



HAL
open science

Performance comparison between a miniaturized and a conventional near infrared reflectance (NIR) spectrometer for characterizing soil carbon and nitrogen

Bernard G. Barthès, Ernest Kouakoua, Michaël Clairotte, Jordane Lallemand, Lydie Chapuis-Lardy, Michel Rabenarivo, Sylvie Roussel

► To cite this version:

Bernard G. Barthès, Ernest Kouakoua, Michaël Clairotte, Jordane Lallemand, Lydie Chapuis-Lardy, et al.. Performance comparison between a miniaturized and a conventional near infrared reflectance (NIR) spectrometer for characterizing soil carbon and nitrogen. *Geoderma*, 2019, 338, pp.422-429. 10.1016/j.geoderma.2018.12.031 . hal-02625503

HAL Id: hal-02625503

<https://hal.inrae.fr/hal-02625503>

Submitted on 4 Jul 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - ShareAlike 4.0 International License

Performance comparison between a miniaturized and a conventional near infrared reflectance (NIR) spectrometer for characterizing soil carbon and nitrogen

Bernard G. Barthès^{1*}, Ernest Kouakoua¹, Michaël Clairotte^{1,2}, Jordane Lallemand³
Lydie Chapuis-Lardy^{4,5}, Michel Rabenarivo⁶, Sylvie Roussel³

¹ Eco&Sols, Université de Montpellier, Cirad, Inra, IRD, Montpellier SupAgro, Montpellier, France. <bernard.barthes@ird.fr> and <ernest.kouakoua@free.fr>

² present address: European Commission Joint Research Centre, Directorate for Energy, Transport and Climate, Sustainable Transport Unit, Ispra, Italy. <michael.clairotte@ec.europa.eu>

³ Ondalys, Clapiers, France. <jlallemand@ondalys.fr> and <sroussel@ondalys.fr>

⁴ Eco&Sols, Université de Montpellier, Cirad, Inra, IRD, Montpellier SupAgro, Dakar, Senegal. <lydie.lardy@ird.fr>

⁵ LMI Iesol, IRD, Dakar, Senegal.

⁶ Laboratoire des Radio-Isotopes, Université d'Antananarivo, Antananarivo, Madagascar. <miarabenarivo@yahoo.fr>

*Corresponding author: +33 499 61 21 36; <bernard.barthes@ird.fr>

Declarations of interest: none

Highlights

- The performances of miniaturized NIR spectrometers have been poorly studied
- Such a device was compared with a common spectrometer for predicting soil C and N
- The microspectrometer yielded independent validation results almost as good
- Its spectra required bias correction for C prediction, but not for N prediction
- (Moderately) less accurate performances were attributed to narrower spectral range

Abstract

Miniaturized near infrared spectrometers are now available, at more affordable prices than conventional spectrometers, but their performances have been poorly studied to date. This paper aimed at comparing the performances of the JDSU MicroNIR 2200 spectrophotometer (weight < 0.1 kg) with those of a conventional bench-top instrument for predicting carbon and nitrogen contents in laboratory conditions, on a range of representative Malagasy soils.

Though its noticeably narrower and less resolved spectra (1151-2186 nm at 8.15 nm step vs. 1100-2498 nm at 2 nm step), the microspectrometer yielded predictions in independent

validation that were almost as accurate as those of the conventional instrument (standard errors of prediction were 4.6 vs. 3.4 gC kg⁻¹, but 3.9 vs. 3.4 gC kg⁻¹ after bias correction, and 0.36 vs. 0.35 gN kg⁻¹, respectively). Due to noisy features, the MicroNIR spectra needed mathematical pretreatment (e.g. standard normal variate SNV), and bias correction for C, for providing accurate predictions, while the raw absorbance spectra from the conventional instrument did not. Furthermore, building multivariate models with MicroNIR spectra required less latent variables than with their conventional counterparts, and these models were less prone to performance degradation when applied to independent validation samples. Fitting the spectra of the conventional instrument to those of the MicroNIR (1150-2182 nm at 2 or 8 nm step) showed that (moderately) less accurate MicroNIR predictions could be firstly attributed to narrower spectral range rather than to poorer resolution.

Considering their performances, such microspectrometers could thus represent a cost-effective alternative to conventional spectrometers. They have now to be tested in field conditions.

Keywords

Near infrared reflectance spectroscopy (NIRS); soil organic carbon; soil total nitrogen; microspectrometer; Madagascar.

1. Introduction

Facing the increase in the global food demand while limiting the carbon footprint of agroecosystems requires optimizing soil management, which in turn requires characterizing soil properties more extensively (Krishna, 2014; Oelbermann, 2014). This can hardly be achieved using conventional characterization approaches, especially physico-chemical analyses, which are often time-consuming and expensive. Near infrared reflectance (NIR) spectroscopy (NIRS) has been reported to provide accurate determination of many soil properties time- and cost-effectively (Stenberg et al., 2010; Soriano-Disla et al., 2014). However, even though characterizing one sample by NIRS is cheap, as it does not require any laboratory supply, buying a NIR spectrometer remains rather expensive (> 40 k€ in general). Nowadays, a new generation of spectrometers is available, much smaller in size and at more affordable prices; but the performances of these spectrometers have been poorly studied to date (O'Brien et al., 2013; Sun et al., 2016; Urraca et al., 2016), especially regarding the prediction of soil properties. Altinpinar et al. (2013) and Peng et al. (2016) used ultra-portable infrared spectrometers for predicting soil attributes in laboratory conditions: the formers

studied hydrocarbon contamination in experimental mixtures of silty sand or clayey loam and diesel or oil, and achieved very accurate predictions; the latter studied dissolved salts and soluble ions in four fields, and got accurate results in general. But the performances of such instruments have not been compared with those of usual bench-top spectrometers.

The possibility of working on-site, in the field, is an important advantage of portable spectrometers, which allows characterizing soil attributes, and even addressing their spatial variability at fine scales, without having to transport the samples to the laboratory except for calibration purposes (Yang et al., 2012). But portability is not the only interest of ultra-portable spectrometers: the price may be an important reason for choosing these instruments, even for working in laboratory conditions; moreover, they may be easily transported for scanning samples in laboratory conditions but close to sampling sites, to avoid sample transport.

The aim of the present study was to compare the performances of a NIR microspectrometer (weight <0.1 kg) with those of a conventional bench-top NIR spectrometer for predicting carbon (C) and nitrogen (N) concentrations on a range of topsoil samples from Madagascar, in laboratory conditions.

2. Materials and methods

2.1. Soil collection and conventional analyses

The soil population studied is representative of the main agricultural soils in Madagascar. The 360 samples, all collected at 0-5 cm depth using a cylinder, originated from eight experimental sites from four regions with contrasted pedoclimatic conditions (Table 1). The sampled plots were (i) under manual tillage or direct seeding mulch-based (DMC) cropping systems, with rainfed rice as main crop (maize in Tulear due to aridity) often associated with legume cover crop in DMC systems, with annual application of cattle manure and, possibly, mineral fertilizers; or (ii) natural fallow. Soil samples were air dried, sieved at 2 mm, and an aliquot was finely ground to pass a 0.2 mm sieve. Conventional determinations of soil C and N concentrations were carried out on 0.2 mm ground and oven-dried (at 40°C during 24 h) aliquots by dry combustion using an Elemental Analyzer CHN Carlo Erba NA 2000 (Milan, Italy). Samples were carbonate free, which was tested using diluted chlorhydric acid; thus all carbon was considered organic. More information on the soil sample population has been provided in Rabenarivo et al. (2013).

