Proximal sensing for soil carbon accounting

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Abstract. Maintaining or increasing soil organic carbon (C) is important for securing food production, and for mitigating greenhouse gas (GHG) emissions, climate change and land degradation. Some land management practices in cropping, grazing, horticultural and mixed farming systems can be used to increase organic C in soil, but to assess their effectiveness, we need accurate and cost-efficient methods for measuring and monitoring the change. To determine the stock of organic C in soil, one

5 needs measurements of soil organic C concentration, bulk density and gravel content, but using conventional laboratory-based analytical methods is expensive. Our aim here is to review the current state of proximal sensing for the development of new soil C accounting methods for emissions reporting and in emissions reduction schemes. We evaluated sensing techniques in terms of their rapidity, cost, accuracy, safety, readiness and their state of development. The most suitable technique for measuring soil organic C concentrations appears to be vis–NIR spectroscopy and for bulk density active gamma-ray attenuation. Sensors for

10 measuring gravel have not been developed, but an interim solution with rapid wet-sieving and automated measurement appears useful. Field-deployable, multi-sensor systems are needed for cost-efficient soil C accounting. Proximal sensing can be used for soil organic C accounting, but the methods need to be standardised and procedural guidelines need to be developed to ensure proficient measurement and accurate reporting and verification. This is particularly important if the schemes use financial incentives for landholders to adopt management practices to sequester soil organic C. We list and discuss the requirements for

15 the development of new soil C accounting methods that are based on proximal sensing, including requirements for recording, verification and auditing.

1 Introduction

Soil is the largest terrestrial store of organic carbon (C) (Batjes, 1996). Soil organic C is an indicator of soil quality because it affects nutrient cycling, aggregate stability, structure, water infiltration and vulnerability to erosion (Tiessen et al., 1994;

20 Lal, 2013). Management of soil organic C is central to maintaining soil health, ensuring food security and mitigating climate change (Lal, 2004, 2016b). This is why stabilizing or increasing the stocks of organic C in soil, through the identification and implementation of locally appropriate agronomic and environmental management practices, has become a political imperative (ITPS, 2015).

Maintaining or increasing soil organic C stocks is an important consideration in addressing land degradation, which was

25 recognized under the United Nations Sustainable Development Goal 15, sustainable development of life on land (Nations, 2015). Used in concert with data on land cover and land productivity, soil organic C stock will be the initial metric used to

quantify Indicator 15.3.1, the 'Proportion of land that is degraded over total land area' (Decision 22/COP.11, (UNCCD, 2013)). The United Nations Convention to Combat Desertification (UNCCD) will use soil organic C stock as one of its indicators to monitor progress towards achieving land degradation neutrality (Orr et al., 2017).

Sequestration of soil organic C has been considered as a possible solution to mitigate climate change (Lal, 2016a). Both
5 policy-makers and scientists expect a large potential for sequestration in agricultural soils due to the large historical losses experienced by agroecosystems (Cole et al., 1997). Studies over several decades have demonstrated that improved land use and management can help to sequester organic C in soil and to reduce greenhouse gas (GHG) emissions (Smith et al., 2008; Ogle et al., 2005; Poeplau and Don, 2015). This opportunity was the motivation behind the '4 pour 1000' initiative, launched at the COP21 meeting in Paris, which aims to increase global soil organic matter stocks by 4 parts per 1000 (or 0.4 %) per year as
10 a compensation for global GHG emissions from anthropogenic sources. Engagement in '4 pour 1000' involves stakeholders voluntarily committing to implementing farming practices that maintain or enhance soil organic C stocks in agricultural soil and to preserving C-rich soil (Lal, 2016a). In addition to increasing soil organic C, the initiative provides an opportunity to implement transparent and credible protocols and methods for C accounting, monitoring, reporting and verification that are compatible with national GHG inventory procedures (Chambers et al., 2016).

15 Although there is good potential for changes in agricultural land use and management to sequester soil organic C (Machmuller et al., 2015), their implementation requires efficient new methods for measurement and monitoring of the C stocks. To determine baselines and to assess the success of management practices for sequestering soil organic C, the variability in soil organic C stock needs to be quantified in both space (laterally across the landscape and vertically down the soil profile) and time. Changes in soil organic C stock that are due to changes in land use and management or climate, occur slowly (*e.g.* compared to
20 changes in biomass C), and must be measured over longer periods of more than 5 to 10 years (Smith, 2004). Changes are also likely to be small relative to the large C stock that is present in the soil, which is highly variable. New measurement methods are also needed to delineate the potential benefits and liabilities of establishing soil C projects and C accounting activities (IPCC, 2007). Methods for soil organic C sampling and analysis must be accurate, practical, inexpensive and cost-efficient, and when used for monitoring, they must consider the minimum detectable difference (Batjes and van Wesemael, 2015). Additionally, the
25 new methods should accurately quantify the magnitude and uncertainty of soil C change that could be attained by introducing defined agricultural management practices (Paustian et al., 2016).

Quantification of soil organic C stock change requires the measurement of soil organic C concentration, bulk density and gravel content over time. Conventional methods to measure soil organic C stocks involve field soil sampling, followed by sample preparation and laboratory analysis. For determination of soil C concentration, dry combustion (e.g. Nelson and Som-
30 mers, 1996) is the benchmark method because of the vast experience acquired in using it, and because of its accuracy. For bulk density, conventional measurements are made using the volumetric ring method, or the clod method for soil containing a lot of rock fragments (Blake and Hartge, 1986). For gravel content, the conventional method involves manual separation of gravel from the fine earth fraction (McKenzie et al., 2002). These methods are time consuming and expensive, particularly for measuring at depth.

Sensors can provide rapid, accurate, inexpensive, non-destructive measurements of soil organic C stocks and other soil properties. Their measurements are accurate and cost-efficient (Viscarra Rossel, R. A. and Brus, 2018). While there are several reviews on the use of sensors for measuring soil organic C concentration (e.g Bellon-Maurel and McBratney, 2011; Izaurralde et al., 2013; Reeves et al., 2012; Stenberg et al., 2010; Viscarra Rossel, R.A. et al., 2011), few studies report on sensors for

5   measuring bulk density or gravel (Lobsey and Viscarra Rossel, 2016; Fouinat et al., 2017), or report on the integration of sensing methods for the purpose of soil organic C accounting. Our objective here is to review the current state of proximal sensing for soil C accounting. Specifically, our aims were to review: (1) soil C accounting for emissions reporting and in emissions reduction schemes, (2) the current state of proximal sensing for measuring soil organic C stocks and monitoring its change and (3) the use of proximal sensors in the development of new soil organic C accounting methodologies.

10   ## 2   Soil organic carbon accounting

Improved measurement methods to account for change in soil organic C stocks are relevant to two key areas of national GHG policy and reporting: international emissions reporting obligations under the United Nations Framework Convention on Climate Change (UNFCCC) (*i.e.* national inventory reporting); and domestic schemes that seek to reduce or offset emissions through a range of activities, including improved land management practices.

15   The UNFCCC, and later the Kyoto Protocol, set up a system of national communications and national inventory reporting to be compiled by Parties and published by the UNFCCC. To estimate GHG emissions and to monitor changes in C stocks, including soil organic C, the International Panel on Climate Change (IPCC) developed a tiered methodology that relates data on land use and management activities to emissions and storage factors to estimate fluxes from the activities (IPCC, 2006). The three-tiered approach depends on the scale, capability and availability of data. Where country-specific data are currently

20   lacking, a global default (Tier 1) approach can be used. Tier 1 methods use default equations with data from globally available land cover classes and global defaults for reference soil organic C stocks, change factors and emission factors. Tier 2 methods include nationally derived land cover classes and data for reference soil organic C stocks, change factors and emission factors specific to local conditions. Tier 3 methods might include national data from the integration of ongoing ground-measurement programs, earth observation and mechanistic models. Tier 2 and Tier 3 approaches are thought to produce estimates with

25   reduced uncertainty.

Soil monitoring networks at the national scale can provide information on changes in soil organic C stocks relative to a defined baseline through repeated measurements across a defined network of sites over time. This can provide a set of observations that represent the variation in climate, soil or land use management at a national scale (Batjes and van Wesemael, 2015). However, there are trade-offs between the ability to detect change and the size of the network and the number of

30   measurements required, which is directly related to cost (Conant and Paustian, 2002). Conventional analytical methods for soil monitoring are likely to be cost-inefficient. Sensing on the other hand can be used to cost-efficiently measure soil organic C stocks, to estimate baselines for national inventory reporting and monitoring (e.g. Viscarra Rossel, R.A. et al., 2014).

