

Carbon stored per unit area and moisture in a Canadian wetland determined by NIRS

D.F. Malley,^a C. McClure,^a P.D. Martin,^a G. Goldsborough^b and M. Sheppard^c

^a*PDK Projects, Inc., #2-12 McGillivray Place, Winnipeg MB R3T 1N4, Canada*

^b*University Field Station (Delta Marsh), University of Manitoba, Winnipeg MB R3T 2N2, Canada*

^c*ECOMatters Inc., Suite 105, W.B. Lewis Business Centre, 24 Aberdeen Ave., Pinawa MB R0E 1L0, Canada*

Introduction

Wetlands, including peatlands, contain the highest density of carbon of all land-based ecosystems. Canada contains 24% of the world's wetlands¹. Wetlands cover approximately 14% of Canada's land surface¹ and contain over 150 Gt of C, about 60% of Canada's C stock. As well as serving as C sinks, peatlands are at risk of being large C sources through burning as they dry out with climate warming. Rapid, cost-effective, practical methods for quantifying C inventories in wetlands, determining C quality, and monitoring impacts of climate change, such as changes in moisture and C quality, are important in facilitating management of global wetland carbon.

Near-infrared spectroscopy (NIRS) is a good candidate for such a rapid, cost-effective method. It has been reported by a number of authors to accurately determine total C, organic C, and moisture in soils (see review by Malley et al.²) but little work has been published using NIRS for these purposes in wetlands. The purpose of this study was to develop a rapid and potentially field-portable method using NIRS to determine the content of moisture and total C in core profiles and then to estimate the C inventory cm⁻². The study sites were three representative habitats in a large lacustrine marsh. Samples were analyzed by NIRS in the field-moist and dried and ground states. Samples were scanned using a laboratory and a field-portable NIR instrument.

Material and methods

Sampling and sample analysis

Sampling was performed at Delta Marsh, a "Wetland of International Significance" under the Ramsar Convention, on the shore of Lake Manitoba, Manitoba Canada³. The marsh is about 2,500 y old. Three sites were sampled varying in degree of terrestriality, a) a small isolated pond close to the beach ridge, b) a large bay unconnected to the lake, and c) a large, deep bay connected to Lake Manitoba through a channel. Cores were collected of the bottom soil/sediment through the ice (> 1 m thick) and water column (0.5 to 1 m deep) in April 2002. They were collected in 7.5 cm i.d. PVC tubes. Two cores were collected within a few m of each other at each site.

Cores, 52 to 75 cm in length, were sectioned into 1-cm thick sections to comprise samples (n = 370). After samples had been scanned in the field-moist state, moisture content was determined by

weighing the samples wet, drying them to constant weight at 110° C, and reweighing. Dried samples were pulverized using a mortar and pestle and 192 of the samples were analyzed for C by the Dumas combustion method using an Exeter Analytical CE440 Elemental Analyzer.⁴

NIRS scanning

NIR spectra were recorded using a Foss NIRSystems Inc (Silver Spring, MD) Model 6500 visible/NIR scanning spectrophotometer in the reflectance mode. Field-moist, i.e., "as is", soil samples were placed in a standard 7.4 cm o.d. Foss sample cell and scanned from 400 to 2500 nm in the standard sample transport. The dried and pulverized samples in borosilicate glass scintillation vials were scanned from 1100 to 2500 nm with the 6500 configured with the Rapid Content Sampler. The model 6500 records absorbance at 2 nm intervals.

At the same time as with the 6500, the field-moist samples in the Foss cell were scanned from 360 to 1700 nm on a Zeiss Corona® 45 VISNIR 1.7 Spectrometer (Carl Zeiss, Jena, Germany). The dried samples in the glass vials were positioned on the sensor head at the correct height in a custom-designed sample holder. They were also scanned from 360 to 1700 nm. The Corona records absorbance at ~ 6 nm intervals.

Statistical analysis and calibration

Spectra from the two instruments were imported into The Unscrambler® 7.6 (CAMO ASA Oslo, Norway). The Zeiss spectra were interpolated to 2 nm intervals. Areas of obvious noise were eliminated from the spectra for each instrument. Principal component analysis (PCA) was performed on the spectral data of the field-moist and the dried samples from each of the two NIR instruments. Scores plots provided information about patterns, groupings, similarities or differences among the samples.

