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Nuclear Methodology for Non-Destructive Multi-Elemental Analysis of Large Volumes of Soil

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1. Introduction

The extent of global warming is determined by the net difference between the sun's incoming energy and that reflected back into the space. Changes in the reflected energy that depend on the conditions of the land's surface and of the atmosphere alter the global energy-budget, stimulating global warming. The dominant factor forcing climate change is the increasing concentrations of atmospheric greenhouse gases (GHGs), in particular that of CO₂ [Solomon et al., 2007]. The rise in CO₂ level from the pre-industrial revolution value of about 260 ppm to present-day concentrations of about 380 ppm, viz., ~46% increase, is recognized widely, albeit some dispute its anthropogenic origin [IPCC, 2007; Tans, 2011]. Extensive farming, the ever-increasing consumption of fossil fuels, land-management practices, the cement industry, and deforestation are the main drivers disrupting the tenuous balance between natural carbon release by the soil's biota and plant respiration, and carbon uptake by the photosynthesis of aboveground plants [Denman, 2007]. This active soil-atmosphere carbon exchange is an inextricable part of the global carbon cycle: hence, it plays a pivotal role in possibly slowing down, stopping, or even reversing this perilous escalation of global warming. With the predicted increase in fossil-fuel consumption, combating global warming necessitates a multi-pronged approach, including improvements in energy efficiency and the use of alternative energy sources. However, by themselves, these are insufficient unless we modify the ways in which we use and produce energy, specifically, the way we manage carbon. Restoring the depleted organic-carbon pools in soil by terrestrial sequestration worldwide is critical for controlling global warming, and for restoring the soil's quality, productivity, and so assuring food security [Lal et al., 2004; Lal et al., 2005]. Central to improving carbon management is having a better understanding of the belowground carbon processes and the ability to quantify them. However, gaining this knowledge poses special challenges because these processes are invisible to us. Soil is a dynamic, living system, a mix of living and dead-plant matter, and a mélange of belowground biota embedded in a matrix of solids, liquids, and gases [Johnston et al., 2004]. The current state-of-the-art in soil analysis comprises taking soil samples and subsequently analyzing them chemically by dry combustion in a laboratory. This method, although very

well established, is destructive, time-consuming, labor intensive, and provides only point information in time and space. The throughput of the method is highly inadequate for present demands for precise soil analyses over large areas in a variety of soil types and ecosystems.

The centrality of soil carbon in the global carbon cycle, in soil-quality management practices, in land restoration, in monitoring terrestrial sequestration, and in precision farming are only but few examples implicating soil carbon as vital in extensive research worldwide. The specific research objective in this chapter is to demonstrate the feasibility and the unique characteristics of a novel nuclear method for non-destructive multi-elemental analysis in large soil volumes over large areas. To this end Section 2 briefly reviews the current standard chemical-methods for analyzing soil and the emergence of new modalities that improve upon the existing shortcomings. Section 3 reviews the basic nuclear-physics processes necessary for understanding the unique characteristics of the promoted system. Section 4 describes the promoted system, its response function, and simulations of it using probabilistic Monte Carlo methodology. In addition, section 4 discusses the issues with spectral analysis, interferences, calibration, and its unique characteristics. Section 5 demonstrates the feasibility and the uniqueness of the system in numerous field studies and various soil types. Section 6 summarizes the research, and Section 7 contains the bibliography used in this chapter.

2. Methodologies for soil analysis

2.1 *Ex situ* chemical analysis

Chemical analysis of soil samples in a laboratory, occasionally referred to as an *ex situ* method, evolved over about the last 150 years. In the 19th century, Rogers and Rogers (1848) reported that dichromate-sulfuric-acid solution could oxidize organic substances. After unsuccessful attempts by Warrington and Peake (1880), and Cameron and Breazeale (1904), Ames and Gaither (1914) accomplished a high recovery of organic substances with this mixture. Schollenberger (1927) introduced the titrimetric determination of unused chromic acid in the oxidation reaction with ferrous ammonium sulfate using several indicators; diphenylamine, o-phenanthroline, or N-phenylanthranilic acid. This method generally is referred to as wet combustion.

Rather (1917) introduced the technique of estimating soil organic matter (SOM) from the weight loss of soils on ignition (LOI), and later, Tabatabai and Bremner (1970) offered an automated CO₂ analyzer based on thermal-conductivity measurements of the effluent gases. These analyzers, founded on Walkley-Black procedures (dry combustion) [Walkley, 1935] have widely recognized limitations and are both lengthy and labor-intensive; nevertheless, they become the standard method used for measuring SOM for many years. Tabatabai and Bremner (1991) defined the principles for upgrading dry combustion via automated total C analyses; it still is considered as the method of choice for assessing carbon in soil. Extensive efforts over the years went into characterizing and testing this approach, thereby establishing it as the state-of-the-art method for analyzing carbon and nitrogen in soil. Numerous books document the protocols for implementing soil analysis by dry combustion [Allison, 1965; Tiessen, 1993; Tan 2005; Chatterjee, 2009]. However, again, this method is lengthy and labor intensive as it entails collecting core samples,

occasionally by excavating them, and transporting them to a laboratory. Before analysis, the samples are weighed, dried, weighed again, ground, and sieved to below 2 mm; thereafter, subsamples again are ground, and then weighed aliquots are analyzed and percent carbon by weight determined. However, for assessing the total carbon stored in the field, knowing the soil's bulk density is essential, which is problematic since the natural variability in the field must be accounted for [Ellert, 2001]. Finally, the information gained from soil analysis by dry combustion represents a point measurement in space and time that poses a problem when extrapolating to fields at the landscape-, regional-, or a higher level. Accordingly, in the last decade new approaches for soil analysis were introduced and tested that circumvent some of the constraints imposed by the chemical methodologies.

2.2 *In situ* new modalities

The increasing need and interest in assessing, and reassessing carbon inventories in soil, and clarifying its dynamics on large spatial- and temporal-scales with reduced uncertainties, not possible at earlier, stimulated novel implementations of three independent, well-established techniques. These are near-infrared spectroscopy (NIR) [Sudduth and Hummel 1996; Christy et al., 2003], laser-induced breakdown spectroscopy (LIBS) [Ebinger et al., 2003], and inelastic neutron scattering (INS) [Wielopolski, 2006], the last one being the subject of the present chapter. These three techniques respectively entail spectroscopy on the molecular-, atomic-, and nuclear-levels.

2.2.1 LIBS

LIBS is a well-established atomic-emission technique extensively applied for surface analyses in research and industry (Balzer et al., 2005; Essington et al., 2009; Merdes et al., 2007). It involves focusing a pulsed laser-beam $\sim 50 \mu\text{m}$ diameter on a sample and ablating a small amount, $\sim 10^{-9} \text{ cm}^3$, of the material (Martin et al., 2010). When sufficient energy is focused on the irradiated target, matter is vaporized, and its atomic- and molecular-constituents are ionized. Thus, the micro-plasma so created is apparent as a spark that expands rapidly, reaching local thermodynamic equilibrium within 0.5- to 1.0- μs , depending upon the sample's conditions. Thereafter, as the micro-plasma starts to cool down, ionized species within the plasma are populated with concomitant emissions of light from atomic- and molecular-transitions (Buckley, 2006; De Lucia et al., 2009; Hahn, 2009). Recently, this method was applied successfully for soil analyses [Cremers et al., 2001; Ebinger et al., 2003; Martin et al., 2003]. Since the volumes analyzed by the LIBS are very small, a fraction of a cm^3 , samples from heterogeneous materials, like soils, require averaging the signals from up to 100 laser shots per spot. The entire LIBS spectra, rather than the peaks alone, are analyzed using principal-component analysis. This approach supports investigations of the impact of experimental parameters on the systems' mode of data collection, such as the laser's irradiation-wavelength and power [Martin, 2010].

2.2.2 NIR

William Herschel in 1800 discovered the infrared (IR) region of the electromagnetic spectrum, spanning the red end of visible light and microwaves; for over a century, it has

been used as a diagnostic tool. It is utilized intensively for surface analyses since IR can penetrate a few cm in the most advantageous cases. The IR region of the spectrum is divided arbitrarily into three regions: The near-, mid- and far-infrared, named for their distance relative to the visible spectrum. The far-infrared, approximately 1,000–30 μm ($400\text{--}10\text{ cm}^{-1}$), lying adjacent to the microwave region, has low energy and is employed in rotational spectroscopy. The mid-infrared, approximately 30–2.5 μm ($4,000\text{--}400\text{ cm}^{-1}$), is valuable in exploring fundamental vibrations and the associated rotational-vibrational structures. The higher energy near-IR, approximately 2.5–0.8 μm ($4,000\text{--}4,000\text{ cm}^{-1}$), can excite overtone- or harmonic- vibrations. Hence, infrared spectroscopy is a tool responding to material structures on the molecular level, in particular to the C-C, C-H, N-H, and O-H bonds. Diffuse reflectance spectroscopy relies upon detecting the scattered part of the focused incident beam on a sample where it undergoes reflection, scattering, and transmission through the material. Numerous publications discuss employing IR in agricultural research and soil analyses; this information appears in recent reviews [Reeves, 2010; Shepherd and Walsh 2007]. IR spectra are complex and require advanced chemometrics wherein measured reflectance spectra are acquired from each sample, and statistical procedures are used to correlate reflectance and the data obtained from soil analyses in laboratories. Awiti (2008) and Reeves (2010) discuss the intricacies of analyzing IR spectra. The IR method is destructive, requiring sampling of soils, or alternatively plowing through them with a sensor mounted on the tip of a shank [Christy et al., 2003].

