				Calibration set							Validation set							
Constituent	Unit	preprocessing	Ν	out	n1	Mean	SD	SECV	R_{c}^{2}	RPD _c	n2	Mean	SEP(c)	R ² v	RPDv	SD	Slope	Bias
NIRS																		
$\mathbf{P}_{\mathrm{tot}}$	mg kg⁻¹	none 2441	104	4	100	318.0	236.1	184.8	0.38	1.3	42	424.4	295.8	0.32	1.2	163.4	1.1	84.8
P _{resin}	mg kg ⁻¹	none 1441	104	5	99	0.9	0.9	0.6	0.56	1.5	42	2.1	0.7	0.06	1.0	0.7	-3.3	1.4
P _{rem}	mg kg ⁻¹	none 1441	104	4	100	24.0	9.1	5.0	0.70	1.8	42	21.5	8.7	0.53	1.5	8.7	6.6	1.4
MIRS																		
P _{tot}	mg kg ⁻¹	none 1441	104	6	98	361.3	256.4	167.0	0.57	1.5	42	314.7	0.8	0.16	1.1	177.0	0.6	-29.9
P _{resin}	mg kg ⁻¹	snv 1441	104	8	96	0.7	0.8	0.6	0.43	1.3	42	1.0	6.4	0.36	1.3	0.8	0.7	0.0
P _{rem}	mg kg ⁻¹	snvd 0011	104	3	101	23.3	9.5	5.0	0.73	1.9	42	23.6	260.0	0.50	1.4	7.0	6.4	-1.1

Table 2	2.	Calibration	and	validation	statistics	of soil	phosphorus	properties.	using	NIRS	and MIRS.

none: without treatment / snv : Standard Normal Variate / snvd : Standard Normal Variate and Detrend / N : total nb of sample of calibration, out : nb of outlier, n1 : N - out, Mean of calibration: mean of prediction / SD : Standard deviation / SECV: Standard Error of Cross Validation / R²c: Correlation of determination of SECV / RPDc: Ratio Performance Deviation (SD/SECV) / n2: number of validation set / Mean of validation : mean of measured value/ SEP(c): Standard Error of Prediction / R²v: coefficient of determination of SEP / RPDv: 1/[racine (1-R²)]

			Calibration set							Validation set								
Constituent	Unit	preprocessing	Ν	out	n1	Mean	SD	SECV	R ² _c	RPD _c	n2	Mean	SEP(c)	R²v	RPDv	SD	Slope	Bias
NIRS																		
Kt	g kg ⁻¹	None 2441	104	5	99	309.3	308.9	95.0	0.60	1.6	42	329.2	125.5	0.37	1.3	127.1	0.7	-28.0
Gb	g kg ⁻¹	None 0011	104	34	70	138.4	138.8	67.8	0.60	1.6	42	173.8	83.5	0.51	1.4	92.9	0.9	10.5
Fe ₂ O _{3 CBD}	g kg ⁻¹	Msc 2551	104	9	95	36.9	37.0	11.8	0.80	2.2	42	50.9	21.3	0.63	1.6	27.2	1.0	1.4
C	g kg ⁻¹	none 1441	104	4	100	1.3	1.3	0.5	0.79	2.1	42	1.5	0.4	0.81	2.3	0.8	0.9	-0.2
Clay	g kg ⁻¹	None 0011	104	4	100	311.4	136.4	97.7	0.49	1.4	42	397.7	114.6	0.33	1.2	74.6	1.1	49.3
Silt	g kg ⁻¹	Snv 1441	104	3	101	214.9	127.2	99.0	0.39	1.3	42	208.0	132.4	0.02	1.0	99.9	0.1	-18.8
Sand	$g kg^{-1}$	Snv 1441	104	4	100	480.1	182.5	127.9	0.58	1.5	42	431.6	143.7	0.40	1.3	133.1	0.9	-37.3
pH_{water}	0 0	snv 2441	104	4	100	5.46	0.4	0.3	0.37	1.3	42	5.5	0.7	0.27	1.2	0.3	1.5	0.2
MIRS																		
Kt	g kg ⁻¹	None 0011	104	6	98	298.9	140.1	90.3	0.59	16	41	312.3	126.4	0.30	1.2	93.1	0.9	8.5
Gb	g kg ⁻¹	None 0011	104	25	79	149.4	116.2	78.4	0.54	1.5	41	121.5	67.8	0.45	1.3	78.0	0.8	11.9
Fe ₂ O _{3 CBD}	g kg ⁻¹	Detrend 1441	104	6	98	40.9	25.6	16.7	0.57	1.5	41	38.9	22.5	0.72	1.9	24.6	1.4	5.7
C	g kg ⁻¹	Snvd 1441	104	7	97	1.1	0.9	0.3	0.85	2.6	41	1.4	0.4	0.87	2.8	0.9	1.2	0.0
Clav	g kg ⁻¹	Snv 210101	104	6	98	349.4	131.1	87.3	0.56	1.5	41	334.4	117.5	0.55	1.5	105.6	1.2	6.2
Silt	$g kg^{-1}$	Snv 2551	104	4	100	218.2	116.6	76.5	0.58	1.5	41	192.9	107.4	0.32	1.2	119.4	0.5	-39.6
Sand	$g kg^{-1}$	Snv 0011	104	2	102	440.4	186.9	110.0	0.66	1.7	41	442.4	115.4	0.76	2.0	177.5	1.1	30.3
pH_{water}	00	Snvd 0011	104	7	97	5.5	0.4	0.4	0.24	1.1	41	5.4	0.5	0.38	1.3	0.3	1.2	0.1