2.2. *Spectrum acquisitions*

Reflectance was measured on samples that had been air dried, 0.2 mm ground, then oven-dried just before being scanned (24 h at 40°C), using two spectrophotometers. Firstly, it was measured with a Foss NIRSystems 5000 (Laurel, MD, USA), a monochromator-type bench spectrometer equipped with a scanning grating as dispersive element and a PbS detector, which provides spectra between 1100 and 2498 nm at 2 nm step (i.e. 700 variables), with 5-nm spectral resolution (width at half maximum). It is composed of a sample transport module which holds ring cups. The scan was performed on a 42 mm² area of a ca. 5 g subsample packed in a ring cup. Each spectrum was the average of 32 co-added scans (this could be parametrized by the operator, while integration time could not). The spectrometer is equipped with a ceramic plate as internal white reference.

Secondly, reflectance was measured with a JDSU MicroNIR 2200 spectrophotometer (Milpitas, CA, USA), which relies on a linear variable filter as dispersive element. This ultra-portable spectrometer is equipped with an uncooled, extended wavelength range InGaAs array detector and provides spectra between 1151 and 2186 nm at 8.15 nm step (i.e. 128 variables), spectral resolution being about 12.5 nm at 1000 nm and 25 nm at 2000 nm. The scan was performed on an 8 mm² area of a ca. 5 g sample packed in a Petri dish, the spectrometer being covered with a windowed collar for protection and uniform sample presentation. Integration time was set to 500 µs per scan (the minimum proposed by the spectrum acquisition software is 100 µs; the manufacturer recommends less than 1000 µs); and 1000 co-added scans were performed then averaged. Before every spectrum acquisition, external white reference (> 99% reflectance, achieved with a disk of clean Spectralon, i.e. compressed polytetrafluoroethylene powder) and black reference (< 1% reflectance, achieved by scanning the space in front of the operator, with no light source around) were scanned.

The two spectrometers differ strongly from an optical viewpoint (dispersive elements, detectors, resolution, etc.), but this does not necessarily matter much from a practical (i.e. end-user's) viewpoint. Other technical differences matter from a practical viewpoint, beside noticeably smaller MicroNIR spectral range: sample spectrum acquisition is automatic with the Foss but manual with the MicroNIR; and internal white reference scanning is also automatic with the Foss, while external white and black references have to be scanned manually before every MicroNIR scan, which is somewhat tedious. Furthermore, the two spectrometers differ considerably in weight and price: > 20 kg and > 40 k€ for the Foss NIRSystems 5000, and < 0.1 kg and < 10k€ for the JDSU MicroNIR 2200.

The spectra were recorded in absorbance ($\log [1/\text{reflectance}]$). Spectral data analyses were conducted using the WinISI IV software (Infrasoft International, LCC, State College, PA, USA) and the *pls* package (Mevik et al., 2013) of the R software (R Development Core Team, 2012).

2.3. Analysis of spectral data

Several mathematical pretreatments were evaluated for spectrum pre-processing in order to reduce baseline variations, enhance spectral features, reduce the particle-size scattering effect, remove linear or curvilinear trends of each spectrum, or remove additive or multiplicative signal effects (Bertrand, 2000): standard normal variate transform (SNV), detrending (D), both SNV and detrending (SNVD), multiplicative scatter correction (MSC), or no correction (denoted None), in conjunction with first-order derivation with 4-, 15- or 20-point gap and 4- or 5-point smoothing (denoted 144, 1155 and 1205, respectively) or no derivation (denoted 001). Second order derivation was not used because previous works demonstrated that it often resulted in poor predictions of soil properties (Brunet et al., 2007).

The sample set was then divided into a calibration set, which included the 312 samples from all sites except that of Andranomanelatra, and an external validation set, which included 41 samples from Andranomanelatra. This site was the only one where most samples were well represented by the population of the seven other sites together. This was evaluated by carrying out a principal component analysis on raw absorbance data of all but one site, then calculating the Mahalanobis distance H between the centre of this seven-site population and the samples of the eighth site (Mark and Tunnell, 1985). Andranomanelatra was the only site where most samples had $H < 3$; it included 48 samples but seven were poorly represented by the seven other sites together ($H > 3$) and were removed. This design was the only one that allowed relevant independent validation; because independent validation on samples that are poorly represented by the calibration set is not particularly relevant.

Calibration models for predicting C and N concentrations (reference values) from absorbance spectra were built using modified partial least square (PLS) regression: PLS reduces the spectral data to a few orthogonal combinations of all absorbances, called latent variables (LV) or terms, that account for most spectral information and covary with the reference values. Cross-validation is recommended for estimating the optimal number of LV in order to avoid overfitting. The modification included in the modified PLS algorithm consists in normalizing the residuals (Shenk and Westerhaus, 1991a, 1991b). Cross-validation was performed by dividing the calibration set into four groups in a cyclical way (i.e. "Venetian blinds"), after

having ranked the samples according to increasing C or N concentration (i.e. the first, fifth, ninth samples, etc., were in the first group; the second, sixth, tenth samples, etc., in the second group, and so on). All but one group were used for developing the model and one for testing it, the procedure being performed four times to use all samples for both model development and testing. The residuals of all predictions were pooled to calculate the standard error of cross-validation (SECV). The number of terms (LV) after which final SECV no longer decreased meaningfully determined the optimal number of terms of the model. A prediction model that used all calibration samples was built with this number of LV, and its performance was evaluated according to standard error of calibration (SEC). The model performance was then evaluated on the external, independent validation set (which had not been used for model development), according to four figures of merit: (i) the standard error of prediction (SEP); (ii) the standard error of prediction corrected for bias (SEPC; bias is the mean residual); (iii) the coefficient of determination between predicted and measured values (R^2_{val}); and (iv) the RPD_{val} (ratio of standard deviation of measured values in the validation set to SEPC). According to Chang et al. (2001), prediction of soil properties with $\text{RPD}_{\text{val}} \geq 2$ has been considered accurate. The mathematical pretreatment that minimized SEPC (thus maximized RPD_{val}) was considered the most appropriate.

An attempt was made to perform cross-validation after dividing the calibration set into groups corresponding to sites. This resulted in very poor results, probably because the soils used for calibration differed between sites, as was observed when trying to find a validation site (cf. above); thus a model built on some sites was often not appropriate for the other sites (data not shown).

3. Results and discussion

3.1. Conventional and spectral data

The distributions of C and N concentrations in the total set and in the calibration and validation sets are presented in Table 2. C and N were closely correlated (e.g. $R = 0.98$ for the total set, $n = 360$, $p < 0.001$), which is consistent because both are dominantly found in soil organic matter. The validation set included samples that were relatively rich in C and N, and some of them were even richer than any calibration sample; nevertheless, as stated previously, they were well represented by the calibration set ($H < 3$, cf. section 2.3). It should be reminded that the main objective of the study was to compare spectrometer performances, not to build robust calibrations, which would have required that the calibration set fully represents any prediction set. This was not fully met here, as predictions were sometimes carried out in

extrapolation conditions, and as a consequence, issues were expected, especially regarding the slope of the regression line (Estienne et al., 2001); but these issues were presumably similar for both spectrometers.

