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Soil analytical quality control by traditional and spectroscopy techniques: Constructing the future of a hybrid laboratory for low environmental impact

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ABSTRACT

Soil analysis is an important information in agriculture and environmental monitoring. It is usually performed by wet chemical analysis with high cost and chemical products consumption. In the world, it is estimated that 1.5 billion ha is used as agricultural area. If every 5 ha 2 samples (2 depths) were collected, we would have 600 million soil samples for chemical and granulometric analysis. Considering just the analysis of organic matter (OM) by wet combustion method in the laboratory as an example, we would be utilizing about 840 thousand kg of dichromate and ammonium ferrous sulfate and 3 million L of sulfuric acid. The use of these reagents can have a huge ecological consequence if they do not have an adequate final disposal. An alternative methodology such as proximal sensing can be utilized with low environmental impact. Therefore, the objective of this study was to: i) evaluate the analytical quality of soil attributes via different traditional laboratories and sensors, ii) evaluate the prediction of the models using sensors, iii) assess the uncertainties of lime recommendation analyzed by the laboratories. We applied 96 soil samples at two depths collected in São Paulo State, Brazil. The determination of 15 soil attributes was performed by four different routine laboratories, and they were predicted by 4 sensors (400–2500 nm). Results indicate that the determination of attributes via chemical analysis with low quality led to high error in spectral models. The great predictive performances of clay, OM, cation exchange capacity (CEC), and pH enable the use of sensors in the evaluation of these attributes. Overall, the criteria for classification of analytical results showed that sand, silt, clay, pH, OM, CEC, and base saturation were the attributes that can be determined by the spectroscopy technique with high-quality outcome. The lime recommendation derived from proximal sensor analysis can be used as an efficient method, since it presented a high correlation with the laboratory result. In this sense, a hybrid laboratory analysis can be developed to optimize analysis with better quality control, which is indicated as a great opportunity in the near future.

1. Introduction

Soil is one of the most important resources for humanity. The chemical and granulometric characteristics of soils are responsible for water dynamics, climate, organisms, forests, carbon and others. In addition to their environmental importance, they are the basis for food production. FAO indicates that in the next 30 years we will increase by 35% in population, going from 7.6 to 10.26 billion people in the world. How to feed so many people? This concern was also discussed in McBratney et al. (2014), in which the authors introduced the term “soil security”, indicating that it is imperative to take care of soils or we will likely have environmental problems in several areas.

The study of soil attributes (i.e., clay, carbon, nutrients) implies on the determination of its analytical value. Soil attributes mapping is recommended prior to soil management, as soil analyses are essential for assessment and monitoring of its chemical and physical conditions, indicating the need for fertilization, liming and conservation techniques. The most applied chemical methods in laboratories are those called traditional wet analysis.

Considering Brazil, the agriculture area is around 60 million ha with a potential to expand to 70 million in the coming years. Nowadays, Brazil uses precision agriculture (PA) techniques in approximately 10% of its farmland, which involves between 100,000 and 200,000 soil analyses per year. The number of soil analyses is even more impressive

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when considering sampling at two depths (0–20 and 20–40 cm, in general), which can reach 400,000 soil analyses. Considering the world demand, there is an estimate that > 600 million soil samples can be analyzed every year.

However, the numbers of analyses are not exactly the main issue. One analysis takes about 3 to 15 days for delivering results, which is not adequate considering the speed required in PA. Despite the longtime, the traditional laboratory analysis uses several types of chemical substances. For instance, to determine the soil organic matter (OM), the wet combustion method is predominantly applied, which uses dichromate ($Cr_2O_7^{2-}$) (0.196 g), ammonium ferrous sulfate hexahydrate ($Fe(NH_4)_2(SO_4)_2.6H_2O$) (1.20 g), and sulfuric acid (H_2SO_4) (5 mL) for only one sample. Considering just the analysis of OM, 1.396 g and 5 mL of these reagents are used, reaching a disturbing number of 698 kg and 2500 L of these toxic chemical compounds per year. Considering the potential of 600 million soil samples to be analyzed globally, it will consume about 840 thousand kg of dichromate and ammonium ferrous sulfate and 3 million L of sulfuric acid. Besides, for OM, it is estimated a cost of US$ 5.00 per sample, with an annual expenditure of US$ 2.5 million. We have to emphasize that this is not a local problem. Countries with established agriculture, especially the developing ones (from Latin America and Africa) that have a lot of land for agricultural expansion, are the most affected.

Soil analyses are subject to several errors due to sampling, products, methods, humans, and others (Olsen and Sommers, 1982). In fact, O'Rourke and Holden (2011) stated that routine analyses have some limitations, i.e., reagents quality, brands of equipment and extensive sequence of steps. Consequently, repeated analysis of the same sample may show variations. These variations are only acceptable if they are within a certain interval. This was ratified by Cantarella et al. (2006) that identified differences for a same sample in the same or between laboratories. These issues took the community of soil scientists on the investigation of new techniques for soil analysis. The main focus was how to reach soil results in a fast, simple, more stable and no-pollutant method.

In this sense, years of experiments took many authors to observe proximal sensing as a promising technique that can bring light to the issue. Indeed, first findings of Zheng and Schreier (1988) quantified soil patterns and field fertility using spectral reflection. Ben-Dor and Banin (1995) created the near infrared analysis (NIRA), which is an approach to examine the capability for predicting soil properties from the reflectance curves in the near infrared region of arid and semiarid soils of Israel.

Spectroscopy is a proximal sensing technique based on the detection of the electromagnetic radiation reflected by the soil. In the same way, spectroscopy in the visible (Vis: 400–700 nm), near infrared (NIR: 701–1100 nm) and short-wave infrared (SWIR: 1101–2500 nm) regions of the electromagnetic spectrum associated with chemometric methods has allowed the quantification of physical, chemical and mineralogical attributes (Viscarra Rossel and Behrens, 2010). Vis-NIR-SWIR spectroscopy technique emerges as a promising new option for soil analysis, with advantages such as: the possibility of predicting several attributes in just one spectral reading, facility of data acquisition from large amounts of samples, it is a rapid analysis and without the use of environmentally hazardous chemicals (Minasny and McBratney, 2008; Viscarra Rossel and Behrens, 2010). Nanni and Demattê (2006) reached important correlation between traditional and spectroscopic methods, but the authors emphasized the necessity of more research in this regard. Although spectroscopy is promising, results are variable as reviewed by Soriano-Disla et al. (2014) and Nocita et al. (2015). O'Rourke and Holden (2011) highlighted that with the spectroscopic methods it is possible to have costs reduction for OM of about 90%, with the potential to read 720 samples per day. In addition, the soil attributes quantification via reflectance spectroscopy technique is based on multivariate statistical methods, generating calibration models that correlate the spectral with the analytical values obtained from laboratories with standardized methodologies. Thus, the predictive quality of the models depends on the precision and accuracy of the reference laboratory determinations (Rayment et al., 2012; Reeves III, 2010).

The types and the range of spectral sensors also influence the quantification of soil characteristics. This method of determining soil attributes by sensors has gained prominence due to two fundamental factors, namely fast information and the environmental appeal regarding the use of a safe methodology. Hence, the quantification of soil attributes must be performed to generate necessary information about it and ensure proper management of this natural resource.

Techniques using spectral data have been applied and shown promising success in the quantification of soil attributes worldwide (Viscarra Rossel et al., 2016). However, few scientific studies compared the analytical results between different laboratories to evaluate how their data impact on the spectral models. If we assure that the variation on the results are real, can sensors detect this variation? How much of the sensor prediction performance is affected by the reference value of laboratory analysis? Can a sensor perform better applying the most accurate reference value or applying an average reference value? The answers for these questions are still unknown.

Regarding the variations of soil spectral features considering different sensors, Romero et al. (2018) observed that there is low difference between sensor measurements, which leads to a more stable technique. Taking into consideration these low differences, caused by geometry and equipment variation, Ben-Dor et al. (2015) determined a protocol to standardize measurements between sensors. This takes spectroscopy methodology a step ahead of traditional ones.

Seeking the increase of food production for the human needs, optimization of fertilizers in agricultural production, and the decreasing of chemical products in the soil analyses, it is essential to search for alternatives and thereby reduce the environmental impact. In this sense, understanding the variations between laboratories is a fundamental part of this study. We intend to demonstrate the advantages and limitations of soil analysis methodologies and the impact of different laboratories and sensors in the prediction of attributes, thus allowing better decisions for soil management. We understand that it is not possible to substitute traditional soil analysis completely, because reflectance is a dependent variable. The objective of the present study was to: i) evaluate the analytical quality of soil attributes via different laboratories and sensors, ii) evaluate the prediction of the models using sensors, and iii) assess the uncertainties of lime recommendation analyzed by the laboratories. Therefore, the focus is to bring light on the development of a hybrid laboratory analysis approach, where one would have in simultaneous both measurements: 80% of soil samples analyzed by spectroscopy and only 20% by traditional analysis.

