#### Synthèse

Les coûts des analyses en laboratoire et les temps nécessaires aux manipulations constituent toujours une contrainte majeure à l'évaluation de la fertilité des sols via leurs propriétés physico-chimiques. Cette contrainte est de plus en plus importante dès qu'il s'agit de travailler sur un grand nombre d'échantillons. La caractérisation des constituants et des propriétés physico-chimiques des sols par les techniques classiques nécessite des moyens coûteux en termes d'analyse. L'utilisation de techniques moins coûteuses, comme la Spectrométrie Moyen Infrarouge (SMIR) et Proche Infrarouge (SPIR), permettrait de multiplier les analyses des sols à réaliser. Ceci est particulièrement vrai pour les éléments minéraux des sols : les analyses minéralogiques nécessitent généralement l'utilisation d'équipements sophistiqués non disponibles dans la plupart des laboratoires d'analyses des sols. Toutefois, du fait de l'importance de ces éléments minéraux dans les processus d'échange, la rétention ou la (bio)disponibilité des nutriments, la quantification des teneurs des constituants minéraux serait d'un intérêt majeur.

Ce chapitre présente les résultats de nos recherches sur l'utilisation de la spectroscopie de réflectance infrarouge comme outil d'estimation des constituants minéraux du sol, évaluée sur une large gamme de sols fortement altérés à Madagascar.

À ce jour, seul un nombre limité d'études ont tenté de prédire quantitativement la composition minéralogique des sols tropicaux par la spectrométrie infrarouge (Soriano-Disla *et al.*, 2014 ; Vendrame *et al.*, 2012). Quelques résultats encourageants ont été obtenus pour quantifier les oxydes de fer (Ben-Dor *et al.*, 2006 ; Viscarra Rossel *et al.*, 2009). Pour la kaolinite et la gibbsite, les deux types d'argile les plus importants des sols tropicaux fortement altérés, Vendrame *et al.* (2012) ont fait des prédictions quantitatives du contenu minéralogique de sols brésiliens en utilisant des méthodes chimiométriques. Madeira *et al.* (1995) ont proposé une méthode utilisant des pics spécifiques de kaolinite et de la gibbsite. Néanmoins, des recherches sur ce thème sont encore nécessaires (Soriano-Disla *et al.*, 2014).

Les objectifs de cette étude étaient donc (i) d'étudier l'intérêt de la SMIR et de la SPIR pour mesurer la composition minéralogique sur une large gamme de sols fortement altérés à Madagascar; (ii) de comparer l'utilisation de méthodes chimiométriques, qui utilisent l'ensemble de spectres en tant que données d'entrée, et celle de méthodes basées sur l'analyse de pics spécifiques de minéraux.

Pour estimer les constituants minéraux du sol, diverses méthodes ont été testées afin de les modéliser à partir de SMIR et SPIR. Les résultats obtenus avec la SPIR se sont révélés être plus intéressants que ceux obtenus avec la SMIR. Les résultats obtenus avec la SPIR ont ainsi fait l'objet d'un article accepté à la revue Catena (Cf. Annexe 10), présenté ci-dessous. Des résultats sur la SMIR ont été présentés en tant que données complémentaires, en annexe de la thèse (Cf. Annexe 7). Une déconvolution des spectres SMIR a été également testée pour les analyses qualitatives des teneurs en oxydes et hydroxydes de Fe et d'Al et en kaolinite. Les corrélations entre les teneurs des constituants minéraux et les surfaces des pics déconvolués sont mauvaises et ne sont pas exploitables. Les résultats de la déconvolution sont également présentés à titre d'information à la fin de la thèse (Cf. Annexe 7). Article accepté par la revue Catena le 19 juillet 2017

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# Mineralogical analysis of ferralitic soils in Madagascar using NIR spectroscopy

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#### Abstract

The applicability of near-infrared reflectance spectroscopy (NIRS) as tool for estimating mineral soil constituents was assessed over a wide range of highly weathered soils in Madagascar. The predictions were based on two types of methods, chemometric methods using multivariate calibration models from partial least squares (PLS) regressions, and the use of spectral signatures of specific minerals. The predictions of mineralogical properties of soils using chemometric methods were poor, except for the quantification of iron oxides extracted with citrate-bicarbonate dithionite (CBD) ( $R_{cv}^2 = 0.80$ ). Soil minerals (kaolinite, gibbsite, goethite and hematite) were also estimated by NIRS but with less accuracy ( $R_{cv}^2 = 0.50 - 0.80$ ). The predictions of kaolinite and gibbsite contents were improved by the use of the peak intensity of the first derivative spectra, situated at around 2 205 nm for kaolinite and 2 265 nm for gibbsite. The results indicate that NIRS can be used as a rapid analytical technique to simultaneously estimate the main minerals of highly weathered ferralitic soils with acceptable accuracy. *Keywords:* Diffuse reflectance spectroscopy; Chemometrics; Diagnostic absorption peak; Soil mineral composition; Highly weathered tropical soils.