Figure 1 presents the raw absorbance spectra ($\log 1/R$) of three example samples from the validation set, acquired with both spectrometers. These raw spectra were noticeably noisier when acquired with the MicroNIR spectrometer.

3.2. NIRS predictions

3.2.1. Number of PLS terms

Figure 2 presents the relationship between the number of PLS terms (latent variables, LV) and SECV for C prediction, with no pretreatment (None001). Using MicroNIR spectra, SECV decreased rapidly until the number of terms reached 7, it was slightly lower for 8 terms, then increased; thus identifying the optimal number of PLS terms was easy, because there was a clear minimum, after which SECV did not decrease anymore. Using Foss spectra, SECV decreased rapidly when using up to 6 terms, then it decreased moderately until 15 terms, beyond which it remained almost constant. In such conditions, identifying the number of PLS terms after which SECV did not decrease meaningfully, thus optimizing the number of PLS terms, was less easy.

Actually the WinISI software does not allow the operator to choose the number of PLS terms but just to set its maximum; then it selects as optimum the number of terms beyond which SECV does not decrease meaningfully. In a first step, this maximum number of terms was set to 16, considering empirically that more terms would result in overfitting. In such conditions, with no pretreatment (None001), the optimal number of PLS terms proposed by WinISI for both C and N was 7 with the MicroNIR spectra but 15 with the Foss spectra (Figure 2 and Tables 3 and 4).

3.2.2. Comparison between predictions using MicroNIR and full Foss spectra

With no pretreatment (None001), the MicroNIR spectra yielded noticeably worse cross- and independent external validation results than the Foss spectra (e.g. almost twice larger SEPc for both C and N). Prediction accuracy was not improved by the pretreatment of Foss spectra (data not shown), but was noticeably improved by the pretreatment of MicroNIR spectra (Table 3 for C and Table 4 for N): using the most appropriate pretreatments, the MicroNIR spectra still yielded noticeably worse cross-validation results than the Foss spectra (50-60% larger SECV); but the results of independent validations, after bias correction, were just

slightly worse with MicroNIR than with Foss spectra (15% and 3% larger SEPc for C and N, respectively). Validation results indeed show there were bias issues using MicroNIR spectra for C prediction (bias > 0.5 SEP), but not for N prediction, possibly due to C models being based on signal fingerprints closer to the noise level, which caused sensitivity to spectral perturbations (cf. section 3.3.3. on regression coefficients). Even though bias is not negligible matter, bias correction is common procedure when applying NIR models to spectra that differ from calibration spectra to some extent: this is for instance the case in many agricultural applications, where a few representative samples of every new harvest are analyzed conventionally beside spectral analysis, for possible bias (and slope) correction (Shenk et al., 2001). And here, indeed, validation samples were more clayey and often richer in C and N than calibration samples (cf. Tables 1 and 2). For both MicroNIR and Foss spectrometers, validation results also show some slope issues (regression slope differing noticeably from 1), which was expected due to higher maximum C and N values in the validation than in the calibration set (extrapolation conditions; Estienne et al., 2001). Figure 3 presents comparisons between conventional measurements and predictions of C and N contents made using optimally pretreated Foss or MicroNIR spectra, in independent external validation. It is worth noting that N predictions were similar using Foss and MicroNIR spectra.

Interestingly, using the most appropriate pretreatment (i.e. no pretreatment for Foss spectra), SEPc was 35-40% larger than SECV using MicroNIR spectra, but 80-110% using Foss spectra. Thus there was less reduction in prediction accuracy from cross-validation to independent validation using MicroNIR than Foss spectra.

In order to try to achieve more robust models with Foss spectra, the maximum possible number of PLS terms (LV) was reduced: for C and N predictions, it was set respectively to 9 and 5, which were the optimum numbers of LV with pretreated MicroNIR spectra. When compared with 15-LV Foss models, this reduction in the number LV yielded noticeably degraded C and N predictions with no pretreatment (80-100% larger SEPc), and still degraded predictions with the most appropriate pretreatments (30-40% larger SEPc). Moreover, this constraint on the number of LV did not result in more robust Foss models (SEPc was 90-170% larger than SECV with reduced LV vs. 80-110% larger with 15 LV). In addition, such constrained Foss models yielded less accurate predictions than MicroNIR models having the same number of terms (7-10% larger SEPc without pretreatment, 10-40% larger SEPc with pretreated spectra). The maximum number of LV used for calibrating Foss spectra was also set to 13 and 11, with no improvement in robustness in general when compared with 15 LV (data not shown).

Thus less PLS terms were needed with MicroNIR than with Foss spectra for achieving accurate predictions. Needing more LV for processing the wider and denser Foss spectra is relevant a priori but nevertheless seemed to result in some overfitting, which was not easily manageable.

3.2.3. Comparison between predictions using MicroNIR spectra and reduced Foss spectra

To evaluate the possible influence of spectral range and resolution on model performance, Foss spectra were limited to 1150-2182 nm and their digitalization step to 8 nm (i.e. absorbance at 130 wavelength instead of 700), just like MicroNIR spectra ("MicroNIR-fitted Foss" in Tables 3 and 4). Maximum LV was set to 16 and also to 9 for C and 5 for N (tests were also carried out with 11 and 13 LV; data not shown). With either no pretreatment (None001) or the most appropriate ones, MicroNIR-fitted Foss spectra still yielded better cross-validations for C and N than MicroNIR spectra in general (SECV = 1.8-2.7 vs. 2.8-3.2 gC kg⁻¹ and 0.15-0.26 vs. 0.23-0.28 gN kg⁻¹, respectively). Independent external validations were similarly accurate with non pretreated MicroNIR and MicroNIR-fitted Foss spectra (SEP_c = 6.3 vs. 5.8-6.7 gC kg⁻¹ and 0.58 vs. 0.50-0.57 gN kg⁻¹, respectively); but they were more accurate with MicroNIR than with MicroNIR-fitted Foss spectra when the spectra were pretreated appropriately (SEP_c = 3.9 vs. 4.3-4.6 gC kg⁻¹ and 0.36 vs. 0.39-0.54 gN kg⁻¹, respectively).

To study specifically whether poorer predictions using MicroNIR than full Foss spectra resulted firstly from narrower range (1151-2186 vs. 1100-2498 nm) or from wider acquisition step (8.15 vs. 2 nm), predictions using MicroNIR-fitted Foss spectra (1150-2182 nm, 8 nm step) were compared with predictions using non condensed "MicroNIR-ranged Foss" spectra (1150-2182 nm, 2 nm step). In general denser spectra (2 vs. 8 nm) did not improve predictions made using MicroNIR-fitted Foss spectra (Tables 3 and 4; e.g. with no pretreatment, predictions of C or N made with MicroNIR-fitted and MicroNIR-ranged Foss spectra had similar SEP_c for a given number of terms). Thus poorer MicroNIR than Foss predictions could be firstly attributed to narrower spectral range, and not to wider acquisition step. This was confirmed by the results of Yang et al. (2012), who used 400-2499-nm spectra and observed that soil C and N prediction models made using 50-nm interval spectra performed as well as those made using 2-nm interval spectra.

