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Review

Near-infrared (NIR) and mid-infrared (MIR) spectroscopic techniques for assessing the amount of carbon stock in soils – Critical review and research perspectives

Véronique Bellon-Maurel [a,*], Alex McBratney [b,1]

[a] Montpellier Supagro, UMR ITAP, 2 place Viala, 34000 Montpellier Cedex 1, France
[b] ACPA, Faculty of Agriculture, Food & Natural Resources, The University of Sydney, Sydney NSW 2006, Australia

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ABSTRACT

This paper is an extensive review of the research that has been undertaken on near-infrared (NIR) and mid-infrared (MIR) spectroscopy applied to soil particularly for determining carbon (C) content. The objective is to determine which acquisition method (NIR, MIR, in the field or in the laboratory) might be recommended for the purpose of C stock measurement with a particular interest in carbon credit trading. For this purpose, an optimal method has to satisfy the dual constraints of low-cost and high throughput analysis. The various methods proposed in the literature are compared. In order to make comparisons as reliable as possible, special attention has been paid to the conditions of data acquisition (sample preparation), and to calibration and validation procedures. In particular, whether the validation has been carried out on fully independent samples or on samples similar to the ones of the calibration set greatly influences the results. Also, for C stock measurement, it is absolutely necessary to measure the bias of the prediction in order to be conclusive about the feasibility of the method. However, only few researchers provide this parameter and we recommend including it as a matter of course in future reports. Finally, although MIR on dried and ground samples is the most accurate method, on-the-go and in-field sensors provide predictions accurate enough to show promise in being a valuable component of technologies that would be used for C-credit purposes. But in order to meet the cost/accuracy trade-off, the main issue using such field sensors is to be able to simultaneously measure the bulk density or, better, to directly measure the volumetric concentration of C in soil. This circumvents the costs of field extraction and laboratory analysis. This is the next great challenge to be met by soil scientists.

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1. Introduction

1.1. The need for rapid methods to assess soil organic C content

In order to mitigate climate change due to emissions of greenhouse gases (GHGs), the Kyoto Protocol proposed targets for GHG reductions and set up trading credits that corresponded to verified removal of greenhouse gas from the atmosphere (United Nations Framework Convention on Climate Change[2]). One of the main options for C mitigation identified by the IPCC is the sequestration of organic C in soils (Metz et al., 2007). Not only can soil C sequestration help to offset GHG emissions, but storing C in soil also provides environmental benefits (Lal et al., 1997). There are two ways to design contracts to purchase C-credits, either practice-based contracts or credit-based contracts, and studies have shown that credit-based contracts are more efficient than practice-based contracts (Mooney et al., 2007). But the same authors stated that (i) the biggest difference between transaction costs under credit-based and practice-based contracts was the cost associated with measuring the amount of C-credit sequestered, and (ii) another factor influencing transaction costs is uncertainty related to the quantity of credits produced, which could affect the payments received by the producers.

This converges with Smith's view (2002) who also warns: "without quantified knowledge of the precision of the measurement, one runs the risk that sampling designs installed now will fail to detect much of the changes between now and re-measurement in 5 or 10 years. At the same time, measurement cost must be less than the market price of the amount of sequestration detected by the measurement." This author and others (McCarty and Reeves, 2006; Morgan et al., 2009; Reeves, 2009) converge with unanimity on the fact that the issue of C sequestration assessment

* Corresponding author. Fax: +33 4 67 04 63 06.
E-mail addresses: bellonv@supagro.inra.fr, veronique.bellon@cemagref.fr (V. Bellon-Maurel), A.McBratney@sydney.edu.au (A. McBratney).
[1] Fax: +61 2 9351 3706.
[2] http://unfccc.int/kyoto_protocol/items/2830.php.

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is two-fold, i.e., it has to be accurate and low-cost. Reeves (2009) outlined the trade-off of accuracy versus speed and quantity of samples to be analyzed, "the question exists as to whether better overall estimate of C can be made by using large amounts of fair quality data versus much smaller amounts of highly accurate data". He outlined that this question was related to the inherent heterogeneity of soils. Finally, he suggested that "for large-scale studies, large amounts of more easily acquired surface data be integrated with little amounts of harder to get core/subsurface data to provide an accurate estimate of the total C content within a given area-volume of soil".

1.2. Near- and mid- infrared spectroscopy

Among the low-cost and easy-to-use alternative techniques, spectroscopic techniques such as Near-Infrared (NIR) and Mid-Infrared (MIR) spectroscopy are very attractive for C content measurement in soil. These techniques have been extensively developed in agriculture in the last 40 years, with a boom starting in the late 80's, measuring composition of cereals, fruit and vegetables, meat, etc. In some cases, such as cereals, they have replaced classical laboratory analysis in inspection programs carried out by GIPSA (Grain Inspection, Packers and Stockyards Administration)[3] or CGC (Canadian Grain Commission) in US and Canada (Williams et al., 1998), respectively. The main difference between both ranges is that absorption in mid-infrared spectroscopy corresponds to fundamental bands of molecular vibrations, whereas absorptions in NIR correspond to overtones and combinations of these fundamental bands (Williams and Norris, 1987). The consequence is that (i) absorption coefficients (also called extinction coefficients) are much smaller in the NIR range, which allows light to better penetrate into the matter, but on the other hand (ii) the NIR spectrum is much more encumbered because of the abundance or combination and overtone bands. Therefore, the specificity of bands is less in the NIR range compared with MIR. Another point is that diffusion of light is much greater in the NIR than in the MIR range. Therefore, NIR spectra will be much more affected by factors which affect the diffusion of light such as: the physical structure (size of aggregates, porosity), but also the presence of water which changes the refractive index and therefore the diffusion of light (Williams and Norris, 1987).

The practical consequence is that NIR requires less sample preparation than MIR and is best fitted for in-field analysis, with lesser specificity requirements, whereas MIR generally shows a better specificity and reproducibility, but requires more sample preparation in order to optimize the sample/light interaction. The two classical modes of MIR analysis of soils are diffuse reflectance on dried/ground soils, as shown in several articles cited by Viscarra Rossel et al. (2006) or Attenuated Total Reflectance (ATR) applied to soil pastes especially when ions, like nitrate, ammonium etc., are assayed (Jahn et al., 2006; Du and Zhou, 2009). Therefore, up to now, MIR has been restricted to laboratory analysis, although its use in the field has been reported (Reeves, 2009).

1.3. NIR and MIR spectroscopy applied to soil attributes – a booming interest

Although research on NIR/MIR spectroscopy for soil analysis started later than for agricultural products, this research area has been experiencing a boom over the last 10 years, with a current apparent exponential growth (see Fig. 1). More than 210 publications have been produced in the last 15 years, with almost 50% of them in the last 3 years. Numerous investigations have been carried out measuring the properties of soil, in different configurations (i.e., in laboratory, in the field by sampling, or on-the-go with sensors embedded on a tractor). But up to now, bibliographic studies and reviews on this subject have been very scarce, may be because the rapid growth of NIR/MIR studies dedicated to soil is only recent. Viscarra Rossel et al. (2006) compiled a very complete table of the various soil attributes measured by NIR/MIR. Recently, as the result of a first NIR conference dedicated to soil in France, Cécillon et al. (2009) made an extensive review of all the available NIR technologies (proximal sensing-, laboratory analysis, remote sensing) for assessing soil quality and concluded that the most urgent need was for international databases. Kusumo et al. (2008) focused on C issues. Reeves (2009) recently wrote a review emphasizing laboratory versus on-site NIR and MIR analysis of C and pointing out the various advances and bottlenecks of this technique. He ended up with a list of nine questions which are deemed important for the future large-scale implementation of calibration for C content assessment either for C sequestration needs or for improving farming techniques in general. These key points are: 1. The calibration extent (local, regional etc.); 2. The spectrum acquisition procedure (in laboratory, in the field etc.); 3. The calibration transfer issue; 4. The reference measurement accuracy; 5. The trade-off between accuracy versus speed and number of sample analyzed; 6. The need for additional measurements (for instance bulk density) to provide relevant information (for instance Mg C ha^{-1}); 7. Which C form is to be measured with regard to its stability; 8. Can NIR predict sequesterable C from source material? and finally 9. Which is the best chemometric method for calibration development?