2.2.3 INS

Inelastic neutron scattering, the last of the three newly emerging modalities for carbon analysis in soil in the field, differs fundamentally from LIBS and IR in that it does not require collecting soil samples. It is non-destructive and analyses large volumes, approximately 0.3 m^3 , in static- and large fields in scanning-modes of operation. The INS approach is based on the spectroscopy of gamma rays induced by nuclear interactions of fast- and thermal-neutrons with the nuclei of the elements present in soil. The spectra, measured during and after the end of irradiation are recognized, respectively, as prompt- and delayed-gamma-ray spectra. The former consist of two separate, but concurrently acquired spectra from inelastic neutron- scattering reactions during the fast neutron pulse, about 25 μs long, and from thermal neutron-capture (TNC) reactions occurring in the 75 μs between the neutron pulses. The delayed gamma-ray spectra are measured at the end of the total period of irradiation. Since all the measured gamma-ray spectra result from the nuclear reactions of neutrons with atomic nuclei, they are insensitive to the chemical state of the element, and the intensity of the measured signal is proportional to the total number of atoms of a given element in the interrogated volume. A unique capability of the INS system is its ability for scanning arbitrarily large areas, so providing a single mean value for its entirety [Wielopolski et al., 2011]. A description, characterization, and the results from using the INS system are detailed hereafter. Table 1 briefly summarizes the key characteristics of the new techniques; comparative reviews of the various methodologies are given in the literature [Chatterjee, 2009; Gehl and Rice, 2007; Schumacher, 2002].

Method	Principle	Penetration in soil (cm)	Sampled volume (cm ³)	Features
Dry Combustion	Small subsample is fully oxidized and amount of CO ₂ measured	Depends on core size	Arbitrary, ~0.1 g analyzed	Destructive, labor-intensive, and time-consuming
Laser induced breakdown spectroscopy (LIBS)	Laser-ablated sample forms micro plasma that, upon cooling, emits light from the ionized atomic- and molecular-species	0.1	~10 ⁻²	Destructive, with high spatial resolution, ~1 mm, minimal sample preparation, presence of roots and rocks increases variability in carbon signal necessitating its normalization
Mid- and Near-infrared reflectance spectroscopy (MIRS/NIRS)	NIRS (0.4-2.5 μm) and MIR (2.5-25 μm) region utilized to quantify soil C; based on the absorption of C-H, N-H and O-H groups found in organic constituents	0.2-1	~10	Destructive, isotopic and carbon specie sensitive, strong matrix interferences, minimal sample preparation
Inelastic neutron scattering (INS)	Based on spectroscopy of gamma rays induced by high, 14 MeV, and low energy neutrons	30	~10 ⁵	Non-destructive, no sample preparation, multi-elemental, analyzes large volumes with scanning capability, provides true sequential measurements, has analytical expression for the response function

Table 1. Key features of the *in situ* soil carbon determination techniques

3. Neutron- and gamma-ray transport in matter

3.1 Neutrons

3.1.1 Neutron interactions with matter

Neutrons interact with atoms' nuclei via nuclear reactions, and so are insensitive to the chemistry of the elements in the sample. These interactions are stochastic, and depend on the neutron's energy that loosely is categorized as fast above 1 MeV, epithermal between 1

MeV and 2.7 eV, and thermal below the latter. The neutrons interact with matter via numerous types of interaction that are divided roughly into scattering and absorption. Elastic scatterings occur when a fast neutron collides with a scattering atom, and transfers energy to it, after which the neutron continues to move at a somewhat degraded speed through the medium. In this process, no nuclear excitation occurs. Alternatively, a neutron may scatter inelastically (INS), wherein the nucleus is raised temporarily to an excited state that instantaneously decays to a ground state with concomitant emission of a neutron with lower energy than the incident one, and of specific gamma rays. Inelastic reactions are typified by threshold energies below which this reaction cannot occur. There also are processes by which a thermalized neutron is absorbed resulting in prompt- and delayed gamma rays, whereas for fast neutrons, the absorption reactions are accompanied by the emission of a particle and gamma rays [Evans, 1955]. Fig.1 summarizes these reactions, and partially list elements that were analyzed *in situ* in soil.

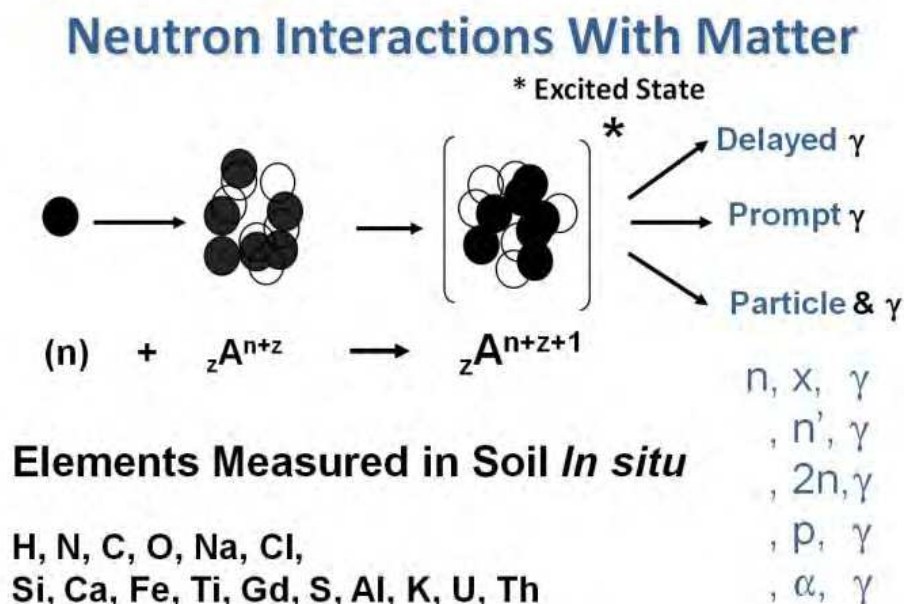


Fig. 1. The decay modes of excited nuclei following the absorption of a neutron, and a partial listing of the elements measured *in situ* in soil.

The path of an incident fast neutron intercepting the soil medium is random, and depends on the cross-sections (probabilities) for various reactions. Figure 2 depicts the conceptual temporal- and spatial-dependence of the excitations of the various elements in a large intact soil volume. Fast 14 MeV neutrons would penetrate the soil and, within 10^{-12} to 10^{-9} sec, induce gamma rays from inelastic reactions; alternatively, they may thermalize, slow down, and following more than 30 collisions, be absorbed, inducing prompt- and delayed-gamma rays.

3.1.2 Neutron attenuation in matter

Under the simplifying assumptions that neutrons are monoenergetic and non-changing in a perfectly narrow well-collimated beam, then the intensity of a neutron beam penetrating

thickness x , I_x is given by $I_0 \cdot \exp(-\Sigma_t \cdot x)$. Here, I_0 is the incident beam's intensity and Σ_t is the macroscopic cross-section, i.e., it is the probability per unit path-length that a neutron will undergo some kind of interaction as it moves about in the medium. For materials containing several elements, Σ_t is given as weighed summation of the individual cross-sections. However, in reality, we do not have a collimated beam, and neutrons change their energy as they slow down [Lamarsh, 1975]. Thus, in principle, the sampled soil is semi-infinite in size; however, practically the three mean free paths, $1/\Sigma_t$, in which 99% of the beam is attenuated are several tens of centimeters deep.

