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Near infrared spectroscopy for soil bulk density assessment

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Summary

Soil bulk density values are needed to convert organic carbon content to mass of organic carbon per unit area. However, field sampling and measurement of soil bulk density are labour-intensive, costly and tedious. Near-infrared reflectance spectroscopy (NIRS) is a physically non-destructive, rapid, reproducible and low-cost method that characterizes materials according to their reflectance in the near-infrared spectral region. The aim of this paper was to investigate the ability of NIRS to predict soil bulk density and to compare its performance with published pedotransfer functions. The study was carried out on a dataset of 1184 soil samples originating from a reforestation area in the Brazilian Amazon basin, and conventional soil bulk density values were obtained with metallic "core cylinders". The results indicate that the modified partial least squares regression used on spectral data is an alternative method for soil bulk density predictions to the published pedotransfer functions tested in this study. The NIRS method presented the closest-to-zero accuracy error (-0.002 g cm^{-3}) and the lowest prediction error (0.13 g cm^{-3}) and the coefficient of variation of the validation sets ranged from 8.1 to 8.9% of the mean reference values. Nevertheless, further research is required to assess the limits and specificities of the NIRS method, but it may have advantages for soil bulk density predictions, especially in environments such as the Amazon forest.

Introduction

In the past few decades, considerable efforts have been made to quantify carbon (C) dynamics and fluxes in the environment as affected by climate change, rising greenhouse gas levels and global warming. In this context, tropical rain forests such as the Brazilian Amazon represent significant sources/sinks of trace gases and are an important component within the global C cycle (Cerri *et al*., 2007).

The soil is considered the largest terrestrial pool of carbon (excluding carbonate rocks), with 1500–2000 Pg C stored in the upper 100 cm of the soil profile (Batjes, 1996; García-Oliva & Masera, 2004). Accurate estimates of soil carbon stocks (C_t) depend on the availability of soil carbon content (in g C kg^{-1} soil) and bulk density (D_b). In order to obtain accurate predictions of D_b, labour-intensive and time-consuming field measurements are required (Manrique & Jones, 1991). In addition, field methods for measuring D_b are limited in their ability to provide reliable, complete and uniform soil data (Bernoux *et al*., 1998b). Many conventional soil analytical techniques have been used in an attempt to establish the relationship between soil physical and chemical properties and individual soil components, often disregarding their complex, multi-component interactions (Viscarra Rossel *et al*., 2006). Pedotransfer functions (PTFs) for soil bulk density have been estimated from soil properties in the Amazon basin (clay, sand and silt contents, organic carbon and pH) using a stepwise multiple regression procedure (Bernoux *et al*., 1998b) and multiple linear regressions (Tomasella & Hodnett, 1998).

Near-infrared reflectance spectroscopy (NIRS) offers an alternative method to assess field soil variation. NIRS is a physically non-destructive, rapid, reproducible and low-cost method that characterizes materials according to their reflectance in the wavelength range between 800 and 2500 nm (Stevens *et al*., 2006; Brunet *et al*., 2007). In this region of the electromagnetic spectrum, each constituent of a complex organic mixture (C, N, H, O, P and S atoms) has unique absorption properties due to stretching and bending vibrations in molecular bonds (Odlare *et al*., 2005). The technique has been used in the past two decades to assess total carbon and nitrogen, nitrate-nitrogen ($N\text{-}NO_3^-$), ammonia-nitrogen ($N\text{-}NH_4^+$), respirometry, pH, cation exchange capacity, Ca, Mg, K,

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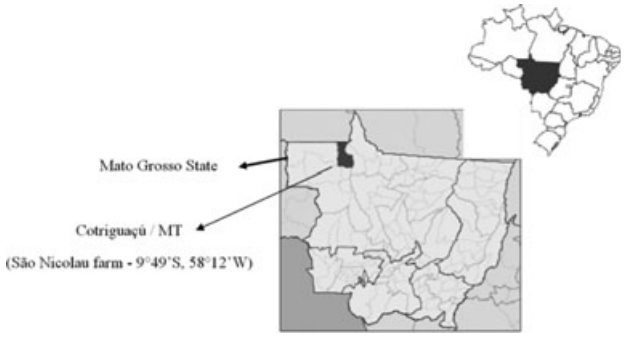