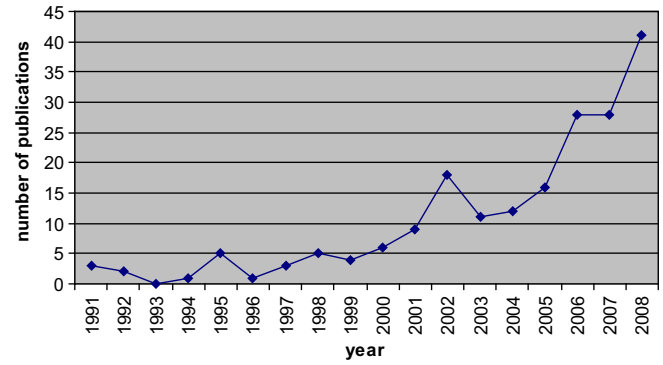

Fig. 1. Temporal trend of the publications devoted to NIR–MIR spectroscopy for soil analysis (excluding soil chemical contamination issues).

His analysis investigates the state of the art to determine "where we are and what needs to be done". Here we shall be much more focused on a critical analysis of the procedures carried out and results obtained so far for C measurement in soil, in order to address some of these questions.

Soils raise very interesting scientific issues for NIR/MIR spectroscopy. Soil is a very diffusive and absorptive medium. So, soil spectra must be acquired in diffuse reflectance, not in transmission (except of samples diluted in non-absorbing materials like KBr). The incident light is diffusely reflected back when reflecting, diffusing and diffracting on the macro- and micro-optical interfaces of soil particles to create a reflectance spectrum R. The transmitted and reflectance flux can be modelled by the Kubelka–Munk's (K–M) law which describes light transfer in an absorbing and diffusing medium. But more classically, to get a spectrum in which the intensities are linearly linked to the concentrations of interest, the reflectance spectrum is turned into an absorbance spectrum, by

[3] http://www.gipsa.usda.gov/GIPSA/webapp?area=home&subject=lr&topic=hb-nirt.

applying a Log(Ro/R) function, where Ro is the reflectance of a diffusing and non-absorbing medium. Reflectance – and consequently absorbance – spectra contain both chemical and physical information linked to scattering and specular reflectance. In soil, this last effect, i.e., the physical effect, mainly related to soil structure, is particularly important because soil structure and particle size can vary greatly and therefore can affect the spectrum (Boonmung and Riley, 2003; Richter et al., 2009; Wu et al., 2009b) and should be removed (Bogrekci and Lee, 2005). In MIR spectroscopy, which has higher absorption coefficients, strong specular reflection effects can be observed, which is another cause of noise. Drying and finely grinding samples or working in ATR mode are two ways to avoid this effect, but this requires sample preparation and makes in-field use of MIR difficult.

In addition to these effects due to soil structure, other physical effects can be encountered when one has to carry out NIR measurements in-field, such as soil temperature variations (Wu et al., 2009a) and soil moisture variations (Boonmung and Riley, 2003; Wu et al., 2009b). These additional external factors alter the spectrum and cause discrepancy in predictions.

1.4. Objective

Our aim was to investigate the research work on NIR/MIR analysis of soil C content, whatever its form (total C, inorganic C, organic C). This review is based on a very detailed analysis of the methodologies carried out in order to enable us to correctly compare their performance strengths. In particular, factors such as the size and exhaustiveness of the calibration database, the closeness of calibration/validation samples, sample preparation (dry/moist, ground/non ground etc.), the type of instrument, the mathematical process for calibration (Partial Least Squares Regression or PLS, Principal Component Regression or PCR, Multiple Linear Regression or MLR etc.), the spectra pre-treatment etc. have been thoroughly studied to reveal common approaches to the NIR/MIR analysis of soil C. This will help one who reads a publication on NIR/MIR for soil analysis to develop a critical assessment of the performance values presented in this publication.

This analysis will lead us to analyze how far we are from using NIR/MIR techniques as routine measurement techniques, based on a metrological approach and to propose research paths for reaching this goal of having NIR/MIR spectroscopy as a recognized method for assessing C content in soil.

2. Analysis of the literature

2.1. Preliminary caveat

2.1.1. How do we deal with the diversity of methods when comparing spectroscopy-based models?

Measuring C or organic matter in soil has been carried out by numbers of researchers, mainly in laboratory conditions but also in the field. Therefore, it is always very confusing to analyze such studies because they are very diverse with regard to (i) the technique used (MIR/NIR) and the way it is applied i.e., in the laboratory on dried/ground samples or on fresh/moist samples, or in the field on extracted cores or top-soils, in drilled holes (using fibre optics) or on-the-go with sensors embedded on machines; (ii) the range of the soils tested, i.e., samples coming from a single field to large-scale studies; (iii) the way the validation has been carried out i.e., either by using samples with the same origin as the calibration samples (this occurs when the calibration and validation samples all come from a limited number of fields, which is often – but not always – the case) or by trying to create fully independent sets. Therefore it is of prime importance to carefully examine these conditions when one compares prediction performances. The second point to be aware of is which chemometric parameters (i.e., Standard Error of Prediction or SEP, Ratio of Performance Deviation or RPD, bias etc.) to use when comparing the performance of the models.

2.1.2. Performance parameters used to compare the models

As NIR/MIR spectroscopy is to be used as a future reference measurement, the measurement procedure must be compatible with metrology requirements and, in particular, with a precise expression of the performance and/or uncertainty of the measurement. The performance parameters generally used are the coefficient of determination r^2, the standard error of prediction SEP, the Ratio to Performance Deviation RPD, the Coefficient of Variation, and the bias (Davies and Fearn, 2006). Some researchers based their analysis on r^2, which gives the degree of relationship which exists between two sets of data (here the true and predicted values for C content). This indicator is definitely not the best one as far as quantitative analysis is dealt with. As shown in Davies and Fearn (2006), r^2 depends on the measurement range.

In NIR/MIR studies, the most used indicator is the Standard Error of Prediction (SEP). This parameter is very relevant because it determines the limits of the confidence interval in which a future prediction Yp is to be found for a new sample (Draper and Smith, 1966). Therefore, to reduce uncertainty on the prediction, SEP must be reduced.

SEP is generally related to the range of the quantity to be measured (for instance C content), i.e., the bigger the range, the bigger the standard error of prediction. To standardize this SEP, two indices are generally proposed, i.e., the first one is the coefficient of variation (named hereafter CV%) but it is scarcely used:

$$CV\% = SEP/Mean$$

The most popular is the RPD for Ratio of Performance to Deviation, computed using SD the standard deviation of the quantity to estimate.

$$RPD = SD/SEP$$

This ratio has been proposed for many years by scientists applying NIR measurement in agricultural applications. It was first used in soil science by Sudduth and Hummel (1993) and has been widely adopted by the soil community since the paper of Chang and Laird (2002) who set up RPD thresholds to gauge the performance of the prediction. It is used to attempt to standardize the value of the SEP, with respect to the natural dispersion of the samples. Larger values of RPD indicate better fitting models. Although the relevance of this parameter is highly questionable, because it depends on the range and distribution of the population (Bellon-Maurel et al., 2010), due to its widespread appearance in the literature, we have decided to include it in the following tables.

Another very relevant parameter of the performance of the calibration is the bias which may appear in the validation step. The bias is the difference of the average of the true values and the average of the predicted values in the validation sample set. The square of the standard error of prediction SEP – which also called Root Mean Square Error of Prediction or RMSEP – can therefore be modelled as the quadratic sum of two errors i.e., the bias and the bias-corrected SEP (SEPc) which has a null average:

$$SEP^2 = Bias^2 + SEPc^2$$

The bias is an offset that cannot be reduced by averaging the predicted values. The only way to mitigate it is to reduce the causes of errors during the calibration/validation procedure. Therefore, the

bias is as important parameter as the SEP for model performance analysis.

2.1.3. Comparison of C prediction based on IR spectroscopy

We carried out an exhaustive analysis of the papers involving C in whatever form i.e., organic, inorganic, carbonates, total or organic matter. In contrast to what is found in other reviews, the objectives were to provide the reader with details, not only on the mathematical results, but also on the way the measurement had been carried out, and on how the validation has been conducted. This is absolutely necessary when one wants to estimate how far we are from a real application. The performance indices given are the SEP, the RPD, the CV, but also, when available, the bias and the laboratory error (to be compared to SEP). Tables have been created based on the form of C the authors focus on, i.e., inorganic C/carbonates, charcoal, organic matter/organic C and total C.

