



Near infrared reflectance spectroscopy for estimating soil characteristics valuable in the diagnosis of soil fertility

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Soil fertility diagnostics rely not only upon measurement of available nutrients but also upon the ability of the soil to retain these nutrients. Near infrared (NIR) reflectance spectroscopy is a rapid and non-destructive analytical technique which allows the simultaneous estimation of standard soil characteristics and does not require the use of chemicals. Previous studies showed that NIR spectroscopy could be used in local contexts to predict soil properties. The main goal of our research was to build a methodological framework for the use of NIR spectroscopy on a more global scale. The specific goals of this study were (i) to identify the best spectral treatment and processing—LOCAL versus GLOBAL—regression methods, (ii) to compare the performance of NIR to standard chemical protocols and (iii) to evaluate the ability of NIR spectroscopy to predict soil total organic carbon (TOC), total nitrogen (TN), clay content and cationic exchange capacity (CEC) for a wide range of soil conditions. We scanned 1300 samples representative of the main soil types of Wallonia under crop, grassland or forest. Various sample preparations were tested prior to NIR measurement. The most appropriate options were selected according to analysis of variance and multiple means comparisons of the spectra principal components. Fifteen pre-treatments were applied to a calibration set and the prediction accuracy was evaluated for GLOBAL and LOCAL modified partial least square (MPLS) regression models. The LOCAL MPLS calibrations showed very encouraging results for all the characteristics investigated. On average, for crop soil samples, the prediction coefficient of variation (CV_p) was close to 15% for TOC content, 7% for TN content and 10% for clay content and CEC. The comparisons of repeatability and reproducibility of both NIR and standard methods showed that NIR spectroscopy is as reliable as reference methods. Prediction accuracy and technique repeatability will allow the use of NIR spectroscopy within the framework of the soil fertility evaluation and its replacement of standard protocols. LOCAL MPLS can be applied within global datasets, such as the International global soil spectral library. However, the performance of LOCAL MPLS is linked to the number of similar spectra in the dataset and more standard measurements are needed to characterise the least widespread soils.

Keywords: NIR, LOCAL MPLS calibration, carbon, nitrogen, clay, cation exchange capacity, soil spectral library

Introduction

Soil fertility is the ability of a soil to provide, at the right time, essential plant nutrients in adequate amounts and suitable proportions to sustain plant growth.¹ The chemical aspect of

soil productivity is usually expressed by a set of properties which relates to nutrient availability. Appropriate decisions about nutrient management, such as use of fertilisers, should

rely upon efficient soil testing. In the Walloon Region, the general scheme to provide appropriate fertility diagnosis faces two major problems. The first one is the lack of measurement of clay, total nitrogen (TN) content and cation exchange capacity (CEC) of the soil samples, even though these properties are keys to entering regional reference systems.² Indeed, Ca, Mg and K levels are compared to an ideal cationic balance of the soil exchange complex while P availability in soils depends on pH, TOC and clay content. Up to now, the laboratories use regional mean values of clay content or CEC with a risk of a biased diagnosis and subsequent wrong estimation of the nutrient requirement. The second concern is linked to the use of analytical methods which generate chemical waste and are time-consuming.³ As NIR spectroscopy is known to be a physical, non-destructive, rapid, reproducible and low-cost method for predicting several soil properties simultaneously,^{4,5} its ability to produce reliable estimates of properties that set up the framework of fertility evaluation needs to be investigated and verified for each region.

NIR spectroscopy is an analytical technique that characterises materials according to their reflectance in the wavelengths ranging between 800 nm and 2500 nm. Spectral signatures of materials are defined by their reflectance (R), or absorbance ($\log 1/R$), as a function of wavelengths. Under controlled conditions, the signatures are due to electronic transitions of atoms and vibrational stretching and bending of structural groups of atoms that form molecules and crystals. The fundamental vibrations of most soil materials can be found in the mid-infrared region, with overtones and combinations found in the near-infrared region.⁶

Soil is a non-ideal system because it is chemically and mineralogically more complex than the "pure" systems often studied using traditional laboratory procedures. Mechanisms of soil processes are only partially understood and the fundamental links between measured soil chemistry and particular soil attributes or properties may be complex.^{4,7} Indeed, the near infrared spectra of soil are influenced by the liquid and solid phases of the soil material: soil moisture, organic content, CaCO_3 , iron content and mineral composition. Spectra are also influenced by their physical structure: the size and shape of the particles, the voids between them and their arrangements affect the length of the light transmission passing through a sample and, therefore, influence reflectance.⁸

Viscarra-Rossel *et al.*⁴ reviewed literature about the capacity of UV, visible, NIR and mid-infrared (MIR) to predict soil attributes. Most of them relate to soil fertility through acidic, organic, or mineral status. CEC and clay content also appear in the list of studied attributes. As soil properties are often interrelated, many of them may be directly or indirectly determined by IR spectroscopy.⁹ However, the ability of NIR spectroscopy to predict P, K and microelements should be considered cautiously because results from calibration data sets have failed to be validated using other data sets.⁹ As summarised in Stenberg *et al.*,¹⁰ some authors have already studied the prediction of TOC, TN, clay content and CEC by NIR spectrometry.^{3-8,11-33} Most authors concluded that this technique

is a promising method, but some of the NIR studies related to prediction of soil properties were limited in one way or another by (i) small sample set size and/or weak diversity of soil types⁸ and (ii) small extent of the area of interest in comparison to the Walloon territory (~ 16,800 km²) characterised by more than 6000 soil units (series and phases) according to the Digital Soil Map of the Walloon Region. For TOC content, Shepherd and Walsh²³ and McCarty and Reeves³⁰ worked with large sample sets (more than 500 samples) but close data ranges (0% to around 5% of TOC). They obtained a standard error of calibration (SEC) of 0.22% and 0.16% respectively. Chang *et al.*⁸ and Brown *et al.*⁶ worked with large sample sets and large data ranges (0% to 50% of TOC). They obtained a SEC around 0.80%. For TN content, Chang *et al.*,⁸ working with the same data sets, obtained a SEC of 0.62%. Islam *et al.*²⁷ and McCarty and Reeves,³⁰ working with large data set but narrow data range, obtained a SEC around 0.20 g kg⁻¹. For clay content, Chang *et al.*⁸ and Brown *et al.*,⁶ working with the same data set as for TOC content, obtained a SEC of 5.4% with a data range of 0% to 90%. McCarty and Reeves³⁰ working with close data set (11% to 29%) obtained a SEC of 1.8%. For CEC, Chang *et al.*⁸ and Brown *et al.*⁶ obtained a SEC of 3.82 cmol(+) kg⁻¹ and 5.5 cmol(+) kg⁻¹ for a data range of 2 to 90 and 0.2 to 165, respectively. Some authors, as summarised in Cécillon *et al.*³⁴ and Viscarra Rossel,³⁵ emphasised the interest of building a spectral library representative of soil diversity of the studied population (region, country or continent) in soil monitoring.

The quantitative analysis of the sample constituents by NIR spectroscopy requires multivariate calibration. A soil characteristic is thus predicted thanks to the relationship between this property (Y) and the absorbance for each selected wavelength (X_x). Several alternatives exist to build equations allowing the prediction of the unknown soil characteristic from the observed absorbance: principal components regression (PCR), partial least square regression (PLSR), stepwise multiple linear regression (SLMR), locally weighted regression (LWR), boosted regression trees (BRT) and artificial neural networks (ANN) are the most used multivariate calibration techniques. None of those proposed calibration techniques have achieved universal acceptance because a calibration model that works well for one application may be unacceptable for another.⁸ Each technique requires a calibration stage on a sample set where the studied soil characteristics are known for every sample and can be compared to the absorbance at some wavelengths. It appears that PLS methods have been fully used for predicting soil characteristics,^{3-6,19-21,24,25,27,28,32,33,36-60} but some authors working on regional calibration^{6-9,11-23} emphasised the use of non-linear techniques to give more accurate predictions. Brown *et al.*,⁶ using their international spectral library of around 4200 spectra, found that BRT clearly outperformed PLS regression. Shepherd and Walsh²³ worked with a multivariate adaptive regression (MARS) splines application to predict several soil properties on a spectral library of 1000 topsoil samples from eastern and southern Africa. They concluded that this approach is appropriate for large multivariate data sets when little theoretical knowledge is available

to guide the model building process. In the “Chimiometric 2006” meeting, a large set of soil data was given to the participants to test their ability for using regression methods based on NIR data and to compare several methods.⁶¹ Five chemometric methods were compared: back propagation neural network (BPNN), B-splines basis and radial basis function network (Bsplines+RBFN), least square support vector machine (LS SVM), PLS regression and LOCAL PLS regression. The best predictions were obtained following LOCAL PLS regression. The LOCAL PLS regression is based on local linear modeling and can be used for non-linear relations.⁶² It matches the sample to be predicted with a small homogeneous group of samples selected from the calibration set. Each unknown sample is compared to the calibration set and the closest samples are selected from the spectra database. Then, based on selected samples, a new equation is built to predict the sample. The similarity index used to choose the small homogeneous group of samples is a correlation coefficient between spectra. Two samples having a correlation of one must have the same composition.⁶¹

A result obtained by NIR spectroscopy or by a traditional analytical method is always linked to uncertainty which has to be evaluated. Some authors compared their results to an analytical error. For instance, Ben-Dor and Banin¹³ obtained a CV_p [$SEP \times 100 \times (\max - \min)^{-1}$] of 14% for the CEC and a CV_a [$\text{analytical error} \times 100 \times (\max - \min)^{-1}$] of 2%. For the TOC content, they obtained a CV_p of 13% and a CV_a of 2%. Fyströ¹⁹ obtained similar results for the TOC and TN contents. Repeatability and reproducibility are useful concepts in the evaluation of the quality of analytical results. The repeatability conditions are conditions where independent test results are obtained with the same method on identical test items in the same laboratory, by the same operator, using the same equipment within short intervals of time. The repeatability standard deviation (s_r) is the standard deviation of test results obtained under repeatability conditions. The repeatability limit (r) is the value under to which the absolute difference between two test results obtained under repeatability conditions is expected to be, with a probability of 95%. The reproducibility conditions are valid when test results are obtained with the same method on identical test items in different laboratories, with different operators using different equipment.⁶³

The general objective of the paper was to build up an assessment methodology for NIR determination of soil TOC, TN, clay content and CEC in the framework of a land fertility evaluation process. The strategy is (i) to evaluate the ability of NIR spectroscopy to predict accurately TOC, TN, clay content and CEC of Walloon soil samples by comparing several spectral data pre-treatments using scatter correction techniques, detrending and derivatives and chemometric methods based on GLOBAL and LOCAL MPLS regression, (ii) to assess the robustness of the models compared to the reference analytical method and for a generalisation to other soil laboratories and operators and (iii) to lay the foundations for the development of a spectral library for all Wallonia. For the first point, the aim was to evaluate the gain of using the LOCAL MPLS to

take into account the non-linearity of the spectral response in comparison to a GLOBAL approach. We limited our study to GLOBAL and LOCAL MPLS as only these options are available in the ISI SCAN software used in our laboratories.