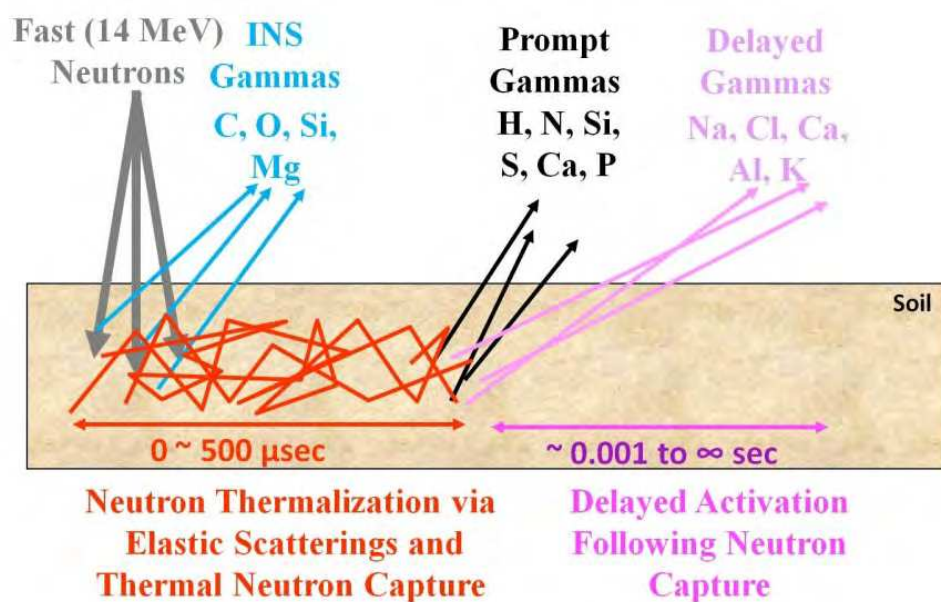


Fig. 2. Temporal- and spatial-neutron reactions with an incident 14-MeV neutron beam.

3.2 Neutron sources

Neutron sources are classified as small, medium, and large depending upon their size, operational complexity, energy, and intensity. Clearly, nuclear reactors are the largest, most prolific sources of neutrons; however, their industrial applications are extremely limited, except for generating electricity. Medium-sized neutron sources are based on plasma, light-ion accelerators, and high-energy photons devised for producing neutrons and for physics research. Small neutron sources are the most suited for field applications. They include certain isotopes that emit neutrons following spontaneous fission, as for example, a ^{252}Cf source with a half life of 2.6 years, and an emission rate between 10^7 to 10^9 neutrons per second.

Another family of neutron sources is based on radioisotopes that decay via alpha particles, viz., radium, plutonium, and americium that impinge upon a low-Z elemental matrix, such as lithium, beryllium, carbon, or oxygen. Usually the source is prepared as a mixture of powders of the two materials. Typical emission rates for alpha-reaction

neutron sources range from 1×10^6 to 1×10^8 neutrons per second. The useful lifetime for such sources is highly variable, depending upon the half-life of the radioisotope that emits the alpha particles. Usual combinations of materials are plutonium-beryllium (PuBe), and americium-beryllium (AmBe).

Radioisotopes that decay by gamma emissions exceeding the neutron-binding energy co-located with beryllium or deuterium stimulate gamma-reactions. Two examples of this reaction with their decay products are 1) ${}^9\text{Be} + >1.7 \text{ MeV photon} \rightarrow 1 \text{ neutron} + 2 \text{ } {}^4\text{He}$; and, 2) ${}^2\text{H} + >2.26 \text{ MeV photon} \rightarrow 1 \text{ neutron} + {}^1\text{H}$.

Sealed-tube neutron generators are the most popular neutron source in industry. They can be turned off at the end of use, so terminating radiation production, and they are operable either continuously or in a pulsed mode. A unique feature in more advanced neutron generators, referred to as associate particle neutron generators, is that the emitted neutrons can be tagged making their direction known. The sealed-tube neutron generators are designed as hermetic, sealed tube, compact accelerators that use deuterium-deuterium (D-D) and deuterium-tritium (D-T) reactions; $\text{D} + {}^2\text{H} \rightarrow {}^3\text{He} + \text{n}$ $Q = 3.270 \text{ MeV}$, $\text{D} + {}^3\text{H} \rightarrow {}^4\text{He} + \text{n}$ $Q = 17.590 \text{ MeV}$. These accelerators respectively generate neutrons of ~ 2.5 and $\sim 14.1 \text{ MeV}$ [Csikai, 1987]. Nominally, these sources produce between 10^7 to 10^{11} neutrons per second, and thousands of such small, relatively inexpensive systems were built over the past five decades. The number and variety of their applications are growing steadily [Chichester and Simpson, 2004].

3.3 Gama-ray interactions and attenuation

Gamma-rays interact with matter in several ways; however, we only need to take three processes into account. These are the photoelectric effect, significant for gamma-rays below 100 keV, Compton scattering that dominates above 100 keV and below 2MeV, and pair production above 2 MeV. These processes will attenuate and change the energy of the emitted gamma radiation that is recorded during gamma-ray spectroscopy. However, the elemental information is stored in the spectral peaks that represent the un-collided gamma-rays that traveled from the point of origin to the detector.

The attenuation of gamma-rays in a medium is similar to that of neutrons but it is governed by an attenuation coefficient, μ that equals $\mu_{pe} + \mu_C + \mu_{pp}$. The attenuation coefficient depends on the gamma-rays' energy and the soil's composition.

4. INS system

4.1 System description

INS system for quantitative elemental soil analysis is based on the spectroscopy of gamma rays induced by the fast neutrons inelastic scattering, and the prompt gamma-rays resulting from thermalized-neutron capture. An INS system comprises the following: A pulsed neutron generator operated at 10 kHz and a 25% duty cycle; NaI gamma-ray detectors; shadow-shielding material between the detectors and the neutron generator; nuclear spectroscopy electronics; and data acquisition on a laptop. The entire system is mounted on a cart about 30 cm above the ground and is powered by a 1 kW power generator, or by a bank of four 12 V batteries with a total capacity of 400 Ah feeding a 110 V inverter. During operation, when fully loaded, the system draws about 1.3 A. The INS system can be operated when it is positioned stationary in a fixed place, or in a scanning mode when towed across field. The INS system is shown in Fig. 3.

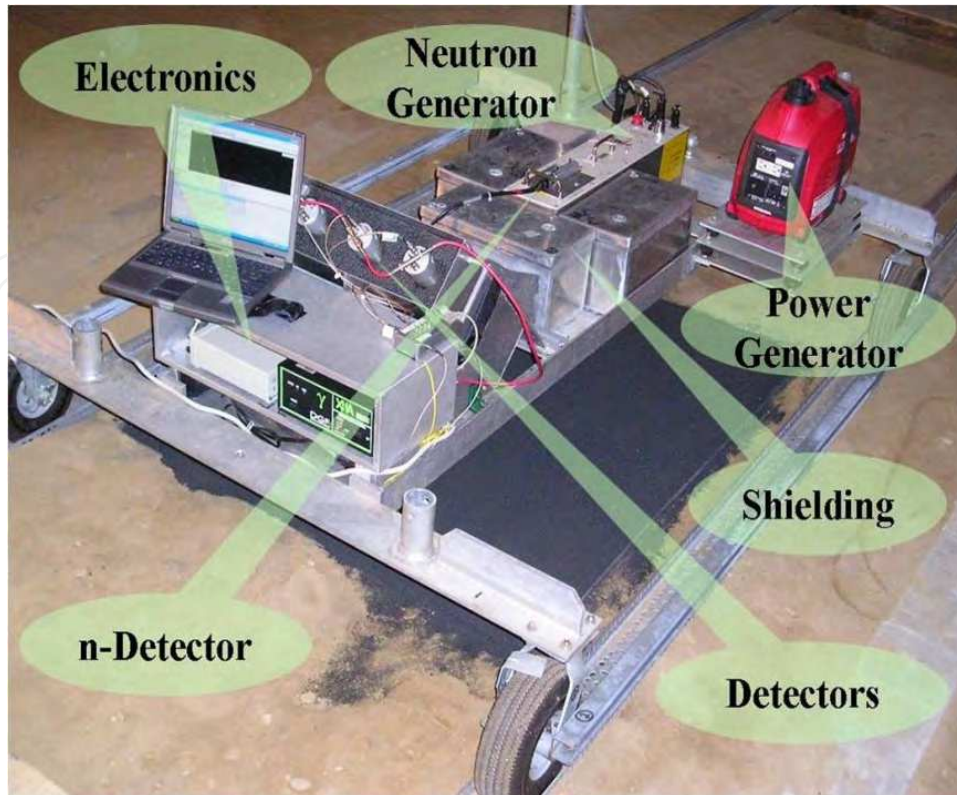


Fig. 3. Alpha prototype of an INS system with its main components marked.

The data typically are acquired for 30- to 60- minutes and displayed as INS and TNC spectra, as for example in Fig. 4; those particular spectra were acquired in a pine stand. A carbon peak is apparent in the INS spectrum, whereas nitrogen is shown in the TNC spectrum. The signal-to-noise ratio in these spectra can be improved using associated particle-neutron generators. The spectroscopy of gamma-rays induced by neutrons was discussed extensively for example [Alfasi and Chung, 1995; Nargolwalla and Przybylowicz, 1973].