Figure 1 Location of the study area in the northwest of Mato Grosso State, Brazil.

exchangeable Al, total P, electrical conductivity, particle size distribution, moisture, clay content and $CaCO_3$ (e.g. Dalal & Henry, 1986; Henderson *et al*., 1992; Chang *et al*., 2001; Velasquez *et al*., 2005; Barthès *et al*., 2006; Viscarra Rossel *et al*., 2006; Brunet *et al*., 2007).

Reliable tools to quantify C stocks and verify sequestration in soils from the Brazilian Amazon would be a very valuable addition to existing methodologies for C offset negotiations (Cerri *et al*., 2007). The use of NIRS to assess soil parameters including soil bulk density can therefore contribute to increasing knowledge of carbon dynamics in tropical environments at reduced cost.

The objective of the present study was to (i) investigate the ability of NIRS to predict soil bulk density and (ii) compare the performance of nine published pedotransfer functions (PTFs) with the proposed method (NIRS), using a dataset of 1184 measured soil density values.

Materials and methods

Study site

The analyses were performed on soil samples originating from the Amazon Basin, from an experimental field (São Nicolau Farm - 9°49′S; 58°12′W) located in the north-west of Mato Grosso State, Brazil, as a part of a reforestation project sponsored by Peugeot SA and ONF (National Forest Office). The farm covers an area of 10 134 ha, composed of 7000 ha of natural forest, 2000 ha of pasture (targets of reforestation) and 1000 ha of degraded forests along the Juruena River (Figure 1). The reforestation project was established in 1999 and planting was developed between 1999 and 2003, with more than 50 native species and one exotic species (*Tectona grandis*). The history of land use can be described as follows: clearing of native forest (1981–1999), establishment of pasture (1981–1999), burning of pasture (1999–2003) and planting of trees (1999–2003).

The climate of the region is humid tropical, characterized by an annual mean daily temperature of 25°C. The annual rainfall is 2300 mm and the dry season lasts from May to October. The relief is flat to gently sloping with an altitude between 200 and 250 m above sea level.

Table 1 Details of soil samples

Management system	Number of samples (% of 1184 samples)	Texture (% of management system)
Pasture	144 (12.2)	Clayey (25) Loamy (75)
Reforestation	992 (83.8)	Very clayey (1.8) Clayey (29.5) Loamy (68.7)
Native forest	8 (4)	Clayey (25) Loamy (62.5) Sandy (12.5)

Soil samples

A total of 1184 soil samples was collected from four layers (0–5, 5–10, 10–20 and 20–30 cm depths) using a soil sampler and metallic core cylinders of 100 cm^3 volume (Table 1). According to Cerri *et al*. (2000), 57% of the carbon stored in the first 100 cm of the Amazon soil profile is found in the 0–30 cm depth. Soil sampling was carried out in three management systems (native forest, pasture and reforestation), including 50 different stands (2, 6 and 42 stands, respectively, for each management system). Six samples from each depth were collected in each stand, with some exceptions. The experimental design used for sampling can be considered completely randomized, consisting of 50 stands (considered as treatments), each with six pseudo-replications in different topographic situations (Hurlbert, 1984). The species growing in each stand were all native to the Amazon forest (except for *Tectona grandis*, an exotic plant). The stands had different characteristics such as density of plants, spacing between plants and combinations of species.

Soils belong to the Oxisol order (Soil Survey Staff, 1999). According to EMBRAPA (2006), the soil samples were classified as very clayey (clay $>$ 60%), clayey (35–60% clay), medium (clay + silt $\geq$ 15% and clay $<$ 35%), and sandy (clay + silt $\leq$ 15%).