Table 3. Calibration and validation statistics of physico-chemical and mineralogical soil properties, using NIRS and MIRS.

none: without treatment / snv : Standard Normal Variate / snvd : Standard Normal Variate and Detrend / N : total nb of sample of calibration, out : nb of outlier, n1 : N - out, Mean of calibration: mean of prediction / SD : Standard deviation / SECV: Standard Error of Cross Validation / R²c: Correlation of determination of SECV / RPDc: Ratio Performance Deviation (SD/SECV) / n2: number of validation set / Mean of validation : mean of measured value/ SEP(c): Standard Error of Prediction / R²v: coefficient of determination of SEP / RPDv: 1/[racine (1-R²)]



Figure 2. Correlation between absorption intensities of specific peaks for kaolinite (a) and gibbsite (b) and their contents analyzed by wet chemistry. IKt and IGb are the heights of the first derivatives of absorption peaks of kaolinite and gibbsite, respectively.



Chapitre 3. Prédiction de la sorption et de la disponibilité de P des sols ferrallitiques par la spectrométrie infrarouge

Figure 3. Partial least square loading weights for the PCA transformed NIR reflectance values after the best pre-treatments for the prediction of soil minerals: (a) NONE 1441 for Pres in NIRS; (b) SNV 1441 for Pres in MIRS; (c) SNV 1441 for P_{rem} in NIRS; (d) SNVD 0011 for P_{rem} in MIRS. NONE: no treatment; SNV: Standard Normal Variate; SNVD : Standard Normal Variate and Detrend.

3.3 Development of a PTF for soil phosphorus using other soil variables prediction through chemometric approach

Simple regression statistics (Table 4) indicated a significant linear relationship between P_{rem} and C, clay, silt, sand, $Fe_2O_{3_CBDcbd}$ and Gb, whereas pH_{water} and Kt were not significantly related to P_{rem} . Among the different soil properties, gibbsite content was the most closely and significantly correlated with P_{rem} (r = -0.59). The amount of crystallized oxides was also significantly correlated with P_{rem} (r = -0.49), however, the relationship with gibbsite was better than with iron oxides. Strong relationships between P_{rem} and the clay (r = -0.53) and sand (r = 0.51) contents were observed, with a negative coefficient for the former and a positive one for the latter. The clay fraction was highly correlated to gibbsite and iron oxide contents (r = 0.35 and 0.54, respectively) which also had significant negative correlations with P_{rem} . The sand fraction behaved opposite to the clay fraction. The C content was negatively

correlated with P_{rem} , which was a surprising result, because organic matter is supposed to reduce phosphorus retention (Haynes and Mokolobate, 2001), and thus increase P_{rem} . Soil minerals (kaolinite, gibbsite, iron oxides) play a key role in the stabilization of organic matter (Kaiser and Guggenberger, 2003) and thus explain the significant correlation between C and Gb (r = 0.24). The chemical reaction of the soil (pH_{water}) does not seem to contribute much to the sorption of P, in line with the review paper of Gérard (2016), explaining that the binding capacity of Fe/Al oxides varies moderately in the pH range of Madagascar soils. Regression between P_{res} and soil properties showed that pH_{water}, silt and sand contents were the only significant variables (Table 4).