2.2. Carbonates/inorganic C

Measuring carbonates or inorganic C may be important because not only are carbonates generally a stable form of sequestered C, generally with a long residence time, they may be lost rapidly by management changes such as irrigation. An estimate of changes in soil inorganic C may be important in high-pH soils to obtain a figure on net soil C sequestration. Carbonates are conventionally determined by a calcimeter based on the Scheibler method, i.e., the soil is acidified and the volume of released carbon dioxide (CO_2) is measured. However, this method is time-consuming (1 h) and suffers from a lack of accuracy. Spectroscopic methods can therefore be used as an alternative. Carbonates are easy to find in MIR because of the strong absorption bands at 2910, 2850, 1796, 2506, 1415, 871 and 712 cm^{-1} (Tatzber et al., 2007; Du and Zhou, 2009). In the NIR range, the carbonate peak appears at 2381 nm (Lagacherie et al., 2008; Reeves and Smith, 2009), but is weak.

As shown in Table 1, the performance of NIR spectroscopy for measuring carbonates or inorganic C is very variable. On the one hand, very good results have been obtained even in the harshest prediction conditions. For instance Morgan et al. (2009) obtained an RPD of 2.73 when predicting inorganic C in field conditions, on moist samples, and with fully independent validation samples (one field out of six). The performance could have been further improved because one of the validation fields was an outlier. After removing it, the SEP would have been 1.9 g kg^{-1} and the RPD would have jumped to 9.3. However the same authors also showed predictions which, although carried out on samples similar to the calibration samples, have high bias values (2.2–2.9) which should be avoided. Other authors have shown similarly good results obtained on fully independent samples in laboratory conditions. For example, McCarty et al. (2002) and Brown et al. (2006) obtained SEP equal to 6.2 and 4.4 g kg^{-1} and bias equal to −0.4 and −0.1 g kg^{-1} for fully

Table 1
Carbonate or inorganic carbon content quantification by NIR/MIR spectro-metry.

#	N/M	Sample	Validation set	Data processing	SEP (bias) g kg^{-1}	RPD	Mean g kg^{-1}	Range in μm & brand
1 a	N	Lab/oven dried grnd <2 mm	4184 s./world V = 1/6 indep.	1st D − BRT	6.2 (−0.4)	3.35	Med = 0	0.4–2.5 ASD
b	N	Lab/oven dried grnd <2 mm	3793 s./world V = 1/6 indep.	1st D (% sand[a])−BRT	5.6 (−0.3)	3.71	Med = 0	0.4–2.5 ASD
2 a	M	Lab/dried grnd	720 s./220 f. V = 50%	PLS	2.6**	1.4	6**	2.5–25 Digilab
b	N	Lab/dried grnd	720 s./220 f. V = 50%	PLS	4.9**	0.7	6**	0.4–2.5 Digilab
3 a	N	Lab/air dried-intact	540 s./6 f. V = 30%	PLS on reflectance	7.8 (2.8)	2.23	10.3	0.3–2.5 ASD
b	N	Field/moist-intact	540 s./6 f. V = 30%	PLS on reflectance	8.7 (2.2)	2.02	10.3	0.3–2.5 ¤ ASD
c	N	Field/moist-smeared	540 s./6 f. V = 30%	PLS on reflectance	9.0 (2.9)	1.94	10.3	0.3–2.5 ¤ ASD
d	N	Field/moist-intact	540 s./6 f. V = 1 field out of 6	PLS on reflectance	6.4*	2.73	10.3	0.3–2.5 ¤ ASD
4 a	M	Lab/dried grnd	273 s./14 f. V = 25% random	Av & norm − PLS	1.2 (0.3)	5.2	10.8	2.5–25 Digilab
b	N	Lab/dried grnd	273 s./14 f. V = 25% random	Av & norm − PLS	3.1 (−0.1)	2.0	10.8	1.1–2.5 Foss
c	M	Lab/dried grnd	273 s./14 f. V = 1 f. out (16 s.)	Av & norm − PLS	0.7 (−0.3)	–	–	2.5–25 Digilab
d	N	Lab/dried grnd	273 s./14 f. V = 1 f. out (16 s.)	Av & norm − PLS	4.4 (−0.1)	–	–	1.1–2.5 Foss
5 a	M	Lab/ND	237 s./West US V = 25%	PLS	12** (3.3)**	0.9	6.2**	2.5–25 Digilab
b	N	Lab/ND	237 s./West US V = 25%	PLS	31.4** (−0.1)**	0.34	6.2**	0.4–2.5 Digilab
6	N	Field/hole & trench	100 s./4 f. V = 22%	1st D − PLS	69	–	222*	0.4–2.45 ASD
7 a	N	Lab/ND	52 s./1 f. 2 dates V = looCV	CR − LR 1 wl	52	–	0–450	0.4–2.5 ASD
b	N	Field/topsoil	19 s./1 f. 2 dates V = looCV	CR − LR 1 wl	79	–	–	0.4–2.5 ASD

1-(Brown et al., 2006), 2-(Reeves and Smith, 2009), 3-(Morgan et al., 2009), 4-(McCarty et al., 2002), 5-(Reeves, 2009), 6-(Ben-Dor et al., 2008), 7-(Lagacherie et al., 2008); N/M: NIR/MIR; Mean: mean of the sample set content, *: calculated; **: value converted from % to g kg^{-1}; ND: Non Determined; grnd: ground; siev: sieved; s.: samples; f.: fields; V: validation mode − ex V = 22% means that 22% of the samples are kept for validation; (loo)CV: (leave-one-out) Cross-Validation; 1st D: 1st derivative; (M)LR x wl: (Multiple) Linear Regression on x wavelengths; CR: Continuum Removal; BRT: Boosted Regression Tree; Med.: median; ¤ best results for range >1600 nm.

[a] Percentage of sand has been added as a co-variable.

Table 2
Char content quantification by NIR/MIR spectrometry.

#	N/M	Sample	Validation set	Data processing	SEP g kg^{-1}	RPD	Mean g kg^{-1}	Range in μm & brand
1a	M	Lab/grnd	121 s./Sev. f. V = 12%	Av. + baseline corr + PLS	0.04	–	3.2	2.5–25 BioRad
2 a	M	Lab/grnd	56 s./2 f. V = CV	Norm + PLS	–	16*	–	2.7–9.4 Bruker
b	N	Lab/grnd	432 s./2 f. V = CV	2nd D + PLS	–	100*	–	0.4–2.5 Foss

1-(Janik et al., 2007), 2-(Michel et al., 2009); N/M: NIR/MIR; Mean: mean of the sample set content, *: calculated; –: Non Determined; grnd: ground; s.: samples; f.: "fields"; V: validation mode – ex V = 22% means that 22% of the samples are kept for validation; CV: Cross-Validation; Av: Averaged; Norm: Normalized; 2nd D: 2nd derivative; PLS: Partial Least Square.

independent samples, respectively. The small bias was particularly surprising in both cases due to the fact that the heterogeneity of sample origin is so large and that the validation set is really different from the calibration set. On the other hand, predictions can be disappointing in same cases, with low RPDs, although the samples have been studied in laboratory conditions and are carried out on samples which have got the same origin as the calibration samples (Reeves and Smith, 2009). Finally, knowing the amount of carbonates can also be very useful for improving calibration models on organic C because the presence of carbonates degrades the prediction of organic C (McCarty et al., 2002; Reeves and Smith, 2009). McCarty et al. (2002) suspected that the absorption bands of the carbonate ion CO_3^{2-} mask the ones of the organic C. Reeves (2009) showed that not only carbonates degrade the results for soil organic carbon (SOC) but they can result in non-linear calibrations of SOC. He identifies the question of "how best to develop calibrations when carbonates are present" as "one of the big questions that remain to be properly answered about calibrations for soil carbon".

2.3. Char

Certain soils contain high amount of charcoal from anthropogenic sources (as in Terra Preta) and/or from natural origins (forest, savannah and grassland fires). Charcoal is very relevant to C sequestration issues because it can persist in the soil for centuries, and apparently is a useful soil amendment, especially in tropical soils (Lehmann, 2007). Being able to quantify this type of stable organic C separately from the other C pools would be a plus, both for providing data for models of C turnover but also to more accurately assess the soil potential for C sequestration. Biochar may be determined analytically by several methods, as described in Hammes et al. (2007). These methods are time-consuming (they generally require from 2 to 24 h) and many of them are expensive. That is why some researchers have initiated studies on how to measure soil char content by spectroscopic methods. The investigations listed in Table 2 shows that both MIR and NIR spectroscopy appear very good for measuring char in soil. But in the study of Michel et al. (2009), all the soil organic matter had been removed by heating at 650 °C prior to mixing the soil with various charred materials, i.e., prior to IR analysis. As stated by Reeves et al. (2008) "the similarity between the functional groups found in charred materials and materials such as humic acids etc… already present in soils does raise the question of whether charred material will be quantifiable by NIRS or DRIFTS when present in soil samples".

