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Organic Matter and Sand Estimates by Spectroradiometry: Strategies for the Development of Models with Applicability at a Local Scale

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ABSTRACT

The development of spectral prediction models for soil attributes has been extensively studied in the last 10 years. However, one of the problems encountered during this period concerns the representativeness of the samples selected for model generation, which are often unable to capture the existing variability in agricultural areas, generating imprecise models. Thus, it is necessary to establish strategies for selecting soil samples, as well as for making them more representative within the model. Considering this, the aim of the present study was to evaluate strategies for soil sample selection and the recalibration of large models using samples from a smaller area, in a process called spiking, and its effect on soil attribute estimations. A total of 425 soil samples were used for the generation of the state models, as well as 200 soil samples from a target site for attribute recalibration and prediction. From these 200 samples, 10 (subset) were selected by different methods for state model recalibration (spiking), and 190 were used in the prediction. Another 5 and 10 copies of the subsets were also used as extra-weight to recalibrate the models. Models spiked with samples located in the center of the spectral space associated with extra-weight (10 copies) showed better accuracy in sand prediction (RPD = 2.20; r^2 = 0.80; RMSEP = 71.6 g kg^{-1}). For organic matter, the use of selected samples based on 5 clusters associated with extra-weight (10 copies) slightly improved the RMSEP and RPD in most cases, reaching a maximum value of 6.1 g dm^{-3} and 1.20, respectively. However, the subsets selected at the target site were not able to indicate the entire variability of the local samples concerning organic matter, damaging the expansion of the recalibrated state models.

Keywords: Spiking; Sand; Organic Matter; Spectroradiometry.

1. Introduction

Detailed mapping of soil attributes involves the collection of a high number of samples. In addition to high economic cost, this leads to the generation of dangerous residues derived from chemical analyses.

For this reason, the search for analysis tools that are easily applied, inexpensive, precise and with low negative ambient impacts (clean) is key in studying soil on a large scale, especially in countries such as Brazil, where the need for laboratory analysis increases each year, with hundreds or thousands of samples requiring analysis. In this regard, Vis-NIR-SWIR spectroscopy combines all these desirable characteristics and can be applied to obtain soil attributes (Dunn et al., 2002; Shepherd and Walsh, 2002; Islam et al., 2003; Brown et al., 2006).

Vis-NIR-SWIR spectra are complex signals that contain useful information for analytical pursposes. An empirical approach can be applied for the use of the significant amount of information contained in a spectrum, employing calibrations (or models) constructed using multivariate regression techniques (Naes et al., 2002; McBratney et al., 2006).

The samples used to construct the models, termed calibration samples, must be representative of the population of samples to which this model will be applied. The establishment of spectral calibration libraries derived from a high number of representative samples that contain the necessary variability has been suggested (Shepherd and Walsh, 2002; Brown et al., 2005, 2006; Viscarra Rossel et al., 2008). However, this premise is not easy to fulfill, especially in areas with high edaphic diversity, because, even though the acquired calibrations are based on a large number of samples, the number of samples does not always guarantee that the fitted model can be successfully applied in new areas (Viscarra Rossel et al., 2008; Wetterlind et al., 2010).

In this case, the application of calibrated models in new areas, which have no representative samples in the spectral library, can contribute to incorrect soil attribute predictions (Brown et al., 2006; Brown, 2007; Sankey et al., 2008). Thus, regional models (generated with samples from a particular region) may not be useful for estimating soil properties from other regions presenting different properties and edaphic attributes.

This problem is more evident in regions presenting greater edapho-diversity, since it is very complex to include all factors that interfere in soil variability in the spectral library.

Likewise, models developed at the local scale (generated with samples from a certain area) will not be valid for regional or even national scales.

Recent studies suggest that the best way to solve this problem is through calibration spiking with samples from the target study site (D'Acqui et al., 2010; Wetterlind and Stenberg, 2010; Guerrero et al., 2014; Guy et al., 2015). After spiking, the recalibrated model tends to display greater precision when applied to samples taken from the target study site (Wetterlind et al., 2010; Guerrero et al., 2010). Currently, the spiking process seems to be most adequate when applied to model expansion (Shepherd and Walsh, 2002; Viscarra Rossel et al., 2008; Minasny et al., 2009).

The central question regarding spiking concerns the type and adequate number of samples to be selected for model recalibration, since has a direct influences on the prediction result. A high number of local samples for the spiking subset tends to raise model accuracy (Brown, 2007; Guerrero et al., 2010), but, on the other hand, reduces the advantages of using spectroscopy as a quick and low-cost analytical method (Guerrero et al., 2014).

The use of a small spiking subset displays the advantage of low-cost, but a disadvantage regarding the possibility of inaccuracies in recalibrated models. To circumvent these problems, Guerrero et al. (2014) suggest the addition of several copies (extra-weight) of the spiking subsets within the calibration matrix, in order to increase the relevance of the target site samples and improve model fit.

In this context, this study had as its first objective to select the most influential samples from a target site for spiking subsets. The second objective was to evaluate the prediction accuracy for sand and organic matter content in the target site after assigning extra-weight to the spiking subsets.

2. Materials and methods

2.1. Soil sampling in the state of Paraná

A total of 425 soil samples were collected from different areas in the state of Paran's - Brazil, a region delimited by the geographic coordinates 22º29'30′ ′ to 26º42'59′ ′ south and 48º02'24′ ′ to 54º37′ 38′ ′ west. According to the World Reference Base (2014), the soil classes in the state comprise mainly Lixisols, Cambisols, Chernozems, Podzols, Gleysols, Ferralsols, Regosols, Nitisols and Histosols. These soil classes are developed on different lithologies such as migmatites, quartzites, basalt, sandstone, phyllites, siltstones, granites and micaxists, among others (EMBRAPA, 1984). The samples were collected from different landscape areas, toposequences and soil, forest and draining conditions.

2.2. Soil sampling in the target site

A total of 200 samples were collected from a target site located in northwestern Paraná - Brazil, delimited by the geographic coordinates 22º57´19´´ to 22º52´59´´ south and 52º3´47´´ to 51º59´0.7´´ west, comprising 2,500 ha. The soil classes found in the area, according to the World Reference Base (2014) are Ferralsols, Nitisols, Lixisols, Cambisols and Regosols. It is worth mentioning that, although this area is located within the state of Paraná, no samples were collected from this area to form the group of 425 samples described in Section 2.1

2.3. Soil sample laboratory and spectral analyses

After collection, the samples were submitted to laboratory analyses for determination of physical and chemical attributes, as well as spectral characterization. The samples were air-dried and sieved through a 2 mm mesh. A hydrometer was used for the determination of total sand content (Kiehl, 1979). Organic matter content was measured according to Walkley and Black (1934). These attributes were chosen because they must be identified in a laboratory, which uses chemical reagents with the potential to contaminate the environment, in addition to increasing the time and cost of the analysis.

The samples designated for spectral reading were dried at 45 °C for 24 h and sieved (mesh 2 mm) for size particle homogenization and reduction of humidity and sampling effects (Epiphânio et al., 1992). Subsequently, each sample was placed on a Petri dish (9 cm diameter and 1.5 cm height) and submitted to spectral readings using a ASD FieldSpec 3 JR spectroradiometer with a spectral range from 350 to 2.500 nm. The equipment was programmed to perform 50 readings for each sample, thereby generating an average spectral curve.

For data acquisition, a Spectralon standard white plate calibrated for 100% reflectance was used, in accordance to the Labsphere Reflectance Calibration Laboratory (LRCL, 2009). An optical-fiber reader was placed on the support platform in a vertical position 8 cm distant from the samples. The reading area cmprised approximately 2 cm^2. The light source was a 650 W light bulb with a noncollimated beam located 35 cm from the platform and at a 30° angle relative to the horizontal plan.

The spectral readings were repeated three times, with successive displacement of the Petri dish 120° clockwise and successive scans, anlysing the entire sample. Subsequently, a simple arithmetic means of the three readings for each sample was determined, based on the recommendations by Nanni and Demattê (2006) and Fiorio et al. (2010).

2.4. Data processing and statistical analyses

Each spectral curve was submitted to baseline and light scattering correction by the Multiplicative Scatter Correction (MSC) method, according to Buddenbaum and Steffens (2012). For noise reduction, a 1st order polynomial Savitzky-Golay Smoothing with seven smoothing points was used. The calibration models (empirical calibration functions) were constructed from regressions for the partial squared minimums (PLSR) using Unscrambler version 10.3 (CAMO, Incorporation, Oslo, Norway).

The predictive ability of the models was evaluated through the calculation of the determination coefficient (r^2), the root-mean-square error for prediction (RMSEP; Eq.1), the standard error (SEP; Eq.2) for prediction, the systematic error (BIAS; Eq.3) and the Ratio of performance to deviation (RPD; Eq.4).

The RPD has been used as a useful indicator of precision for PLS prediction. For analytical performance quality, this value must be applied to at least 3 agricultural applications, (Williams and Sobering, 1993; Chang, 2001; Fearn, 2002; Cozzolino and Moron, 2006; Janik et al., 2007), whereas an RPD between 2 and 3 is considered “good”, 1.5 to 2, average and < than 1.5, poor (D’ Acqui et al., 2010). Theses parameters are defined as:

$$RMSEP = \sqrt{\sum_{i=1}^{n} (Dif_i)^2 / n} \qquad (1)$$

Dif_i = ŷi (estimated or predicted value by model VIS/NIR); ‘y’ edaphic property (sand, p.e.) of the sample ‘i’, and n is the number of samples;

$$SEP = \sqrt{\sum_{i=1}^{n}(Dif_i - bias)^2/n - 1} \quad (2)$$

- with the bias' (or deviation) a measure of the systematic error;

$$BIAS = \frac{\sum_{i=1}^{n}(\hat{y}_{pred} - y_{ref})}{n} \quad (3)$$

- obtained by calculating the difference between reference and predicted values (means) by VIS/NIR;

$$RPD = \frac{SD_y}{SEP} \quad (4)$$

- obtained by calculating the relationship between the standard deviation and SEP for the data set in the prediction phase.

In addition, the T^2 Hotteling test at $P<0.001$ probability was also applied to the predicted values for the target area (local scale, to aid in evaluating the performance of the spiked state models, spiked and extra-weight state models, unspiked state models and local models).

2.5. Calibration Models

2.5.1. Unspiked State Models

The unspiked state models were constructed using 425 soil samples (dataset) collected from different areas in Paraná.

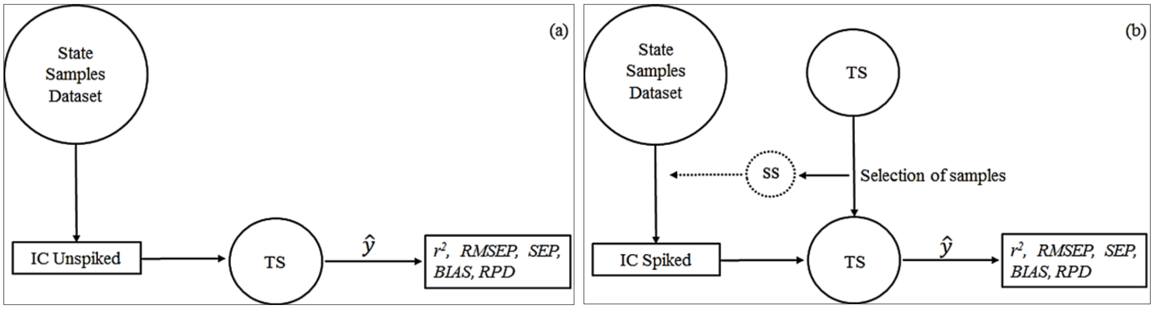
2.5.2. Spiked State Models

At this stage, 5% of the target site samples (subset) were selected as outlined below and added to the unspiked state models (Paraná models) for recalibration. Thus, the recalibrated models were extended to incorporate the variability of the target site. The strategies to select the subset used for spiking state models were based on the spectral characteristics of the target site samples.

