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Introduction to Carbon Sensing in Soil

A SURFACE-LEVEL REVIEW OF TRADITIONAL AND ALTERNATIVE METHODS OF SOIL CARBON MEASUREMENT

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Introduction

Soil carbon can be divided into two categories: organic and inorganic. Soil inorganic carbon (SIC) is present in carbonate minerals in the soil and is often found in dry, arid regions [1], [2]. Examples of SIC include calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$), both of which play important roles in soil health. Soil organic carbon (SOC) is found in fresh plant matter (available SOC) and as humus or charcoal (inert SOC) [1]. Both types of carbon act as storage in the global carbon cycle [3], as shown in Figure 1.

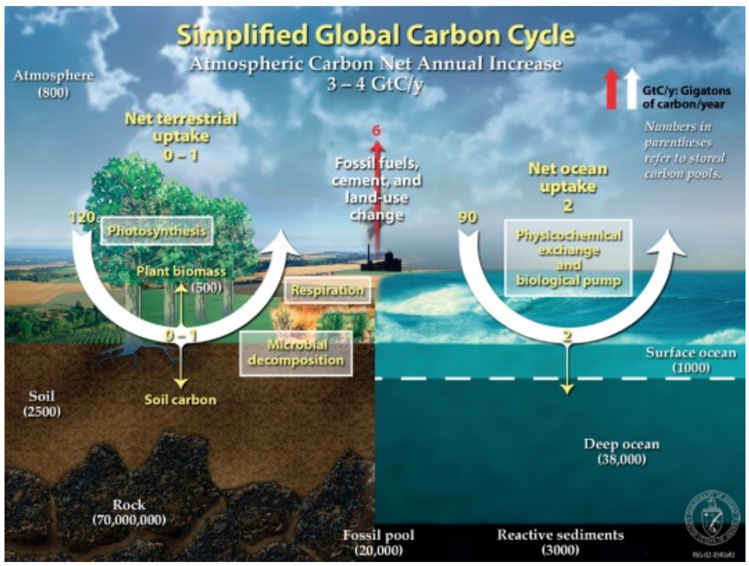

Fig 1: Soil carbon acts as carbon storage, or sink, in the global carbon cycle [3]

As a carbon sink, soil carbon has the potential to store carbon that would otherwise remain in the atmosphere as CO_2, one of the primary greenhouse emissions. As such, soil is under increasing attention and research to be used as a sequestration (i.e., isolation) method to reduce the amount of carbon in the atmosphere. This type of carbon sequestration is called biological sequestration. SOC typically stores carbon for several decades (depending on decomposition rates) while SIC can store carbon for more than 70,000 years [2], [4]. Common sequestration techniques for SOC usually fall under the category of land management: planting perennials, keeping plant residue and composting, reducing tilling, and other agricultural practices that vary by region [5]. SIC sequestration through carbonates naturally takes thousands of years but there have been studies to increase SIC sequestration through the addition of silicates [6].

The amount of carbon, both organic and inorganic, in soil is referred to as carbon stock The SOC stock is highly dependent upon environmental conditions such as heat, humidity, rainfall, vegetation, and similar factors, and varies between areas, leading to difficulties with accurately measuring the SOC stock [5], [7], [8]. SIC stock is also difficult to track due to issues with differentiating types of carbonates in the soil [4]. Additionally, because of the long-term nature of carbon stocks, since they are built up over millions of years, it is nearly impossible to measure the carbon stock directly; instead,9 carbon measurements are considered against background carbon measurements for that area, resulting in measurements of the change in carbon stock [9]. The recommended calculation for changes in SOC stock is to multiply organic carbon measurements with bulk density measurements for a fixed depth of 0-30 cm. The result of this calculation should be reported as mass of carbon/unit area in tons organic carbon/hectare [9]. Based on this international standard proposed by the 1997 Intergovernmental Panel on Climate Change, bulk density plays an important role in soil carbon measurements.

To understand the effect of bulk density on soil carbon measurements, it is important to understand what bulk density is and how it is measured. According to the USDA Natural Resources Conservation Service, bulk density represents soil compaction and is calculated as the dry weight of the soil divided by its volume, expressed in units of g/cm^3 [10]. Generally, bulk density is measured by driving a corer with known volume into the soil to the desired fixed depth, as shown in Figure 2, and the soil mass is measured after being oven dried [9]. However, some current research focuses on using faster and cheaper soil sensors to evaluate bulk density and SOC. One project proposes using gamma-ray attenuation and visible – near infrared (vis-NIR) spectroscopy to measure *ex situ* the bulk density of wet soil cores immediately after sampling [9]. The gamma-ray attenuation measures the density of the soil core samples while the vis-NIR spectroscopy can account for the effect of water on the gamma-ray measurements [9]. Overall, the sensors eliminate the need for laboratory measurements and reduce the overall cost of this key soil measurement in evaluating SOC stocks.