2.4. Organic matter/organic C

Organic matter and organic C are conventionally measured by dry combustion and subtraction of inorganic C, or by chemical

Table 3
Organic matter content quantification by NIR/MIR spectrometry.

#	N/M	Sample	Validation set	Data processing	SEP (bias) %	RPD	Mean or range %	Range in μm & brand
1	N	Lab/fresh	575 s./1 f. V = 70%	PLS	0.39	–	–	0.4–2.5 Foss
2 a	N	Lab/grnd <2 mm moisturized	180 s./30 f. (A) V = 33%	PLS on 24 aver. values	0.24	2.4	–	1.65–2.5 Custom
b	N	Lab/grnd <2 mm moisturized	180 s./30 f. (A) V = 33%	MLR 6 wl	0.24	2.4	–	1.65–2.5 Custom
c	N	Lab/grnd <2 mm moisturized	216 s./2 f. (A + B) V = 33%	PLS on 24 aver. values	0.18	4.1	–	1.65–2.5 Custom
d	N	Lab/grnd <2 mm moisturized	216 s./2 f. (A + B) V = 33%	MLR 6 wl	0.19	3.9	–	1.65–2.5 Custom
3	N	Lab/oven dried + grnd	108 s./1 f. V = looCV	1st D – PLS	4.6	–	Range 43–95	0.4–2.5 Foss
4 a	N	Field/on-the-go	105 s./8 f. V = looCV	SNV – 1st D – PCR	0.4	2.2	2.24	0.7–1.7 Control Dvpt
b	N	Field/on-the-go	105 s./8 f. V = 1/8 CV	SNV – 1st D – PCR	0.44	2.0	2.24	0.7–1.7 Control Dvpt
c	N	Field/on-the-go	105 s./8 f. V = 1 f. out	SNV – 1st D – PCR	0.54	1.63	2.24	0.7–1.7 Control Dvpt
5	N	Field/hole & trench	100 s./4 f. V = 22%	MSC – 1st D – PLS	2.1**	–	17**	0.4–2.45 ASD

1-(Van Vuuren et al., 2006); 2-(Sudduth and Hummel, 1993); 3-(Rinnan and Rinnan, 2007); 4-(Christy, 2008); 5-(Ben-Dor et al., 2008); N/M: NIR/MIR; Mean: mean of the sample set content, Mean: mean of the sample set content; *: calculated; **: value converted from g kg^{-1} to %; ND: Non Determined; grnd: ground; siev: sieved; f.: "fields"; s.: samples; A (+B): horizon A (+B); V: validation mode – ex V = 22% means that 22% of the samples are kept for validation; looCV: leave-one-out Cross-Validation; MSC: Multiple Scattering Correction; SNV: Standard Normal Variate; 1st D: 1st derivative; MLR x wl: Multiple Linear Regression on x wavelengths; PCR: Principal Component Regression; PLS: Partial Least Square.

Table 4
Organic Carbon content quantification by NIR/MIR spectrometry.

#	N/M	Sample	Validation set	Treatment	SEP (bias) g kg^{-1}**	RPD	Mean g kg^{-1}**	Range in μm & brand
1 a	N	Lab/oven dried + grnd <2 mm	3793 s./world V = 1/6 indep	1st D – BRT	9.0 (−0.4)	2.3	Med = 4.7	0.4–2.5 ASD
b	N	Lab/oven dried + grnd <2 mm	3793 s./world V = 1/6 indep	1st D (+ % sand[a]) – BRT	7.9 (−0.3)	2.63	Med = 4.7	0.4–2.5 ASD
2 a	N	Lab/fresh cores	1570 s./16 f. (B) V = 30%	Stepwise MLR MLR 8wl	0.64%	2.00	–	1.6–2.5 Custom
b	N	Lab/fresh cores	1900 s./16 f. (all) V = 30%	Stepwise MLR MLR 9wl	0.79%	2.06	–	1.6–2.5 Custom
3	M	Lab/grnd	734 s./sev. f. V = 78%	Av – auto baseline corr – PLS	0.62	–	18.1	2.5–25 BioRad
4 a	M+	Lab/dried grnd	720 s./220 f. V = 50% sp	ND – PLS	1.9%	1.2	1.8%	2.5–25 Digilab
b	N	Lab/dried grnd	720 s./220 f. V = 50% sp	ND – PLS	1.9%	1.2	1.8%	0.4–2.5 Digilab
5 a	N	Lab/core. dried grnd (<2 mm)	697 s./10 f. V = 1/10 CV	Av & norm – PLS	0.24	3.11	0.83*	1.7–2.5 ASD
b	N	Lab/tops. dried grnd <2 mm	167 s./10 f. V = 1/10 CV	Av & norm – PLS	0.32	2.09	–	1.7–2.5 ASD
6 a	N	Lab/air dried-intact	540 s./6 f. V = 30%	1st D – PLS	4.6 (1.2)	1.92	9.7	0.35–2.5 ¤
b	N	Field/moist-intact	540 s./6 f. V = 30%	1st D – PLS	5.4 (1.1)	1.45	9.7	0.35–2.5 ¤
c	N	Field/moist-smeared	540 s./6 f. V = 30%	1st D – PLS	5.7 (1.6)	1.4	9.7	0.35–2.5 ¤
d	N	Field/moist-intact	540 s./6 f. V = 1/6 f. out	1st D – PLS	5.82*[b]	1.08	9.7	0.35–2.5 ¤
7 a	N+	Lab/grnd <0.2 mm	415 s./12 f. V = 45%	Smoothed – PCR	0.5%	2.0	1.4%	0.25–2.5 Varian
b	M	Lab/grnd <0.2 mm	415 s./12 f. V = 190 s.	Smoothed – PCR	0.55%	2.6	1.4%	2.5–22 PE
8	N	Lab/air dried siev <2 mm	393 s./13 f. V = looCV	1st D – MSC – PLS	6.25	5.75	50	0.8–2.63 Bruker
9	N	Lab + on-the-go/fresh soil	306 s./2 f. V = looCV	MSC – 1st D – PLS	0.48%	1.97	1.62%	0.3–1.7 Zeiss
10 a	M+	Lab/dried grnd	277 s./14 f. V = 25%	Av & norm – PLS	3.2 (0.01)	4.1	12.1	2.5–25 Digilab
b	N	Lab/dried grnd	277 s./14 f. V = 25%	Av & norm – PLS	5.5 (0.1)	2.4	12.1	1.1–2.5 Foss
c	M+	Lab/dried grnd	277 s./14 f. V = one f. out	Av & norm – PLS	6 (−2.7)	2.2	–	2.5–25 Digilab
d	N	Lab/dried grnd	277 s./14 f. V = one f. out	Av & norm – PLS	7.1 (−2.8)	1.86	–	1.1–2.5 Foss
11	N	Field/on-the-go	261 s./6 f. V = looCV	ND – PLS	0.08–0.22%	1.8–3.1	–	0.45–2.2 VERIS
12 a	N+	Lab/air-dried grnd	237 s./14 f. V = 20%	MSC – 2nd D – PLS	0.831%	1.64	1.46%	0.4–2.5 Foss
b	M	Lab/air-dried grnd	237 s./14 f. V = 20%	MSC – 1st D – PLS	0.354%	3.87	1.46%	2.5–25 Digilab
13 a	M+	Lab/ND	237 s./west US V = 25%	PLS	2.42% (0.55)	0.6	1.21%	2.5–25 Digilab
b	N	Lab/ND	237 s./west US V = 25%	PLS	5.77% (−1.1)	0.23	1.21%	0.4–2.5 Foss
14 a	N	Field/fresh core section	189 s./7 f. × 2 d. V = 50% pedo criteria	1st D – PLS	1.21 & 1.36%	1.78 & 2.01	4.42%	0.5–2.45 ASD
b	N	Field/fresh core section	189 s./7 f. × 2 d. V = 50% Rank – 1/2[c]	1st D – PLS	1.28 & 1.27%	1.92–1.91	4.42%	0.5–2.45 ASD
c	N	Field/fresh core section	189 s./7 f. × 2 d. V = 50% Eucl. dist in PC plot[d]	1st D – PLS	1.40 & 1.16%	1.80–1.97	4.42%	0.5–2.45 ASD
d	N	Field/fresh core section	189 s./7 f. × 2 d. V = 50% Id. by quadrant	1st D – PLS	1.47 & 1.32%	ND 1.74–1.76	4.42%	0.5–2.45 ASD
e	N	Field/fresh core section	189 s./7 f. × 2 d. V = 25% quadrant	1st D – PLS	1.00–1.74%	1.06–1.47	4.42%	0.5–2.45 ASD
15	N	Lab/fresh	172 s./1 f. V = 88%	PLS	0.29%	3.5	1.85%	0.9–1.65 Perten