A total of 10 samples were selected, located at the periphery of the spectral space and constituting the first two principal components carried out previously with the target-site samples (subset 1), 10 located in the center of the spectral space and constituting the first two principal components (subset 2), 10 located along of the spectral space and constituting the first two principal components (subset 3) and, finally, 10 samples belonging to different clusters (k-means clustering method) based on Euclidean distance (subset 4).

2.5.3. Spiked and Extra-weighted State Models

The unspiked state models were spiked and extra-weighted with additional copies of the target site spiking subsets, to evaluate whether sample extra-weighting could be used to improve calibration models for sand and organic matter estimates from the target site, as described by Guerrero et al. (2014) and Guy et al. (2015). In each of the four above-mentioned ways to selected samples, the number of times (copies) of the spiking subset were increased 5- and 10-fold, totaling 475 (425 + 50) and 525 (425 + 100) samples for recalibration. A general overview of the four methods is displayed in Figure 1.



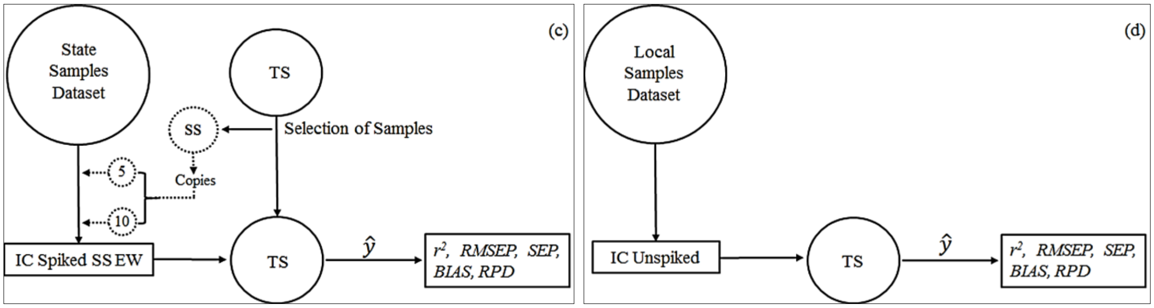


Figure 1. Scheme used to represent the experiment. (a) Initial calibration (IC) unspiked model constructed only with state samples; (b) Initial calibration spiked with a spiking subset (SS) selected from a target site (TS); (c) Initial calibration spiked with a spiking subset (SS) selected from the target site (TS) associated with extra-weight. (d) Initial calibration constructed only with local samples. Fonte: Adapted from Guerrero et al. (2014).

After recalibration of the unspiked state models, they were applied to the prediction of target site attributes. In this stage, samples not selected from the target site (95% of the remaining samples) were used as an unknown dataset.

2.5.4. Local models

Two local models from the target site were generated, one for sand and another for organic matter, with the intention of comparing the prediction results with the results obtained by spiked state models, spiked and extra-weighted state model and unspiked state models. In this phase, 10 soil samples (5%) were used for the calibration of the local models, and 190 (95%) for sand and organic matter prediction. The datasets used in the generation of the local models were the selected subsets in the target site with the best results in the cross-validation of the spiked state models.

3. Results

3.1. Descriptive results (reference methods)

The results obtained applying the reference methods are displayed in Table 1. Sand and organic matter attributes presented high variability for both datasets.

Table 1. Descriptive statistics of the set of samples collected throughout the state of Paraná and from the target site.

Statistical parameters	Paraná state samples [1]		Target site samples [2]	
	O.M[3] (g dm^{-3})	Sand (g kg^{-1})	O.M (g dm^{-3})	Sand (g kg^{-1})
Means	22.6	566.7	12.3	611.8
Minimum	3.4	70.0	3.4	180.0
Maximum	98.3	950.0	49.5	940.0
SD[4]	16.6	201.7	7.3	157.9
SE[5]	0.81	9.8	0.5	11.2
CV[6] (%)	73.5	36.0	59.2	26.0
N[7]	425	425	200	200

[1] Samples used in the generation of the state models; [2] Samples used in the generation of the local models; [3] Organic Matter; [4] Standard Deviation; [5] Standard Error; [6] Coefficient of Variation; [7] Number of Samples.

High sand content variability (CV=36.0%) is explained by the presence of different materials present in Paraná soil, such as migmatites, quartzites, basalt, sandstone, phyllites, siltstones, granites, and micaxists, among others (EMBRAPA, 1984), which comprise varied mineralogical constitution. The high variability (CV=73.5%) in organic matter content is due to the disparity of the climatic conditions of the state (Caviglione et al., 2000), as well as altitude (100 to 2000 meters), and soil use, contributing to the occurrence of significant differences in the accumulation of organic matter in the different sample regions. Of the 425 soil samples, 41.17% (175 samples) presented organic matter values above 20 g dm^{-3}, and, thus, significantly influence soil spectral behavior, as reported by Baumgardner et al (1970).

On the other hand, although the results obtained for the set of samples from the target site presented variability, was still lower than the set of samples collected from the state of Paraná. The variation coefficient was of 59.2% for organic matter and 26.0% for sand content. This lower variability is due, mainly, to the fact that the soils were derived predominantly from two lithologies, sandstone and basalt (EMBRAPA, 1984), and are currently covered by two types of vegetation, sugar cane and forest. Of the 200 samples, 15.5% (31 samples) presented organic matter values above 20 g dm^{-3}.

3.2. Unspiked State Models

3.2.1. Calibration and prediction

Calibration results for sand and organic matter content are presented in Table 2.

Table 2. Cross-validation results obtained during the calibration phase of the unspiked state models (*n* = 425).

Attribute	$r^{2(1)}$	RMSECV[2]	SECV[3]	BIAS[4]	RPD[5]	N.F[6]
Sand (g kg^{-1})	0.95	136.2	136.3	-0.73	1.48	10
O.M (g dm^{-3})	0.86	10.5	10.5	0.01	3.37	13

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error; [5] Ratio of performance to deviation; [6] Number of Factors. *n:* Number of Soil Samples.

The model for sand presented a high determination coefficient, however, RMSECV and SECV were around 14%, with a value of 136.2 g kg^{-1} and 136.3 g kg^{-1}, respectively. On other hand, organic matter presented a lowed determination coefficient, but better BIAS and RPD indicators. A near-zero BIAs indicates that the organic matter model is not biased, i.e. the difference between the observed mean measurement and the reference value is very small. If, during the calibration of the unspiked state models, organic matter generally presented better quality indicators in the prediction phase employing a set of unknown samples (target area), it was evident that the unspiked state model developed for the sand fraction presented better results (Table 3).

Table 3. Prediction results obtained from the target site using unspiked state models (n = 200).

Attribute	$r^{2(1)}$	RMSEP^2	SEP^3	BIAS^4	RPD^5	N.F^6
Sand (g kg^{-1})	0.74	80.4	80.6	-0.62	2.00	10
O.M (g dm^{-3})	0.24	6.3	6.8	1.45	1.15	13

O.M: Organic Matter; ^{1} Determination Coefficient; ^{2} Root-Mean-Square Error; ^{3} Standard Error; ^{4} Systematic Error, ^{5} Residual Predictive Deviation; ^{6} Number of Factors. *n:* Number of Soil Samples.

The determination coefficient for sand presented value of 0.74, indicating a reasonable adjustment of the state model to the target area dataset (local scale). An RPD of 2.00 was determined, indicating good analytical performance of the model in predicting this attribute, which was not found for organic matter, at 1.15, considered poor for agricultural studies, according to Chang et al. (2001) and D' Acqui et al. (2010).

The sand RMSEP and SEP were lower when compared to those obtained in Table 2, decreasing 55.8 g kg^{-1} and 55.7 g kg^{-1}, respectively. A similar result was observed for organic matter, albeit with significant BIAS (1.45), which can be observed by the organic matter scatter plot (Figure 4) (unspiked state model). Most of the points are scattered above the 1:1 line, especially considering the lower organic matter values (4 to 12 g dm^{-3}). This indicates that the measurements for this value are higher than the reference values.

The limited capacity of the unspiked state model in predicting organic matter values suggests that the model did not cover the range of variation found at the target site for this attribute (Viscarra Rossel et al., 2009; Guerrero eta al., 2014), even using a medium state model, consisting of 425 soil samples. This inaccurate prediction may be related to the size of the target site, larger (2,500 ha) and more diversified in terms of soil and soil use in relation to other target sites described in the literature (Guerrero et al., 2014; Guy et al., 2015), which are small and densely sampled.

Therefore, organic matter values tend to be more variable in our study area, in agreement with the maximum (49.5 g dm^{-3}) and minimum (3.4 g dm^{-3}) results obtained for the target site. It is clear that the difference between both levels (46.1 g dm^{-3}) is high, reflecting in very different spectral responses and predictions by theunspiked state model.

3.3. Spiked State Models / Spiked and extra-weighted state model

3.3.1. Recalibration

The spiked state models presented the same trend for statistical parameters already discussed for the unspiked state models. Table 4 displays the multivariate statistics obtained after the recalibration of the unspiked state models with the selected samples from the target site.

Table 4**.** Cross-validation results of the unspiked state model after recalibration with different spiking subsets (*n* = 435).

Attribute	Subset	r$^{2(1)}$	RMSECV^{2}	SECV^{3}	BIAS^{4}	RPD^{5}	N.F^{6}
Sand (g kg^{-1})	1	0.95	136.7	136.8	-1.08	1.47	10
Sand (g kg^{-1})	2	0.95	134.5	134.9	-0.26	1.52	10
Sand (g kg^{-1})	3	0.95	135.0	135.0	-1.43	1.49	10
Sand (g kg^{-1})	4	0.94	135.5	135.6	-0.47	150	10
O.M (g dm^{-3})	1	0.85	10.7	10.7	-0.01	3.30	13
O.M (g dm^{-3})	2	0.85	10.6	10.6	-0.04	3.33	13
O.M (g dm^{-3})	3	0.85	10.7	10.7	-0.01	3.30	13
O.M (g dm^{-3})	4	0.86	10.3	10.4	0.04	3.40	13

O.M: Organic Matter; ^{1} Determination Coefficient; ^{2} Root-Mean-Square Error; ^{3} Standard Error; ^{4} Systematic Error, ^{5} Ratio of performance to deviation; ^{6} Number of Factors. *n:* Number of Soil Samples.

The results obtained for the sand fraction using the spiked state model presented a maximum r^2 of 0.95, while organic matter values were lower, at around 0.86. The BIAS values were insignificant for organic matter, indicating a random distribution of the regression line points. On the other hand, the sand BIAS was satisfactory only when using subsets 2 and 4 for recalibration of the unspiked state models. The RPD ranged from 1.47 to 1.52 for sand and from 3.30 to 3.40 for organic matter. Similar behavior was noted when state models were spiked and extra-weighted with additional copies of the target site subsets (Table 5).

Table 5**.** Cross-validation results of the state model after recalibration with different spiking subsets and extra-weight (*n* = 475 and 525).