4.2 System response function

The transport of neutrons and gamma-ray radiation in matter is very complicated and necessitates solving a five-dimensional integration over neutron energy, time, and space where there are two different spaces; the outside world denoted, x, y, z , and the inner world of the gamma-ray detector identified as x', y', z' . Assuming steady-state conditions independent of time, the time integration becomes a simple time-multiplier. Under these conditions, the INS's response function is derived from basic principles and based on fundamental parameters can be written as Eq. 1;

$$C_N = k \int_T dt \int_E \int_V \varphi_n(x, y, z, E_n) \sigma(E) C_c(x, y, z) \rho_b(x, y, z) \Omega(x, y, z) At(E, x, y, z) dE dx dy dz \int_D \text{Det}(E_\gamma, x', y', z') dx' dy' dz' \quad (1)$$

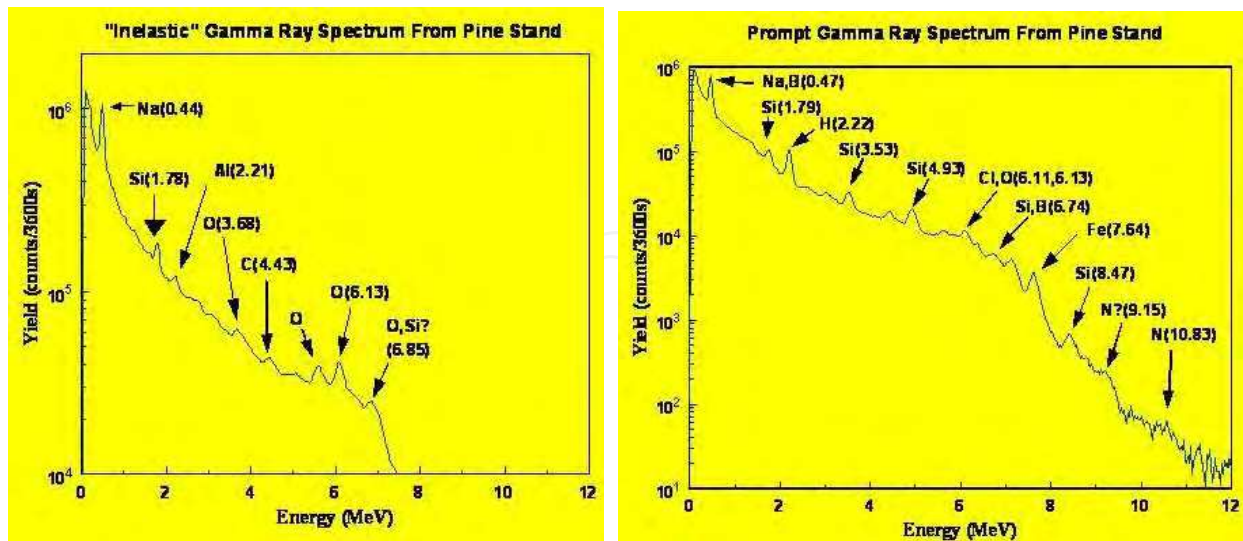


Fig. 4. A typical inelastic gamma-ray spectrum on the left, and prompt gamma-ray from neutron capture spectrum on the right. These spectra were acquired for 30 min in a pine stand.

where T is the time domain, E is neutron energy from incident energy of 14 MeV down to thermal energies 0.025eV, V the soil dimensions, which are semi-infinite in all directions. The simulation is limited to a parallelepiped volume 250 long by 200 cm wide and 50 cm deep, and D is the space occupied by the detectors. Inherent lateral homogeneity is assumed in this model. Thus, the number of counts in the carbon peak, C_N , given in Eq. 1 depends on the depth distributions of the various components in the equation; these components are shown in Fig. 5 in which

- $\phi_n(x,y,z,E_n)$ (n/cm²) is the calculated neutron-flux depth-distribution that decreases with depth;
- $\sigma(E)$ (cm²) is the neutron cross-section that only depends on the neutron's energy;
- $C_c(x,y,z)$ (gC/cm³), the carbon-depth profile usually decreases, although it may assume different distributions;

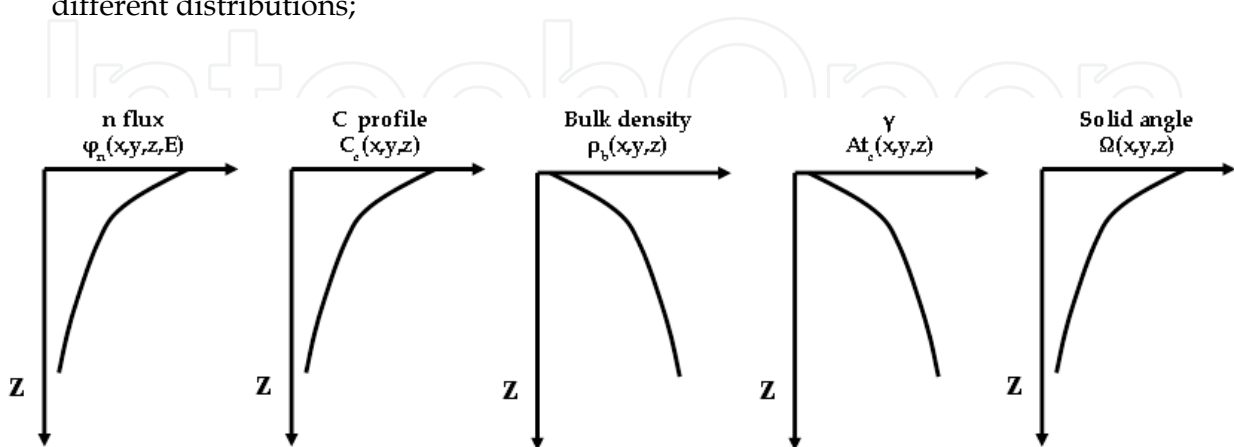


Fig. 5. Conceptual changes with depth in the key components in the INS system's response function.

- $\rho_b(x,y,z)$ (g/cm³), the soil's bulk density increases with depth;
- $\Omega(x,y,z)$ (fraction), the solid angle subtended by the detectors from the emission point of the gamma-rays in the soil;
- $At(E_\gamma,x,y,z)$ (fraction), the attenuation of gamma-rays on their way to the detector, increases with depth; and,
- $Det(E_\gamma,x',y',z')$ (photopeak counts) complete the energy deposition in a detector and allocation in a spectrum.

There is no closed-form analytical solution to Eq. 1, regardless of the existence or lack of boundary conditions. Instead, the integral equation is estimated using the stochastic process of random-number generation and following the individual history paths for each particle. This approach is feasible since all the processes are well-defined. The mean probability of success from many histories is the estimate of the value of the integrals in Eq.1. This stochastic numeric approach is known as the Monte Carlo (MC) method [Lux and Koblinger, 1990]. In the following paragraph the MC methods is used for estimating various parameters of the INS system.

4.3 MCNP simulations

The INS system was simulated using a Monte Carlo neutron photon (MCNP) transport code [Breisemeister, 1993; Pelowitz, 2005]. The simulation started with a neutron emission at the source, and terminated with a photon intercepting a detector. In some cases, the simulations was carried out for 10^{10} incident neutrons and soil composition was taken from mean values of the world soil's composition, Table 2 [Frank and Tolgyessy, 1993]; the soil bulk density was assumed as 1.4 g/cm³.

Element	O	Si	Al	Fe	C	Ca	K	Na	Mg	Ti	N	S	P
Weight (%)	49.0	33.0	7.10	3.80	2.00	1.37	1.36	0.63	0.63	0.46	0.10	0.09	0.08

Table 2. The median values of the distributions of the average top thirteen elements from the world soil series; soil bulk density is 1.4 g/cm³.

Because of the exponential attenuation of radiation in soil, the volume sampled by the INS is semi-infinite; however, a signal arriving from a large distance would be asymptotically vanishing. Instead, an effective sampling volume is defined as a volume from which 90-, 95-, or 99- percent of the detected signal arrives. Clearly, this volume would depend on the carbon's distribution in soil. For example, in the extreme case where the entire carbon content is located on the soil's surface the sampled volume would be zero according to this definition. Thus, these sampling volumes are calculated for the conservative condition when carbon is homogenously distributed throughout the soil's volume. Figure 6 illustrates the results of the latter, derived from 2.5×10^6 1 cm³ voxels; Table 3 summarizes the calculated maximum depth, defined as the height of the vortex, the footprint, the volumes, and sampled mass using a soil bulk density of 1.4 g/cm³.