Accurate and cost-efficient methods to quantify changes in C stocks are also needed for a growing number of national and sub-national emissions reduction and C accounting and trading schemes that incorporate mitigation from soil organic C sequestration following changes in land management (ICAP, 2017). In this context, how to measure, report on and verify the impacts of mitigation actions is important for decision-makers because access to financial payments depends on the ability to

5 demonstrate the sequestration or emissions reductions that might be attained. To date, however, relatively few methodologies have been developed for quantifying change in soil organic C stock from changes in land management. Those that have been developed are based on approaches that use either direct measurement or mechanistic modelling (Table 1). Under such schemes, endorsed methodologies set out the rules for estimating emissions reductions or C offsets from different activities. Proponents that change some permissible aspect of their land management, which leads to increases in C stocks or reductions in emissions,

10 can use these methods to earn payments. Information from these activities can then also contribute to national inventories.

For example, the Australian government established the Emissions Reduction Fund (ERF) to encourage the adoption of management strategies that result in either the reduction of GHG emissions or the sequestration of atmospheric CO_2. The ERF is enacted through the Carbon Credits (Carbon Farming Initiative) Act 2011 (CFI Act), and under it, carbon credits can be earned by anyone (*e.g.* landholders, businesses and community groups) undertaking a project that aims to reduce emissions

15 or sequester C (Australian Government, 2011). Projects must comply with approved methods that define the activities that are eligible to earn C credits, how the abatement is measured, verified and reported. These methods[1] must comply with the Off-sets Integrity Standards described in the CFI Act, which require that any C abatement generated through the implementation of a method can be used to meet Australia's climate change targets under the Kyoto Protocol or other international agreements. Legislation ensures that only authentic emissions reductions are credited; that the methods used in the ERF are eligible,

20 evidence-based (supported by relevant scientific results), measurable, verifiable, conservative, additional, and permanent (25 or 100 years); and that there is no leakage. Thamo and Pannell (2016) discuss these requirements and the challenges they pose for development of policy for soil C sequestration. Once a method is implemented by a proponent it can be used to produce Australian Carbon Credit Units (ACCUs). A single ACCU corresponds to sequestration or emission avoidance of 1 tonne of CO_2-equivalent, which proponents can sell to generate income.

25 The Australian ERF currently has two soil C sequestration methods: (i) 'Sequestering carbon in soils in grazing systems' (Australian Government, 2014) that aims to quantify changes in soil organic C stocks over time using conventional soil composite sampling and laboratory analysis; and (ii) 'Estimating sequestration of carbon in soil using default values' (Australian Government, 2015) that uses default values for the rates of soil C change from different activities, predicted with the Full Carbon Accounting Model (FullCAM), which is used in the Australian National Greenhouse Gas Inventory. A new method under

30 the Australian ERF, currently awaiting ministerial approval, will: allow the use of covariates and prior information to inform the sampling design; include additional land management activities; and allow the use soil sensors — visible–near infrared (vis–NIR) and mid infrared (mid-IR) spectrometers and gamma attenuation densitometers — to measure and monitor changes in soil organic C stocks (DoEE, 2018). This will be the first methodology in the world to legislate sensing for monitoring and accounting of soil organic C stocks.

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[1]www.environment.gov.au/climate-change/emissions-reduction-fund/methods

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Table 1. Examples of methodologies for estimating change in soil organic C for mitigation actions related to changed management of agricultural land. Emissions Reduction Fund (ERF); Climate Change and Emissions Management Act (CCEMA); Alberta Offset System (AOS); Climate Policy Framework (CPF)

Country	Policy setting	Developer	Methodology	Activity	Approach
Australia	ERF	Australian Government	Sequestering carbon in soils in grazing systems (Australian Government, 2014)	Changed management of grassland	Direct measurement
Australia	ERF	Australian Government	Estimating sequestration of carbon in soil using default values (Australian Government, 2015)	Changed management of cropland	Modelling
Canada	CCEMA, AOS	Government of Alberta	Conservation Cropping Protocol[1]	Changed management of cropland	Sequestration coefficients from measurement and modelling
Canada	No monetization of soil C offsets	Government of Saskatchewan and other stakeholders	Prairie soil carbon balance project[2,3]	Changed management of cropland and grassland	Modelling and direct measurement
Mexico	CPF	Climate Action Reserve	Grassland Project Protocol[4]	Avoided conversion of grassland to cropland	Emissions factors from modelling

[1] http://aep.alberta.ca/climate-change/guidelines-legislation/specified-gas-emitters-regulation/documents/ProtocolConservationCropping-Apr2012.pdf

[2] http://www.usask.ca/soilsncrops/conference-proceedings/previous_years/Files/cc2000/docs/posters/018_post.PDF

[3] http://ssca.ca/images/new/PSCB.pdf

[4] http://www.climateactionreserve.org/how/protocols/grassland/

3 Soil sampling, measurement and estimation of soil organic C stocks

3.1 Measuring soil organic C stocks

Effective accounting of changes in soil organic C stocks requires measurement of the stocks and their uncertainty for a defined baseline and over the monitoring period. Internationally, the default method to determine soil organic C stock (C_s) for the accounting of change is to multiply measurements of soil organic C concentration, bulk density and gravel content at a fixed depth of 0–30 cm, and to report the stock as a mass of carbon per unit area in tonnes of organic C per hectare (IPCC, 1997):

$$C_s = C_m \times \rho \times (1 - \frac{g}{100}) \times d \qquad (1)$$

where C_m is the mass of soil organic C in the soil (%), ρ is the soil bulk density (g cm^{-3}), g is the gravel content (%) and d is the thickness of the layer (cm). Our definition of soil organic C used here extends that of the IPCC Guidelines (IPCC, 2006), which address the measurement of soil organic C in mineral soil in the 0–30 cm layer, by extending to deeper soil layers. Based on typical rooting depths found in agricultural crops and pastures, and the capacity of deeper soil horizons to sequester

relatively large amounts of soil organic C, there is evidence to suggest that measurements should extend to deeper layers (e.g. Fan et al., 2016; Lorenz and Lal, 2005; Viscarra Rossel, R.A. et al., 2016b).

Conventionally, measurement of soil organic C stocks involves soil sampling (see section 3.2), followed by sample preparation and laboratory analysis. For the analytical determination of soil C concentration, sample preparation typically entails

5   drying, crushing, grinding, sieving, sub-sampling, quantification of the sample's water content and further fine-grinding for dry combustion analysis (e.g. Nelson and Sommers, 1996; Rayment and Lyons, 2011). Conventional measurements of soil bulk density typically involve using the volumetric ring method, where a pit is dug and a metal core of known volume is driven into the soil at the fixed depth. The bulk density of the soil is then determined by dividing the oven-dry soil mass of the sample by the volume of the core (Blake and Hartge, 1986). Alternatively, the clod method (e.g. Hirmas and Furquim, 2006; Cunningham

10   and Matelski, 1968; Muller and Hamilton, 1992) has been used for soil with abundant rock fragments, where clods of soil are sampled, sealed (*e.g.* with paraffin), and the volume of the sample is determined by its displacement of water in a vessel. Gravel content is conventionally measured by breaking the soil cores into specific depth intervals, drying in an oven, crushing the soil with a mortar and pestle and then sieving to separate the fine earth ($\leq$2 mm) fraction from the gravel.

Equation (1) can be used to quantify and report the change in soil organic C stocks at fixed depth intervals. However,

15   this method can systematically overestimate or underestimate C stocks if bulk densities increase or decrease, respectively, from changes in land use or land management practices (*e.g.* changes in cultivation). Where bulk densities differ between management practices or over time periods, more accurate estimates of the C stock and its change can be derived using measures of cumulative or equivalent soil masses per unit area (Wendt and Hauser, 2013). Various studies have recognized the importance of this approach, which also reduces the effect of depth of sampling errors (Ellert et al., 2001; Gifford and

20   Roderick, 2003; Lee et al., 2009; VandenBygaart and Angers, 2006; Wendt and Hauser, 2013). Both the current (Table 1; Australian Government, 2014) and the new (Australian Government, 2018) direct measurement method under the Australian ERF use an equivalent soil mass (ESM) approach to quantify soil organic C stock change.

