Rapid determination of soil organic matter quality indicators using visible near infrared reflectance spectroscopy

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ABSTRACT

Assessment and monitoring of soil organic matter (SOM) quality are important for determining and developing management practices that will enhance and maintain the productivity of agricultural soils. This requires routine analysis of multiple soil parameters, which can be time-consuming and expensive. Research has suggested that visible near infrared reflectance spectroscopy (VNIRS) may be used as a rapid and cost-efficient tool for SOM quality assessment. In this study, VNIRS (400–2498 nm) was used for the first time to simultaneously predict microbial biomass nitrogen (MBN), water-extractable organic N (WEON), light fraction organic matter N (LFOMN), particulate organic matter N (POMN), soil total N (TN), soil organic carbon (SOC) and soil C/N ratio as soil SOM quality indicators in Chernozemic soils of western Canada. The soil samples ($n = 200$) were collected at the 0–15 cm depth from a crop rotation experiment conducted at 6 sites in 2010 and 2011. After removal of outliers (five samples) identified by principal components analysis (PCA), 75% of the sample set was randomly selected for calibration ($n = 146$) and the remainder used for validation ($n = 49$). Modified partial least squares regression with cross-validation was used to develop prediction models. The reliability of the models was assessed using the coefficient of determination in validation (R^2_V) and the ratio of standard deviation of the reference data in the validation set to the standard error of prediction (RPD_V). The VNIRS predictions were considered reliable for LFOMN, POMN, TN, and SOC ($R^2_V > 0.80$, $RPD_V > 2.4$), as well as for MBN ($R^2_V = 0.74$, $RPD_V = 1.93$), but less reliable for WEON ($R^2_V = 0.67$, $RPD_V = 1.70$) and soil C/N ratio ($R^2_V = 0.54$, $RPD_V = 1.45$). This study showed that VNIRS has the potential as a non-destructive and cost-efficient tool for rapid determination of SOM quality indicators.

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1. Introduction

Soil organic matter (SOM) is a key indicator of soil quality since it affects physical, chemical and biological functions, which in turn influence soil productivity (Gregorich et al., 1994; Haynes, 2005). Quantitative assessment of SOM quality is therefore important for understanding SOM dynamics and for providing valuable information for determining management practices that might maintain or increase SOM. Crop rotation is one of the most important agricultural practices that have been shown to improve and/or maintain SOM quality. Soil total N (TN), soil organic carbon (SOC) and soil C/N ratio measurements, which represent the quantity and quality of SOM, are some of the most widely recommended indicators of SOM quality (Gregorich et al., 1994). However, changes in TN and SOC occur quite slowly and do not provide adequate information on important short-term changes in SOM quality. Labile organic

nitrogen (N) fractions such as microbial biomass N (MBN), water-extractable organic N (WEON), and light fraction and particulate organic matter (LFOMN, POMN) are more sensitive to management-induced changes and therefore can serve as early indicators of possible changes in SOM quality (Chantigny, 2003; Gregorich et al., 1994; Haynes, 2005).

Soil microbial biomass is the living component of SOM, and is mostly responsible for the decomposition of organic materials in soils. The MBN represents both a source (substrate) and sink (immobilization) of mineral N (Brookes, 2001). The WEON is composed of molecules generally reflecting the composition of SOM and is frequently used as a substitute for dissolved organic N in soil solutions (Chantigny, 2003). The WEON is derived from microbial decomposition of above- and below-ground residues, hence, practices that influence SOM quantity and quality as well as soil microbial activity may also have an impact on WEON dynamics (Chantigny, 2003). The LFOMN and POMN are composed of partially decomposed plant residues together with microbial by-products, and are major sources of N for microbes (Gregorich et al., 2006). However, LFOM contains greater concentrations of carbohydrates and aliphatic

compounds than POM and is thought to be primarily of plant origin, while POM contains relatively more decomposed organic matter than LFOM (Gregorich et al., 2006). The extent to which these SOM quality indicators respond to changes may depend on inherent soil characteristics, such as texture (Franzluebbers et al., 1996; Hassink, 1995). Unfortunately, conventional soil analyses for these SOM quality indicators are either expensive, time-consuming and/or require the use of hazardous chemicals.

