Rapid, non-destructive carbon analysis of forest soils using neutron-induced gamma-ray spectroscopy

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A R T I C L E   I N F O

A B S T R A C T

Forest soils are pivotal to understanding global carbon (C) cycling and evaluating policies for mitigating global change. However, they are very difficult to monitor because of the heterogeneity of soil characteristics, the difficulty of representative sampling, and the slow time scale of response to environmental change. Here we demonstrate that use of gamma-ray spectroscopy facilitates *in situ* non-destructive analysis of C and other elements in forest soils. In this approach the element-specific gamma-rays are induced by fast and thermal neutrons interacting with the nuclei of the elements present in the soil. Background gamma-rays emanating from naturally occurring radionuclides in the forest are recorded as well. We applied this approach in a mature northern hardwood forest on glacial till soils at the Bartlett Experimental Forest in New Hampshire, USA. The inelastic neutron scattering (INS) system yielded strong signals in gamma-ray counts/h, from C and other elements present in the soil matrix that included silicon, oxygen, hydrogen, iron, aluminum, manganese and potassium. The INS sensitivity for carbon was 20.656 counts h^{-1} kg^{-1} C m^{-2} based on current net C gamma-ray counts and the data for the O horizon and mineral soil to a depth of 30 cm obtained from a nearby quantitative soil pit (7.35 kg C m^{-2}). We estimate the minimum detectable change to be ~0.34 kg C m^{-2}, which is ~5% of the current soil C content, and the minimum detectable limit to be ~0.23 kg C m^{-2}. Eight % reproducibility from 11 measurements was limited, in part, by the large variability in the system counting geometry due to the uneven forest microtopography. The INS approach has the potential to revolutionize belowground monitoring of C and other elements, because the possibility of detecting a 5% change in forest soils has not been possible with destructive sampling methods.

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1. Introduction

Forest ecosystems play a pivotal role in regulating carbon (C) fluxes between land and the atmosphere (Waring and Running, 1998). Accurate estimation of forest C requires monitoring C sequestration in aboveground and belowground biomass (Zerihun and Montagu, 2004). Accurately quantifying C budgets is important for forest management and for shaping climate policy. In addition, assessments of C and nutrients in biomass and soil pools are critically important to ecologists and climate modelers (Kulmatiski et al., 2003; Galbraith et al., 2003).

Forest soils are much more difficult to sample than the aboveground biomass because of their inaccessibility, high spatial variability, and presence of rocks and coarse root systems. Current methods of measuring soil and belowground biomass for C and nutrient contents are slow, requiring collecting, drying, sieving, weighing, and laboratory analysis of samples. Additionally, these analyses are expensive, as they require many samples from large and heterogeneous areas to accurately characterize soil properties (Nurthup et al., 1977). It is well recognized that every step in the sample preparation and in the process of field sampling and sub-sampling for analysis contribute to the error. Cohran (1977) described a method for minimizing error propagation while optimizing the cost function for the two stages of sampling: (1) collecting samples in the field and (2) sampling in the laboratory for the analysis. A method that would eliminate these steps would be highly desirable. In addition, C budget determination requires measuring or estimating bulk density and soil volume, which in the presence of rocks and roots, as in a forest, is both difficult and destructive. Extrapolating from soil cores or excavated pits to field sites or land-use treatments magnifies small-scale measurement uncertainties, making it impossible to detect change in C stocks over time spans shorter than decades. Forest science and manage-

ment, together with C-credit trading, would benefit greatly from a new approach to measuring forest soils that is fast, non-destructive, and analyses large areas.

