

Prediction of organic carbon, nitrogen and phosphorus in freshwater sediments using near infrared reflectance spectroscopy

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Introduction

Organic matter is the least understood chemical component of sediments. It is ultimately derived from biological activity on watersheds and within bodies of water. It is a food source for sediment-dwelling organisms. It is the site of sorption of many inorganic and organic contaminants and its character may influence the behaviour of these contaminants.

Sediments are routinely analysed for % dry weight organic matter (e.g. by loss on ignition) or for organic C concentration as a way of characterising them and as a basis for expressing trace metal or organic contaminant concentrations. Organic C, N and P in sediments are also of interest in understanding the mass balance of these elements in lakes. The plant nutrient, P, is often measured in sediments because of its role in eutrophication. Conventional analytical methods are destructive of the sample, time-consuming and, therefore, costly. Concentration of C and N may be determined by combustion using a CNS Analyzer.¹ Phosphorus is measured by combustion/digestion and colorimetry.² Some of the analytical methods for C respond non-selectively to material of both inorganic and organic origin, requiring two procedures to determine organic constituents. Methods that greatly improve the efficiency of quantification of C, N and P in sediments would have wide application.

Near infrared (NIR) spectroscopy, described in detail by Osborne and Fearn³ and Williams and Norris,⁴ has been used to predict C and N in soils;⁵ C, N and P in suspended matter from lakes;^{6,7} and % organic matter in sand.⁸ This study examined the feasibility of using NIR

spectroscopy for the estimation of C, N and P in freshwater sediments. In a range-finding trial, two types of sediments—low-organic sand and high-organic, deeper sediments—were examined by NIR spectroscopy.

Methods

Field sampling

The first sampling site was a shallow bay of Roddy Lake (Lake 468) (290 ha in surface area; ~25 m maximum depth) in the Experimental Lakes Area (ELA), north-western Ontario. The ELA is a research preserve of 57 small lakes, typical of near-pristine Precambrian Shield lakes.^{9,10} Surface water at the Roddy sampling site on 24 July 1990 had conductivity, 29 $\mu\text{S cm}^{-1}$ at 25°C; pH, 7.36; and alkalinity, 126 $\mu\text{moles L}^{-1}$.

Eighty cores were taken from the sandy bottom at 1.6 to 1.8 m water depth from 14 to 20 July 1992. Sediments were sampled with a 5 cm internal diameter Plexiglass corer fastened to a 3 m long pole. The corer was pressed into the sediment and a rubber stopper, attached to a second pole, was inserted into the corer before it was removed from the sediment. The corer and both poles were brought to the lake surface where a second stopper was inserted into the bottom of the corer before it was brought out of the water. Cores were placed upright in a pail of lake water and transported within 0.5 h to the ELA field lab. There, water was siphoned off the top of the core, the sediment was extruded and layers of 2 cm were removed and stored in polyethylene bags at -40°C until analysis. Only 0–2 cm slices were analysed in this study.

The second sampling site was Colville Lake, north-west of Great Slave Lake, Northwest Territories. Water chemistry data are not available. One sediment core was taken on 19 April 1993 at 67° 7' 46" N latitude and 125° 55' 16" W longitude at 14.5 m water depth. The core was taken through the ice using a 10 cm diameter KB type gravity corer. The 62 cm long core was immediately sliced in 1 cm thick slices down to 30 cm and in 2 cm slices thereafter. The top 10 slices were analysed in this study.

Sample preparation

Each 1 or 2 cm thick core slice comprised a sample. Samples from Roddy Lake were freeze-dried on a Lab Con Co. Freeze Dry 5 (Fisher Scientific Co., Winnipeg, MB) at -68 to -75°C and a pressure of 0.5 to 1 Pa for at least 120 h. Samples, essentially sand with small amounts of gravel, clay and wood chips, were sieved through a #10 sieve (2.00 mm opening) to remove large organic and inorganic particles and ground for 30 sec using a Tekman Model A-10 analytical mill fitted with a tungsten-carbide blade. Equipment specifications indicate that samples should be reduced to 125 μm mean particle size after grinding. Ground samples were stored in glass scintillation vials in a desiccating cabinet.