Materials and methods

The developed methodology to achieve our aims and to build the most accurate models for predicting soil properties includes the following steps:

1. Evaluating the population diversity for the four studied soil characteristics in Wallonia.⁶⁴
2. Set-up of a representative sample set from this population (see section on “Soil sampling strategy and chemical procedures”)
3. Analysis of the samples following standard procedures (see section on “Soil sampling strategy and chemical procedures”)
4. Elaboration of a procedure for soil sample preparation before scanning (see section on “NIR spectroscopy measurements”)
5. Scanning in replicate all the samples following this procedure (see section on “NIR spectroscopy measurements”).
6. Division of sample set between calibration, tuning and validation sub-sets (see section on “Selection of tuning and validation sample sets”).
7. Elaboration of a predictive model for each soil characteristics (see sections on “Spectral data pre-treatment and GLOBAL MPLS calibration” and “LOCAL MPLS calibration”).
8. Evaluating the repeatability and reproducibility of the method (see section on “Evaluation of the repeatability and reproducibility of the method”).
9. Transferring and implementing the spectral library in the laboratory network (results not presented in this paper).

Soil sampling strategy and chemical procedures

One thousand three hundred soil samples were collected across the Walloon region. Both soil properties and land use (crop, grassland or forest) drove the sampling strategy. The number of samples to be selected was defined proportionally to the area covered by crossing the soil nature (following the Main Soil Types of Wallonia, Figure 1) and land use (Table 1 and Figure 2). For instance, “crop loamy soils with good natural drainage” cover 17% of the Walloon Region and are, consequently, the most representative group in our spectral library. In each cluster, samples were selected from topsoil but also from some subsoil as reference. The interest in considering both top and subsoil is mainly linked to the determination of the CEC, where one aim was to evaluate the prediction accuracy taking into account the influence of both TOC and clay content. All samples were air-dried, crushed and sieved at 2 mm. For the reference TOC and TN determinations, a fraction was ground at 200 μm .

Samples were analysed according to standard procedures: TOC content (Springer-Klee method⁶⁵)—TN content (Kjeldhal method⁶⁶)—clay content (chain hydrometer method

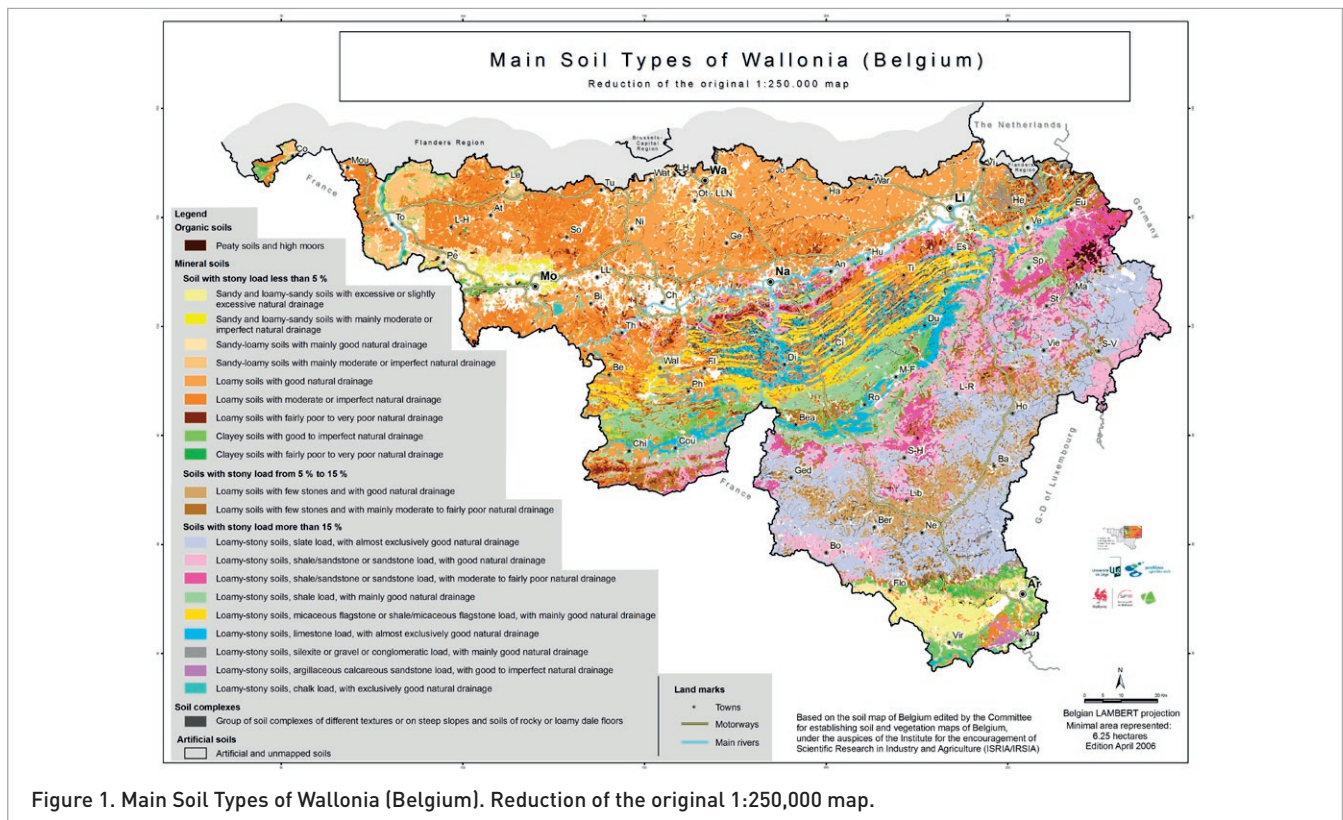


Figure 1. Main Soil Types of Wallonia (Belgium). Reduction of the original 1:250,000 map.

Table 1. Number of samples constituting the spectral library per soil type (texture/drainage) according to the Main Soil Types of Wallonia classification and to land use.

Main soil type		Total number of samples	Crop soil samples	Grassland soil samples	Forest soil samples
Texture	Natural drainage				
Sandy and loamy-sandy soils	Excessive or slightly excessive	79	6	11	62
	Moderate or imperfect	11	3	3	5
Sandy-loamy soils	Good	51	20	10	22
	Moderate or imperfect	31	16	6	10
Loamy soils	Good	334	290	29	15
	Moderate or imperfect	119	77	21	21
	Fairly poor to very poor	28	6	3	19
Clay soils	Good to imperfect	43	9	23	11
	Fairly poor to very poor	20	4	9	7
Loamy soils with few stones	Good natural drainage	64	8	9	47
	Moderate to fairly poor	45	14	3	28
Loamy-stony soils on					
- slate	Good	98	6	23	69
- shale/sandstone	Good	117	15	6	96
	Moderate to fairly poor	49	7	4	38
- shale	Good	68	18	14	36
- micaceous siltstone	Good	59	24	9	26
- limestone	Good	47	16	18	13
- siliceite, gravel or conglomeratic	Good	35	13	15	7
TOTAL		1300	546	216	538

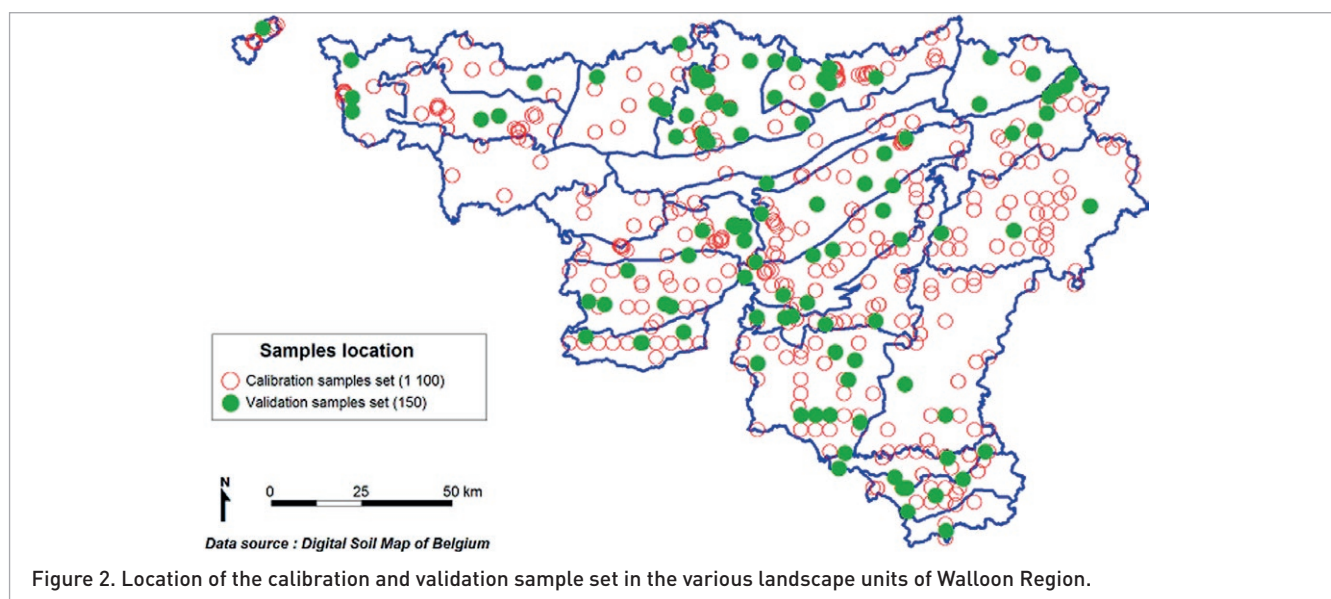


Figure 2. Location of the calibration and validation sample set in the various landscape units of Walloon Region.

or De Leenheer system)—CEC (derived Metson method). The Springler–Klee method relies on the oxidation of organic matter by potassium dichromate in a hot acid environment. The excess of potassium dichromate is then titrated with ammonium iron sulphate. The Kjeldhal method consists in digesting soil with sulphuric acid. The addition of sodium hydroxide to the digestion solution produces ammonium which is evaporated by steam distillation and condensed in a flask with boric acid solution. The ammonia is then titrated with chlorhydric acid. The chain hydrometer system (or De Leenheer system) measures the density at constant depth of a suspension of clay and silt soil fractions. Prior to measurements, clay and silt fractions are suspended in a solution with sodium hexametaphosphate as the dispersing agent after removal of cementing agents and before sand separation. CEC determination is realised through saturation of the exchange complex with ammonium acetate at pH 7, washing, displacement and measurement of the ammonia by steam distillation and titration with chlorhydric acid. Detailed protocols may be found in Page *et al.*⁶⁷ and Pansu and Gautheyrou.⁶⁸

NIR spectroscopy measurements

Before scanning soil samples, a preparation procedure (quarter cup packing with soil material) had to be defined. In order to be used for routine work in laboratories, the procedure should be easy to apply and give similar spectra regardless of the laboratory, the technician or the physical nature of the soil sample. Furthermore, the same spectra scattering should be observed whatever the soil texture. Based on the literature review,^{3,5,19,21} it was decided to work with 2 mm crushed and sieved soil samples. Those authors studied the effects of the sample conditioning on the prediction quality. They compared the effect of samples sieved at 2 mm and ground at 200 μm on the accuracy and did not observe highly significant differences.