Constraints and limitations of the traditional approaches for soil analysis are outlined in the literature (Schumacher, 2003; Chatterjee et al., 2009). Three new methods developed specifically for *in situ* analyses were reviewed by Wielopolski (2006), Gehl and Rice (2007), and Chatterjee et al. (2009). These methods are based on fundamentally different physical principles and include two surface methods: (1) near infrared reflectance spectroscopy (NIRS) and (2) laser-induced breakdown spectroscopy (LIBS), and one volumetric method, inelastic neutron scattering (INS). In NIRS the surface of a soil sample is illuminated by a broadband IR source and the absorbance spectrum of the diffusely reflected component of this light is acquired by an IR spectrometer. The spectral structure of the reflected light depends on the extent of organic C bonds in the sample (Janik et al., 1998; Reeves et al., 2001; McCarty et al., 2002; McCarty and Reeves, 2006). The LIBS technique is based on spectroscopy of the atomic emission resulting from a laser pulse focused on a soil sample. The high temperatures and electric fields break the chemical bonds in a small amount (about 10^{-9} m^3) of the material and vaporize it into a white-hot gas of atomic ions known as "micro-plasma". The resulting emission spectrum is then measured using a spectrometer covering a spectral range from 190 to 1000 nm (Radziemski and Cremers, 1989; Moenke-Blankenburg, 1989; Rusak et al., 1997). The INS method is based on nuclear spectroscopy of gamma-rays induced by fast and thermal neutrons interacting with the nuclei of the soil elements as described below. While the NIR and LIBS methods are destructive, the INS method is not, and the volume analyzed by INS is orders of magnitude larger than that analyzed by the other methods. The INS systems had not been tested in a natural forest setting until now. Here we demonstrate the feasibility of using the INS method in a northern hardwood forest ecosystem at the Bartlett Experimental Forest, in the White Mountain region of New Hampshire.

2. Materials and methods

2.1. Site description

We tested the INS system in June 2009 at the Bartlett Experimental Forest in Bartlett, New Hampshire (44°3′N, 71°18′W). We selected the study site for its low slope (~2–5%), proximity to a road, and existing data on soil texture, bulk density, coarse fraction, C content, and root mass from quantitative soil pits excavated in 2004 (Yanai et al., 2006; Park et al., 2007). The stand is a mature northern hardwood forest, dominated by sugar maple (*Acer saccharum* Marsh.) and American beech (*Fagus grandifolia* Ehrh.), with white ash (*Fraxinus americana* L.), yellow birch (*Betula alleghaniensis* Britton), basswood (*Tilia americana* L.) and hemlock (*Tsuga canadensis* L.) also found in the overstory. Analysis of tree rings and USFS records show that the site was cutover in the early 1880s. The site is located in a toe-slope position at 330 m elevation with a northeast aspect. The soil is a Spodosol (isotic, frigid Typic Haplorthod) developed on a sandy loam with ~10–50% coarse fraction (>2 mm) by volume.

The main area in which we took INS measurements (Fig. 1) had five sugar maples (31–48 cm diameter) and one American beech (24 cm diameter) in the canopy. A sparse shrub layer consisted of occasional hobblebush (*Viburnum lantanoides* Michx.) and young beech. For a forest soil in rocky till, the surface of the area we sampled was relatively even without surface boulders or dramatic pit-and-mound microtopography. The presence and depth of belowground obstructions (large roots or boulders) was tested by inserting a 6 mm diameter metal probe into the soil at 25 cm inter-

val. The area we tested was relatively free of shallow rocks and large roots (Fig. 1), similar to the nearby soil pit (9% coarse fraction by volume to a depth of 50 cm).

2.2. Conventional soil analysis

Three soil pits were excavated quantitatively by horizon in this site in 2004 (Park et al., 2007). Some disturbance to the surrounding forest floor likely resulted from the pit excavation. For the purpose of soil carbon estimation, roots were assumed to be 50% C on a dry mass basis (Saugier et al., 2001). Root sampling methodology is described by Park et al. (2007). Carbon was measured in an elemental analyzer; total Si was measured on an ICP, after fusion with lithium metaborate. Relevant soil data to 50 cm depth from the soil pit nearest to our measurements are shown in Table 1.