Attribute	Subset	Copy	$r^{2(1)}$	RMSECV^2	SECV^3	BIAS^4	RPD^5	N.F^6	n^7
Sand (g kg^{-1})	1	5	0.95	132.5	132.6	0.10	1.52	10	475
Sand (g kg^{-1})	2	5	0.95	128.8	128.9	-1.11	1.56	10	475
Sand (g kg^{-1})	3	5	0.95	131.4	131.5	-0.35	1.53	10	475
Sand (g kg^{-1})	4	5	0.95	132.4	132.6	-1.20	1.52	10	475
Sand (g kg^{-1})	1	10	0.96	129.9	130.1	-0.40	1.55	10	525
Sand (g kg^{-1})	2	10	0.96	122.0	122.1	-0.45	1.65	10	525
Sand (g kg^{-1})	3	10	0.96	124.1	124.2	-0.02	1.62	10	525
Sand (g kg^{-1})	4	10	0.96	128.2	128.3	-1.05	1.57	10	525
O.M (g dm^{-3})	1	5	0.87	10.0	10.1	-0.03	3.50	13	475
O.M (g dm^{-3})	2	5	0.85	10.3	10.3	0.01	3.43	13	475
O.M (g dm^{-3})	3	5	0.85	10.2	10.2	-0.03	3.46	13	475
O.M (g dm^{-3})	4	5	0.87	9.9	9.9	-0.01	3.57	13	475
O.M (g dm^{-3})	1	10	0.85	9.7	9.8	-0.01	3.61	13	525
O.M (g dm^{-3})	2	10	0.85	10.1	10.1	0.02	3.50	13	525
O.M (g dm^{-3})	3	10	0.86	9.7	9.8	0.03	3.60	13	525
O.M (g dm^{-3})	4	10	0.86	9.5	9.6	-0.01	3.61	13	525

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error; [5] Ratio of performance to deviation; [6] Number of Factors. [7] *n*=475: Total number of samples for recalibration of unspiked state models with 5 copies of the selected samples from the target site;[7] *n* = 525: Total number of samples for recalibration of unspiked state model with 10 copies of the selected samples from the target site.

With the extra-weight increment (5 and 10 times), the spiked state models for sand presented slightly better results than those obtained without any weighting (Table 4). A decrease in RMSECV was observed, reaching 122.0 g kg^{-1} when using 10 repeats for selected samples in the center of the spectral space (representing the mean spectrum of the target site). On the other hand, increases in RPD were observed, reaching a maximum value of 1.65 for these samples.

However, it is worth noting that, although the RMSECV values were reduced after the use of extra weight, these results are considered high when compared to those obtained by Terra et al. (2015) and Pinheiro et al. (2017), obtaining 25.22 g.kg^{-1} and 114.74 g kg^{-1} for sand, when studying Brazilian soils. On the other hand, when compared to the latter, BIAS values are considered low, at a maximum value of -1.20 (Table 5) against -17.37.

Organic matter showed a slight improvement in RMSECV, with values ranging from 9.5 to 10.3 g dm^{-3}. The RPD indicator was higher than the unspiked state model, ranging from 3.43 to 3.61. The best result was observed when extra-weight (10 copies) was used in subset 4 selected from 5 clusters (two samples per cluster).

3.3.2. Prediction

The results of the model predictions are presented in Table 6.

Table 6. Prediction results obtained by spiked state models using the remaining samples from the target site (n = 190).

Attribute	Subset	$r^{2(1)}$	RMSEP[2]	SEP[3]	BIAS[4]	RPD[5]	N.F[6]
Sand (g kg^{-1})	1	0.74	78.3	78.6	2.35	1.96	10
Sand (g kg^{-1})	2	0.74	82.1	82.3	1.16	1.95	10
Sand (g kg^{-1})	3	0.75	78.7	78.7	-5.14	2.00	10
Sand (g kg^{-1})	4	0.75	78.1	78.3	-1.11	2.01	10
O.M (g dm^{-3})	1	0.33	5.9	5.9	0.29	1.23	13
O.M (g dm^{-3})	2	0.33	5.6	5.6	-0.59	1.25	13
O.M (g dm^{-3})	3	0.28	6.1	6.2	0.50	1.18	13
O.M (g dm^{-3})	4	0.23	6.3	6.9	1.68	1.14	13

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error, [5] Ratio of performance to deviation; [6] Number of Factors. *n:* Number of Soil Samples.

The best estimate results were obtained for sand, and, all forms of sample selection led to more precise values for r^2 and RPD statistical parameters, with a maximum determination coefficient of 0.75 and RPD ranging from 1.95 and 2.01. In accordance to D'Acqui et al. (2010) these RPD values demonstrate that the spiked models present average potential for estimating sand content. RMSEP and SEP values were also reduced after spiking, using subsets 1, 3 and 4.

Regarding organic matter, slight improvements in prediction were observed with the use of most subsets for spiking, reaching 5.9 g dm^{-3}, 0.33 and 1.25, for RMSEP, r^2 and RPD, respectively. However, although this improved RPD to below 1.5, these values still demonstrate low prediction precision, making the use of these models for analytical use impractical. This is probably related to the size of the subsets used for spiking the models. Guy et al. (2015), while studying soil organic carbon, demonstrated that spiking models with 10 or fewer samples causes little improvement in model performance. Probably, the low number of samples used for spiking was not able to allow for recalibrated models to cover the organic matter range of variation to be predicted in the target site, independent of the sample selection methods, in agreement with Viscarra Rossel et al. (2009).

One point concerning the use of spiking is that the performance parameters of the models did not follow the cross-validation trend with the use of different subsets. For example, subset 4 based on 5 clusters for spiking of the state model in the cross validation presented better results for organic matter, but, at the prediction phase using 190 target site samples, the best result was obtained with the use of subset 2 referring to samples located in the center of the spectral space. This is due to the lower spectral variability of these samples selected for recalibration, which present reflectance values at all wavelengths that approximate most of the samples that make up the population of the target area used for the model prediction test.

On the other hand, although the cluster analysis was statistically robust, the selection of samples based on 5 clusters was not efficient for recalibration of the state models and organic matter prediction using an independent set of samples, because, although two spectrally similar samples inside of the spectral space existed for each cluster, a higher Euclidean distance between clusters were observed, leading to the re-calibration of the models with very dissimilar samples, not representing the 190 samples of the target area used in the prediction of soil attributes.

Attribute estimation using extra-weight in the spiked state model demonstrated that the sand results were better when compared to organic matter for all quality parameters except BIAS (Table 7).

Table 7**.** Prediction results of the state model after recalibration with different spiking subsets and extra-weight (*n* =190).

Attribute	Subset	Copy	r^2(1)	RMSEP[2]	SEP[3]	BIAS[4]	RPD[5]	N.F[6]	*n*[7]
Sand (g kg^{-1})	1	5	0.76	75.7	75.8	-4.30	2.03	10	190
Sand (g kg^{-1})	2	5	0.74	81.9	82.2	1.35	2.00	10	190
Sand (g kg^{-1})	3	5	0.76	77.0	75.9	-14.03	2.10	10	190
Sand (g kg^{-1})	4	5	0.77	74.3	74.4	-3.42	2.11	10	190
Sand (g kg^{-1})	1	10	0.76	74.4	74.3	-6.19	2.10	10	190
Sand (g kg^{-1})	2	10	0.80	71.6	71.6	-6.26	2.20	10	190
Sand (g kg^{-1})	3	10	0.75	78.3	75.0	-23.21	2.02	10	190
Sand (g kg^{-1})	4	10	0.79	71.6	71.6	-5.24	2.17	10	190
O.M (g dm^{-3})	1	5	0.33	6.2	6.2	-0.66	1.22	13	190
O.M (g dm^{-3})	2	5	0.24	5.9	6.6	1.66	1.20	13	190
O.M (g dm^{-3})	3	5	0.30	6.0	6.9	1.93	1.22	13	190
O.M (g dm^{-3})	4	5	0.30	6.1	6.2	-0.13	1.23	13	190
O.M (g dm^{-3})	1	10	0.24	6.3	6.3	0.89	1.20	13	190
O.M (g dm^{-3})	2	10	0.20	6.1	7.3	2.29	0.82	13	190
O.M (g dm^{-3})	3	10	0.25	6.2	7.1	1.94	1.20	13	190
O.M (g dm^{-3})	4	10	0.30	6.1	6.1	-0.14	1.20	13	190

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error, [5] Ratio of performance to deviation; [7] *n*: Number of soil samples from the target site used for prediction of sand and organic matter through the recalibrated state models.

Likewise, when compared to Tables 3 and 6, the use of extra-weighting resulted in prediction accuracy improvements for sand, with RPD ranging from 2.00 to 2.11 (5 copies) and from 2.00 to 2.20 (10 copies). Decreases in RMSEP and increases in determination coefficients were also noted, with the latter reaching a maximum value equal to 0.80, when recalibrating unspiked state model using subset 2, and 10 copies. However, the models recalibrated with subset 3 did not present satisfactory results, generating high bias values for sand, at -14.03 (5 copies) and -23.21 (10 copies).

The improvement in RMSEP, SEP and RPD was dependent on the type of sample selected to form the subsets used for spiking (Capron et al., 2005; Guerrero et al., 2014) and the number of copies used for extra weight. Satisfactory results were not observed for organic matter, with little differences among spiked and extra-weighted state models and spiked state models. This may be related to the low number of copies used in the spiked model, since for medium and large models, large extra-weight of spiking subsets may be necessary (Guerrero et al., 2010, 2014; Guy et al., 2015) to improve prediction performance of some soil attributes.

3.4. Local Model (target site)

3.4.1. Calibration and prediction

A total of 10 samples located in the center of the spectral space and 10 samples selected by 5 clusters were used to generate the local models for sand and organic matter, respectively. These samples belong to the target site and were chosen due to the improvement provided in the spiked state models in cross-validation stage. The results are presented in Table 8.

Table 8. Cross-validation results obtained during the calibration phase of the local models ($n = 10$).

Attribute	$r^{2(1)}$	RMSECV^{2}	SECV^{3}	BIAS^{4}	RPD^{5}	N.F^{6}
Sand (g kg^{-1})	0.97	93.0	98.6	6.04	1.08	3
O.M (g dm^{-3})	0.37	12.8	14.7	3.23	0.62	2

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error, [5] Ratio of performance to deviation; *n:* Number of Soil Samples.

Notable differences were observed between the quality parameters from the local models for both sand and organic matter, when comparing the elements displayed in Table 8 with those in Tables 2, 4 and 5. The local models showed low estimation potential in the cross-validation phase when compared to spiked and unspiked state models. BIAS values were high, whereas RPD values remained below ideal for use in agricultural studies.

Similarly, the prediction results were lower than expected. The r^2 and RPD for sand and organic matter were lower when comparing the information in Table 9 to that displayed in Tables 3, 6 and 7.

Table 9. Prediction results obtained for the target site using local models (*n* = 190).

Attribute	$r^{2(1)}$	RMSEP[2]	SEP[3]	BIAS[4]	RPD[5]	N.F[6]
Sand (g kg^{-1})	0.67	91.6	91.8	1.49	1.75	3
O.M (g dm^{-3})	0.10	6.8	6.9	0.02	0.96	2

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error, [5] Ratio of performance to deviation; *n:* Number of Soil Samples.

This result is in disagreement with those obtained by Wetterlind and Stenberg (2010), who, working with organic carbon, sand and other soil attributes, observed that local models presented better estimation results than spiked national models.