A fraction (~ 25 g) of the 2 mm sieved, air-dried sample was poured in a quarter cup. Four filling-up protocols (T) were evaluated in order to select the most robust:

1. tipping the soil in the quarter cup;
2. filling up the quarter cup with a spoon;
3. filling up the quarter cup with a spoon and packing down the soil with the spoon;
4. filling up the quarter cup with a spoon and packing down the soil with a lid.

Six samples (S) characterised by a large range of clay content (3% to 54%) and TOC content (0.1% to 5.1%) were used for each test. Two quarter cups (QC) were filled for each sample and each QC was scanned in duplicate. Two operators (O) participated in the experimentation to compare the robustness of each testing method. Forty eight spectra were thus recorded for each of the four tests. Statistical analyses were performed on the spectra. First, a principal component analysis (PCA) was applied and the first five components, which explained 99.7% of the variability, were selected. Second, the significance of differences between protocols was evaluated through a variance analysis (ANOVA) based on a partially nested design. The factors “test–T–”, “operator–O–” and “sample–S–” are crossed; factor “quarter cup–QC–” is nested to the three others. Factors “O”, “S” and “QC” are random. The variance components were evaluated for each of the four tests, for the factors “O”, “QC” and for the interactions. Third, a multiple means comparison was performed to identify which way of filling up the cup produced different spectral response from the others. The principal components (PCs) were studied separately as these are not correlated.

All samples were scanned using a NIRSystems spectrometer (model 5000, FOSS NIRSystems Inc., Laurel, MD, USA) model from 1100 nm to 2498 nm by 2 nm steps. The spectrophotometer was equipped with a dispersive monochromator, a tungsten lamp and two PbS detectors at 45°. A ceramic tile

was used as reference. Each spectrum, averaged from 32 scans, was recorded as absorbance ($\log 1/R$). Each sample was scanned in duplicate, meaning that two QCs were filled for each sample, and the spectra averaged and recorded in the spectra database or spectral library (SDB—where all Y and X_λ of each sample from the calibration set are recorded). An internal standard was scanned, following this procedure, every 20 samples. Information about absorbance (for each wavelength), land use, topsoil/subsoil, nature of soil, texture, geographical location and data analysis (TOC, TN and clay content and CEC) were recorded in this spectral library.

Before recording the average spectrum in the SDB, the root mean square (RMS) between the two spectra of each sample was measured to check whether they were close enough. If the observed RMS was higher than a fixed limit, the average spectrum was discarded and the sample was scanned again in duplicate. To determine the fixed limit between two replicates, a t -student test was conducted with the first 300 scanned samples. Considering a confidence interval of 99%, the obtained limit RMS was 9850 $\mu\log$ averaged to 10,000 $\mu\log$. The mean RMS between the two replicates was 3100 $\mu\log$ (based on the same 300 spectra) when the RMS between two scans of the same quarter cup was 380 $\mu\log$.

Detection of spectral outliers

Chang *et al.*⁸ and Islam *et al.*⁷ defined an outlier as a sample having a difference between measured and predicted values higher than three times the SEC or standard error of prediction (SEP). In order to detect the outliers in our spectral library before applying the calibration stage, the methodology followed by Fyströ¹⁹ and Brunet *et al.*⁵ was applied: a PCA was carried out after the application of an SNV pre-treatment of the spectra. The aim was to calculate Mahalanobis distance (H), which illustrates the way the spectra deviates from the average spectrum. The spectra with $H > 3$ were considered as outliers and were eliminated from further investigations.⁶⁸ Fifty three samples out of 1300 were detected as outliers. Those statistics were made using the WinISI (Infrasoft International, LLC, State College, PA, USA) and Minitab 15 (Minitab Inc., State College, PA, USA) software.

Selection of tuning and validation sample sets

Most authors^{3,4,5,18,19,21,25,28,33} using PLS regression, split the sample set in two parts, one for calibration goal, obtaining SEC or standard error of cross validation ($SECV$) and one for the validation of the predictive model, based on the SEP . In LOCAL MPLS regression, an optimisation stage is needed and to avoid overestimation, the set used to optimise the model has to be different from the one used to check its accuracy. LOCAL calibration, therefore, needs three independent sets. To avoid misunderstanding, the three sets were also considered for GLOBAL MPLS regressions. The first, called calibration set, was treated as our spectral database. The second, called tuning set, was used to compare all the studied models and select the most accurate. The third set, called validation

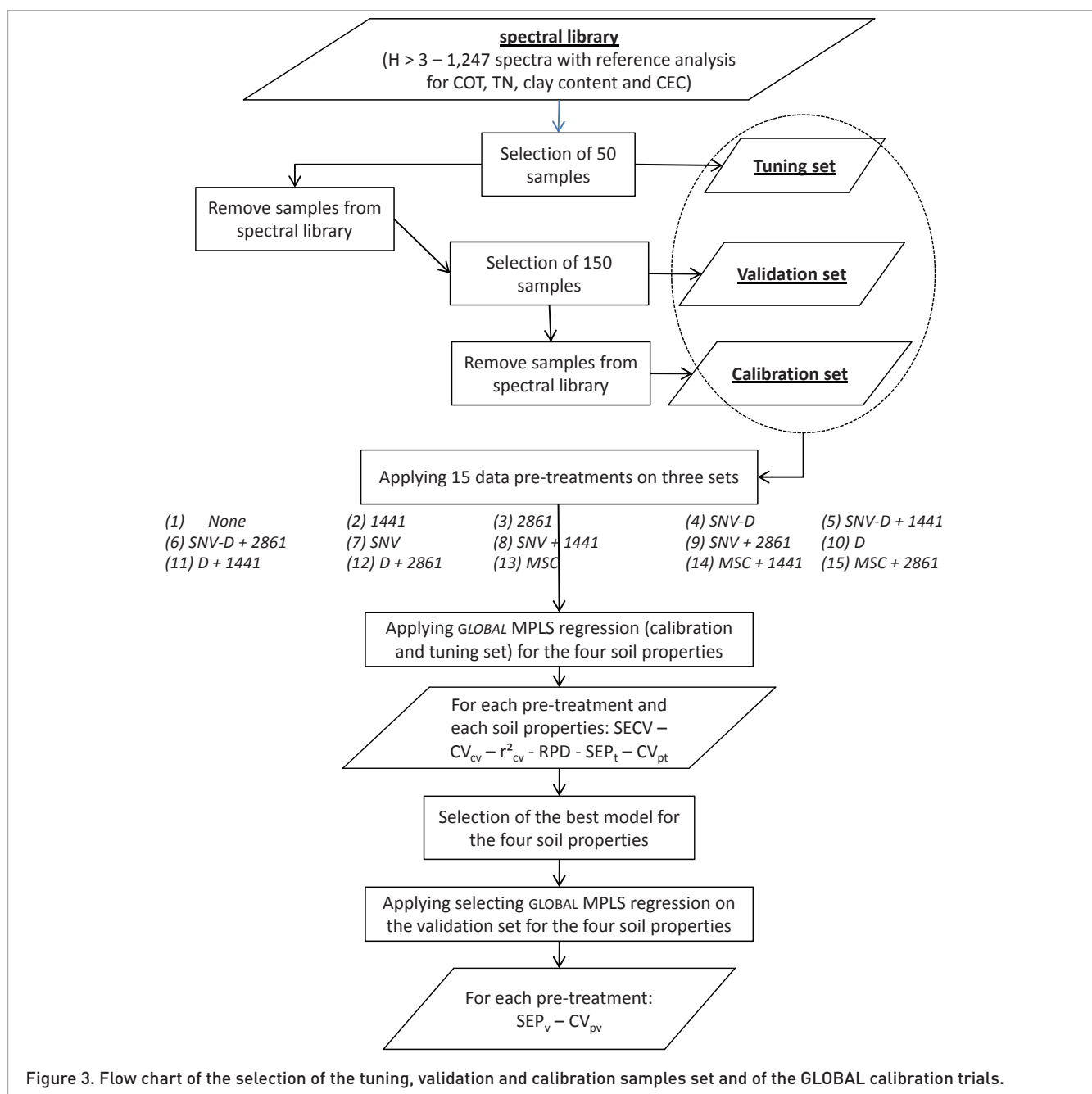
set, was considered to validate the choice of model for both GLOBAL and LOCAL approaches.

First, 50 soil samples were selected to form the tuning sample set. This number was determined to take into account both study feasibility and soil representativeness by selecting the samples on the basis of ancillary information. All the samples were classed following the criteria "land use", "topsoil/subsoil" and "soil units". Then, in each class, samples were randomly selected proportionally to the number of data in these classes. These 50 samples were therefore deleted from the spectral database. Then, the spectral database was split up into calibration and validation sets. To build a validation set representative of the population diversity, the methodology proposed by Minasny and McBratney⁷⁰ and applied by Viscarra-Rossel *et al.*⁷¹ was followed. This method, called "conditioned Latin hypercube sampling—cLHS", allows the selection of a representative sample set by taking into account the location of the samples, some ancillary information and the main NIR spectral characteristics. These last were defined as the first five PCs of the PCA, after a SNV pre-treatment. The algorithm was carried out on MatLab software, v7.1 (The Mathworks, Inc., Natick, MA, USA). One hundred and fifty samples, covering all the Walloon Region and representative of the soils and spectral diversity were therefore selected from the spectral library to compose the validation sample set. The remaining samples constituted the calibration sample set (Figure 2).

Once the calibration stage is achieved, the original spectral library containing all the spectra of the three sets, outliers excluded, will be used by the soil laboratories to routinely predict the studied soil properties, as suggested by Dardenne and Fernandez-Pierna⁷²—"Using a tuning set is useful and necessary to optimise the parameters of the modelling, but we suggested, by experience, keeping everything equal, to recalculate the final model, the one which will be used in real time in the lab by using all the information available." This means merging calibration, tuning and validation sets.

Spectral data pre-treatment and GLOBAL MPLS calibration

GLOBAL calibrations were obtained by using a MPLS regression technique available in the WinISI software (Infrasoft International, LLC). This method is the classical PLS algorithm with a standardisation of the X residuals at each iteration. This regression technique requires cross-validation to prevent over-fitting, by partitioning the calibration set into several groups (ten in this study). As NIR spectra are affected by particle size, scatter coefficient and pathlength variation, pre-treating the spectral data, before applying MPLS calibration, improves the prediction.⁶² The full spectrum can be corrected in several ways and the best spectral pre-treatment, which may be a combination of several pre-treatments, has to be chosen and can differ for each predictive parameter. Fifteen pre-treatments were compared for each soil characteristic and that, given the more accurate results, was selected based on the tuning set. Then the selected model was applied on the validation set.



The fifteen pre-treatments are a combination of those four:

- (i) detrend (D) removes the linear and quadratic curvature of each spectrum;⁵⁵
- (ii) standard normal variate (SNV) reduces the light scattering caused by particle size effects. Each corrected value is the original absorbance from which the mean of the whole spectrum is subtracted and divided by the standard deviation of the spectrum;⁶²

- (iii) multiplicative scatter correction (MSC) eliminates or reduces the difference in light scatter between samples.

