

A NON-INVASIVE METHOD OF DETECTING CARBON IN SOIL: COMPARISON WITH SOIL CORES AND EXCAVATIONS

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Abstract

Our need for a non-destructive, precise, and rapid determination of the soil's elemental composition poses special challenges because of the complexity of the soil matrix and lack of instrumentation for such belowground measurements. Although the availability of such instrumentation would significantly promote our understanding of subsurface processes and balances, today's gold standard is core samples and excavations. Preliminary results of calibrations in a sandpit and in two field studies of our novel multi-elemental soil analysis (MESA) system clearly demonstrate its value in non-destructively measuring carbon in soil. We discuss the system's basic operating characteristics and performance, and its potential applications.

Key Words: Soil analysis, carbon sequestration, neutrons, gamma rays, spectroscopy

1. Introduction

Recent national- and international-concerns about identifying and implementing effective options for reducing atmospheric CO₂ prompted a search for new technologies to determine the role of soils in sequestering carbon. The soils' large capacity to store carbon [Lal et al. 2003] is reflected in the increasing concentrations or pools of soil organic matter (SOM), as assessed by simple grab sampling and subsequent estimation of carbon by dry- or wet-combustion techniques. These destructive strategies require sealing the samples immediately after their removal and transporting them back to the laboratory where, after extensive separation of solids and woody matter, they are dried and analyzed. Although this method served as a gold standard for soil analysis in countless studies, criticism levied at the procedures of collecting, preparing, and analyzing the samples called into question some findings [Johnston et al., 2004].

Two recent alternative methods to measure carbon in soil *in situ*, based on laser-induced breakdown spectroscopy (LIBS) [Cremers et al., 2001] and near- and mid- infrared spectroscopy [McCarty et al., 2002], might replace the current slow, cumbersome, and labor-intensive combustion analyses. However, their drawback is that they are destructive. In LIBS, a small volume of soil (~50 µL) is vaporized and the resulting spectral emission measured; in the infrared method, a sensor, mounted on the tip of a shank ploughs through the soil at a set depth and senses the carbon down to a few millimeters beneath it.

We propose a third novel method for soil analysis that is entirely non-destructive as an alternative to the current sampling methods for carbon analysis. Our multi-elemental soil analysis (MESA) system is based on the spectroscopy of gamma rays induced by inelastic neutron scattering (INS) and thermal neutron capture in the various elements present in the soil [Wielopolski et al., 2000, Wielopolski et al., 2003, and Wielopolski et al., 2004]. MESA enables true serial measurements in exactly the same spot over short and long periods. Furthermore, it can be used in a stationary mode or in a contiguous scanning mode over arbitrarily large fields. The sampled volume is over 100 liters, resulting in a sampled mass of over 150 kg. The sampled depth in the soil is estimated as 20- to 30-cm [Wielopolski L., Dioszegi I., Mitra, S., 2004].

We initially calibrated the system in a homogeneous mixture of sand with carbon, and then compared the findings with those from two field studies, one at Brookhaven National Laboratory (BNL) and the other at the C-H₂O research site in the Blackwood Division of Duke Forest, NC. The MESA system clearly demonstrated its ability to measure carbon under extreme conditions of 100% water saturation and in rocky forest fields. We discuss the findings below. Despite this success, we recommend making a thorough careful calibration under well-defined conditions before its widespread use in the field.

2. Experimental Set-up and Sampling Procedures

2.1 INS Set-up

The use of neutrons for analytical purposes has been described extensively; the reader is referred to three basic references [Alfassi and Chung, 1995, Chrien and Kane, 1979, and Nargolwalla et.al., 1973]. The MESA system consists of a deuterium-tritium (d,t) neutron generator (NG) producing 14 MeV neutrons [Csikai, 1987], gamma-ray NaI scintillation detectors, and a shadow-shielding between the NG and the detector to reduce direct exposure. Originally, measurements were taken by placing the system shown in Fig. 1 (configuration A) on the ground (as described in detail in Wielopolski et al., 2003, 2004) Subsequently, we found that adding two more detectors and raising the system about 30 cm above the ground improved the system's response. These changes increased the footprint of the system and the detectors' counting yield, while reducing the neutron depth gradient, thus improving the uniformity of exposure to the neutron field.