The Colville Lake samples were already relatively fine-grained. They were dried at 104°C and ground to pass through a #100 mesh sieve (150 μm opening).

Reference analyses for C, N and P

Ground Roddy and Colville Lake samples were analysed for total C, N and P. Ground Colville Lake samples only were analysed for inorganic C. Unground Roddy Lake samples were analysed for % organic matter by loss on ignition.⁸ Colville Lake samples were not analysed for % organic matter.

Ground samples were subsampled for chemical determination of total C and total N by weighing 1–10 mg into aluminium foil cups. The cups were placed in nickel sleeves and inserted into the autosampler of a Control Equipment Corporation CHN analyser. Samples were analysed

by high temperature combustion in an O₂ atmosphere. C and N are determined as CO₂ and N₂ as described in the method for suspended C and N by Stainton *et al.*² The CHN analyser was calibrated with acetanilide; MESS-1 reference sediment (National Research Council of Canada) was used for QA/QC. This method determines total C. For the Roddy samples organic C was equivalent to total C since there was negligible inorganic C in these ELA sediments. For the Colville samples, organic C was calculated as total C less inorganic C.

Inorganic C was measured using an O.I. Corporation Model 700 TOC Analyzer. Samples of 8–20 mg ground sediment were weighed into platinum boats then transferred to 10 mL pre-ignited glass ampoules. To each ampoule were added 10 mL H₂O and 20 µL Ultrex sulphuric acid. Ampoules were then flame-sealed. Blanks and CaCO₃ standards were run with each sample batch. The sealed ampoules were autoclaved for 2 h. After cooling, the CO₂ content of the ampoules was measured in the TOC Analyzer. This method dissolves CO₃⁼ while leaving the organic matter intact.

Reproducibility of the reference method for total C and N was determined by analysing a sample of sediment from Clay Lake, ON, 20 times. Carbon averaged (mean \pm SD) 19.5 \pm 1.15 mg g⁻¹ dry weight in the sediment and values ranged from 17 to 21. Nitrogen averaged 0.56 \pm 0.08 mg g⁻¹ dry weight; range from 0.4 to 0.8.

Samples for the determination of sediment P were handled identically as for C and N, except that the aluminum cups were not digested. The samples were transferred into glass vials for digestion. Thereafter, the procedure was the same as for suspended P.² Samples were ashed at 500°C to oxidise organic P followed by hydrolysis at 104°C for 2 h and colorimetric analysis of PO₄-P. The instrument was calibrated using PO₄-P standards; MESS-1 and NBS Orchard Leaf were used for QA/QC.

Determination of organic C, N and P using NIR spectroscopy

Eighty Roddy Lake and 10 Colville Lake samples were scanned over the wavelength range 1100 to 2498 nm using a model 6500 visible/NIR spectrophotometer (NIRSystems, Silver Spring, MD) and NSAS (Near-infrared Spectral Analysis Software). The instrument was equipped with a Rapid Content Sampler (NIRSystems, Silver Spring, MD).¹¹ This presentation method allows

Table 1. Compositional data (mg g⁻¹ d.w.) determined by reference methods for calibration and prediction sets for sediments from Roddy and Colville Lakes.

Parameter	Calibration Set			Prediction Set		
	Organic C	N	P	Organic C	N	P
Mean	19.54	2.30	0.19	21.41	2.54	0.20
SD	35.95	4.63	0.39	38.74	5.03	0.42
High	134.8	17.70	1.63	139.8	18.3	1.81
Low	4.0	0.40	0.04	6.0	0.5	0.03
Range	130.8	17.30	1.59	133.8	17.8	1.78
n	45	45	45	45	45	45

samples to be scanned in standard glass scintillation vials without transfer to the sample cup. Samples were scanned alternatively with an external ceramic reference and the reference spectrum was automatically subtracted from each sample spectrum.

