic techniques to predict several soil properties. Australian Journal of Soil Research 43:713–721

Reeves JB III, McCarty GW 2001. Quantitative analysis of agricultural soils using near infrared reflectance spectroscopy and a fibre optic probe. Journal of Near Infrared Spectroscopy 9:25–34.

Reeves JB III, McCarty GW, Hively WD 2008. Mid-versus near-infrared reflectance spectroscopy for on-site determination of soil carbon. Proceedings of the 1st Global Workshop on High Resolution Digital Soil Sensing and Mapping, held under the auspices of the International Union of Soil Sciences (IUSS), Working Group on Digital Soil Mapping, Sydney, Australia, 5–8 February 2008. CDROM.

Reeves III J, McCarty G, Mimmo T 2002. The potential of diffuse reflectance spectroscopy for the determination of carbon inventories in soils. Environmental Pollution 116:S277–S284.

Reichstein M, Falge E, Baldocchi D, Papale D, Aubinet M, Berbigier P, Bernhofer C, Buchmann N, Gilmanov T, Granier A, Grünwald T, Havránková K, Ilvesniemi H, Janous D, Knohl A, Laurila T, Lohila A, Loustau A, Matteucci G, Meyers T, Miglietta F, Ourcival J, Pumpanen J, Rambal S, Rotenberg E, Sanz M, Tenhunen J, Seufert G, Vaccari F, Vesala T, Yakir D, Valentini R 2005. On the separation of net ecosystem exchange into assimilation and ecosystem respiration: review and improved algorithm. Global Change Biology 11:1424–1439.

Ross DJ, Tate KR, Scott NA, Feltham CW 1999. Land-use change: Effects on soil carbon, nitrogen and phosphorus pools and fluxes in three contrasting ecosystems. Soil Biology and Biochemistry 31:803–813.

Ross DJ, Tate KR, Scott NA, Feltham CW 2002. Afforestation of pastures with *Pinus radiata* influences soil carbon and nitrogen pools and mineralisation and microbial properties. Australian Journal of Soil Research 40:1303–1318.

Ruark GA, Zarnoch SJ 1992. Soil carbon, nitrogen, and fine root biomass sampling in a pine stand. Soil Science Society of America Journal 56:1945–1956.

Russel CA 2003. Sample preparation and prediction of soil organic matter by near infra-red reflectance spectroscopy. Communications in Soil Science and Plant Analysis 34:1557–1572.

Rutledge S, Campbel, DI, Baldocchi D, Schipper LA 2010. Photodegradation leads to increased CO_2 losses from terrestrial organic matter. Global Change Biology (in press).

Saby NPA, Bellamy PH, Morvan X, Arrouays D, Jones RA, Verheijen FGA, Kibblewhite MG, Verdoodt A, Berényi Üveges J, Freudenschuß A, Simota C 2008. Will European soil-monitoring networks be able to detect changes in topsoil organic carbon content? Global Change Biology 14:2432–2442.

Schipper LA, Baisden WT, Parfitt RL, Ross C, Claydon JJ, Arnold G 2007. Large losses of soil C and N from soil profiles under pasture in New Zealand during the past 20 years. Global Change Biology13:1138–1144.

Schipper LA, McLeod,M 2002. Subsidence rates and carbon loss in peat soils following conversion to pasture in the Waikato Region, New Zealand. Soil Use and Management. 18: 91–93.

Schipper LA, Sparling GP 2000. Performance of soil condition indicators across taxonomic groups and land uses. Soil Science Society of America Journal 64:300–311.

Scott NA, Tate KR, Ford-Robertson JR, Giltrap DJ, Tattersall Smith C. 1999. Soil carbon storage in plantation forest and pastures: Land-use change implications. Tellus 51B:326–335.

Shonk JL, Gaultney LD, Schultze DG, Van Scoyoc GE 1991. Spectroscopic sensing of soil organic matter content. Transactions of the ASAE 34:1978–1984.

