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### ► To cite this version:

Bernard G. Barthès, Didier Brunet, Edmond Hien, Frank Enjalric, Sofian Conche, et al.. Determining the distributions of soil carbon and nitrogen in particle size fractions using near-infrared reflectance spectrum of bulk soil samples. *Soil Biology and Biochemistry*, 2008, 40 (6), pp.1533-1537. 10.1016/j.soilbio.2007.12.023 . hal-01195059

**HAL Id: hal-01195059**

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Submitted on 5 Jul 2023

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# Determining the distributions of soil carbon and nitrogen in particle size fractions using near infrared reflectance spectrum of bulk soil samples

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## Abstract

This study aimed at assessing the potential of near infrared reflectance spectroscopy (NIRS) for determining the distribution of soil organic matter (SOM) in particle size fractions, which has rarely been attempted. This was done on sandy soils from Burkina Faso (three sites) and Congo-Brazzaville (one site). Over the total sample set, NIRS accurately predicted carbon (C) and nitrogen (N) concentrations ( $\text{g kg}^{-1}$  fraction) in the fraction  $< 20 \mu\text{m}$ . When considering Burkina Faso only, predictions were improved in general; those of C and N amounts ( $\text{g kg}^{-1}$ ) became accurate for the fraction  $< 20 \mu\text{m}$  but not for the coarser fractions, probably due to heterogeneous SOM repartition. However, most SOM being  $< 20 \mu\text{m}$  in general, NIRS could be considered promising for determining SOM size distribution.

*Keywords:* Soil organic matter; Particle size fractions; Near infrared reflectance spectroscopy (NIRS)

## Introduction

Near infrared reflectance spectroscopy is a rapid and low-cost approach that uses regression methods to express a property as a function of sample reflectance. It has been applied for determining different SOM pools, such as mineralizable or microbial SOM (Chang et al., 2001; Ludwig et al., 2002). However, though the distribution of SOM in particle size fractions

provides useful information, due to the different composition and dynamics of SOM size fractions (Christensen, 1992; Feller et al., 2001), very few studies have attempted characterizing it using NIRS (Móron and Cozzolino, 2004; Cozzolino and Móron, 2006). Yet, this would be relevant because usual fractionation procedures are tedious, while measuring soil reflectance requires ca. one minute per sample. The present work aimed at assessing whether NIRS could facilitate characterizing the particle size distribution of SOM, by studying the accuracy of NIRS determinations based on bulk soil spectra.

## **Materials and methods**

The 193 studied soil samples originated from three sites in Burkina Faso and one site in Congo-Brazzaville (Table 1). The particle size fractionation of SOM (reference method) was carried out on 2-mm sieved air-dried soil samples of 20 g, following Gavinelli et al. (1995). The procedure involved chemical dispersion; shaking; wet-sieving at 200 then 50  $\mu\text{m}$ ; ultrasonication of the suspension  $< 50 \mu\text{m}$  when dispersion seemed incomplete; wet-sieving at 20  $\mu\text{m}$ ; withdrawing of an aliquot of the suspension  $< 20 \mu\text{m}$ ; fraction oven-drying (40°C) then weighing; C and N analyses by dry combustion. Four samples from Saria were fractionated in triplicate and four samples from Pointe-Noire in duplicate.

Reflectance was measured between 1100 and 2500 nm at 8 nm intervals with a Foss NIRSystems 5000 spectrometer (Silver Spring, MD, USA), on two 5-g subsamples per sample (2-mm sieved, oven-dried at 40°C). Each spectrum, averaged from 32 scans, was recorded as absorbance ( $\log [1/\text{reflectance}]$ ). Data analyses were conducted using the WinISI III-v.1.61 software (Infrasoft International, LCC, State College, PA, USA). According to preliminary results, spectra were mean centred and variance-scaled, then a first derivate was applied. A principal component analysis was carried out on spectral data for calculating the Mahalanobis distance  $H$ , and samples with  $H > 3$  were eliminated; then the sample set was divided into a calibration subset including the 100 most representative samples, and a remaining validation subset (Shenk and Westerhaus, 1991a). Calibration models were derived from spectra and reference values using modified partial least square regression (Shenk and Westerhaus, 1991b). Cross validation was performed on the calibration subset and the number of factors giving the smallest standard error of cross validation (SECV) determined the optimal number of factors of the model. The calibration performance was assessed using coefficient of determination ( $R^2_{\text{cal}}$ ), SECV (as absolute value or as % of the mean), and RPD (ratio of standard deviation to SECV). The prediction accuracy was evaluated on the validation subset, using validation  $R^2$  ( $R^2_{\text{val}}$ ) and relative standard error of prediction (SEP).

