

Advanced Instrumentation for *In Situ* Field Monitoring of Soil Carbon Sequestration

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Introduction

Atmospheric CO₂ concentrations have increased considerably since the mid-1800s and are projected to increase even further during the coming century. This rapid increase in CO₂ concentration corresponds with increases in the combustion of fossil fuel, changes in agricultural land use, and deforestation since the beginning of the industrial age. These observations have prompted scientists and policy-makers to consider options for stabilizing energy-related increases in atmospheric CO₂ concentration. A continued move towards energy conservation and a commitment to renewable energy resources offers a range of socially-acceptable options for mitigating further increases in CO₂ concentrations. Additional mitigation opportunities also exist, including the implementation of innovative technologies for carbon sequestration in geologic formations, ocean sequestration, direct capture and separation, advanced biological and chemical approaches to carbon management, and enhanced carbon sequestration in terrestrial ecosystems (DOE Carbon Sequestration Roadmap, 1999).

Carbon sequestration in the terrestrial biosphere, or more specifically the storage of carbon in plant biomass and soils, offers an attractive option for carbon management. Soil organic carbon (SOC) represents an especially large pool of carbon in many ecosystems and there has been increasing emphasis placed on enhancing carbon sequestration in this pool through timely manipulation of agricultural and forest lands. Unfortunately, non-invasive, remote and/or otherwise rapid-throughput techniques for measuring changes in SOC that might result from implementing these carbon sequestration strategies are lacking. Existing methodologies for measuring SOC are time-consuming, analytically expensive and often require unreasonable replication in order to identify statistically significant differences between or among treatments (Garten and Wullschleger, 1999). In addition, efforts to examine carbon quality or the chemical

nature of SOC have also been limited. Many of the techniques used to assess changes in SOC quality require chemical and/or physical fractionation of samples that are themselves time consuming, require destructive sampling, and thus often preclude broad-scale application across a range of sites. As a result, there is little information on the chemical form of carbon stored in soils as a result of land conversion activities, nor information about how chemical constituents of SOC may change over time.

Objectives

Because SOC represents a large pool of carbon, there has been great interest in developing strategies to enhance SOC through manipulating agricultural and forest lands. The extent to which such manipulations will lead to the long-term enhancement of SOC will depend on the amount (*quantity*) and on the chemical composition (*quality*) of carbon stored within the soil profile. Instrumentation for characterizing SOC is, however, lacking. Therefore, to address this deficiency, we have initiated a project designed to address the following objectives:

- to develop an advanced Raman/SERS fiberoptic-based device for the analysis of carbon concentration and characterization in soil,
- to test the qualitative and quantitative performance of the system against agricultural and forest soils of known SOC concentration and for soils that have been physically and chemically fractionated to labile and recalcitrant SOC pools, and

Approach

Raman spectroscopy offers several distinct features that are important for field monitoring of complex environmental systems and thus make this general spectroscopic technique attractive for potentially monitoring changes in SOC. One disadvantage with the normal Raman effect for trace detection of chemical constituents, however, is its very weak nature, as only 10^{-7} (or less) of the incident photons exhibit the Raman scattering effect. A phenomenon that can significantly enhance the Raman intensity is the surface-enhanced Raman scattering (SERS) effect. In the SERS technique, a laser beam is focused onto a nano-structured surface (or substrate) and scattered radiation is collected and analyzed (Vo-Dinh, 1989). If the substrate is coated with a target compound, the scattered light contains compound-specific information useful for both qualitative and quantitative chemical analysis. The intensity of the normally weak Raman scattering process is increased by factors as large as 10^8 for compounds adsorbed onto a SERS substrate, allowing for trace-level detection.

Several projects have applied various RAMAN-based approaches to the study of humic and fulvic acids extracted from soils (Francioso et al. 1996, 1998, 2000), and generally found both SERS and FT-Raman useful in this regard. Francioso et al. (1998) observed that the study of fulvic acids extracted from an Irish peat was possible with SERS using a surface coating of a rough metallic substance like silver, which effectively enhances the Raman signal and quenches the otherwise high fluorescence. Francioso et al. (1996) had earlier used this same approach to characterize humic acids from peat, and successfully obtained SERS spectra for this class of SOC across a range of molecular weights. It was concluded that further development of these techniques would help to discern structural features of humic substances of different origins and

therein increase our knowledge concerning the application of humic and fulvic acids to the fields of agronomy and forestry.