3.3. Regression coefficients

3.3.1. Carbon

Figure 4 presents the regression coefficients of C prediction models using MicroNIR spectra (1151-2186 nm every 8.15 nm; $LV \leq 16$), Foss spectra (1100-2498 nm every 2 nm; $LV \leq 16$) and MicroNIR-fitted Foss spectra (1150-2182 nm every 8 nm; $LV \leq 9$). The models considered were those which yielded the best independent validation results without spectrum derivation, because regression coefficients are difficult to interpret when derivatized spectra are used. Indeed, with first derivatives, peaks correspond to regions where absorbance varies the most, which is not necessarily informative; and as mentioned above, previous work showed that second order derivation often resulted in poor predictions of soil properties (Brunet et al., 2007). For MicroNIR spectra, SNVD001 pretreatment yielded $RPD_{val} = 2.2$ with 5 LV instead of 2.3 with SNV1205 and 9 LV, which was the most appropriate pretreatment. For full and MicroNIR-fitted Foss spectra, the best independent validations were achieved without derivation. When considering the regression coefficients, some regions were somewhat noisy, for instance for MicroNIR data the serrated bands at 1450-1600 and 1650-1800 nm, and for Foss data (full spectra) the region between 1900 and 2500 nm. Strong contributions to C prediction could be attributed to the following regions (assigned according to Workman and Weyer, 2008, except when otherwise mentioned):

- for MicroNIR spectra, positively, to several bands around 1470-1540 (amines, amides, proteins) and 1690-1720 nm (aliphatic compounds) and at 2130 nm (amides); and negatively, to the region around 1800 nm (possibly lignin; Matson et al., 1994);
- for full Foss spectra, positively to the regions around 1800 nm (possibly lignin; Matson et al., 1994), and to a lesser extent around 1590-1600 (amides), 1650-1660 (carbonyl, Ciurczak, 2001, and/or iron sesquioxides, Haest et al., 2012), 1480 (amines, amides, proteins) and 1210 nm (aliphatic compounds); and negatively, to the regions around 1290 nm (not easily assignable), and to a lesser extent around 1450 and 1550-1560 nm (amines, amides, proteins) and at 1880 (chlorinated compounds possibly) and 2400 nm (aromatic compounds);
- for MicroNIR-fitted Foss spectra, positively to the regions around 1690-1700 (aliphatic organic compounds), 1740-1750 (aromatic compounds), and to a lesser extent 1580 (water), 1450-1460 (amines, amides, proteins), 1200 and 1220 nm (aliphatic compounds); and negatively, to the region around 1870 nm (chlorinated compounds possibly), and to a lesser extent around 1490 (amines, amides, proteins) and 1720 nm (aliphatic compounds).

3.3.2. Nitrogen

Figure 5 similarly presents the regression coefficients of N prediction models using MicroNIR spectra ($LV \leq 16$), full Foss spectra ($LV \leq 16$) and MicroNIR-fitted Foss spectra ($LV \leq 16$; with 5 LV, which was the optimum for predicting N using MicroNIR spectra, predictions with MicroNIR-fitted Foss spectra were very poor thus examining the regression coefficients that yielded these predictions had little interest). The models considered were also those which yielded the best independent validation results without spectrum derivation. For MicroNIR-fitted Foss spectra, best validation results without derivation were achieved using SNV001, with $RPD_{val} = 1.82$ instead of 1.84 with SNVD144, which was the most appropriate pretreatment. For the other spectrum types, the best independent validations were achieved without derivation. As already seen for C, the variations of regression coefficients with wavelength showed noisy regions (1450-1600 and 1650-1800 nm for MicroNIR, 1900-2500 nm for full Foss). Strong contributions to N prediction could be attributed to the following regions (assigned according to Workman and Weyer, 2008, except when otherwise mentioned):

- for MicroNIR spectra, positively, to the regions around 1485 (amides, amides, proteins) and 1721 nm (aliphatic compounds), and to a lesser extent around 1469 and 1509 nm (amides, amides, proteins) and 1689 and 1738 nm (aromatic compounds), and negatively, to 1803 nm (possibly lignin; Matson et al., 1994) and to a lesser extent 1363 nm (aliphatic compounds);
- for full Foss spectra, positively, to 1656 (carbonyl, Ciurczak, 2001, and/or iron sesquioxides, Haest et al., 2012) and 1802 nm (possibly lignin; Matson et al., 1994), and to a lesser extent 1196 nm (aliphatic compounds); and negatively to 1548 (amines, amides, proteins), 1880 (chlorinated compounds possibly) and 2402 nm (aromatic compounds); surprisingly, no region assigned to N compounds contributed positively to N prediction, probably due to limited consideration of soil biochemistry in spectral libraries to date (e.g. the regions around 1656 and 1802 nm could relate to soil N compounds without demonstration yet);
- for MicroNIR-fitted Foss spectra, positively, to 1654 (carbonyl, Ciurczak, 2001, and/or iron sesquioxides, Haest et al., 2012), 1790 (water) and 1590 nm (amides), and negatively, to 1630 (aliphatic compounds) and 1766 nm (methylene i.e. CH_2).

3.3.3. Comparisons between C and N predictions and between spectrum types

At first sight, similar regions of MicroNIR spectra contributed heavily to C and N predictions (e.g. groups of positive peaks around 1500 and 1700 nm, and negative peak at 1800 nm); however the specific contribution of a given region might differ between C and N predictions.

Bias issues when predicting C but not N suggested that spectral perturbations might have affected regions important for predicting C but not N. MicroNIR spectra were noisy from 1151 to 1370 nm, and to a lesser extent, from 1500 to 1850 nm (cf. Figure 1); and it is possible that these regions contributed more to C than N prediction (though this could not be evidenced easily when examining regression coefficients, cf. Figures 4 and 5). Using full Foss spectra, there was less similarity between regions that contributed heavily to C and N predictions, especially below 1700 nm; and in particular, the regions around 1290, 1480 and 1590 nm contributed heavily to C prediction but not to N prediction. Using MicroNIR-fitted Foss spectra, no region contributed markedly to both C and N predictions. Nevertheless, using a given spectrum type, the chemical compounds that contributed most to C and N predictions were often the same (several regions have often been assigned to a given type of compound), though their respective weights often varied:

- aliphatic and N organic compounds (positively), and possibly lignin (negatively), using MicroNIR spectra;
- lignin possibly, carbonyl or sesquioxides (positively), and N, aromatic and possibly chlorinated compounds (negatively), using full Foss spectra;
- amides and water (positively) and aliphatic compounds (negatively) using MicroNIR-fitted spectra.

Moreover, the regions that contributed to a given prediction (C or N) varied according to the spectrum type in general. For instance, the region around 1290 nm had a strong negative contribution to C prediction using full Foss spectra but marginal contribution using MicroNIR spectra. Such discrepancies could be seen for almost every region that contributed heavily to prediction using a given spectrum type. Discrepancies could even be dramatic: the contributions of the regions around 1650 and 1800 nm to C and N predictions were strongly positive using full Foss spectra but strongly negative using MicroNIR spectra. Nevertheless the regions around 1480 nm, and to a lesser extent around 1510 and 2130 nm, had a strong positive contribution to C prediction using both MicroNIR and full Foss spectra. Some regions of both spectrum types also contributed comparably to N prediction (e.g. 2065 nm).

Though the contributing regions were not necessarily the same, the chemical compounds that contributed to a given prediction were often similar using different spectrum types. In particular, aliphatic and N organic compounds contributed positively to C and N predictions in general.