- (iv) first (1_4_4^a) or second (2_8_6) derivatives of the data to remove part of the particle size influence;⁸

The flow chart of the GLOBAL calibration trials, including the selection of the three data sets, is given in Figure 3. The number of PLS components to be used for those models was chosen by minimising the SEP_t . The models were compared according to

^a1_4_4 or 2_8_6: first number represented the number of the derivative (first or second derivative), second number represented the gap between wavelength over which derivative is calculated and third number represented the smoothing of the points

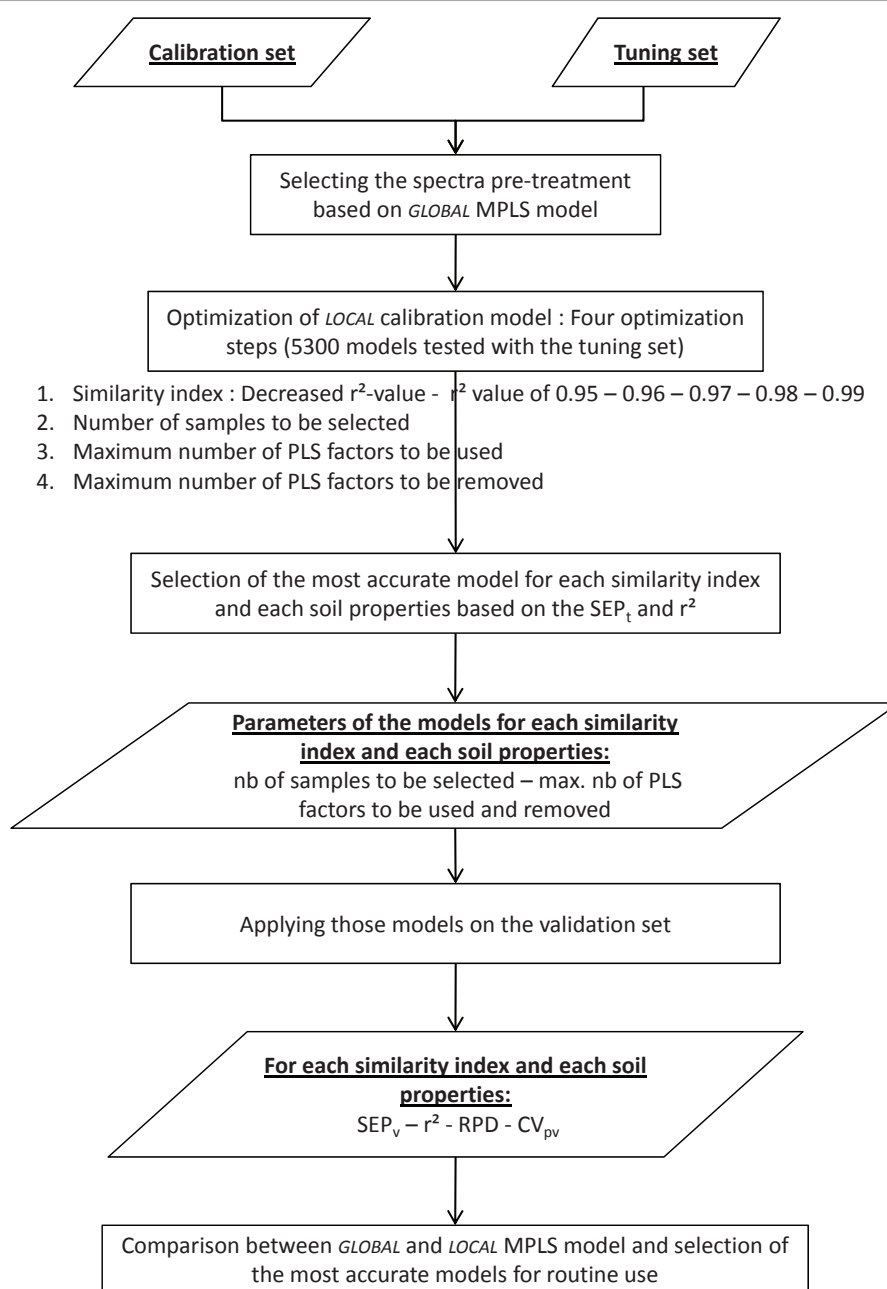


Figure 4. Flow chart of the LOCAL calibration trials.

the following criteria: $SECV$, SEP_t (SEP obtained with the tuning set) or SEP_v (SEP obtained with the validation set), the determination coefficient (r^2 value), the ratio of prediction to determination = SD/SEP (RPD), the cross-validation coefficient of variation, ratio of the $SECV$ to the calibration sample set mean, expressed in % (CV_{cv}) and the prediction coefficient of variation, ratio of the SEP to the tuning or validation sample set mean, expressed in % (CV_{pt} or CV_{pv}). The RPD criterion takes into account the variability of the database. It is a useful indicator to compare results obtained using diverse databases, or results in the literature. In comparison to the $SECV$ or SEP , working with the CV allows a comparison between the methods whatever the mean value, the set, or the studied property.

LOCAL MPLS calibration

The LOCAL calibrations were performed using the same pre-treatments as for the GLOBAL calibration. As considered by Sinnavee *et al.*,⁶² it was assessed that the best pre-treatment in the GLOBAL calibration step would also be the best in the LOCAL procedure. As detailed in the flow chart in Figure 4, four calibration parameters remained to be optimised, based on the tuning set. Then the validation set samples were analysed using the best optimised model. These four parameters were⁶¹:

(i) the similarity index, based on the r^2 value between the spectrum to be predicted and the spectra to be selected in the calibration set. The neighbourhood distance was not

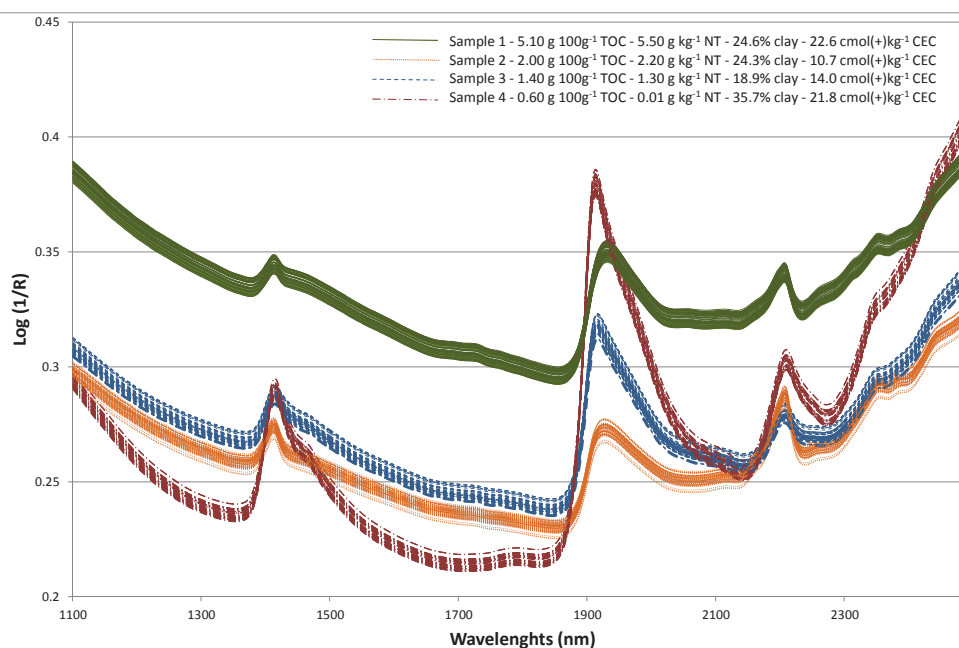


Figure 5. Spectra of the four samples used for the repeatability and intra-laboratory reproducibility evaluation.

considered in this study, as the final users of the model (REQUASUD network laboratories) work with the ISIScan software in which the LOCAL MPLS regression is based on r^2 value. The model selects the fixed number of samples by decreasing r^2 value. Furthermore, checks were made by fixing the similarity index (r^2 value) between the spectra. This means that if there were not enough correlated samples based on the fixed r^2 value, the sample was not predicted. The tested fixed r^2 values were: 0.95, 0.96, 0.97, 0.98 and 0.99;

(ii) the number of the closest samples in the spectral space to be used in the MPLS regression, the tested progressive number of sample was between 50 and 260 samples with steps of 10;

(iii) the maximum number of PLS components. Three to 21 PLS factors were tested with steps of 2;

(iv) the maximum number of PLS components which may be ignored. Three to 11 PLS factors to be removed were tested with steps of 2.

Testing all those criteria meant trying 5300 possibilities for each of the 50 samples of the tuning set.

Finally, the model was applied to the validation set in order to evaluate the prediction accuracy and was compared to that obtained with the GLOBAL model.

Evaluation of the repeatability and reproducibility of the method

In order to evaluate the repeatability and reproducibility of the technique for the four soil characteristics (TOC, TN, clay content and CEC), the sensitive spots of the method were identified and a methodology to evaluate them was elaborated. They were (i) machine error, (ii) sample presentation error–QC–,

(iii) operator error–O– and (iv) time error–Ti–. Four samples used in the section on NIR spectroscopy measurements (S) were selected, to check if the repeatability and reproducibility errors depend on the concentrations. Two hundred and eighty-eight spectra (Figure 5) were thus recorded in a spectral database.

To evaluate machine error, each QC was scanned three times without removing it from the spectrometer. For the sample presentation error, four QCs were filled up for each sample and by each operator. Two operators lead this experimentation which was repeated three times to evaluate the time error. Only the intra-laboratory reproducibility (intermediate precision) was evaluated, meaning that the test was performed in the same laboratory with an added time factor. In the next paragraph, intra-laboratory reproducibility is called reproducibility.

The predictions were made for each spectrum and for the four soil characteristics using the selected LOCAL MPLS model. An outlier detection test (Cochran and Grubs tests⁷³) was then carried out on the predicted values. The Cochran method is used to identify outliers between replicated objects. The Grubbs test aims at detecting the outlier based on the mean. The means of each three repetitions were compared to identify which one was too far from the scatter diagram. For the estimation of repeatability and reproducibility, the variance components were evaluated through ANOVA based on a partially nested design. The factors “time –Ti–”, “operator –O–”, “sample –S–” are crossed and random. The repeatability standard error corresponds to the residual error⁷³ (1), while the reproducibility standard error is the sum of all the errors (time, operator, sub sampling, interactions and residual error)⁷³ Equation (2).

$$s_r = s_{error} = \sqrt{MS_{error}} \quad (1)$$

$$s_R = \sqrt{vc_{Tl}^2 + vc_0^2 + vc_{Tl*0*s}^2 + s_r^2}; \quad vc = \text{variance component} \quad (2)$$

The repeatability is equal to Equation (3):

$$r = 1.96 \times \sqrt{2} \times s_r \quad (3)$$

and the reproducibility (intermediate precision) is determined by Equation (4):

$$R = 1.96 \times \sqrt{2} \times s_R \quad (4)$$

The precision of the NIR technique can be determined by this methodology and compared to reference chemical procedures. The global predictive error (*SEP*) includes the reproducibility error of the NIR technique, but also the analytical reproducibility error (s_{Ra}) and the lack of fit (s_{lf}). As, in this study, the samples were scanned in duplicate, the relationship between *SEP* and s_R is as follows [Equation (5)].

$$SEP^2 \sim s_{lf}^2 + \frac{s_R^2}{2} + s_{Ra}^2 \quad (5)$$

Results and discussion

Analytical results of the three sample sets

The characteristics of the three sample sets are presented in Table 2. A wide range of values was covered for each parameter in the calibration set which is representative of the whole population diversity.⁶⁴ We observed that even if the selection of the validation set was not based on the analytical results, the range of values covered is similar to those observed for the calibration sub-set. For the TN content, the validation sub-set included a smaller number of samples due to the fact that reference chemical analyses were not performed on every subsoil samples.