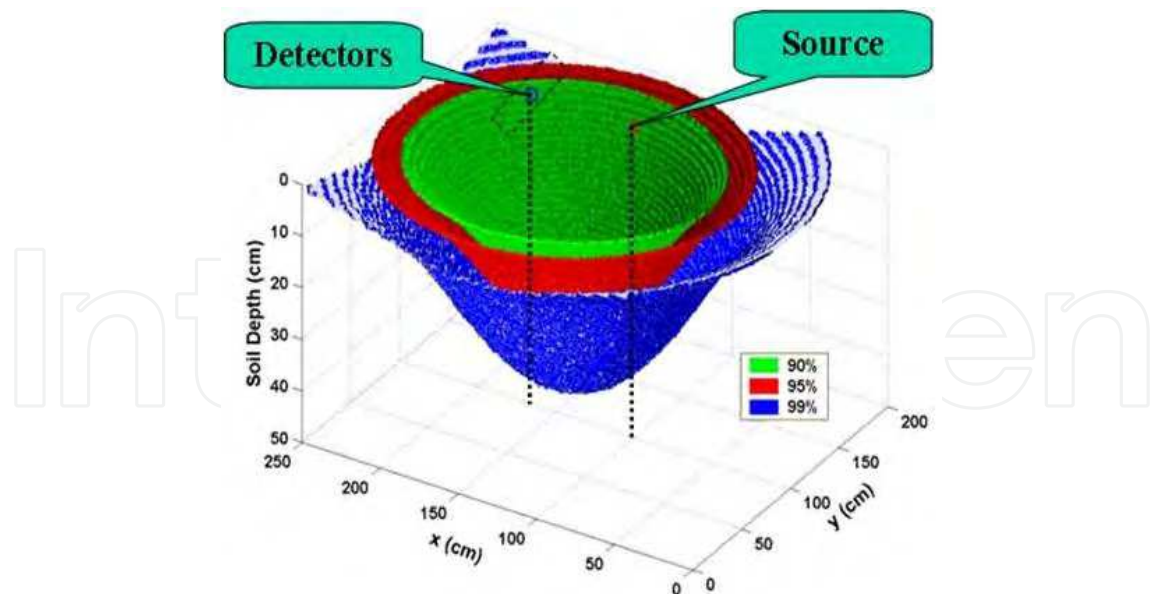


Fig. 6. Monte Carlo-calculated surfaces ascribing the volumes from which 90% (green), 95% (red), and 99% (blue) of the total detected carbon-signal emanated.

Carbon Response %	Depth (cm)	Footprint (m ²)	Volume (m ³)	Mass (kg)
90	25	2.4	0.23	326
95	31	3.3	0.37	522
99	44	7.1	0.79	1105

Table 3. Results from MCNP simulations derived from a test box of 200x250x50 cm³ containing 2,500,000 one cm³ voxels, and soil mass with bulk density 1.4 g/cm³.

Figure 7 depicts the impact of changing the carbons depth profile from a homogeneous to a linear one, starting at 10% by weight at the surface and decreasing to 2% every 5 cm, it shifted the calculated height of the vortex from about 25 cm to 20 cm. The very large volumes obtained in these simulations are unique and counterintuitive to conventional wisdom in standard practice that use fixed very small volumes. These very different volumes relate to the system's calibration and are addressed in the next section.

4.4 System correlation versus calibration

Comparing the INS readings with those obtained by chemical analysis of soil samples is referred to as the calibration of the INS system. However, the term calibration in this context is misused; instead, the process should be referred to simply a correlation between them. To clarify these two concepts and provide consistency in their use, they are briefly reviewed here. Calibration is the validation of specific measurement techniques and equipment against another measurement acquired, in way as similar as possible, from a second device with known- or assigned- correctness and termed the primary standard. Thus, standards and certified reference materials have designated value based on fundamental parameters or by

direct comparison with a reference base. A primary standard usually is under the jurisdiction of a national standards body, such as the National Institute of Standards and Technology (NIST) in the United States. Therefore, at its simplest, two basic requirements constitute a calibration: (i) Using a device with known or assigned correctness in an absolute sense, or a primary- or secondary- device certified or traceable to the NIST's standard materials; and, (ii) measuring a secondary device in way as similar as possible to that of the primary device.

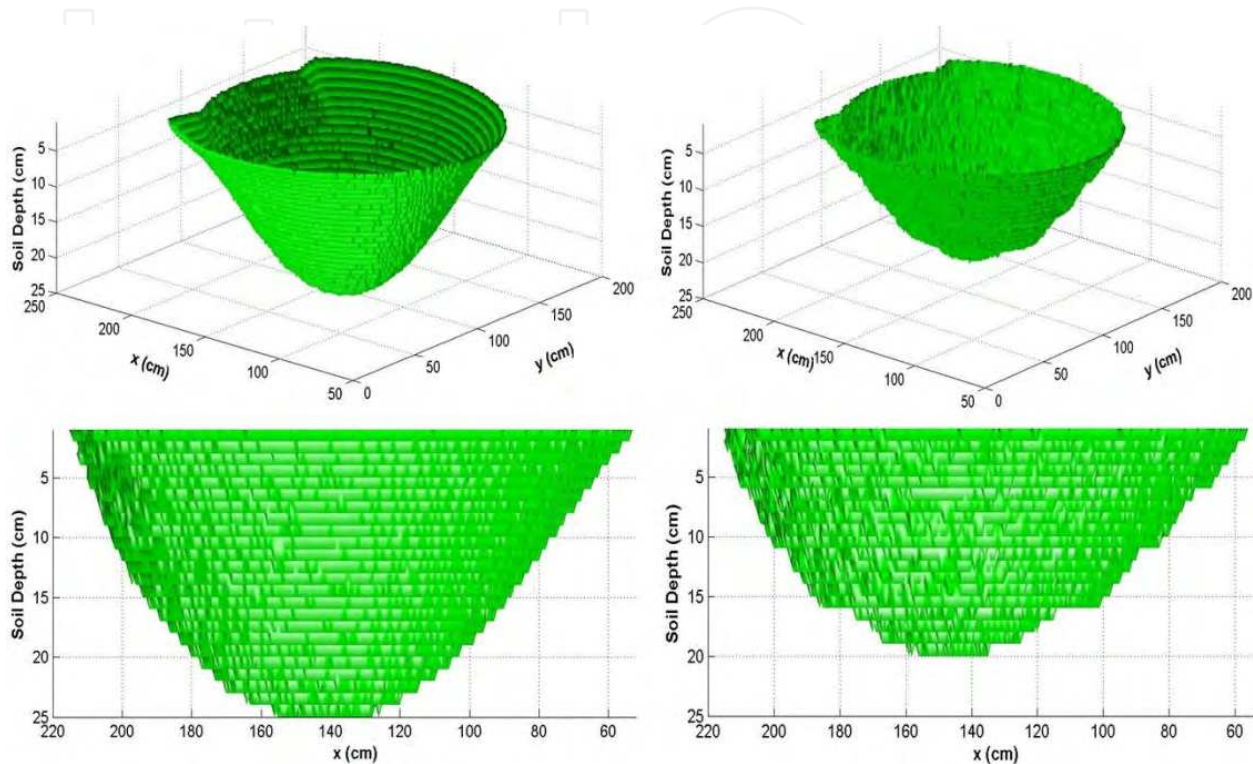


Fig. 7. Changes in the carbon depth profiles from (left) a homogeneous one to (right) a linear one affect the depth of the apex. The ruggedness of the surface on the right is due to lower statistics.

Certainly, soil analysis by the DC method does not qualify as a primary calibration device or as one with a calibrated reading. The standard materials used for initially calibrating a DC analyzer differ substantially from the various soil matrices being analyzed. In addition, as discussed above, the very large differences in the volumes sampled by each method, combined with the high heterogeneity in the field, represent different domains necessitating differing underlying assumptions. These conditions negate the possibility of calibrating any of the two methods discussed. Instead, two independent variables are compared using correlation, indicating the strength and direction of a linear relationship between these two random variables. In other words, correlation tests the hypothesis whether two independent variables are co-related, and measures the strength (departure) of two random variables from independence. In this broad sense, there are several correlation coefficients (Pyzdek, 2003) measuring the degree of correlation, adapted to the nature of the data; these are not discussed here.

In principle, each of the soil analytical methods could be calibrated in a strict sense against a known amount of carbon, albeit with a great deal of difficulty in preparing a proper standard material with a matrix identical to that of the soil. The slopes of true calibration lines, sensitivities of the methods, i.e., readings per gram carbon, would differ because of the

diverse interactions involved and the varying number of carbon atoms in the dissimilar volumes sampled by each method. However, since all the methods attempt to assess the same entity, carbon, they would retain, for different but fixed volumes some proportionality. Therefore, it is logical that without any abrupt changes in the carbon profile, and within the instruments' linear domains, there will be a linear correlation between any two of the methods. In fact, under the ideal condition of no sampling errors, the slope of the correlation line would be the ratio of the sensitivities of each method.

We tested the proportionality concept by comparing INS readings against chemical analysis by dry combustion of soil samples drawn from an excavation of 40 cm by 40 cm and 40 cm deep. The soil was removed in layers 0-5, 5-10, 10-20, 20-30, and 30-40 cm thick, and prepared for analysis. Subsequently, three samples from each layer were pulverized further, and two aliquots from each sample analyzed for carbon. The INS reading was plotted against total surface carbon derived from each depth, Fig. 8 [Wielopolski et al., 2010]. The regression improves with increasing depth and beyond some depth the proportionality changes very little; there is little carbon in deeper layers.