## Results and discussion

The cumulative yields of fraction masses, C and N averaged 100, 89 and 96%, respectively, rather low recoveries being attributed to soluble SOM (Christensen, 1992). Most samples were sandy, but the fraction  $< 20 \mu\text{m}$  generally included the highest proportion of SOM (Table 2). Coefficients of variation of fraction C and N were 2-3% for the fraction  $< 20 \mu\text{m}$  and 12-21% for the other fractions in Saria, and 22-32% in Pointe-Noire.

The NIRS analysis was first carried out over the complete sample set (Table 3). Calibration and prediction were accurate for all fraction masses and for C and N concentrations ( $\text{g kg}^{-1}$  fraction) in the fraction  $< 20 \mu\text{m}$ , but not for fraction C and N amounts ( $\text{g kg}^{-1}$  soil). They were reasonably accurate for C/N in the fractions  $< 50 \mu\text{m}$  but not in the coarser ones. Moreover, they were rather accurate for total soil C (Ct) and N (Nt), and very accurate for Ct/Nt. Calibrations and predictions were more accurate in general when considering only the 159 samples from Burkina Faso. This was clear for the fraction  $< 20 \mu\text{m}$  as regarded C and N concentrations ( $R^2_{\text{val}} = 0.94\text{-}0.97$ ,  $\text{SEP} = 12\%$ ), C amount ( $R^2_{\text{val}} = 0.87$ ,  $\text{SEP} = 24\%$ ), N amount ( $R^2_{\text{val}} = 0.71$ ,  $\text{SEP} = 19\%$ ), and C/N ( $R^2_{\text{val}} = 0.82$ ,  $\text{SEP} = 11\%$ ), and also for Ct and Nt ( $R^2_{\text{val}} = 0.84\text{-}0.94$ ,  $\text{SEP} = 17\%$ ).

Accurate NIRS determinations of Ct and Nt have been extensively reported, especially for rather homogeneous textural sets (Dalal and Henry, 1986; Morra et al., 1991; Brunet et al., 2007). Several studies have also reported NIRS determination of Ct/Nt (Chang and Laird, 2002; Ludwig et al., 2002). Here Ct/Nt was more accurately predicted than Ct and Nt, suggesting that spectra include precise information on SOM quality. The prediction accuracy of fraction masses was similar in the present study and in those involving comparably homogeneous sets (Chang et al., 2001; Chang et al., 2005; Madari et al., 2006). Here fraction mass was less accurately predicted for the fraction  $< 20 \mu\text{m}$  than for the others, probably due to less precise reference determination (aliquot withdrawing).

For the fraction  $< 20 \mu\text{m}$ , which included most SOM in general, NIRS predictions of C and N were accurate, especially when considering Burkina Faso only. By contrast, C and N were poorly predicted in the fractions  $> 20 \mu\text{m}$ , probably due to heterogeneous SOM repartition. Indeed, due to its low SOM content, every fraction  $> 20 \mu\text{m}$  included a limited number of organic particles. Depending on the subsample, a couple of organic particles more or less could thus affect fraction SOM content, leading to discrepancies between replicates, or between reference and NIRS analyses. This underlined that the apparent imprecision of NIRS predictions might actually reflect imprecise reference determinations, and that more attention

should be paid to using the same subsample for spectral then conventional analyses, NIRS being non-destructive. Fraction C/N was reasonably predicted for fine fractions, confirming that spectra include relevant information on SOM quality, but predictions were poor for coarse fractions, probably due to heterogeneous SOM repartition. Very few studies have attempted predicting the size distribution of SOM using NIRS. Mórón and Cozzolino (2004) and Cozzolino and Mórón (2006) used visible and near infrared reflectance spectra to study topsoil samples representing different Uruguayan soils. Texture was not described precisely but SOM data suggest that most samples were rather clayey. On the whole, predictions regarding the fractions  $< 50 \mu\text{m}$  or N were more accurate in these studies than in the present one, but those regarding the fractions  $> 50 \mu\text{m}$  or C/N were more accurate in the present one, whereas no clear difference between studies could be found for C.