Results of the sample preparation study

As detailed in Table 3, differences between tests, operators and sub-samplings were highlighted, meaning that the four tests (tipping, spoon filling, spoon filling and packing, spoon filling and lid packing) gave different responses. The variance linked to the sample was not taken into account in our interpretation as its variability did not affect our study. Effect of operator and also interaction between test and samples were significant. As interactions were significant, ANOVA was conducted for each test, which also allowed variance components evaluation as detailed in Table 4. The mean comparison test indicated that, except between tests 2 and 3, each test was different. Those results emphasised the importance of applying a sample preparation procedure for both calibration study and routine application. Interactions between samples and operator or test gave interesting information about the influence of the soil nature on the robustness of the procedure. The results of the variance

Table 2. Characterization of the calibration, tuning, and validation subsets for each studied soil properties.

	TOC content (g 100g ⁻¹)		TN content (g kg ⁻¹)		Clay content (%)		CEC (cmol(+) kg ⁻¹)	
	Calibration set	Validation set	Calibration set	Validation set	Calibration set	Validation set	Calibration set	Validation set
Mean	2.2	3.1	1.6	1.83	21.2	19.1	14.6	13.3
Standard deviation	2.66	2.20	2.05	1.29	9.65	7.26	8.36	6.42
Minimum	0.1	0.8	0.1	0.20	1.5	6.6	0.6	0.8
First quartile	0.6	1.3	0.3	1.00	15.6	13.4	9.7	10.0
Median	1.3	2.3	0.8	1.25	19.9	18.6	13.0	12.4
Third quartile	2.7	4.6	1.6	2.23	24.9	23.4	16.8	14.5
Maximum	24.1	9.4	10.4	5.40	70.6	48.1	91.6	37.0
Number of samples according to land use								
All	1121	50	138	62	786	50	1105	148
Crop	425	26	59	29	335	27	424	66
Grassland	121	4	28	14	128	10	128	3
Forest and others	575	20	55	20	323	13	553	25
Number of top and subsoil samples								
Topsoil	602	50	53	43	284	50	543	54
Subsoil	519	0	85	19	502	0	562	94

Table 3: Comparison of the sample preparation procedures: result of the variance analysis, partially nested design, for the five first principal components (PC).

Source of variation	DF	First PC			2 nd PC			3 rd PC			4 th PC			5 th PC		
		MS	F	P	MS	F	P	MS	F	P	MS	F	P	MS	F	P
Test	3	0.011	0.9	0.48	0.048	12.7	0.00	0.004	0.8	0.53	0.008	2.2	0.13	0.003	0.8	0.52
Operator	1	0.018	12.7	0.00	0.036	14.8	0.00	0.057	58.1	0.00	0.010	47.9	0.00	0.007	85.5	0.00
Sample	5	25.882			11.678			7.278			2.659			0.611		
Quarter cup within test, operator and sample	48	0.003	6.0	0.00	0.001	7.8	0.00	0.001	11.1	0.00	0.001	10.3	0.00	0.001	10.1	0.00
Interaction test and operator	3	0.001	0.4	0.79	0.000	0.5	0.70	0.000	0.0	0.99	0.000	1.4	0.25	0.000	0.3	0.83
Interaction test and Sample	15	0.015	6.1	0.00	0.004	14.0	0.00	0.006	12.6	0.00	0.003	11.7	0.00	0.004	16.7	0.00
Interaction operator and sample	5	0.003	1.3	0.29	0.003	9.1	0.00	0.001	3.2	0.01	0.000	0.3	0.89	0.000	0.5	0.75
Interaction test, operator and sample	15	0.002	0.8	1.00	0.000	0.2	0.10	0.000	0.4	0.98	0.000	0.4	0.99	0.000	0.3	0.10
Residual error	96	0.001			0.000			0.000			0.000			0.000		

DF: degree of freedom

F: F observed; P-value. If $P > 0.05$ = reject of the null hypothesis

analysis indicated that the nature of the soil principally affects the variability between the four tests.

To select which of the four procedures to apply, the intra-variability of each test was studied. The variance components linked to the operator error, sub-sampling error, interaction and residual error were estimated (Table 4). The minimum sum of variance components was obtained for test 2 which was therefore applied in the next stages of the study. The intra-variability of test 1 was high in comparison to the other tests, emphasising the importance of particle size effects in NIR analyses. When tipping the soil into the QC, the granulometric differentiation within the cup was far more important than that observed when using a spoon.

GLOBAL PLS model, comparison of 15 spectral pre-treatments

In this section, 15 spectral pre-treatments (first—1 4- and second—2 8 6- derivatives, SNV, detrend, multiplicative scatter correction and a combination of two or three of them) were compared using the MPLS regression. The number of PLS factors was chosen to be at the first minimum of the SEP_t . As detailed in Table 5, the spectral pre-treatments giving the best prediction accuracy (SEP_t or CV_{pt} minimum) were the SNV and detrend for the TOC content, the SNV and first derivative for the TN content, the MSC and second derivative for the clay content and the detrend and second derivative for the CEC. The CV_{pt} were around 30% for clay content, 35% for the TOC and CEC and 75% for TN content. A single spectral pre-treatment for the prediction of the four soil properties is thus not an appropriate solution for our study.

The $SECV$ values obtained for the cross validation were lower than that obtained for the tuning set (SEP_t), except for clay content. Overestimation, due to cross validation, was around 10%, 30% and 60% for TOC, TN content and CEC, respectively.

The $SECV$ or SEP were higher than those linked to the chemical procedures and much higher than those found in the literature for NIR analyses for authors working with more than 500 samples covering different soils units. For TOC content, Chang *et al.*⁸ and Brown *et al.*⁶ obtained a SEC of $0.79 \text{ g } 100 \text{ g}^{-1}$. Shepherd and Walsh²³ and Islam *et al.*²⁷ found a SEC of $0.22 \text{ g } 100 \text{ g}^{-1}$. Finally, Mc Carthy and Reeves³⁰ obtained a SEC of $0.16 \text{ g } 100 \text{ g}^{-1}$. The results found for TN content were 0.62 g kg^{-1} for Chang *et al.*,⁸ 0.22 g kg^{-1} for Islam *et al.*,²⁷ 0.16 g kg^{-1} for McCarty and Reeves.³⁰ For clay content, Chang *et al.*,⁸ obtained a SEC of 4.1%, Shepherd and Walsh²³ and Brown *et al.*⁶ found a SEC of 5.4% and McCarty and Reeves³⁰ obtained a SEC of 1.8%, but for a wider range of value (11.0% to 29.0%). For CEC, results are $3.82 \text{ cmol(+) kg}^{-1}$ for Chang *et al.*,⁸ $2.60 \text{ cmol(+) kg}^{-1}$ for Shepherd and Walsh,²³ $4.88 \text{ cmol(+) kg}^{-1}$ for Islam *et al.*²⁷ and $5.5 \text{ cmol(+) kg}^{-1}$ for Brown *et al.*⁶

The graphics in Figure 6 collate the results obtained for the best GLOBAL PLS model with the reference methods. It can be noticed that the clouds of points obtained for TOC and clay content present a wider scattering with increasing values. On the contrary, clouds of points obtained for TN content and CEC are independent of the data range.

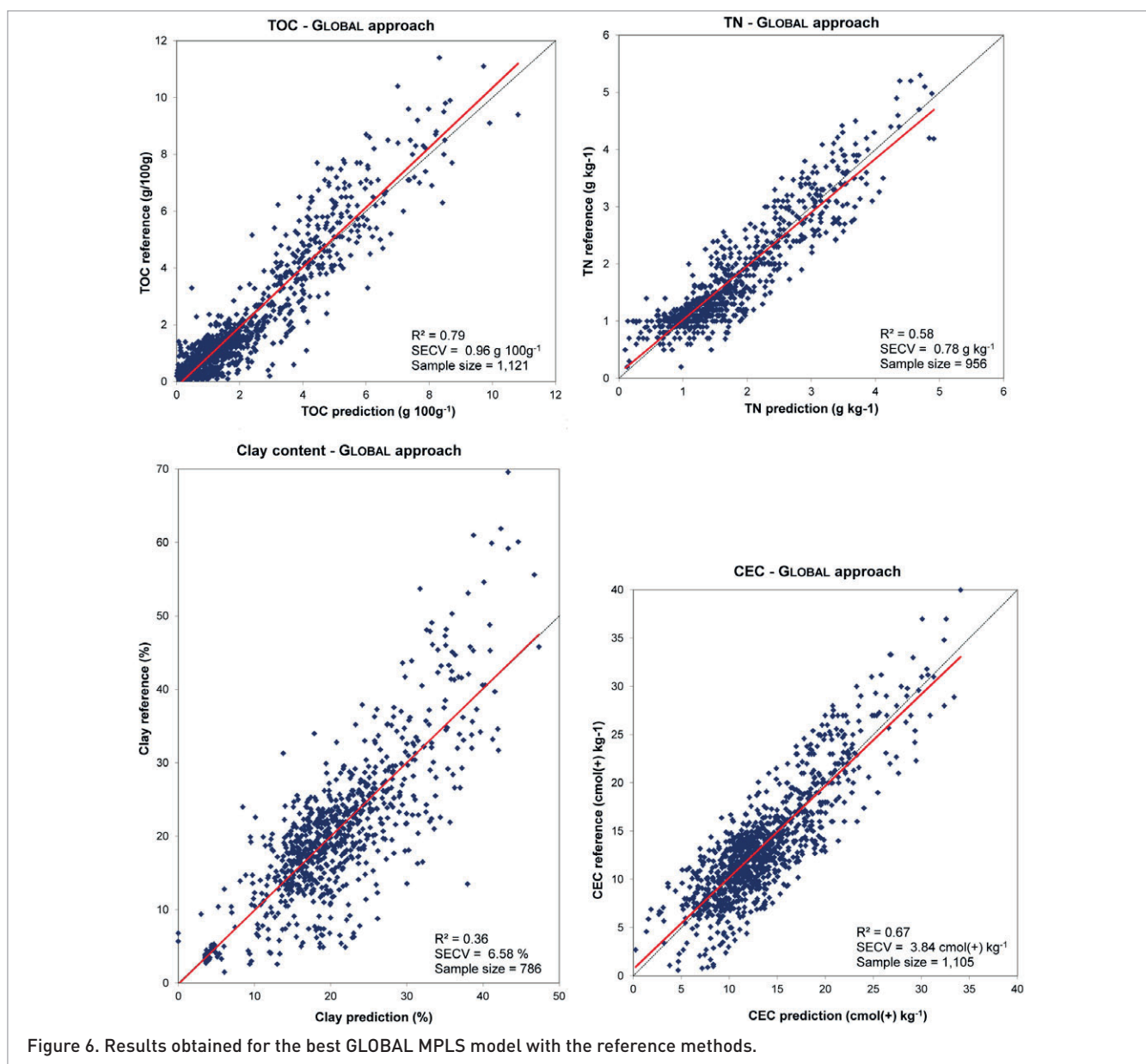
Table 4. Comparison of the sample preparation procedures: sum of the variance components for the four tests and for each of the five principal components (PC).