3.2   Soil sampling and estimation

Before measuring the soil organic C stocks (Equation 1), sampling locations must be determined. Methods to select sampling

25   locations include probability sampling and non-probability sampling, which result in to two widely used sampling philosophies: design- and model-based sampling (Brus and DeGruijter, 1993; de Gruijter et al., 2006; Papritz and Webster, 1995). In design-based sampling, the randomness of an observation originates from the random selection of sampling sites, whereas in model-based sampling, randomness comes from a random term in the model of the spatial variation, which is added to the model because our knowledge of the spatial variation is imperfect. Probability sampling is therefore a requirement for design-based

30   sampling but not for model-based.

Choosing which approach to use depends largely on the purpose (Brus and de Gruijter, 1997). For instance, if one needs estimates of the mean or total soil organic C stock and their accuracy over a given area, whose quality is not dependent on the correctness of modelling assumptions, then design-based sampling might be most suitable. If the aim is to produce a map of the soil organic C stock over the area, then model-based sampling will be preferable. However, because the design-based

approach can also be used for mapping, and the model-based approach can be used for estimation of means or total C stocks, the choice of approach to use can be difficult. Viscarra Rossel, R.A. et al. (2016b) demonstrated the use of probability sampling, which allowed design-based, model-assisted and model-based estimation of the total soil organic C stock across 2837 ha of grazing land in Australia. Spectroscopic and active gamma attenuation sensors were used for estimating soil organic C stocks

5 and their accuracy in the 0–10 cm, 0–30 cm and 0–100 cm layers, and for mapping the stocks in each layer across the study area. Although the design-based, model-assisted and model-based estimates of the total soil organic C stocks were similar, the variances of the model-based estimates were shown to be smaller than those of the design-based methods. The authors noted that the advantage of the design-based and model-assisted methods, unlike the model-based approach, was that their estimates of the baseline soil organic C stocks and their variances did not rely on the assumptions of a model and that although the model-

10 based approach produced the smallest variance of the predicted total soil organic C stocks, the results cannot be generalized to other sample sizes and types of sampling designs. We propose that whatever the method used, careful consideration of the sampling design for the estimation of both baseline soil organic C stocks and for monitoring should be used. Further discussion on the advantages and disadvantages of the sampling approaches can be found in de Gruijter et al. (2006).

4 Sensors for soil organic C accounting

15 We reviewed the literature on proximal soil sensing (see Viscarra Rossel, R.A. et al. (2011) for a definition), to learn about the sensors that can be used to measure the soil properties needed to determine the organic C stock in soil: organic C concentration, bulk density and gravel content (Equation 1). Table 2 provides a summary of our assessment of each sensor technology in terms of their rapidity, accuracy, cost and safety, their readiness for field-deployment and their stage of research and development. Below we also evaluate and report on their suitability for soil organic C accounting and for monitoring its change.

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Table 2. Assessment of relevant proximal sensing technologies against the review criteria in terms of readiness to underpin a carbon accounting methodology. The sensing methods are visible–near infrared (vis–NIR) and mid infrared (mid-IR) diffuse reflectance spectroscopy; laser induced breakdown spectroscopy (LIBS); inelastic neutron scattering (INS); active gamma-ray attenuation (AGA); gamma- and X-ray computed tomography (CT). A ? indicates unknown or not sufficiently developed; Cost: $AU 0–40,000; $$AU 40,000–100,000; $$$AU 100,000+; Active source refers to whether the source of energy used by the sensor is radioactive.

Method	Rapid?	Accurate?	Sensor cost?	Developed?	Field use?	Active source?
SOC						
Colour	yes	no	$	yes	yes	no
vis–NIR	yes	yes	$–$$	yes	yes	no
mid-IR	yes	yes	$$	yes	?	no
LIBS	yes	yes	$$–$$$	yes	?	no
INS	yes	yes	$$$	no	yes	yes
Bulk density						
vis–NIR, mid-IR	yes	no	$–$$	yes	yes	no
AGA transmission	yes	yes	$	yes	yes	yes
AGA backscatter	yes	no	$	yes	yes	yes
CT	no	?	$$$	no	no	yes
Gravel						
Wet-sieve and image analysis	yes	yes	$	no	yes	no
CT	no	?	$$$	no	no	yes

4.1 Sensing of soil organic C concentrations

4.1.1 Soil colour

Because soil organic C content is known to influence the colour of a soil, it is possible to use colour to estimate the organic C content (e.g. Viscarra Rossel, R.A. et al., 2006a; Ibañez Asensio et al., 2013; Liles et al., 2013), for example, using digital cameras (Viscarra Rossel, R.A. et al., 2008a) or mobile phone applications (e.g. Aitkenhead et al., 2016; Stiglitz et al., 2017). While colour has been shown to adequately predict soil organic matter content for some soil types and at regional or larger scales (e.g. Ibañez Asensio et al., 2013; Liles et al., 2013; Viscarra Rossel, R.A. et al., 2008a), a limitation is that it can be difficult to use colour to accurately estimate the soil organic C content of soil types with inherently small C concentrations, and at field–farm scales.

4.1.2 Soil visible, near- and mid-infrared spectroscopy

Spectroscopic methods characterise soil organic C according to absorptions at specific wavelengths in the given spectral region. Visible and infrared spectroscopic techniques are highly sensitive to both the organic and inorganic components of soil, making their use in the agricultural and environmental sciences particularly relevant. Absorptions in the visible (vis: 400–700 nm)

5   portion of the electromagnetic, are due to electronic transitions and are useful for characterising organic matter in soil as well as iron-oxide mineralogy (Sherman and Waite, 1985). Absorptions in the near infrared (NIR: 700–2500 nm) correspond to overtones and combinations of fundamental absorptions that occur in the mid-infrared region (mid-IR: 2500 and 25 000 nm (Williams and Norris, 2001). As a consequence, absorptions in the NIR range are weaker and less distinctive compared to those in the mid-IR. It is useful to combine the vis and NIR ranges as each provides complementary information on soil. Instrument

10 manufacturers have recognised this and many provide spectrometers that measure the vis–NIR range.

Visible–NIR spectroscopy has been used successfully to predict soil organic C concentration, even under field conditions, but in the latter case using a method for correcting or removing the effects of soil water on the vis–NIR spectra (Ji et al., 2015; Minasny et al., 2011). Mid-IR has also been used used to accurately predict soil organic C. However, mid-IR spectroscopy has been moslty used in the laboratory with measurements on oven- or air-dried and finely ground (typically 80–500 μm) soil

15 samples (Le Guillou et al., 2015; Reeves, 2010; Reeves et al., 2012). There are strong water absorptions in the mid-IR, which tend to either mask or deform absorptions due to other soil constituents, thus degrading the calibrations and predictions of soil organic C with mid-IR spectra. There are a number of reviews on the use of vis–NIR and mid-IR spectroscopy for predicting soil properties, including soil organic C concentrations (Bellon-Maurel and McBratney, 2011; Kuang et al., 2012; Soriano-Disla et al., 2014; Stenberg et al., 2010; Viscarra Rossel, R.A. et al., 2016a, 2006b). Readers are directed to those reviews for

20 further detail.

To predict soil organic C, the spectroscopic techniques described above require the development of an empirical model (or calibration) that relates the spectra to corresponding soil data analyzed with a reference analytical method such as dry combustion analysis. This data set, which holds the spectra, the soil analytical data and metadata is referred to as a spectral library. To be useful for site-specific predictions of soil organic C, the spectral library should contain data that represent the local

25 variability of soil organic C concentration. In section 5.2 below, we review the methods that can be used to derive spectroscopic calibrations for predictions of soil organic C concentrations.

4.1.3 Laser Induced Breakdown Spectroscopy (LIBS)

Laser Induced Breakdown Spectroscopy (LIBS) uses atomic emission spectroscopy. A focused laser pulse heats the surface of the soil sample to break the chemical bonds and vaporize it, generating a high temperature plasma on the surface of the sample.

30 The resulting emission spectrum is then analysed using a spectrometer covering a spectral range from 190 to 1000 nm. The different LIBS peaks from the analyzed samples can be used to identify the elemental composition of soil. Information on peak intensities can then be used to quantify the concentration of elements in the sample. Further details of the method are given by Cremers and Radziemski (2006).

