



Short communication

Distinguishing recent and fossil organic matter – A critical step in evaluation of post-mining soil development – using near infrared spectroscopy

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ABSTRACT

Content of soil organic carbon (SOC) is an important parameter for monitoring of reclamation success. In coal mine soils, measurements of SOC are affected by fossil of organic matter in the overburden, such as kerogen and coal.

The objective of this study was to assess the potential of near infrared spectroscopy (NIRS) coupled with partial least square analysis (PLS) for quantifying recently formed and fossil organic matter in post-mining soils near Sokolov, Czech Republic. NIR data were acquired from soil samples ($n = 14$), where recent SOC was quantified by ^{14}C -AMS analysis, and from artificial mixtures ($n = 125$) of overburden, coal and material from fermentation (O_e) layer. 12 PLS analyses were performed on spectra, each separately calibrated to total C (C_{tot}), recent C (C_{rec}), coal C (C_{coal}) and kerogen C (C_{ker}). All models produced correlation coefficient of cross-validation $\text{RCV} > 0.97$. When validated using the independent validation set of soils, addition of soil samples into the calibration set improved soil predictions of C_{tot} and C_{rec} (obtained from cross-validation) considerably. All four models for C_{tot} and C_{rec} were classified as successful as indicated by root mean square error ranging from 0.74 to 1.11. Results showed no clear effect of grinding on predictive accuracy; thus, we conclude that particle size < 2 mm is sufficient for NIRS. Our results demonstrate the ability of NIRS-PLS to quantify fossil and recent carbon in soils.

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1. Introduction

Open pit coal mining has a severe impact on ecosystem. Overburden overlying the coal seam is removed and deposited in heaps leading to distribution of large areas (Bell and Donnelly, 2006). In many cases, overburden material becomes the parent substrate for soil development (Karu et al., 2009; Šourková et al., 2005). Soil organic carbon (SOC) is an important indicator of soil quality (Bodlák et al., 2012) and reclamation success (Courtney et al., 2013). It changes soil structure, sorption properties, affects porosity, water storage, and infiltration rates (Brady and Weil, 1999). Soil organic matter accumulation can lead to sequestration of carbon which can mitigate rising concentration of CO_2 in the atmosphere (Lal, 2004).

In mine soils, besides soil organic matter recently derived from plant residues also fossil forms of organic carbon such as coal or kerogen can be frequently found (Filcheva et al., 2000;

Ussiri et al., 2014). Coal rich in aromatic compounds is the most frequent form of fossil organic carbon in coal mining areas (Vindušková and Frouz, 2013). However, the overburden may contain significant amounts of other organic compounds such as kerogen (Křibek et al., 1998) which is predominantly aliphatic. Fossil organic carbon leads to overestimation of soil organic carbon sequestration. The lack of a generally accepted method for fossil and recent carbon determination severely hampers the evaluation of post-mining soil development, comparison of carbon sequestration among mine soils or comparison of mine soils and natural undisturbed soils (Mukhopadhyay et al., 2013; Vindušková and Frouz, 2013).

The only way to directly quantify recent and fossil carbon in post-mining soils is the radiocarbon (^{14}C -AMS) analysis, introduced by Rumpel et al. (1999), and applied in several studies (Karu et al., 2009; Morgenroth et al., 2004; Rumpel et al., 2003). Radiocarbon method is laborious and costly. There is a lack of a simpler and accessible method for quantifying fossil carbon (Karu et al., 2009).

Cost-effective, non-destructive and simple to use near infrared diffuse reflectance spectroscopy (NIRS) as well as younger mid-infrared spectroscopy (MIRS) has been applied on numerous

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materials such as forages, foods and also soil (Stenberg et al., 2010). When combined with multivariate chemometric techniques, such as partial least-squares (PLS) regression, NIRS can be used for prediction of sample properties based on interaction of particular chemical functional groups with near infrared radiation (Janik et al., 2007).

Soil organic matter has many characteristic absorptions in the NIR (Ben Dor et al., 1997; Michel et al., 2009; Stenberg et al., 2010) which allow estimation of total carbon (TC), as well as different carbon fractions (Janik et al., 2007). However, Pietrzykowski and Chodak (2014) showed that the accuracy of NIRS may be insufficient for the prediction of SOC content in a highly variable data set of mine soils if fossil C is not taken into account during calibration. There has been several attempts to distinguish coal from recent organic matter using NIR or MIRS (Chodak et al., 2007; Michel et al., 2009; Rumpel et al., 2001). No study has yet focused on NIRS application to soils where fossil carbon is found in two chemically different forms.

This paper describes the use of NIRS and PLS for the prediction of TC and recent carbon in soils and investigates the application of NIRS–PLS to distinguish fossil carbon derived from coal or kerogen.

2. Materials and methods

2.1. Geological setting

Study was performed in the Sokolov Brown Coal Basin (NW, Czech Republic) where overburden consists of Miocene lacustrine clay sediments forming the Cypris formation called after a leading fossil *Cypris angusta*. These sediments are characteristic of variable contents of organic matter (2–18% TOC), the bulk of which is kerogen of algal or mixed origin (Kříbek et al., 1998).