Calibrations were developed in The Unscrambler using principal component analysis/partial least squares regression (PCA/PLS1). Using the test set method, calibrations were developed on two-thirds of the samples and validated on the remaining third of the samples. Calibrations were developed and validated on untransformed spectral data and on the spectral data smoothed over 5, 11, 21, or 41 wavelength points (where wavelength points were at 2 nm intervals). Calibrations were also performed on data smoothed over each interval and then transformed to first or second derivative where the derivative interval, or gap, was 5, 11, 21, or 41 wavelength points. This gave a total of 37 trial calibrations. The calibration that resulted in the highest r^2 (coefficient of determination) between the NIR-predicted values in the validation set and the chemically-measured, reference values, and in the lowest Standard Error of Prediction (SEP) was selected as the best. Also calculated was the ratio of the SD (standard deviation) of the reference values in the validation set to the SEP termed the RPD, and the ratio of the range of the reference values in the validation set to the SEP termed the RER. The regression statistics, r^2 , SEP, RPD, and RER were tabulated.

Estimation of carbon per unit area

Using the calibrations for C in samples on a wet weight basis, C content in those samples not subject to combustion analysis was predicted. From the C content and the wet weight of the samples, the mass of C in each slice was calculated. Masses of C in slices were summed down the cores.

Results and discussion

Composition

The samples ($n = 370$) from the six cores in this study varied in moisture from 21.7 to 83.8% (mean $\pm$ SD, $51.6 \pm 15.1\%$ weight basis) and in C from 15 to 137 mg g^{-1} d.w. (mean $\pm$ SD, $74.3 \pm 24.5 \text{ mg g}^{-1}$ d.w.). Carbon calculated on a wet weight basis varied from 11.4 to 53.4 mg g^{-1} w.w. (mean $\pm$ SD, $32.6 \pm 7.9 \text{ mg g}^{-1}$ w.w.). Moisture and C were generally highest at the top of the core and lowest at the bottom. A previous student project⁵ on moisture and C in soil of three emergent plant communities in the marsh determined that moisture ranged from 54.0 to 88.0% and total C from 24.7 to 78.3% w.w.). Thus, the present study covered most but not all of the range of these constituents in the marsh.

Moisture and C in the field-moist samples were not correlated (r , 0.065). Correlation between C on a wet weight and on a dry weight basis was 0.534.

Spectral data

Figure 1 shows the scores for the field-moist samples recorded with the Corona. The first two PCs accounted for 59 and 12% of the variance in the spectral data, respectively. Duplicate cores, A and B; C and D; and E and F; tended to be similar to each other. PC1 is largely related to moisture in cores. Samples ranged along PC1 from high moisture on the left to low moisture on the right.

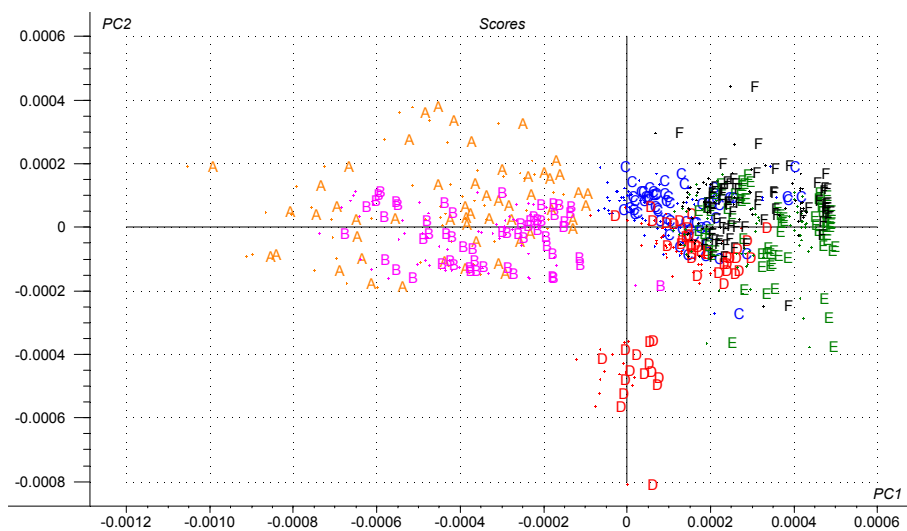


Figure 1. Scores plot for the 370 samples from the six cores in this study on the first two principal components explaining the variability in the spectral data (426 - 1600 nm). The spectra were recorded using the Corona and the samples were in the field-moist, "as is", state. The spectra were smoothed and transformed to the second derivative. Cores A and B, C and D, and E and F were pairs from each of three sampling sites in Delta Marsh.

When PCA plots of loadings of individual constituents on the PCs explaining the variance in constituents are compared side by side with the scores plots, samples in particular quadrants in the scores plots will tend to have high values for the constituents in the same quadrants in the loadings

plot. Thus, changes in relative positions of samples in the scores plot over time, such as might be detected in an environmental monitoring program, may be associated with overall changes in the concentrations of certain constituents, such as moisture or C fractions. These general changes can be detected rapidly in the field from the spectral data alone.