(*continued on next page*)

Table 4 (*continued*)

#	N/M	Sample	Validation set	Treatment	SEP (bias) g kg^{-1}**	RPD	Mean g kg^{-1}**	Range in μm & brand
16	N	Lab/air dried	161 s./11 f. V = 40%	No pretreat – PCR	0.44%	1.7	1.17%	0.7–2.5 Varian
17 a	N	Field/tops.	162 s./>13 f. V = 25%	1st D – PLS	3.3 (−0.1)	1.79	26.4*	0.45–2.5 ASD
b	N	Field/dry tops. only	101 s./>13 f. V = 25%	1st D – PLS	2.4 (0.08)	2.33	26.4*	0.45–2.5 ASD
18 a	N	Lab/air dried grnd siev	117 s./1 f. V = 33%	PLS	1.2	2.03	13.4	0.45–2.5 ASD
b	N	Field/tops.	201 s./3 f. × 2 d. V = 33%	Smoothing – PLS	7.03	1.21	17.7	0.45–2.5 ASD
c	N	Field/tops.	136 s./3 f. × 2 d. V = 1 d. out (37 s.)	1st D – PLS	4.56 (−0.45)	1.09	–	0.45–2.5 ASD
19	N	Field/surface	146 s./2 f V = looCV	PLS	0.61%	1.69	1.28%	0.35–2.5 ASD
20 a	N	Lab/thawed coarse	133 s./40 f. V = 48 s. CV	SNV – De – 2nd D – PLS	5.7 (0.6)	2.7	29.5	0.4–2.5 Foss
b	N	Lab/dried coarse	133 s./40 f. V = 48 s. CV	SNV – De – 2nd D – PLS	6.7 (1.1)	2.2	29.5	0.4–2.5 Foss
c	N	Lab/dried grnd (<0.5 mm)	133 s./40 f. V = 48 s. CV	SNV – De – 2nd D – PLS	6.8 (1.9)	2.2	29.5	0.4–2.5 Foss
21 a	N	Lab/air-dried – grnd <2 mm	120 s./3 f. V = 40%	MLR 3 wl	0.3%	–	0.97%	1.1–2.5 InfraAlyzer
b	N	Lab/air-dried – grnd <0.25 mm	120 s./3 f. V = 40%	MLR 3 wl	0.22%	–	0.97%	1.1–2.5 InfraAlyzer
22	N	Lab/ND	120 s./2 f. V = 2/3	SNV – De – 1st D – PLS	12.5	–	–	0.4–2.5 Foss
23 a	N+	Lab/oven dried grnd siev <2 mm	118 s./1 f. V = looCV	PLS	1.8 (0)	1.56	13.4	0.8–2.4 Varian
b	M	Lab/oven dried grnd siev <2 mm	118 s./1 f. V = looCV	PLS	1.5 (0)	1.87	13.4	1.2–20 BioRad
24 a	N	Lab/fresh & siev <2 mm	113 s./18 f. × 2 d. V = looCV	SNV – De – 2nd D – PLS	0.15	4.6	1.76	0.4–2.5 Foss
b	N	Lab/freeze-drying + grnd	109 s/18 f. × 2 d. V = looCV	SNV – De – 1st D – PLS	0.18	3.8	1.76	0.4–2.5 Foss

1-(Brown et al., 2006); 2-(Hummel et al., 2001); 3-(Janik et al., 2007); 4-(Reeves and Smith, 2009); 5-(Lee et al., 2009); 6-(Morgan et al., 2009); 7-(Pirie et al., 2005); 8-(Zornoza et al., 2008); 9-(Mouazen et al., 2007); 10-(McCarty et al., 2002); 11-(Kweon et al., 2008); 12-(Reeves et al., 2006); 13-(Reeves, 2009); 14-(Kusumo et al., 2008) 15-(Van Vuuren et al., 2006); 16-(Islam et al., 2003); 17-(Stevens et al., 2006); 18-(Stevens et al., 2008); 19-(Gomez et al., 2008); 20-(Fystro, 2002); 21-(Dalal and Henry, 1986); 22-(Ludwig et al., 2008); 23-(Viscarra Rossel et al., 2006); 24-(Terhoeven-Urselmans et al., 2008); N/M: NIR/MIR; g kg^{-1}**: value in g kg^{-1}, except otherwise mentioned; Mean: mean of the sample set content; *: calculated; ND: Non Determined; grnd: ground; siev: sieved; f.: fields; s.: samples; d.: date; tops.: topsoil; B: horizon B; all: all horizons; V: validation mode – ex V = 22% means that 22% of the samples are kept for validation; looCV: leave-one-out Cross-Validation; "sp" means that the validation set has been build by choosing spectra similar to those of the calibration set; De: pre-processed by Detrend; SNV: preprocessed by Standard Normal Variate; Av & Norm: preprocessed by Average and Normalization;1st (2nd) D: 1st (2nd) derivative; MSC: Multiple Scattering Correction; (M)LR x wl: (Multiple) Linear Regression on x wavelengths; BRT: Boosted Regression Tree; Med.: median; PCR: Principal Component Regression; PLS: Partial Least Square.

[a] Percentage of sand has been added as a co-variable.

[b] Computed as quadratic mean of the RMSE from Table 3 in Morgan et al. (2009).

[c] The samples are ranked with regard to their chemical values and then, every second sample in the ranking is selected for the validation sample.

[d] A PCA is carried out and samples are ranked with regard to their Euclidean distance to 0. Every second sample in the ranking is kept for validation.

oxidation as in the Walkley–Black method. They are the soil properties that are certainly most studied using NIR and MIR spectroscopy, and involved analytical devices from laboratory to on-the-go sensors (for herbicide variable rate application for instance). Results are expressed either in g C kg^{-1} soil or in %. Because there is no conventional factor to predict SOC from SOM values (Pribyl, 2010), the results are given in two different tables (Table 3 and Table 4). As shown in Table 3, very good assessment of organic matter has been obtained, using NIR spectroscopy, even, in-field conditions and using on-the-go sensors, as shown by experiment #4 (Christy, 2008). RDP values as high as 3.9 have been obtained in presumed leave-one-out cross-validation procedures. In the case of independent validation sets (Christy, 2008), RPD of 1.6 were attained. This shows that measuring the organic matter using NIR spectroscopy is possible, even with stiff tests (outdoor conditions and really independent validation set). Another interesting point shown in Table 3 is the importance of variable selection. For example, one of the best predictions in Table 3 (SEP = 0.19 g kg^{-1}) was obtained with only six wavelengths selected from the 1700–2500 nm range (Sudduth and Hummel, 1993). This would open new opportunities for the design of a low-cost NIR spectrometer dedicated to OM measurement. Unfortunately, however, in these papers, no data were given on the bias encountered.

More extensive results are given for organic C, and except two or three studies, the analysis is generally carried out by using NIR, even in in-field conditions (Table 4). Analyzing this table leads us to the following conclusions about common features encountered in all over these research studies:

1) *Is NIR or MIR better suited for soil C analysis*? When NIR/MIR coupled experiments are carried out on the same samples (see in Table 4, column "N/M" marked by +), MIR generally provides slightly better results. It is also interesting to compare the bias of NIR versus MIR measurements, in NIR/MIR coupled

Table 5
Determination of Total Carbon content by NIR/MIR spectrometry.