Reports that use LIBS for measuring soil organic C generally use large benchtop instruments with prepared samples and calibrations to predict soil organic C from the measured elemental C (Bel'kov et al., 2008; Cremers et al., 2001; Ebinger et al., 2003; Knadel et al., 2017). These studies reported good correlations between LIBS measurements and those from dry combustion, particularly for soil with similar morphology (Cremers et al., 2001; Ebinger et al., 2003). They also reported that

5 LIBS measurements are rapid (less than a minute per sample).

The primary limitations of LIBS for soil C measurements are sample preparation, and whether the samples are representative because only a very small volume of soil is ablated for the measurement (Izaurralde et al., 2013). Chatterjee et al. (2009) suggested that either intact soil cores or discrete, pressed samples could be used for analysis, and that LIBS spectra could be recorded along a soil core or from each discrete sample. However, we have not found studies reporting on LIBS measurements

10 of soil organic C on intact cores, or cores under field conditions. There is potential to account for the spatial variability of organic C concentrations in soil profiles by the ability of LIBS to analyze and average multiple 'spots' (Chatterjee et al., 2009). However, we did not find any studies that demonstrate the use of LIBS on intact soil cores or samples that are under field condition.

Although there are some portable LIBS systems that are commercially available (Harmon et al., 2005), there are few reports

15 on their use for measuring soil organic C. Izaurralde et al. (2013) used 'SUV-portable' LIBS equipment for field measurements of soil organic C, but pre-processing, including breaking up cores and pelletising sub-samples in a hydraulic press, was required before measurements. Although the study mentioned the potential for such equipment to measure intact soil cores under field conditions (wet), albeit with reduced accuracy, this was only speculation.

4.1.4 Inelastic Neutron Scattering (INS)

20 Inelastic Neutron Scattering (INS) involves spectroscopy of gamma rays induced by fast- and thermal-neutrons interacting with the nuclei of the elements in soil. Fast neutrons, generated by a neutron generator, penetrate the soil and stimulate gamma-rays that are then detected by an array of scintillation detectors such as NaI. Peak areas in the measured spectra are proportional to the elemental composition of the soil. Using information on the peak intensities (counts) of the measured spectra and an established calibration, the results are reported immediately in units of g C m^{-2} (Wielopolski et al., 2008).

25 The suggested benefits of INS include the ability to interrogate large volumes of soil over a relatively large footprint and the ability to measure to a depth of approximately 30–50 cm (Chatterjee et al., 2009). Thus there is good potential for using it to non-invasively measure soil organic C (volumetrically) to a depth of around 30 cm. There is also no sample preparation required. Wielopolski et al. (2011) reported on the feasibility of an INS instrument for measuring soil organic C. The sensor used high-energy neutrons and photons to sample soil volumes up to about 0.3 m^3 and from approximately 20 to 30 cm deep,

30 with a 150-cm-diameter footprint. Although this technology appears useful, it is not yet sufficiently developed, the equipment is expensive and there are concerns around the safe use of fast neutron generators in farms (Izaurralde et al., 2013).

4.2 Sensing of soil bulk density

4.2.1 Active gamma-ray attenuation (AGA)

Active gamma-ray attenuation (AGA) measures the attenuation of the radiation by the soil, as defined by Beer-Lambert's Law, and provides a direct measure of the soil density. Because the mass attenuation coefficient of soil is a function of both photon

5 energy and the elemental composition of the soil, attenuation is affected by soil texture and mineralogy. Measurement of bulk density by AGA can be made using either the scattering method or the transmission method; the first is applied to mostly surface determinations, mainly using gamma/neutron surface gauges, while the latter is used for measurements at depth, which can be made in the laboratory or in the field (Pires et al., 2009).

AGA with a gamma (or neutron) surface gauge and a source of radiation that is lowered into the soil to the effective

10 measurement depth, can be used to measure soil density. The backscattered gamma radiation that originates from the source, loses some of its energy on the way back to the scintillation detector at the surface, and the energy of the detected radiation is proportional to the density of the soil. The technique requires considerable soil preparation and correction for soil water to derive soil bulk density. Soil surface preparation requires that there are no gaps between the soil and the sensor and, for measurements at depth, a pit needs to be dug to the effective measurement depth into which the active gamma source is

15 lowered. Reports on the accuracy of these measurements are variable (Holmes et al., 2011; Timm et al., 2005). This might be due to problems with uneven soil surfaces and other soil preparation issues. Relationships between bulk density measured with a neutron density meter and those using the conventional ring method were not strong and were variable among sites (R^2=0.14-0.47, N=75; Holmes et al. (2011)), while others required new calibrations for different soil types or bulk densities $<1.4\,\mathrm{g\,cm}^{-3}$ (C'assaro et al., 2000; Rousseva et al., 1988). By comparison, other studies have shown that bulk densities measured using a

20 neutron-gamma surface gauge tended to be lower than the conventional ring method (e.g. Timm et al., 2005; Bertuzzi et al., 1987; Rawitz et al., 1982), although this difference was not statistically significant.

AGA using measurements of transmission can be used to measure soil density. In this case, the measurements are made axially through a soil core and the attenuation of gamma radiation passing through it to the scintillation detector is proportional to the density of the soil. Pires et al. (2009) and Lobsey and Viscarra Rossel (2016) provide descriptions of the measurement

25 principles. The method requires sampling of intact soil cores and when measurements are made on soil under field condition, corrections for water, θ, are needed. No other sample preparation is required.

The bulk density of the soil cores, ρ_b, can be derived with (Lobsey and Viscarra Rossel, 2016):

$$\rho_\mathrm{b} = \frac{1}{x\mu_\mathrm{s}}\ln(\frac{I_0}{I}) - \frac{\mu_\mathrm{w}}{\mu_\mathrm{s}}\rho_\mathrm{w}\theta, \qquad (2)$$

where I is the incident radiation at the detector, I_0 is the un-attenuated radiation emitted from the source and x is the sample

30 thickness in cm, μ_s is the mass attenuation coefficient of dry soil in $\mathrm{cm^2\,g^{-1}}$, μ_w is the mass attenuation coefficient of soil water at 0.662 MeV, ρ_w is the density of water (taken as $1\,\mathrm{g\,cm}^{-3}$) and θ is the volumetric water content of the soil in $\mathrm{cm}^{-3}\,\mathrm{cm}^{-3}$.

Good agreement between measures of bulk density with an AGA transmission sensor and the conventional volumetric ring method have been found for dry samples in the laboratory (Pires et al., 2009). More recently, Lobsey and Viscarra Rossel

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(2016) showed that this method with vis–NIR corrections for water can accurately and rapidly (on average 35 seconds per measurement) measure, $ex\,situ$, the bulk density of soil cores sampled (wet) under field condition. The method facilitates the measurement of soil bulk density at fine depth resolution enabling characterisation of the spatial variability of soil bulk density in lateral and vertical directions. Lobsey and Viscarra Rossel (2016) report that the accuracy of measurements was

5   similar to that obtained using the conventional single ring method (RMSE=0.06 g cm^{-3}, R^2=0.90, N=32). Further, the authors show that the method can be used to determine organic C stocks on a fixed-depth or equivalent soil mass basis (Lobsey and Viscarra Rossel, 2016).

4.2.2   Computed tomography (CT)

The use of computed tomography (CT) in soil science was introduced several decades ago (Petrovic et al., 1982), and has

10   since been used to assess porosity and pore size distribution (inversely related to bulk density), tortuosity, soil structure and compaction (Lopes et al., 1999; Pires et al., 2010). CT is based on the principle that electromagnetic radiation (commonly X- or gamma rays), is attenuated by matter. Similar to the AGA described above, attenuation follows the Beer-Lambert Law. CT is used to convert the attenuation of the radiation by matter into CT numbers called tomographic units (TUs), and the soil mass attenuation coefficient is used to derive soil density. The techniques can produce cross-sectional images to create a

15   three-dimensional model, and hence they have good potential for measuring soil bulk density (and gravel content, see section 4.3.1 below) of intact soil core samples.

   Only few studies have demonstrated that gamma-ray CT can be used to measure soil bulk density (Pedrotti et al., 2005; Timm et al., 2005). Timm et al. (2005) compared measurements of bulk density with gamma-ray CT to several other methods, including the conventional volumetric single ring method and found the CT technique to be more accurate. In an evaluation of

20   the potential for X-ray microtomography for measuring the bulk density of soil with different textures and at different depths, Segnini et al. (2014) found only moderate linear agreement with the conventional volumetric ring method (R^2=0.58, N=12). They concluded that factors such as the 'beam hardening' effect (see Cnudde and Boone (2013)) and the polychromatic nature of X-ray microtomography make it difficult to directly measure soil bulk density. However, further evaluation is required. An advantage of the CT methods is that they can provide detailed analysis of soil bulk density profiles at a fine resolution. Cnudde

25   and Boone (2013) provide a review of the applications and limitation of X-ray CT.