Project Description

In keeping with objectives stated above, three tasks are currently being undertaken as part of a two-year project to explore the utility of Raman/SERS as a non-invasive tool for monitoring soil carbon sequestration. These include:

Task 1. Assemble Raman System for SOC Detection and Optimize Experimental Parameters

A Raman-based system for laboratory analysis of SOC is being assembled that will use a continuous-wave laser as an excitation source for spectral resonance Raman measurements. The utility of resonance Raman spectroscopy as an analytical technique depends upon the quality of the data and reliability of the methodologies used to translate these data into information. Fortunately, the theoretical framework of Raman spectroscopy has advanced in response to new experimental challenges (Myers and Mathies, 1987).

Task 2. Develop Advanced Raman Detection System (ARS)

The components required for a prototype Raman or SERS system would be composed of an excitation module, a detection module, and a network of fiberoptic probes (Figure 1). The excitation and detection modules could be combined into a single unit which ultimately might be hand-held, or at least portable (depending on the laser selection).

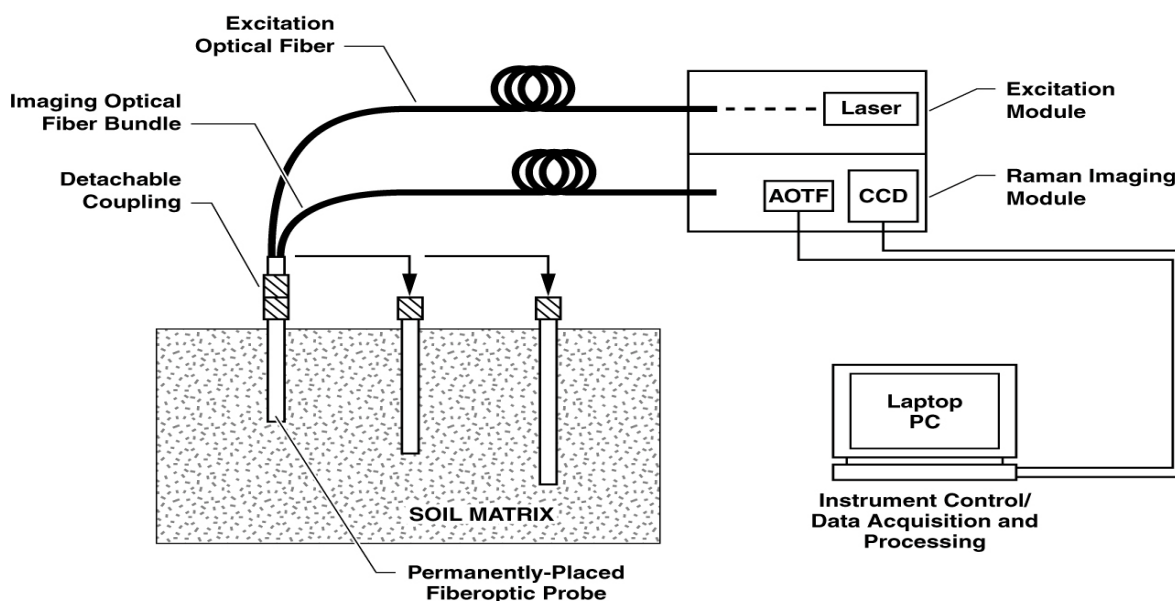


Figure 1. Schematic diagram of an imaging-capable AOTF-based Raman instrument with fiberoptic probes having detachable coupling with excitation/imaging module.

The detection module itself would be composed of the AOTF and a CCD detector (Figure 1). As with the excitation module, the Raman image collection fiberoptic bundle could be connected to the frame of the detection module via an SMA connector. The divergent signal beam exiting the fiberoptic would then be collimated, directed through the AOTF, and focused onto the CCD detector with an image-quality lens.

Task 3. Establish Correlation Between Raman Spectra and Different Forms of Soil Carbon

Soil samples are available for use in testing and calibration of the proposed Raman sensing system (Garten and Wullschleger, 1999). These samples have been taken to a depth of 60 cm and characterized in 10-cm depth increments for carbon concentration. Additionally, soil organic matter in all increments has been separated into two compositional pools by chemical and wet-sieving methods (Garten and Wullschleger, 2000). We will measure, where appropriate, the Raman and SERS Raman spectra associated with the above-mentioned soil samples and establish a spectral library for these samples taking into account differences in SOC with depth of original sample collection.