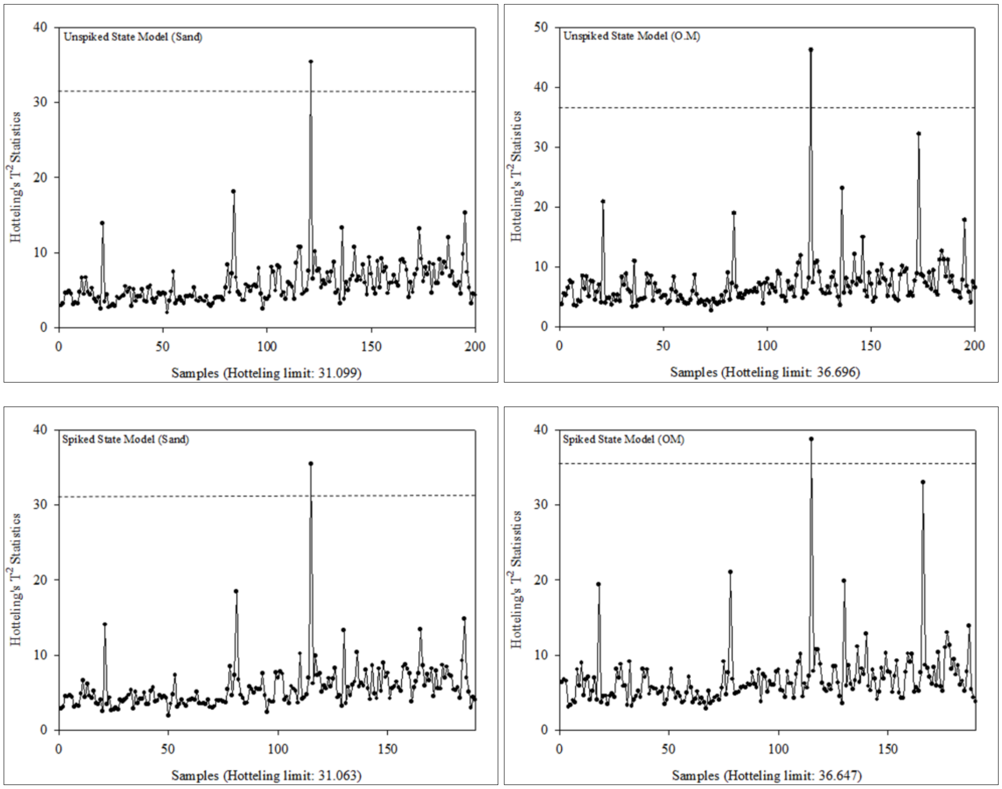
The low efficiency of the estimation for both attributes can be related to the small size of the local model, which was adjusted with only 10 samples (Guy et al., 2015). The selected samples were not able to represent the variability in the study area, reflecting in low accuracy. These results are in agreement with those reported by Guerrero et al. (2014), demonstrating the difficulty in obtaining site-specific calibration models using a small number of samples.

However, although these results were obtained, it is evident that i sand attribute presented better results when compared to organic matter all phases of the study. Similar results were obtained by Demattê et al., (2000), Nanni and Demattê (2006), and Cezar et al., (2013) when studying Brazilian soils. This is related to the high sand content found in the soil samples, which presents high spectral response due to the predominance of quartz in this fraction (Hunt and Salisbury, 1971., Al-Abbas et al. 1972., White at al. 1997).

Of the 425 soil samples collected in the state of Paraná, 273 (64.23%) presented sand contents above 50%. In some cases, values close to 90% were detected. Of the 200 soil samples collected in the target area, 154 (77.0%) presented sand contents above 50%. It is concluded, therefore, that, although the energy reflected by the samples is characterized as a function of the soil constituents, in this case the sand overlaps with the other elements, becoming the most significant parameter influencing the spectral response.

3.5. Additional evaluation of the model performance

The results obtained through the T^2 Hotteling test demonstrated that the spiked and unspiked state models presented medium performance, being able to maintain most of values within the control limit (associated with $p< 0.001$) established for the test (Figure 2).



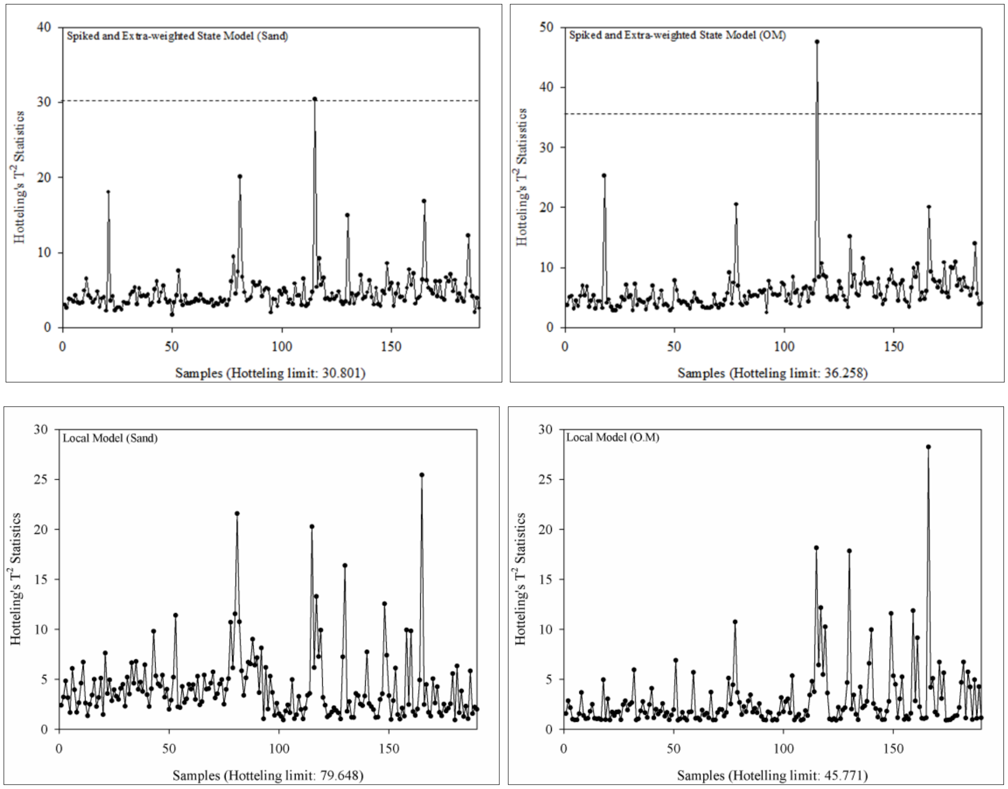


Figure 2. Graphs obtained through the T² Hotteling test in the prediction phase. The dashed line represents the critical limit. The spiked state model and spiked and extra-weighted state model (10 copies) for sand represents the recalibrated model with 10 samples (subset 2); The spiked state model and spiked and extra-weighted state model (10 copies) for organic matter represents the recalibrated model with 10 samples (subset 4).

Only one T² Hotteling value was above the critical limit for the two attributes, a sample belonging to the Regosol class. In this case, the models presented low potential to adequately estimate the value for this sample. However, the spiked and extra-weighted state model was very close in incorporating sample variability and obtaining a satisfactory result for sand, since it was close to the maximum limit.

The value above the critical limit is probably due to the high spectral response obtained for the sample, which presented a higher reflectance factor than the other samples comprising the target site set (Figure 3).

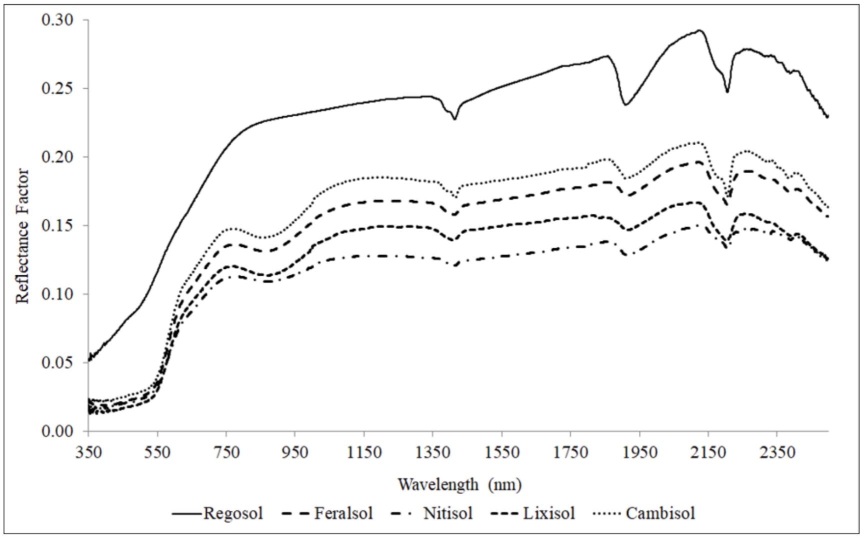
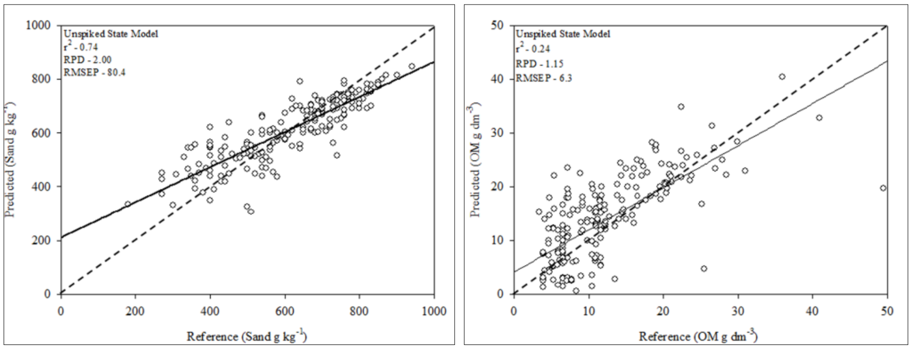


Figure 3. Spectral curves representative of the soil classes found at the target site.

The high spectral response was influenced mainly by sample sand content, with values close to 69.0%, in agreement with that described by Hunt and Salisbury (1971). On the other hand, the use of local models did not present values above the critical limit established by the T^2 Hotteling test, indicating that all values estimated for the samples are under statistical control (without any outliers). However, during soil attribute prediction, no satisfactory results were obtained, demonstrating high data dispersion as presented by scatter-plots (Figure 4), especially for organic matter.