Such discrepancies in the contributions of spectral regions were probably an effect of multivariate analysis. Indeed, PLS regression combines and weights the contributions of

different spectral regions assigned to a given type of compounds involved in the prediction of the variable of interest (C or N contents here), in order to optimize the fitting of spectra to this variable.

4. Conclusions

When compared with Foss spectra (1100-2498 nm every 2 nm), MicroNIR spectra (1151-2186 nm every 8.15 nm) resulted in a little less accurate C and N prediction models, provided spectra were mathematically pretreated, and for C, bias correction was performed (with optimal pretreatment, SEP = 4.6 vs. 3.4 gC kg⁻¹ and SEP_c = 3.9 vs. 3.4 gC kg⁻¹, for N SEP = SEP_c = 0.36 vs. 0.35 gN kg⁻¹, respectively); but MicroNIR models required less PLS terms and were less prone to performance degradation when applied to independent validation samples (after bias correction for C). Actually, more PLS terms were necessary to calibrate Foss spectra but this seemed to result in some overfitting; and reducing the number of PLS terms did not increase prediction accuracy or robustness. Reducing Foss spectra to MicroNIR pattern showed that (moderately) less accurate MicroNIR predictions could be firstly attributed to narrower spectral range rather than to wider acquisition step.

In short, the JDSU MicroNIR spectrometer, though it produced spectra 25% narrower and four times rougher than the Foss NIRSystems spectrometer, could be considered a cost-effective alternative for NIRS prediction of soil properties in laboratory conditions. One important advantage of such ultra-portable instruments is the possible use on-site, thus further work is needed to evaluate the performances of the micro-spectrometer considered in field conditions.

5. Acknowledgements

We thank Lilia Rabeharisoa, director of the Laboratoire des Radioisotopes (University of Antananarivo, Madagascar), for her support. An anonymous reviewer is also thanked for fruitful recommendations.

6. References

- Altinpinar, S., Sorak, D., Siesler, H.W., 2013. Near infrared spectroscopic analysis of hydrocarbon contaminants in soil with a hand-held spectrometer. *Journal of Near Infrared Spectroscopy*, 21, 511–521.
- Bertrand, D., 2000. Prétraitement des données spectrales, in: Bertand, D., Dufour, E. (Eds.), *La Spectroscopie Infrarouge et ses Applications Analytiques*. Editions Tec & Doc, Paris, pp. 351–370.
- Brunet, D., Barthès, B.G., Chotte, J.-L., Feller, C., 2007. Determination of carbon and nitrogen contents in Alfisols, Oxisols and Ultisols from Africa and Brazil using NIRS analysis: Effects of sample grinding and set heterogeneity. *Geoderma*, 139, 106–117.

- Chang, C.W., Laird, D.A., Mausbach, M.J., Hurburgh, C.R.J., 2001. Near-infrared reflectance spectroscopy—principal components regression analyses of soil properties. *Soil Science Society of America Journal*, 65, 480–490.
- Ciurczak, E.W., 2001. Principles of near-infrared spectroscopy, in: Burns D.A., Ciurczak E.W. (Eds.), *Handbook of Near-Infrared Analysis*, 2nd edition. CRC Press, Boca Raton, FL, USA, pp. 7–18.
- Estienne, F., Pasti, L., Centner, V., Walczak, B., Despagne, F., Jouan Rimbaud, D., de Noord, O.E., Massart, D.L., 2001. A comparison of multivariate calibration techniques applied to experimental NIR data sets: Part II. Predictive ability under extrapolation conditions. *Chemometrics and Intelligent Laboratory Systems*, 58, 195–211.
- Haest, M., Cudahy, T., Laukamp, C., Gregory, S., 2012. Quantitative mineralogy from infrared spectroscopic data. I. Validation of mineral abundance and composition scripts at the Rocklea Channel Iron Deposit in Western Australia. *Economic Geology*, 107, 209–228.
- IUSS (International Union of Soil Science) Working Group WRB (World Reference Base), 2014. *World Reference Base for Soil Resources 2014. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*. World Soil Resources Reports, 106. FAO, Rome.
- Krishna, K.R., 2014. *Agroecosystems: Soils, Climate, Crops, Nutrient Dynamics and Productivity*. Apple Academic Press, Oakville, ON, Canada.
- Mark, H.L., Tunnell, D., 1985. Qualitative near-infrared reflectance analysis using Mahalanobis distances. *Analytical Chemistry*, 57, 1449–1456.
- Matson, P., Johnson, L., Billow, C., Miller, J., Ruiliang, P., 1994. Seasonal patterns and remote spectral estimation of canopy chemistry across the Oregon transect. *Ecological Applications*, 4, 280–298.
- Mevik, B.-H., Wehrens, R., Liland, K.H., 2013. pls: Partial least squares and principal component regression. R package, v2.4-3. <http://ftp.igh.cnrs.fr/pub/CRAN/> (accessed 8 April 2014).
- O'Brien, N., Hulse, C.A., Pfeifer, F., Siesler, H.W., 2013. Near infrared spectroscopic authentication of seafood. *Journal of Near Infrared Spectroscopy*, 21, 299–305.
- Oelbermann, M. (Ed.), 2014. *Sustainable Agroecosystems in Climate Change Mitigation*. Wageningen Academic Publishers, Wageningen, The Netherlands.
- Peng, J., Ji, W., Ma, Z., Li, S., Chen, S., Zhou, L., Shi, Z., 2016. Predicting total dissolved salts and soluble ion concentrations in agricultural soils using portable visible near-infrared and mid-infrared spectrometers. *Biosystems Engineering* 152, 94–103.
- R Development Core Team, 2012. *R: A language and environment for statistical computing*. <https://cran.r-project.org/doc/manuals/r-release/fullrefman.pdf> (accessed 5 August 2016).
- Rabenarivo, M., Chapuis-Lardy, L., Brunet, D., Chotte, J.-L., Rabeharisoa, L., Barthès, B.G., 2013. Comparing near and mid-infrared reflectance spectroscopy for determining properties of Malagasy soils, using global or LOCAL calibration. *Journal of Near Infrared Spectroscopy*, 21, 495–509.
- Shenk, J.S., Westerhaus, M.O., 1991a. Population definition, sample selection and calibration procedures for near infrared reflectance spectroscopy. *Crop Science*, 31, 469–474.
- Shenk, J.S., Westerhaus, M.O., 1991b. Population structuring of near infrared spectra and modified partial least square regression. *Crop Science*, 31, 1548–1555.
- Shenk, J.S., Workman, J.J., Jr, Westerhaus, M.O., 2001. Application of NIR spectroscopy to agricultural products, in: Burns D.A., Ciurczak E.W. (Eds.), *Handbook of Near-Infrared Analysis*, 2nd edition. CRC Press, Boca Raton, FL, USA, pp. 419–474.
- Soriano-Disla, J.M., Janik, L., Viscarra Rossel, R.A., McDonald, L.M., McLaughlin, M.J., 2014. The performance of visible, near and mid-infrared spectroscopy for prediction of soil physical, chemical and biological properties. *Applied Spectroscopy Reviews*, 49, 139–186.