Visible near infrared reflectance spectroscopy (VNIRS) has been suggested as a viable alternative to conventional methods for assessing and monitoring soil quality (Cécillon et al., 2009; Kinoshita et al., 2012). The VNIRS is an indirect analytical method based on the development of empirical models from which the concentration of a soil constituent is predicted from complex spectral data (Coûteaux et al., 2003). The VNIRS spectra results from electronic transitions of atoms in the visible region (400–700 nm) and weak overtones and combinations of fundamental vibrations that occur in the NIR region due to stretching and bending of chemical bonds, such as C–H, N–H, and O–H found in organic compounds (Stenberg et al., 2010; Viscarra Rossel et al., 2006). Due to broad and overlapping bands, direct quantitative prediction of soil parameters is not possible. As a result, multivariate statistics are required to mathematically extract complex absorption patterns and correlate them with soil parameters (Martens and Naes, 1987; Stenberg et al., 2010). The VNIRS is advantageous since it is rapid, accurate, non-destructive, cost-efficient, requires minimal sample preparation and does not require the use of hazardous chemicals (Chang et al., 2001; Shepherd and Walsh, 2002).

Accurate VNIRS prediction of TN and SOC has been extensively reported (Brunet et al., 2007; Chang and Laird, 2002; Fystro, 2002; Nduwamungu et al., 2009b; Shepherd and Walsh, 2002; Shi et al., 2013; St. Luce et al., 2012; Xie et al., 2011; Zornoza et al., 2008). The VNIRS was also used for prediction of MBN (Coûteaux et al., 2003; Ludwig et al., 2002; Reeves and McCarty, 2001; Terhoeven-Urselmans et al., 2008). However, there are few studies reporting on VNIRS prediction of WEON (Rinnan and Rinnan, 2007) and POMN (Yang et al., 2012) concentrations from whole soil samples. To our knowledge, there is no published study reporting on the VNIRS prediction of LFOMN. Most VNIRS calibration models reported in the literature were achieved with soil samples that were collected in close proximity and involved a limited number of samples. Moreover, there is no published report on the simultaneous prediction of these labile organic N fractions using VNIRS.

This study evaluated the potential of VNIRS to rapidly assess changes in SOM quality by predicting a number of SOM quality indicators (MBN, WEON, LFOMN, POMN, TN, SOC, and soil C/N ratio) using diverse soil samples collected from crop rotation experiments across western Canada, with the aim of creating calibration models for extensive use in this region. The soils in western Canada are located in semi-arid soil moisture regimes and were developed under grasslands.

2. Materials and methods

2.1. Dataset

The soil samples ($n = 200$) used in this study were collected from crop rotation experiments established at five no-till sites in western Canada in 2009 (Exp. 1; $n = 100$) and 2010 (Exp. 2; $n = 100$), respectively. These experiments were designed to investigate the influence of preceding legume and non-legume crops on soil fertility, canola [*Brassica napus* L. (Exp. 1)] and spring wheat [*Triticum aestivum* L. (Exp. 2)] production. Both experiments were designed to accommodate a split-plot two-factor experiment in the subsequent year (2010 and 2011, respectively) with five preceding crops as the main plots and five N fertilizer rates (0, 30, 60, 90 and 120 kg N ha^{-1}) as the sub-plots. Field pea (*Pisum sativum* L.), faba bean (*Vicia faba* L.), faba bean managed for green manure, canola and wheat were established as the main plots in 2009 and 2010 for Exp. 1

and Exp. 2, respectively, with field managed for green manure replacing faba bean at one site in Exp. 2. A more detailed description of Exp. 1 and site history was previously reported by St. Luce et al. (2013). The same details are also applicable for Exp. 2. The sites for Exp. 1 were Brandon, Manitoba, Indian Head, Saskatchewan, Lacombe, Alberta, Lethbridge, Alberta, and Scott, Saskatchewan. The sites were the same for Exp. 2 except that Melfort, Saskatchewan replaced Lethbridge, Alberta. Site locations and some soil characteristics are given in Table 1.