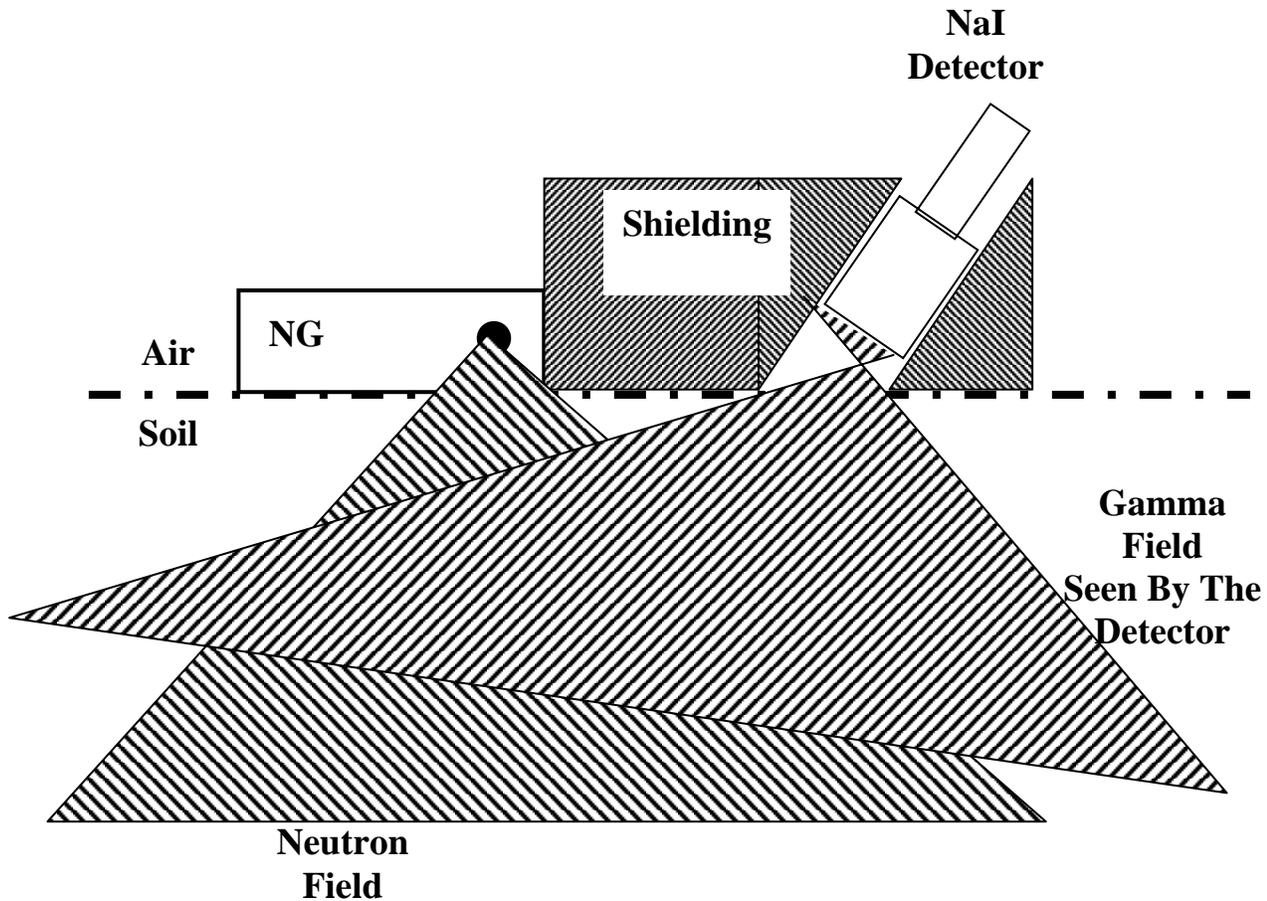


Figure 1. Schematic configuration of the MESA system showing the common volume of the neutron- and gamma-fields that contributes to the gamma-counting yield.

2.2 Measurement Sites and Protocols

The measurements reported here took place at BNL with the system in configuration A and at Duke Forest, NC with the system in configuration B. All INS measurements lasted for 30 min during which two gamma-ray spectra were acquired, inelastic and prompt, and analyzed for carbon peak intensity. At the same time, fast neutron output from the NG was monitored independently with a neutron plastic scintillator detector. At BNL, the system was first calibrated in a sandpit containing homogeneous mixtures of sand and granular carbon prepared with various concentrations of the latter. Figure 2 shows

the system's set-up for these measurements. It was then used in field studies at three different sites. At each site, the INS measurements were followed with five cores spaced over a 30 cm by 30 cm area; these sites and configuration of the cores are shown in Fig. 3. Each core, 5 cm in diameter, was subdivided into 0-5, 50-10, 10-20, 20-30, and 30-40-cm long sections from which duplicates of 1 gram aliquots were taken for standard dry combustion chemical analysis. The sites included a pine stand, an oak forest, a sandy patch: the soil type was predominantly sandy loam typical to Long Island.