Fig 2: Bulk density measurement normally uses cored soil samples [10]

Another obstacle with measuring the carbon stock of an area accurately is the methodology of spatial sampling. One of the most common sampling techniques is called compositing, which involves taking subsamples from multiple locations and mixing them together to form a single composite sample [11], [12]. The number of subsamples within each sample varies by field and region. An issue with this method is the reduction in specific subsample measurements, so overall field measurements can be inaccurate [12]. This issue is resolved by evaluating soil samples individually, which does increase cost and time. However, the increased efforts associated with individual soil sample measurements can be offset with design-based sampling methods based on evaluation requirements or even sampling algorithms to achieve the best distribution of samples within an area [9] - [13].

Despite carbon sensing challenges, it is important to get an accurate measurement of the carbon stock within the soil to track carbon sequestration and evaluate soil health. Accordingly, the aim of this review is to summarize traditional and novel methods to sense carbon in soil and provide potential research avenues for future work in carbon sensing.

Traditional Organic Carbon Sensing Methods

The biggest challenge facing carbon sensing is getting an accurate picture of the carbon stock in an area. Because the carbon stock can vary widely even in a single field, it is difficult to get a good representative sample of soil carbon to run tests on. The usual method to determine the carbon stock of an area is to divide the area into strata, or sections, where individual samples of the soil can be taken and tested to get an overall picture of the area's carbon levels [8], [13]. Typically, soil organic carbon is measured by dry combustion with automatic CO_2 analyzers (direct and indirect measurement) or through chemical oxidation, most commonly with the Walkley-Black method [13] - [14].

Organic Carbon Dry Combustion

The organic carbon dry combustion method works by heating the soil sample at high temperatures to oxidize all the carbon present as CO_2, which is then measured with an infrared detector [15]. Since there is no way to separate the organic and inorganic carbon present in the soil, this method measures the total carbon in the sample, so to find the SOC, the SIC must be measured separately and then subtracted from the value determined after combustion. Generally, this method requires specialized analyzers, so it is more expensive to use and maintain; however, it is also the preferred method in carbon sequestration research because it measures organic carbon directly [13] - [14].

Loss-on-Ignition (LOI) Dry Combustion

The other method that uses dry combustion measures the carbon present in the soil indirectly by weight. The sample is combusted around 360°C to oxidize the carbon and the change in weight upon ignition is measured and taken to be the amount of soil organic carbon [15]. This process is sensitive to loss in weight due to inorganic components, especially hydrated clays, as well as the ignition temperature and the sample size [13], [15], [16]. Despite these issues, LOI is the routine method for measuring SOC commercially due to the relatively low cost and time required [15].

Walkley-Black Procedure

The Walkley-Black Procedure is the original SOC measurement method developed in 1934 but is currently being phased out due to labor and hazardous chemical management requirements [15], [17]. The method uses titration after reacting the soil with potassium dichromate and sulfuric acid to calculate residual oxidant and thus the active carbon present in the sample [15], [17], [18]. There are several issues with this procedure, including inaccurate SOC results that must be corrected against other SOC measurements, lower efficiency on soils with high organic matter since the reagent is consumed, and the issues with working with the hazardous dichromate chemicals and waste [13], [14], [15], [17].

Alternative Organic Carbon Sensing Methods

Emerging techniques to the traditional methods described previously are focused around identifying carbon present in the soil *in situ*, reducing the need for expensive and time-consuming laboratory analysis. These methods can be divided into four categories, with most research going towards spectroscopy techniques and remote sensors, and some research into fractionation and studying carbon fluxes.

Spectroscopy

Most of the spectroscopy techniques work on the diffuse reflectance property of the soil, which depends on the composition of the soil, particle size distribution, organic matter, iron oxides and carbonates present, and soluble salts within the soil [19]. The reflectance spectra are a result of the electronic transitions of atoms and the vibrational stretching and bending of atomic bonds in molecules and crystals [19] - [20]. By comparing the sample spectrum to a library of spectra, the amount of SOC present in the soil can be determined. There are several types of spectroscopies available for carbon sensing: visible and near-infrared (Vis-NIR), mid-infrared (MIR), laser-induced breakdown spectroscopy (LIBS), and inelastic neutron scattering (INS).