4.2.3   Spectroscopic- and pedo-transfer functions

The bulk density of soil is a measure of the amount of pore space in a volume of soil, thus spectroscopy, being a surface measurement, cannot physically measure density, particularly if the soil has been ground and sieved. Nonetheless, it is often suggested that predictions of bulk density using vis–NIR or mid-IR spectra are possible. The reason is that under certain conditions,

30   these spectroscopic models rely on second- or higher-order correlations to other soil constituents that are spectroscopically-active ($e.g.$ minerals, organic matter, water). However, because the predictions are 'indirect', they can be biased. Moreira et al. (2009) found that using vis–NIR spectroscopy on dry soils to predict soil bulk density produced inaccurate results and concluded that further research was needed to assess the limits and specificity of the method. A more recent study by Roudier et al.

(2015), using vis–NIR on wet intact cores, found that predictions of bulk density were relatively accurate (in soil containing no gravel), but calibration was at a very local scale and thus for very specific conditions. Pedotransfer functions (PTFs) are also commonly used to rapidly measure soil bulk density (e.g. Tranter et al., 2007), however such functions are often biased and/or imprecise and therefore unsuitable for determinations of soil organic C stocks even when developed with soil from the

5   same study area (Don et al., 2007). A further disadvantage of using PTFs is that they use other soil properties, which need to be measured, as input variables.

4.3   Sensing of gravel

Gravels are defined as coarse fragments with particles that are coarser than 2 mm (McKenzie et al., 2002). The presence of gravel has a significant effect on the mechanical and hydraulic properties of soil (Brakensiek and Rawls, 1994; Sauer and

10 Logsdon, 2002). If gravel is present but not accounted for, it could bias the measurements of soil organic C stocks (Lobsey and Viscarra Rossel, 2016; Poeplau et al., 2017). For example, the presence of abundant coarse fragments ($>20\%$) adversely affected measurement of soil bulk density by both conventional and AGA using backscatter methods (Holmes et al., 2011). Sensing of gravel is difficult and so it is typically measured manually by drying, crushing, sieving and weighing of the soil and gravel. However, this method is time consuming. A practical and robust method for sensing gravel needs to be developed.

15 ### 4.3.1   Wet sieving and image analysis

Viscarra Rossel, R.A. and Lobsey (2017) developed a wet-sieving system combined with image analysis to more efficiently measure the gravel content of soil core samples in the field. The system enables rapid wet-sieving of the core samples in 10 cm increments. The system is modular and can accommodate soil cores of various lengths. The authors tested the system using four soil types with varying textures and gravel contents. They showed that, for a 1 m soil core, gravel could be separated from

20 the soil, at 10 cm intervals, in 10–20 minutes, which is considerably faster (by a factor of more than 10) than the conventional method. By imaging the resulting gravel and measuring the pixel area or pixel volume occupied by the gravel in the images, they could accurately estimate the gravel content of the different soil types ($R^2=0.79$–0.90, average $R^2=0.85$ over the four soil types Viscarra Rossel, R.A. and Lobsey (2017). The authors suggested that the method showed good promise for use in a soil C stock measuring system and that further testing and improvements of the wet-sieving might include using a dispersing agent

25 ($e.g.$ $(NaPO_3)_6$). A further advantage of the method is that as well as gravel, undecomposed plant materials and roots are also separated (Viscarra Rossel, R.A. and Lobsey, 2017).

4.3.2   Computed tomography (CT)

There is good potential for the development of CT methods to measure gravel (and bulk density). However, there is little research on the topic. Fouinat et al. (2017) tested a novel X-ray CT method to analyse distinct deposits in lake sediment cores.

30 The analysis highlighted the presence of denser >2 mm mineralogical particles ($i.e.$ gravel) in the silty sedimentary matrix. When compared to conventional manual measurements that involved sieving and water displacement to measure volume, they

found that CT measurements overestimated the volume of the gravel by 11.6 %. The authors suggested that the overestimation might be due to pixel resolution issues. Nonetheless, the authors obtained a good positive correlation (ρ=0.81) between the CT measurements and the more conventional method. Further development is required and the issues discussed above for sensing bulk density also apply here for sensing of gravel.

4.4 Evaluation of sensing for soil organic C accounting

Based on our review and assessment of the available sensor technologies above, currently, the most suitable proximal sensing techniques for measuring soil organic C and for monitoring its change are: vis–NIR and mid-IR spectroscopy for estimating soil organic C concentration, and AGA for measuring bulk density. There are no practical or efficient sensors available for measuring gravel. Presently, a possible best option might be wet-sieving to separate the gravel fraction and quantification by weighing or image analysis (Viscarra Rossel, R.A. and Lobsey, 2017). A summary of the benefits and limitations of each of these technologies is given in Table 3, and an assessment of their cost and accuracy is given in Table 4.

The cost of spectrometers can vary widely (Table 4). Portable vis–NIR spectrometers (350–2 500 nm) can be purchased from different manufacturers from approximately AU\$30,000–100,000 (Table 4), although their cost is continually decreasing as technologies develop. Smaller vis–NIR spectrometers that use micro-electromechanical systems (MEMS) technologies are emerging and are less expensive, but not many have been thoroughly tested. Prices for mid-IR portable spectrometers (2500–20,000 nm) are approximately AU\$50 000–70 000, and for mid-IR benchtop spectrometers, approximately AU\$20 000–90 000, depending on the size, type of detector, sensitivity and amount of automation. Spectroscopic measurements of soil organic C concentration in the laboratory are large than measurements under field conditions because of the need for sieving, drying and grinding. mid-IR measurements are more expensive because of the need for fine grinding. Both vis–NIR and mid-IR techniques provide accurate predictions of soil organic C on dry soils (Table 4). Accuracy using vis–NIR on wet soil under field conditions is generally lesser than that for dry soils in the laboratory, although the difference can be relatively small (Table 4).

AGA sensors for measuring bulk density are also quite readily available (Table 4). Measurement costs are significantly smaller for AGA using transmission than for AGA using backscatter because of the additional soil preparation required for the latter. There are few assessments of accuracy of AGA for measurement of bulk density, but these have shown good accuracy for AGA using transmission and variable accuracy for AGA using backscatter. There is no information on the cost and accuracy of wet sieving and image analysis for quantifying gravel (Table 4). Viscarra Rossel, R.A. and Lobsey (2017) suggested that a system could be easily developed and that measurement costs would be small.

4.5 Integrated multi-sensor systems are needed for soil organic C accounting

An integrated multi-sensor approach is needed for measuring and monitoring soil organic C stocks because one needs to simultaneously measure soil organic C concentration, bulk density and gravel. There are two currently-available, field-deployable, proximal multi-sensor systems that could measure soil organic C stocks. One involves inserting the sensors into the soil profile and making measurements $insitu$, while the other requires sampling undisturbed soil cores and measuring the soil $exsitu$.

Table 3. Benefits and limitations of sensing technologies for soil C accounting. vis–NIR, visible and near infrared diffuse reflectance spectroscopy; mid-IR, mid infrared spectroscopy; AGA, active gamma-ray attenuation; ESM equivalent soil mass; SOP standard operating procedure.

Sensing technique	Soil attribute	Advantages	Limitations
vis–NIR	Soil organic C	Rapid and easy to use.	Empirical, requires calibration.
		Inexpensive measurements.	Calibration requires expertise.
		Relatively accurate.	Surface measurement.
		Samples can be wet, under field conditions.	Requires correction for water.
		Non-destructive.	
		No sample pre-treatment required; no harmful chemicals.	
		Effects of water on soil organic C estimation can be corrected.	
		Robust field instruments available and becoming more affordable.	
mid-IR	Soil organic C	Rapid measurement.	Empirical, requires calibration.
		Inexpensive measurements.	Need to dry and grind soil samples.
		No harmful chemicals.	Calibration requires expertise.
		Non-destructive.	Surface measurement.
		Accurate predictions on dried, ground samples.	Corrections for water need testing.
		Few portable instruments but becoming more available.	Few studies on estimating C in the field.
AGA transmission	Bulk density	Rapid.	Requires soil core sampling.
		Accurate.	Needs independent measure of water content.
		Inexpensive sensor and measurements.	Needs construction of a set-up.
		Non-destructive.	Uses active radiation.
		Allows characterisation of variability vertically and laterally.	Requires SOP and regulatory approval.
		Can estimate stocks on fixed-depth and ESM basis.	Requires a licensed operator.
		Instrumentation readily available.	
AGA backscatter	Bulk density	Non-destructive.	Requires pit for active gamma/neutron source.
		Does not require sampling of intact core.	Variable accuracy reported.
		Commercial instrumentation available.	Need independent measure of water content.
			Uses active radiation.
			Requires SOP and regulatory approval.
			Requires a licensed operator.