At Duke Forest, the measurements were taken at three locations with a modified system in configuration B. The soil there is generally classified as an Enon silt loam (a



Figure 2. Sandpit filled with synthetic mixture of sand and 10% carbon by weight with the set-up at configuration A.



Figure 3. Three sites at BNL that were measured by INS and core samples subjected to chemical analysis; a) pine forest, b) oak forest, c) sandy patch. d) Relative location of the five cores.

low fertility Hapludalf, typical of the SE US piedmont). The INS measurements also lasted 30 min, but in addition to the 2.5 cm diameter cores, the measurement sites were excavated into 40 cm by 40 cm by 40 cm pits in layers of the same thickness, when possible, as the cores at BNL. Three large samples were taken from a cleaned and homogenized material from each layer and two 1 g aliquots (subsamples) from each sample underwent combustion analysis. While the core samples at Duke were used mainly to determine moisture, which were taken immediately after the INS measurements, the excavation samples were used for quantitatively determining carbon, solid and woody fractions. During the INS measurements the fields at Duke were about 100% water saturated, 20 to 50 percent by weight, and also very rocky with coarse

fragment varying 5% to 30% by weight. Figure 4 shows the three sites at the Duke Forest.



Figure 4. The three sites selected for measurements at the Duke Forest, NC included a) grassland with the grass in place and, b) removed, c) pine forest, and, d) hardwood, oak forest.

3. Results

3.1 BNL Results

The carbon calibration line in Fig. 5, derived in a sandpit, demonstrates the linearity of the carbon signal with the abundance of carbon. We emphasize that since the device measures carbon in a constant volume, the abscissa of the calibration line is given in terms of carbon concentration, C_c , in units of gC/cc and not in the terms of carbon fraction, C , that has units of gC/g. The widely used carbon fractions are derived from samples with constant weight, implying that different volumes are sampled from soils with different bulk densities. The variability of the soil's density with depth further complicates the assessment of carbon stocks using carbon fractions. The calibration line thus derived is expressed as

$$Y = 73100 \cdot C_c + 5295$$

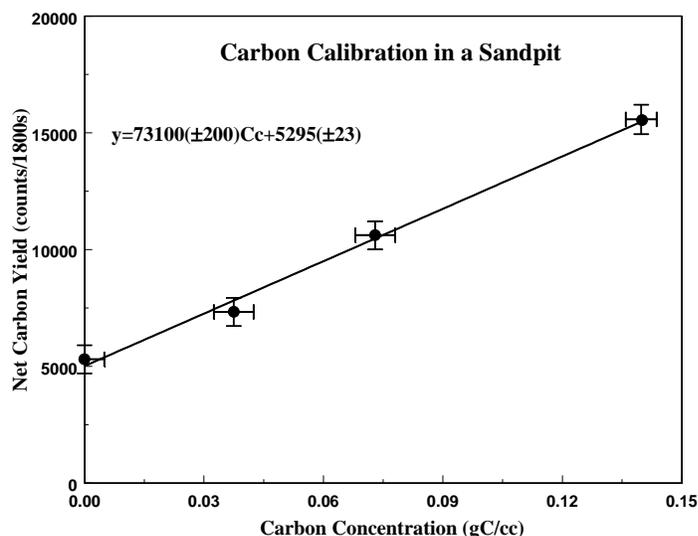


Figure 5. Carbon calibration line derived in the sandpit.

(1)

The sandpit calibration was tested against the values obtained from analyzing the carbon fraction in soil cores taken from three fields at BNL (Fig. 3). Each core section, pine stand, sandy patch, and oak forest, revealed that there were very large lateral and between-depth variations over a small, 30 cm square. For example, these variations in soils from the oak forest are shown in Fig. 6a, where there was a large discrepancy between the chemical analyses of the carbon percentages and INS measurements using the calibration line from the sandpit. However, when the percentages were converted into carbon density, as shown in Fig. 6b, the variability was reduced, and the values agreed with the results by the INS. This is attributed to the varying bulk density with depth. Table 1 summarizes this agreement of the averaged top 5 cm of the five cores at each site with the MESA measurements. The average carbon density over the entire depth is an artificial quantity that exists only when the entire pit has been homogenized in the laboratory,