## Highlights

• NIR spectroscopy allowed estimating the main minerals of highly weathered tropical soils.

• Multivariate calibration with the full spectra was effective to predict iron oxide content.

• Derivatives of specific absorption peaks were effective to predict kaolinite and gibbsite contents.

### **1** Introduction

In highly weathered tropical soils, the dominant residual minerals, i.e. kaolinite, gibbsite, hematite and goethite, play a key role with organic matter, in soil behaviour through their effect on the sorption of nutrients, such as phosphorus (Eberhardt et al., 2008) or exchangeable cations and exchangeable aluminium (Vendrame et al., 2013). Information on soil mineralogical properties is important for effective and sustainable soil fertility management, basis for sustainable productivity. It is of utmost importance in sub-Saharan Africa (SSA), as well as in other tropical regions, where agricultural intensification becomes critical and imperative to overcome the prevailing food insecurity (Nziguheba et al., 2015). There is a great and urgent need for cost and time effective and relatively simple soil analytical methods or procedures that enable local institutions and authorities to obtain relevant information, such as soil quality index for different soils or agroecological regions, that support decision making for sustainable management for agriculture.

Soil analyses using traditional laboratory methodologies are generally expensive and often time consuming, restricting their use. The acquisition of large datasets on soil needs other technologies, such as sensing techniques (aircraft, satellite, on-the-ground spectroscopy etc.), to easily and accurately measure soil properties (Minasny and Hartemink, 2011). Infrared reflectance spectroscopy is accepted as a fast and non-destructive method to evaluate the components and properties of soils, and is considered as a possible alternative to improve or replace the conventional laboratory methods of soil analysis (Janik et al., 1998; Stenberg et al., 2010). Spectroscopy has also advantages over some of the conventional techniques, e.g. it is rapid, less expensive and more environmentally friendly (Viscarra Rossel et al., 2006b).

Extensive literature exploits spectroscopy to predict soil components, soil organic matter and minerals, using spectroscopic techniques (Cécillon et al., 2009; Nocita et al., 2015; Shepherd and Walsh, 2002; Soriano-Disla et al., 2014; Viscarra Rossel et al., 2006b). For tropical soils, a large number of studies deal with the prediction of soil organic carbon as a result of the interest in carbon sequestration. Numerous studies have reported accurate predictions of soil organic matter content (Brunet et al., 2007; Madari et al., 2005; Móron and Cozzolino, 2003; Viscarra Rossel et al., 2006b).

The quantitative prediction of the mineralogical composition of soils using spectroscopic techniques is, however, still limited. Nevertheless, spectral signatures for soil minerals in the visible, near- and mid-infrared regions, for clay and iron oxides, are

numerous (Farmer and Russell, 1964; Soriano-Disla et al., 2014). The lack of useful prediction models is partly due to the fact that conventional analytical data are often unavailable due to the impeding cost of mineralogical analyses that require sophisticated equipment not available in most soil laboratories. However, the type, the proportion, and the concentration of soil minerals determine soil properties, such as cation exchange capacity or phosphorus sorption, and they are important for soil classification (Soriano-Disla et al., 2014), especially in the case of tropical soils.

To date, only a limited number of studies have attempted to quantitatively predict the mineralogical composition of tropical soils with infrared spectrometry (Soriano-Disla et al., 2014; Vendrame et al., 2012). It has been shown that the quantification of iron oxides as well as the distinction between hematite and goethite are efficient (Ben-Dor et al., 2006; Viscarra Rossel et al., 2009) and successfully applied to soil surveys (Ben-Dor et al., 2009). For kaolinite and gibbsite, the two most important clay particles of highly weathered tropical soils, Madeira et al. (1995) proposed a methodology using specific peaks of kaolinite and gibbsite, produced by vibrations of hydroxyl ions (OH<sup>-</sup>) in their crystal lattice, situated between 2 200 and 2 300 nm. More recently, Vendrame et al. (2012) reported quantitative predictions for the mineralogical content of Brazilian soils using NIRS and chemometric methods. Coefficient of determination and ratio of performance to deviation (RPD) values as high as 0.86 and 2.5 (gibbsite) and 0.83 and 2.2 (kaolinite) were obtained from a diverse set of soils.