2. Material and methods

2.1. Characterization of the study area, collection and preparation of soil samples

We collected the soil samples in an area that covers 29 municipalities located at São Paulo State, Brazil. The study areas present tropical climate, with hot and humid summer, cold and dry winter, with average temperatures of 20 °C, with annual thermal amplitude of up to 7 °C. Rainfall varies from 1000 to 1500 mm/year. 48 profiles were collected at two depths of 0–20 cm and 80–100 cm (A and B horizons, respectively) totalizing 96 soil samples. The collected material was dried in 45 °C for 48 h, ground and sieved in a 2 mm mesh.

2.2. Laboratory and spectral analysis

For the reference soil analysis, four laboratories were selected in São Paulo State, which are regularly evaluated by the proficiency test of the Agronomic Institute of Campinas (IAC), Brazil. The 96 soil samples were divided in three replicates (in a total of 288 soil samples) and sent

Table 1
Methods of soil analysis applied by the laboratories.

Soil Attribute[a]	Laboratory			
	1	2	3	4
pH	$CaCl_2$[b]	$CaCl_2$[b]	$CaCl_2$[b]	$CaCl_2$[b]
OM	Walkley-Black	Walkley-Black	Walkley-Black	Walkley-Black
P	Ion exchange resin	Ion exchange resin	Ion exchange resin	Ion exchange resin
K	Ion exchange resin	Ion exchange resin	Ion exchange resin	Ion exchange resin
Ca	Ion exchange resin	KCl[b]	Ion exchange resin	KCl[b]
Mg	Ion exchange resin	KCl[b]	Ion exchange resin	KCl[b]
Al	KCl[b]	KCl[b]	KCl[b]	KCl[b]
H + Al	SMP[b]	SMP[b]	SMP[b]	SMP[b]
SB	(K + Ca + Mg)	(K + Ca + Mg)	(K + Ca + Mg)	(K + Ca + Mg)
CEC	[K + Ca + Mg + (H + Al)]	[K + Ca + Mg + (H + Al)]	[K + Ca + Mg + (H + Al)]	[K + Ca + Mg + (H + Al)]
BS	[(K + Ca + Mg)/(Ca + Mg + K + H + Al)]100	[(K + Ca + Mg)/(Ca + Mg + K + H + Al)]100	[(K + Ca + Mg)/(Ca + Mg + K + H + Al)]100	[(K + Ca + Mg)/(Ca + Mg + K + H + Al)]100
AS	[(Al)/(Ca + Mg + K + Al)]100	[(Al)/(Ca + Mg + K + Al)]100	[(Al)/(Ca + Mg + K + Al)]100	[(Al)/(Ca + Mg + K + Al)]100
Sand	Hydrometer[b]	Pipette	Pipette	Pipette
Silt	Hydrometer[b]	Pipette	Pipette	Pipette
Clay	Hydrometer[b]	Pipette	Pipette	Pipette

[a] Potential of hydrogen (pH), organic matter (OM), exchangeable phosphorus (P), exchangeable potassium (K^+), exchangeable calcium (Ca^{2+}), exchangeable magnesium (Mg^{2+}), exchangeable aluminum (Al^{3+}), potential acidity (H + Al), exchangeable sum of the bases (SB), cation exchange capacity (CEC), base saturation (BS), and Aluminum saturation (AS).

[b] $CaCl_2$: 0.01 mol/L, KCl: 1 mol/L, SMP: buffer solution method of Shoemaker et al. (1961); Hydrometer: Bouyoucos scale.

to the four laboratories. For chemical determinations, the following attributes were analyzed: potential of hydrogen (pH), organic matter (OM), exchangeable phosphorus (P), exchangeable potassium (K^+), exchangeable calcium (Ca^{2+}), exchangeable magnesium (Mg^{2+}), exchangeable aluminum (Al^{3+}), potential acidity (H + Al), exchangeable sum of the bases (SB), cation exchange capacity (CEC), base saturation (BS), and Aluminum saturation by (AS). The particle size distribution composed of sand, silt, and clay fractions were also determined. Table 1 presents the chemical and physical analytical methods used for each attribute and laboratory considered.

Spectral reflectance was obtained by four spectroradiometers in a range of 350 to 2500 nm (Vis-NIR-SWIR) by the Analytical Spectral Devices Inc., Colorado, USA. Petri dishes were used for homogeneous arrangement of the samples of dry and sieved soil, so that the surface was as flat as possible for performing the spectral reading. The sensor has a fiber optic cable located 8 cm from the sample surface registering the reflectance in an area of 2 cm^2. Two 50 W external halogen lamps positioned at 35 cm from the sample and at a 30° zenith angle forming a 90° angle to each other provided the illumination to acquire the spectrum. All sensors were calibrated using a *Spectralon* white plate representing a 100% reflectance pattern. This procedure was done at the beginning and repeated every 25 sensor readings. Also, after each calibration, a standard white sample (homogeneous sand dunes) was scanned according to Ben-Dor et al. (2015). This sequence was necessary to standardize and equalize spectral measurements between sensors.

2.3. Analytical precision and accuracy

According to Cantarella et al. (2016), the precision and accuracy were evaluated regarding the analytical determinations of all laboratories and sensors. The methodology is certified by the National Institute of Metrology, Quality and Technology (INMETRO), Brazil and by the International Proficiency Testing Information System (EPTIS).

Considering the 15 soil attributes determined by the four laboratories and sensors, we calculated the mean, standard deviation (SD), and coefficient of variation (CV) of each soil sample, e.g., three replicates of one sample were analyzed by four laboratories totalizing 12 determinations, from which we calculated the mean, SD, and CV. These parameters were applied in the criteria used for acceptance or rejection of results following Cantarella et al. (2016): if the result of CV > 40%, and the mean is ± 1.0 SD; or 20 ≤ CV ≤ 40% and the mean is ± 1.5 SD; or CV < 20%, and the mean is ± 2.0 SD, then the determination is accepted; if not, the determination is rejected. The results outside the acceptance range are highlighted with an asterisk (penalty) and are taken from the data set. A second and third rounds of calculations were established. New mean, SD, CV, and acceptance ranges are defined. The sum of penalization for each attribute was assessed. Three types of indices were calculated to evaluate the performance of determinations: a) inaccuracy (Eq. (1)), b) imprecision (Eq. (2)), and c) excellence index (EI), which is the overall performance (Eq. (3)). For the EI, each laboratory and sensor were graded as A if this index is ≥90%, B if between 75% and 89%, C if between 50% and 74%, and D if < 50% (Cantarella et al., 2016).

Moreover, to evaluate the impact of the results quality, the lime recommendation (Eq. (4)) was calculated using 50 soil samples considering the results of the laboratories and sensors. The lime recommendation was calculated and then the discrepant results outside the confidence interval (α = 5%) were identified.

$$\text{Inaccuracy} = \frac{\text{number of penalizations}}{\text{number of determinations}} \times 100 \quad (1)$$

$$\text{Imprecision} = \frac{\Sigma\ \text{CV}}{\text{number of determinations}} \quad (2)$$

$$EI = 100 - \frac{(\text{Inaccuracy} * 2) + \text{Imprecision}}{3} \quad (3)$$

$$LR = \frac{CEC * (BS_2 - BS_1)}{10 * RTNP} \quad (4)$$

where: the number of determinations is the total number of soil samples measured; the number of penalties is given by the sum of rejected samples; CV is the coefficient of variation of each laboratory; LR is the lime recommendation expressed in $t\,ha^{-1}$; CEC is the cation exchange capacity expressed in $mmol_c\,dm^{-3}$; BS_1 is the base saturation of the soil; BS_2 is the base saturation that we want to raise to (it was considered BS = 70%); RTNP is the relative total neutralizing power (variable dependent on the liming material employed). The RTNP value of 67% was used. More details of this methodology can be found in Cantarella et al. (2016).

2.4. Prediction models

The modeling for prediction of 15 attributes using the spectral reflectance of four sensors was performed using Alrad Spectra graphical user interface in R (R Core Team, 2017). The total of 288 soil samples was randomly divided in calibration (200 samples, ~70%) and validation set (88 samples, ~30%). The samples of two depths (0–20 cm and 80–100 cm: A and B horizons, respectively) were mixed within the data sets. Aliah Baharom et al. (2015) reported that the best calibration model for soil properties estimation was the one combining depths.