Samples were air-dried before being transported to Piracicaba, São Paulo State, Brazil. They were then oven-dried at 45°C and gently crushed using a mortar and pestle and passed through a 2 mm sieve (10 mesh). Sub-samples were finely ground to pass through a 0.15 mm sieve (100 mesh) for NIRS analysis.

Bulk soil density analyses–reference data

Soil bulk density was determined from the dry mass of 100 cm^3 soil cores (Blake & Hartge, 1986).

NIRS analyses

Spectrum acquisition and pre-processing The reflectance of soil samples was determined using an Antaris MDS-FT-NIR spectrometer (Thermo Electron, Madison, WI, USA) equipped with integrating sphere sampling module and internal reference flag for automatic background collection. Samples (*c*. 3 g) were scanned

in the wave number range of 4000–10 000 cm^{-1} at 4 cm^{-1} resolution with 16 co-averaged scans per spectrum, in glass vials of 2.5 cm in diameter.

For the calculations of the pre-treatments and calibration methods, detailed below, the software (WinISI III-version 1.61e–Foss NIRSystems/Tecator Infrasoft International, Silver Spring, MD, USA) selected the spectral region between 4015 and 6684 cm^{-1}, which is the region where the absorbance variations are the most important. Between 6684 and 10 000 cm^{-1}, there was just one peak of absorbance at 7066 cm^{-1}. Thus, each measurement produced a spectrum with 174 data points.

Spectral data were recorded as absorbance (A) according to the following equation:

$$A = \log(1/\text{Reflectance}). \quad (1)$$

Several pre-processing methods were applied to the spectral data, including a standard normal variate (SNV) transform, a standard normal variate transform with detrending (SNVD) and a standard multiplicative correction (MSC). Derivatives (144) were used to reduce baseline variation and enhance spectral features (Reeves *et al*., 2002). A no-scatter correction (None) was also applied.

The standard normal variate (SNV) transformation is applied to reduce the variation in absorbance intensity. In many situations, spectra present uncontrolled variation in absorbance intensity due to scatter and/or particle size distribution, especially with soil samples. Samples that have a coarse particle size distribution give an absorbance higher than those that have a fine particle size. In addition, in materials such as soil, absorbance spectra tend to be more intense at the longer wavelengths. This trend is linear and becomes curvilinear (Barnes *et al*., 1989). De-trending corrects this trend.

The MSC was applied to eliminate the optical interference that requires a different linearization than chemical ones, as observed by Martens *et al*. (1983). This transformation removes physical effects like particle size and surface blaze from the spectra that do not carry any chemical or physical information (Maleki *et al*., 2007).

Derivatives, denoted as 001 and 144, were also used to reduce baseline variation and enhance spectral features (Reeves *et al*., 2002). The first number is the order of derivative, the second number is the gap in data points over which the derivative is calculated and the third number is the number of data points to be smoothed. The designation '001' was used when no derivative was applied. The third number '1' is given automatically by the software when no derivative is used.

Spectral outliers

To identify spectral outliers, a principal component analysis (PCA) was carried out on the entire spectral set to calculate the Mahalanobis distance H (Mark & Tunnell, 1985). Samples with $H > 3$ were considered spectral outliers and were eliminated from further investigations (Shenk & Westerhaus, 1991a). Depending on the pre-processing method, the number of spectral outliers ranged from 15 to 27, representing less than 3% of the population.