More research about the use of infrared reflectance spectroscopy are still needed to provide quantitative analyses of the mineralogical composition of soils (Soriano-Disla et al., 2014), a key component for highly weathered tropical soils. The objective of this study was to investigate the use of near-infrared reflectance spectroscopy (NIRS) to estimate the mineralogical composition over a wide range of highly weathered soils in Madagascar. Two spectroscopic methods were compared: a method that use the entire near infrared spectra as input data and another that is based on diagnostic absorption peaks of minerals.

#### 2 Materials and methods

#### 2.1 Study sites

The study areas were located in different sites in Madagascar, corresponding mainly to the crystalline basement of the island (Fig. 1.). This basement is formed of strongly metamorphosed Precambrian meta-sedimentary units and is intruded by various

granitic, mafic and mafic-ultramafic rocks (Collins and Windley, 2002). The climate of the island is subtropical, characterized by a mean annual rainfall of more than 3 000 mm along the East Coast to less than 1 000 mm in the south-east region, and varying from 1 000 to 1 800 mm in the highlands. The mean annual temperature depends largely on the altitude, being above 25°C on the coasts and below 20°C in the highlands.

The studied soils were classified as Ferralsols, Cambisols and Nitisols (IUSS Working Group WRB, 2006) and were mostly classified as ferralitic soils in the former French classification system (Commission de Pédologie et de Cartographie des Sols; CPCS, 1967). The selection of the soils was based on field observations, i.e. the presence of a ferralitic horizon, resulting from long and intense weathering.

According to Bond et al. (2008), the central plateau of Madagascar is dominated by grasslands and savannas with, for example, *Aristida rufescens*, *Loudetia simplex*, *Trachypogon spicatus*, *Hyperthelia dissoluta*, *Ctenium concinnum*, whereas the west is dominated by herbaceous savannas represented by species like *Heteropogon contortus*, *Hyparrhenia spp.*, *Loudetia spp.*, *Themeda quadrivalvis*, *Panicum spp*.



**Figure 1.** Sampling sites localization in Madagascar. The island is predominantly formed by strongly metamorphosed Precambrian meta-sedimentary units (crystalline basement) and Mesozoic sedimentary rocks.

#### 2.2 Soil sampling and reference analyses

Soil samples were collected at 120 sites close to the main roads (Fig. 1.) at the top or upper third part of the hills. The sites selected were at least 100 m away from the road, and were relatively undisturbed by human activities, i.e. grasslands used by farmers for extensive grazing. At each of the 120 sites (Fig. 1.), composite samples were taken at 0-0.1, 0.1-0.2, 0.2-0.3, 0.5-0.6 and 0.8-0.9 m depth, using an auger (Edelman auger), resulting in 600 soil samples. The spectra of the 600 samples were acquired, and 148 of those were selected from all the five soil horizons, according to their spectral representativeness, and analyzed by reference methods.

Iron oxides were determined by the citrate-bicarbonate-dithionite (CBD) deferrification method (Mehra and Jackson, 1960). One gram (1 g) of crushed (200  $\mu$ m) soil was placed in a centrifuge tube and mixed with 1 g of dithionite and 50 mL of sodium citrate (78.43 g L<sup>-1</sup>) and sodium bicarbonate (9.82 g L<sup>-1</sup>) solutions. The mixture was warmed up and kept at 40°C for two hours in a water bath. Then, the samples have been being mixed continuously in an end-over-end shaker for 16 hours at 25°C. After that the supernatant was separated by centrifugation at 4 000 rpm for 15 minutes and reserved to determine iron (Fe) and aluminium (Al) by atomic absorption spectroscopy (AAS) (Thermo Scientific ICE 3000 series). The Fe<sub>2</sub>O<sub>3</sub> content determined by the CBD extraction method (Fe<sub>2</sub>O<sub>3\_CBD</sub>) represents the amount of free iron oxides and the Al<sub>2</sub>O<sub>3</sub> content (Al<sub>2</sub>O<sub>3\_CBD</sub>) corresponds to the amount of Al substituting Fe in iron oxides. The ratio of Al substitution (Al<sub>sub</sub>, %) was calculated from the amount of Fe<sub>2</sub>O<sub>3\_CBD</sub> and Al<sub>2</sub>O<sub>3\_CBD</sub> expressed in moles (Jeanroy et al., 1991). The goethite (Gt) and hematite (Hm) contents were computed by combining the two equations as follows (see Reatto et al., 2008, 2009, for more details):