2.3. INS system

In the INS approach, element-specific gamma-rays are induced by fast and thermal neutrons interacting with nuclei present in the soil; those acquired during irradiation with neutrons are known as prompt gamma-rays. In addition, natural background gamma-rays are recorded prior to or following irradiation, and are termed delayed gamma-rays. The prompt gamma-rays are recorded concurrently in two separate spectra; the first resulting from inelastic neutron scattering reactions occurring during the 25 μs neutron pulse and the second resulting from thermal neutron capture (TNC) reactions occurring during the 75 μs interval between neutron pulses. Gamma-ray spectra are histograms of gamma-rays energies converted to pulse heights in the detector, sorted in orderly manner according to their height and stored in energy bins (channels). The INS and TNC spectra resulting from nuclear reactions are insensitive to the chemical state of the element; thus the signal yield is proportional to the total elemental concentration. Additional details of the INS system were published previously (Wielopolski et al., 2004, 2008).

A key advantage of the INS system is its non-destructive quantitative elemental analysis of soil over a large footprint of ~1.5 m^2 and sampling depth to ~30 cm. Since the INS system is mounted on a 30 cm high cart it can be used in stationary or scanning modes of operation. The weight of the INS system is ~150 kg and the cart's dimensions are 132 cm wide, 213 cm long (Fig. 2).

The linearity of the INS signal as a function of C concentration has been demonstrated in synthetic soils (mixtures of clean sand and granular C), with a correlation coefficient r^2 of 0.996 (Wielopolski et al., 2004). This regression represents the INS system calibration, in which net counts of the C photopeak are compared to known C content (kg C m^{-2}) as derived by chemical analysis; the slope of the regression line is the system sensitivity. Field studies that included grassland, a pine forest, and a hardwood forest were carried out in the Duke Forest near Durham, NC. In these studies, the INS signal was highly correlated ($r^2 = 0.965$) with C content estimated by destructive excavation, sub-sampling, and dry combustion analysis (Wielopolski et al., 2008). Detailed discussion of the proportionality of the INS C signal, obtained from a large volume, to that from chemical analysis, obtained from a small volume, was reported by Wielopolski et al. (2010). The INS system has also been used in several field studies ranging from organic soils in Willard, OH to abandon mine fields in PA (manuscripts in preparation).

2.4. INS measurements

First, we measured a spectrum of the natural radioactive background in the forest soils in the tested area and following neutron activation we measured delayed spectra. Subsequently we acquired twelve 1 h spectra marked sequentially in Fig. 1 and Table 3 (point
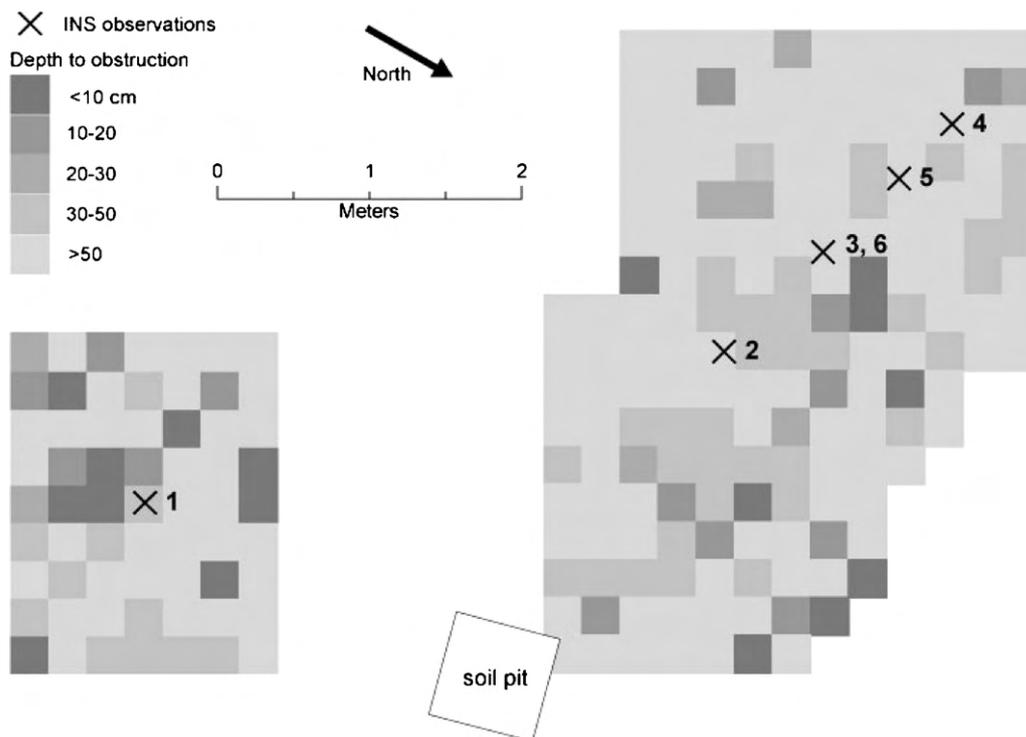
Fig. 1. Location of INS observations points 1–6 taken in June 2009 and soil pit C8-1, which was excavated in August 2004, in Bartlett Experimental Forest compartment 33. The shaded grid indicates depth to obstruction (rock or large root). Observations 7–9 were taken outside this area, to the northeast.