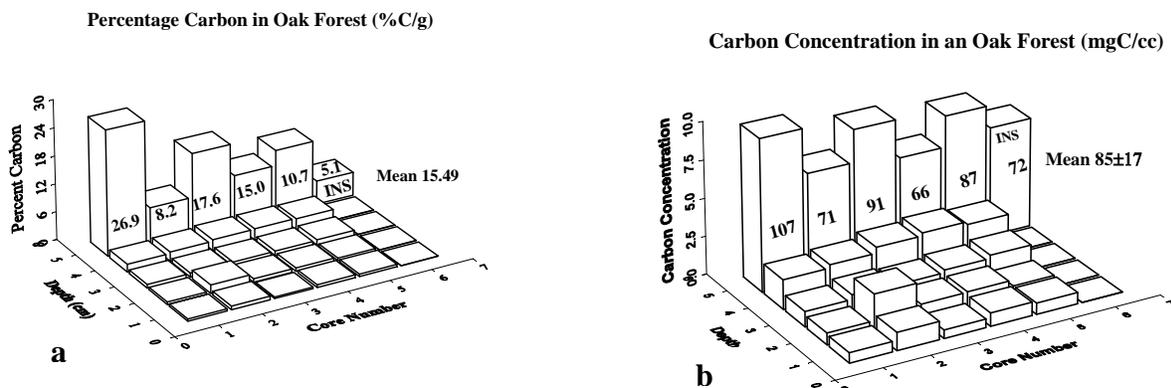


Figure 6. a) Percentage of carbon for the five cores in the oak forest as a function of depth, b) converted to carbon concentration.

or calculated analytically. Thus, since mean carbon density is not a physical quantity in the field, it cannot be measured *in situ* by the MESA system.

Table 1. Carbon concentrations at the top 5-cm layer estimated using the INS method and chemical analysis of the soil samples.

Site	INS (gC/cc)	Chemical Analysis (gC/cc)
Pine Stand (w,l)	0.099 ± 0.005	---
Pine Stand (w/o,l)	0.079 ± 0.005	0.073 ± 0.021
Oak Forest (w/o,l)	0.072 ± 0.004	0.085 ± 0.017
Sandy Patch	0.026 ± 0.003	0.025 ± 0.002
Sand Pit (Cal.)	0.00	0.0004 ± ---

(w/l) with litter

(w/o,l) without litter

It is apparent that the MESA system responds quantitatively to the presence of carbon in soil; however, because of the strong gradients in soil density, it raises the question about the most appropriate way of calibrating the system.

3.2 Duke Forest Results

The approach in the Duke Forest differed from that at BNL in that soil cores taken for analysis from the measurement sites were used only to determine 1 moisture immediately after the INS measurements. Carbon was analyzed after excavating five layers 5, 5, 10, 10, and 10 cm thick of a 40x40 cm square pit. Figure 7 shows calibration attempts using 9 points from three different regions. Line c with the highest r-value that excluded the outlying points P1 and G2 was used as a tentative calibration line of total yield of INS counts versus total carbon in the pit. The exclusion of the points was

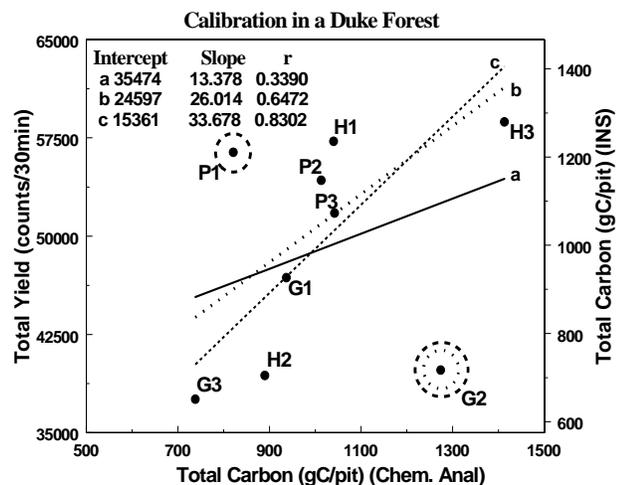


Figure 7. Three potential regression lines; line a- includes all the points, line b- with P1 removed, and line c- with P1 and G2 removed.

arbitrarily based on the r-value; however, subsequently we found that the P1 sample contained a significant amount of very brittle crystalline charcoal that could have been lost when the samples were mechanically ground in preparation for the analysis. That would explain why the INS reading for P1 was higher. No plausible explanation was found for the outlier G2. The calibration line c was applied to create the right-hand side axis on the graph, and to convert the INS counts into carbon content. Table 2 summarizes these results, where G represents grassland, P for pine forest, and H for hardwood oak forest.