The multiple regression analyses developed are presented in Table 5, and illustrated graphically in Figure 4 for P_{rem}. For chemically analyzed variables, the strongest multiple regression (P<0.0001) for P_{rem} included five factors (each significant at $\alpha = 0.05$), representing pH_{water}, texture and mineralogy variables (Eq. 1; Figure 4a). As expected, given their P sorption capacity, Fe/Al oxides (i.e. Gb and Fe₂O_{3 CBD}) had a major effect on P_{rem}. The sand content (i.e. quartz), known for not having significant sorption capacity for P, counteracted the effects of Fe/Al oxides and was useful for the accurate prediction of Prem. The pH_{water}, which was not correlated with P_{rem} (Table 4), was removed without a substantial reduction of the model efficiency (Eq 2). The C content had significant contributions (Eq 1), however, its inclusion in the model improved only the explanation of variability marginally (Eq 3, Figure 4b), presumably, because of collinearity of C with Al oxides (r = 0.24). The root-mean-square error (RMSE) was between 6.5 and 6.9 mg L^{-1} , depending on the models. A multiple regression equation was also obtained for P_{resin} ($R^2 = 0.42$, Eq. 4) using the same five factors than for P_{rem}, but the efficiency of the model was greatly reduced after removing pH_{water} and C content ($R^2 = 0.05$, Eq. 5). The goodness of fit of multiple regressions was lower for P_{resin} than for P_{rem} (Table 5).

We tested the same multiple regression analyses using the variables predicted with the PLS methods (carbon, $Fe_2O_{3_CBD}$, sand) and with the use of the intensity of the derivative of specific peaks (kaolinite, gibbsite). For pH_{water} we used measured values as it could not be predicted with spectral methods. For P_{rem}, the multiple regression equations were approximately of the same quality than those obtained with only the measured variables (Eq 7 to 8 in Table 5; Figure 4c). Moreover, the relationship between P_{rem} predicted with PTF using chemically measured data (Eq 3) and P_{rem} predicted with PTF using spectrally predicted data (Eq 8) were good (slope = 0.83; $R^2 = 0.74$) (Fig. 5.).

		P _{rem} (mg l^{-1})	P_{res} (mg l ⁻¹)				
Variables	Unit	Coefficient	Significance level	Coefficient	Significance level			
Kt	g kg ⁻¹	0.0277	0.7380	-0.050	0.5450			
Gb	g kg ⁻¹	-0.586	0.0000	-0.019	0.8230			
$Fe_2O_{3_CBD}$	g kg ⁻¹	-0.488	0.0000	-0.097	0.2430			
pH_{water}		0.120	0.1470	0.482	0.0000			
Clay	g kg ⁻¹	-0.533	0.0000	0.010	0.9080			
Silt	g kg ⁻¹	-0.167	0.0423	0.260	0.0014			
Sand	g kg ⁻¹	0.507	0.0000	-0.167	0.0431			
С	g kg ⁻¹	-0.284	0.0005	-0.025	0.7600			

Table 4. Pearson coefficients and significance levels for correlation between physico-chemical and mineralogical soil properties and P_{rem} or Pres of the ferrallitic soils studied.

Table 5. Best-fit multiple regression analyses for P_{rem} or Pres of the ferrallitic soils studied using chemically analyzed or values predicted using spectrometry (except pH).