Infrared (IR) spectroscopy is the subject of the most research into soil spectroscopy techniques due to the relatively inexpensive and non-destructive nature of the testing. Depending on the wavelength range used, different features of the molecular vibrations can be determined. Of particular interest are the functional groups present in organic materials, including O–H, C=O, N–H, and C–H [21], [22]. Vis-NIR spectroscopy can detect the overtones and combinations of the fundamental bands of molecular vibrations but can be made inefficient by the large combinations of overtone bands [17], [20], [21], [22]. Mid-IR can detect the fundamental vibration bands and has been reported to give more accurate readings on soil [17], [21], [23], [24]. However, current mid-IR tools are not as well-developed for in-field use, as shown in Figure 3, or for quantitative measurements of soil carbon [17], [21], [25]. Currently, vis-NIR tools are considered the better alternative at the moment due to the relatively high accuracy and in-field use capabilities [17], [20], [21] [22], [26], [27]. Both types of spectroscopy face noise and accuracy issues in-field due to moisture content, surface texture, and particle distribution, as well as the specific area calibrations required for accurate spectra [17], [20] - [23], [25], [26].

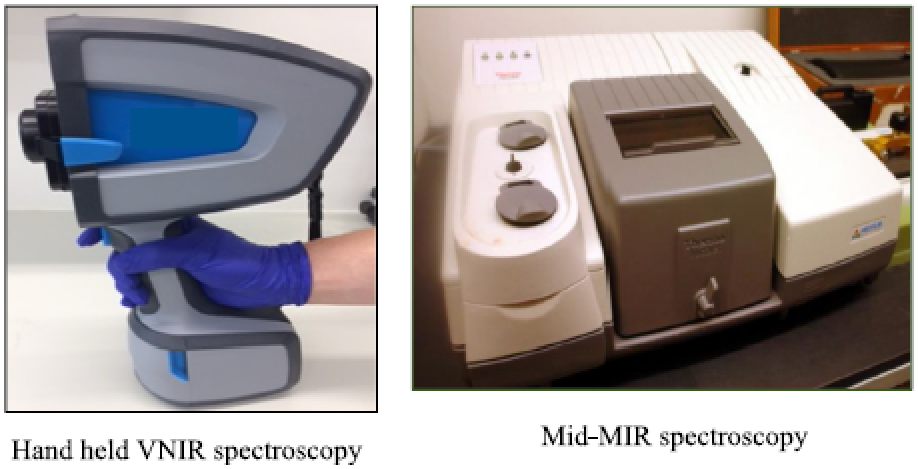

Fig 3: Vis-NIR tools are more readily available for in-field use than MIR tools [17]

LIBS is another interesting area of carbon sensing that can be used in-field. This technique works on the concept of atomic emission spectroscopy, where a pulsed laser is applied to the sample to turn a portion of the sample into a thin plasma with the exact composition of the original sample so that the spectrum will match the composition of the sample [17], [28], [29], [30]. The set-up for LIBS is shown in Figure 4 below. LIBS has the potential to be developed into an *in-situ* field instrument that can quickly test soil carbon levels with accuracy comparable to traditional techniques [28], [29]. However, there are known issues with plasma formation as well as unknown issues in how soil properties such as soil structure and composition affect accuracy [17], [29], [30], [31]. For example, one study using portable LIBS to analyze tropical soils had to use a different carbon spectral line due to the interference of the iron spectral line at the same wavelength [32].

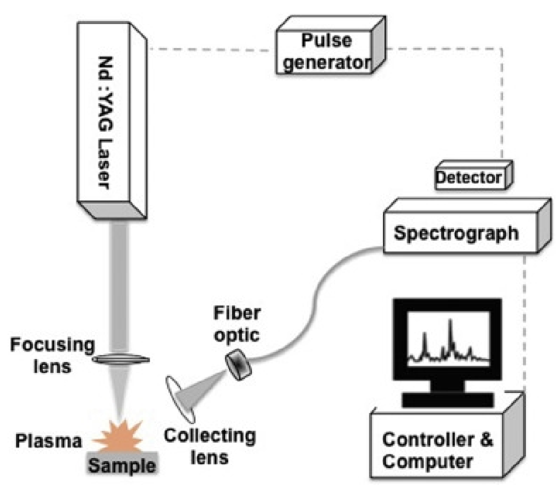

Fig 4: Experimental set-up for laser-induced breakdown spectroscopy (LIBS) for soil carbon sensing [30]