- Stenberg, B., Viscarra Rossel, R.A., Mouazen, A.M., Wetterlind, J., 2010. Visible and near infrared spectroscopy in soil science. *Advances in Agronomy*, 107, 163–215.
- Sun, L., Hsiung, C., Pederson, C.G., Zou, P., Smith, V., von Gunten, M., O'Brien, N., 2016. Pharmaceutical raw material identification using miniature near-infrared (MicroNIR) spectroscopy and supervised pattern recognition using support vector machine. *Applied Spectroscopy*, 70, 816–825.
- Urraca, R., Sanz-Garcia, A., Tardaguila, J., Diago, M.P., 2016. Estimation of total soluble solids in grape berries using a hand-held NIR spectrometer under field conditions. *Journal of the Science of Food and Agriculture*, 96, 3007–3016.
- Workman, J., Jr, Weyer, L., 2008. *Practical Guide to Interpretative Near-Infrared Spectroscopy*. CRC Press, Boca Raton, FL, USA.
- Yang, H., Kuang, B., Mouazen, A.M., 2012. Quantitative analysis of soil nitrogen and carbon at a farm scale using visible and near infrared spectroscopy coupled with wavelength reduction. *European Journal of Soil Science*, 63, 410–420.

Table 1. Presentation of the studied sites.

Site	Region	Latitude, longitude	Climate	Soil type	Clay content	No of samples
Marololo Baiboho	Alaoatra lake, northeast	17°32' S, 48°31' E	mid-altitude tropical	Fluvisol	≈20%	78
Marololo Tanety	Alaoatra lake, northeast	17°32' S, 48°32' E	mid-altitude tropical	Ferralsol	≈20%	54
Andranomanelatra	Antsirabe, centre	19°46' S, 47°06' E	highland tropical	Ferralsol	≈60%	48
Antsapanimahazo	Antsirabe, centre	19°40' S, 47°09' E	highland tropical	Ferralsol	≈35%	18
Ivory	Antsirabe, centre	19°33' S, 46°24' E	highland tropical	Ferralsol	≈30%	30
Andasy	Manakara, southeast	22°12' S, 47°50' E	sub-equatorial	Ferralsol	≈45%	60
Andranovory	Tulear, southwest	23°07' S, 44°13' E	subarid	Cambisol	≈30%	36
Sakaraha	Tulear, southwest	22°54' S, 44°37' E	subarid	Arenosol	≈10%	36

According to the "FAO classification" (IUSS Working Group WRB, 2014).

Table 2. Distributions of soil carbon and nitrogen concentrations (in g kg⁻¹).

Variable	Set	Mean	Standard deviation	Minimum	First quartile	Median	Third quartile	Maximum
Carbon	Total	23.9	13.0	5.2	14.2	18.3	36.0	59.0
Carbon	Calibration	21.1	11.2	5.2	13.5	17.4	28.8	47.5
Carbon	Validation	40.4	8.9	24.5	33.3	40.3	46.6	59.0
Nitrogen	Total	2.04	0.86	0.74	1.39	1.72	2.76	4.67
Nitrogen	Calibration	1.86	0.74	0.74	1.33	1.62	2.34	3.63
Nitrogen	Validation	3.10	0.72	1.95	2.43	3.16	3.68	4.67

Table 3. Cross-validation and independent external validation statistics for soil **carbon** concentration (for the 312-sample cross-validation set, mean and standard deviation were 21.1 and 11.2 gC kg⁻¹ respectively; for the 41-sample independent validation set they were 40.4 and 8.9 gC kg⁻¹ respectively).

Spectro and conditions	Pretreatment	Calibration						Validation					
		LVmax	LV	SEC	SECV	R ² _{cv}	RPD _{cv}	SEP	Bias	SEPC	Slope	R ² _{val}	RPD _{val}
MicroNIR (1151-2186 nm, 8.15 nm)													
≤ 16 LV	None001	16	7	3.1	3.2	0.92	3.5	9.2	6.8	6.3	0.53	0.64	1.4
≤ 16 LV	SNV1205	16	9	2.6	2.8	0.94	4.1	4.6	-2.5	3.9	0.87	0.82	2.3
Foss (1100-2498 nm, 2 nm)													
≤16 LV	None001	16	15	1.7	1.9	0.97	6.0	3.4	0.0	3.4	0.84	0.88	2.6
≤ 9 LV	None001	9	9	2.5	2.5	0.95	4.5	8.9	5.8	6.9	0.37	0.65	1.3
≤ 9 LV	D144	9	9	2.1	2.3	0.96	4.9	4.4	0.0	4.4	0.72	0.82	2.0
MicroNIR-ranged Foss (1150-2182 nm, 2 nm)													
≤ 16 LV	None001	16	14	1.9	2.1	0.97	5.4	7.8	4.3	6.6	0.44	0.67	1.4
≤ 16 LV	D001	16	14	1.8	2.0	0.97	5.8	4.0	1.1	3.9	0.68	0.90	2.3
≤ 9 LV	None001	9	9	2.5	2.6	0.95	4.3	7.3	4.3	6.0	0.44	0.80	1.5
≤ 9 LV	SNVD001	9	9	2.5	2.5	0.95	4.4	4.6	-1.9	4.2	0.75	0.83	2.1
MicroNIR-fitted Foss (1150-2182 nm, 8 nm)													
≤ 16 LV	None001	16	14	1.9	2.1	0.97	5.4	8.1	4.7	6.7	0.50	0.58	1.3
≤ 16 LV	SNVD144	16	15	1.6	1.8	0.97	6.1	4.6	0.6	4.6	0.90	0.74	1.9
≤ 9 LV	None001	9	9	2.5	2.5	0.95	4.6	7.3	4.5	5.8	0.46	0.80	1.5
≤ 9 LV	SNVD001	9	9	2.5	2.7	0.94	4.2	4.4	-1.0	4.3	0.79	0.80	2.1

LV is the number of latent variables for PLS regression, and LVmax its maximum (fixed by the operator); SEC, SECV, SEP and SEPC are the standard errors of calibration, of cross-validation, of prediction, and of prediction corrected for bias, respectively, in gC kg⁻¹; R²_{cv} and R²_{val} are the coefficients of determination for cross-validation and independent validation, respectively; RPD_{cv} is the ratio of the standard deviation of the calibration set to SECV; RPD_{val} is the ratio the standard deviation of the validation set to SEPC; R² and RPD are unitless.

Table 4. Cross-validation and independent external validation statistics for soil **nitrogen** concentration (for the 312-sample cross-validation set, mean and standard deviation were 1.86 and 0.74 gN kg⁻¹ respectively; for the 41-sample independent validation set they were 3.10 and 0.72 gN kg⁻¹ respectively).