	First PC	2 nd PC	3 rd PC	4 th PC	5 th PC	TOTAL
Test 1	0.0079	0.0033	0.0036	0.0023	0.0025	0.0201
Test 2	0.0007	0.0004	0.0008	0.0001	0.0001	0.0022
Test 3	0.0006	0.0007	0.0008	0.0002	0.0002	0.0025
Test 4	0.0012	0.0006	0.0008	0.0003	0.0002	0.0032

Table 5. Results obtained for the global MPLS regression optimised to select the best pre-treatment to be used in a prediction aim (number of PLS factors chosen to be at the first minimum of the SEP_t based on the tuning set).

TOC content															
Pre-treatment	/	144	286	SNV D	SNV D+144	SNV D+286	SNV	SNV+144	SNV+286	D	D+144	D+286	MSC	MSC+144	MSC+286
Nb. PLS factors	6	3	5	8	5	4	10	4	4	7	3	5	4	2	6
SECV	1.12	1.17	0.95	0.96	0.92	0.90	0.87	1.00	0.90	1.10	1.15	0.94	1.25	1.14	0.90
R^2_{cv}	0.72	0.71	0.80	0.79	0.81	0.81	0.82	0.77	0.82	0.75	0.71	0.81	0.63	0.69	0.81
SEP_t (g 100g ⁻¹)	1.44	1.18	1.32	1.06	1.14	1.16	1.07	1.13	1.15	1.28	1.27	1.31	1.29	1.18	1.09
RPD_{pt}	1.53	1.86	1.67	2.07	1.93	1.90	2.06	1.95	1.91	1.72	1.73	1.68	1.70	1.86	2.02
CV_{pt} (%)	46.6	38.2	43.2	34.5	37.2	37.8	34.9	36.8	37.5	41.8	41.4	42.8	41.6	38.1	35.7
TN content															
Pre-treatment	/	144	286	SNV D	SNV D+144	SNV D+286	SNV	SNV+144	SNV+286	D	D+144	D+286	MSC	MSC+144	MSC+286
Nb. PLS factors	3	5	3	4	2	4	3	8	4	4	4	3	2	5	5
SECV	0.88	0.86	0.82	0.92	1.01	0.77	1.01	0.78	0.78	0.86	0.82	0.82	1.06	0.90	0.78
R^2_{cv}	0.39	0.49	0.52	0.34	0.27	0.58	0.20	0.58	0.57	0.45	0.52	0.54	0.15	0.41	0.56
SEP_t (g kg ⁻¹)	1.15	1.07	1.04	1.16	1.17	1.03	1.2	1.01	1.03	1.13	1.06	1.04	1.21	1.07	1.04
RPD_{pt}	1.15	1.23	1.27	1.14	1.13	1.28	1.10	1.31	1.28	1.17	1.25	1.27	1.09	1.23	1.27
CV_{pt} (%)	86.3	80.1	78	87.4	88.0	77.7	90.0	75.9	77.4	85.3	79.3	77.8	91.1	80.8	78.5
Clay content															
Pre-treatment	/	144	286	SNV D	SNV D+144	SNV D+286	SNV	SNV+144	SNV+286	D	D+144	D+286	MSC	MSC+144	MSC+286
Nb. PLS factors	3	2	2	4	1	3	2	5	3	1	2	2	1	3	2
SECV	6.99	6.64	6.5	6.58	7.62	6.25	7.39	6.04	6.19	7.92	6.62	6.48	7.43	6.89	6.58
R^2_{cv}	0.32	0.38	0.37	0.34	0.12	0.42	0.18	0.46	0.42	0.12	0.39	0.37	0.14	0.29	0.36
SEP_t (%)	6.12	5.99	5.80	6.11	6.66	5.96	6.66	5.83	5.93	6.69	6.15	5.83	6.67	5.94	5.62
RPD_{pt}	1.39	1.43	1.41	1.33	1.22	1.37	1.23	1.41	1.37	1.26	1.38	1.40	1.20	1.37	1.46
CV_{pt} (%)	32.1	31.1	30.7	32.3	35.3	31.6	34.9	30.9	31.4	35.4	32.4	30.9	35.1	31.3	29.8
CEC															
Pre-treatment	/	144	286	SNV D	SNV D+144	SNV D+286	SNV	SNV+144	SNV+286	D	D+144	D+286	MSC	MSC+144	MSC+286
Nb. PLS factors	6	4	6	5	3	6	6	6	6	4	3	6	6	5	4
SECV	4.49	4.23	3.79	4.79	4.91	4.00	4.92	4.49	4.02	5.12	4.43	3.84	4.85	4.63	4.29
R^2_{cv}	0.51	0.61	0.68	0.42	0.43	0.62	0.40	0.53	0.62	0.40	0.56	0.67	0.40	0.49	0.55
SEP_t (cmol(+)kg ⁻¹)	7.9	7.3	7.1	7.4	7.7	7.4	7.4	7.6	7.4	7.6	7.5	7.0	7.6	7.4	7.1
RPD_{pt}	1.15	1.24	1.28	1.23	1.18	1.23	1.23	1.20	1.23	1.20	1.21	1.30	1.20	1.23	1.28
CV_{pt} (%)	42.0	38.9	37.3	38.9	40.5	39.1	38.9	40.4	39.1	40.0	39.7	37.2	40.0	39.0	37.6

144: first derivative; 286: second derivative; SNV: standard normal variate; D: detrend; MSC: multiplicative scatter correction; SEP_t : root mean square error of prediction; RPD_{pt} : ratio of prediction to determination; CV_{pt} : prediction coefficient of variation



Even if the CEC is not a primary property of the NIR spectrum,⁸ the prediction worked well, better than that obtained by regressing TOC and clay content. The correlograms between each wavelength and CEC, TOC and clay content for the top- and subsoil samples (Figure 7) clearly illustrates the difference between CEC dependency on TOC and clay content. TOC content influence was dominant for the topsoil sample. A strong dependence on clay content was observed for subsoil samples containing less organic matter. However, other parameters, such as clay mineralogy and organo-mineral complex particularities, may also influence the accuracy of the CEC prediction and further investigations should be conducted.

When the best pre-treatment was selected based on the tuning set, the model was applied on the independent valida-

tion set samples to estimate the actual performance. SEP_v (Table 6) were around 1.14 g 100g⁻¹, 0.84 g kg⁻¹, 6.74%, and 5.10 cmol(+) kg⁻¹ for TOC, TN and clay content, and CEC, respectively. Those values can be considered as the expected error in routine use in laboratories for every new sample coming from the Walloon territory. The range of those errors is similar to that obtained with the tuning set, confirming the robustness of the model for the territory we studied.

The PLS LOCAL regression, comparison with the GLOBAL approach

To build the local model, the following criteria were optimised by predicting all the samples of the tuning set, based on the spectra pre-treatment found in the previous step: (i) similarity index, (ii) maximum number of samples to be selected, (iii)

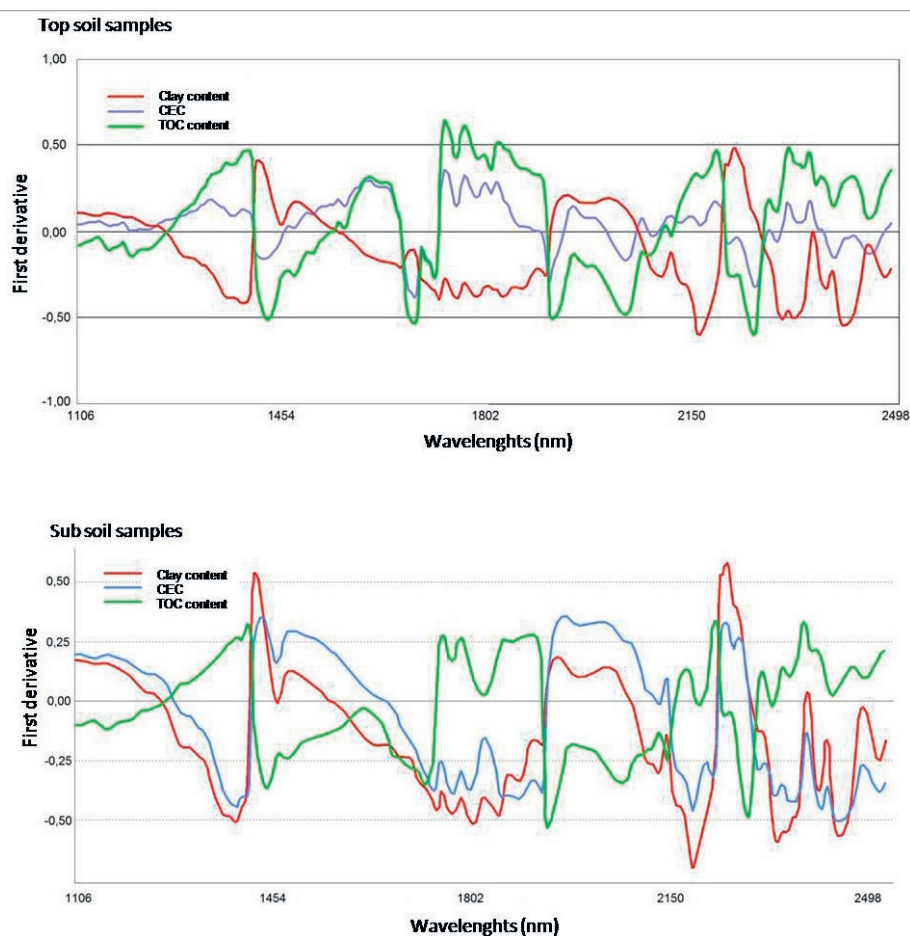


Figure 7. Correlogram between the wavelengths and the CEC, TOC and clay content for the top- and subsoil samples of the calibration data set.

maximum number of PLS factors to be used and (iv) maximum number of PLS factors to be removed. Each sample of the tuning set has been predicted 5300 times by combining all the criteria. For each combination, SEP_t , r^2 , RPD_t , and CV_{pt} were calculated and compared to allow selection of the most accurate model. Those results are not presented in this paper. Then, for each similarity index level, we applied the selected model on the validation sample set, as presented in Table 7, to

check the accuracy of the models. As not all the samples were predicted, mean and standard deviation of only the predicted samples were calculated for each similarity index level and taken into account for the evaluation of the CV_{pv} and RPD_v .

When decreasing similarity index was used ($\downarrow r^2$ value), as for the PLS global regression, this lack of prediction is due to the fact that outliers were removed (samples with a Mahalanobis distance, H , greater than 3). When a fixed similarity index

Table 6. Prediction of the validation set based on the global model for the four soil properties.