Statistical analysis

The calibration procedure for C, N and P was similar to that used to predict % organic matter on a subset of these samples.⁸ For each constituent, the spectra were sorted from lowest to highest constituent values, then divided into a calibration set and a prediction (or validation) set (Table 1). Using NSAS software, calibration equations were computed using the raw optical data ($\log 1/R$ where R is reflectance) smoothed from 4 to 40 wavelength points, or first or second derivative of the $\log 1/R$ data, with several combinations of segment (smoothing) and derivative (gap) sizes. Both stepwise multiple linear regression (MLR) and principal component analysis/partial least squares (PCA/PLS) regression were applied but MLR was slightly superior. Using the calibration equations developed from the calibration set, C, N or P in the prediction set were predicted and correlated to the reference values. The calibration for each constituent yielding the highest r^2 and the smallest standard error of prediction (SEP , the standard deviation of differences between the reference values and the NIR-predicted values) was selected as best.

The RPD (ratio of the SD of the prediction set to the SEP)¹² and the RER (ratio of the range in the prediction set to SEP)¹³ were calculated. $RPDs$ of 3.0 and over are suitable for screening and process control; for the most accurate analysis, $RPDs$ of 5.0 and over are required. RER values should be at least 10.

Results

Prediction of C, N and P in sediments of varying organic content

Roddy Lake samples, consisting of sand, have among the lowest organic content found in freshwater sediments and a low range of variability. The samples, consisting of 0–2 cm slices from 80 cores in a shallow bay, ranged in % organic matter from 0.75 to 2.12% of dry weight (by loss on ignition),⁸ in C from 4 to 11 mg g⁻¹ dry wt, in N from 0.4 to 1.1 mg g⁻¹ dry wt and in P from 0.03 to 0.1 mg g⁻¹ dry wt. Inorganic CO₃⁼ content was negligible. There were statistically significant correlations between % organic matter : C, % organic matter : N and C : N but only the latter was relatively high [Table 2(a)].

Usable calibrations were not obtained for C, N and P on Roddy Lake sand alone. In order to increase the range of organic matter in the sample set, the 10 highly organic Colville Lake samples were combined with samples from Roddy Lake. In the Colville samples, organic C ranged from 100.3 to 139.8 mg g⁻¹ (10.0–14.0%), N from 12.3 to 18.3 mg g⁻¹ (1.23–1.83%) and P from 0.98

Table 2(a). Correlations (r) among constituents in the Roddy Lake data set measured by reference methods. $N = 80$.

	C	N	P	% organic matter ^a
C	-	0.79	-0.08	0.40
N	-	-	-0.17	0.35
P	-	-	-	0.12

Table 2(b). Correlations among constituents in the Colville Lake data set measured by reference methods. *N* = 10.

	Organic C	N	P
Organic C	—	0.978	0.667
N	—	—	0.790

Table 2c. Correlations among constituents in combined Roddy and Colville Lakes data set measured by reference methods. *N* = 90.

	Organic C	N	P
Organic C	—	0.998	0.984
N	—	—	0.990

^aData from Reference 8.

to 1.81 mg g⁻¹ (0.1–0.18%). Content of CO₃⁼ was 6.2–10.2 mg g⁻¹ (0.62–1.02%). Organic C and N were highly correlated [Table 2(b)]. Compared with the calibration and prediction sets for Roddy Lake samples (not shown), those for the combined set (Table 1) had 2–3 times higher means and 20–150 higher ranges for C, N and P. In the combined set, C, N and P were all highly correlated with one another [Table 2(c)].

Calibrations were developed for C, N and P in the combined Roddy–Colville sample set. Linear regression relationships between NIR spectroscopy predicted and reference values had *r*² of 0.988 for each of C and N and 0.974 for P (Table 3; Figures 1 and 2). Although they are a “dumbbells”, the data for C and P in Figures 1 and 2 indicate that the calibration was useful for predicting the C and P concentrations in Colville samples and were useful for screening purposes for those from Roddy Lake. The graphical results obtained for N (not shown) were similar to those for C. For the three constituents, the RPDs were all greater than 5.0 and were particularly high for C and N (Table 3). Values for RER were also high (25–35) for all three constituents and highest for C and N (Table 3).