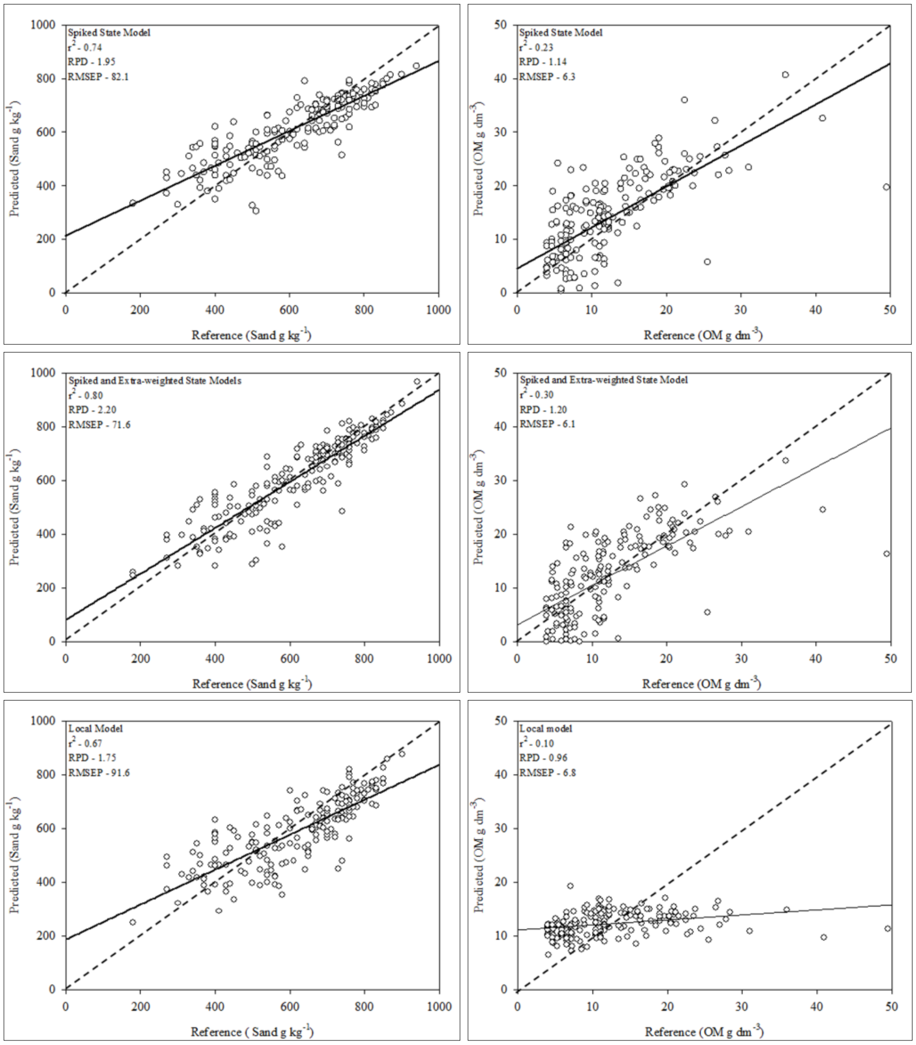


Figure 4. Scatter-plots obtained during the prediction phase. The unspiked state model, spiked state model, spiked and extra-weighted state model and local model are presented. Line 1:1 (dashed); regression line (solid line).

4. Conclusions

The spiked state model, as well as the spiked and extra-weighted state models, presented better sand and organic matter predictions compared to the local model.

Sample selection from the center of the spectral space, associate with extra-weight (mainly 10 copies), was shown to be more effective in sand prediction for the target site.

Selected subsets at the target site were not able to represent the entire the variability of the local samples regarding organic matter, damaging the expansion of the recalibrated state models and estimations for this attribute.

The results obtained in this specific study demonstrate that it is unnecessary to generate local models to estimate sand in the state of Paraná, and that recalibrated state models (spike) can be applied. However, it should be emphasized that new local models must be generated (in Brazilian conditions) from a larger number of samples to evaluate if the prediction results will be similar to those obtained herein.

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Highlights

- The sand attribute showed more direct relationship with de spectral response.
- Spiked and extra-weight state model presented better results for estimating sand.
- Selected subsets did not represent all the variability of the target site for OM.
- It is unnecessary to generate local models to estimate sand in the Parana State.

Organic Matter and Sand Estimates by Spectroradiometry: Strategies for the Development of Models with Applicability at a Local Scale

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ABSTRACT

The development of spectral prediction models for soil attributes has been extensively studied in the last 10 years. However, one of the problems encountered during this period concerns the representativeness of the samples selected for model generation, which are often unable to capture the existing variability in agricultural areas, generating imprecise models. Thus, it is necessary to establish strategies for selecting soil samples, as well as for making them more representative within the model. Considering this, the aim of the present study was to evaluate strategies for soil sample selection and the recalibration of large models using samples from a smaller area, in a process called spiking, and its effect on soil attribute estimations. A total of 425 soil samples were used for the generation of the state models, as well as 200 soil samples from a target site for attribute recalibration and prediction. From these 200 samples, 10 (subset) were selected by different methods for state model recalibration (spiking), and 190 were used in the prediction. Another 5 and 10 copies of the subsets were also used as extra-weight to recalibrate the models. Models spiked with samples located in the center of the spectral space associated with extra-weight (10 copies) showed better accuracy in sand prediction (RPD = 2.20; r^2 = 0.80; RMSEP = 71.6 g kg^{-1}). For organic matter, the use of selected samples based on 5 clusters associated with extra-weight (10 copies) slightly improved the RMSEP and RPD in most cases, reaching a maximum value of 6.1 g dm^{-3} and 1.20, respectively. However, the subsets selected at the target site were not able to indicate the entire variability of the local samples concerning organic matter, damaging the expansion of the recalibrated state models.

Keywords: Spiking; Sand; Organic Matter; Spectroradiometry.

1. Introduction

Detailed mapping of soil attributes involves the collection of a high number of samples. In addition to high economic cost, this leads to the generation of dangerous residues derived from chemical analyses.

For this reason, the search for analysis tools that are easily applied, inexpensive, precise and with low negative ambient impacts (clean) is key in studying soil on a large scale, especially in countries such as Brazil, where the need for laboratory analysis increases each year, with hundreds or thousands of samples requiring analysis. In this regard, Vis-NIR-SWIR spectroscopy combines all these desirable characteristics and can be applied to obtain soil attributes (Dunn et al., 2002; Shepherd and Walsh, 2002; Islam et al., 2003; Brown et al., 2006).

Vis-NIR-SWIR spectra are complex signals that contain useful information for analytical pursposes. An empirical approach can be applied for the use of the significant amount of information contained in a spectrum, employing calibrations (or models) constructed using multivariate regression techniques (Naes et al., 2002; McBratney et al., 2006).

The samples used to construct the models, termed calibration samples, must be representative of the population of samples to which this model will be applied. The establishment of spectral calibration libraries derived from a high number of representative samples that contain the necessary variability has been suggested (Shepherd and Walsh, 2002; Brown et al., 2005, 2006; Viscarra Rossel et al., 2008). However, this premise is not easy to fulfill, especially in areas with high edaphic diversity, because, even though the acquired calibrations are based on a large number of samples, the number of samples does not always guarantee that the fitted model can be successfully applied in new areas (Viscarra Rossel et al., 2008; Wetterlind et al., 2010).

In this case, the application of calibrated models in new areas, which have no representative samples in the spectral library, can contribute to incorrect soil attribute predictions (Brown et al., 2006; Brown, 2007; Sankey et al., 2008). Thus, regional models (generated with samples from a particular region) may not be useful for estimating soil properties from other regions presenting different properties and edaphic attributes.

This problem is more evident in regions presenting greater edapho-diversity, since it is very complex to include all factors that interfere in soil variability in the spectral library.

Likewise, models developed at the local scale (generated with samples from a certain area) will not be valid for regional or even national scales.

Recent studies suggest that the best way to solve this problem is through calibration spiking with samples from the target study site (D'Acqui et al., 2010; Wetterlind and Stenberg, 2010; Guerrero et al., 2014; Guy et al., 2015). After spiking, the recalibrated model tends to display greater precision when applied to samples taken from the target study site (Wetterlind et al., 2010; Guerrero et al., 2010). Currently, the spiking process seems to be most adequate when applied to model expansion (Shepherd and Walsh, 2002; Viscarra Rossel et al., 2008; Minasny et al., 2009).

The central question regarding spiking concerns the type and adequate number of samples to be selected for model recalibration, since has a direct influences on the prediction result. A high number of local samples for the spiking subset tends to raise model accuracy (Brown, 2007; Guerrero et al., 2010), but, on the other hand, reduces the advantages of using spectroscopy as a quick and low-cost analytical method (Guerrero et al., 2014).

The use of a small spiking subset displays the advantage of low-cost, but a disadvantage regarding the possibility of inaccuracies in recalibrated models. To circumvent these problems, Guerrero et al. (2014) suggest the addition of several copies (extra-weight) of the spiking subsets within the calibration matrix, in order to increase the relevance of the target site samples and improve model fit.

In this context, this study had as its first objective to select the most influential samples from a target site for spiking subsets. The second objective was to evaluate the prediction accuracy for sand and organic matter content in the target site after assigning extra-weight to the spiking subsets.

2. Materials and methods

2.1. Soil sampling in the state of Paraná

A total of 425 soil samples were collected from different areas in the state of Paran's - Brazil, a region delimited by the geographic coordinates 22º29'30′ ′ to 26º42'59′ ′ south and 48º02'24′ ′ to 54º37′ 38′ ′ west. According to the World Reference Base (2014), the soil classes in the state comprise mainly Lixisols, Cambisols, Chernozems, Podzols, Gleysols, Ferralsols, Regosols, Nitisols and Histosols. These soil classes are developed on different lithologies such as migmatites, quartzites, basalt, sandstone, phyllites, siltstones, granites and micaxists, among others (EMBRAPA, 1984). The samples were collected from different landscape areas, toposequences and soil, forest and draining conditions.

2.2. Soil sampling in the target site

A total of 200 samples were collected from a target site located in northwestern Paraná - Brazil, delimited by the geographic coordinates 22º57´19´´ to 22º52´59´´ south and 52º3´47´´ to 51º59´0.7´´ west, comprising 2,500 ha. The soil classes found in the area, according to the World Reference Base (2014) are Ferralsols, Nitisols, Lixisols, Cambisols and Regosols. It is worth mentioning that, although this area is located within the state of Paraná, no samples were collected from this area to form the group of 425 samples described in Section 2.1

2.3. Soil sample laboratory and spectral analyses

After collection, the samples were submitted to laboratory analyses for determination of physical and chemical attributes, as well as spectral characterization. The samples were air-dried and sieved through a 2 mm mesh. A hydrometer was used for the determination of total sand content (Kiehl, 1979). Organic matter content was measured according to Walkley and Black (1934). These attributes were chosen because they must be identified in a laboratory, which uses chemical reagents with the potential to contaminate the environment, in addition to increasing the time and cost of the analysis.

The samples designated for spectral reading were dried at 45 °C for 24 h and sieved (mesh 2 mm) for size particle homogenization and reduction of humidity and sampling effects (Epiphânio et al., 1992). Subsequently, each sample was placed on a Petri dish (9 cm diameter and 1.5 cm height) and submitted to spectral readings using a ASD FieldSpec 3 JR spectroradiometer with a spectral range from 350 to 2.500 nm. The equipment was programmed to perform 50 readings for each sample, thereby generating an average spectral curve.

For data acquisition, a Spectralon standard white plate calibrated for 100% reflectance was used, in accordance to the Labsphere Reflectance Calibration Laboratory (LRCL, 2009). An optical-fiber reader was placed on the support platform in a vertical position 8 cm distant from the samples. The reading area cmprised approximately 2 cm^2. The light source was a 650 W light bulb with a noncollimated beam located 35 cm from the platform and at a 30° angle relative to the horizontal plan.

The spectral readings were repeated three times, with successive displacement of the Petri dish 120° clockwise and successive scans, anlysing the entire sample. Subsequently, a simple arithmetic means of the three readings for each sample was determined, based on the recommendations by Nanni and Demattê (2006) and Fiorio et al. (2010).

2.4. Data processing and statistical analyses

Each spectral curve was submitted to baseline and light scattering correction by the Multiplicative Scatter Correction (MSC) method, according to Buddenbaum and Steffens (2012). For noise reduction, a 1st order polynomial Savitzky-Golay Smoothing with seven smoothing points was used. The calibration models (empirical calibration functions) were constructed from regressions for the partial squared minimums (PLSR) using Unscrambler version 10.3 (CAMO, Incorporation, Oslo, Norway).

The predictive ability of the models was evaluated through the calculation of the determination coefficient (r^2), the root-mean-square error for prediction (RMSEP; Eq.1), the standard error (SEP; Eq.2) for prediction, the systematic error (BIAS; Eq.3) and the Ratio of performance to deviation (RPD; Eq.4).