Calibration and validation processes

Modified partial least squares (mPLS) regression was used to correlate spectral data to conventional values of bulk density (Shenk & Westerhaus, 1991b). The sample set was divided into a calibration subset (including the 200 most representative samples) and a validation subset (the remaining samples) (Shenk & Westerhaus, 1991a). Cross-validation was performed on this subset to determine the optimal number of terms to be included in the prediction model. It was split into four groups, three being used for developing the model and one for the prediction. The residuals of the four predictions were pooled to calculate the standard error of cross-validation (SECV). The outliers for calibration (i.e. samples with $t < 2.5$) were removed and another cross-validation was performed. This procedure was carried out twice. The number of factors giving the lowest final SECV determined the optimal number of terms to be used for the calibration. The final model was recalculated with all the samples and the residuals gave the standard error of calibration (SEC). The accuracy of the model was evaluated on the validation subset using the standard error of prediction (SEP) and the CV%, which is the ratio of SEP to the mean reference value (Morra *et al*., 1991).

Validation of different models (PTFs v NIRS)

The performance of the proposed method (NIRS) in relation to nine published models (regression models) was also evaluated with the total set (1184 samples) by complementary indices: the mean prediction error (MPE) (Equation (3)), the root mean square prediction error (RMSPE) (Equation (4)) and its coefficient of determination R^2_p. The MPE (accuracy error) allows the assessment of a positive or negative bias of a regression model, a general trend of overestimation or underestimation, respectively (De Vos *et al*., 2005). The MPE should be as small as possible. The RMSPE is a measure of the overall error of the prediction.

$$MPE = 1/n^{\mathrm{n}}_{\mathrm{i}=1}(\hat{y}_{\mathrm{i}} - y_{\mathrm{i}}) \quad (2)$$

$$RMSPE = \sqrt{1/n^{\mathrm{n}}_{\mathrm{i}=1}(\hat{y}_{\mathrm{i}} - y_{\mathrm{i}})^2}, \quad (3)$$

where y_{i} is the observed soil bulk density of the i^{th} soil sample, y_{i} is the predicted soil bulk density of the i_{th} soil sample, and n is the total number of observations.

The PTF models were selected after consideration of site location (tropical environments), soil type (Oxisol order), sampling depth (surface) and the parameters included in the equations, allowing the selection of suitable models for our data.

Table 2 Conventional determination of soil bulk density: minimum, maximum, mean, standard deviation (SD) and coefficient of variation (CV %) for total set and the management system subsets

Dataset	Bulk density / g cm^{-3}					
	n[a]	Min	Max	Mean	SD	CV[b]%
Total set	1184	0.45	1.95	1.48	0.14	9.5
Native forest	48	1.16	1.51	1.36	0.09	6.3
Pasture	144	0.65	1.68	1.48	0.16	10.6
Reforestation	992	0.45	1.95	1.49	0.14	9.3

[a]n is the number of samples.
[b]CV is the coefficient of variation.

Results

Reference data

The bulk density of the soil samples ranged from 0.45 to 1.95 g cm^3 (Table 2) with a mean of 1.48 g cm^{-3} ($\pm$ 0.14). The data from pasture and reforestation stands (mean of 1.48 and 1.49 g cm^{-3}, respectively) reflect the compaction of these soils, probably by field operations and cattle trampling in both systems.

Calibration and validation statistics

Considering all pre-processing methods, SEC and SECV ranged from 0.10 to 0.12 g cm^{-3}. SEP ranged from 0.12 to 0.13 g cm^{-3}. The CV of validation sets ranged from 8.1 to 8.9% of the mean reference values (Table 3). Based on the calibration R^2, SECV, SEP and CV, the best treatment was the Std MSC with no derivative (0011).

Separate calibration of layers, textures and management systems did not lead to substantial improvement of the prediction quality (data not shown).

Performance of pedotransfer functions and NIRS method

The performance of the mPLS regression used on spectral data (NIRS method) and nine published PTF models are listed in Table 4. The MPE, RMSPE and R_p^2 were calculated for the total dataset ($n = 1184$). The results show that the NIRS method along with model C (Tomasella & Hodnett, 1998) was associated with negative MPE values (-0.002 and -0.012 g cm^{-3}), indicating underestimation of D_b. Nevertheless, the NIRS method presented the closest to zero MPE, which means the least biased prediction. For the total dataset, MPE ranged from -0.012 to 0.322 g cm^{-3}. In general, prediction errors using the published PTFs indicated that these overestimated the Db.