In conclusion, due to the accurate prediction of C and N in the fine fraction, which contribution to total SOM was dominant in general, NIRS could be considered promising for facilitating the determination of SOM distribution in particle size fractions.

### **Acknowledgements**

The authors thank Moussa Barry, Damien Landais, Raphaël Manlay, Dominique Masse, Laurent Saint-André and Sansan Youl for sample collection, and two anonymous reviewers for their recommendations. This work received financial support from the French Ministry of Higher Education and Research (Project MIROT founded by the Action Concertée Incitative “Ecologie quantitative”).

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**Table 1.** Presentation of the studied sites, soils and samples.

Location	Soil type <sup>a</sup> (and % sand <sup>b</sup> )	Mean annual rainfall and temperature	Land use	Number of samples	Sample depth (cm)
Banh (northern Burkina) 14°04'N, 02°26'W	Ferralic Arenosol (48-94%)	600 mm 29°C	Millet with or without manure addition (corralling)	56	0-10 to 80-100
Saria (central Burkina) 12°16'N, 02°09'W	Ferric Acrisol (59-66%)	800 mm 28°C	Sorghum with or without manure and/or fertilizers	51	0-10 and 10-20
Torokoro (southern Burkina) 10°03'N, 04°25'W	Lixisol (68-86%)	1100 mm 27°C	Crops (cotton, yam, sorghum), fallow, orchard, forest	52	0-10
Vicinity of Pointe-Noire (Congo-Brazzaville) 04°S, 12°E	Ferralic Arenosol (91-96%)	1200 mm 25°C	Eucalyptus plantations and savanna	34	0-10

<sup>a</sup> FAO-ISRIC-ISSS (1998).

<sup>b</sup> 50-2000 µm.

**Table 2.** Reference data regarding the mass, C and N concentrations ( $\text{g kg}^{-1}$  fraction) and amounts ( $\text{g kg}^{-1}$  soil), and C/N ratio of particle size fractions and total soil for the total sample set and each site separately.