Results

This project started only recently and thus, only preliminary results are available. Our studies have focused initially on the question of whether Raman spectroscopy could be applied to simple solutions of alcohols (e.g., ethanol and glycerol) and acids (e.g., lactic and citric acids). Raman spectra were easily generated for these simple compounds using an excitation wavelength of 633nm (Figure 2). These studies were repeated for aqueous solutions of fulvic and humic acids (peat and soil) and it was observed that background fluorescence was problematic in terms of obtaining informative spectra. We have since shifted the emphasis of our investigations to SERS and are currently experimenting with various surface coating (e.g., silver) and excitation wavelengths as applied to fulvic and humic acid samples.

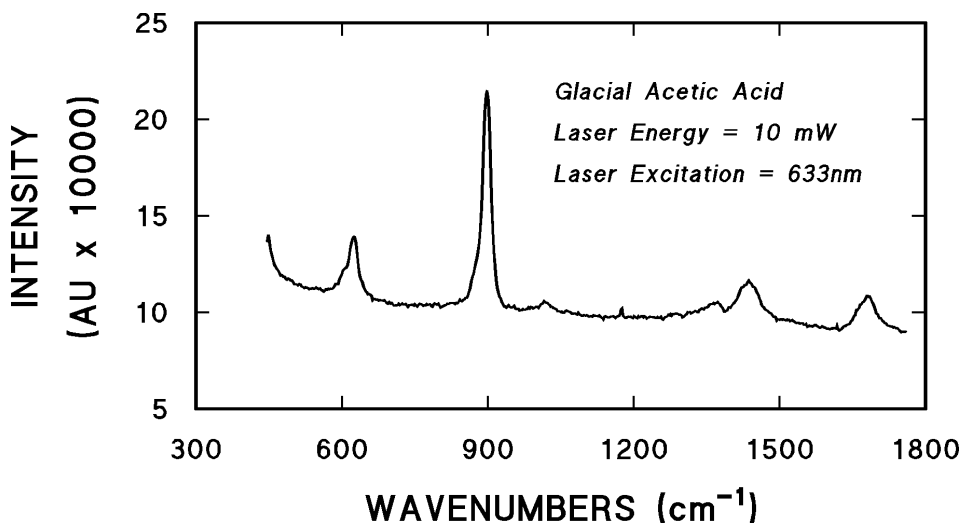


Figure 2. RAMAN spectral characteristics for an aqueous solution of glacial acetic acid.

Application

There is an obvious need for better understanding the amount of organic carbon stored in soils as a result of land management activities and the chemical forms of those SOC pools. Such a need is not currently being met in field carbon sequestration studies and the scientific community must begin to develop instrumentation and associated methodologies so that inventories of SOC can be quantified in the terrestrial biosphere (Post et al., 1999). Developing new approaches to measuring changes in SOC will, however, require improved science and technology as was voiced by the Monitoring and Verification Working Group at the St. Michael's Carbon Sequestration in Soils Workshop (Jastrow, 1999):

“Development of an accurate, portable, non-destructive organic carbon analyzer that can be used relatively quickly by one person in the field would be extremely helpful for monitoring and verification activities. Such an analyzer would allow repeated sampling within relatively small areas without the removal of soil from the field, thus leaving the study area intact. An effective and economical monitoring system...should...take advantage of improvements in monitoring and measurement technologies.”

The instrumentation requirements of the soil carbon management community appear simple, but (in reality) meeting these needs will necessitate significant technical breakthroughs in terms of developing a small, robust, reliable and potentially handheld system for measuring SOC concentration and chemical speciation in the field. Because SOC is present in relatively low concentrations and because changes due to carbon management strategies are likely to be subtle, special attention will need to be given to achieving high signal-to-noise ratios, quantifying acceptable limits of detection, and to resolving potential spectral overlap between various chemical forms of soil carbon. These constraints will alone require significant electronic and engineering attention. Furthermore, the future integration of carbon management into our Nation's forest and agricultural sectors will place additional demands on the use and deployment of instrumentation for detecting changes in SOC and, therefore, the technologies selected for initial examination should be readily adaptable to the market-place.

Future Activities

We are confident that SERS will prove useful for the detection and characterization of fulvic and humic acids. Once a SERS-based system is optimized for these compounds, it will then be applied to the study of SOC extracted from soils of known turn-over times (Garten and Wullschleger, 2000). This effort will serve to establish relationships between SERS-based estimates of SOC and other independent techniques for estimating soil carbon concentration. Depending on the outcome of these activities, SERS will subsequently be applied to solid-phase media either in the form of an artificial soil matrix or to actual soils.

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