The NIRS method and model C also had the lowest RMPSE value (0.13 g cm^{-3}), indicating the lowest prediction error. The opposite was found for the E_1 and E_2 models proposed by Mello (2007), despite being designed for the same soil type and climate conditions as our database (Oxisols from the Amazon Basin).

The R_p^2 varied from 0.01 (Bernoux *et al*., 1998b–model B_2) to 0.14 (NIRS method, see Figure 2). The results showed small variation on this index, and were not as high as we could presume, considering the specificity of the models (i.e. models for tropical soils). However, the NIRS method produced the best soil bulk density prediction. The lowest prediction quality was observed for the PDFs of Bernoux *et al*. (1998b) (B_1 and B_2) and Mello (2007).

Discussion

Calibration of the NIRS method

There are no previous reports on soil bulk density predictions with the NIRS method. Therefore, all comparisons are made in relation to regression models based on published pedotransfer functions (PTFs).

Although the best calibration R^2 obtained by the NIRS method is not high (0.34), it is in the same range as other methods for the same soil order. Manrique & Jones (1991) found that PTFs including the square root of carbon values could be used to estimate soil density of Oxisols, with $R^2 = 0.24$ ($n =$ 173). Similar results were obtained by Bernoux (1998b) ($R^2 =$ 0.25and$n = 62$). The SEC and SECV values ranged from 0.10 to 0.12 g cm^{-3}, and are in agreement with the results presented by Benites *et al*. (2007), where the parameter SE (standard error of estimate) used on Brazilian soils varied from 0.10 to 0.16 g cm^{-3}.

It must be emphasized that compared with other soil properties, soil bulk density does not vary widely, but needs to be as accurate as possible for the estimation of precise soil carbon stocks. Van Groenigen *et al*. (2003), studying the performance of NIRS and MIRS (mid-infrared spectroscopy) of soils for predicting soil and crop properties, reported that there could be low prediction accuracy for some soil parameters (e.g. total C and N) due to the relatively small variation in these parameters. This may be a reasonable explanation for the prediction accuracy of soil bulk density presented in this study. Nevertheless, in an attempt to find an improvement in statistical parameters of calibration, the spectrum preprocessing methods were applied to dataset groups by texture, depth and soil management (data not shown). De Vos *et al*. (2005), developing regression models for the whole pedon, observed that taking calibration and validation samples from all horizons or depths of interest is better than taking them separately.

Tranter *et al*. (2007), building and testing conceptual and empirical models for predicting D_b, found better results with a calibration set of 926 samples for model construction and a validation set of 481 samples. Because one of the advantages of using NIRS is the possibility of reducing the costs of analysis by reducing the number of samples analysed by conventional methods, the calibration model was built using a small number of samples (<200).

Validation of the NIRS method

The SEP values (0.12 to 0.13 g cm^{-3}) are in agreement with previous studies (Bernoux *et al*., 1998b; Benites *et al*., 2007). The

Table 3 Calibration and validation results for soil bulk density and the preprocessing method for the total soil set (1184 samples)

Preprocessing method	n_1[a]	SEC[b]/g cm^{-3}	R^2	SECV[c]/g cm^{-3}	Number of terms	n_2[d]	SEP[e]/g cm^{-3}	CV[f]%
None 001	187	0.10	0.32	0.11	7	959	0.12	8.1
None 144	170	0.12	0.10	0.12	2	960	0.13	8.9
SNV 001	189	0.11	0.21	0.11	4	956	0.13	8.6
SNV 144	171	0.10	0.24	0.11	4	964	0.13	8.6
SNVD 001	182	0.10	0.19	0.11	3	961	0.13	8.5
SNVD 144	167	0.11	0.22	0.12	2	966	0.13	8.7
Std MSC 001	184	0.11	0.34	0.11	6	969	0.12	8.1
Std MSC 144	185	0.10	0.31	0.11	3	963	0.13	8.4

[a]n_1 is the number of samples after the elimination of calibration outliers.
[b]SEC is the standard error of the calibration.
[c]SECV is the standard error of cross-validation.
[d]n_2 is the number of samples used for the validation.
[e]SEP is the standard error of prediction.
[f]CV is the coefficient of variation, defined as the ratio of SEP to the mean.