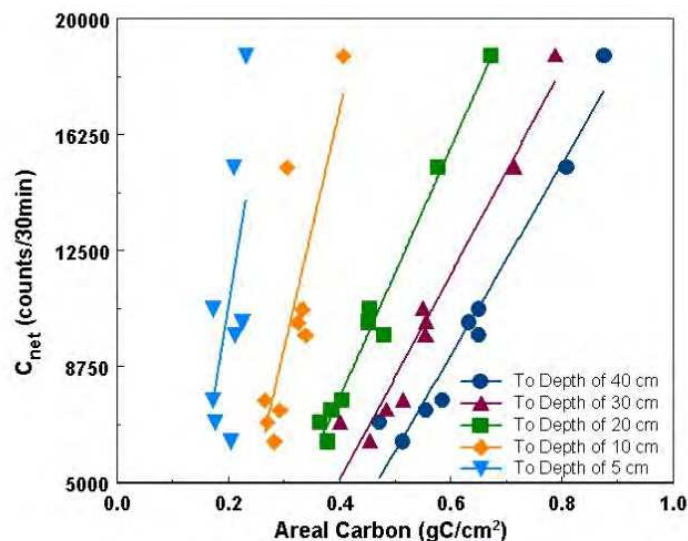


Fig. 8. Correlation of INS readings versus total surface carbon, soil plus roots, derived by chemical analysis of soil samples from various depths and summed-up.

4.5 Data analysis

Data analysis of experimental results is concerned with properly identifying the spectral peaks and with minimizing error propagation in their quantitative analysis. The latter focuses on possible spectral interferences.

4.5.1 Error propagation

The statistical nature of radioactive decay in nuclear counting was recognized soon after its discovery. Hence, in any sample containing a large number of radioactive atoms or excited nuclei, some average number, N , is counted per unit time fluctuating around that average. The statistics of nuclear counting follows a binomial distribution, which for a large number of counts, about $N > 12$, can be approximated by a normal distribution with a mean value, N , and standard deviation (SD) that equals the square-root of N (\sqrt{N}) [Evans, 1955].

By extension, in nuclear spectroscopy, the gamma-ray events in the detector are represented by the number of counts falling into contiguous energy intervals (channels) surrounding a

peak in a spectrum (Fig. 4). The total number of counts in a given energy-interval T_t following counting time of T minutes is due to the incident-signal counting rate, S_r times T , and the background-counting rate, B_r times T . Thus, $T_t = S_r T + B_r T$ are linear with time T , and, conversely, the net number of counts associated with an element (E) of interest, $S_r T$, is given by the difference $T_t - B_r T$. The INS's net counts are converted to conventional units of areal density ($g E/m^2$) by dividing the net signal by the system's sensitivity, s , defined as the number of counts acquired during a counting period T , $S_r T$, per gram element per unit area; k is a proportionality constant with matching units of $g E/m^2$. Thus $s = S_r T/k$, also is the slope of the regression line that correlates INS yield *versus* the soil's carbon concentration. The experimentally determined quantities B_r , S_r and s represent the key performance parameters of an INS system from which other parameters are derived. Using the general uncertainty estimator of a function $f(x,y,z...)$ given, to a first approximation, by Eq. 2 [Bevington, 1969], it can be shown that the SD of $S_r T$, σ_s , equals $\sqrt{T_{tot} + B_r T}$ or to $\sqrt{(S_r + 2B_r)T}$. Thus, the signal is proportional to the counting time and the error is proportional to the square-root of the time. In Eq. 2, the partial derivatives of the function with regard to the parameters x_i that are being search are added in quadrature,

$$\sigma_f^2 = \sum_i [\sigma_i^2 \left(\frac{\partial f}{\partial x_i}\right)^2] \quad (2)$$

Extending the counting time improves the signal, and the error increases correspondingly but at a slower pace [Wielopolski, 2011]. The application of statistics to nuclear counting data is mandatory to assess the precision with which measurements are made. It should be emphasized that only the uncertainty due to the randomness of the counting statistics are addressed here; any other significant sources of uncertainty must be added in quadrature to the overall estimate of the precision.

4.5.2 Methods for spectra analysis

There are several analytical approaches and commercial software for analyzing spectral peaks. The simplest one assumes a linear background under the peak shown in Fig. 9 as a straight line "c" "d".

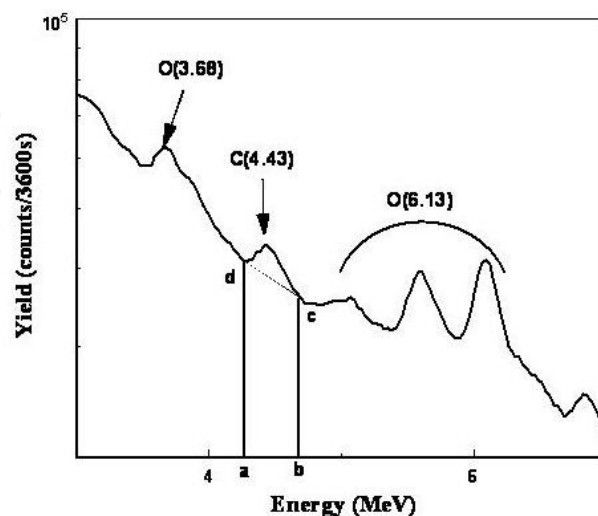


Fig. 9. Expanded INS spectrum in Fig. 4 shows oxygen- and carbon-peaks. The trapezoidal background under the carbon peak is bound between 'a' and "b".

Thus, the net number of counts in the peak is defined as the total counts minus the background delimited by the area enclosed by the trapezoid “abcd”. This approach is valid provided that the peak is clearly defined and there are no overlapping peaks distorting the area with extraneous counts. The least-squares method offers a more advanced analysis wherein the peak is fitted with one or more Gaussian functions, thus partly resolving the problem of overlapping peaks. However, with complete overlap, as might occur when an identical gamma-ray is produced by an interfering element, it is more difficult to resolve. However, since an excited element generally produces more than a single gamma-ray with fixed ratios among them, it is possible to resolve interfering peaks by fitting an entire spectrum instead of the peak alone; this is the library-least-squares method (LLS) [Arinc et al., 1976]. The measured spectra from pure elements, referred to as elemental standard library, are least-squares-fitted to an unknown measured spectrum revealing any discrepancies between the synthetically modeled spectrum and the measured one. The fundamental assertion in the LLS method is that a measured unknown spectrum is a linear superposition of standard reference libraries plus an error term. The multipliers of the standard libraries are found by minimizing the error term, or of the reduced χ^2 given by equation Eq. 3 [Gardner et al., 1975; Wielopolski, 1981; Wielopolski and Cohn].

$$\chi^2 = \sum_{i=1}^n \left[b_i - \sum_{j=1}^m x_j a_{ij} \right]^2 / \sigma_i^2 (n - m), \quad (3)$$

where:

b_i - counting rate in channel i for the composite spectrum;

a_{ij} - counting rate of pure element j in channel i per unit amount of component j ;

x_j - amount of component j in the unknown;

m - number of components;

n - number of channels;

σ_i^2 - variance of the random error in channel i .

The LLS method requires an extra effort in deriving good elemental libraries with good statistics; in turn, this approach reduces the reported error for the analyzed peak intensities.

4.5.3 Peak interferences

During the INS and TNC processes, most elements emit a multiplicity of gamma-rays, some of which may overlap with those emitted from other elements. The gamma-rays emitted by a given element bear fixed relationships among themselves; thus, analyzing an undistorted peak enables the correction of a distorted one with interference. Alternatively, using the LLS method with a good set of elemental libraries, the interfering peaks can be assessed and corrected values obtained. For example, thermal neutron capture in a ^{28}Si yields 4.94-MeV gamma-rays that generate a single escape peak, C_{SEP} , at $4.94 - 0.511 = 4.43$ MeV that overlaps the carbon peak. This peak is generated in the TNC spectrum that, depending on the neutron-generating pulsing regimen, must be adjusted by the ratio of the live times, $LT_{\text{INS}}/LT_{\text{TNC}}$ (Mitra and Wielopolski, 2005). Thus, the contribution of the escape peak to the carbon peak in the INS spectrum is $C_{\text{SEP}} = \text{Si}_{(4.43)} LT_{\text{INS}}/LT_{\text{TNC}}$. A second process affecting the carbon peak is the decay of excited silicon (^{28}Si) to the ground state via several cascades feeding the 1.78-MeV level that, in itself, decays to the ground state. A fraction of these cascades originates at the 6.23-MeV level generating a $6.23 - 1.78 = 4.45$ MeV gamma-rays (C_{CAS}) that overlap the carbon

peak. The ratio between the 4.45 MeV and 1.78 MeV gamma-rays is constant, and was calculated theoretically as 0.0547 [Herman et al., 2007]. Furthermore, the 1.78-MeV Si peak itself must be corrected for $^{28}\text{Si}(n,p)^{28}\text{Al}$ reactions that, with a decay time of 2.25-min half-life, contribute to the 1.78-MeV line. Since all the interferences are associated with peaks acquired concurrently with the carbon peak, the corrections are made for each individually measured spectrum. Thus, $C_{\text{CAS}} = [\text{Si}_{(1.78)} - \text{Al}_{(1.78)} \text{LT}_{\text{INS}}/\text{LT}_{\text{TNC}}]0.0547$. Estimates suggest that the errors associated with these theoretically- and experimentally- determined correction factors are about 10%. Thus, the corrected number of counts, N_c , in the carbon peak with N_p is

$$N_c = N_p - C_{\text{SEP}} - C_{\text{CAS}} \quad (4)$$

Figure 10 shows carbon calibration in a sand pit using a synthetic soil of sand mixed with known different amounts of carbon before and after correcting for silicon interference. The intercept was reduced from 5029 to 348 ± 327 , which includes the 0 value.