#	N/M	Sample	Validation set	Data processing	SEP (bias) g kg^{-1}**	RPD	Mean g kg^{-1}**	Range in μm & Spectro
1 a	N+	Lab/dried grnd	120b + 700a/10 f. C = 120b V = 700a	Av & Norm – ND – PLS	6.13	1.47	20.6	1.1–2.5 Digilab
b	M	Lab/dried grnd	120b + 700a/10 f. C = 120b V = 700a	Av & Norm – ND – PLS	5.12	1.76	20.6	2.5–25 Digilab
c	N+	Lab/dried grnd	120b + 700a/10 f. C = 120b + 35a V = 665a	Av & Norm – ND – PLS	2.84	3.17	20.6	1.1–2.5 Digilab
d	M	Lab/dried grnd	120b + 700a/10 f. C = 120b + 35a V = 665a	Av & Norm – ND – PLS	2.4	3.75	20.6	2.5–25 Digilab
e	N+	Lab/dried grnd	120b + 700a/10 f. C = 120b + 136a V = 564a	Av & Norm – ND – PLS	2.73	3.23	20.6	1.1–2.5 Digilab
f	M	Lab/dried grnd	120b + 700a/10 f. C = 120b + 136a V = 564a	Av & Norm – ND – PLS	1.9	4.73	20.6	2.5–25 Digilab
2 a	M+	Lab/dried grnd	720 s./220 f. V = 50%	PLS	2%	1.2	2.7%	2.5–25 Digilab
b	N	Lab/dried grnd	720 s./220 f. V = 50%	PLS	1.9%	1.2	2.7%	0.4–2.5 Digilab
c	M+	Lab/dried grnd	237 s./14 f. V = 20%	MSC – 1st D – PLS	0.334%	4.55	1.82%	2.5–25 Digilab
d	N	Lab/dried grnd	237 s./14 f. V = 20%	PLS	0.712%	2.13	1.82%	0.4–2.5 Foss
3 a	N	Lab/core. dried grnd siev	697 s./12 f. V = 1/10 CV	Av & Norm. – PLS	0.56	1.7	–	1.7–2.5 ASD
b	N	Lab/topsoil. dried grnd siev	165 s./12 f. V = 1/10 CV	Av & Norm. – PLS	<0.57	1.62	–	1.7–2.5 ASD
4 a	N+	Lab/dried grnd	272 s./1 f. V = looCV	Av & Norm – ND – PLS	1.5	3.27	11	1.1–2.5 Foss
b	M	Lab/dried grnd	272 s./1 f. V = looCV	Av & Norm – ND – PLS	0.94	5.21	11	2.5–25 Digilab
c	N+	Lab/dried grnd	544 s./1 f. V = 2/3	1st or 2nd D – PLS	1.6	3.06	11	0.4–2.5 Foss
d	M	Lab/dried grnd	544 s./1 f. V = 2/3	1st or 2nd D – PLS	1.1	4.45	11	2.5–25 DigiLab
5 a	M+	Lab/dried grnd	277 s./14 f. V = 25%	Av & Norm – ND – PLS	3.4 (0.4)	4.56	18.3	2.5–25 Digilab
b	N	Lab/dried grnd	277 s./14 f. V = 25%	Av & Norm – ND – PLS	5.4 (−0.3)	2.87	18.3	1.1–2.5 Foss
c	M+	Lab/dried grnd	277 s./14 f. V = 1 f. out	Av & Norm – ND – PLS	7.6 (3.9)	–	–	2.5–25 Digilab
d	N	Lab/dried grnd	277 s./14 f. V = 1 f. out	Av & Norm – ND – PLS	10.9 (−5.8)	–	–	1.1–2.5 Foss
6 a	M+	Lab/ND	237 s./West US V = 25%	ND – PLS	3.42% (0.4)	0.39	1.83%	2.5–25 Digilab
b	N	Lab/ND	237 s./West US V = 25%	ND – PLS	5.41% (−0.3)	0.27	1.83%	0.4–2.5 Foss
7	N	Lab/oven dried grnd siev	193 s./4 f. V = 45%	1st D – PLS	1.2	2.92	5.2	1.1–2.5 Foss
8	N	Lab/fresh soil	173 s./2 f. V = looCV	MSC – 1st D – PLS	0.27%	1.92	1.43%	0.3–1.7 Zeiss
9 a	N	Lab/air-dried finely grnd	144 s./1 f. × 2 d. V = 2nd date.	SNV – De – 1st D – Stepwise MLR	0.095% (−0.06)	1.38	0.85%	1.1–2.5 Foss
b	N	Lab/air-dried finely grnd	144 s./1 f. × 2 d. V = 2nd date.	SNV – De – 1st D – PLS	0.116% (−0.08)	1.13	0.85%	1.1–2.5 Foss
10	N	Lab/–	120 s./2 f. V = 2/3	SNV – De –1st D – PLS	14.5	ND	95	0.4–2.5 Foss
11 a	N	Lab/oven dried grnd siev	97 s./2 regions clayey soil V = 30%	1st D – PLS	1.92	3.98	14.6*	0.4–2.5 ASD
b	N	Lab/oven dried grnd siev	97 s./2 regions clayey soil V = 30%	1st D – PLS	3.45	2.22	14.6*	1.1–2.5 ASD
c	N	Lab/oven dried grnd siev	66 s./sandy soils V = 30%	2nd D – PLS	0.8	2.1	4.7	0.4–2.5 ASD
d	N	Lab/oven dried grnd siev	66 s./sandy soils V = 30%	1st D – PLS	0.77	2.0	4.7	1.1–2.5 ASD

(*continued on next page*)

Table 5 (*continued*)

#	N/M	Sample	Validation set	Data processing	SEP (bias) g kg^{-1}**	RPD	Mean g kg^{-1}**	Range in μm & Spectro
12	N	Lab/dried grnd	56 s./several f. V = looCV	SNV – De – PLS	90	–	Range: 0–466 g	0.4–2.5 Foss

1-(Reeves et al., 2008), 2-(Madari et al., 2006), 3-(Lee et al., 2009), 4-(McCarty and Reeves, 2006), 5-(McCarty et al., 2002), 6-(Reeves, 2009), 7-(McCarty et al., 2002), 8-(Mouazen et al., 2007), 9-(Confalonieri et al., 2001), 10-(Ludwig et al., 2002), 11-(Brunet et al., 2008), 12-(Terhoeven-Urselmans et al., 2006); N/M: NIR/MIR; g kg^{-1}**: value in g kg^{-1}, except otherwise mentioned; Mean: mean of the sample set content; *: calculated; ND: Non Determined; grnd: ground; siev: sieved; f.: "fields"; s.: samples; a: Aggregated Soil Fraction,; b: bulk soil; V: validation mode – ex V = 22% means that 22% of the samples are kept for validation; looCV: leave-one-out Cross-Validation; De: preprocessed by Detrend; SNV: preprocessed by Standard Normal Variate; Av & Norm: preprocessed by Average and Normalization; 1st or 2nd D: 1st or 2nd derivative; MSC: Multiple Scattering Correction; (M)LR: (Multiple) Linear Regression.

experiments. The bias has been given for experiments #10a/b, 10c/d, 13a/b, 23a/23b. Although the number of experiments is small, general trends can be observed. When validation uses cross-validation carried out on samples highly processed (dried ground) and very similar, i.e., samples coming from one field, both NIR and MIR validations give a low bias (see exp. #23a/23b in Table 4). This can be due to the fact that all sources of errors which can affect both NIR and MIR have been reduced. When NIR and MIR validation as cross-validation is carried out on a more heterogeneous sample set, i.e., made up of different fields, the variety of the sources of errors increases. Instrumental errors (lack of reproducibility of the device from one day to another etc.) and, to a smaller extent, some modelling errors (lack of fit of the model to new samples) can be found. As NIR is more sensitive than MIR to instrumental errors, bias may be higher for NIR- than for MIR-based models. This is the case of experiments #10a/b and #13a/b (Table 4). However, when the validation samples become too dissimilar from calibration samples, the main error source for both MIR and NIR is the bias. Therefore not only is the bias very high, but it is also similar with NIR and MIR measurements, as can be seen in experiments #10c/d (Table 4).

2) *What is the influence of calibration/validation datasets*? The performance, for instance given by the RPD, is very sensitive to the type of validation. Leave-one-out cross-validation always gives the best results. This is quite normal because in most – but not all – cases of soil databases, validation samples have an origin similar to the ones of the calibration set, and moreover, they could have been scanned in the same batch. Therefore, there are not independent. However, leave-one-out cross-validation would be rigorously independent if the samples themselves were highly independent. Performance is altered when the validation set is built by dividing the sample set into two (one calibration and one validation set), because the calibration database is then reduced. Finally, when the validation sample set is really independent, i.e., with soil samples analyzed which are not "spatial neighbours", the performance drops as shown by #6, 10 and 18 (McCarty et al., 2002; Stevens et al., 2008; Morgan et al., 2009). Christy (2008) assessed the impact on the prediction quality of increasing the number of different fields added in the calibration set (Table 3, exp #4). He found out that globally, the prediction error decreased but local discrepancies could be encountered. Going further, Brown et al. (2006) got an RPD of 2.3 with a worldwide database of more than 4000 samples, with one sixth being fully independent samples, which is a very satisfying result. A particular attention has to be given to this issue (quality of the calibration database and origin of the validation database), when comparing performances from different authors.