2.2. Soil sampling and laboratory analyses

The soil samples from the 0–15 cm depth were a composite of two to four random samples per plot, collected from the control plots (0 kg N ha^{-1}) before fertilizer application and crop establishment in spring of 2010 (Exp. 1) and 2011 (Exp. 2), respectively. The samples were then air-dried and passed through a 2-mm mesh sieve in preparation for laboratory analyses. A sub-sample was ground further with a mortar and pestle to pass a 250 μm sieve for TN and organic C analyses, and for spectral acquisition. Determination of the labile organic N fractions, TN, and organic C was described in detail by St. Luce et al. (2013). Briefly, 10 g of air-dried soil was incubated in a dark climate controlled chamber at 25 °C and 60% water-filled pore space for 7 d. Subsequently, chloroform fumigation-direct extraction (Brookes et al., 1985; Voroney et al., 2008) followed by potassium persulfate digestion (Cabrera and Beare, 1993) was used to determine the MBN concentrations. Water-extractable organic N was determined after gently stirring 7.5 g (air-dry basis) of soil with 15 mL of 5 mmol CaCl$_2$ L^{-1} for 1 min (Chantigny et al., 2008). The WEON was calculated as the difference between total dissolved N concentration in potassium persulfate digest and mineral N (NH$_4$-N + NO$_3$-N) in fresh filtrate. The LFOM was separated from 25 g air-dried soil by shaking in a heavy sodium iodide solution (NaI; specific gravity of 1.8 g cm^{-3}) for 1 h and allowing the soil mineral particles to settle for 48 h before recovering the floating LFOM, which was then dried at 50 °C (Gregorich and Beare, 2008). To isolate the POM, 25 g of air-dried soil was dispersed by shaking in 100 mL of deionized water and 10 glass beads (6 mm) for 16 h. The dispersed soil was passed through a 53-μm sieve and dried at 50 °C. Total N in LFOM and POM, and the total N and organic C in whole soil samples were determined by dry combustion using an Elementar CN Analyzer (Elementar Analysensysteme GmbH, Hanua, Germany). Organic C in whole soil samples was determined after treating the soil with H$_2$SO$_4$ to remove the carbonates (Skjemstad and Baldock, 2008). All measurements, except soil C/N ratio, were reported as mg or g per kg of dry soil.

2.3. VNIRS analysis

2.3.1. Spectral acquisition and pre-treatment

Absorbance [log (1/R), where R is the reflectance] of the soil samples (7.5 mL) was recorded in the visible and near infrared region between 400 and 2498 nm at 2-nm intervals with the spinning (ring) cup of a NIRSystems model 6500 Instrument (Foss NIRSystem, Silver Spring, MD). Each spectrum was the average of 32 co-added scans. The acquired spectra were processed with WinISI IV software (ver. 4.6.8, Infrasoft International, LLC, State College, PA, USA).

Pre-treatment included scatter correction using the standard normal variate and detrending (SNVD) to reduce the scatter and particle size effect, and also to remove the linear or curvilinear trend of each spectrum (Barnes et al., 1989). The SNVD was applied to all spectra with the WinISI IV software, using the following math treatments that were previously evaluated by St. Luce et al. (2012) to improve the calibration models: 0-0-1, 0-10-10, 0-5-5, 1-1-1, 1-4-4, 1-5-5, 1-8-6, 1-10-10, 2-1-1, 2-2-2, 2-4-4, 2-5-5, 2-8-6, and 2-10-10. These three numbers (e.g. 0-0-1) are derivative treatments and were used to remove baseline variation and accentuate spectral features. The first number stands for the order of the derivative, the second for the gap over which the derivative is to be calculated and, the third for the smoothing of the points. The