The RPD has been used as a useful indicator of precision for PLS prediction. For analytical performance quality, this value must be applied to at least 3 agricultural applications, (Williams and Sobering, 1993; Chang, 2001; Fearn, 2002; Cozzolino and Moron, 2006; Janik et al., 2007), whereas an RPD between 2 and 3 is considered "good", 1.5 to 2, average and < than 1.5, poor (D' Acqui et al., 2010). Theses parameters are defined as:

$$RMSEP = \sqrt{\textstyle\sum_{i=1}^{n}(Dif_i)^2/n} \qquad (1)$$

Dif_i = ŷi (estimated or predicted value by model VIS/NIR); 'y' edaphic property (sand, p.e.) of the sample 'i', and n is the number of samples;

$$SEP = \sqrt{\textstyle\sum_{i=1}^{n}(Dif_i - bias)^2/n - 1} \tag{2}$$

- with the bias' (or deviation) a measure of the systematic error;

$$BIAS = \frac{\sum_{i=1}^{n}(\hat{y}_{pred} - y_{ref})}{n} \tag{3}$$

- obtained by calculating the difference between reference and predicted values (means) by VIS/NIR;

$$RPD = \frac{SD_y}{SEP} \tag{4}$$

- obtained by calculating the relationship between the standard deviation and SEP for the data set in the prediction phase.

In addition, the T^2 Hotteling test at $P<0.001$ probability was also applied to the predicted values for the target area (local scale, to aid in evaluating the performance of the spiked state models, spiked and extra-weight state models, unspiked state models and local models).

2.5. Calibration Models

2.5.1. Unspiked State Models

The unspiked state models were constructed using 425 soil samples (dataset) collected from different areas in Paraná.

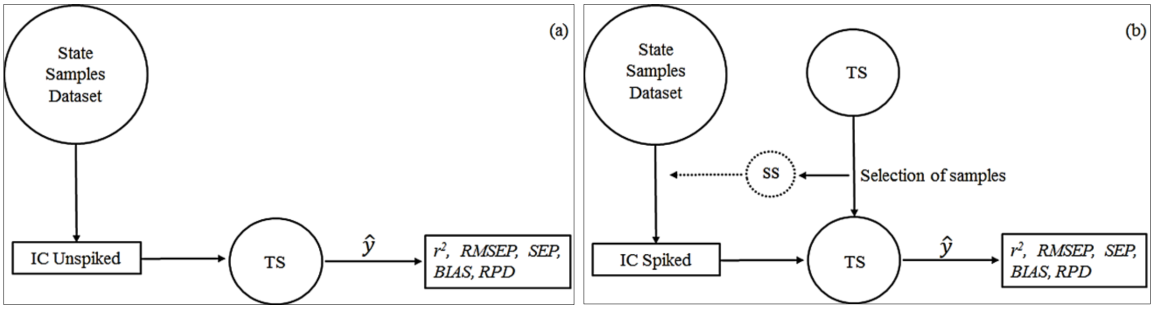
2.5.2. Spiked State Models

At this stage, 5% of the target site samples (subset) were selected as outlined below and added to the unspiked state models (Paraná models) for recalibration. Thus, the recalibrated models were extended to incorporate the variability of the target site. The strategies to select the subset used for spiking state models were based on the spectral characteristics of the target site samples.

A total of 10 samples were selected, located at the periphery of the spectral space and constituting the first two principal components carried out previously with the target-site samples (subset 1), 10 located in the center of the spectral space and constituting the first two principal components (subset 2), 10 located along of the spectral space and constituting the first two principal components (subset 3) and, finally, 10 samples belonging to different clusters (k-means clustering method) based on Euclidean distance (subset 4).

2.5.3. Spiked and Extra-weighted State Models

The unspiked state models were spiked and extra-weighted with additional copies of the target site spiking subsets, to evaluate whether sample extra-weighting could be used to improve calibration models for sand and organic matter estimates from the target site, as described by Guerrero et al. (2014) and Guy et al. (2015). In each of the four above-mentioned ways to selected samples, the number of times (copies) of the spiking subset were increased 5- and 10-fold, totaling 475 (425 + 50) and 525 (425 + 100) samples for recalibration. A general overview of the four methods is displayed in Figure 1.



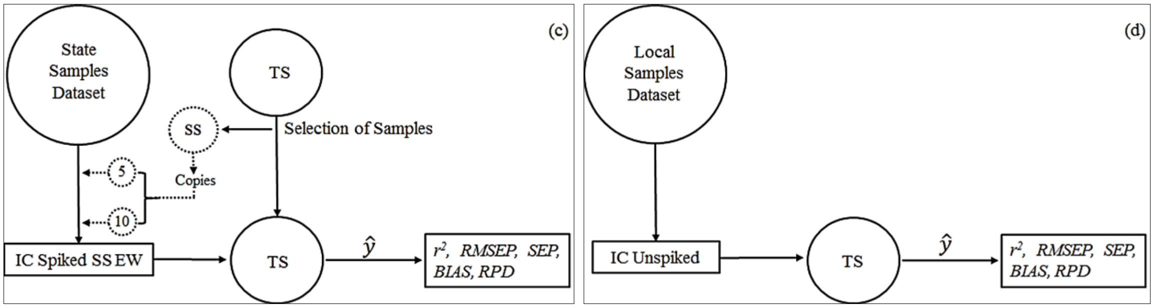


Figure 1. Scheme used to represent the experiment. (a) Initial calibration (IC) unspiked model constructed only with state samples; (b) Initial calibration spiked with a spiking subset (SS) selected from a target site (TS); (c) Initial calibration spiked with a spiking subset (SS) selected from the target site (TS) associated with extra-weight. (d) Initial calibration constructed only with local samples. Fonte: Adapted from Guerrero et al. (2014).

After recalibration of the unspiked state models, they were applied to the prediction of target site attributes. In this stage, samples not selected from the target site (95% of the remaining samples) were used as an unknown dataset.

2.5.4. Local models

Two local models from the target site were generated, one for sand and another for organic matter, with the intention of comparing the prediction results with the results obtained by spiked state models, spiked and extra-weighted state model and unspiked state models. In this phase, 10 soil samples (5%) were used for the calibration of the local models, and 190 (95%) for sand and organic matter prediction. The datasets used in the generation of the local models were the selected subsets in the target site with the best results in the cross-validation of the spiked state models.

3. Results

3.1. Descriptive results (reference methods)

The results obtained applying the reference methods are displayed in Table 1. Sand and organic matter attributes presented high variability for both datasets.

Table 1. Descriptive statistics of the set of samples collected throughout the state of Paraná and from the target site.

Statistical parameters	Paraná state samples [1]		Target site samples [2]	
	O.M[3] (g dm^{-3})	Sand (g kg^{-1})	O.M (g dm^{-3})	Sand (g kg^{-1})
Means	22.6	566.7	12.3	611.8
Minimum	3.4	70.0	3.4	180.0
Maximum	98.3	950.0	49.5	940.0
SD[4]	16.6	201.7	7.3	157.9
SE[5]	0.81	9.8	0.5	11.2
CV[6] (%)	73.5	36.0	59.2	26.0
N[7]	425	425	200	200

[1] Samples used in the generation of the state models; [2] Samples used in the generation of the local models; [3] Organic Matter; [4] Standard Deviation; [5] Standard Error; [6] Coefficient of Variation; [7] Number of Samples.

High sand content variability (CV=36.0%) is explained by the presence of different materials present in Paraná soil, such as migmatites, quartzites, basalt, sandstone, phyllites, siltstones, granites, and micaxists, among others (EMBRAPA, 1984), which comprise varied mineralogical constitution. The high variability (CV=73.5%) in organic matter content is due to the disparity of the climatic conditions of the state (Caviglione et al., 2000), as well as altitude (100 to 2000 meters), and soil use, contributing to the occurrence of significant differences in the accumulation of organic matter in the different sample regions. Of the 425 soil samples, 41.17% (175 samples) presented organic matter values above 20 g dm^{-3}, and, thus, significantly influence soil spectral behavior, as reported by Baumgardner et al (1970).

On the other hand, although the results obtained for the set of samples from the target site presented variability, was still lower than the set of samples collected from the state of Paraná. The variation coefficient was of 59.2% for organic matter and 26.0% for sand content. This lower variability is due, mainly, to the fact that the soils were derived predominantly from two lithologies, sandstone and basalt (EMBRAPA, 1984), and are currently covered by two types of vegetation, sugar cane and forest. Of the 200 samples, 15.5% (31 samples) presented organic matter values above 20 g dm^{-3}.

3.2. Unspiked State Models

3.2.1. Calibration and prediction

Calibration results for sand and organic matter content are presented in Table 2.

Table 2. Cross-validation results obtained during the calibration phase of the unspiked state models (*n* = 425).

Attribute	$r^{2(1)}$	$RMSECV^2$	$SECV^3$	$BIAS^4$	RPD^5	$N.F^6$
Sand (g kg^{-1})	0.95	136.2	136.3	-0.73	1.48	10
O.M (g dm^{-3})	0.86	10.5	10.5	0.01	3.37	13

O.M: Organic Matter; ^{1} Determination Coefficient; ^{2} Root-Mean-Square Error; ^{3} Standard Error; ^{4} Systematic Error; ^{5} Ratio of performance to deviation; ^{6} Number of Factors. *n:* Number of Soil Samples.

The model for sand presented a high determination coefficient, however, RMSECV and SECV were around 14%, with a value of 136.2 g kg^{-1} and 136.3 g kg^{-1}, respectively. On other hand, organic matter presented a lowed determination coefficient, but better BIAS and RPD indicators. A near-zero BIAs indicates that the organic matter model is not biased, i.e. the difference between the observed mean measurement and the reference value is very small. If, during the calibration of the unspiked state models, organic matter generally presented better quality indicators in the prediction phase employing a set of unknown samples (target area), it was evident that the unspiked state model developed for the sand fraction presented better results (Table 3).

Table 3. Prediction results obtained from the target site using unspiked state models (*n* = 200).

Attribute	$r^{2(1)}$	RMSEP[2]	SEP[3]	BIAS[4]	RPD[5]	N.F[6]
Sand (g kg^{-1})	0.74	80.4	80.6	-0.62	2.00	10
O.M (g dm^{-3})	0.24	6.3	6.8	1.45	1.15	13

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error, [5] Residual Predictive Deviation; [6] Number of Factors. *n:* Number of Soil Samples.

The determination coefficient for sand presented value of 0.74, indicating a reasonable adjustment of the state model to the target area dataset (local scale). An RPD of 2.00 was determined, indicating good analytical performance of the model in predicting this attribute, which was not found for organic matter, at 1.15, considered poor for agricultural studies, according to Chang et al. (2001) and D' Acqui et al. (2010).

The sand RMSEP and SEP were lower when compared to those obtained in Table 2, decreasing 55.8 g kg^{-1} and 55.7 g kg^{-1}, respectively. A similar result was observed for organic matter, albeit with significant BIAS (1.45), which can be observed by the organic matter scatter plot (Figure 4) (unspiked state model). Most of the points are scattered above the 1:1 line, especially considering the lower organic matter values (4 to 12 g dm^{-3}). This indicates that the measurements for this value are higher than the reference values.

The limited capacity of the unspiked state model in predicting organic matter values suggests that the model did not cover the range of variation found at the target site for this attribute (Viscarra Rossel et al., 2009; Guerrero eta al., 2014), even using a medium state model, consisting of 425 soil samples. This inaccurate prediction may be related to the size of the target site, larger (2,500 ha) and more diversified in terms of soil and soil use in relation to other target sites described in the literature (Guerrero et al., 2014; Guy et al., 2015), which are small and densely sampled.