Table 1
Soil characteristics of the soil pit located within the INS testing area.

Soil horizon	Soil mass (kg m^{-2})	Rock mass >2 mm (kg m^{-2})	Total root mass (kg m^{-2})	Soil content in fraction <2 mm (kg m^{-2})		Total C (kg m^{-2})
				C	Si	
O_{ie}	1	0	0.1	0.5	0.02	0.55
O_a	6	0	0.2	1.3	1.8	1.40
0–12 cm (A,E,B_h,B_s)	57	12	1.0	2.0	24	2.50
12–30 cm (B_s)	126	21	0.6	2.6	60	2.90
30–52 cm (B_s)	168	27	0.5	2.2	72	2.45

Fig. 2. INS system taking measurements at the Bartlett Experimental Forest.

8 was acquired for only 30 min due to system failure and renormalized to 1 h measurement). Points 2a, 2b, and 2c were separated by small (~5 cm) movements of the cart, to test the sensitivity of the INS positioning. Due to the small movement relative to the 1.5 m^2 measurement footprint, these can be considered remeasurements of the same location. Spectra 4a and 4b were acquired similarly. Points 7, 8, and 9 were made outside the test area on a 30 m long transect to the northeast of the test area shown in Fig. 1. Points 7 and 8 were located over shallow and deep soil depressions, and point 9 was selected purposely over a large surface boulder partially covered in soil. The gamma-ray spectra were analyzed using a basic trapezoidal method in which the background, B, under the peak is assumed to be linear and its area is calculated as a trapezoid at the base of the peak. Thus the net counts, N, in a peak equals to the total count, T, minus B.

3. Results

The pre-activation spectrum was dominated by photopeaks from naturally occurring radionuclides ^{40}K and ^{208}Th, with additional photopeaks from bismuth, thallium, and actinium. This measurement was taken at point one before activating the neutron generator. The post-activation spectra were acquired in subsequent

Table 2

Peaks identified in the measured background spectra before and after soil irradiation with neutrons. The channel number is the centroid of the photopeaks in a spectrum and the energy is derived from the energy calibration of the detection system. The underlined italic elements denote induced activity.

Channel number	Energy (keV)	Element
39.5	352	^{214}Pb
56.8	511	*Annihilation*
66.0	609	^{214}Bi
94.4	847	^{56}*Mn*
103.0	911, 969	^{228}Ac
123.5	1120	^{214}Bi
152.5	1368	^{24}*Na*
161.0	1461	^{40}K
193.5	1764	^{214}Bi
234.5	2119	^{214}Bi
244.0	2204	^{214}Bi
287.5	2615	^{208}Tl
300.0	2754	^{24}*Na*

measurements within 1 m from the point one; these showed four additional photopeaks; two from ^{24}Na (2754.0 and 1368.6 keV), one from ^{56}Mn (847 keV), and one photopeak at 511 keV due to the electron–positron annihilation process (Table 2, Fig. 3). The difference between the post- and pre-activation spectra indicates delayed activation (Fig. 3). These spectra are normalized to the same counting times but have not been corrected for surface microtopography, which affects counting geometry.