Variables	Multiple regression equation	R ² _c	RMSE	
	Chemically analyzed variables			
P _{rem}	$P_{rem} = 22.323 + 1.553 pH_{water} - 0.127 C - 0.009 Kt_{as} - 0.039 Gb_{cbd} - 0.065 Fe_2O_{3_CBD} + 0.008 S C_{bb} - 0.008 C_{bb} - 0.00$	0.52	6.49	Eq 1
	$P_{rem} = 25.775 - 0.13 \text{ C} - 0.031 \text{ Gb}_{cbd} - 0.062 \text{ Fe}_2O_{3_CBD} + 0.012 \text{ S}$	0.49	6.69	Eq 2
	$P_{rem} = 25.610 - 0.035 \text{ Gb}_{cbd} - 0.072 \text{ Fe}_2O_{3_CBD} + 0.010 \text{ S}$	0.46	6.89	Eq 3
P _{res}	$P_{res} = -0.208 + 0.053C - 0.001 \text{ Gb}_{cbd} + 0.001S$	0.42	0.70	Eq 4
	$P_{res} = 0.284 + 0.001S$	0.05	0.90	Eq 5
,	Spectrally predicted variables			
P _{rem}	$P_{rem} = 20.787 + 1.285 \ pH_{water} - 0.290 \ C - 0.007 \ Kt_{as} - 0.029 Gb_{cbd} - 0.105 Fe_2 O_{3_CBD} + 0.020 \ S_{abc} + 0.020 \ $	0.50	6.61	Eq 6
	$P_{rem} = 24.897 - 0.261 \text{ C} - 0.027 \text{ Gb}_{cbd} - 0.099 \text{ Fe}_2O_{3_CBD} + 0.019 \text{ S}$	0.49	6.72	Eq 7
	$P_{rem} = 24.160 - 0.030 \text{ Gb} - 0.111 \text{ Fe}_2O_{3_CBD} + 0.015 \text{ S}$	0.43	7.09	Eq 8
P _{res}	$P_{res} = 0.847 + 0.058 \text{ C} - 0.001 \text{ Kt}_{as} - 0.001 \text{ Gb}_{cbd} - 0.007 \text{ Fe}_2O_3 _{CBD}$	0.41	0.71	Eq 9
	$P_{res} = 1.777 - 0.002 \text{ Kt}_{as} - 0.001 \text{ Gb}_{cbd} - 0.007 \text{ Fe}_2O_{3_CBD}$	0.20	0.84	Eq 10



Figure 4. Relationships between the measured data and the predicted using the best-fit pedotransfert function (Eq 1, a), a simplified function without C and pH (Eq 3, b), a simplified function without C and pH (Eq 8, c).



Figure 5. Relationships between the P_{rem} predicted with PTF using chemically measured data (Eq 3) and PTF using spectrally predicted data (Eq 8).

4 Discussion

4.1 Use of infrared spectroscopy to develop P availability indices with chemometric methods

Phosphorus is an essential nutrient required by crops in large amounts. Soil testing is one of the most cost-effective nutrient management tools available to farmers and crop advisers. Soil tests provide an index of the labile plant-available P by extracting a fraction of the P that is related to the yield response of crops (Fixen and Grove 1990).

Soriano-Disla *et al.* (2014) have recently reviewed the performance of visible, near-, and mid-infrared reflectance spectroscopy for the prediction of soil physical, chemical, and biological properties using multivariate chemometric regression modeling. For P availability indices, with few exceptions of soil sets representing special or unusual conditions, most predictions of extractable P in soils resulted either in low R^2_v values (0.5–0.7) or were considered to be completely unreliable ($R^2 < 0.50$). At regional or country scales, most of the results are unreliable with both NIRS (Chang *et al.*, 2001; Vendrame *et al.*, 2012) and MIRS (Shepherd and Walsh, 2002; Minasny *et al.*, 2009; Forrester *et al.*, 2015). An exception was reported by Morón and Cozzolino (2007) who found low accuracy prediction, using NIRS, for resin and Bray extractable P ($R_v^2 = 0.61$ and 0.58, respectively) for soils from Uruguay. Our

results, presenting even lower coefficients ($R_v^2 = 0.06$ for NIRS and 0.36 for MIRS), are comparable to the majority of studies conducted on a similar scale.

Sorption of P in the soil controls its chemical mobility and bioavailability (Hinsinger, 2001). The ability of soil to bind phosphorus (P sorption) can be also a useful index of P availability. Good predictions were reported in the study of Soriano-Disla *et al.* (2014) for P sorption with MIR (moderately successful predictions, median $R^2_v = 0.83$). However, the number of studies and geographic area studied (i.e. west Australia) are very limited (Janik *et al.*, 2009; Minasny *et al.*, 2009; Forrester *et al.*, 2015). Studies using the Vis-NIR were less successful ($R^2_v = 0.69$) (Cohen *et al.*, 2007). Our results showed lower accuracy prediction, with $R^2_v = 0.53$ and 0.50 for NIRS and MIRS, respectively, than the reported studies. However, these predictions could be used as acceptable soil quality indices for evaluating soil quality or fertility by African farmers who have no access to the soil analysis due to high prices.