3) *Is it possible to directly analyze C in fresh samples by NIR spectrometry*? This question is crucial as we target to make in-field measurements. The answer is positive, i.e., NIR measurements on fresh samples (either on cores or topsoil) can deliver satisfying results. RPD ranking from 1.45 to over 3 (for leave-one-out Cross-Validation or looCV) could be obtained, as shown in Table 4, experiments #6, 11, 14, 15, 18, 19, 20 (Fystro, 2002; Gomez et al., 2008; Kusumo et al., 2008; Kweon et al., 2008; Stevens et al., 2008; Morgan et al., 2009).

4) *Should we analyze topsoil or profile samples*? When topsoil and cores of the same locations are studied in parallel, the core analysis (Table 4 experiments #5 and 6) give better results (Lee et al., 2009; Morgan et al., 2009); this is due to the presence of non degraded or partly degraded organic material in the topsoil, which increases the prediction uncertainty.

5) *What is the best spectral range in NIR for C analysis*? The 1650–2500 nm range is often cited as the most relevant for measuring organic C, as can be seen in Table 4, experiments #2, 5 and 6 (Hummel et al., 2001; Lee et al., 2009; Morgan et al., 2009).

6) *Is it feasible to get a good prediction ability with discrete wavelengths instead of a full spectrum*? Calibration models based on selected wavelengths are quite satisfactory, as RPD values over 2, CV values lower than 25% or r^2 values over 0.75 have been obtained as shown in Table 4, in experiments resp. #2, 5 and 21 (Dalal and Henry, 1986; Hummel et al., 2001; Lee et al., 2009). This paves the way for the development of low-cost wavelength-based sensors to measure organic C, which will ultimately reduce measurement costs.

7) *Is there any trend explaining bias occurrence in the prediction*? As explained above, knowing the bias is of primary interest, because the bias shows a lack of fit of the model (Draper and Smith, 1966) and cannot be removed by averaging the measurements, irreversibly creating a bad prediction. The trend that comes out of the literature is that the bias is higher when the validation is carried out on a really independent sample as in the one-field-out procedure (see experiment #10d in Table 4) or when the samples are more heterogeneous like smeared samples (see experiment #6c in Table 4), resp. 40% and 25% of the total error. On the contrary, when validation is carried out on samples very similar to the ones which have been used for calibration, low bias can be found (0 to less than 20% of the total error). However exceptions can be found in two directions, i.e., exceptionally high bias, 25% of the total error, has been found for a random selection of validation samples (experiment #20b in Table 4) whereas a small bias, of less than 10% of the error has been found for one-date-out validation procedure.

Finally, in addition to these conclusions, attention must also be drawn on another issue which affects the organic C prediction, i.e., non-linear effects. When a calibration is carried out using PLS on large sample sets, non-linear effects occur both on NIR and MIR spectra, as shown by Reeves (2009) in his study of 699 samples from across the USA. The origin of this non-linearity would not be due to the heterogeneity of the database but to the presence of carbonates which provide highly non-linear calibration models both in NIR and MIR. The ability to develop a reliable calibration for organic C when carbonates are present remains an open question.

2.5. Total C

Several studies have been conducted on the measurement of total C (Table 5). The conclusions are very similar to the ones obtained with organic C. In particular, MIR is slightly superior to NIR with prediction errors always lower than the ones obtained with NIR. Also, the bias can be very small (around 0) even with validation samples extracted at a different time than calibration samples (Table 5, experiments #9a/b), which shows a good model fitting for this experiment (but we have to notice that the experiments were carried out in a single field). But, as found above, when one-field-out validations are carried out, huge bias can occur (Table 5, experiment #5c/d).

3. Discussion and conclusions

The aim of this bibliographic study was to make a critical review of the various studies using either NIR or MIR to measure C content in soil, with a future objective of applying it in the context of Kyoto Protocol requirements. The objective of the review was to draw trends and conclusions about the best appropriate technique (including spectral range choice, sample preparation requirement, influence of calibration/validation sample sets etc…) for a low-cost and reliable assessment of soil C content. To do so, we analyzed the recent literature through the filter of metrology (the science of measurement) by studying the calibration and validation parameters which affected the measurement quality, namely the bias and standard error of prediction. The following conclusions can be drawn from our analysis.

1. The first conclusion deals about the preference of using MIR or NIR for soil analysis. MIR spectroscopy is slightly better than NIR for measuring C, with prediction errors generally 10–40% lower than with NIR. When calibration and validation samples are very similar to each other (i.e., of same origin), the difference is larger because MIR spectroscopy is more reproducible than NIR. When validation and calibration samples are very different, both NIR and MIR show large prediction errors mainly accounted for by the bias due to lack of fit to the new samples. This also means that if NIR will be used, special procedures will have to be found to enhance its reproducibility (see the paragraph about bias).
2. The second conclusion deals with the influence of calibration and validation dataset on the apparent performance of the model. Leave-one-out cross-validation, especially when carried out on a dataset created from a limited number of fields, leads to over-optimistic performance. The performance drops when one uses really independent samples, which is however what is most likely to be encountered in reality. This comes from the fact that the model is influenced by other parameters than the target variable, such as the texture and in some cases (e.g., in in-field conditions) by other properties such as soil structure or moisture etc. Two conclusions can be drawn from that. First, when comparing performances from different authors, it is necessary to be aware about the procedure used for the validation to make safe interpretations. Secondly, in order to cope with the issue of model instability, it is necessary to create as large and exhaustive as possible calibration database. That database could be then used either to create local models or to build a generic model not sensitive to texture and other secondary parameters. For instance, Brown et al. (2006) concluded from their study on more than 4000 samples coming from all the 50 U.S. states and 36 other countries that viable empirical calibrations might be constructed with very large but obtainable spectral libraries of the order of 10^4–10^5 samples. They outlined the issue of correct database construction for soil analysis, with regard to what is required for biological product NIR analysis: "*Reliable calibrations for materials like wheat grains and forages can be constructed with just a few thousands samples, but these materials are compositionally constrained by plant genetics. Soil composition is, unfortunately, not so constrained, which makes the problem of VNIR-DRS soil characterization both different and more challenging than that of grain or forage analysis*". This idea of a global library, which was first suggested by Shepherd and his team (Shepherd and Walsh, 2002; Brown et al., 2006), is now supported by the Soil Spectroscopy Group, managed by Viscarra Rossel (Viscarra Rossel, 2009; Stenberg et al., 2010), under the auspices of the Working Group on Proximal Soil Sensing of the International Union of Soil Sciences (IUSS).
3. The third conclusion deals with the feasibility of analyzing directly fresh samples with NIR. Fresh or field samples can provide satisfactory prediction accuracy.
4. The fourth conclusion addresses the issue of using either topsoil or cores in NIR analysis. Topsoil scanning provides less accurate prediction than core scanning due to the high amount of partly degraded organic matter which can bias the result.
5. The fifth conclusion deals with the relevant spectral range for NIR analysis of C. In the NIR range, the best range is 1650–2500 nm, as shown by many researchers (Hummel et al., 2001; Mouazen et al., 2007; Lee et al., 2009; Morgan et al., 2009).
6. The sixth conclusion corresponds to the issue of using a full spectrum or only some wavelengths, which paves the way to filter instruments. MLR can perform as well as PLS, as shown by the results obtained in for total C in Confalonieri et al. (2001) and for organic C in Dalal and Henry (1986), Hummel et al. (2001), and Lee et al. (2009).
7. The seventh conclusion is related to the bias which irreversibly lowers the prediction performance. The bias can be very high when the validation samples come from quite a different provenance. Indeed, such samples can contain new soil components which are not present in the calibration samples. A bias will appear and its value is the scalar product of the spectrum of these components and of the b-coefficient. To reduce the bias, three approaches, which can be used jointly, are possible: (i) reducing instrumental sources of errors by developing standard samples to be scanned for calibration transfer, (ii) accounting for sources of spectral variations due to the environment (soil moisture content, temperature…) and, if possible, getting rid of them in the calibration step, and (iii) using as few variables as possible in the calibration, in application to the parsimony principle (Seasholtz and Kowalski, 1993). This last point could explain why PLS might not be the best data-processing technique for soil composition analysis. Due to large prediction errors obtained today, some researchers even consider the objective of C sequestration measurement as unreachable: Morgan et al. (2009) concluded that "*the future of Vis–NIR DRS for soil measurement in situ is promising. […] The result of our study and other published papers indicate that Vis–NIR DRS alone do not provide sufficient accuracy for stand-alone C sequestration measurement, monitoring and verification. However, in situ proximal sensing with Vis–NIR DRS could be used to map soil variability for more efficient sampling and laboratory determination of soil carbon.*" Reducing the bias is an inescapable issue to meet the challenge of stand-alone C sequestration measurement.
8. Finally, this review also revealed that various forms of C can be predicted, in particular the presence of biochar which has a much longer half-life in soil and therefore has a positive effect on C sequestration.