Concurrently acquired INS and TNC spectra at all locations are shown in Fig. 4a and b, respectively. We calculated the net number of counts according to $N = T - B$ for the main Si, H, C, and O photopeaks and summarized in Table 3. The natural variability in the elemental contents in addition to the large variability in the counting geometry of the INS system resulted in a standard deviation of about 7.6% in the net counts in the C peak (Table 4). The average value of C counts from 11 spectra was 151,820, with a standard deviation of 11,477 (excluding point 9). Note the decrease in the C photopeak intensity at point 9, when the INS system was placed above a boulder about 150 cm long and 80 cm wide. At point 9 we observed a reduction in the counts of all the peaks, except silicon, by several standard deviations. These are summarized as deltas in the last row of Table 4.

We estimated the C sensitivity (s) of the INS system at 20.656 counts h^{-1} kg^{-1} m^{-2}, by relating the INS mean net C counts of 151,820 (Table 4) to the total C content of 7.35 kg C m^{-2} (including soil and roots), measured in 2004 in the nearby soil pit to a depth of
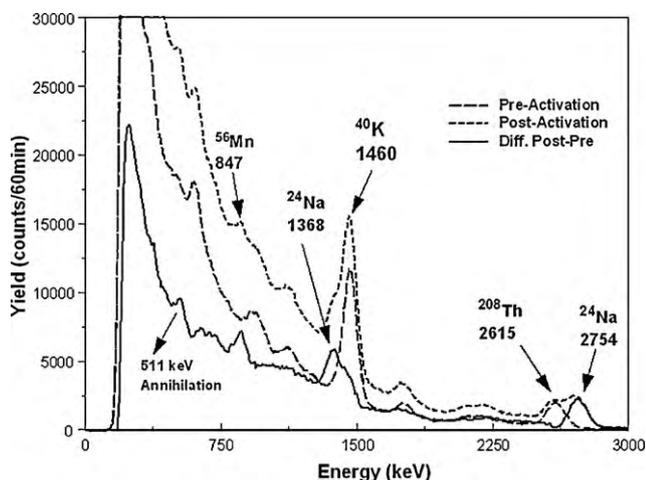
Fig. 3. Pre- and-post-activation gamma-ray spectra, plus their difference in soil at the Bartlett Experimental Forest. Data are normalized to the same counting time but are not corrected for variation in counting geometry.
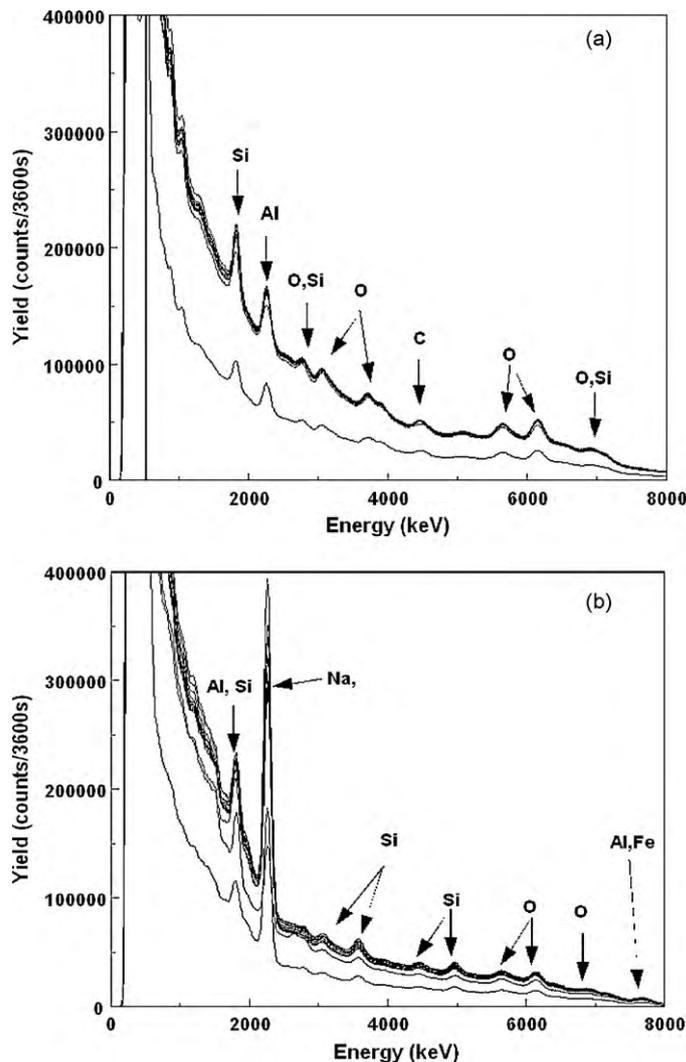
Fig. 4. (a) INS and (b) TNC spectra acquired concurrently for 1 h at Bartlett Experimental Forest. The lowest spectrum was counted for half of the time due to a computer error.