4.2 Use of PTF to relate P availability indices to soil properties

The extent to which a soil adsorbs P (buffering capacity or sorption capacity) differs widely among different soils. Factors controlling phosphate binding in soils have been the focus of research efforts in recent decades (e.g. McGechan and Lewis, 2002; Gérard, 2016). P sorption tends to be high in soils with high proportion of small-size particles such as clay and, hence, high specific surface area (McGechan and Lewis, 2002). Aluminium and iron oxides are considered as the main phosphate adsorbents in soils (Gérard, 2016 and references therein). Accordingly, close relationships were found between the amounts of adsorbed phosphate and certain aluminium and iron forms, which lead to the creation of pedotransfer functions for predicting adsorbed phosphate sorption have been also demonstrated recently (Gérard, 2016). The effect of pH and organic matter on phosphate sorption by clay minerals and Fe/Al oxides have been also extensively studied (Muljadi *et al.*, 1966; Haynes and Mokolobate, 2001).

Chemical properties that are related to the mineral and organic components can be predicted spectrometrically because of the interaction between the soil properties and the active soil components: organic matter, clay minerals and oxides (Minasny and Hartemink, 2011). Therefore, adsorption-desorption reactions, such as P availability or P sorption, can be predicted if quantitative mineralogy and chemical analysis of various properties are available. However, detailed mineralogical measurements and some specific analysis are expensive and

rarely made in soil surveys. There exist a few PTF that relates P sorption to aluminium and iron oxide contents (Borggaard *et al.*, 2004). Our results showed that, in addition to Fe/Al oxides, sand and carbon content are key parameters. These compounds have been predicted with a relatively good accuracy (Soriano Disla *et al.*, 2014). Demattê *et al.* (2006) and Vendrame *et al.* (2012) demonstrated the use of NIR spectroscopy for identifying major soil mineralogy in tropical Brazil. Numerous studies have reported accurate predictions of soil total C and N content (e.g. Madari *et al.*, 2005; Viscarra Rossel *et al.*, 2006; Brunet *et al.*, 2007). Accurate calibration for sand using MIRS or combined visible-NIR have been found, with R^2_v between 0.70 and 0.99 (Chang *et al.*, 2001; Schepherd and Walsh, 2002; Morón and Cozzolino, 2003; Madari *et al.*, 2006; Vendrame *et al.*, 2012).

Our results are in the range of most published results with reliable spectroscopy-based soil analysis for soil compounds used in our PTF, with R^2_v of 0.87 for C (with MIRS and PLS calibration); 0.76 for sand (MIRS-PLS); 0.72 for Fe₂O_{3_CBD} (MIRS-PLS); and 0.75 for gibbsite (NIRS, height of the first derivative of specific peak at 2,265 nm) (Table 3 and Figure 2.). The fit of multiple regression analyses for P_{rem} or P_{resin}, using data obtained by chemical analyses and predicted values through spectrometry, were similar (Table 5) and a good relationship between the PTFs obtained by the two approaches was shown for P_{rem} (Fig. 5.).

5 Conclusion

Highly weathered soils cover large areas in the tropics. The reactive minerals, i.e. clay minerals (kaolinite) and Al/Fe oxides (gibbsite, goethite, hematite), play a key role, together with organic matter, in the physico-chemical functioning of these soils, especially on P sorption. To overcome the widespread P deficiency in the agricultural soils of Sub-Saharan Africa and promote adequate soil P management, rapid and low cost soil testing for P availability or P sorption capacity are needed. While numerous studies have been conducted to quantify the soil organic matter with infrared spectral methods (see Soriano-Disla et al., 2014), research on the prediction of P sorption capacity or P availability in soils using this approach is still scarce. Although these methods are ineffective in predicting available P (P_{resin}), we showed that reliable spectroscopy-based analyses of a P buffering index (P_{rem}) can be obtained with both NIR and MIR spectrometry using mPLS. The development of pedotransfer functions (PTF) based on carbon content, texture and mineralogical properties of soils predicted with chemometric methods is also useful for predicting P_{rem} and through that in the understanding of the effects of the most important soil components controlling P sorption. Therefore, the P sorption capacity of the soil can be predicted based on the amounts

of aluminium and iron oxides (gibbsite and $Fe_2O_{3_CBD}$), that both increase P sorption, and the amount of sand, that counteract the effects of Fe/Al oxides. These soil components being fairly well predicted by IR-spectrometry, a rapid and low cost procedure for the estimation of P sorption capacity can be proposed. The hereby presented models represent encouraging results and foresee the need for similar studies on tropical soils in different environments to improve the method.

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