Table 4. Assessment of the accuracy and cost of sensing technologies for soil C accounting. The methods are visible–near infrared (vis–NIR) and mid infrared (mid-IR) diffuse reflectance spectroscopy; active gamma-ray attenuation (AGA) and wet sieving and image analysis. The accuracy for soil organic C is represented by median values for dry soils at a local scale, and for bulk density, for wet soil corrected for water with vis–NIR measurements. The statistics reported are the root mean square error of validation (RMSEv); the coefficient of determination (R^2v) and the ratio of performance to deviation (RPDv). N are the number of local sites at which accuracy was assessed.

Method	Instrument cost	Measurement cost	Accuracy			
	('000 \$AU)	per sample (\$AU)	N	RMSEv	R^2v	RPDv
Soil organic C /%						
vis–NIR, dried ground	30–100	8	29-35	0.41	0.85	2.4
vis–NIR, field condition	30–100	0.8	9-10	0.47	0.81	2.3
mid-IR, dried, finely ground	20–90	15	4-8	0.11	0.93	3.7
Bulk density /g cm^{-3}						
AGA transmission	15	0.5	1	0.06	0.90	-
AGA backscatter	5	10	3	-	0.33	-
Gravel /%						
Wet-sieving and image analysis	100	-	4	-	0.85	-

Veris® Technologies produces commercial sensors for precision agriculture (www.veristech.com), including several field-deployable systems which can measure electrical conductivity, pH, penetration resistance, and also record the vis–NIR spectra of soil. The system that is particularly relevant to soil organic C accounting is the P4000, which uses a hydraulic probe system to insert four sensors into the soil to characterize the profile. The sensors are a vis–NIR spectrometer (350–2200 nm), an

5   electrical conductivity (EC) sensor and an insertion force sensor. The system does not measure bulk density. Using insertion force as a surrogate for bulk density might be possible but would be prone to errors. Wetterlind et al. (2015) tested the accuracy of predictions of soil organic matter (SOM) using the P4000 system and evaluated whether the predictions were improved when the sensors were combined. They found that the accuracy of predictions of SOM content using the vis–NIR alone was good, but the inclusion of insertion force only improved the accuracy of predictions of SOM content by about 10%. They

10   concluded that these small improvements did not provide strong support for combining vis–NIR sensor measurements with measurements of insertion force. However, there was no testing of bulk density.

The Soil Condition Analysis System (SCANS) (Viscarra Rossel, R.A. et al., 2017) uses a combination of proximal sensing technologies, smart engineering and data analytics to characterize soil laterally across the landscape and vertically down the profile. The SCANS has an automated soil core sensing system, which can be used in the laboratory or in the field, with

15   a vis–NIR (350–2500 nm) spectrometer, an AGA densitometer and digital cameras that measure intact soil core samples

that are either (wet) under field condition, or dry, at user-defined intervals over the length of 1.2 m soil cores. The system can measure soil organic C content and composition (particulate, humus and resistant C), bulk density, clay content, cation exchange capacity, volumetric water content, available water capacity, pH, iron and clay mineralogy (Viscarra Rossel, R.A. et al., 2017). Each measurement with the sensors takes approximately 35 seconds, so that measuring a 1 m core at 2 cm intervals

5   (*i.e.* 50 measurements along the core) takes approximately 30 minutes. Viscarra Rossel, R.A. et al. (2016b) showed that the sensing system can be used to accurately baseline soil C stocks for accounting purposes. The system was use to derive baseline estimates of soil organic C stocks (Viscarra Rossel, R.A. et al., 2016b) and its efficiency and reliability for soil C accounting was assessed by Viscarra Rossel, R. A. and Brus (2018). They found that compared to more conventional methods that use composite sampling and laboratory analysis, sensing with the SCANS is more cost-efficient in that it provides a good balance

10 between accuracy and cost.

5   Developing a soil organic C accounting methodology with proximal sensing

5.1   Development of spectral libraries

Measurement of soil organic C using spectroscopy (*e.g.* vis–NIR, mid-IR) requires calibration of the spectra to soil organic C content using multivariate statistics or machine-learning algorithms. The calibrations can be derived using existing large

15 spectral libraries (ESLs) (e.g. Viscarra Rossel, R.A. and Webster, 2012; Shepherd and Walsh, 2002; Stevens et al., 2013), or using new site-specific libraries developed with local soil samples (LSLs). Using an ESL to predict soil organic C incurs no immediate cost but it is likely that the predictions at local site (farm- or field-scales) will be biased (Clairotte et al., 2016; Guerrero et al., 2014b). Using a LSL will produce more accurate (unbiased) predictions but will incur cost because soil needs to be analysed in the laboratory to derive the local model.

20 Significant investment has been made in developing large regional, country and global spectral libraries (Shepherd and Walsh, 2002; Brown et al., 2006; Viscarra Rossel, R.A. et al., 2016a), and there will be value in using these for developing site-specific calibrations. These ESLs could reduce the need for site-specific data. Various approaches have been proposed to make better use of ESLs for local predictions of soil properties. They are based on either constraining the ESL with spectral or sample similarities, or augmenting the ESL with site-specific samples.

25 Memory based learning (MBL) methods aim to constrain the ESL with spectral information, and derive calibrations for each unknown sample on a case-by-case basis. By selecting a subset of the ESL to predict each unknown sample, these methods effectively derive site-specific (*i.e.* local) calibrations. Methods include the LOCAL (Shenk et al., 1997) and locally weighted regression (LWR) (Naes et al., 1990) algorithms, and their variants. Essentially, the methods select calibration samples from the ESL with a distance metric (*e.g.* Mahalanobis distance) in the multivariate space between the calibration and the unknown

30 samples. In LWR weighting the calibration samples are also weighted according to their spectral dissimilarity (distance) to the unknown samples.

Ramirez-Lopez et al. (2013) proposed spectrum base learning (SBL), which is a type of MBL. The spectrum-based learner selects nearest neighbours from an ESL using distance metrics calculated in the principal component space and optimizing the

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number of components used to identify the nearest neighbours in the selection. Spectroscopic modelling is then carried out with both the selected neighbours and the matrix of distances to the unknown samples as the training data set.

The ESL can also be constrained with other information such as soil order, type, texture and parent material (e.g. Vasques et al., 2010; Sankey et al., 2008a). Shi et al. (2015) proposed the use of both spectral similarities and geographically constrained

5   local calibrations to predict soil organic C content. They reported improvements in the accuracy of predictions when the ESL was constrained to the geographic region from which the unknown samples originated. Viscarra Rossel, R.A. and Webster (2012) developed general ESL calibrations for Australian soil using the machine learning algorithm CUBIST. The authors showed that the algorithm makes inherently local predictions because CUBIST partitions the spectra into local subsets that are each modelled separately.

10   There are two techniques that use the augmenting approach. They are 'spiking', which uses several local spectra to augment the calibration made with an ESL (e.g. Guerrero et al., 2010; Sankey et al., 2008b; Viscarra Rossel, R.A. et al., 2009), and spiking with extra-weighting (Guerrero et al., 2014a), which uses multiple copies of the local samples to improve their leverage in the calibrations. Guerrero et al. (2014a) showed that the approach improved on spiking and suggested it might be more appropriate with larger spectral libraries.

15   Lobsey et al. (2017) developed a new approach, which they call RS-LOCAL, that makes best use of ESLs and minimises the number of site-specific, local samples for deriving calibrations. The method is data-driven and makes no assumptions on spectral or sample similarities. Using data from farms in Australia and New Zealand, they showed that by combining 12–20 local with a well-selected set of samples from an ESL, the robustness and accuracy of the predictions was improved compared predictions made using a 'general' calibration and other methods tested. The authors suggested that RS-LOCAL can reduce

20   analytical cost and improve the financial viability of soil spectroscopy.