The modeling was performed by partial least square regression (PLSR) method. Predictive models for each attribute were developed to estimate the soil attribute value using two approaches of reference values and the Vis-NIR-SWIR spectral data of four sensors. The reference value approaches were i) the mean value of all laboratories, and ii) the value of best laboratory for each attribute. In the text, they will be referred as "mean" and "best". The best laboratory was selected for each attribute based on the best EI of four laboratories. As we reached the best fitted model for each attribute, the predicted value was used to perform the statistical criteria proposed by Cantarella et al. (2016). The models were evaluated by the following indices: coefficient of determination (R^2) and root mean square error (RMSE). The R^2 provides the percent of variance that is explained by the model. The RMSE is an easily interpreted error metric because it has the same data units of the attributes analyzed.

3. Results and discussion

3.1. Descriptive statistics

Observing the results for all laboratories, some attributes presented a high range of minimum and maximum values, e.g. P, H + Al, CEC, SB, and BS (Table 2). The laboratory 1 presented biased median values for nearly all attributes, which may increase the inaccuracy and impair the performance of the models. For each attribute the SD varied in all laboratories, showing that this parameter had no tendency. The lowest CV values were found for pH, sand and clay and the highest value was found for K. The CV values for all attributes were below 32.4%. This statistical parameter can influence the error evaluation increasing the imprecision. In contrast, the low values of SD found for pH determinations from all laboratories were an indicative of the low error estimation as proposed by Cantarella et al. (2016). The large range of each attribute contents directly reflects the representativeness and will positively influence the stability of the predictive models (Debaene et al., 2014).

3.2. Predictive performance of soil attributes by sensors

The predictive results for pH were generally low applying the best laboratory as reference value (Table 3). The R^2_{val} ranged from 0.52 to 0.71 considering all laboratories. The highest result was found applying sensor 1 ($R^2_{val} = 0.71$ and $RMSE_{val} = 0.36$). Tekin et al. (2013) explored the potential of Vis-NIR-SWIR spectroscopy for on-line measurement of soil pH, with the intention to produce variable rate lime recommendation maps. The authors obtained very good accuracy with the on-line measured spectra ($R^2 = 0.81$, RMSE = 0.20).

For OM, the predictive performances of sensors using the mean of all laboratories and the best laboratory were similar. For validation results, comparing both approaches only sensor 1 performed better for mean ($R^2_{val} = 0.83$, $RMSE_{val} = 4.54\,g\,kg^{-1}$). Concerning the prediction using the best laboratory, the highest result was found for sensor 2 ($R^2_{val} = 0.82$, $RMSE_{val} = 4.70\,g\,kg^{-1}$). The predictive performance of models is in accordance with the results found in the literature (Araújo et al., 2014; Nawar et al., 2016; Wang et al., 2015), where the overall performance of OM models presents R^2 around 0.8.

However, the predictive result of P was not as good as for OM. The models that used mean of all laboratories as reference value performed poorly compared to models using the best laboratory as standard value. In the first approach, regardless of the sensor used, the R^2_{val} did not exceed 0.36. The best prediction result for P was found applying sensor 3 with the best laboratory: $R^2_{val} = 0.60$ and $RMSE_{val} = 29.62\,mg\,dm^{-3}$. The poor prediction results for P may be attributed to the high variance of minimum and maximum values (Table 2) and also to its high lability in the soil, which makes difficult its precise determination.

The models applying the best laboratory also showed the best result for K, in particular for the sensor 1 ($R^2_{val} = 0.72$ and $RMSE_{val} = 1.52\,mmol_c\,dm^{-3}$). The predictive performances of Ca and Mg models were moderate. For both attributes, the models using the mean of all laboratories showed the best performance. Besides, for both attributes, sensor 3 presented the best results (Ca: $R^2_{val} = 0.77$ and $RMSE_{val} = 11.24\,mmol_c\,dm^{-3}$; Mg: $R^2_{val} = 0.76$ and $RMSE_{val} = 6.61\,mmol_c\,dm^{-3}$).

The predictions of Al and H + Al were good. Sensor 1 presented the best prediction for Al in both reference value approaches (mean: $R^2_{val} = 0.86$, $RMSE_{val} = 4.47\,mmol_c\,dm^{-3}$, and best: $R^2_{val} = 0.69$, $RMSE_{val} = 6.32\,mmol_c\,dm^{-3}$). For H + Al, sensor 1 with the mean of all laboratories achieved an impressive $R^2_{val} = 0.89$ and $RMSE_{val} = 5.98\,mmol_c\,dm^{-3}$. The AS presented a good prediction result ($R^2_{val} = 0.79$ and $RMSE_{val} = 11.39\%$, for mean of all laboratories), however slightly below Al and H + Al results. The Al presented very good prediction results compared to other papers. For instance, Viscarra Rossel et al. (2006) applied diffuse reflectance spectroscopy in distinct spectral ranges for simultaneous assessment of various soil properties. The highest R^2 value achieved for Al in their study was 0.61 applying near-infrared reflectance.

The prediction of SB, CEC, and BS achieved a great performance. Sensor 1 with the mean of all laboratories approach reached the best prediction for SB with an $R^2_{val} = 0.85$ and $RMSE_{val} = 15.07\,mmol_c\,dm^{-3}$. For the same reference value approach, CEC showed a good prediction for sensor 2 ($R^2_{val} = 0.92$ and $RMSE_{val} = 15.41\,mmol_c\,dm^{-3}$). The BS presented the best result using sensor 1, with the best laboratory ($R^2_{val} = 0.79$ and $RMSE_{val} = 10.34\%$).

For particle size fractions, the greatest R^2 for validation set of all attributes was found for clay content. The sensor 1 presented the best predictive performance for sand, silt, and clay (sand: $R^2_{val} = 0.91$ and $RMSE_{val} = 5.82\%$; silt: $R^2_{val} = 0.89$ and $RMSE_{val} = 3.59\%$; and clay: $R^2_{val} = 0.91$ and $RMSE_{val} = 4.95\%$). Both reference value approaches achieved similar prediction performance. These results are considered very good comparing with some studies (Casa et al., 2013; Vasques et al., 2016), especially for sand and silt.

The great performances of the predictive models enable the use of sensors in the evaluation of soil attributes. The prediction of some soil attributes, e.g. clay, OM, CEC, and pH, via sensors has huge consequences in the context of precision agriculture. This proximal sensing technique is able to assist the soil analysis in order to diminish the volume of soil samples to be analyzed by the routine laboratory. Instead

Table 2
Descriptive statistic of the analytical attributes for all soil samples.

		Attribute[a]														
		pH	OM	P	K	Ca	Mg	Al	H + Al	SB	CEC	BS	AS	Sand	Silt	Clay
Parameters	Laboratory	CaCl$_2$	g kg^{-1}	mg dm^{-3}	mmol$_c$ dm^{-3}							%				
Minimum	1	3.8	1.0	0.3	0.2	1.0	1.0	0.5	2.0	0.5	23.4	3.0	0.3	11.5	1.0	5.3
	2	3.7	1.0	1.0	0.0	0.4	0.4	0.0	10.0	1.1	0.7	4.4	0.0	10.8	1.6	2.5
	3	3.8	3.0	1.0	0.1	2.0	1.0	0.0	11.0	3.6	26.7	7.6	0.0	8.1	2.6	6.6
	4	3.8	5.7	0.7	0.0	3.1	1.9	0.5	9.2	5.6	26.9	13.9	0.2	6.8	1.9	5.0
Maximum	1	6.2	48.0	302.0	14.1	115.0	46.0	86.0	313.0	168.2	335.7	93.0	86.0	93.1	55.2	81.5
	2	6.7	53.0	307.0	20.7	161.4	87.3	116.9	297.0	242.1	452.7	94.5	83.6	85.7	59.0	75.4
	3	7.0	66.0	347.0	18.4	141.0	60.0	90.0	319.0	204.6	362.4	94.1	78.8	86.5	58.9	71.8
	4	7.1	41.3	712.7	13.2	145.1	64.5	91.9	198.8	205.7	309.0	93.9	73.9	87.0	55.2	73.0
Median	1	4.8	15.3	12.4	2.3	18.8	8.3	5.7	42.1	29.4	71.7	41.1	18.4	45.0	12.0	43.0
	2	4.8	18.3	14.1	2.9	27.5	15.2	7.3	38.1	45.5	83.3	52.1	16.4	43.8	16.3	39.9
	3	4.9	17.4	16.4	2.9	25.5	12.0	6.6	45.5	40.3	85.9	46.9	16.4	42.0	17.3	40.7
	4	4.9	15.8	14.9	2.5	32.0	13.9	6.5	32.1	48.4	80.5	58.7	12.0	43.2	17.1	39.7
Standard deviation	1	0.1	1.1	2.2	0.4	3.3	1.2	1.4	6.3	4.3	8.0	5.1	2.6	1.4	3.1	2.7
	2	0.1	0.9	1.8	0.4	4.2	1.6	1.1	6.3	5.9	11.5	2.7	0.9	0.8	1.8	1.5
	3	0.0	4.7	1.3	0.2	1.8	0.9	0.6	3.5	2.7	5.1	1.8	1.4	0.5	1.0	0.8
	4	0.1	1.3	6.7	0.4	3.4	2.5	1.5	4.2	4.4	7.5	2.7	2.7	1.9	2.5	2.2
Coefficient of variation in %	1	2.6	9.3	31.3	21.8	26.7	16.3	12.2	14.0	20.6	10.7	17.3	17.9	3.7	32.4	6.8
	2	2.3	6.3	27.1	14.5	15.8	10.8	26.4	15.2	13.2	14.1	6.6	24.6	2.4	13.3	4.9
	3	1.0	28.5	14.3	11.2	8.1	8.4	12.8	7.5	7.7	6.1	5.2	14.1	1.4	7.9	2.4
	4	2.4	9.5	39.7	28.8	9.9	18.3	18.0	10.9	8.3	8.4	5.5	21.7	5.7	16.0	6.4