$$Fe_2O_{3\_CBD} = 0.8989 \times Gt + Hm$$

where Gt and Hm are the goethite and hematite contents (g kg<sup>-1</sup>) of the sample, respectively,  $Fe_2O_{3\_CBD}$  is the  $Fe_2O_3$  content of the sample determined with CBD extraction (in g kg<sup>-1</sup>), 0.8989 the specific proportion of  $Fe_2O_3$  in a goethite (for goethite assumed to be not Al substituted), RI is the red index according to (Santana, 1984) and equalled to RI = M + V/C, with M a parameter related to the hue, C the chroma and V the value of the Munsell notation.

(1)

Kaolinite (Kt) and gibbsite (Gb) were estimated after extraction with sulphuric acid (SA; 1:1 distilled water / conc.  $H_2SO_4$  volume ratio, SA). The SA extraction is a widely

used method for the quantitative characterization of the mineralogy of highly weathered tropical soils (Reatto et al., 2008). This acid attack enables dissolution of the clays, Fe oxyhydroxydes and Al hydroxides (Schaefer et al., 2008). The SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> extracted with sulfuric acid were used to compute the kaolinite (Kt) and gibbsite (Gb) contents as follows (adapted from Reatto et al., 2008):

$$Kt = SiO_{2}SA / Kt_{SiO2}$$

(3)

where Kt is the kaolinite content (g kg<sup>-1</sup>) of the sample,  $SiO_{2_SA}$  is the SiO<sub>2</sub> content of the sample determined with SA extraction (g kg<sup>-1</sup>), and Kt\_SiO<sub>2</sub> is the specific proportion of SiO<sub>2</sub> of the kaolinite set equal to 0.465.

 $Gb = [Al_2O_{3\_SA} - Al_2O_{3\_CBD} - (Kt \times Kt_{Al_2O3})] / Gb_{Al_2O3}$ (4)

where Gb is the gibbsite content (g kg<sup>-1</sup>) of the sample,  $Al_2O_{3\_SA}$  is the  $Al_2O_3$  content of the sample determined with SA extraction (g kg<sup>-1</sup>),  $Al_2O_{3\_CBD}$  is the  $Al_2O_3$  content of the sample determined with CBD extraction, Kt is the kaolinite content, Kt\_Al2O3 is the specific proportion of  $Al_2O_3$  in the kaolinite, equal to 0.395 and Gb\_Al2O3 is the specific proportion of  $Al_2O_3$  in the gibbsite, equal to 0.654. Eqs. (1) and (2) assume that kaolinite and gibbsite have no substitution in their formula.

The Ki, Kr and R<sub>KGb</sub> molar ratios [Ki = SiO<sub>2\_SA</sub>/Al<sub>2</sub>O<sub>3\_SA</sub>; Kr = SiO<sub>2\_SA</sub>/(Al<sub>2</sub>O<sub>3\_SA</sub> + Fe<sub>2</sub>O<sub>3\_SA</sub>); R<sub>KGb</sub> = Kt/(Kt + Gb)] were also calculated ((Reatto et al., 2008; Vendrame et al., 2012). These indexes indicate the soil weathering degree (Demattê and da Silva Terra, 2014).

#### 2.3 NIR spectral reflectance measurements

The reflectance of the soil samples was determined in the near-infrared region using a Foss NIRSystems 5000 spectrophotometer (Silver Spring, MD, USA). Samples (ca. 5g) were scanned using a ring cup of 5-cm diameter. Each sample spectrum, averaged from 15 spectra, was recorded as the logarithm of the inverse of the reflectance (Log [1/R]). Measurements were made from 1 100 to 2 498 nm. The data sets were reduced by keeping the wavelengths separated by 2 nm and removing the four first data points of the range, yielding 696 data points per spectrum. Data were analysed using the WinISI III – V 1.63e software (Foss NIR Systems/Tecator Infrasoft International, LLC, Silver Spring, MD, USA).