Table 3 summarises the mathematical treatments and wavelengths used in the development of the NIR calibration equations. First or second derivative treatments of the log 1/*R* raw optical signals are effective in correcting for baseline drift and for the variance due to differences in mean particle size and particle size distribution among individual samples.¹⁴ Wavelengths used in the calibrations included OH stretching and deformation combination (1420, 1900) and bands associated with protein (1980, 2160).⁴

Discussion

The samples in this study represent a wide range of organic content in freshwater sediments, from low organic, sandy ELA sediments, to the highly organic Colville Lake samples. The high *r*² values between the reference organic C, N and P concentrations and the NIR spectroscopy-predicted values indicate that NIR spectroscopy has the capacity to predict organic C, N and P in

Table 3. Accuracy of prediction, mathematical treatments and wavelengths for C, N and P from the scanning of fine sediments combined from Roddy and Colville Lakes. Wave-

Statistic	C	N	P
r^2	0.988	0.988	0.974
SEP^a	3.95	0.508	0.069
RPD^b	9.34	9.45	6.05
RER^c	34.89	35.83	25.65
Math ^d	D2OD	D1OD	Log 1/R
Seg./Gap ^e	10/10	10/10	20
1 ^f	1420	2000	1900
2	1980	1120	2220
3	2160	—	1880
4	—	—	2400

^astandard error of prediction.

^bratio of *SD* of prediction set to *SEP* (*SD/SEP*).

^crange in the prediction set/*SEP*.

^dMathematical treatments: **D1OD** = first derivative, **D2OD** = second derivative, Log 1/R is raw optical data.

^eSegment = degree of smoothing; gap = derivative size, or distance in wavelength points between beginning and end of the derivative.

^fThese are the wavelengths used in the calibration equation.

a range of types of freshwater sediments. The r^2 values obtained here compare favourably with those determined for C, N and P in suspended material from ELA lakes of 0.91 to 0.99⁶ and 0.88 to 0.97,⁷ possibly reflecting that suspended material and the organic matter of upper sediments are similar in chemical nature.

Calibrations for C, N and P were not successfully developed for Roddy Lake sandy sediments alone but were developed when the range of constituent values represented in the sample set was greatly extended by adding the high organic Colville Lake sediments. Nevertheless, C and N in the Roddy sediments were predictable for screening purposes from the Roddy–Colville calibrations. Dalal and Henry⁵ report that NIR spectroscopy was useful for predicting C and N ($r^2 > 0.92$) in air-dried soils containing 0.27–2.1% C and 0.02–0.17% N. Their lowest levels of about 0.3% C (3 mg g⁻¹ dry weight) and 0.025% N (0.25 mg g⁻¹ dry weight) were not well predicted. These may be the lower limits of values currently measurable by NIR spectroscopy in sediments and soils. Alternatively, these results may reflect the difficulty of analysing low level samples by the reference methods. In the present study, the C and N in the Roddy samples were within the overall