[a] Potential of hydrogen (pH), organic matter (OM), exchangeable phosphorus (P), exchangeable potassium (K^+), exchangeable calcium (Ca^{2+}), exchangeable magnesium (Mg^{2+}), exchangeable aluminum (Al^{3+}), potential acidity (H + Al), exchangeable sum of the bases (SB), cation exchange capacity (CEC), base saturation (BS), and Aluminum saturation (AS).

of sending all soil samples to the routine laboratory analysis, the farmer can analyze around 80% or even more of the total collected amount in the Vis-NIR-SWIR spectroscopy laboratory. We are calling that as hybrid laboratory analysis.

The reflectance spectroscopy technique has been applied as an alternative for routine agronomic soil analyses since early 1990's. For instance, Cohen et al. (2007) showed that for some attributes (pH, P, Ca, and K) the accuracy was moderate, whereas K, Cu, Mg, Mn, Zn, and Fe exhibited low accuracy. They recommended the refinement of standard laboratory procedures before measurement by the sensor as a viable alternative to improve modeling results. Furthermore, the authors demonstrated that Vis-NIR-SWIR reflectance spectroscopy error rates were comparable to laboratory analytical error rates (being smaller in some cases), suggesting that the observed poor performance of prediction models may be attributed to the uncertainty inherent in laboratory data.

Most attributes achieved great prediction results (Table 3). For OM, K, CEC, BS, sand, silt, and clay attributes this technique appeared as a potential alternative to reduce the cost and time in soil analysis, as it maintains high accuracy. However, the type of sensor influenced the calibration of the models. The spectral reading of each sensor can vary in: calibration of the equipment, number of reading repetitions, time in reading the Spectralon plate, angle and distance of the sensor in relation to the sample and sources of light. As all these variables were controlled and remained unchanged, the differences in the prediction of the same attribute can be mainly due to the regression modeling, and the dissimilarity between spectroradiometer brand and internal calibration. In Ge et al. (2011), the authors developed models investigating sets with and without a controlled scanning protocol. The authors concluded that the establishment of a protocol decreases the variations that are related to extraneous effects due to multiple instruments/scanning.

The use of reflectance spectroscopy method may have the same analytical quality as the traditional laboratory method for some attributes. The studies over the years demonstrated that Vis-NIR-SWIR reflectance spectroscopy can be used to determine accurately important soil constituents, such as organic carbon, clay, sand, and CEC. This technique possibly will be employed as a hybrid laboratory method in estimating rapidly, non-destructively, accurately, and at low-price some attributes in soil samples, demonstrating its applicability to characterize agricultural soils. In the next section, the criteria for classification of analytical results proposed by Cantarella et al. (2016) will be discussed.

3.3. Results of inaccuracy and imprecision indices

All analytical quantifications are subject to uncertainties, although there are boundary ranges for it. The number of soil samples penalized (discrepant results outside the confidence interval) was evaluated in the laboratory. The determinations with the highest number of penalized samples by laboratories (sum of all laboratories) were found for P, K, Ca, Mg, Al, SB, AS, and silt (Fig. 1). These attributes presented a sum of penalties above 100 samples out of the total 1152. The least penalized attributes were CEC, sand, pH, H + Al, and clay.

The number of penalized samples predicted by sensors followed the same trend for laboratories (Fig. 1). The attributes with the highest number of penalized samples were equivalent to laboratories. In particular, the attributes P, K, Ca, Mg, Al, H + Al, SB, and AS showed over 150 penalized samples. The attributes pH, OM, CEC, BS, sand, silt, and clay were less penalized compared to laboratories. Observing the results of sensors using the mean of all laboratories and best laboratory as reference values in the prediction, the number of penalized samples were analogous, given the low CV values (Table 2) and the close predictive performance of models for these attributes (Table 3).

The inaccuracy of attributes for all laboratories was low (Fig. 2a). The highest inaccuracy was found for attribute AS in laboratory 1 and 2 (Fig. 2a). Regarding the imprecision index of laboratories (Fig. 2d), which represents the incompatibility in the reproduction of values for the same sample, Ca presented the highest percentage (48.6% for laboratory 4). The following attributes presented imprecision above 20% for at least one laboratory, representing weak reproducibility: Mg (26.7% and 35.3%, laboratories 1 and 4, respectively), H + Al (20% and 22.4%, laboratories 1 and 4, respectively), SB (32.4% and 22%, laboratories 2 and 4, respectively), Al (32.7%, laboratory 1), K (34.9%,

Table 3
Prediction performance of attributes applying PLSR method for four sensors.

		Calibration				Validation			
		Mean of all laboratories[a]		Best laboratory[b]		Mean of all laboratories[a]		Best laboratory[b]	
Attribute	Sensor	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE
pH (CaCl$_2$)	1	0.95	0.12	0.72	0.27	0.71	0.36	0.40	0.41
	2	0.68	0.33	0.60	0.30	0.61	0.35	0.42	0.42
	3	0.65	0.33	0.59	0.33	0.60	0.41	0.61	0.30
	4	0.77	0.28	0.68	0.29	0.52	0.42	0.46	0.37
OM (g kg^{-1})	1	0.85	3.39	0.87	3.95	0.83	4.54	0.78	4.41
	2	0.95	2.19	0.88	3.43	0.79	4.38	0.82	4.70
	3	0.88	3.32	0.87	3.83	0.76	4.44	0.76	5.37
	4	0.92	4.29	0.86	3.85	0.79	4.29	0.81	4.97
P (mg dm^{-3})	1	0.39	25.95	0.35	25.23	0.35	32.17	0.42	43.09
	2	0.24	29.92	0.34	36.57	0.25	32.71	0.23	25.39
	3	0.85	15.50	0.95	6.73	0.27	27.12	0.60	29.62
	4	0.43	26.25	0.74	20.25	0.36	28.93	0.36	32.34
K (mmol$_c$ dm^{-3})	1	0.98	0.36	0.94	0.74	0.71	1.19	0.72	1.52
	2	0.97	0.47	0.87	0.99	0.66	1.74	0.71	1.87
	3	0.67	1.46	0.61	1.68	0.64	1.72	0.70	1.92
	4	0.62	1.58	0.70	1.56	0.61	1.72	0.65	1.82
Ca (mmol$_c$ dm^{-3})	1	0.87	8.16	0.89	8.69	0.72	9.82	0.70	11.52
	2	0.72	11.75	0.71	13.05	0.64	11.84	0.62	15.85
	3	0.95	4.42	0.96	5.60	0.77	11.24	0.74	10.63
	4	0.83	8.98	0.93	6.64	0.68	11.65	0.55	16.41
Mg (mmol$_c$ dm^{-3})	1	0.95	4.81	0.88	3.77	0.81	10.16	0.71	6.27
	2	0.67	5.74	0.63	6.64	0.69	6.66	0.60	7.41
	3	0.89	3.45	0.87	3.80	0.76	6.61	0.72	6.65
	4	0.69	5.08	0.88	3.69	0.64	8.22	0.64	7.14
Al (mmol$_c$ dm^{-3})	1	0.95	2.2	0.78	6.08	0.86	4.47	0.69	6.32
	2	0.83	5.46	0.76	5.84	0.81	6.78	0.61	7.03
	3	0.93	3.54	0.73	6.64	0.87	5.74	0.67	5.61
	4	0.98	2.2	0.85	5.09	0.85	4.58	0.63	5.13
H + Al (mmol$_c$ dm^{-3})	1	0.91	3.86	0.89	16.13	0.89	5.98	0.79	18.71
	2	0.81	18.04	0.78	19.06	0.77	20.77	0.78	25.25
	3	0.92	12.92	0.90	15.36	0.70	17.42	0.80	19.25
	4	0.98	5.98	0.97	7.82	0.86	15.37	0.86	23.00
SB (mmol$_c$ dm^{-3})	1	0.92	8.77	0.92	9.71	0.85	15.08	0.77	19.96
	2	0.54	21.7	0.70	21.04	0.49	26.67	0.58	22.88
	3	0.98	4.64	0.95	6.96	0.76	14.8	0.73	24.34
	4	0.84	11.39	0.83	14.17	0.62	28.7	0.62	25.65
CEC (mmol$_c$ dm^{-3})	1	0.94	7.87	0.92	16.21	0.83	14.9	0.87	19.54
	2	0.98	7.52	0.95	7.97	0.92	15.41	0.82	24.47
	3	0.93	12.86	0.90	14.37	0.9	18.09	0.86	30.84
	4	0.95	11.46	0.93	15.24	0.82	22.23	0.87	18.53
BS (%)	1	0.97	3.99	0.88	7.22	0.68	11.43	0.79	10.34
	2	0.72	10.86	0.73	11.16	0.7	11.73	0.56	13.56
	3	0.83	8.6	0.83	8.61	0.67	11.17	0.62	15.50
	4	0.76	9.6	0.81	9.17	0.7	12.27	0.71	11.34
AS (%)	1	0.95	4.78	0.91	7.01	0.79	11.39	0.61	12.55
	2	0.73	11.87	0.62	14.40	0.47	13.27	0.61	14.28
	3	0.74	10.68	0.75	10.46	0.59	14.62	0.65	14.91
	4	0.95	4.82	0.89	7.50	0.65	13.39	0.66	13.15
Sand (%)	1	0.94	5.2	0.95	5.07	0.91	5.82	0.90	6.90
	2	0.83	9.00	0.76	10.64	0.84	8.27	0.78	10.85
	3	0.90	6.76	0.89	6.93	0.85	8.71	0.86	8.70
	4	0.94	4.96	0.94	5.21	0.89	7.89	0.89	7.64
Silt (%)	1	0.96	2.04	0.95	1.82	0.89	3.59	0.89	3.47
	2	0.61	6.21	0.83	4.84	0.64	6.54	0.74	5.31
	3	0.96	2.03	0.95	2.40	0.86	3.87	0.86	4.91
	4	0.92	2.87	0.96	2.28	0.81	4.61	0.83	4.51
Clay (%)	1	0.95	3.79	0.95	14.03	0.90	5.20	0.91	4.95
	2	0.87	6.29	0.92	5.09	0.88	6.05	0.89	5.70
	3	0.88	5.97	0.97	3.24	0.86	6.57	0.86	6.98
	4	0.94	4.28	0.94	4.41	0.86	6.51	0.86	6.23