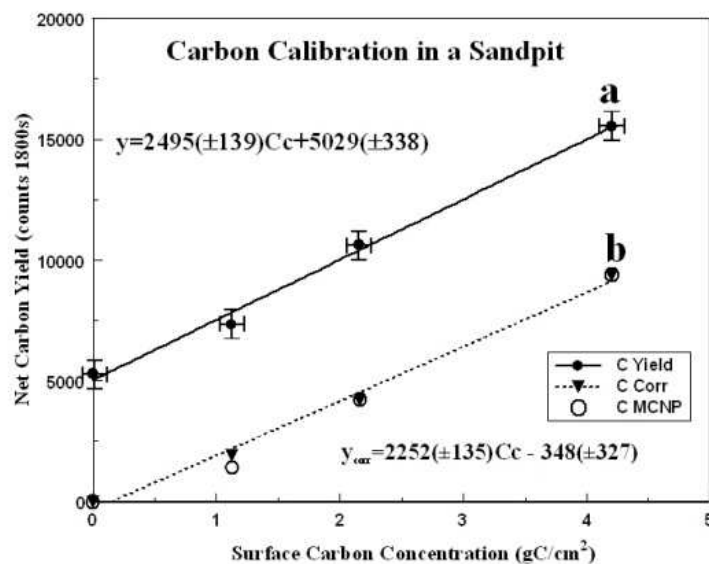


Fig. 10. Calibration of an INS system over a sand pit filled with synthetic soils; (a) Calibration before correction for Si interference, and, (b) after correcting using Eq. 4, for the silicone interference with the carbon peak. The circles indicate simulation of calibration using Monte Carlo calculations normalized at point b.

Differences may occur in a correction factor when operating the system in a scanning mode due to differences in delayed activation detected by the detectors when they operate in the stationary mode versus scanning when they are moved away from an activated area. Large changes in the soil's composition, particularly the presence of aluminium, may affect the correction [Wielopolski et al., 2008].

4.6 Mean field value (scanning)

The INS and TNC processes are very fast, $\sim 10^{-9}$ s, and the INS's footprint is very large, about 2.5 m². Thus, in one millisecond, a very long time for nuclear processes to occur, the INS system towed at a speed of 10 km/h (or about 2800 mm/s) would move about 3 mm, a distance that is negligible in relation to the footprint; hence, the system can be perceived as stationary. Thus, continuous scanning of a large field at reasonably constant speed yields a

single value that represents a physically averaged value for the field. The assessed mean from continuous scan of the entire field is analogous to a simple mean or a geo-statistically average of a set of discrete samples measured by conventional chemical methods. This scanning capability introduces significant changes in conventional wisdom in soil sampling and analysis. This consideration was tested by comparing INS stationary measurements with conventional analysis of core samples taken from the same sites, and then by comparing the calculated mean value with that determined by scanning a transect containing the sampled sites. There was a good agreement in organic soil; however, further clarification is required in a pasture [Wielopolski et al., 2011].

5. Results

Using an INS alpha prototype system, numerous field measurements were carried out across Montana, Arizona, Alabama, North Carolina, Maryland, New Hampshire, Pennsylvania, and Ohio. They were taken on federal-, state-, and privately owned lands; each required a different permit to operate a neutron generator, i.e., a radiation-producing device (RPG). The soil types tested included pure organic soils, histosols, various types of agricultural soils, abandoned surface mine fields, and forests.

5.1 Correlation between INS and chemical analysis

One study was carried out in the Blackwood Division of the Duke Forest near Durham, NC (35°58'41.430" N, 79°5'39.087" W). This is a complex site with woody and rocky components in the soil matrix; it included grassland, a pine forest, and a hardwood forest. The grassland, dominated by the C3 grass shrub, *Festuca arundinacea*, was mowed at least once annually for hay. The pine site was planted in 1983 with loblolly pine (*Pinus taeda* L.) in the overstory, and has been unmanaged since. The hardwood site is an unevenly aged, 80- to 100-yr-old oak (*Quercus* sp.)-hickory (*Carya* sp.) forest, also never managed [Wielopolski, et al., 2008, 2010]. Three INS static measurements were taken on each site; nine excavations, 40x40x40 cm³ at the same INS locations gave soil samples for chemical analyses by dry combustion. The results from the three sites were combined to correlate the INS measurements with chemical assays; these were corrected for the solid fraction of the soil.

Similar results were combined from three sites in Ohio. The first site, designated pastureland, is located at the USDA's North Appalachian Experimental Watersheds (NAEW) in Coshocton County OH (40°16'19"N and 81°51'35"W). The soil is derived from a fine-loamy, mixed, mesic Typic Hapludultsoess-like silty deposit overlying a loamy textured material weathered from sandy shale and siltstone bedrock. Orchard grass (*Dactylis glomerata* L.) is the dominant species in the watershed under pasture, and the watershed's slope is about 10% [Kelley et al., 1975].

The second location sited at the Ohio Agricultural Research and Development Center (OARDC) Muck Crops Branch in Willard, OH, (41°0'37.80"N and 82°44'0.39"W). The soils are classified as the Linwood muck, a loamy mixed euic, mesic, Terric Halosaprist (Elder and Lal, 2008). This soil contains almost 80% organic matter; the main crops grown there are lettuce (*Lactuca sativa*), radish (*Raphanus sativus*), and other leafy species. The third location is an unmanaged natural forest adjacent to the cultivated organic soil, dominated by white oak (*Quercus alba* L.) and red oak (*Quercus rubra* L.), also in Willard, Ohio. The measured soil bulk densities varied from 0.37 to 1.7 g/cm³ [Wielopolski et al., 2011]. Fig.11 illustrates the correlations for Duke Forest and the Ohio sites; the former also shows the 95% confidence limits.

5.2 Scanning

The capability of the INS system to non-destructively scan fields continuously and provide a mean value for the scanned field was highlighted previously and evaluated by comparing a transect scan with mathematical averaging of discrete points on the transect. Two scans performed in a wheat field, 100 m by 100 m, in Montana, and in a 30 m by 30 m corn field in Maryland demonstrated the feasibility for scanning arbitrarily large areas. Figure 12 shows the global positioning system (GPS) traces of the scans in the wheat- and corn-fields. The large wheat field allowed well-structured scans whereas random scanning was more suitable for the small corn field

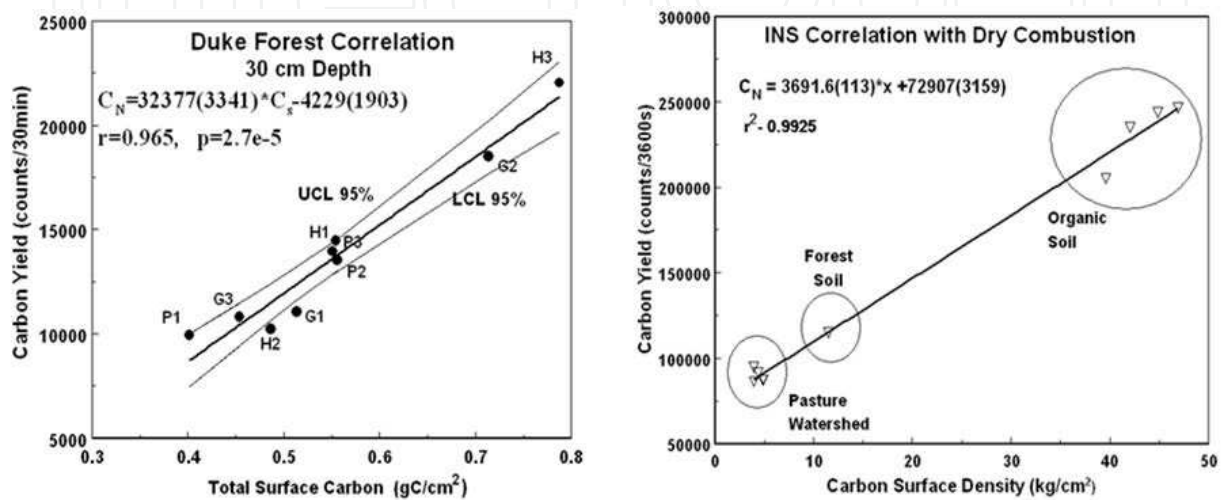


Fig. 11. Regression lines between INS yield and chemical analysis of soil samples from Duke Forest on the left, and from the Ohio sites on the right. The symbols G, P, and H, respectively, stand for grass, pine forest, and hardwood forest, respectively.