5.2 Spectroscopic modelling: training, validation and prediction

As described above, to measure and monitor soil organic C with spectra, a local spectroscopic model needs to be developed to ensure that the estimates of organic C are unbiased. Therefore, once the soil in a study area has been sampled, according to an appropriate soil sampling design (see section 3.2), the spectra of the sampling units in the sample should be recorded using

25   standardised protocols and guidelines, such as those described by the Global Spectral Library in Viscarra Rossel, R.A. et al. (2016a). Following a spectral outlier analysis to identify erroneous spectra (due to rocks, roots and other non-soil materials), the spectra of the sample, which characterises the variability in the study area, is used to guide the selection of data for the spectroscopic modelling and prediction, *i.e.* the training, validation and prediction sets.

The training set should be selected with a method that ensures that the training spectra adequately represent the sample,

30   *e.g.* Kennard-Stone (Kennard and Stone, 1969), or Duplex (Snee, 1977) algorithms. The validation set, should be selected by random sampling to ensures unbiased assessment of the spectroscopic model predictions. How many spectra to use for training and for validation depends on the available budget, because the selected sampling units will need to be analysed with conventional laboratory methods, and on the heterogeneity of the sample. Spectroscopic models for prediction of soil organic C that are developed and validated with too few data can lead to unstable and erroneous results (Reeves et al., 2012). Once the

total number of sampling units are selected for the spectroscopic modelling, a general rule of thumb is to use two-thirds for training and the remaining third for validation, although this is not a hard rule and the choice might depend on the total number of sampling units that are selected. The prediction set is made up of the data that remains in the sample after the training and validation sets have been selected.

5   Once the spectra for the modelling have been selected, soil aliquots of the respective sampling units need to be prepared for the analysis of soil organic C concentrations in the laboratory, *e.g.* by LECO (Laboratory Equipment Corporation), combustion analysis. It is important to note that the inaccuracy and imprecision of analytical results are directly related to the sampling, handling and analytical procedure (Viscarra Rossel, R.A. and McBratney, 1998). Therefore, soil sample preparation (drying, crushing, grinding, sub-sampling) and analytical measurements should be made with certified methods and in an accredited

10   laboratory that conduct regular technical and inter-laboratory proficiency programs, *e.g.* in Australia accreditation is though the National Association of Testing Authorities (NATA) and the Australian Soil and Plan Analysis Council (ASPAC). We recommend that an independently assessment of the analytical accuracy is performed by including a small but representative proportion of 'blind' duplicates (*e.g.* 15 %) in the analysis. If the 'blind' duplicate samples exceed a pre-determined threshold value (*e.g.* 0.05 % soil organic C), then the samples should be re-analysed by the laboratory. As with any type of modelling,

15   the dictum when developing spectroscopic calibrations is 'garbage in=garbage out' and conversely 'quality in = quality out' (Viscarra Rossel, R.A. et al., 2008b).

The spectra and analytical data in the training set should then be analysed and if necessary, transformed, preprocessed and pretreated. For example, if the algorithm for the modelling assumes that the response variable is normally distributed, then the analytical data will need to be checked and if necessary transformed (*e.g.* with logarithmic transforms) to approximate

20   a normal distribution. Similarly, the spectra may need transformation to apparent absorbance, it may need smoothing and baselining (*e.g.* using a Savitzky-Golay filter with a first derivative (Savitzky and Golay, 1964)). The spectra may also need to be mean-centred and if recorded at field conditions, it may need corrections to remove the effects of water on the spectra (*e.g.* with either the external parameter orthogonalisation (EPO) (Minasny et al., 2011), or direct standardisation (DS) (Ji et al., 2015). A recent comparison of EPO and DS is given by Roudier et al. (2017). It is important to note that whatever

25   transformations, preprocessing and pretreatments are applied to the training set, they must also be applied to the validation and prediction sets.

Before embarking on the modelling it is sensible to objectively check for outliers and influential data in training set. This can be done by calculating Studentized residuals (Cook and Weisberg, 1982), to check for observations with unusually large residuals, or data that deviate greatly from their mean, *i.e.* those with high leverage (Martens and Naes, 1989). If outliers are

30   detected, then further checks for data entry and other errors should be made. Unless there is reasonable evidence to suggest that the data are in error, they should not be removed.

Spectroscopic models should be developed by cross-validation to obtain optimal parameterisation of the models and to minimise or prevent problems with under- or over-fitting. Once a model is developed, model diagnostics should be performed to interpret the model and also to check that the statistical assumptions of the particular algorithm being used are not violated.

35   For example, this could simply be done by calculating the residuals of the data in the training set and plotting these against

the estimated soil organic C concentrations. This plot can help to diagnose dependence of the predicted value, non-constant (or heteroscedastic) variances, and non-linear trends that indicate the need for data transformations or alternate curvilinear modelling methods (see for example, (Martens and Naes, 1989)).

5   If all assumptions about the model are correct and the model has a good diagnosis, then the optimised model should be validated with the independent validation set, which were selected at random and that were not used in the training process. The type of algorithm used (*e.g.* partial least squares regression (PLSR), support vector machines (SVM), regression trees) is not critical as long as the optimisation and validation are done well. Modelling uncertainties could be derived with a Monte Carlo (e.g. Viscarra Rossel, R.A., 2007), or with Bayesian methods.

     The predictions on the validation set should be assessed with statistics that completely describe the errors in the same 10 units as the analyte (*i.e.* soil organic C content). For this we recommend the use of the root mean square error (RMSE), which measures the inaccuracy of the model predictions, the mean error (ME), which measures their bias and the standard deviation of the error (SDE), which measures their imprecision. Inaccuracy may be defined as combining both bias and imprecision, so that $RMSE^2=ME^2+SDE^2$ (Viscarra Rossel, R.A. and Webster, 2012). Other indices that are commonly reported are the coefficient of determination (R^2), the ratio of performance to deviation (RPD) (Williams and Norris, 2001), or the ratio of performance 15 to interquartile range (RPIQ) (Bellon-Maurel et al., 2010) and the concordance correlation coefficient (Lin, 1989).We do not recommend the use of the R^2 alone because it does not account for bias in the model predictions, or the RPD or RPIQ alone because their categories are rather subjective and variable (Reeves and Smith, 2009).

     If the independent model validation statistics are not too dissimilar to those reported in the literature for soil organic C predictions at the field and farm-scales, *e.g.* for vis–NIR spectroscopy 0.1–1.0 % organic C, with a median value of 0.3 % 20 organic C (Viscarra Rossel, R.A. et al., 2016a), we recommend that additional sampling units be selected to augment and potentially extend the range of the training set. These values should serve only as guidelines and if the validation statistics fall outside of these ranges after augmentation of the training set, then it might not be sensible to proceed with spectroscopy for the estimation of organic C.

     The optimised and validated spectroscopic model may then be applied to all of the spectra: the training, validation and 25 prediction sets, to estimate in a consistent manner, the soil organic C concentration of the entire sample set and their uncertainty. If the model was developed on a transformed organic C scale (*e.g.* square root or logarithmic), then the estimates need to be back-transformed to the original units.