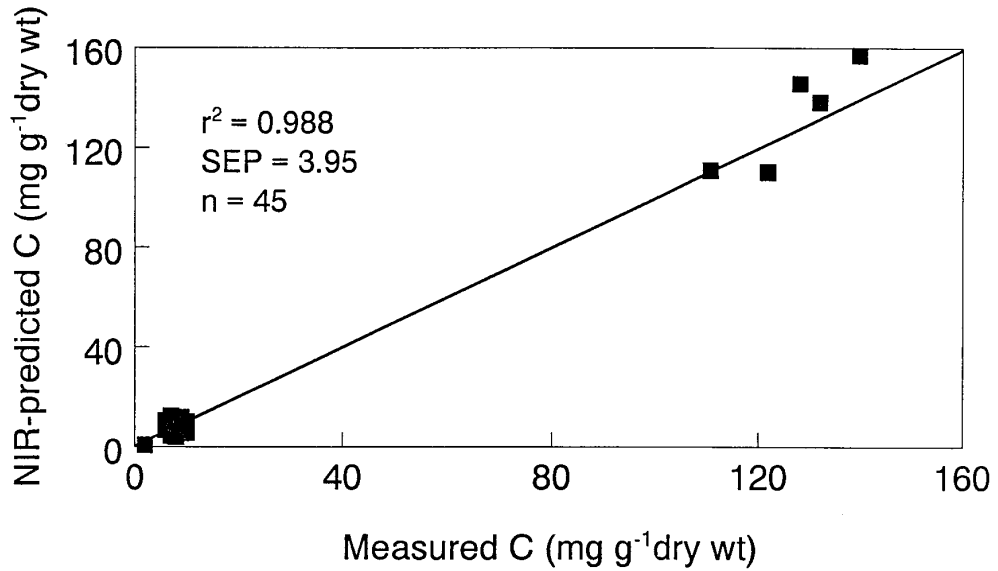


Figure 1. Linear regression relationship between NIR-predicted and reference values for C in sediments from Roddy and Colville Lakes.

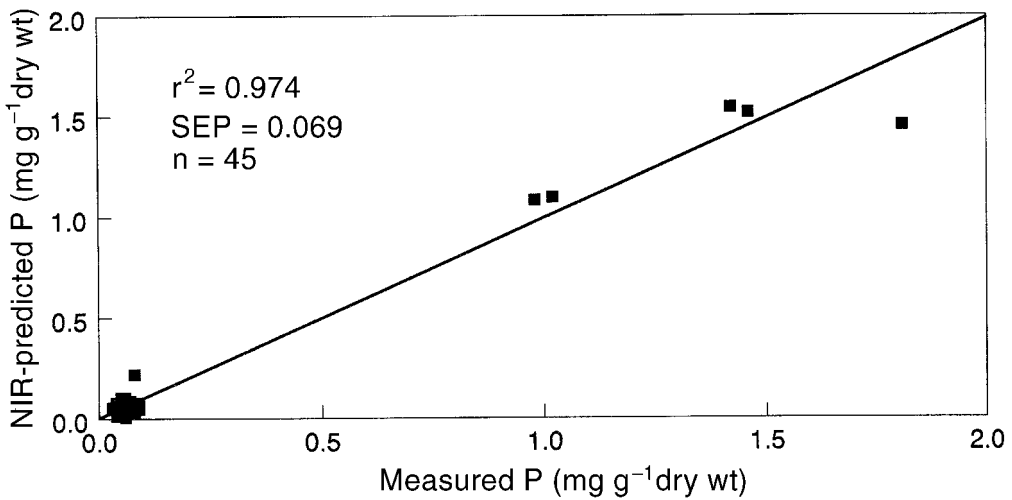


Figure 2. Linear regression relationship between NIR-predicted and reference values for P in sediments from Roddy and Colville Lakes.

range of those in the Dalal and Henry soil study, but were of smaller range, (0.4–1.1% C, 0.04–0.11% N). Either the ranges of C and N in the Roddy sediments alone were not high enough or the analytical errors in the reference method were too large for the development of successful calibrations.

This study indicates that NIR spectroscopy has the potential to increase greatly the efficiency of prediction of C, N and P in sediments. NIR spectroscopy does not replace conventional analytical methods since a proportion of samples, e.g. 10–15%, should be routinely analysed by the reference methods to verify the calibration and maintain accuracy. Calibrations are valid for samples demonstrating the variability present in the original calibration sets. Samples from new geographical locations that may be outliers to the calibration set should be analysed by the reference methods and an updated calibration prepared.

Although NIR spectroscopy can predict % organic matter, C, N and P in sediments, it is anticipated that NIR spectroscopy will make an even greater contribution to sediment analysis by providing information on the complex chemical composition of the organic matter in sediments. At present, there is no satisfactory method for determining the components to which metals bind in natural sediments.¹ Since NIR spectroscopy detects bonds between C, H, O and N, rather than quantifying the elements *per se* as in the reference analyses, it may prove capable of predicting such fractions as protein, lipids, cellulose and other carbohydrates and lignin. Differences among sediments in their behaviour toward contaminants may then become more understandable.

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