Table 4 Evaluation indices of proposed and existing models for soil bulk density estimation

Model source[a]	Function[b]	MPE[c]	RMSPE[d]	R_p^{2e}
NIRS	mPLS[f]	−0.002	0.13	0.14
B_1	D_b = 1.524 - 0.0038(Clay) - 0.050(OC) - 0.045(pH) + 0.0010(Sand)	0.236	0.27	0.06
B_2	D_b = 1.371 - 0.0048(Clay)	0.126	0.19	0.01
B_3	D_b = 1.419 - 0.0037(Clay) - 0.061(OC)	0.152	0.20	0.12
C	D_b = 1.578 - 0.054(OC) - 0.006(Silt) - 0.004(Clay)	−0.012	0.13	0.12
D_1	D_b = 1.660 - 0.318(OC)$^{1/2}$	0.024	0.14	0.12
D_2	D_b = 1.509 - 0.098(OC)	0.098	0.16	0.12
D_3	D_b = 1.396 - 0.185(OC)$^{1/2}$	0.204	0.24	0.12
E_1	D_b = 1.15 - 0.0062(Clay) + 0.0029(Sand)	0.322	0.35	0.12
E_2	D_b = 1.33 - 0.08(OC)	0.254	0.29	0.12

[a]B_1, B_2, B_3, Bernoux *et al*. (1998b); C, Tomasella & Hodnett (1998); D_1, D_2, D_3, Manrique & Jones (1991); E_1, E_2, Mello (2007).
[b]D_b, soil bulk density (g cm^{-3}); OC, organic carbon (g 100 g soil).
[c]Mean prediction error (accuracy error).
[d]Root mean square prediction error.
[e]Prediction coefficient of determination.
[f]Modified partial least square regression method.

range of values obtained for the validation CV % was 8.1–8.9%. The validation CV may be a better indicator of soil bulk density prediction than the SEP values, considering the small variation in this parameter. Brunet *et al*. (2007), studying the effects of sample grinding and set heterogeneity using NIRS analysis on Brazilian soils (two Typic Haplustox and one Typic Hapludox), observed validation CV for total carbon between 6.8 and 25%. The inverse correlation between *D*b and C has been described in the literature (Bernoux *et al*., 1998b; Tomasella & Hodnett, 1998; Benites *et al*., 2007; Mello, 2007).

A recent study (Minasny *et al*., 2008) examined the use of mid-infrared spectroscopy (MIRS) for prediction of various physical and mechanical properties of soil, including bulk density. Based on RMSE (0.09 g cm^{-3}), RPD (defined as the ratio of standard deviation to SECV) (1.16 g cm^{-3}) and the relative error (0.92 g cm^{-3}), the authors concluded that MIRS is not able to predict bulk density in samples from agricultural areas.

Performance of the PTFs and NIRS methods

Although the sampling in this study was carried out mostly in reforested areas, there are important sources of variation introduced by the tree species used for reforestation, management practices, sampling depth, differences in soil biotic activity and land use history. Furthermore, spatial variability is increased in forest plantation environments, due to the absence of homogenization of agricultural practices (De Vos *et al*., 2005).