Therefore, organic matter values tend to be more variable in our study area, in agreement with the maximum (49.5 g dm^{-3}) and minimum (3.4 g dm^{-3}) results obtained for the target site. It is clear that the difference between both levels (46.1 g dm^{-3}) is high, reflecting in very different spectral responses and predictions by theunspiked state model.

3.3. Spiked State Models / Spiked and extra-weighted state model

3.3.1. Recalibration

The spiked state models presented the same trend for statistical parameters already discussed for the unspiked state models. Table 4 displays the multivariate statistics obtained after the recalibration of the unspiked state models with the selected samples from the target site.

Table 4**.** Cross-validation results of the unspiked state model after recalibration with different spiking subsets (*n* = 435).

Attribute	Subset	r$^{2(1)}$	RMSECV^{2}	SECV^{3}	BIAS^{4}	RPD^{5}	N.F^{6}
Sand (g kg^{-1})	1	0.95	136.7	136.8	-1.08	1.47	10
Sand (g kg^{-1})	2	0.95	134.5	134.9	-0.26	1.52	10
Sand (g kg^{-1})	3	0.95	135.0	135.0	-1.43	1.49	10
Sand (g kg^{-1})	4	0.94	135.5	135.6	-0.47	150	10
O.M (g dm^{-3})	1	0.85	10.7	10.7	-0.01	3.30	13
O.M (g dm^{-3})	2	0.85	10.6	10.6	-0.04	3.33	13
O.M (g dm^{-3})	3	0.85	10.7	10.7	-0.01	3.30	13
O.M (g dm^{-3})	4	0.86	10.3	10.4	0.04	3.40	13

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error, [5] Ratio of performance to deviation; [6] Number of Factors. *n:* Number of Soil Samples.

The results obtained for the sand fraction using the spiked state model presented a maximum r^2 of 0.95, while organic matter values were lower, at around 0.86. The BIAS values were insignificant for organic matter, indicating a random distribution of the regression line points. On the other hand, the sand BIAS was satisfactory only when using subsets 2 and 4 for recalibration of the unspiked state models. The RPD ranged from 1.47 to 1.52 for sand and from 3.30 to 3.40 for organic matter. Similar behavior was noted when state models were spiked and extra-weighted with additional copies of the target site subsets (Table 5).

Table 5**.** Cross-validation results of the state model after recalibration with different spiking subsets and extra-weight (*n* = 475 and 525).

Attribute	Subset	Copy	$r^{2(1)}$	RMSECV[2]	SECV[3]	BIAS[4]	RPD[5]	N.F[6]	*n*[7]
Sand (g kg^{-1})	1	5	0.95	132.5	132.6	0.10	1.52	10	475
Sand (g kg^{-1})	2	5	0.95	128.8	128.9	-1.11	1.56	10	475
Sand (g kg^{-1})	3	5	0.95	131.4	131.5	-0.35	1.53	10	475
Sand (g kg^{-1})	4	5	0.95	132.4	132.6	-1.20	1.52	10	475
Sand (g kg^{-1})	1	10	0.96	129.9	130.1	-0.40	1.55	10	525
Sand (g kg^{-1})	2	10	0.96	122.0	122.1	-0.45	1.65	10	525
Sand (g kg^{-1})	3	10	0.96	124.1	124.2	-0.02	1.62	10	525
Sand (g kg^{-1})	4	10	0.96	128.2	128.3	-1.05	1.57	10	525
O.M (g dm^{-3})	1	5	0.87	10.0	10.1	-0.03	3.50	13	475
O.M (g dm^{-3})	2	5	0.85	10.3	10.3	0.01	3.43	13	475
O.M (g dm^{-3})	3	5	0.85	10.2	10.2	-0.03	3.46	13	475
O.M (g dm^{-3})	4	5	0.87	9.9	9.9	-0.01	3.57	13	475
O.M (g dm^{-3})	1	10	0.85	9.7	9.8	-0.01	3.61	13	525
O.M (g dm^{-3})	2	10	0.85	10.1	10.1	0.02	3.50	13	525
O.M (g dm^{-3})	3	10	0.86	9.7	9.8	0.03	3.60	13	525
O.M (g dm^{-3})	4	10	0.86	9.5	9.6	-0.01	3.61	13	525

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error; [5] Ratio of performance to deviation; [6] Number of Factors. [7] *n*=475: Total number of samples for recalibration of unspiked state models with 5 copies of the selected samples from the target site;[7] *n* = 525: Total number of samples for recalibration of unspiked state model with 10 copies of the selected samples from the target site.

With the extra-weight increment (5 and 10 times), the spiked state models for sand presented slightly better results than those obtained without any weighting (Table 4). A decrease in RMSECV was observed, reaching 122.0 g kg^{-1} when using 10 repeats for selected samples in the center of the spectral space (representing the mean spectrum of the target site). On the other hand, increases in RPD were observed, reaching a maximum value of 1.65 for these samples.

However, it is worth noting that, although the RMSECV values were reduced after the use of extra weight, these results are considered high when compared to those obtained by Terra et al. (2015) and Pinheiro et al. (2017), obtaining 25.22 g.kg^{-1} and 114.74 g kg^{-1} for sand, when studying Brazilian soils. On the other hand, when compared to the latter, BIAS values are considered low, at a maximum value of -1.20 (Table 5) against -17.37.

Organic matter showed a slight improvement in RMSECV, with values ranging from 9.5 to 10.3 g dm^{-3}. The RPD indicator was higher than the unspiked state model, ranging from 3.43 to 3.61. The best result was observed when extra-weight (10 copies) was used in subset 4 selected from 5 clusters (two samples per cluster).

3.3.2. Prediction

The results of the model predictions are presented in Table 6.

Table 6. Prediction results obtained by spiked state models using the remaining samples from the target site (*n* = 190).

Attribute	Subset	$r^{2(1)}$	RMSEP[2]	SEP[3]	BIAS[4]	RPD[5]	N.F[6]
Sand (g kg^{-1})	1	0.74	78.3	78.6	2.35	1.96	10
Sand (g kg^{-1})	2	0.74	82.1	82.3	1.16	1.95	10
Sand (g kg^{-1})	3	0.75	78.7	78.7	-5.14	2.00	10
Sand (g kg^{-1})	4	0.75	78.1	78.3	-1.11	2.01	10
O.M (g dm^{-3})	1	0.33	5.9	5.9	0.29	1.23	13
O.M (g dm^{-3})	2	0.33	5.6	5.6	-0.59	1.25	13
O.M (g dm^{-3})	3	0.28	6.1	6.2	0.50	1.18	13
O.M (g dm^{-3})	4	0.23	6.3	6.9	1.68	1.14	13

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error, [5] Ratio of performance to deviation; [6] Number of Factors. *n:* Number of Soil Samples.

The best estimate results were obtained for sand, and, all forms of sample selection led to more precise values for r^2 and RPD statistical parameters, with a maximum determination coefficient of 0.75 and RPD ranging from 1.95 and 2.01. In accordance to D'Acqui et al. (2010) these RPD values demonstrate that the spiked models present average potential for estimating sand content. RMSEP and SEP values were also reduced after spiking, using subsets 1, 3 and 4.

Regarding organic matter, slight improvements in prediction were observed with the use of most subsets for spiking, reaching 5.9 g dm^{-3}, 0.33 and 1.25, for RMSEP, r^2 and RPD, respectively. However, although this improved RPD to below 1.5, these values still demonstrate low prediction precision, making the use of these models for analytical use impractical. This is probably related to the size of the subsets used for spiking the models. Guy et al. (2015), while studying soil organic carbon, demonstrated that spiking models with 10 or fewer samples causes little improvement in model performance. Probably, the low number of samples used for spiking was not able to allow for recalibrated models to cover the organic matter range of variation to be predicted in the target site, independent of the sample selection methods, in agreement with Viscarra Rossel et al. (2009).

One point concerning the use of spiking is that the performance parameters of the models did not follow the cross-validation trend with the use of different subsets. For example, subset 4 based on 5 clusters for spiking of the state model in the cross validation presented better results for organic matter, but, at the prediction phase using 190 target site samples, the best result was obtained with the use of subset 2 referring to samples located in the center of the spectral space. This is due to the lower spectral variability of these samples selected for recalibration, which present reflectance values at all wavelengths that approximate most of the samples that make up the population of the target area used for the model prediction test.

On the other hand, although the cluster analysis was statistically robust, the selection of samples based on 5 clusters was not efficient for recalibration of the state models and organic matter prediction using an independent set of samples, because, although two spectrally similar samples inside of the spectral space existed for each cluster, a higher Euclidean distance between clusters were observed, leading to the re-calibration of the models with very dissimilar samples, not representing the 190 samples of the target area used in the prediction of soil attributes.

Attribute estimation using extra-weight in the spiked state model demonstrated that the sand results were better when compared to organic matter for all quality parameters except BIAS (Table 7).

Table 7**.** Prediction results of the state model after recalibration with different spiking subsets and extra-weight (*n* =190).

Attribute	Subset	Copy	r^{2}(1)	RMSEP[2]	SEP[3]	BIAS[4]	RPD[5]	N.F[6]	*n*[7]
Sand (g kg^{-1})	1	5	0.76	75.7	75.8	-4.30	2.03	10	190
Sand (g kg^{-1})	2	5	0.74	81.9	82.2	1.35	2.00	10	190
Sand (g kg^{-1})	3	5	0.76	77.0	75.9	-14.03	2.10	10	190
Sand (g kg^{-1})	4	5	0.77	74.3	74.4	-3.42	2.11	10	190
Sand (g kg^{-1})	1	10	0.76	74.4	74.3	-6.19	2.10	10	190
Sand (g kg^{-1})	2	10	0.80	71.6	71.6	-6.26	2.20	10	190
Sand (g kg^{-1})	3	10	0.75	78.3	75.0	-23.21	2.02	10	190
Sand (g kg^{-1})	4	10	0.79	71.6	71.6	-5.24	2.17	10	190
O.M (g dm^{-3})	1	5	0.33	6.2	6.2	-0.66	1.22	13	190
O.M (g dm^{-3})	2	5	0.24	5.9	6.6	1.66	1.20	13	190
O.M (g dm^{-3})	3	5	0.30	6.0	6.9	1.93	1.22	13	190
O.M (g dm^{-3})	4	5	0.30	6.1	6.2	-0.13	1.23	13	190
O.M (g dm^{-3})	1	10	0.24	6.3	6.3	0.89	1.20	13	190
O.M (g dm^{-3})	2	10	0.20	6.1	7.3	2.29	0.82	13	190
O.M (g dm^{-3})	3	10	0.25	6.2	7.1	1.94	1.20	13	190
O.M (g dm^{-3})	4	10	0.30	6.1	6.1	-0.14	1.20	13	190

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error, [5] Ratio of performance to deviation; [7] *n*: Number of soil samples from the target site used for prediction of sand and organic matter through the recalibrated state models.

Likewise, when compared to Tables 3 and 6, the use of extra-weighting resulted in prediction accuracy improvements for sand, with RPD ranging from 2.00 to 2.11 (5 copies) and from 2.00 to 2.20 (10 copies). Decreases in RMSEP and increases in determination coefficients were also noted, with the latter reaching a maximum value equal to 0.80, when recalibrating unspiked state model using subset 2, and 10 copies. However, the models recalibrated with subset 3 did not present satisfactory results, generating high bias values for sand, at -14.03 (5 copies) and -23.21 (10 copies).