Multivariate calibration models were performed using modified partial least squares regression (mPLS) to link the spectra with the measured mineralogical parameters. To build the NIR calibration models we selected the most accurate spectral pre-processing

techniques of the software: gap over which the derivative is calculated, ranging from 0 to 10; first smoothing over 1 to 10 data points; no second smoothing; full cross-validation; two passes for the number of outlier elimination (T > 2.5). In the pre-processing step, classical background correction methods were used, such as first derivative, second derivative, standard normal variate (SNV) and multiplicative scatter correction (MSC). SNV scales each spectrum to have a standard deviation of 1.0 to help reduce particle size effects. MSC is a processing step that attempts to account for scaling and offset (baseline) effects. The notation of the pre-processing included the pre-treatment (NONE, MSC, SNV) and four successive numbers corresponding to the derivatives (0, 1 and 2: no derivation, first and second derivatives, respectively), the number of point gap (0, 4, 5, 10), the number of point for first smoothing (1, 4, 5, 10), and the number of point for second smoothing (always 1).

The performance of the calibration model was assessed using the coefficient of determination of cross validation  $(R^2_{cv})$  and the ratio of performance to deviation  $(RPD_{cv})$ , which is the ratio of standard deviation to the standard error of cross validation (SECV), and was considered acceptable for  $RPD_{cv} > 2$ , and  $R^2_{cv} > 0.75$  (Chang et al., 2001; Malley et al., 2004). The prediction accuracy of the model was evaluated on the validation subset (which had not been used for model development), using the validation  $R^2_{v}$  and  $RPD_{v}$ .

#### 2.4 Analyses of specific diagnostic absorption peaks for kaolinite and gibbsite

Some attributes can be predicted directly from spectra, based on the presence of characteristic chemical bonds or molecules that absorb at specific wavelengths (Viscarra Rossel, 2011; Soriano-Disla et al., 2014). This means that we can measure their abundances directly from the spectra using their corresponding diagnostic absorption peaks. The main kaolinite and gibbsite reflectance bands, produced by vibrations of hydroxyl ions OH<sup>-</sup> in their crystal lattice, are expressed in the near infrared range by two specific peaks situated at around 2 205 nm for kaolinite and 2 265 nm for gibbsite. Madeira et al. (1995) demonstrated the possibility of using the absorption intensity of these two peaks for quantitative determination of kaolinite and gibbsite in highly weathered soils. We, therefore, used the 2 150 to 2 350 nm range of the spectrum (Fig. 2). Two modifications were introduced in the original methodology of Madeira et al. (1995) to measure the heights of the derivative peaks of the two minerals: the use of derivate spectra; and the selection of normalized point for determination of the baseline

of the peaks of kaolinite and gibbsite. The first derivative was used to reduce baseline variation and enhance spectral features (Ben-Dor and Banin, 1994; Reeves et al., 2002). The first derivatives of the peak of maximum reflectance intensity were shifted by nearly 7-13 nm with respect to non-derivative spectra: i.e. between 2 212-2 214 nm for kaolinite (P1) and between 2 272-2 284 nm for gibbsite (P3) (Fig. 2.). A point of minimum variation of reflectance, situated between the peaks of kaolinite and gibbsite, was chosen as the baseline to measure the heights of the derivative peaks of the two minerals. Two points were tested (Fig. 2): the minimum variation of reflectance between P1 and P3, situated between 2 234 and 2 248 nm (P2) and the intersection point of the derivative spectra, situated between 2 256 and 2 268 nm (P2\*). The points P2 and P2\* were the best baseline points for kaolinite and gibbsite, respectively. Thus, the heights of the derivative peaks were calculated as follows:

$$I_{Kt} = P1 - P2 \tag{5}$$

$$I_{Gb} = \mathbf{P3} - \mathbf{P2^*} \tag{6}$$

where  $I_{Kt}$  and  $I_{Gb}$  are the first derivatives of absorption intensities of kaolinite and gibbsite, respectively, P1 and P3 the maximum intensities of kaolinite and gibbsite peaks, respectively, and P2 and P2\*, the best minimum reference points for kaolinite and gibbsite, respectively.

Linear or polynomial regressions were used to build the models relating kaolinite or gibbsite contents with their respective absorption intensities. A first regression model provided a prediction interval (p = 0.90). The samples outside this prediction interval were removed. The final regression model was assessed on the basis of the remaining samples and we computed the coefficient of determination ( $R^2$ ), the standard error (SE) and the p-value. The data processing was performed by R software (R Core Team, 2015).