The final type of spectroscopy covered in this review is INS, which is based on the inelastic scattering of neutrons from organic carbon nuclei. The resulting gamma rays' response is measured through gamma ray spectroscopy [17], [33], [34] . The interactions between the fast- and thermal-neutrons result in prompt- and delayed-gamma ray spectra measured during and after the irradiation process. One of the advantages of this method is that it can sense both inorganic and organic carbon because the spectroscopy will measure the total number of carbon atoms present in the scanned area [33], [34]. Another advantage of this technique is the ability to scan large areas, reducing total time and effort in measuring the SOC of an area [17], [33], [34]. This method is not as developed as the previous methods described, so the challenges that it faces include high cost, missing optimization and calibration, and lack of field models ready for research and testing [17]. A team at the Lawrence Berkeley National Lab developed a neutron imaging system based on INS mechanisms that is currently being tested on real soil, outside of the lab [35], [36]. Their system is represented by the image in Figure 5, showing how the neutron scattering events are detected and translate to the carbon present in the soil.

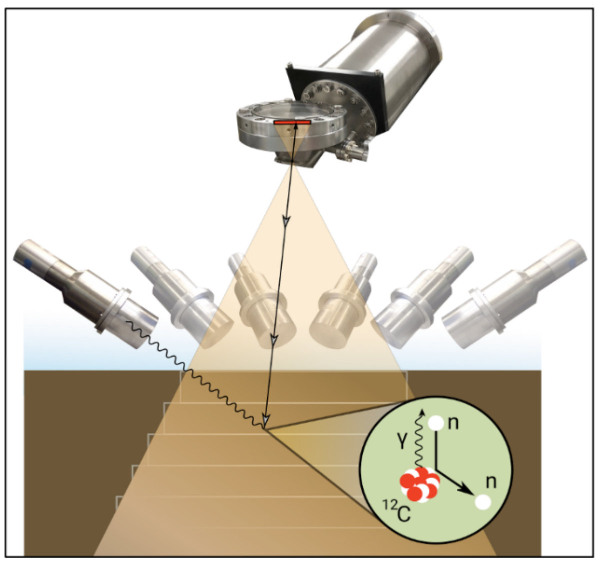

Fig 5: The new system by Berkeley Labs can determine carbon amounts by INS mechanisms without disturbing the soil [35]

A summary of the advantages and disadvantages of the above spectroscopy techniques are listed in Table 1 below. The factors examined in this analysis include amount of current research and development into that technique, relative cost, accuracy (in comparison to traditional methods), and size of measurement area. This table is not intended to be comprehensive, but instead serves as an overview of soil carbon spectroscopy techniques.

Table 1: Summary of comparison of soil carbon spectroscopy methods

	Vis-NIR	MIR	LIBS	INS
Prep work required	Soil core required	Soil core required	Soil core required	None
Amount of current research	Extensive; focused on field use	Extensive; mainly lab but some field use	Somewhat extensive; focused mainly on lab use	Some; still in lab use focus
Relative cost	Lowest cost (most developed technology)	Still too high for feasible field tools	High cost	Highest cost
Accuracy	Decent (probably sufficient for most field use)	Good (better than NIR, at least in lab tests)	High; dependent upon other soil components	Highest accuracy
Measurement area	Small; requires many measurements	Small; requires many measurements	Small; requires many measurements for a single area	Small and large-scale
Calibration curve?	Required; reproducible after significant calibration	Required	Required; reproducible	Required; reproducible
Portability	High; can run off a portable battery	High; can run off a portable battery	Decent; requires gas and a power source	Limited (radiation transportation limitations)

Remote Sensing

On the larger scales of regional SOC and global SOC, it is difficult to measure SOC content using field or lab techniques. That's where remote sensing techniques come in. Most remote sensors work by passively capturing the radiation reflected or emitted by objects near or on Earth's surface. Optical sensors, such as hyperspectral sensors, use the Sun's radiation as an illumination source to capture object wavelengths in the visible, near infrared, and shortwave infrared spectral regions [37]. These sensors are often mounted on aircraft or satellites and the resulting spectra are analyzed to improve the accuracy of the model. Recent advances in remote sensing for soil carbon sensing include the integration of machine learning and unmanned aircraft systems to improve the hyperspectral capabilities [38], [39].