30 cm (Table 1) (unpublished, private communication M. Vadeboncoeur and S. Hamburg). Using this sensitivity the minimum detection limit (MDL $= 3\sqrt{(B)}$/s is ~0.23 kg C m^{-2} and the minimum detectable change (MDC $= 3\sqrt{(T+B)}$/s is ~0.34 kg C m^{-2} or ~5% of the total C. On average the error in the recorded net C peak ($\sqrt{(T+B)}$/s is about 1.4%. Measurements repeated with small displacement of the system show smaller variability then the 7.6% reported above (Table 3).

4. Discussion

We selected a continuously forested site on glacial till soils in the White Mountain region of New Hampshire to evaluate the suitability of the INS system for non-destructive analysis of C and other elements *in situ*. The specific site selected for testing was slightly sloped and free from underground obstacles (Fig. 1). However, the modest microtopographic variations introduced variability in the system geometric counting efficiency, i.e. changes in the relative distances between the neutron source, the soil, and the counting detectors, making positioning of the cart in a reproducible manner more difficult. Furthermore, this would increase the variance of the reported mean value from different sites that, if needed, could be assessed separately. At two loca-

Table 3
Net counts in the peaks in the TNC and INS spectra at nine measurement points in a forest stand at the Bartlett Experimental Forest.

	Silicon		Hydrogen		Carbon		Oxygen	
	TNC	INS	TNC	INS	TNC	INS	TNC	INS
1	713,938	682,674	2,752,689	548,624	70,506	145,112	357,158	570,484
2a	673,797	675,003	2,541,932	503,547	80,511	154,958	384,122	635,882
2b	661,128	607,618	2,978,648	520,766	82,239	156,328	367,527	617,471
2c	697,345	624,056	2,949,443	536,814	82,839	159,011	378,192	626,975
3	670,762	642,376	2,746,527	518,604	78,380	142,860	375,258	618,241
4a	751,590	716,554	2,346,603	480,241	84,437	149,389	373,193	614,297
4b	719,212	711,176	2,326,724	456,573	90,991	138,774	381,314	606,155
5	739,502	701,907	2,366,435	478,772	80,084	143,312	384,664	613,437
6	682,439	664,908	2,343,836	478,763	83,749	142,657	395,498	621,711
7	649,401	546,499	3,613,120	616,770	71,799	178,816	361,826	623,239
8	736,759	590,027	3,226,304	561,463	76,780	158,807	388,057	633,689
9	514,655	700,510	859,688	330,652	43,571	98,127	327,703	508,140

Table 4
Summary statistics of the net counts in the measured spectra given in Table 3.