[a] Model generated considering as reference value the mean of all laboratories.
[b] Model generated considering as reference value the best laboratory based on the best Excellence Index.

laboratory 3), BS (25.2% laboratory 1), sand (21.2%, laboratory 1), and silt (21.8%, laboratory 1).

Observing the inaccuracy calculated for sensors using the mean of all laboratories (Fig. 2b), all attributes presented low inaccuracy regarding sensors, with the exception of P (inaccuracy of 47% for sensor 3) (Fig. 2b). In the results for sensors using the best laboratory (Fig. 2c), Al showed the highest inaccuracy (36.8%, sensor 4) followed by P (34.7%, sensor 4), AS (26%, sensor 1), K (25%, sensor 1), Ca (23%, sensor 4), and Mg (21.5%, sensor 4). The worst performance in general was found for sensor 4.

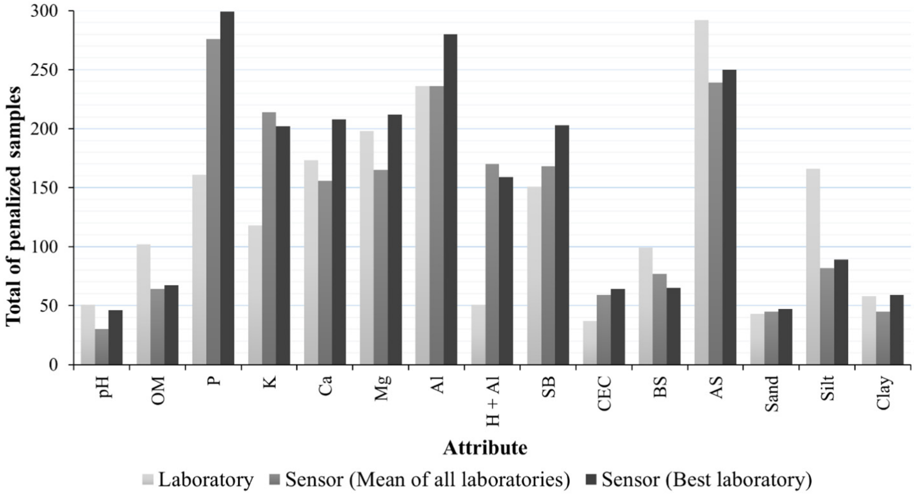


Fig. 1. Total number of penalized samples for each soil attribute obtained by the laboratory and sensor.

The imprecision index for sensors using mean of all laboratories was high for three attributes: K, H + Al, and sand (Fig. 2e). For K, sensor 3 presented the poorest performance (78.6%). For H + Al, sensors 1, 2, and 4 were the ones with highest imprecision indexes (71.1%, 72.4%, and 72.6%, respectively), and for sand, sensors 1 and 4 (57.5%, and 69.6%, respectively). However, the lowest imprecision indices for the sensors applying the best laboratory as reference value were found for different attributes (Fig. 2f). In this case, P, Al, and AS showed high imprecision. For P, sensor 3 and 4 achieved imprecision of 91.9% and 74.9%, respectively; for Al, sensor 4 had 71.8%; and for AS sensors 1 and 4 had 63.4% and 60.6% of imprecision, respectively (Fig. 2f). Besides these attributes, K, Ca, and Mg presented imprecision above 40%. The sensor 4 revealed high imprecision in average (30.9%) followed by sensor 1 (23.3%).

In general, the imprecision index presented higher percentage compared to inaccuracy because the imprecision formula takes into consideration the CV values of each soil sample and the CVs were high for some attributes, e.g. K, Ca, Mg, Al, H + AL, SB, CEC, and sand. As for the inaccuracy, it considers the number of soil samples penalized and this number was low. In summary, the soil attributes that were classified with relatively high imprecision indices represent incompatibilities in the reproduction of values for the same sample. On the other hand, the attributes that presented high inaccuracy indices represent consequent uncertainties of measurements outside the

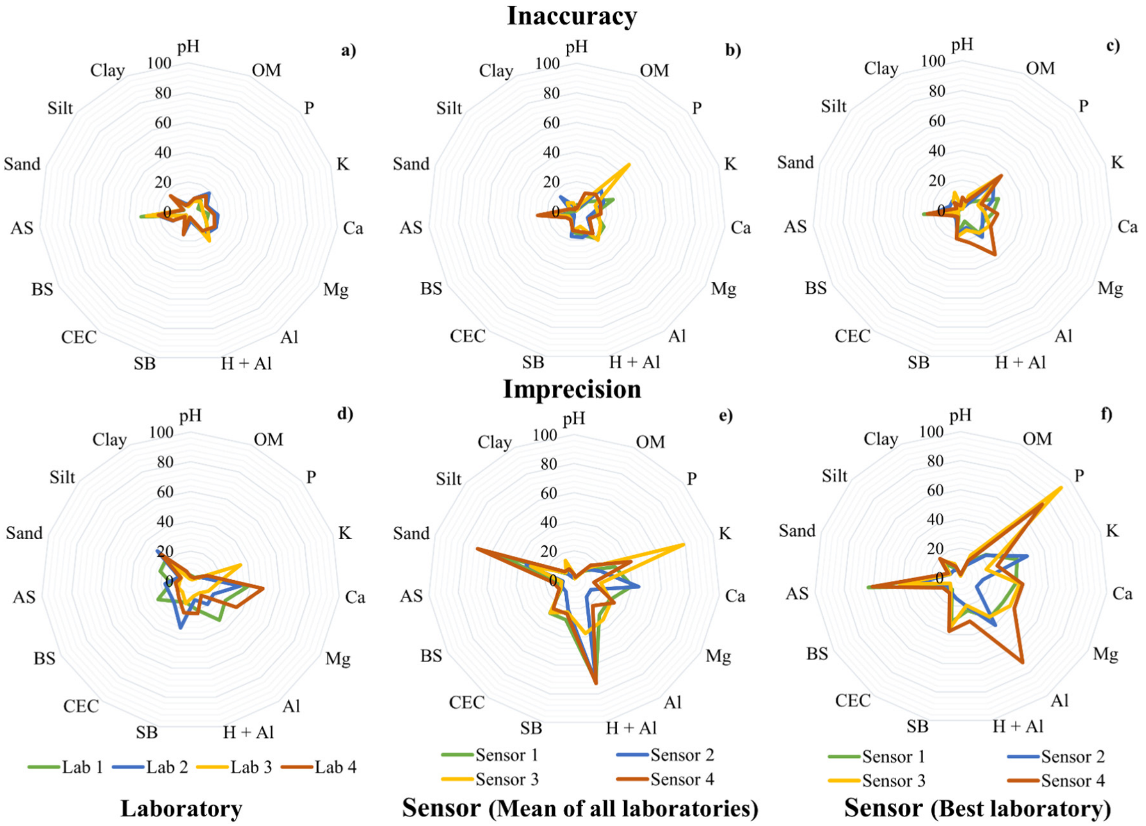


Fig. 2. Inaccuracy and Imprecision for laboratory (a and d), sensor using the mean of the reference values for all laboratories (b and e), and sensor using the reference values from the best laboratory (c and f).