Spectro and conditions	Pretreatment	Calibration						Validation					
		LVmax	LV	SEC	SECV	R ² _{cv}	RPD _{cv}	SEP	Bias	SEPC	Slope	R ² _{val}	RPD _{val}
MicroNIR (1151-2186 nm, 8.15 nm)													
≤ 16 LV	None001	16	7	0.21	0.23	0.90	3.2	0.72	0.44	0.58	0.47	0.48	1.2
≤ 16 LV	SNVD001	16	5	0.26	0.28	0.86	2.7	0.36	-0.09	0.36	0.87	0.77	2.0
Foss (1100-2498 nm, 2 nm)													
≤16 LV	None001	16	15	0.16	0.17	0.95	4.4	0.35	-0.05	0.35	0.93	0.77	2.1
≤ 5 LV	None001	5	5	0.28	0.28	0.86	2.7	0.64	0.18	0.62	0.32	0.45	1.1
≤ 5 LV	D144	5	5	0.23	0.23	0.90	3.2	0.50	0.11	0.50	0.50	0.69	1.4
MicroNIR-ranged Foss (1150-2182 nm, 2 nm)													
≤16 LV	None001	16	11	0.18	0.18	0.94	4.0	0.60	0.35	0.50	0.44	0.74	1.4
≤16 LV	SNVD001	16	14	0.16	0.17	0.95	4.3	0.45	0.11	0.44	0.57	0.75	1.6
≤ 5 LV	None001	5	5	0.26	0.26	0.88	2.9	0.68	0.38	0.57	0.24	0.86	1.2
≤ 5 LV	SNVD001	5	5	0.31	0.31	0.82	2.4	0.61	0.39	0.49	0.46	0.76	1.5
MicroNIR-fitted Foss (1150-2182 nm, 8 nm)													
≤ 16 LV	None001	16	11	0.18	0.19	0.94	4.0	0.61	0.35	0.50	0.45	0.72	1.4
≤ 16 LV	SNVD144	16	12	0.14	0.15	0.96	4.9	0.39	0.00	0.39	0.79	0.73	1.8
≤ 5 LV	None001	5	5	0.26	0.26	0.88	2.8	0.68	0.38	0.57	0.24	0.86	1.2
≤ 5 LV	D144	5	5	0.25	0.26	0.87	2.8	0.70	0.46	0.54	0.42	0.67	1.3

LV is the number of latent variables for PLS regression, and LVmax its maximum (fixed by the operator); SEC, SECV, SEP and SEPC are the standard errors of calibration, of cross-validation, of prediction, and of prediction corrected for bias, respectively, in gN kg⁻¹; R²_{cv} and R²_{val} are the coefficients of determination for cross-validation and independent validation, respectively; RPD_{cv} is the ratio of the standard deviation of the calibration set to SECV; RPD_{val} is the ratio the standard deviation of the validation set to SEPC; R² and RPD are unitless.

Figure 1. Raw absorbance ($\log 1/R$) spectra of three example samples of the validation set acquired with two spectrophotometers: JDSU MicroNIR 2200 vs. Foss NIRSystems 5000.

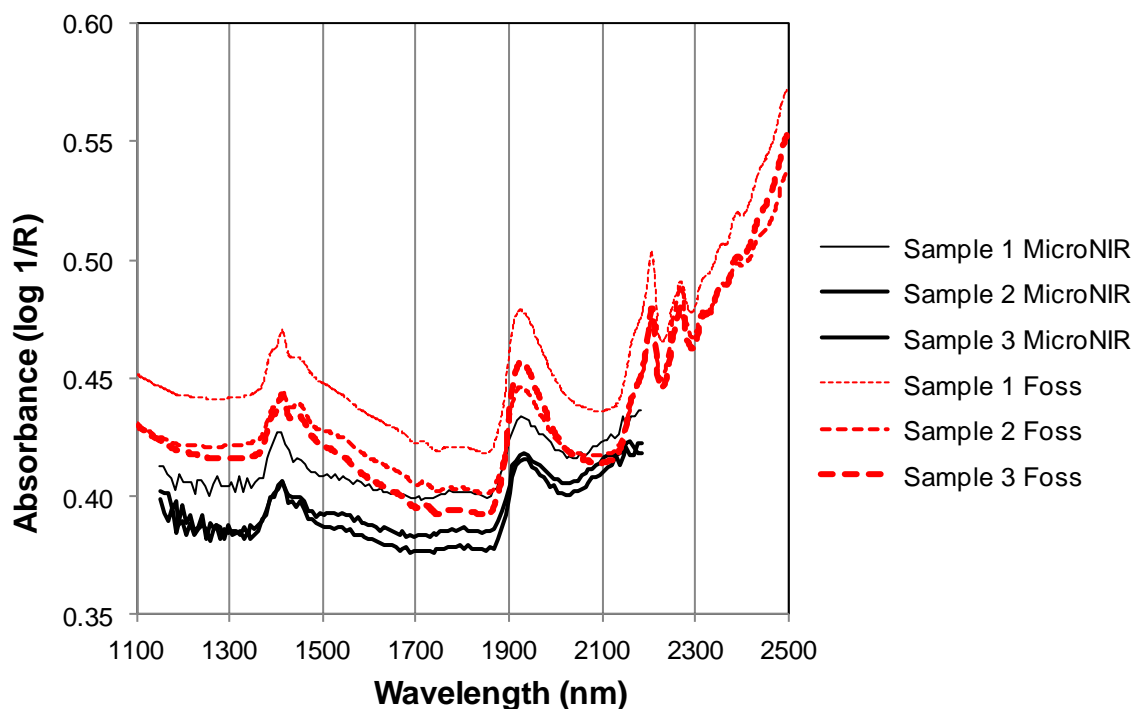


Figure 2. Relationship between the number of PLS terms (latent variables) used for cross-validation and standard error of cross-validation (SECV) for C prediction, for non-pretreated absorbance spectra (None001).

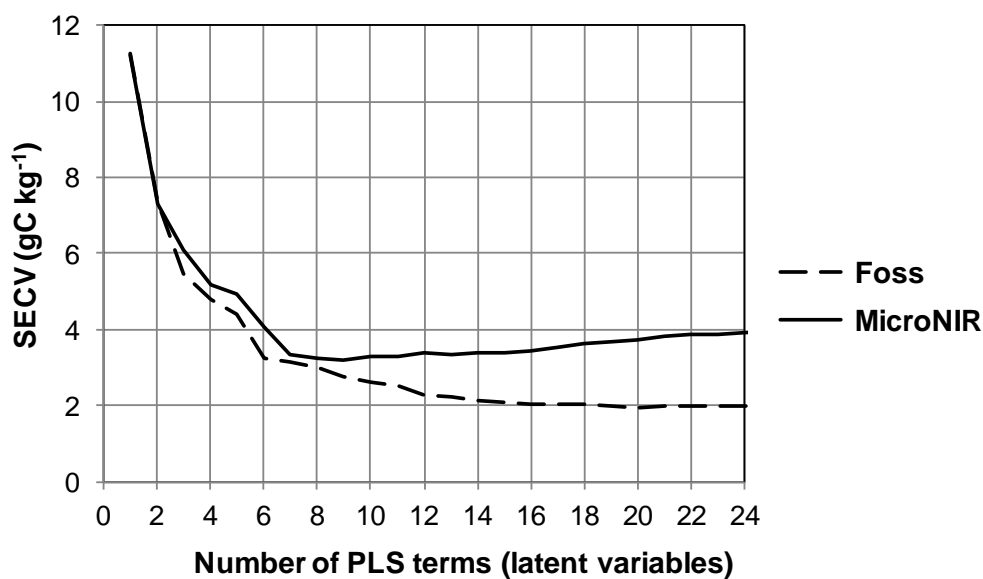


Figure 3. Comparisons between conventional measurements of soil C and N concentrations and predictions (independent external validation) using full Foss or MicroNIR spectra (best results, achieved with no pretreatment for Foss spectra, and with SNV1205 and SNVD001 for predicting C and N with MicroNIR spectra, respectively).