	Si		H		C		O	
	TNC	INS	TNC	INS	TNC	INS	TNC	INS
Mean[a]	699,625	651,163	2,744,751	518,267	80,210	151,820	376,983	616,507
STDEV	34,732	54,408	419,629	46,292	5,811	11,476	11,511	17,595
STDEV/mean (%)	4.96	8.35	15.28	8.93	7.24	7.56	3.05	2.85
(mean-observation 9)/STDEV	5.32	−0.91	4.49	4.05	6.30	4.68	4.28	6.16

[a] The mean values excluded the observation at point 9, where the INS was placed over a large boulder.

tions we looked into the impact of small, ∼5 cm, displacements of the system on the signals that yielded only minor changes in the counts (Table 3). It is speculated that the large footprint of the INS system eliminates fluctuations due to small displacements. Nevertheless, our findings clearly indicate the ability of the INS system to quantify local elemental abundance in forest soils in terms of mass per unit area. A better estimate of the conversion factor used in this work could be obtained by calculating the slope of a regression between INS counts and the analysis of soils from multiple locations with a wide range of soil C content.

Previous studies of C in forest floors using destructive sampling were unable to detect changes of less than 20% (Yanai et al., 2003). Thus the possibility of detecting changes of ∼5% presents a significant improvement. However, the reported MDL and MDC depend on the sensitivity of the INS, which in turn depends on the quality of the determination of the carbon content in the forest soil. For example, Lichter and Costellp (1994) claim that volume excavation technique generates bulk density values up to 9% lower than the core sampling technique. Bulk density can be measured using various methods (clod, core, excavation, and radiation) which are fully reviewed by Blake et al. (1986). These methods have been developed largely for agricultural soils which are low in large coarse fragments. Soils in forests and arid lands often contain substantial amounts of large coarse fragments (rocks, cobbles, and boulders) that require quantitative pits (Johnson et al., 2002; Page-Dumroese et al., 1999). These are usually made by excavation methods that are difficult, time consuming and destructive to the site being sampled. Hamburg (1984) outlined a quantitative pit procedure for measurement of bulk density and large coarse fragments in very stony soils in Hubbard Brook, New Hampshire.

To assess changes in soil C, the current INS system can be used in its current configuration provided that it can be repositioned accurately at specific locations for the purpose of serial measurements. However, when averaging over larger area, changes in counting geometry will increase the uncertainty in the results. To monitor percent change in soil C, no calibration is necessary, i.e., no conversion from C counts in the photopeak to mass per unit area is required, since these are linearly correlated. However, for moni-

toring C sequestration for "credits" the results of C stocks must be expressed in units of mass per unit area.

The residual peaks in the post- and pre-activation difference spectrum (Fig. 3) clearly show ^{24}Na and ^{56}Mn peaks whereas the remaining peaks may result from imperfect normalization of the spectra due to variable counting geometry. The source of delayed ^{24}Na gamma line may originate in soil from capture of thermal neutrons Na or as a result of fast neutrons via a n,γ reaction with Al. Similarly, the source of the delayed activation of ^{56}Mn could be thermal neutron capture by stable Mn in soil or a fast neutron n,p reaction with ^{56}Fe. These issues could be elucidated experimentally by measuring soils with known composition or across sites with varied and known local bedrock and soil composition (e.g. Billings and Wilson, 1965; Schaller et al., 2010). Since there are emissions of several gamma lines associated with each element, implementing an advanced spectral-analysis package such as the library least squares method would assist in resolving and identifying overlapping peaks (Wielopolski, 1981). This would also improve the correlation between INS analysis and C determination by conventional collection and analysis of soil samples.

5. Conclusions

We demonstrated the utility of an INS system for soil analysis in a forest ecosystem. To fully implement INS for quantitative soil analysis in forestry, additional characterization of the INS system and better understanding of the system response to forest specific variables such as large roots, boulders, and topography will be required. Additional work is required to establish a proper conversion factor of INS readings to conventional units. The INS system has the potential to detect smaller changes in soil elemental composition than is currently possible with conventional methods.

Acknowledgements

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