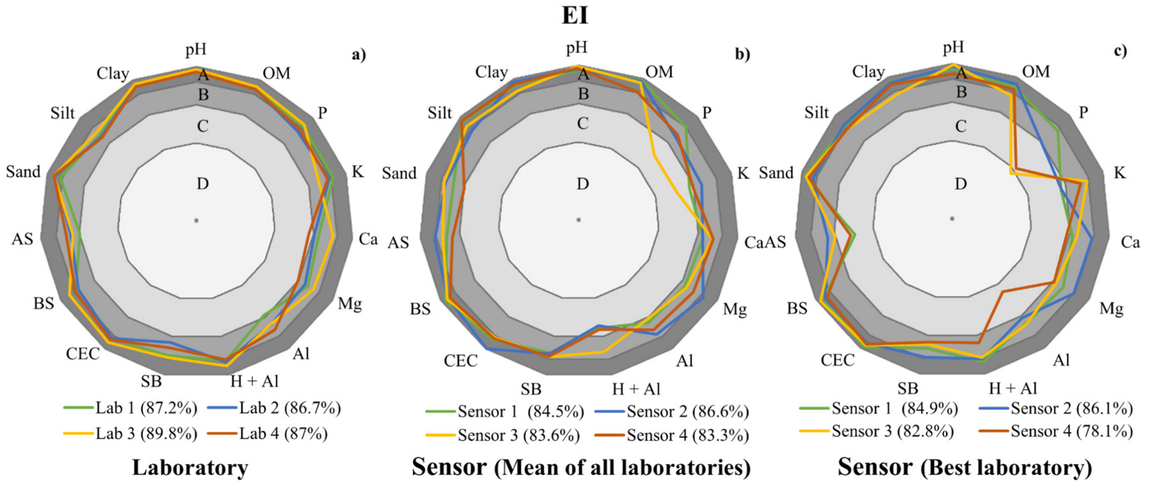


Fig. 3. Excellence Index (EI) obtained by each laboratory and sensor. The colors represent the EI classification: A ≥ 90%, B between 75% and 89%, C between 50% and 74%, and D < 50% performed for each approach. In parenthesis are the average EI of all attributes.

interval of true value acceptance (Cantarella et al., 2016).

The majority of soil attributes analyzed presented high EIs. In general, the attributes with low quantity in soil (e.g. the ones measured in $\text{mmol}_c\ \text{dm}^{-3}$) are likely to present high percentage of inaccuracy and imprecision. In fact, the laboratory measurements can increase rapidly their uncertainty as the attribute concentrations decline (Rayment et al., 2012). The EI for all laboratories is shown in Fig. 3a. Overall, few attributes had results placed in concept C. The attributes Ca (72.2%) and Mg (74.8%) presented the lowest EI (graded C) for laboratory 4, and Al (73.6%) and AS (74.3%) for laboratory 1. The pH, OM, H + Al, CEC, sand, and clay were the attributes classified as A for all laboratories (Fig. 3a). This type of inter-laboratory evaluation is an effective measure for the determination of analytical accuracy. In general, the laboratory 2 presented the lowest performance regarding the criteria for classification of analytical results. The laboratory 3 reached the highest EI (average EI of lab 3 = 86.7%) and the lowest inaccuracy and imprecision indices.

Regarding the quantification methods using the sensors, in the first sensor approach (Fig. 3b), the attributes P, K, H + Al, and sand reached the lowest quality certification by IAC (grade C). The best classification (grade A) was achieved to clay, pH, OM, CEC, and BS. In general, the best performance was found for sensor 2 with an average EI of 86.6%. On the other hand, the second sensor approach (Fig. 3c), using the best laboratory as reference value to predict the attributes, showed poor results for P, which was the only one that reached concept D for sensor 3 and concept C for sensor 4. Al and AS also presented concept C for sensor 4. The attributes sand, silt, clay, pH, OM, CEC, and BS presented EI well-classified, with the majority of them being within class A. For these attributes, all sensors had a great performance reproducing a reliable analytical value. The pH attribute presented the highest concept (A) for all sensors in both approaches (Fig. 3b and c). This result is due to the small pH variation of the samples, which leads to a low standard deviation and CV values. In summary, sensor 2 presented the best performance over all sensors and the sensor 4, the worst.

Considering the quality of the predictions resulting from the four sensors, some attributes denoted inaccurate values. The errors of the sensor predictions are mainly due to the use of inadequate laboratory references, which do not represent precise and accurate values (Soriano-Disla et al., 2014). Sensor 2 presented the best average EI, indicating that the prediction performance of soil attributes modeling applying sensor 2 leads to more accurate results. Overall, the criteria for classification of analytical results showed that sand, silt, clay, pH, OM, CEC, and BS can be determined by the spectroscopy technique with high-quality outcome.

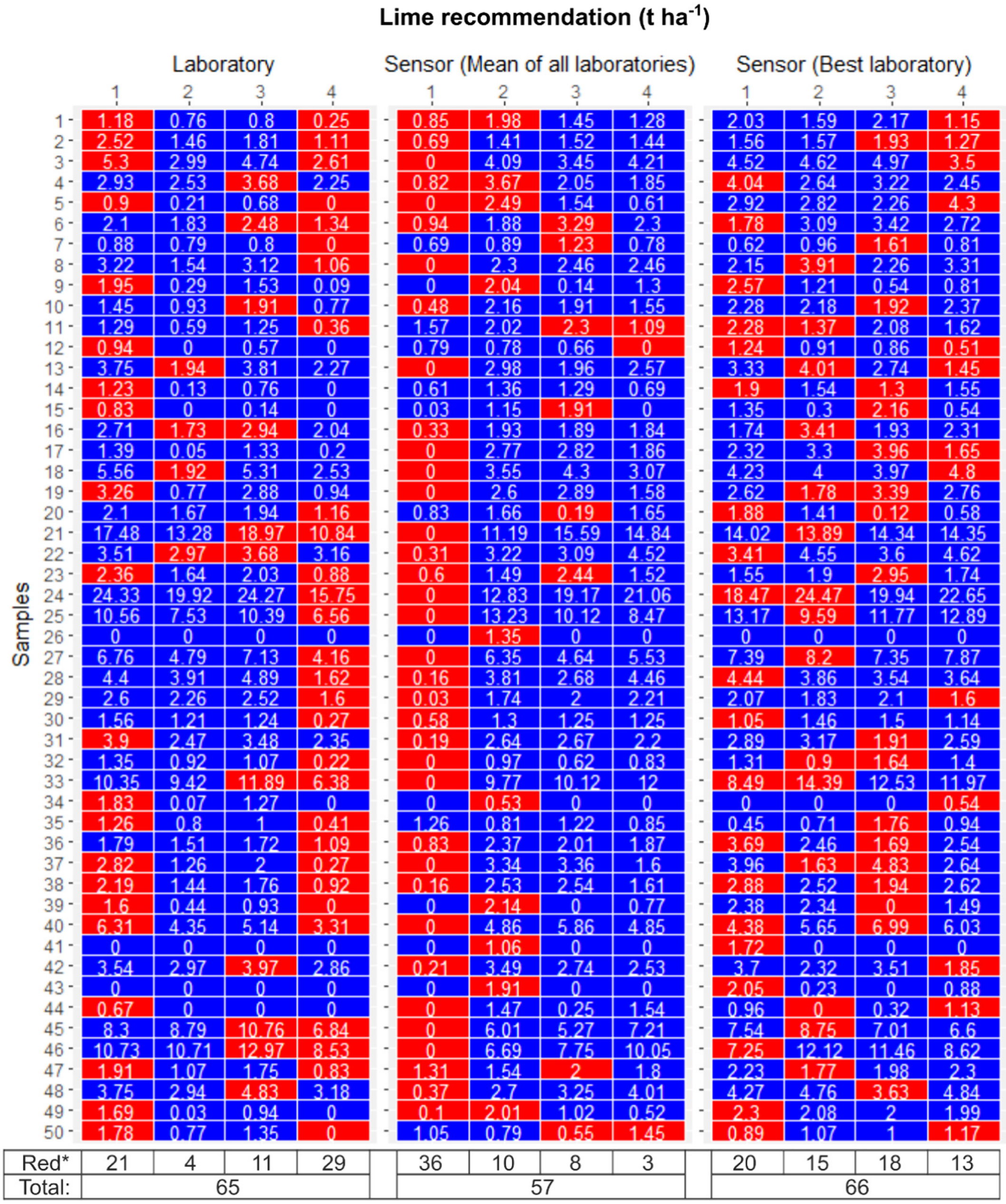
The reliability of the measurements in laboratories directly influences the quality of the models via sensor data. Bernardi et al. (2002) assessed the analytical quality of soil fertility laboratories methods in Brazil and revealed that in 2000, 63% of the 79 laboratories obtained grades A or B, or reached the acceptable minimum requirement to get the authorized seal of Embrapa (regulatory agency of Brazil). Also, they indicated that the human error may always be integrated to the measurement process. Analytical results are exposed to inaccuracies and imprecisions mainly due to the lack of required quality assurance programs in laboratories, and the inherent variable nature of soil (Viscarra Rossel and McBratney, 1998). Thus, the analytical quality of sensor-based models is rather dependent on the quality of traditional laboratory data.