Eddy Covariance and Carbon Flux

Another method of carbon sensing on the global scale is by measuring the carbon fluxes in the atmosphere around agricultural lands and other areas where there is significant carbon exchange between the soil and the air. Typically, these carbon fluxes are measured with the eddy covariance method which works by collecting turbulent flux data through wind velocity covariance calculations [40]. The data needed for these calculations is obtained through anemometers and highly efficient gas-analyzers with high sampling frequency and rapid response time [41]. Measuring carbon flux is generally used to track long-term changes in the land carbon sequestration as well as major fluxes in CO_2 [17]. Challenges with this method of measuring carbon sequestration include inherent uncertainties with the flux estimation and biomass sampling as well as the development of hardware that can rapidly and accurately analyze turbulent flux data [17] [41].

Fractionation

Another important method to understand carbon sequestration and the amount of SOC in soil samples is soil fractionation. The SOC present can be divided into groups, or fractions, based on their properties. The division of fractions depends on what you are looking for when analyzing the samples, but some common SOC fractions include microbial biomass carbon (MBC), particulate organic carbon (POC), readily oxidizable carbon (ROC), and water-soluble carbon (WSC) [17], [42]. Fractionation methods are either physical, where the soil components are physically separated through sieving, sonication, or slaking, or chemical, where the soil components are separated by using solubility and mineralogy rules [17], [43]. There are generally no issues with the accuracy of this carbon sensing method, although it is very time-consuming. Accordingly, this method is better suited to understanding the roles of different soil carbon fractions in overall soil health. This could lead to better understanding of the mechanisms of carbon sequestration for both long-term and short-term [17].

Gaps in Organic Soil Carbon Sensing Research

Most of the current research into measuring organic soil carbon is focused on improving the efficiency and portability of NIR and MIR spectroscopy as well as LIBS and INS for use in the field. However, there are some other methods that so far have not been explored as thoroughly as the methods described previously. One technique is the use of fluorescence spectroscopy to measure the degree of humification in the soil. Humification is the formation of mature organic matter from decomposed plant remains, which increases the amount of carbon present in the soil and is one of the main methods of carbon sequestration [44]. Based on this, there is some research going into estimating humification degree using laser-induced fluorescence spectroscopy (LIFS). The fluorescent material present in SOC (lone pairs of electrons like C=O, aromatic, phenolic, and unsaturated conjugated aliphatic systems) is excited by the laser and releases fluorescent emissions [45]. The carbon content of the soil normalizes the area under the fluorescence emission and is defined as the SOM humification index, giving a measurement of the stable carbon in the soil and therefore a measurement of the amount of carbon sequestration [45]. There is some development of portable LIFS systems but research into using LIFS to analyze soil is focused on the humification degree rather than the amount of stable organic carbon in the soil.

Another route for potential research includes correlating soil electrical conductivity and SOC. In soil, electrical conductivity can represent how much water the soil can carry as well as a measure of the salinity of the soil. In cases where the salinity of the soil is low, the apparent electrical conductivity (EC_a) may also be used to estimate SOC [46]. In one study by Longo et al., there was a strong correlation between EC_a and soil properties including organic carbon content due to the ability of humus (mature organic material) to retain positively charged ions [47]. While it is not enough to accurately measure SOC content, EC_a has the potential to improve overall soil characterization and soil sampling strategies [46]. There is little research done so far in correlating EC and SOC because of the heavy influence on conductivity from other properties of the soil. However, there is potential for future research into this method due to the relative ease of measurement, either through direct sensors in the soil or through electromagnetic induction from no-contact sensors above the soil [47]. Both methods are shown below in Figure 6. Currently, most of the research into EC in soil is focused on using the method to improve soil management strategies.