The building of existing PTF models needs one or more parameters obtained by conventional analysis for each sample, and therefore requires additional analysis, commonly costly. On the other hand, one of the advantages of the NIRS method is that

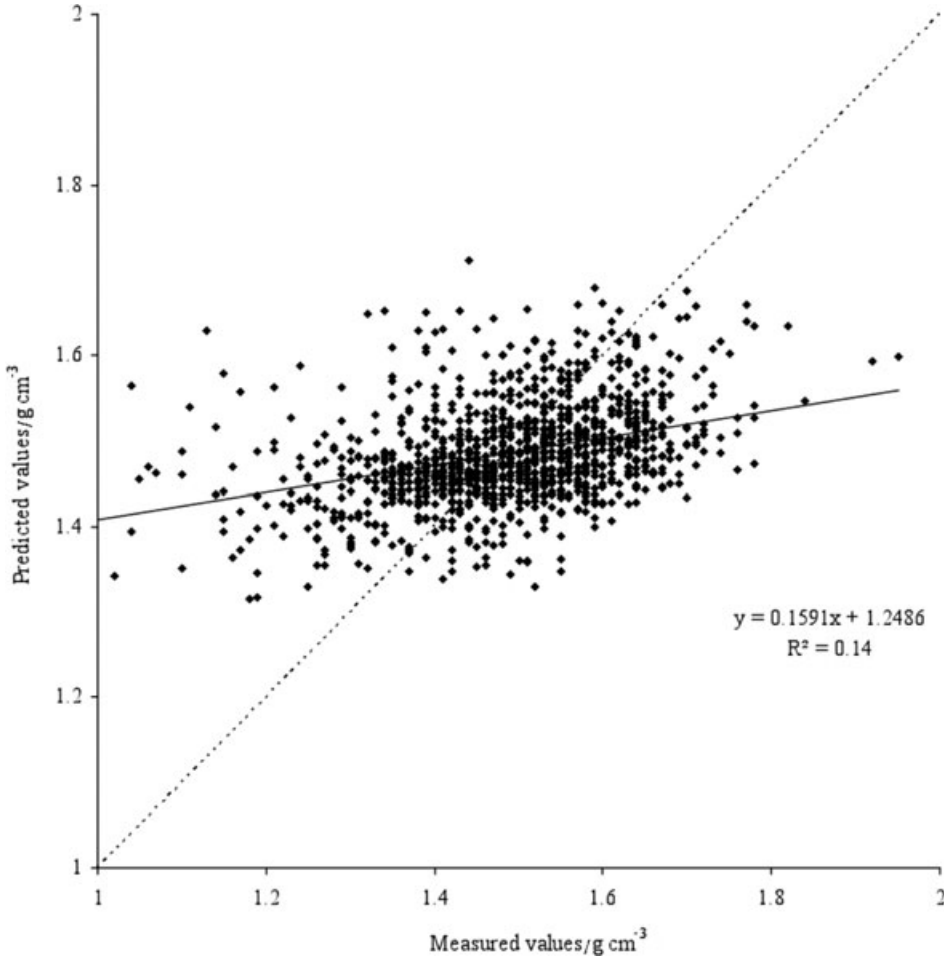

Figure 2 Measured versus predicted values of soil bulk density using near-infrared spectroscopy.

it requires only a minimum determination of D_b reference values to establish prediction models.

Conclusions

This study shows that even if the NIRS method furnishes good and satisfactory estimates of bulk density, it should be recognized that results are not markedly better than predictions using pedotransfer functions. However, the latter requires the availability of other parameters, which are not always reported, or reported using different analytical methods (Jolivet *et al*., 1998). The potential of the NIRS method is important for soil studies in which a large number of soil bulk density determinations or estimations are requested, such as networks for soil carbon monitoring (Morvan *et al*., 2008; Saby *et al*., 2008), or in vertical distribution models of soil carbon based on volumetric concentration (Bernoux *et al*., 1998a).

Although further research is required to assess the limits and specificities of the proposed method, its advantages (rapidity, reproducibility and low-cost) must be considered for soil bulk density predictions. The performance of the estimation procedures might be improved by using, for instance, procedures capable of dealing with linear and nonlinear multivariate calibration, and able to resolve multivariate calibration problems, such as the Least Squares Support Vector Machines.

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