Although it is evident that all of the attributes results may vary from sensor to sensor, the question remaining is: can the variations on different sensors influence the measurement performance? Observing the errors assessment of each sensor, the sensor 2 had the best indices (Fig. 3). However, all sensors presented good ability to reproduce similar values for the same attribute, which is expressed in the inaccuracy index. The similar EI classification assigned to the laboratories and sensors demonstrates the sensors' ability to provide results within an acceptable limit. Alternatively, Rosero-Vlasova et al. (2016) compared the soil reflectance obtained with three laboratory setups, each one with a different spectroscopy accessory (integrating sphere, illuminator lamp and contact probe) and the results showed no statistical differences. Therefore, the variations in the spectral responses found here were not substantial for sand, silt, clay, pH, OM, CEC, and BS attributes.

The general variations in reflectance output result from the interaction of different factors, which can be divided into two main categories: spectroradiometer domains (signal-to-noise ratio, spectral configuration, detector performance, fore and fiber optic characteristics, stray light contribution, warm-up time, and calibration quality) and sampling domains (reference method and condition, homogeneity of the sample, and operator input) (Pimstein et al., 2011). According to Rayment et al. (2012), models involving Vis-NIR-SWIR reflectance spectroscopy depend on the precision, accuracy, and robustness of the reference laboratory analysis. In fact, these factors are prominent over issues related to the sensor domain.

3.4. Lime recommendation (LR) variability

The LR values for each soil sample considering all laboratories and sensors are shown in Fig. 4. In the LR for the soil sample n. 1 (row 1), the laboratories 1 and 4, and sensors 1, 2, and 4 presented results outside the confidence interval (red color). The LR for this soil sample was considered low (average of $1.29\ \text{t ha}^{-1}$). The total of samples



Lime recommendation (t ha^{-1})

Samples	Laboratory				Sensor (Mean of all laboratories)				Sensor (Best laboratory)			
	1	2	3	4	1	2	3	4	1	2	3	4
1	1.18	0.76	0.8	0.25	0.85	1.98	1.45	1.28	2.03	1.59	2.17	1.15
2	2.52	1.46	1.81	1.11	0.69	1.41	1.52	1.44	1.56	1.57	1.93	1.27
3	5.3	2.99	4.74	2.61	0	4.09	3.45	4.21	4.52	4.62	4.97	3.5
4	2.93	2.53	3.68	2.25	0.82	3.67	2.05	1.85	4.04	2.64	3.22	2.45
5	0.9	0.21	0.68	0	0	2.49	1.54	0.61	2.92	2.82	2.26	4.3
6	2.1	1.83	2.48	1.34	0.94	1.88	3.29	2.3	1.78	3.09	3.42	2.72
7	0.88	0.79	0.8	0	0.69	0.89	1.23	0.78	0.62	0.96	1.61	0.81
8	3.22	1.54	3.12	1.06	0	2.3	2.46	2.46	2.15	3.91	2.26	3.31
9	1.95	0.29	1.53	0.09	0	2.04	0.14	1.3	2.57	1.21	0.54	0.81
10	1.45	0.93	1.91	0.77	0.48	2.16	1.91	1.55	2.28	2.18	1.92	2.37
11	1.29	0.59	1.25	0.36	1.57	2.02	2.3	1.09	2.28	1.37	2.08	1.62
12	0.94	0	0.57	0	0.79	0.78	0.66	0	1.24	0.91	0.86	0.51
13	3.75	1.94	3.81	2.27	0	2.98	1.96	2.57	3.33	4.01	2.74	1.45
14	1.23	0.13	0.76	0	0.61	1.36	1.29	0.69	1.9	1.54	1.3	1.55
15	0.83	0	0.14	0	0.03	1.15	1.91	0	1.35	0.3	2.16	0.54
16	2.71	1.73	2.94	2.04	0.33	1.93	1.89	1.84	1.74	3.41	1.93	2.31
17	1.39	0.05	1.33	0.2	0	2.77	2.82	1.86	2.32	3.3	3.96	1.65
18	5.56	1.92	5.31	2.53	0	3.55	4.3	3.07	4.23	4	3.97	4.8
19	3.26	0.77	2.88	0.94	0	2.6	2.89	1.58	2.62	1.78	3.39	2.76
20	2.1	1.67	1.94	1.16	0.83	1.66	0.19	1.65	1.88	1.41	0.12	0.58
21	17.48	13.28	18.97	10.84	0	11.19	15.59	14.84	14.02	13.89	14.34	14.35
22	3.51	2.97	3.68	3.16	0.31	3.22	3.09	4.52	3.41	4.55	3.6	4.62
23	2.36	1.64	2.03	0.88	0.6	1.49	2.44	1.52	1.55	1.9	2.95	1.74
24	24.33	19.92	24.27	15.75	0	12.83	19.17	21.06	18.47	24.47	19.94	22.65
25	10.56	7.53	10.39	6.56	0	13.23	10.12	8.47	13.17	9.59	11.77	12.89
26	0	0	0	0	0	1.35	0	0	0	0	0	0
27	6.76	4.79	7.13	4.16	0	6.35	4.64	5.53	7.39	8.2	7.35	7.87
28	4.4	3.91	4.89	1.62	0.16	3.81	2.68	4.46	4.44	3.86	3.54	3.64
29	2.6	2.26	2.52	1.6	0.03	1.74	2	2.21	2.07	1.83	2.1	1.6
30	1.56	1.21	1.24	0.27	0.58	1.3	1.25	1.25	1.05	1.46	1.5	1.14
31	3.9	2.47	3.48	2.35	0.19	2.64	2.67	2.2	2.89	3.17	1.91	2.59
32	1.35	0.92	1.07	0.22	0	0.97	0.62	0.83	1.31	0.9	1.64	1.4
33	10.35	9.42	11.89	6.38	0	9.77	10.12	12	8.49	14.39	12.53	11.97
34	1.83	0.07	1.27	0	0	0.53	0	0	0	0	0	0.54
35	1.26	0.8	1	0.41	1.26	0.81	1.22	0.85	0.45	0.71	1.76	0.94
36	1.79	1.51	1.72	1.09	0.83	2.37	2.01	1.87	3.69	2.46	1.69	2.54
37	2.82	1.26	2	0.27	0	3.34	3.36	1.6	3.96	1.63	4.83	2.64
38	2.19	1.44	1.76	0.92	0.16	2.53	2.54	1.61	2.88	2.52	1.94	2.62
39	1.6	0.44	0.93	0	0	2.14	0	0.77	2.38	2.34	0	1.49
40	6.31	4.35	5.14	3.31	0	4.86	5.86	4.85	4.38	5.65	6.99	6.03
41	0	0	0	0	0	1.06	0	0	1.72	0	0	0
42	3.54	2.97	3.97	2.86	0.21	3.49	2.74	2.53	3.7	2.32	3.51	1.85
43	0	0	0	0	0	1.91	0	0	2.05	0.23	0	0.88
44	0.67	0	0	0	0	1.47	0.25	1.54	0.96	0	0.32	1.13
45	8.3	8.79	10.76	6.84	0	6.01	5.27	7.21	7.54	8.75	7.01	6.6
46	10.73	10.71	12.97	8.53	0	6.69	7.75	10.05	7.25	12.12	11.46	8.62
47	1.91	1.07	1.75	0.83	1.31	1.54	2	1.8	2.23	1.77	1.98	2.3
48	3.75	2.94	4.83	3.18	0.37	2.7	3.25	4.01	4.27	4.76	3.63	4.84
49	1.69	0.03	0.94	0	0.1	2.01	1.02	0.52	2.3	2.08	2	1.99
50	1.78	0.77	1.35	0	1.05	0.79	0.55	1.45	0.89	1.07	1	1.17
Red*	21	4	11	29	36	10	8	3	20	15	18	13
Total:	65				57				66			