2.2. Samples and analytical procedures

A set of 14 composite soil samples were collected from 7 sites at Podkrušnohorská spoil heap (GPS: N 50° 14.234' E 12° 39.55'). Soils were sampled at the top of mineral soil (0–10 cm) and the 40–50 cm depth. In addition, artificial mixtures were also produced by mixing different amounts of claystone, coal and partially decomposed litter (sampled from fermentation layer at one of the sites with organic carbon content (TOC) of 39.6%). Unweathered samples of coal (TOC=62.4%) and two types of claystone differing in organic C content (C-poor/C-rich) were collected in a nearby abandoned mine, near intersection with Jiří mine (GPS: N 50° 11.836' E 012° 40.199'), from a depth of 50–100 m. C-poor claystone (from the top of the lower part of Cypris formation) is a blue–gray kaolinite clay with a small admixture of siderite (TOC=4.12%, TIC (inorganic carbon)=0.51%). C-rich claystone (from the base of the upper part of Cypris formation) is a brown–gray illite–kaolinite claystone with a considerable admixture of siderite (TOC=13.32%, TIC=0.01%).

Soil samples were hand-picked to remove visible roots and non-clay rock fragments. Fermentation layer sample (O_e material hereafter) was sieved through a 2 mm mesh. Clay rock fragments and aggregates were crushed and left within the sample – samples were not sieved but crushed and homogenized to prevent underestimation of total soil C (Zabowski et al., 2011). The soil, claystone, coal, and O_e material samples were air-dried and coarse-ground in a IKA Analytical Grinding Mill A 11 and sieved through a 2 mm mesh. After the first NIRS measurement of coarse-ground samples, both soils and artificial mixtures were ball-milled to come through a 0.125–mm mesh (fine-ground hereafter) and measured again.

In studied sites, carbonate content was low (Šourková et al., 2005); therefore, samples were not pretreated to remove carbonates before NIRS. Conversely, carbonates were removed from samples before radiocarbon dating using the “rinse method” (Brodie et al., 2011).

For the artificial mixtures, the two types of claystone were mixed in 5 different ratios (1:0, 0:1, 1:3, 3:1, 1:1). After that, both O_e material and coal were added to each of these mixtures in ratios 0:100, 1:100, 2:100, 5:100 and 30:100; thus, 125 (=5³) mixtures were made. The content of total organic carbon (C_{tot}) in mixtures was calculated as a sum of C_{rec} , C_{coal} and C_{ker} assuming all organic C in claystone was kerogen, all C in O_e was recent and all C in coal was coal. Total organic carbon (TOC) content in mixture materials and soils was calculated as a difference of total carbon (TC) and total inorganic carbon (TIC) determined using elemental analyzers ELTRA CS 530 and ELTRA CS 500 with a TIC modul, respectively.

¹⁴C radiocarbon AMS analysis of soils was carried out in the University of Georgia's Center for Applied Isotope Studies. Content of recent carbon in soils was calculated according Rumpel et al. (2003) as TOC multiplied by ¹⁴C activity measured in samples divided by ¹⁴C activity of recent organic matter for which 115 pMC was used as in earlier studies (Morgenroth et al., 2004; Rumpel et al., 1999).

2.3. NIRS

NIR spectra were recorded on an Antaris II FT-NIR spectrophotometer (Thermo Electron Corporation, Madison, USA), equipped with an interferometer, an integrating sphere working in diffuse reflection, plus an indium and gallium arsenide (InGaAs) detector. Approximately 30 g of each sample was placed in a 5 cm diameter spinning cup and scanned 64 times in a spectral range from 10,000 to 4000 cm⁻¹ (equivalent to 1000–2500 nm) in 2 cm⁻¹ intervals. The spectra were converted to absorbance units by ($A = \log [1/\text{reflectance}]$). The 64 sub-scans were averaged to produce the final sample spectrum using software Omnic 7.3 (Nicolet Instruments Co., Madison, USA). No transformation of spectra was performed, since the untransformed spectra provided satisfactory calibrations.

Partial least square (PLS) regression was used to establish calibrations for C_{tot} (%), C_{ker} (%), C_{coal} (%), and C_{rec} (%). Separate models were developed for spectra collected after coarse and fine grinding. Where data for soils were available (C_{tot} , C_{rec}), separate models were developed using only the mixtures ($n=125$) or including also the soil spectra ($n=125+14=139$). For C_{coal} and C_{ker} , soils could not be included in calibration since their values in soils are unmeasurable. The calibrations were validated by full (hold-out-one) cross-validation. The optimum number of PLS factors used in calibration was determined using the prediction residual error sum of squares (PRESS) from the cross-validation procedure. Outliers, i.e., spectra different from the other spectra in calibration set, were identified as those with large residuals, i.e., differences between reference and predicted value (Michel et al., 2009).

All calibration models were described by a correlation coefficient (R), correlation coefficient of cross-validation (RCV), root mean square error of calibration (RMSEC), and root mean square error of cross-validation (RMSECV). To quantify the predictive capabilities of our models exclusively for soil samples, more indicators, i.e., RMSE(C)V, RPD, RSC and EF (described further) were calculated using only the predicted and measured values of C_{tot} and C_{rec} in soils. For these four parameters, negative predictions (<0) were converted to 0. Furthermore, in the calculation of these parameters, the soil outliers excluded from the calibration set were included again in order not to overrate the potential of NIRS.

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