Variable	Fraction ( $\mu\text{m}$ )	Total set				Banh (Burkina)				Saria (Burkina)				Torokoro (Burkina)				Pointe-Noire (Congo)			
		Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
Mass ( $\text{g } 100 \text{ g}^{-1}$ )	> 200	37.0	13.8	14.5	78.9	22.5	3.5	14.5	35.2	31.8	1.9	23.7	35.0	49.0	9.2	28.4	65.2	50.2	11.8	26.7	78.9
	50-200	38.5	12.2	17.6	66.8	51.1	9.1	33.7	66.2	30.1	2.2	25.1	36.1	30.2	7.0	17.7	48.1	43.4	11.5	17.6	66.8
	20-50	8.4	6.9	0.6	22.6	5.4	1.9	0.6	9.9	19.2	1.1	16.6	22.6	5.4	1.8	2.8	11.1	1.5	0.5	0.8	2.8
	< 20	16.3	7.8	2.7	43.7	22.1	9.0	5.1	43.7	18.7	2.2	14.8	22.9	14.9	3.3	9.5	26.3	5.1	1.3	2.7	8.1
C concen- tration ( $\text{g kg}^{-1}$ fr.)	> 200	1.9	2.3	0.2	24.8	1.3	3.3	0.2	24.8	1.4	1.6	0.2	7.9	2.5	1.4	0.9	8.5	2.9	2.1	0.6	9.3
	50-200	2.9	3.1	0.2	20.4	0.8	1.2	0.2	9.1	1.3	1.3	0.2	6.8	4.4	2.3	1.4	14.1	6.3	4.2	1.6	20.4
	20-50	11.5	19.4	0.2	84.6	2.1	2.5	0.7	18.8	1.1	0.7	0.2	4.0	6.4	4.0	2.4	20.9	50.4	15.5	22.2	84.6
	< 20	21.0	16.1	2.8	65.4	9.5	7.1	2.8	47.5	10.6	3.9	6.3	19.7	24.9	6.0	17.1	45.4	49.7	8.8	32.3	65.4
C amount ( $\text{g kg}^{-1}$ soil)	> 200	0.8	0.9	$\varepsilon_1$	6.6	0.3	0.9	$\varepsilon_1$	6.6	0.5	0.5	0.1	2.5	1.2	0.6	0.5	3.8	1.5	1.2	0.3	5.7
	50-200	1.0	1.2	0.1	7.2	0.4	0.8	0.1	6.0	0.4	0.4	0.1	2.1	1.3	0.6	0.6	4.0	2.6	1.5	0.6	7.2
	20-50	0.3	0.3	$\varepsilon_1$	1.6	0.1	0.1	$\varepsilon_1$	0.6	0.2	0.1	$\varepsilon_1$	0.8	0.3	0.2	0.1	1.4	0.8	0.4	0.2	1.6
	< 20	2.5	1.4	0.8	11.8	1.7	0.5	0.8	3.1	2.0	0.7	1.0	3.7	3.8	1.9	2.0	11.8	2.5	0.8	1.2	4.7
	total soil	5.2	3.5	1.2	21.3	2.5	2.2	1.2	18.0	3.8	1.8	1.9	10.1	7.5	3.2	3.8	21.3	8.1	3.4	4.2	17.7
N concen- tration ( $\text{g kg}^{-1}$ fr.)	> 200	0.11	0.17	0.01	2.15	0.09	0.29	0.01	2.15	0.10	0.11	0.02	0.57	0.12	0.07	0.06	0.45	0.12	0.08	0.03	0.39
	50-200	0.17	0.17	$\varepsilon_2$	0.90	0.06	0.12	$\varepsilon_2$	0.90	0.10	0.10	0.02	0.53	0.27	0.13	0.10	0.80	0.31	0.17	0.07	0.81
	20-50	0.70	1.14	0.01	4.69	0.19	0.24	0.05	1.83	0.09	0.06	0.01	0.34	0.34	0.20	0.13	1.17	3.01	0.77	1.08	4.69
	< 20	1.88	1.28	0.40	6.40	1.13	0.85	0.40	6.21	1.15	0.40	0.69	2.23	1.89	0.38	1.44	3.17	4.19	0.81	2.80	6.40
N amount ( $\text{g kg}^{-1}$ soil)	> 200	0.04	0.05	$\varepsilon_2$	0.57	0.02	0.08	$\varepsilon_2$	0.57	0.03	0.04	$\varepsilon_2$	0.19	0.06	0.03	0.02	0.18	0.06	0.05	0.02	0.19
	50-200	0.06	0.07	$\varepsilon_2$	0.59	0.03	0.08	$\varepsilon_2$	0.59	0.03	0.03	0.01	0.16	0.08	0.04	0.03	0.23	0.13	0.06	0.03	0.33
	20-50	0.02	0.02	$\varepsilon_2$	0.10	0.01	0.01	$\varepsilon_2$	0.05	0.02	0.01	$\varepsilon_2$	0.07	0.02	0.01	0.01	0.08	0.05	0.02	0.01	0.10
	< 20	0.23	0.09	0.11	0.83	0.20	0.06	0.11	0.41	0.21	0.07	0.12	0.39	0.29	0.12	0.15	0.83	0.21	0.06	0.12	0.34
	total soil	0.37	0.20	0.14	1.73	0.27	0.21	0.14	1.73	0.35	0.15	0.16	0.93	0.48	0.20	0.26	1.45	0.39	0.11	0.21	0.75
C/N	> 200	18.4	4.7	10.8	37.3	17.5	4.2	10.8	27.3	14.5	1.2	11.8	17.5	20.2	3.6	13.9	31.7	22.9	5.2	14.7	37.3
	50-200	15.5	3.4	7.7	27.7	13.9	2.8	7.7	20.5	13.5	1.1	10.6	15.9	16.4	2.1	12.1	23.8	19.5	4.3	11.9	27.7
	20-50	14.4	3.5	6.8	23.6	11.4	1.8	6.8	14.9	12.3	1.1	10.4	14.6	18.2	2.4	12.5	23.6	16.7	2.5	13.2	22.5
	< 20	10.5	2.5	5.4	19.4	8.2	1.4	5.4	10.9	9.2	0.6	8.0	10.5	13.2	1.6	10.8	19.4	12.0	1.5	8.9	16.3
	total soil	13.3	4.5	5.6	32.7	9.6	1.4	5.6	12.0	10.9	1.2	7.5	13.9	15.3	1.2	13.3	18.4	20.5	4.2	15.4	32.7

SD is the standard deviation.