To improve the credibility of the regression lines for this limited number of points (9), and their non-parametric distribution, a bootstrap method was applied. In this method, the set of nine points is re-sampled with returns to create an alternative set. This process is repeated n times and n new regression

lines are calculated. Figure 8 shows the distribution of the regression r-values where n equals 5000 with the various confidence levels around the most likelihood estimate (MLE) of the r-value. This distribution is positively skewed, and at 50% confidence level, the r-values are completely positive thus indicating an overall positive correlation between these two methods of carbon analysis in soil. Plots of the slope “a” and the intercept “b” distributions also were positively correlated, but were narrower than that of the r-values. Thus, although the number of points is very limited, there is a correspondence between these two methodologies for carbon analysis.

Table 2. Data points used for calibration line together with coarse fragments and moisture in the pits.

Site	INS (gC/pit)	Duke (gC/pit)	Coarse Fragment (%)	Mean (0-10cm) Moist (%)
G1	934	937	16.8	24.7
G2	717	1274	13.9	27.4
G3	654	738	8.2	25.1
P1	1210	821	12.0	25.8
P2	1147	1013	9.4	28.8
P3	1073	1042	12.2	23.9
H1	1235	1040	4.2	21.8
H2	705	890	29.3	24.4
H3	1279	1413	9.6	35.9

3.3 Error Propagation

Proper analysis of error propagation in determining soil carbon is critically important for quantitatively evaluating the stocks of, and changes in, the soil’s carbon content. Error analysis is also crucial for extrapolating local measurements to entire fields, and to regional-, and global-predictions based on analytical models. Generally, the error for any calculated quantity F with an arbitrary functional dependence $f(x_i, \dots)$ can be propagated

according to the general estimator given by Eq. 2, or it can also be determined by repetitive measurements and calculation of the mean value and the standard error of the mean. However, both these approaches are prohibitively time-consuming and labor-intensive. Eq. 2 requires knowledge of every step in the calculations and the errors associated with each step.

$$\sigma_F = \sqrt{\sum_i \left(\frac{\partial f}{\partial x_i} \right)^2 (\sigma_{x_i})^2} \quad (2)$$

This error analysis does not include the natural variability in the field that is time- and space- dependent. Consequently, the widely applied normal statistics for sampling is erroneous and instead geostatistical considerations should be applied, for example, in deciding upon the number of excavations. In light of this, the error associated with core sampling requires many sampling points to reach a desired confidence level. The number of core samples might be reduced by replacing it with site excavations, which, although more involved and cumbersome, reduce the error for a given site. Moreover, excavations provide samples with large volumes thus lowering the number of errors due to lateral variations, for example, as seen in the variability among core samples shown in Fig 6. However, because the INS method samples large volumes its errors are comparable to those of large excavations, but the results are obtained at extensively reduced effort and time. The value and significance of this is further compounded when considering scans of large fields in which the total scanning time might be the same as that needed for a single measurement in stationary mode, thus giving the same error for the large area as that obtained in a single stationary measurement.

As an example of error propagation, we consider the three excavations from the Duke Forest grassland summarized in Table 3. In this case, three samples were collected from each layer and two

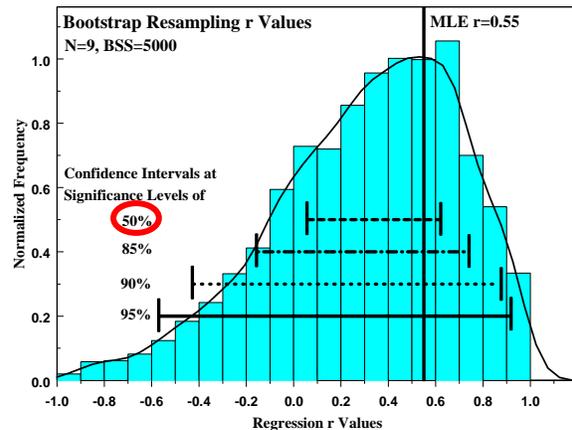


Figure 8. Bootstrap distribution of the regression r-values.