	TOC content ($\text{g } 100\text{g}^{-1}$)	TN content (g kg^{-1})	Clay content (%)	CEC ($\text{cmol}(+) \text{kg}^{-1}$)
Sample pre-treatment	SNV-D	SNV+144	MSC+286	D+286
Nb. Predicted samples	137/138	62/62	150/150	148/148
SEP_v	1.14	0.84	6.74	5.10
R^2_{pv}	0.70	0.61	0.41	0.43
RPD_v	1.80	1.54	1.30	1.26
CV_{pv} (%)	71.2	45.9	31.9	38.3

144: first derivative; 286: second derivative; SNV: standard normal variate; D: detrend; MSC: multiplicative scatter correction; SEP : root mean square error of prediction; RPD : ratio of prediction to determination; CV_p : prediction coefficient of variation

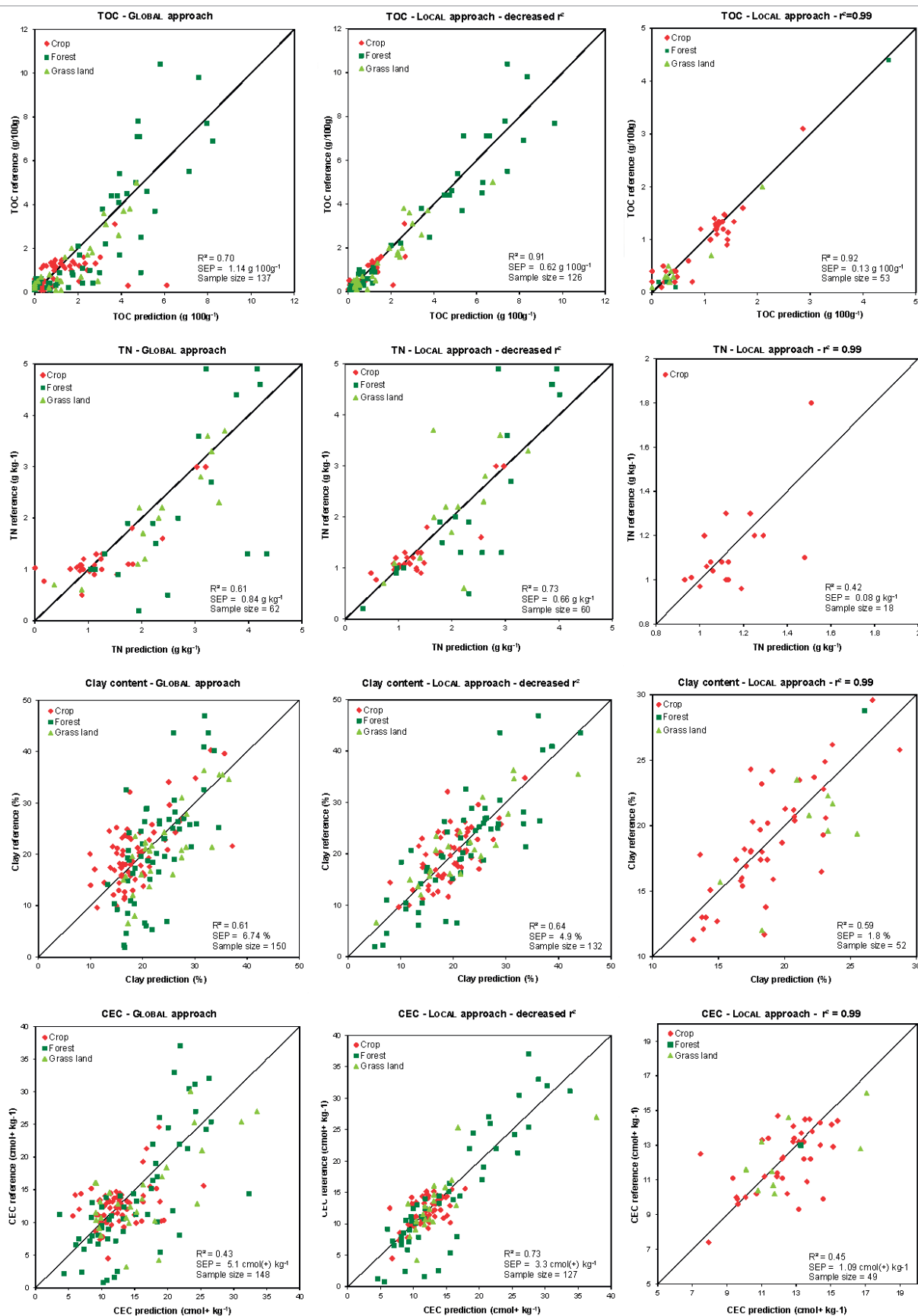


Figure 8. Results of the PLS GLOBAL and LOCAL regression models for the validation samples set.

Table 7. Accuracy of local MPLS model on the entire validation set after an optimisation based on the tuning set.

TOC content						
	Decreased r^2	Fixed r^2 0.95	Fixed r^2 0.96	Fixed r^2 0.97	Fixed r^2 0.98	Fixed r^2 0.99
Samples pre-treatment	SNV-D					
Max. nb. Samples ⁽¹⁾	70	70	100	70	60	170
Max. nb. PLS factors ⁽¹⁾	11	11	21	21	13	13
Max. nb. PLS factors to be removed ⁽¹⁾	9	9	3	11	11	11
Nb. Predicted samples ⁽²⁾	126/138	112/138	98/138	82/138	76/138	53/138
Av±sd of predicted samples (g 100 g ⁻¹) ⁽²⁾	1.59±2.11	1.57±1.98	1.57±1.92	1.66±2.01	1.37±1.85	0.85±0.79
SEP _v (g 100 g ⁻¹) ⁽²⁾	0.62	0.59	0.53	0.34	0.25	0.13
R ² _{pv} ⁽²⁾	0.91	0.90	0.92	0.92	0.92	0.92
RPD _v ⁽²⁻³⁾	3.40	3.36	3.62	5.91	7.40	6.08
CV _{pv} (%) ⁽²⁻³⁾	39.6	38.2	33.8	20.5	18.3	15.3
TN content						
	Decreased r^2	Fixed r^2 0.95	Fixed r^2 0.96	Fixed r^2 0.97	Fixed r^2 0.98	Fixed r^2 0.99
Samples pre-treatment	SNV+1441					
Max. nb. Samples ⁽¹⁾	70	150	120	120	120	110
Max. nb. PLS factors ⁽¹⁾	21	9	19	21	17	17
Max. nb. PLS factors to be removed ⁽¹⁾	11	9	15	11	11	11
Nb. Predicted samples ⁽²⁾	60/62	50/62	35/62	39/62	24/62	18/62
Av±sd of predicted samples (g kg ⁻¹) ⁽²⁾	1.85±1.29	1.92±1.27	1.71±1.20	1.68±1.11	1.29±0.51	1.13±0.20
SEP _v (g kg ⁻¹) ⁽²⁾	0.66	0.40	0.32	0.34	0.15	0.08
R ² _{pv} ⁽²⁾	0.73	0.87	0.93	0.86	0.79	0.42
RPD _v ⁽²⁻³⁾	1.95	3.18	3.75	3.26	3.4	2.5
CV _{pv} (%) ⁽²⁻³⁾	35.7	20.8	18.7	20.2	11.6	7.08
Clay content						
	Decreased r^2	Fixed r^2 0.95	Fixed r^2 0.96	Fixed r^2 0.97	Fixed r^2 0.98	Fixed r^2 0.99
Samples pre-treatment	MSC+2861					
Max. nb. samples ⁽¹⁾	70	150	120	120	120	110
Max. nb. PLS factors ⁽¹⁾	21	9	19	21	17	17
Max. nb. PLS factors to be removed ⁽¹⁾	11	9	15	11	11	11
Nb. Predicted samples ⁽²⁾	132/150	111/150	80/150	76/150	59/150	52/150
Av±sd of predicted samples (%) ⁽²⁾	20.65±8.09	20.28±6.69	20.06±6.66	19.12±5.88	18.98±5.63	18.88±4.73
SEP _v (%) ⁽²⁾	4.9	3.68	3.13	2.84	2.07	1.82
R ² _{pv} ⁽²⁾	0.64	0.66	0.65	0.61	0.68	0.59
RPD _v ⁽²⁻³⁾	1.65	1.82	2.13	2.07	2.72	2.60
CV _{pv} (%) ⁽²⁻³⁾	23.8	17.7	15.6	14.7	10.9	9.6
CEC						
	Decreased r^2	Fixed r^2 0.95	Fixed r^2 0.96	Fixed r^2 0.97	Fixed r^2 0.98	Fixed r^2 0.99
Samples pre-treatment	D+2861					
Max. nb. samples ⁽¹⁾	50	140	50	50	50	70
Max. nb. PLS factors ⁽¹⁾	20	22	8	8	10	18
Max. nb. PLS factors to be removed ⁽¹⁾	5	3	5	5	5	5
Nb. Predicted samples ⁽²⁾	127/148	99/148	89/148	77/148	55/148	49/148
Av±sd of predicted samples (cmol(+)kg ⁻¹) ⁽²⁾	13.15±6.31	13.35±6.54	13.19±6.21	12.83±5.36	11.93±3.32	11.98±2.38
SEP _v (cmol(+)kg ⁻¹) ⁽²⁾	3.29	2.81	2.49	1.68	1.42	1.09
R ² _{pv} ⁽²⁾	0.73	0.76	0.73	0.81	0.58	0.45
RPD _v ⁽²⁻³⁾	1.92	2.33	2.49	3.19	2.34	2.18
CV _{pv} (%) ⁽²⁻³⁾	25.0	21.0	18.9	13.1	11.9	9.1

(1) The selection of the most accurate number of samples, maximum number of PLS factors and maximum number of PLS factors to be removed were optimised by predicted the tuning set for each studied combination. The results obtained for each combination were not presented in the paper.

(2) Those parameters were determined on the validation sample set using the optimised parameters determined in (1)

(3) To obtain the RPD_v and the CV_{pv}, the standard deviation and the average of the predicted values were taken to avoid an over-estimation of those parameters as all the samples are not predicted.

Nb. Predicted samples: number of samples of the validation set predicted by the model; Av±sd of predicted samples: average and standard deviation of the predicted samples, as the number of predicted samples may be lower than the number of samples of the validation set; SEP: root mean square error of prediction; RPD: ratio of prediction to determination; CVp: prediction coefficient of variation

was applied, some samples were also considered as outliers and others were not predicted because of lack of correlated samples in the calibration sub-set. This explains why the number of predicted samples decreases when the value of the fixed similarity index increases.

Compared to the PLS global model, SEP_v or CV_{pv} with PLS local regression using decreasing similarity index ($\searrow r^2$ value), show an improvement in prediction accuracy for every soil characteristics (Figure 8). The CV_{pv} for global and local models are 71% vs 39%, 46% vs 36%, 32% vs 24% and 38% vs 25% for TOC, TN, clay content and CEC, respectively. The same observations were made for the RPD which increased when using PLS local model in comparison to global model (Tables 6 and 7). The RPD for global and local models were 1.80 vs 3.40, 1.54

vs 1.95, 1.30 vs 1.65 and 1.26 vs 1.92 for TOC, TN, clay content and CEC, respectively.

When using a fixed similarity index of 0.99, the accuracy of the models was improved (CV_{pv} of 10% in average) but the number of predicted samples decreased significantly; only one third of the samples being predicted. Two hypotheses may explain the more accurate predictions obtained when working with a higher similarity index, as observed in Table 7: (i) it might be due to the fact that the number of predicted samples decreases when the similarity index increases and, therefore, only the easily-predicted samples were kept which improved the overall prediction precision; (ii) the use of a higher similarity index allows a better selection of the spectra used to predict the unknown sample and, therefore, improves the

Table 8. Accuracy of global and local MPLS predictions for the “well-predicted” subset of validation set (v2).