Shepherd KD, Walsh MG 2002. Development of reflectance spectral libraries for characterization of soil properties. Soil Science Society of America Journal 66:988–998.

Sleutel S, de Neve S, Singier B, Hofman G. 2007. Quantification of organic carbon in soils: A comparison of methodologies and assessment of the carbon content of organic matter. Communications in Soil Science & Plant Analysis 38:2647–2657.

Smith P, Chapman SJ, Scott WA, Black HIJ, Wattenbach M, Milne R, Campbell CD, Lilly A, Ostle N, Levy PE, Lumsdon DG, Millard P, Towers W, Zaehle S, Smith JU 2007. Climate change cannot be entirely responsible for soil carbon loss observed in England and Wales, 1978-2003. Global Change Biology 13:2605–2609.

Soon YK, Abboud S 1991. A comparison of some methods for soil organic carbon determination. Communications in Soil Science & Plant Analysis 22: 943–954.

Sowerby BD 2009. Nuclear techniques for the on-line bulk analysis of carbon in coal-fired power stations. Applied Radiation and Isotopes 67:1638–1643.

Sowerby BD, Tickner JR. 2007. Recent advances in fast neutron radiography for cargo inspection. Nuclear Instruments and Methods in Physics Research A580:799–802.

Sparling GP, Shepherd TP, Schipper LA 2000. Topsoil characteristics of three contrasting New Zealand soils under long-term land uses. New Zealand Journal of Agricultural Research 43:569–583.

Sterner RW, Elser JJ 2002. Ecological Stoichiometry: The Biology of Elements from Molecules to the Biosphere. Princeton University Press, Princeton, NJ. 584 p.

Stolbovoy V, Montanarella L, Filippi N, Jones A, Gallego J, Grassi G 2007. Soil sampling protocol to certify the changes of organic carbon stock in mineral soil of the European Union. Version 2. EUR21576 EN/2. 56 pp. Office for Official Publications of the European Communities, Luxembourg. ISBN: 978-92-79-05379-5.

Sudduth RS, Kitchen NR, Sadler EJ, Drummond ST, Myers DB 2008. VNIR spectroscopy for estimation of within-field variability on soil properties. Proceedings of the 1st Global Workshop on High Resolution Digital Soil Sensing and Mapping, held under the auspices of the International Union of Soil Sciences (IUSS), Working Group on Digital Soil Mapping, Sydney, Australia, 5–8 February 2008. CDROM.

Sudduth KA, Kitchen NR, Wiebold WJ, Batchelor WD, Bollero GA, Bullock DG, Clay DE, Palm HL, Pierce FJ, Schuler RT, Thelen KD 2005. Relating apparent electrical conductivity to soil properties across the north-central USA. Computers and Electronics in Agriculture 46:263–283.

Tang J, Baldocchi DD, Qi Y, Xu L 2003. Assessing soil CO_2 eflux using continuous measurements of CO_2 profiles in soils with small solid-state sensors. Agricultural and Forest Meteorology 118:207–220.

Tate KR, Wilde RH, Giltrap DJ, Baisden WT, Saggar S, Trustrum NA, Scott NA, Barton JP 2005. Soil organic carbon stocks and flows in New Zealand: System development, measurement and modelling. Canadian Journal of Soil Science 85:481–489.

Ulmer MG, Swenson LJ, Patterson DD, Dahnke WC 1992. Organic carbon determination by the Walkley-Black, Udy dye, and dry combustion methods for selected North Dakota soils. Communications in Soil Science & Plant Analysis 23:417–429.

Underwood MC, Dyos CJ. 1986. Inelastic neutron scattering reactions in fluid saturated rock as exploited in oil well logging. International Journal of Radiation Applications and Instrumentation. Part A. Applied Radiation and Isotopes 37:475–481.

van Gorsel E, Delpierre N, Leuning R, Black A, Munger JW, Wofsy S, Aubinet M, Feigenwinter C, Beringer J, Bonal D, Chen B, Chen J, Clement R, Davis KJ, Desai AR, Dragoni D, Etzold S, Grünwald T, Gu L, Heinesch B, Hutyra LR, Jans WWP, Kutsch W, Law BE, Leclerc MY, Mammarella I, Montagnani L, Noormets A, Rebmann C, Wharton S 2009. Estimating nocturnal ecosystem respiration from the vertical turbulent flux and change in storage of CO_2. Agricultural and Forest Meteorology 149:1919–1930.