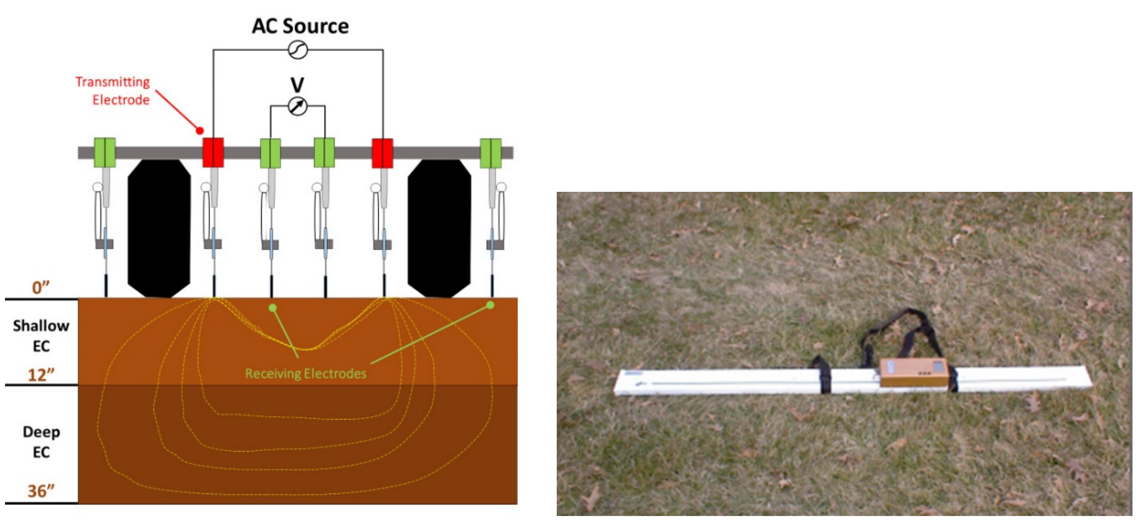

Fig 6: A contact sensor system for soil EC (right) and a typical electromagnetic inductor for non-contact EC measurement [47]

Another gap in soil carbon research is the lack of a library of soil spectra for use in the technologies described in the previous section. A standard soil spectra library that includes data from across the country would allow for improved use of the NIR and MIR technology. The difficulties with this include developing a standard for measurement (which has not been done yet), gathering baseline measurements (the Soil Health Institute has done this somewhat), and instituting an overarching measurement management system. A March 2022 report by Carbon180 called the Soil Carbon Moonshot proposed an interagency plan and related recommendations to invest government funds more efficiently. The full report can be found at https://static1.squarespace.com/static/5b9362d89d5abb8c51d474f8/t/62292045a84bb233211775e7/1646862413364/Carbon180-SoilCarbonMoonshot.pdf.

An earlier report by the Cleantech group in July 2021 laid out the current situation with managing carbon sequestration, with the biggest issue being a lack of regulatory policy or guidance. According to the author, Chris Sworder, there are already many existing methods for soil carbon measurement and modelling. Figure 7 shows the breakdown of existing technologies according to the industry professionals across the field. The full report can be found at https://www.cleantech.com/soil-mapping-technologies-regenerative-agriculture-soil-carbon-sequestration-and-ecosystem-service-payments/.

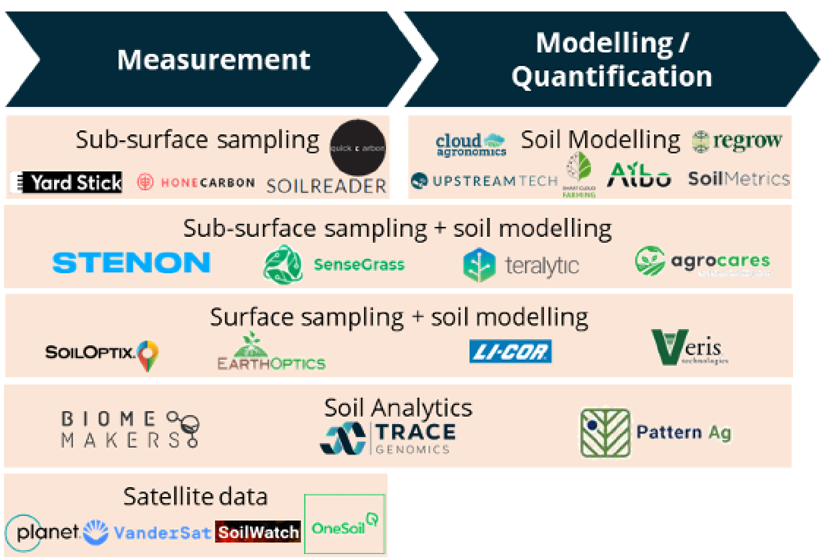

Fig 7: Breakdown of existing measurement and modelling systems for soil carbon content [48]

Conclusions on SOC Measurement Research Prospects

The above research is a surface-level summary of organic carbon concepts and measurements by someone with no prior experience in the field. Accordingly, the following conclusions are based purely on the relatively brief list of sources covered in this review and do not rely on comprehensive knowledge of the subject.