TOC content	GLOBAL	LOCAL					
		Decreased r^2	Fixed r^2 0.95	Fixed r^2 0.96	Fixed r^2 0.97	Fixed r^2 0.98	Fixed r^2 0.99
Nb. Predicted samples -v2-		53/53					
Av \pm sd of predicted samples -v2- (g 100 g ⁻¹)		0.85 \pm 0.79					
SEP_{v2} (g 100 g ⁻¹)	0.50	0.20	0.20	0.17	0.19	0.20	0.13
RPD _{v2}	1.58	3.95	3.95	4.65	4.16	3.95	6.08
CV _{pv2} (%)	58.8	23.5	23.5	20.0	22.3	23.5	15.3
TN content	GLOBAL	LOCAL					
		Decreased r^2	Fixed r^2 0.95	Fixed r^2 0.96	Fixed r^2 0.97	Fixed r^2 0.98	Fixed r^2 0.99
Nb. Predicted samples -v2-		18/18					
Av \pm sd of predicted samples -v2- (g kg ⁻¹)		1.13 \pm 0.20					
SEP_{v2} (g kg ⁻¹)	0.24	0.19	0.14	0.16	0.15	0.15	0.08
RPD _{v2}	0.83	1.05	1.43	1.25	1.33	1.33	2.5
CV _{pv2} (%)	21.2	16.8	12.4	14.1	13.3	13.3	7.08
Clay content	GLOBAL	LOCAL					
		Decreased r^2	Fixed r^2 0.95	Fixed r^2 0.96	Fixed r^2 0.97	Fixed r^2 0.98	Fixed r^2 0.99
Nb. Predicted samples -v2-		52/52					
Av \pm sd of predicted samples -v2- (%)		18.88 \pm 4.73					
SEP_{v2} (%)	4.55	3.8	2.85	3.29	3.11	3.11	1.82
RPD _{v2}	1.04	1.24	1.66	1.44	1.52	1.52	2.60
CV _{pv2} (%)	24.1	20.1	15.1	17.4	16.5	16.5	9.6
CEC	GLOBAL	LOCAL					
		Decreased r^2	Fixed r^2 0.95	Fixed r^2 0.96	Fixed r^2 0.97	Fixed r^2 0.98	Fixed r^2 0.99
Nb. Predicted samples -v2-		49/49					
Av \pm sd of predicted samples -v2- (cmol(+) kg ⁻¹)		11.98 \pm 2.38					
SEP_{v2} (cmol(+) kg ⁻¹)	3.03	2.59	2.01	2.72	2.72	3.15	1.09
RPD _{v2}	0.78	0.92	1.18	0.88	0.88	0.76	2.18
CV _{pv2} (%)	25.3	21.6	16.8	22.7	22.7	26.3	9.1

Nb. Predicted samples: number of samples of the validation set predicted by the model; Av \pm sd of predicted samples: average and standard deviation of the predicted samples, as the number of predicted samples may be lower than the number of samples of the validation set; SEP: root mean square error of prediction; RPD: ratio of prediction to determination; CV_p: prediction coefficient of variation

prediction accuracy. To verify these two hypotheses, only the well-predicted samples with an r^2 value of 0.99 were selected from the validation sample set (53, 18, 52, and 49 samples for TOC, TN, clay content and CEC, respectively, as detailed in Table 7). The various models (global model, decreasing similarity index, fixed r^2 value of 0.95, 0.96, 0.97 and 0.98) were applied to predict these samples (validation sub-set, called v2) and the SEP_{v2} and CV_{pv2} were evaluated. All the samples were consequently well-predicted whatever the model (Table 8). Our interpretation of the obtained SEP_{v2} and CV_{pv2} was based on the following reasoning: the same SEP_{v2} or CV_{pv2} for every model would mean that an equal quality between the models was obtained and, therefore, that a higher similarity index is only an indicator to evaluate the prediction precision; a more reliable indicator than the Mahalanobis distance, as more samples are dismissed. In contrast, if the SEP_{v2} or CV_{pv2} decreases with higher similarity index, it would mean that it improves the prediction accuracy by a better selection of the correlated spectra and, thus, that the global accuracy of the model is improved. Data in Table 8 indicate that a similarity index of 0.99 improves the prediction accuracy. The global model gives the highest values of SEP_{v2} and working with a similarity index of 0.95, 0.96, 0.97 or 0.98 gives similar results as working with decreasing similarity index. However, if an r^2 value of 0.99 is used, then the CV_{pv2} are significantly minimised and prediction accuracy improved; hypothesis 2 is thus verified. For routine applications, it is therefore advised to use a similarity index of 0.99 when working with local PLS regression for the prediction of the four studied soil characteristics in the Walloon region.

As illustrated in Figure 8, the crop soil samples were better predicted than those from grassland or forest. On average, 80% to 90% of the crop soil samples in the validation set were well predicted when using and R^2 of 0.99 as the similarity index. It therefore means that the number of crop soil samples in the calibration sub-set is nearly optimal to predict those soils. In contrast, the number of recorded grassland and forest soil samples was not sufficient. It is essentially linked to higher variability for those soils than for the crop soils. Consequently, there were not enough correlated samples in the calibration data set to predict the grassland or forest soil samples. This hypothesis will be confirmed when NIR analyses are used

in routine applications; the non-predicted samples will be analysed following reference chemical analysis and will be added to the spectral library.

For routine applications, it is advisable to work with the LOCAL model based on the fixed r^2 value of 0.99. If the sample is predicted with this model, the results should be very reliable. If it is only predicted by using the model with decreasing r^2 value, more caution should be taken. It should only be considered as a correct estimation of the true value of the sample.

To improve, in the long term, the prediction precision, the principle of the spectral library developed by Shepherd and Walsh²³ will be applied: a selection of the unpredicted samples will be analysed following the standard procedures and added to the spectral library. In a further study, the rules to select the most contrasted spectra which should be analysed and added in the spectral library to improve the prediction accuracy will be determined.

Evaluation of the repeatability and reproducibility of the NIR technique

The outlier detection test highlighted one result for TOC content (following the Cochran test), three for TN content (Cochran), clay content (one following the Cochran test and two following the Grubbs test) and CEC (Cochran). Those results may suggest that the determination of TOC content by NIR spectroscopy is less sensitive to the sample heterogeneity (particle size effect) than the three other soil properties. The partially nested analysis of variance was applied to the results in order to evaluate the variance components and thus to calculate repeatability and reproducibility (Table 9) of each parameter.

Similar repeatability values were obtained for TOC and TN content, with an $r\%$ lower than 5%. The highest value was observed for clay determination. The same observations were made for reproducibility values. In ISO 14235⁶⁵ (TOC content analysis), the estimated repeatability value is 6.5%, thus higher than that obtained with NIR spectroscopy. In ISO 11261⁶⁶ (TN content analysis), the given repeatability values for four samples (1.9 g kg^{-1} to 10.9 g kg^{-1}) are 17% to 7%, thus higher than those calculated for NIR. The reproducibility values were 77% to 23% for the same samples, thus also higher than for NIR spectroscopy. For the clay content and the CEC, there are no data in the ISO standards; values obtained with NIR

Table 9. Results of the repeatability and intra-laboratory reproducibility studies for TOC, TN and clay content, and CEC.

	Repeatability				Reproducibility			
	s_r	$s_r\%$	r	$r\%$	s_R	$s_R\%$	R	$R\%$
TOC content ($\text{g } 100\text{g}^{-1}$)	0.001	1.62	0.11	4.48	0.008	3.82	0.25	10.59
TN content (g kg^{-1})	0.002	1.55	0.12	4.30	0.005	2.63	0.20	7.29
Clay content (%)	0.83	3.50	2.30	9.71	1.82	7.67	5.04	21.27
CEC ($\text{cmol}(+) \text{kg}^{-1}$)	0.19	2.49	1.22	6.91	0.81	5.10	2.49	14.14

s_r : standard error of repeatability (%; expressed in percent); r : repeatability error (%; expressed in percent); s_R : standard error of reproducibility (%; expressed in percent); R : reproducibility error (%; expressed in percent)

Table 10. Weight of the standard error of reproducibility (s_R) in the *SEP* in comparison to the lack of fit (s_{lf}) and the reproducibility analytical error (s_{Ra}).

	<i>SEP</i>	s_R	s_{Ra}^*	s_{lf}
TOC content (g 100 g ⁻¹)	0.62	0.008	0.03	0.61
TN content (g kg ⁻¹)	0.66	0.005	0.05	0.65
Clay content (%)	4.9	1.82	2.0	4.3
CEC (cmol(+) kg ⁻¹)	3.3	0.81	1.3	3.0

s_{Ra} as observed in the Soil Science Unit of Gembloux Agro-Bio Tech (University of Liege)

techniques can be compared to studies led in our laboratory where r^2 is around 8% for clay content and CEC. This study indicates that NIR analysis is as reliable as the analytical methods for determination of TOC, TN, clay content and CEC.

The relationship (5) was used to evaluate the weight of the repeatability and reproducibility standard error in the *SEP*. Even if this equation is an approximation, the results (Table 10) indicate that the parts of the reproducibility error due to NIR analysis and to analytical methods are negligible in comparison to the lack of fit for the four studied soil properties.

Conclusion and perspectives

NIR spectroscopy can be used as a rapid analytical technique to simultaneously estimate several soil characteristics (TOC, TN, clay content and CEC) with acceptable accuracy in a very short time and, therefore, can be used to improve the fertility diagnosis.

The LOCAL MPLS models, using a similarity index, r^2 value of 0.99, gives the most accurate results for the four soil properties, in comparison to the GLOBAL MPLS regression. In the Walloon Region, it is thus recommended for routine work to apply the LOCAL MPLS model with a similarity index of 0.99. At present, the soil crop samples are well predicted for the four studied soil characteristics. However, in the spectral library, a lack of samples covering the diversity of the grassland and forest soils has been emphasised, meaning that few grassland and forest soil samples are well-predicted. To improve, in the long term, the precision of prediction, the unpredicted samples should be analysed following standard procedures in order to add spectra and reference analysis in the spectral library. Thus, in a short period of time, if all the laboratories of the Walloon Region contributed to this action, the spectral library variability could be well covered and the prediction accuracy improved. The number of chemical analyses would then decrease every year.

The repeatability and reproducibility of the NIR technique are similar or lower than those obtained following chemical analysis. This technique is therefore as reliable as reference analysis and the lack of fit explains the major part of the standard error of prediction.

In this study, the similarity index was only based on the correlation between the sample to be predicted and some

spectra of the spectral library. Some further investigations will be conducted to test if the prediction accuracy would be improved by complementing this index with other criteria such as pedological information (based on texture or mineralogy for instance) and land use.

Even if the CEC is not a primary property of the NIR spectrum, the prediction worked well, better than that obtained by regressing TOC and clay content. It certainly means that other parameters such as the clay mineralogy and the organo-mineral complex particularities are taken into account by the NIR calibration model. Further investigations have to be conducted to evaluate the ability of the NIR technique to predict clay mineralogy and soil properties allowing an evaluation of the quality of the organic matter. These soil properties, which are not analysed routinely, may contribute to the diagnosis of soil fertility.

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