     Figure 1 summarises the procedures for the spectroscopic measurement, modelling and prediction of soil organic C.
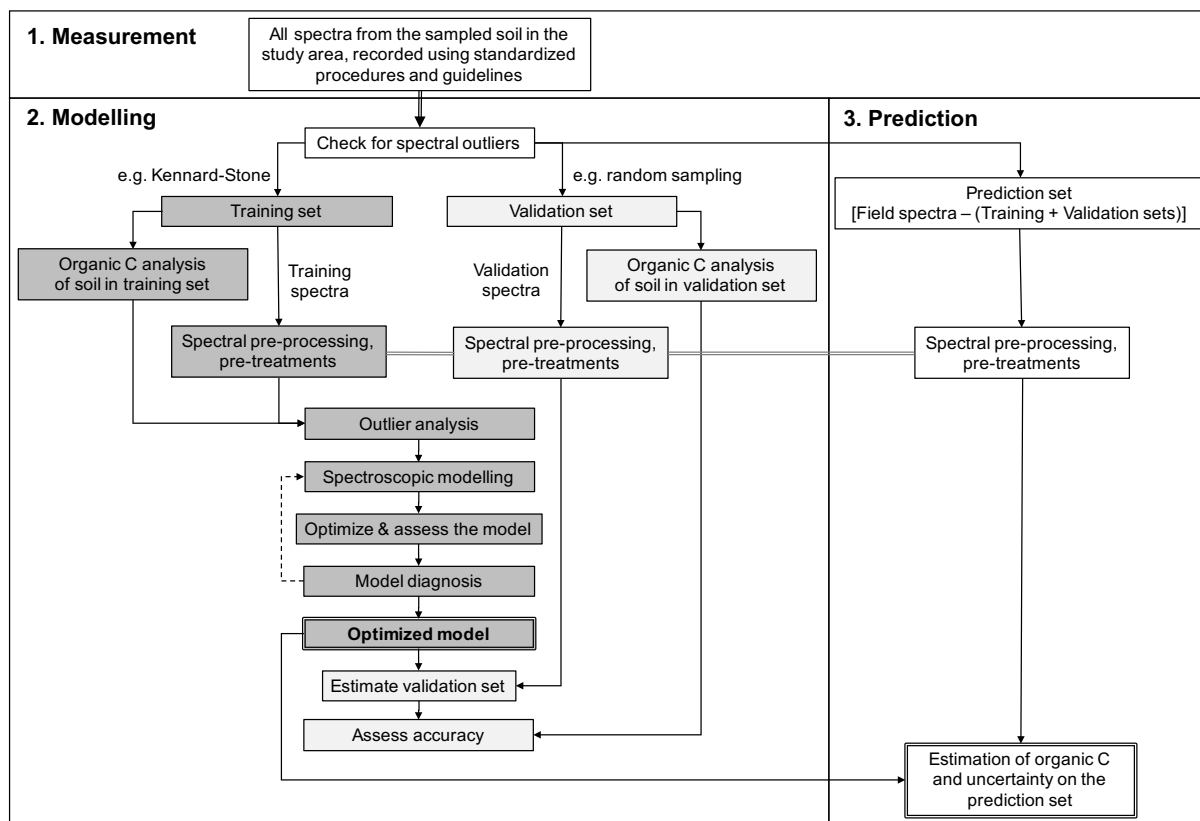
Figure 1. Framework for spectroscopic measurement, modelling and prediction of soil organic C.

5.3 Standards for auditing and verification

Standardisation of the sensing methods and their procedural guidelines are needed if sensing is to underpin methodologies that help to account for soil organic C stock change. This is particularly important for international initiatives like the '4 pour1000', which aim to demonstrate that soil can play an important role to mitigate climate change. Standards and guidelines are also

5 essential in schemes that use financial incentives for landholders to adopt C sequestration practices (see Table 1). In this case, standards will help to ensure that only authentic abatement is credited. In the Australian ERF, methods need to comply with Offsets Integrity Standards, which require that abatement is additional, eligible, measurable and verifiable, evidence based, statistically defensible, supported by relevant scientific results, permanent, with no leakage and conservative (see Section 2 above).

10 Bispo et al. (2017) reported that a number of standards exist for the analysis of soil properties, including organic C, but suggested that new standards are needed for the measurement of soil C stocks and for the verification of C change. In Table 5, we propose a list of data and information that needs to be reported when developing a sensing methodology for soil C accounting. These include, for instance, the type of sensor used, the requirements for calibration, the number of reference analyses to use, the requirements for validation, the statistics to report, and the information that must be recorded for auditing and verification.

Table 5. Data to be recorded for auditing and verification in a soil organic C accounting method.

Sensor specifications	Manufacturer and model number.
	Spectral range.
	Source of radiation.
	Type of detector.
	Instrument calibration procedures.
	Materials of calibration standards.
Sensor measurements	Condition of the soil: air dry / oven dry / wet / ground, sieved / intact core.
	Total number of spectra recorded from the study area.
	Number of spectral outliers and outlier method used.
	Number of training and number of validation spectra and methods used for selection.
	Experimental values for x, μ_s, μ_w, θ see Equation 2.
	Sensor outliers and method used to identify them.
Laboratory analysis.	Laboratory method used laboratory code and accreditation.
	Number of 'blind' duplicates and the measured standard error of the laboratory (SEL).
	Mean, standard deviation, minimum, median, maximum values of the measured data.
	Analytical outliers and method used to identify them.
Transformations pre-processing, pre-treatments.	Type of transformations used on the laboratory and sensor data.
	Pre-processing methods used on the sensor data.
	Pre-treatment methods used on the sensor data.
	Method used for correcting the effects of water on the sensor data.
Spectroscopic modelling: training.	Number of data in the spectral library.
	The algorithm used for modelling.
	The cross-validation method used.
	The optimised setting of the model and the model RMSE and R^2.
	The model diagnostics and residuals plot.
Spectroscopic modelling: validation.	If appropriate, method for back-transformation of the response variable.
	The validation RMSE, ME, SDE and concordance correlation.
	Plot of the observed vs. predicted validation data.
Spectroscopic modelling: prediction of 'unknowns'.	Mean, standard deviation, minimum, median, maximum values of the predicted data.
Data sets.	All sensor data collected from the study area.
	The training and validation data.
	The analytical data used for calibrating sensors.
	Sample identification numbers.
	Geographic locations (WGS84) and depth layers where measurements were taken.
	Date and time of measurements.

Of course, the list in Table 5, is additional to data on the project area, the sampling design used, the soil sampling method, the method for estimation and the preparation of the samples for analysis.

6 Final remarks

For cost-efficient soil C accounting one needs a field-deployable, integrated multi-sensor and data analytics system to derive estimates of organic C stocks. Currently, the most suitable proximal sensing techniques are vis–NIR spectroscopy for predicting soil organic C concentration, and active gamma attenuation with measurements of transmission, for bulk density. The use

5 of mid-IR spectrometers for measurements under field condition needs further investigation and development. Laboratory measurements of soil with mid-IR are possible, but sample preparation by additional fine grinding may be expensive. Sensing with vis–NIR and active gamma attenuation sensors provide accurate, rapid and cost-efficient measures of C stocks, which can be on either a fixed-depth or an equivalent soil mass basis.

Currently, there are no practical or efficient sensors for measuring gravel, but the development of CT for quantifying both

10 gravel and bulk density appears promising. Portable CT scanners exist for medical and other applications, including soil, but further research and development, or significant modification of existing systems are needed to measure bulk density and gravel content for C accounting. The system would need to have: 1) ability to rotate the soil core around fixed sensors or rotate the sensors around the core; 2) short measurement times to produce images of appropriate resolution; 3) adequate emission energies and appropriate shielding; 4) specialised software for the reconstruction of images and measurement of bulk density

15 and gravel; and 5) appropriate size and weight to allow routine field deployment. Of course, a vis–NIR sensor for measuring soil organic C concentration would need to be used with it. In the meantime, however, separation of gravel by rapid wet-sieving and quantification by automated weighing or by image analysis, might be an efficient interim.

Sensing of soil organic C concentration with spectrometers require multivariate calibrations. There has been significant investment over the past decades in developing large regional, country and global spectral libraries, and there is value in

20 using them. Statistical data-driven methods that use such libraries to reduce the need for local samples for deriving site-specific calibrations are being developed. For example, the RS-LOCAL methods can help to improve the cost-efficiency of soil spectroscopy for C accounting.

The rationale for using sensing in a methodology for soil organic C accounting is that although sensing may not be as precise per individual measurement compared to laboratory analysis, sensing is more cost-efficient, that is, sensing provides a good

25 balance between accuracy and cost. Because sensing is cheaper, simpler and more practical to use, many more measurements can be made across space (laterally and vertically) and time, so that as an ensemble, the data are more informative. Sensing can also be non-destructive, allowing soil to be stored in archives for future measurement should auditing and verification be required. The archived soils can then also ensure that there is consistent temporal data for use in dynamic models or for the testing of new technologies and approaches as they become available.

30 Sensing can be used evaluate land use and soil management practices that aim to increase soil organic C stocks, improve soil health, increase agricultural production and mitigate GHG emissions. But, to underpin soil C accounting methodologies, the sensing methods should be standardised and procedural guidelines developed to ensure proficient measurement and accurate reporting and verification. This is particularly important in schemes that use financial incentives for landholders to adopt management practices to sequester soil organic C. The new soil C method under the Australian Emissions Reduction Fund

will allow the use of sensors for C accounting. The method is awaiting ministerial approval and it gets it, it might provide a template for other countries to follow.

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