Calibrations for moisture and carbon

Calibrations developed for moisture in the six cores were judged to be excellent for both NIR instruments (Table 1, Fig. 2). That developed for C on a dry weight basis from spectra recorded with the 6500 was excellent and better than that for the Corona (Table 1), whereas those for C on a wet weight basis were similar for the two instruments (Table 1, Fig. 3). Although C was predicted in moist soil less well than in dry, the calibrations for moist soil were good, with RPDs close to 3.0. The advantage to monitoring programs to have a technique that can be used in the field to predict concentrations of moisture and total C on samples with virtually no sample preparation, including drying, will likely outweigh the modest loss in precision compared with dry samples. Where the laboratory NIR instrument provides more precise data, samples can be brought to the laboratory for drying, grinding, and rescanning.

Table 1. Accuracy of predictions for NIR calibrations in 370 samples for moisture and 192 samples for C from six cores in this study.

Statistic	Moisture		Carbon			
	6500	Corona	6500		Corona	
	Wet	Wet	Dry	Wet	Dry	Wet
Wavelength Range, nm	630 - 2498	434 - 970, 990 - 1634	1100-2498	400-2498	434 - 970, 990 - 1634	434 - 1634
r^2	0.927	0.938	0.953	0.857	0.898	0.867
SEP ¹	3.89	3.66	5.32	2.81	7.46	2.68
RPD ¹	3.69	4.02	4.61	2.80	3.28	2.93
RER ¹	20.01	19.44	22.91	14.96	16.35	15.65
a^2	4.55	3.10	0.49	4.27	7.18	4.27
b^3	0.940	0.914	0.995	0.869	0.903	0.869
Math ⁴	Log 1/R	Log 1/R	1 st derivat.	2 nd derivat.	2 nd derivat.	1 st derivat.
Gap ⁵			21	41	41	11
Seg ⁶	21	21	5	41	41	21

¹SEP, RPD and RER are defined in the text.

² a is the y-intercept of the linear regression line, $y = a + bx$, fitted to the x,y points for each of the 6500 and Corona predictions where x values are reference values, and y values are NIR-predicted values.

³ b is the slope of the linear regression line, $y = a + bx$, fitted to the x,y points for each of the 6500 and the Corona predictions.

⁴ Math is the mathematical pretreatment of the spectral data before the calibration is performed. For moisture, the raw spectral data expressed as log 1/R where R is reflectance, were used without transformation to first or second derivative.

⁵ Gap is the number of wavelength points over which the derivative is taken where wavelength points are 2 nm apart.

⁶ Seg is the number of wavelength points over which the spectral data were smoothed.

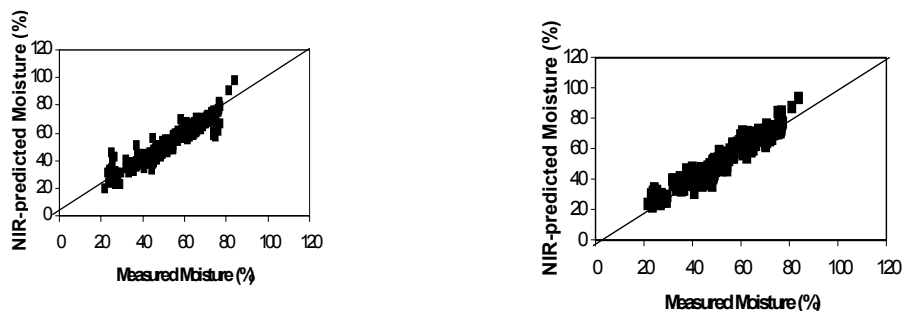


Figure 2. Linear regression relationships between the NIR-predicted values for moisture and values for moisture determined by oven drying for calibrations developed for the 6500 (left) and the Corona (right). Statistics are given in Table 1.

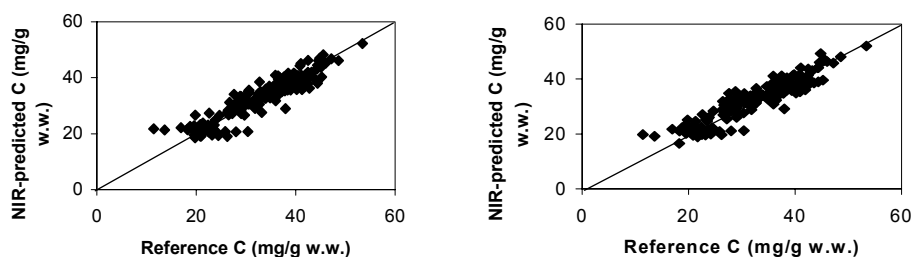


Figure 3. Linear regression relationships between the NIR-predicted values for C (wet weight basis) and values for C calculated from combustion analyses for calibrations developed for the 6500 (left) and the Corona (right). Statistics are given in Table 1.