Viscarra Rossel RA 2008. ParLes: software for chemometric analysis of spectroscopic data. Chemometrics and Intelligent Laboratory Systems 90:72–83.

Viscarra Rossel RA 2009. The Soil Spectroscopy Group and the development of a global soil spectral library. NIR News 20 (4):17–18.

Viscarra Rossel RA, McBratney AB 1998. Soil chemical analytical accuracy and costs: implications from precision agriculture. Australian Journal of Experimental Agriculture 38:765–775.

Viscarra Rossel RA, Walvoort DJJ, McBratney AB, Janik LJ, Skjemstad JO 2006. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. Geoderma 131:59–75.

Wallace D 2010.University of Waikato, Hamilton (in preparation).

Webster R 1985. Quantitative Spatial Analysis of Soil in the Field. Advances in Soil Science 3:1–69.

Webster R, Oliver MA 2007. Geostatistics for environmental scientists. 2nd Ed. John Wiley and Sons, UK.

Westman CJ, Hytönen J, Wall A 2006. Loss-on-ignition in the determination of pools of organic carbon in soils of forests and afforested arable fields. Communications in Soil Science and Plant Analysis 37:1059–1075.

Wetterlind J, Stenberg B, Soderstrom M 2008. The use of near infrared (NIR) spectroscopy to improve soil mapping at the farm scale. Precision Agriculture 9:57–69.

Wielopolski L, Hendrey G. 2002. US Patent 20020150194. Method and device for non-invasive soil carbon content and distribution measurements.

Wielopolski L, Hendrey G, Johnsen KH, Mitra S, Prior SA, Rogers HH, Torbert HA. 2008a. Nondestructive system for analyzing carbon in the soil. Soil Science Society of America Journal 72:1269–1277.

Wielopolski L, Mitra S, Doron O. 2008b. Non-carbon-based compact shadow shielding for 14 MeV neutrons. Journal of Radioanalytical And Nuclear Chemistry 276:179–182.

Wielopolski L, Orion I, Hendrey G, Rogers H. 2000. Soil carbon measurements using inelastic neutron scattering. IEEE Transactions on Nuclear Science 47:914–917.

Wielopolski L, Song Z, Orion I, Hanson AL, Hendrey G. 2005. Basic considerations for Monte Carlo calculations in soil. Applied Radiation and Isotopes 62:97–107.

Williams PC 2001. Implementation of near-infrared technology. In Near-infrared technology in the agriculture and food industries. P Williams, K Norris, Eds. p. 145–169, American Association of Cereal Chemist, Inc., Minnesota, USA.

Wilson K, Goldstein A, Falge E, Aubinet M, Baldocchi D, Berbigier P, Ceulemans R, Dolman H, Field C, Grelle A, Ibrom A, Law B, Kowalski A, Meyers T, Moncrieff J, Monson R, Oechel W, Tenhunen J, Valentini R, Verma S 2002. Energy balance closure at FLUXNET sites. Agricultural and Forest Meteorology 113:223–243.

Wisbrun R, Schechter I, Niessner R, Schroeder H, Kompa KL 1994. Detector for trace elemental analysis of solid environmental samples by laser plasma spectroscopy. Analytical Chemistry 66:2964–2975.

Wu C, Wu J, Luo Y, Zhang L, DeGloria SD 2009. Spatial prediction of soil organic matter content using cokriging with remotely sensed data. Soil Science Society America 73 4:1202–1208.

Yanai RD, Stehman SV, Arthur MA, Prescott CE, Friedland AJ, Siccama TG, Binkley D 2003. Detecting change in forest floor carbon. Soil Science Society of America Journal 67: 1583–1593.