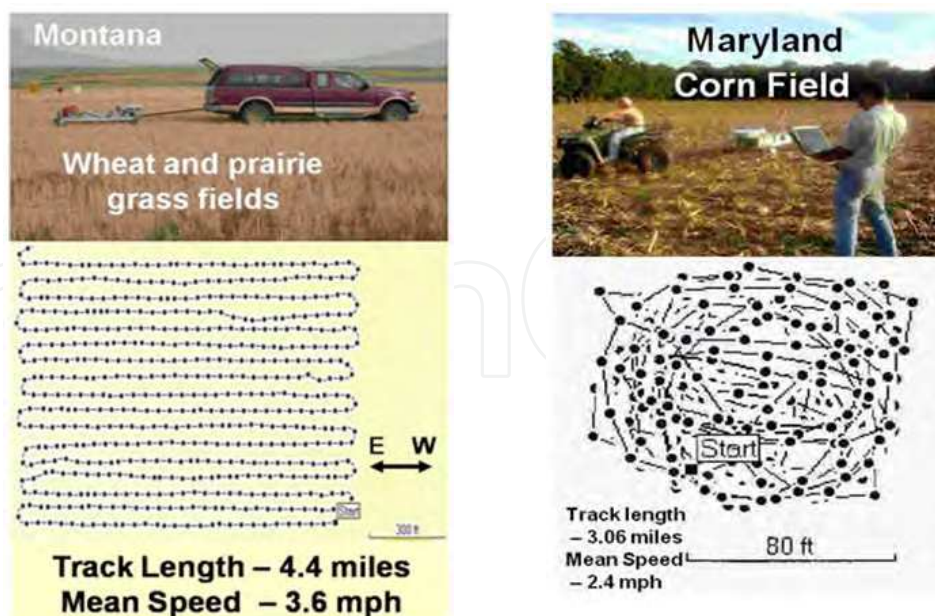


Fig. 12. GPS traces of the scans obtained from of a wheat- and a corn-field by towing the INS system over them. The figures show the total length of the scans and the mean speeds. In the corn field (right), the scan was monitored in real time on a slave computer to assure better coverage of the field.

5.3 Forest and mine fields

It is difficult to estimate the effect on the soils carbon stores of forest-management practices because of the long time-scale of the response and the heterogeneity of forest soils. With traditional sampling methods, changes in forest soils have been impossible to detect, even following clear-cutting; repeated sampling rarely detected changes of less than 20% [Johnson et al., 1992; Yanai et al. 2003]. Furthermore, the logistics of sampling in forests are uniquely complex not only in bringing the equipment to the site, but in dealing with the presence of boulders and fallen woody logs; accordingly, the sampling and analysis protocols must be reformulated. Testing the INS system in a forest environment [Wielopolski, Yanai et al., 2010] led us to the realization that the system's weight must be reduced before it was usable on regular basis. In comparison, conventional sampling of forest soil is especially troublesome due to the frequency of boulders; a better approach is to excavate quantitative pits, but this is a very time-consuming procedure and its scope limited. Figure 13 illustrates using the INS system in Bartlett forest, NH, and sampling there with a motorized coring machine. The difference in the footprints of both methods is apparent, making the use of the INS less error-prone.

Similarly, sampling abandoned minefields under restoration poses challenges because of the rocks therein. There are nearly 3.2 Mha of permitted mine lands in the United States, almost 75% of which are located in the Northeast Appalachian coal-mining region. Estimates of potential carbon sequestration in reclaimed mined land soils in the northeastern US are widely divergent: -0.02- [Amichev et al., 2004], 0.25- [Intergovernmental Panel on Climate Change, 1998], and 1.9-Mg C ha⁻¹ yr⁻¹ (Akala and Lal, 2000). Mine land soils typically are highly heterogeneous, even at very small scales; their drainage, texture, mineralogy, rock fragments, bulk density, and pH differ greatly, all of which influence the soils carbon dynamics and sequestration. The INS's unique capabilities will augment tremendously the monitoring of the restored mine lands. Figure 14 shows an example of minefield soil riddled with stony material; the value of using the INS instrument is contrasted with the effort of conventional soil sampling when it is possible, if at all.



Fig. 13. On the left an INS set up measures the forest soil. On the right, a mechanized coring tool is used to sample soil from the forest floor. Many cores were abandoned because of the belowground rocks.



Fig. 14. Comparison of sampling abandoned minefield restored with its original overburden using the INS system on the left, and an attempt using conventional coring on the right, many cores could not be sampled deeper than 10 cm.

5.4 Geological sequestration

We demonstrated the value of employing the INS to monitor belowground changes in carbon content caused by CO₂ leakage from a zero-emission research and technology (ZERT) facility that tests instrumentation for assurance-monitoring of geological sequestration. The explored hypothesis was as follows: An increase of CO₂ in the soil's atmosphere would slow and/or kill the growth of roots that would decrease the belowground level of carbon. In two consecutive tests over two years, a decrease in carbon content of 15% and 7% was registered [Wielopolski and Mitra, 2010; Wielopolski, 2011]. The correlation between the CO₂ leak and belowground carbon level is yet to be determined. All surface monitoring devices used for monitoring geological sequestration offer point-in time and in-space measurement that may prove insensitive to the expected very low leakages from the storing formations. Alternatively, using INS offers the possibility of monitoring a time-integrated signal that might be more sensitive. Moreover, the INS provides an area-integrated signal, invaluable where prior knowledge of the leakage site might be unknown.

6. Conclusions

Inelastic neutron scattering is a newly emerging modality for soil analysis that differs fundamentally from all other modalities, new and past. However, for better understanding of the INS's unique characteristics, since not all soil researchers may be familiar with the nuclear spectroscopy features, some basic principles involved with it were introduced. The INS is based on well-understood fundamental principles of nuclear physics and demonstrates very unique capabilities that extend beyond those of the current state-of-the-art in soil sampling paradigms while at the same time revolutionize the existing ones. For

example, the INS's larger footprint than in conventional coring is apparent in Figs. 13 and 14. Using an advanced AP neutron- generator, it is possible to extend the measurements non-destructively to gain information on a depth profile of an element, or to monitor repeatedly changes in a region at a specified depth in soil. These data, in turn, enable the development of new models for assessing carbon stocks to a depth of 100 cm. The key outstanding features of INS comprise its non-destructive, i.e., remote, analysis of large samples of soil in static- and scanning-modes of operation and multi-elemental analysis in true sequential order, i.e., measurements taken at the same spot. A brief review of other modalities highlighted the uniqueness of the INS system. Because of the lateral variability in carbon distribution, the large footprint of the INS provides a better-averaged value, hence changing sampling requirements. This is particularly true when scanning large areas where a single scan provides a mean value of a field that otherwise would require tens or more sampling spots. Although not shown, economic advantages of the INS system can be demonstrated.

Using INS alpha prototype demonstrated the correlation between INS signal and that measured by the standard chemical method by dry combustion; the difference between correlation and calibration when comparing signals from different domains was emphasized. It is important to understand that when comparing vastly different modalities proportionality is important.

Thus, we demonstrated the feasibility of the INS system as a viable new modality for carbon analysis in soil. Its unique characteristics improved and expanded the scope of possibilities to observe in depth the belowground processes that otherwise are not visible to naked eye without disturbing the environment. The INS capabilities to monitor soil carbon may prove invaluable in promoting trading with carbon credits. Overall, it is an important addition to the arsenal of instrumentation improving our understanding and monitoring of carbon and other elements in soil.

7. References

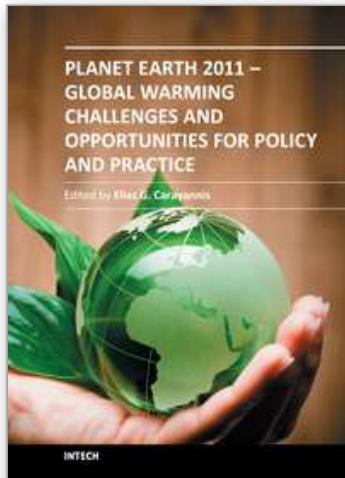
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The failure of the UN climate change summit in Copenhagen in December 2009 to effectively reach a global agreement on emission reduction targets, led many within the developing world to view this as a reversal of the Kyoto Protocol and an attempt by the developed nations to shirk out of their responsibility for climate change. The issue of global warming has been at the top of the political agenda for a number of years and has become even more pressing with the rapid industrialization taking place in China and India. This book looks at the effects of climate change throughout different regions of the world and discusses to what extent cleantech and environmental initiatives such as the destruction of fluorinated greenhouse gases, biofuels, and the role of plant breeding and biotechnology. The book concludes with an insight into the socio-religious impact that global warming has, citing Christianity and Islam.

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