$\varepsilon_1 < 0.1 \text{ g kg}^{-1}$ ;  $\varepsilon_2 < 0.01 \text{ g kg}^{-1}$ .



**Table 3.** Calibration and validation results for the mass, C and N concentrations ( $\text{g kg}^{-1}$  fraction) and amounts ( $\text{g kg}^{-1}$  soil), and C/N ratio of particle size fractions and total soil for the total sample set.

Variable	Fraction	Calibration					Validation			
		$n_1$	$R^2_{\text{cal}}$	SECV (absol. value)	SECV (%)	RPD	$n_2$	$R^2_{\text{val}}$	SEP (absol. value)	SEP (%)
Mass	> 200 $\mu\text{m}$	93	0.783	6.3	16.1	2.2	86	0.819	5.3	15.7
	50-200 $\mu\text{m}$	96	0.787	6.1	15.8	2.2	86	0.798	5.4	14.0
	20-50 $\mu\text{m}$	93	0.948	1.5	19.8	4.4	86	0.961	1.4	14.4
	< 20 $\mu\text{m}$	95	0.813	3.0	20.2	2.3	86	0.891	2.7	14.4
C concen- tration	> 200 $\mu\text{m}$	84	0.801	0.5	24.4	2.2	86	0.533	0.9	66.7
	50-200 $\mu\text{m}$	97	0.797	1.1	33.8	2.2	86	0.699	1.2	63.0
	20-50 $\mu\text{m}$	88	0.914	4.0	30.3	3.4	86	0.915	4.5	60.1
	< 20 $\mu\text{m}$	90	0.945	3.4	14.4	4.2	86	0.953	3.4	20.3
N concen- tration	> 200 $\mu\text{m}$	88	0.833	0.03	24.9	2.4	86	0.515	0.06	81.4
	50-200 $\mu\text{m}$	91	0.825	0.05	25.6	2.4	86	0.776	0.06	47.5
	20-50 $\mu\text{m}$	88	0.908	0.25	30.5	3.3	86	0.907	0.29	59.6
	< 20 $\mu\text{m}$	93	0.869	0.39	18.7	2.8	86	0.929	0.30	20.1
C amount	> 200 $\mu\text{m}$	89	0.765	0.3	29.6	2.1	86	0.649	0.3	64.2
	50-200 $\mu\text{m}$	90	0.857	0.3	26.7	2.7	86	0.775	0.4	60.0
	20-50 $\mu\text{m}$	91	0.668	0.1	41.3	1.7	86	0.690	0.1	57.1
	< 20 $\mu\text{m}$	93	0.742	0.5	17.6	2.0	86	0.700	0.8	34.6
	total soil	88	0.810	1.1	18.9	2.3	86	0.831	1.2	28.2
N amount	> 200 $\mu\text{m}$	86	0.832	0.01	23.4	2.4	86	0.657	0.02	56.7
	50-200 $\mu\text{m}$	87	0.804	0.02	27.7	2.2	86	0.674	0.03	62.5
	20-50 $\mu\text{m}$	93	0.671	0.01	48.5	1.7	86	0.647	0.01	45.0
	< 20 $\mu\text{m}$	92	0.617	0.04	16.1	1.6	86	0.518	0.06	25.5
	total soil	94	0.771	0.06	16.2	2.1	86	0.776	0.07	22.5
C/N ratio	> 200 $\mu\text{m}$	91	0.604	2.7	14.5	1.6	86	0.348	3.7	21.0
	50-200 $\mu\text{m}$	94	0.461	2.1	13.2	1.4	86	0.345	2.7	17.5
	20-50 $\mu\text{m}$	96	0.775	1.6	10.8	2.1	86	0.683	1.9	13.9
	< 20 $\mu\text{m}$	97	0.748	1.1	10.4	2.0	86	0.764	1.3	13.4
	total soil	94	0.874	1.3	9.2	2.8	86	0.878	1.3	10.6

$n_1$  is number of samples in the calibration set after the elimination of calibration outliers.

$n_2$  is the number of samples in the validation test.

SECV and SEP are standard error of cross-validation and of prediction, respectively, and are expressed as absolute values or as proportions of the mean.

RPD is the ratio of standard deviation to SECV.