aliquots were drawn from each sample, resulting in six samples per layer. The actual size of the sample analyzed for carbon content is identical to that from core samples, i.e., it is about one gram, although in each case they represent a different volume that has been homogenized. The first three columns (G1, G2, and G3) represent the maximum relative difference between any two out of six, subsamples at a given layer and excavation site. So, this represents the variability in individual subsamples that, in this case, reached 44%. When the six subsamples are averaged with the relative standard deviation summarized in the next three columns, the differences are reduced in comparison to the variations in the individual subsamples. Finally, the reported standard error in the mean value of the percent carbon fraction for a given layer is further lowered by a factor square root of the number of samples n (n=6). These values are summarized in the last three columns. Table 4 summarizes the results when propagated for the entire pit (summed up over five layers), together with the single measurement by the MESA system. We mention that extending the counting time, thus achieving a desirable error or confidence level, can further reduce the error in the INS method. This example of error propagation is based only on the variability of the six subsamples and did not include contributions from errors associated with determining the volume and solid fragments, and or any other contributing factors.

Table 3. Error propagation in the analysis of soil carbon from excavated samples in the grassland field of the Duke Forest.

Depth (CM)	Max. Diff. In Set of 6 Δ_{\max} / \bar{x} (%)			SD In Set of 6 σ_{n-1} / \bar{x} (±%)			Carbon Fraction (%) $\bar{x} \pm SE_{Mean}$		
	G1	G2	G3	G1	G2	G3	G1	G2	G3
0-5	21	14	15	8.2	5.4	5.9	3.6 (3.3)	3.7 (2.2)	2.6 (2.4)
5-10	12	29	8	3.7	11	2.8	1.8 (1.5)	2.5 (4.5)	1.5 (1.1)
10-20	16	22	16	5.8	9.2	5.8	1.2 (3.3)	3.6 (3.3)	3.6 (3.3)
20-30	16	15	17	6.2	5/6	5.6	0.7 (2.5)	1.1 (2.3)	0.4 (2.3)
30-40	37	44	32	14	17	12	0.5 (5.9)	0.6 (6.9)	0.4 (5.0)

Table 4. Relative SE of the Soil Carbon Content in a Pit

	Excavation (%)	INS (%)
G1	1.4	4.1
G2	1.7	4.8
G3	1.3	5.0

4. Discussion

The INS method using the MESA system clearly demonstrated its capability to measure carbon in soil under poor conditions, such as water saturation or in rocky soils. The effort associated with taking these measurements is significantly less than those entailed in the current gold standard of core sampling or excavations. Consequently, adopting this methodology would permit sampling a larger number of sites for the same level of effort, thereby better characterizing a field that might be of a particular significance in forestry. A unique advantage of the system not discussed here is its ability to operate in a continuous scanning mode thus increasing the sampled volume to any arbitrarily large field. In the scanning mode, the carbon estimate represents the true mean value for the scanned field.

The best way to calibrate the system remains undetermined. Clearly, MESA values cannot be used to assess the carbon fraction by weight. However, carbon density appears to be a proper value for calibration; when used over large areas, it might represent an effective mean value for the entire area. It also might be possible to calibrate the MESA system in terms of total carbon.

An extremely valuable feature of MESA is that it can monitor changes in carbon density at a single point with little or no calibration. This would suffice to develop an index proportional to the carbon content; for example, the number of carbon counts in the original spectrum could serve as such an index, and the changes in that index could be monitored. Then it might be possible to establish several index points within a forest or field, and simply monitor the change in the index over time. Repeated MESA measurements, year after year, would reveal any change in carbon stocks.

For an accurate calibration, more homogeneous fields should be selected and more plots excavated. Based on statistical analysis of the Duke Forest results, achieve 85%, 90%, and 95% confidence levels in the calibration line the required number of excavations is 18, 27, and 40, respectively. We are planning to demonstrate that a thorough calibration of MESA for a particular type of soil will be required only once, and that will be suitable for other types of soils. Then, any subsequent measurements with MESA would occasionally entail obtaining a few more points to verify the appropriateness of the calibration for that soil type. These statistical considerations may change in future due to different ways of measuring and representing carbon content in large fields. The sensitivity of the current system over the initial one with a single detector on the ground improved by a factor of 8.54 (results not presented here); further improvements are expected with increase in number of detectors used. Our latest system is mounted on wheels and is being prepared for scanning.

Acknowledgement

This work was supported by the U.S. Department of Energy under contract No. DE-AC02-98CH10886.

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