Fig. 4. Lime recommendation in tons per hectare (t ha^{-1}) analyzed by four laboratories and four sensors for 50 soil samples (numbers were left in sequence). *Red color: represents discrepant results outside the confidence interval (α = 0.05), Blue color: represents the acceptable results of lime recommendation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

outside the confidence interval for laboratories 1, 2, 3, and 4 were 21, 4, 11, and 29, respectively. The results of CEC and BS for laboratory 4 were the least accurate and, therefore, influenced the calculation of the LR, which led to a large number of penalized samples. Particularly in the laboratory 4, 58% of soil samples analyzed presented a result outside of the confidence interval.

In the sensors applying the reference value of mean of all laboratories, sensor 1 showed the largest number of samples outside the confidence interval (36), followed by sensor 2 (10), sensor 3 (8), and sensor 4 (3) (Fig. 4). For sensors applying the best laboratory as reference value, the LR results were similar, but had a larger number of samples outside the confidence interval for sensors 2, 3, and 4. Only sensor 1 presented less samples outside the confidence interval (20) compared to the same sensor using the mean of all laboratories (36). However, this sensor presented the worst accuracy for LR in both prediction approaches considered.

Uncertainties of LR may undermine the productive potential of agriculture. The LR results showed a significant variability in relation to the confidence interval. This discrepancy is due to the fact that the CEC and BS values presented elevated ranges, resulting in inaccurate LR. Overall, 67.5% of LR for all soil samples determined by the laboratories were within the confidence interval. Similar results were described in Cantarella et al. (2006), in which 84 commercial laboratories were evaluated, and 74% of the LR was within acceptable limits. The consequences of errors in lime application will lead to direct profit losses and will also influence the nutrient availability, which may be difficult to fix if the rates are higher than those actually required (Cantarella et al., 2006).

Considering the total number of samples outside the confidence interval (57 samples penalized), the sensors using the mean reference value of all laboratories revealed the best performance with only 28% of samples penalized (Fig. 4). This result shows the potential

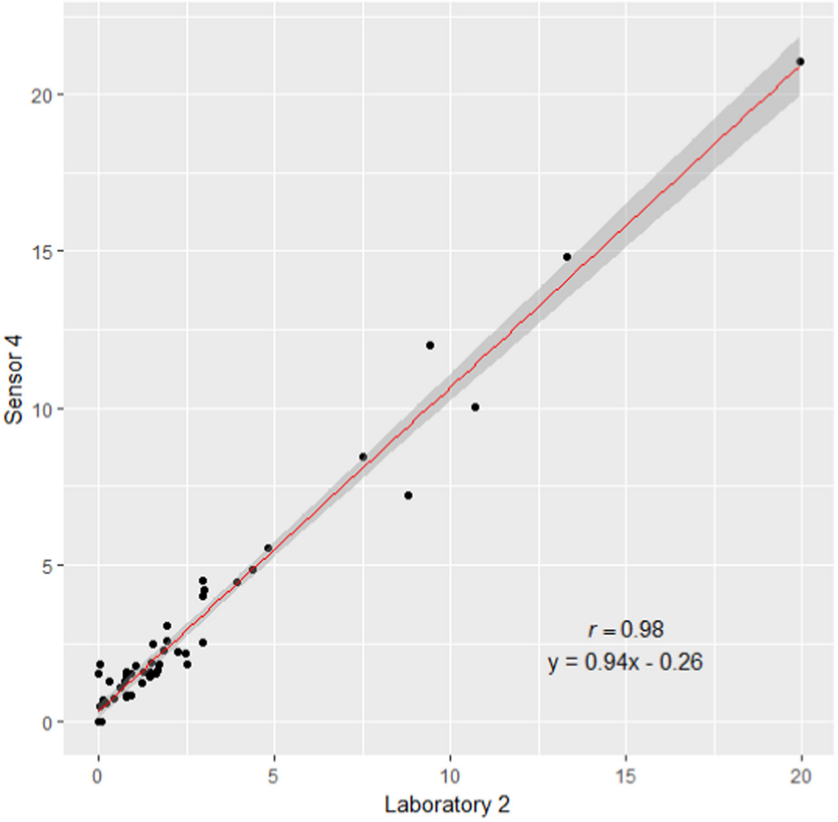


Fig. 5. Correlation between lime recommendation (t ha^{-1}) of laboratory 2 and sensor 4.

application of reflectance spectroscopy in the LR. The under- or over-application of lime influence the absorption of micronutrients, and most important, increase the environmental footprint of the agricultural activity. Tekin et al. (2013) explored the potential of the on-line Vis-NIR-SWIR sensor for pH prediction and derived meaningful lime recommendations.

A more detailed assessment comparing the LR results of the sensors and laboratories was performed by calculating the correlation coefficient of the best laboratory and sensor results (Fig. 5). Considering that the best LR result was achieved for laboratory 2 and sensor 4, the correlation coefficient between both was strongly positive (r = 0.98). The majority of LR was between 0 and 5 t ha^{-1} and few samples presented elevated LR values. This outcome indicated that the LR derived from proximal sensor analysis can be used as an efficient method, since it presented a high correlation with the laboratory result.

The use of sensors is a promising technique with high potential for meeting the soil monitoring requirements. Applying Vis-NIR-SWIR spectroscopy to search the viability of rapidly assessing the essential quality indices of commercial organic fertilizers, Wang et al. (2014) reached accurate predictions for pH, concluding that the reflectance spectroscopy can be used as a valuable industrial and research tool to rapidly and accurately assess the quality of commercial organic fertilizers.

The demand to develop technologies that maximize the fertilizer efficiency in agroecosystems is increasing. The application of fertilizer, lime, and other soil amendments inputs requires a precise management. Soil reflectance spectroscopy has shown capability in providing a rapid assessment of various physical and chemical soil attributes. Soil measurements through sensors can be performed in laboratory conditions or directly in the field.

In this context, hybrid laboratories must be developed in order to efficiently maximize the use of agricultural inputs. The hybrid laboratory analysis works as follows: spectral information of a 100% of the soil samples is obtained and 20% of the samples have their attributes determined by wet chemical analysis. These samples will be used to calibrate models for prediction of soil attributes. The 80% remaining samples will have their attributes estimated by the calibrated model. The term hybrid refers to a small part of the samples being analyzed by the traditional method and most of them being predicted by reflectance spectroscopy. In fact, the ratio 20% and 80% is an estimate and will depend on other factors such as the total sample size, the total cost of the analyses and the accuracy of the prediction model. This approach allows information to be obtained in a faster and cheaper way and reduces the use of toxic compounds in traditional analyses. Hybrid laboratories analyses will have a great impact on how to manage the soil, as by generating soil information rapidly and at low costs, they will enable farmers to have better access to such information.

4. Conclusion

It was possible to quantify the degree of acceptable uncertainties in the determinations of soil attributes with different laboratories and sensors. The performance of the predictive models was influenced by the analytical precision and accuracy of the reference laboratories. Overall, predictions of soil attributes using different sensors showed high reproducibility, which is associated with the analytical capacity of the reflectance spectroscopy technique. The quality of the spectral prediction models led to great results for sand, silt, clay, OM, CEC, K, and pH.

The classification of analytical performance presented good results for sand, silt, clay, pH, OM, CEC, and BS attributes, which are important for agricultural production. The soil attributes are used for the diagnosis of soil fertility and for determining the rates of application of lime, fertilizer, and others nutrient managements. The LR derived from spectral analysis can be used as an efficient method, since it presented a high correlation with the laboratory result. Thus, variation in the LR has economic and environmental implications. For example, the same sample may show a variation of the LR from 1 to 2 t ha^{-1}, i.e. 100% increase, doubling the cost.

The Hybrid Laboratory Analysis is dependent of the quality (accuracy/precision) of traditional analysis. On the other hand, sensors can improve and optimize traditional laboratory operations. The Vis-NIR-SWIR reflectance spectroscopy technique can complement the traditional methods, reducing costs, demanded time, and the use of harmful toxic elements for the characterization of soil attributes.

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