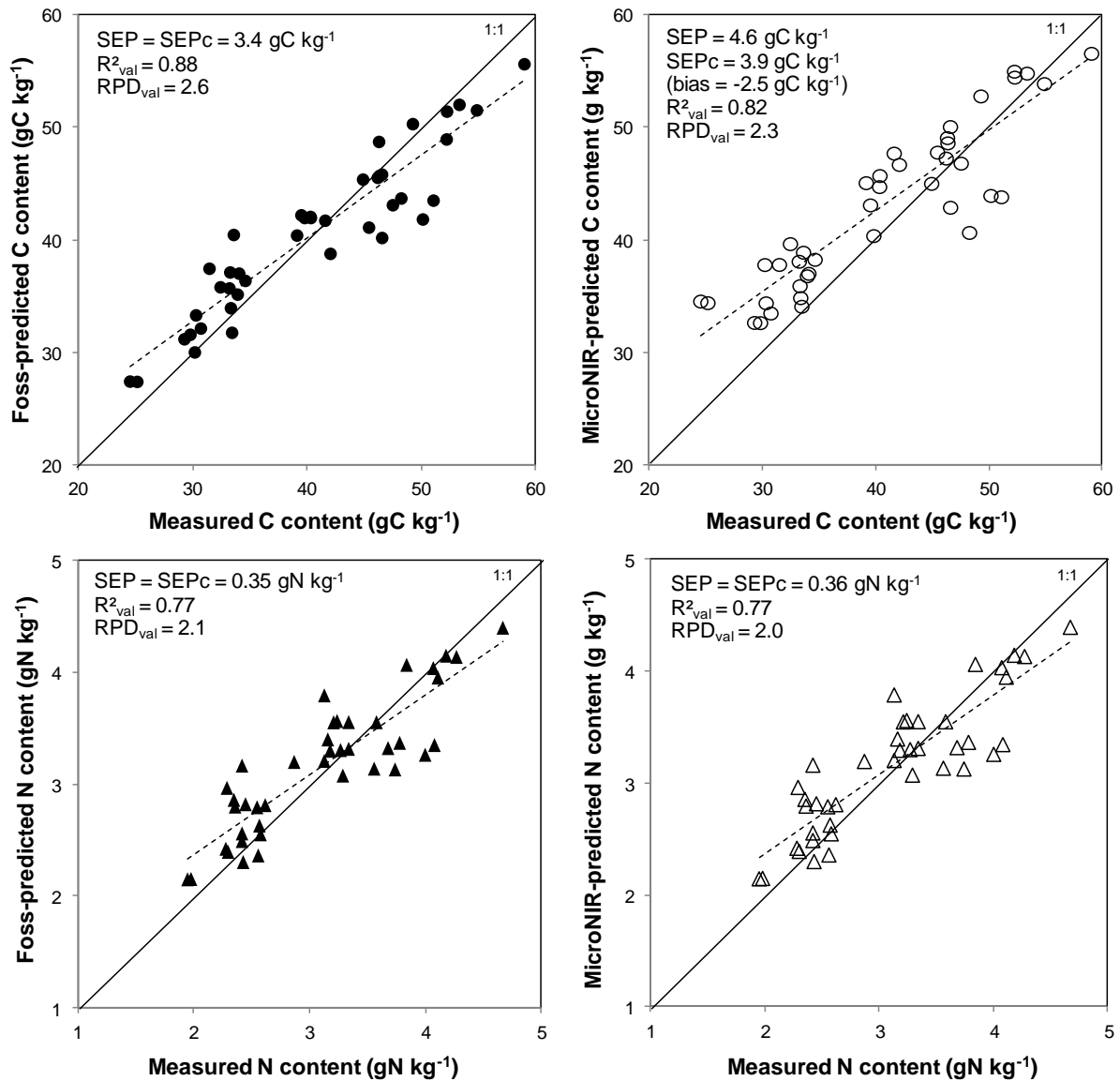


Figure 4. Regression coefficients of C prediction models using three types of absorbance spectra: acquired with JDSU MicroNIR 2200 (1151-2186 nm every 8.15 nm), with Foss NIRSystems 5000 (1100-2498 nm every 2 nm), and acquired with Foss NIRSystems 5000 but reduced to the same range and interval as MicroNIR spectra (1150-2182 nm every 8 nm). The models considered were those which yielded the best validation results without spectrum derivation.

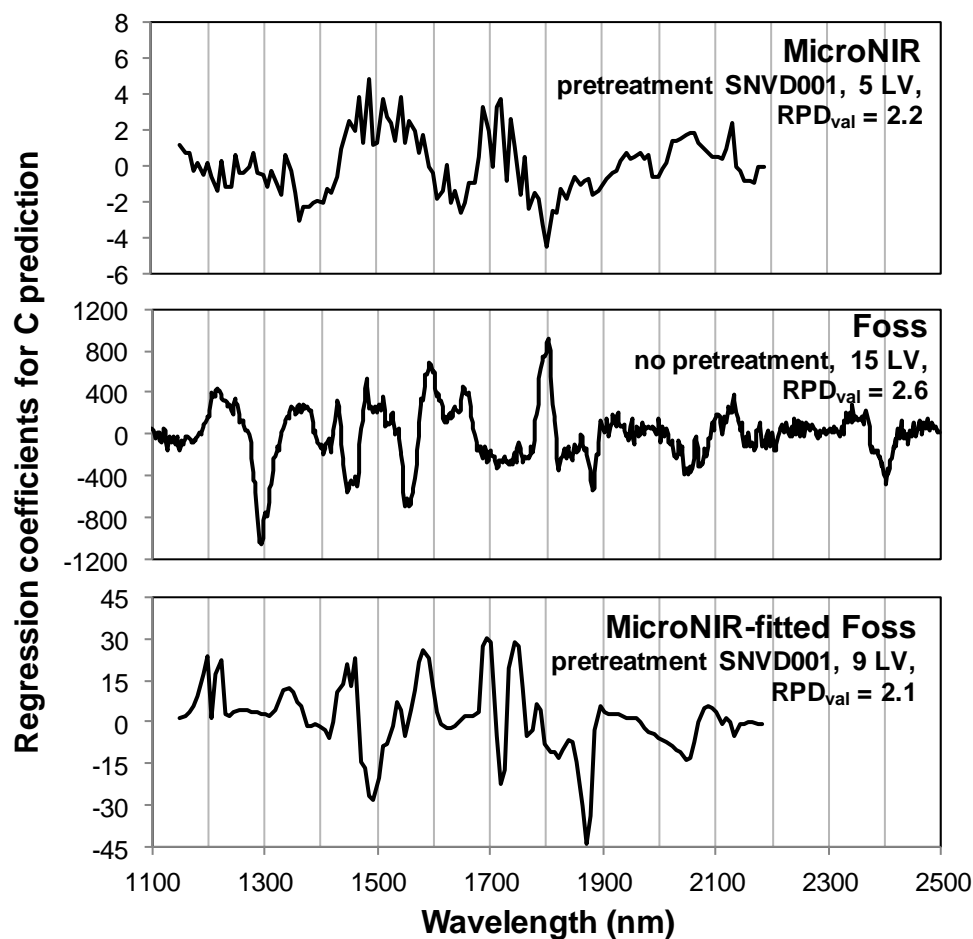


Figure 5. Regression coefficients of N prediction models using three types of absorbance spectra: acquired with JDSU MicroNIR 2200 (1151-2186 nm every 8.15 nm), with Foss NIRSystems 5000 (1100-2498 nm every 2 nm), and acquired with Foss NIRSystems 5000 but reduced to the same range and interval as MicroNIR spectra (1150-2182 nm every 8 nm). The models considered were those which yielded the best validation results without spectrum derivation.