Carbon per Unit Area

On a cm^{-2} basis, the inventory of C in the six cores predicted by the Corona was A, 2.6 g; B, 2.8 g; C, 3.0 g; D, 2.4 g; E, 3.2 g, and F, 2.9 g. The results achieved using the calibrations for C developed for the 6500 were very similar to those for the Corona. None of the six cores collected in this project represented the entire 2,500 y history of organic accumulation of the marsh. For example, previous work on the large bay connected to Lake Manitoba sampled here indicated that the paleoecological accumulation was ~ 1 m in depth⁶. Extrapolating cores E and F from 74 and 71 cm, respectively, to 100 cm length, the areal inventory was estimated as 4.03 and 4.24 g cm^{-2} , respectively. Further work is required to estimate the C inventory at other sites, including the other two sampled.

Conclusions

This paper established that NIRS is a feasible method for the determination of C content of cores in wetlands for the determination of C inventories and for monitoring drying from climate change. Some of the samples from cores from sampling sites would be analyzed for moisture by drying and for C by combustion analysis. Together with spectral data on the samples, calibrations

can be developed that are used to predict moisture and C contents in those samples not analyzed chemically. These calibrations can then be used to predict these constituents in future cores taken from these sampling sites over time for the purpose of environmental monitoring. The technique has potential for efficient determination of C inventories when combining a) effective sampling of the full depth of the organic C layer, b) appropriate sampling of the variability of the depth of the organic layer within representative habitats, and c) measurement of areal extent of the representative habitats.

Although this study demonstrated that the NIR method was useful for determining moisture and C in lake-shore wetland soils, the wetlands of greater interest for C inventory are peatlands. In addition to total C, determination of changes in C quality in peatlands over time would also be valuable. The literature suggests that application of NIRS to "as is" peat is feasible. Moisture, as well as bulk density, degree of humification, identifiable *Sphagnum*, unidentified organic material, and remains of several plant species on dried samples were determined from a blanket bog in Great Britain.⁷

The availability of field-portable NIR instruments permits most of the work following calibration to be done at the field site resulting in large savings in time, and in sample handling, transportation, storage, and laboratory analysis costs. For monitoring of large geographical areas for changes in C quantity or quality or to identify areas that are drying and becoming increasingly at risk for fire, principal component analysis of spectra alone can be a powerful, rapid monitoring tool.

Acknowledgments

This study received funding from the Manitoba Climate Change Action Fund of the Govt. of Manitoba, Canada. In-kind support of Foss NIRSystems Inc. (Silver Spring, MD, USA) and Carl Zeiss AB (Jena, Germany) are gratefully acknowledged. We thank Dr. D. Wrubleski, P. Badiou, N. Firlotte, B. Sanipelli, and B. Hauser for assistance in the field or laboratory.

References

1. Statistics Canada. *Human Activity and the Environment 2000*. CD Rom, Catalogue No. 11-509-XPS (2000).
2. D.F. Malley, E. Ben-Dor and P.D. Martin. Application in analysis of soils. Chapter 25 in C. Roberts, J. Workman, and J.B. Reeves III (eds). *Near Infrared Spectroscopy in Agriculture*. Tri-Societies Monograph (submitted for publication).
3. D.F. Malley, C. McClure, P.D. Martin, N. Firlotte, G. Goldsborough and M. Sheppard. Evaluation of near-infrared spectroscopy as a rapid method for estimating the carbon stored per unit area in a wetland. *Final Report to the Manitoba Climate Change Action Fund on Project #15*, December, 49 pp. (2002).
4. M.P. Stainton, M.J. Capel and F.A.J. Armstrong. *The Chemical Analysis of Fresh Water*. 2nd. Ed. Can. Fish. Mar. Serv. Spec. Publ. 25 (1977).
5. L. Mathias. *Exploring the Use of Near-infrared Spectroscopy for Estimating Carbon Stores in Wetland Soils*. International Baccalaureate Extended Essay, Silver Heights Collegiate, Winnipeg MB. Unpublished (2000).
6. T.A. Sproule. A paleoecological investigation into the post-glacial history of Delta Marsh, Manitoba. M.Sc. Thesis, Department of Botany, University of Manitoba. 49 pp. (1972).
7. K.B. McTiernan, M.H. Garnett, D. Mauquoy, P. Ineson and M.-M. Couëteaux. The Holocene **8**, 729 (1998).