- There are already many existing research projects into developing cost-effective and portable carbon measurement techniques (see Soil Health Institute Briefing and Figure 7 above).
- Soil carbon sensing is highly dependent upon the properties of the soil under analysis, and it is likely that there is no one-size-fits-all technology that can accurately measure soil carbon content.
- A repeating factor throughout the research done was the lack of a standardized carbon measurement system and the lack of a driving agency behind the money thrown at soil carbon research. In short, there are some issues with soil carbon measurement technology, but the bigger and more pressing issues are management and policy challenges.

Traditional Inorganic Carbon Sensing Methods

Soil inorganic carbon, or SIC, is typically stored in soil as carbonates, so traditional SIC measurement techniques are focused on the reaction between the carbonates and a strong acid (usually HCl), with the quantification of the resulting CO_2 product [49]. The CO_2 product can be measured gravimetrically, volumetrically, through back-titration, or through acid consumed during a neutralization reaction [49], [50]. The most common methods are the acid neutralization technique and the volumetric procedure, but SIC can also be determined through the dry combustion technique described in the Traditional Organic Carbon Sensing Techniques [50].

Alternative Inorganic Carbon Sensing Techniques

Generally, SIC is found by determining the amount of total carbon and subtracting the SOC content. Conversely, where SOC cannot be determined directly, it is calculated by determining total carbon and subtracting the SIC content. This relationship comes into play with any measurement technique that does not easily distinguish between SOC and SIC, including spectroscopy techniques. In fact, almost all the spectroscopy techniques described in the Alternative Organic Carbon Sensing Methods section determine the total carbon present in the sample. However, there is some work into investigating the use of MIR spectroscopy to determine SIC specifically [51]. This research is particularly helpful when analyzing soils with high levels of carbonates present, at which point it is difficult to distinguish between organic and inorganic carbon in the sample. Otherwise, most of the existing work into sensing SIC is bundled into sensing total carbon using the techniques described previously.

Gaps in Inorganic Soil Carbon Sensing Techniques

The biggest gap in SIC research is the lack of research into looking for SIC specifically, rather than just the total carbon content of the soil. While SIC plays an important role in soil health, it is not as much a concern when looking purely at carbon content. However, the growing understanding of the permanence of SIC vs SOC indicates a need for a separate evaluation of SIC. Based on the research presented above, it appears that it is nearly impossible to separate diffuse reflectance spectroscopy measurements of SOC and SIC. Similar reasons stand for INS, which measures the amount of carbon atoms and thus does not distinguish between organic and inorganic carbon. Despite this need, there is little-to-no research into sensing SIC for *in situ* measurements. Perhaps due to the permanence of SIC, there is less need for field measurements to track carbon sequestration, particularly since SIC tends to be found more in minerals, which are more predictable than biologically active soil that contains SOC.

For lab use, there is current research into using the thermal gradient method for dry combustion, also called ramped combustion, which uses two different but sequential temperatures during dry combustion to simultaneously measure SIC and SOC [49], [52]. There is also the potential for carbon isotope analysis to distinguish between SIC and SOC [53]. Another possible route for future research could use the distinguishing marker between organic and inorganic carbon: hydrogen. Organic carbon possesses hydrogen and usually some amount of hydrogen bonding whereas inorganic carbon does not. One example of this is CO_2, which is classified as inorganic because it does not contain hydrogen. Spectroscopy techniques can identify the presence of hydrogen bonds, which is why they are useful to measure SOC, but it is difficult to distinguish between organic and inorganic carbon as stated previously.

Conclusions on SIC Measurement Research Prospects

Based on the brief research described above, there is a key conclusion about research prospects on SIC. While lab research allows for the separation of SOC and SIC, it is difficult to separate the identification of organic carbon from the identification of inorganic carbon in field soil samples. Techniques used out in the field such as NIR and MIR spectroscopy will measure the total carbon present in the soil, with some distinction between organic and inorganic carbon due to the presence of hydrogen bonds. Accordingly, there are fewer research prospects in identifying inorganic carbon separate from organic carbon using field instruments. Fortunately, it seems that most of the focus in carbon sensing is on measuring total carbon and organic carbon, which is the more volatile fraction of soil carbon.

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