Table 6
Comparison of the performance and cost of organic carbon prediction or organic matter prediction (see OM in the first column) using different methods; (+ in the I.V. column: experiments involving a really independent validation, called I.V.; f.: field, s.: sample, d: dates, CV%: coefficient of variation = SEP/Mean, *: SEP and bias in %).

Method	SEP g kg^{-1} (bias)	CV % (RPD)	Extraction	Lab. prep.	Lab. anal	Bulk dens	Validation	I.V.	Reference
Reference = ignition	1–2		$$$		$$$	$$			(Fystro, 2002; Ben-Dor et al., 2008; Stevens et al., 2008)
MIR lab						$$			
Dried & ground	0.62	3.4	$$$	$$$	$		Sever. f./734 s. V = 78%		(Janik et al., 2007)
Dried & ground	6 (−2.7)	20 (2.2)	$$$	$$$	$		14 f./277 s. V = 1 f. out (16 s.)	+	(McCarty et al., 2002)
NIR lab						$$			
Dried & ground	0.24	29 (3.11)	$$$	$$$	$		10 f./637 s. core + tops V = 1/10 CV		(Lee et al., 2009)
Dried & ground	7.9 (−0.3)	168 (2.63)	$$$	$$$	$		World wide f./3793 s. V = 1/6 fully indep s.		(Brown et al., 2006)
Fresh	0.29*	16 (3.5)	$$$	–	$		1 f./172 s. V = 88%		(Van Vuuren et al., 2006)
Thawed coarse	5.7 (0.6)	19.3 (2.7)	$$$	–	$		40 f./133 s. core + tops. V = 48 s. indep	+	(Fystro, 2002)
NIR field						$$ or 0			
Intact core	1.29*	29 (1.97)	$$	–	$$		7 f. × 2 d./189 s. V = 50% Eucl. dist in PC plot[a]		(Kusumo et al., 2008)
Intact core	5.82[b]	60 (1.37)	$$	–	$$		6 f./540 s. V = 1/6 whole f. out	+	(Morgan et al., 2009)
Hole	2.2 (OM)	12.4	$	–	$$		4 f./100 s. V = 22%		(Ben-Dor et al., 2008)
On-the-go (OM)	0.4*	19 (2.2)	–	–	$$		8 f./105 s. V = looCV		(Christy, 2008)
On-the-go (OM)	0.54*	24 (1.63)	–	–	$$		8 f./105 s. V = 1/8 whole f. out	+	(Christy, 2008)

[a] A PCA is carried out and samples are ranked with regard to their Euclidean distance to 0. One out of two samples is kept for validation.
[b] Computed as quadratic mean of the RMSE from Table 3 in Morgan et al. (2009).

From a practical point of view, there are trade-offs between low-cost measurement and accuracy. In Table 6, we have reported the best results for organic C (and exceptionally organic matter) quantification, i.e., mass concentration (g C kg^{-1} soil) found in the literature for each approach. The approaches correspond to various data acquisition configurations (MIR, NIR, in laboratory, in-field…). They are indicated in the first column, from the most "reliable" (i.e., in laboratory, on dry and ground samples) to the one with the lowest cost (i.e., in-field, with on-the-go sensors). For each category, we tried, when possible, to find an experiment in the literature, which showed leave-one-out cross-validation (looCV) and fully independent validation, the first one giving the expected prediction error, provided all model lack-of-fit errors have been removed, the second one giving the present best error found under realistic conditions. When available, the bias has been indicated. The accuracy is given either in g kg^{-1} or in % (when specified with *). The coefficient of variation, CV%, defined above is given as another performance index, i.e., the smaller, the better. Table 6 shows that the best CV% is obtained for lab-MIR but satisfactory results can also be obtained with NIR in the field (resp. 12 and 19% with "probe-in-hole" and "on-the-go" measurements). Moreover, Table 6 provides qualitative information about the total cost of analysis, shared into the extraction cost, laboratory preparation cost, analysis cost, with the reference method (ignition) as a standard for both cost and accuracy. The costs drop dramatically when no sample has to be taken in the field. This last remark would encourage the use of NIR systems mounted on probes or on "on-the-go" devices.

However, to match Kyoto requirements, we must carry out a volumetric assessment of C content, whereas all the publications have focused on measuring the mass concentration of C (i.e., mass of C per mass of soil). This means that, even if we are able to measure the mass concentration of C in the field, samples must be extracted and brought back to the laboratory for bulk-density measurement, generating additional costs as shown in Table 6 ("Bulk dens" column). As outlined by Reeves (2009), this would lead to a drop in economic justification of in-field NIR measurement of C content. Two ways are nevertheless possible to avoid this dead-end. Either the bulk density is measured in the field, using NIR spectrometry – or any other sensor such as a gamma probe – or the calibration is made directly with respect to the volumetric concentration of C (mass C per unit volume of soil). These alternatives would generate no cost, as shown by "0" in the bulk density column in Table 6.

Measuring bulk density by NIR spectrometry has been carried out by few researchers. In their attempt to quantify degrading soils, Omuto (2008) obtained coefficients of determination r^2 equal to 0.81 and 0.76 resp. with the calibration and validation sets, when trying to predict the bulk density from near-infrared spectra and SEP of 0.02 g cm^{-3}, whereas the mean for this property is 1.4 g cm^{-3}, meaning that the prediction is satisfactory. When using the in-hole probe, Kweon et al. (2008) collected soil electrical conductivity (EC) and soil penetration resistance values in addition to NIR values and obtained satisfactory results for the bulk-density estimation in three of the six fields studied. Baxter et al. (2008) attempted to predict the bulk density of samples of peat and casing soil dedicated to mushroom production. A SEP of 59 g L^{-1} was obtained, giving a poor value of 1.3 for RPD. Also, with regard to the standard error of laboratory (3.5 g L^{-1}), this SEP value was not considered as correct. Recently, Moreira et al. (2009) investigated the ability of NIR spectroscopy to predict soil bulk density. They obtained SEP equal to 0.13 g cm^{-3}, for a 1184-sample set, ranging from 0.45 to 1.95 g cm^{-3} with a mean of 1.48 g cm^{-3} and a SD of 0.14 g cm^{-3}, but performances for RPD (1.05) and r^2p, the

coefficient of determination of the prediction ($r^2p = 0.14$) were poor. As the samples were ground before analysis, it is difficult to understand how a real relationship could be obtained between NIR and bulk density. As bulk density is to some extent related to the C content and the texture, we think that the NIR prediction of bulk density could be based on the spectral features related to these variables (Tranter et al., 2008) and not on the sample structure. So, direct calibration for bulk density would not be efficient on soil samples measured in field, which may be of similar composition but have different structures (e.g., degree of compaction), and bulk densities.

Because measuring bulk density is not easy with NIR as shown above and because computing a volumetric concentration from a NIR-predicted C density and a NIR-predicted bulk density would lead to additional error due to the error propagation law, we recommend attempting the second approach, i.e., directly predicting the volumetric C concentration. This is a main issue researchers have to work on to have NIR spectrometry accepted as a sustainable method for C sequestration assessment.

In conclusion, in-field NIR measurement of soil C content appears a most appealing technique to meet the trade-off of low-cost versus accuracy. There are three practical issues to be dealt with by research. These are (i) bias reduction by increasing reproducibility – in order to meet the overall accuracy requirement, (ii) the ability to make an assessment of the volumetric content, and not only the mass content, of C in the field – in order to meet the low-cost requirement, (iii) the potential for measurement of the living root C for improved soil C permanence estimation.

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