The improvement in RMSEP, SEP and RPD was dependent on the type of sample selected to form the subsets used for spiking (Capron et al., 2005; Guerrero et al., 2014) and the number of copies used for extra weight. Satisfactory results were not observed for organic matter, with little differences among spiked and extra-weighted state models and spiked state models. This may be related to the low number of copies used in the spiked model, since for medium and large models, large extra-weight of spiking subsets may be necessary (Guerrero et al., 2010, 2014; Guy et al., 2015) to improve prediction performance of some soil attributes.

3.4. Local Model (target site)

3.4.1. Calibration and prediction

A total of 10 samples located in the center of the spectral space and 10 samples selected by 5 clusters were used to generate the local models for sand and organic matter, respectively. These samples belong to the target site and were chosen due to the improvement provided in the spiked state models in cross-validation stage. The results are presented in Table 8.

Table 8. Cross-validation results obtained during the calibration phase of the local models (*n* = 10).

Attribute	$r^{2(1)}$	RMSECV^2	SECV^3	BIAS^4	RPD^5	N.F^6
Sand (g kg^{-1})	0.97	93.0	98.6	6.04	1.08	3
O.M (g dm^{-3})	0.37	12.8	14.7	3.23	0.62	2

O.M: Organic Matter; ^{1} Determination Coefficient; ^{2} Root-Mean-Square Error; ^{3} Standard Error; ^{4} Systematic Error, ^{5} Ratio of performance to deviation; *n:* Number of Soil Samples.

Notable differences were observed between the quality parameters from the local models for both sand and organic matter, when comparing the elements displayed in Table 8 with those in Tables 2, 4 and 5. The local models showed low estimation potential in the cross-validation phase when compared to spiked and unspiked state models. BIAS values were high, whereas RPD values remained below ideal for use in agricultural studies.

Similarly, the prediction results were lower than expected. The r^2 and RPD for sand and organic matter were lower when comparing the information in Table 9 to that displayed in Tables 3, 6 and 7.

Table 9. Prediction results obtained for the target site using local models (*n* = 190).

Attribute	$r^{2(1)}$	RMSEP^2	SEP^3	BIAS^4	RPD^5	N.F^6
Sand (g kg^{-1})	0.67	91.6	91.8	1.49	1.75	3
O.M (g dm^{-3})	0.10	6.8	6.9	0.02	0.96	2

O.M: Organic Matter; [1] Determination Coefficient; [2] Root-Mean-Square Error; [3] Standard Error; [4] Systematic Error, [5] Ratio of performance to deviation; *n:* Number of Soil Samples.

This result is in disagreement with those obtained by Wetterlind and Stenberg (2010), who, working with organic carbon, sand and other soil attributes, observed that local models presented better estimation results than spiked national models.

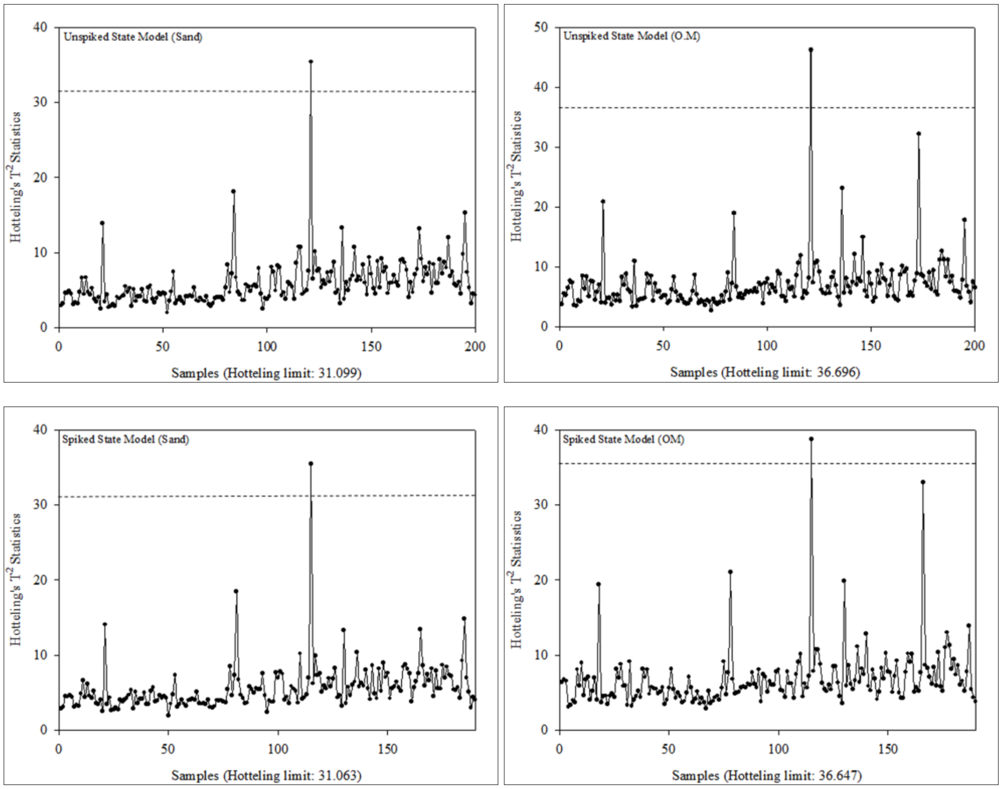
The low efficiency of the estimation for both attributes can be related to the small size of the local model, which was adjusted with only 10 samples (Guy et al., 2015). The selected samples were not able to represent the variability in the study area, reflecting in low accuracy. These results are in agreement with those reported by Guerrero et al. (2014), demonstrating the difficulty in obtaining site-specific calibration models using a small number of samples.

However, although these results were obtained, it is evident that i sand attribute presented better results when compared to organic matter all phases of the study. Similar results were obtained by Demattê et al., (2000), Nanni and Demattê (2006), and Cezar et al., (2013) when studying Brazilian soils. This is related to the high sand content found in the soil samples, which presents high spectral response due to the predominance of quartz in this fraction (Hunt and Salisbury, 1971., Al-Abbas et al. 1972., White at al. 1997).

Of the 425 soil samples collected in the state of Paraná, 273 (64.23%) presented sand contents above 50%. In some cases, values close to 90% were detected. Of the 200 soil samples collected in the target area, 154 (77.0%) presented sand contents above 50%. It is concluded, therefore, that, although the energy reflected by the samples is characterized as a function of the soil constituents, in this case the sand overlaps with the other elements, becoming the most significant parameter influencing the spectral response.

3.5. Additional evaluation of the model performance

The results obtained through the T^2 Hotteling test demonstrated that the spiked and unspiked state models presented medium performance, being able to maintain most of values within the control limit (associated with $p< 0.001$) established for the test (Figure 2).



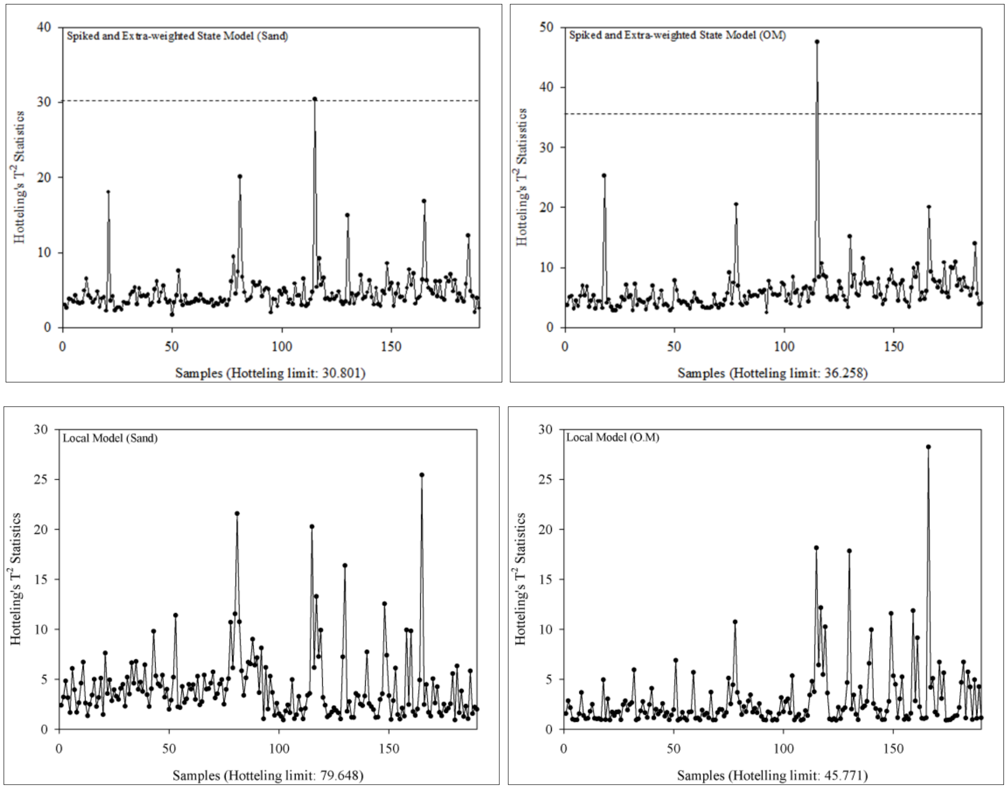


Figure 2. Graphs obtained through the T^2 Hotteling test in the prediction phase. The dashed line represents the critical limit. The spiked state model and spiked and extra-weighted state model (10 copies) for sand represents the recalibrated model with 10 samples (subset 2); The spiked state model and spiked and extra-weighted state model (10 copies) for organic matter represents the recalibrated model with 10 samples (subset 4).

Only one T^2 Hotteling value was above the critical limit for the two attributes, a sample belonging to the Regosol class. In this case, the models presented low potential to adequately estimate the value for this sample. However, the spiked and extra-weighted state model was very close in incorporating sample variability and obtaining a satisfactory result for sand, since it was close to the maximum limit.

The value above the critical limit is probably due to the high spectral response obtained for the sample, which presented a higher reflectance factor than the other samples comprising the target site set (Figure 3).

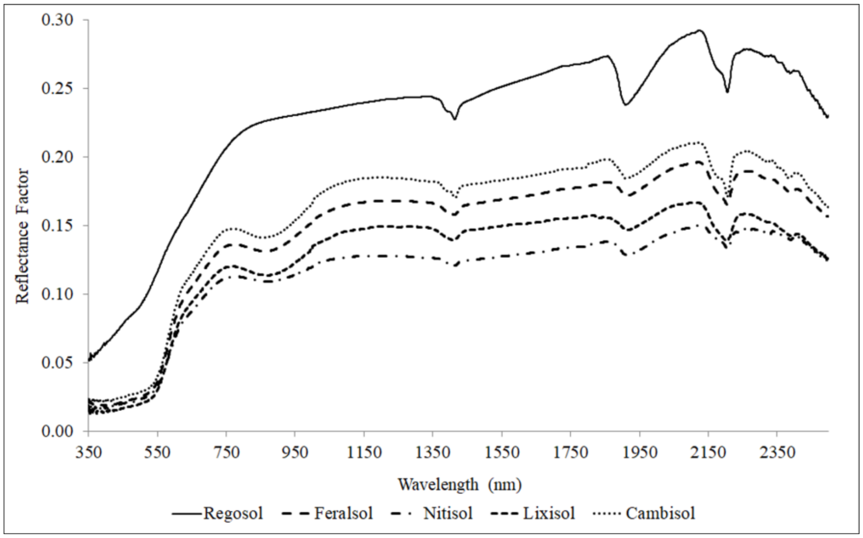
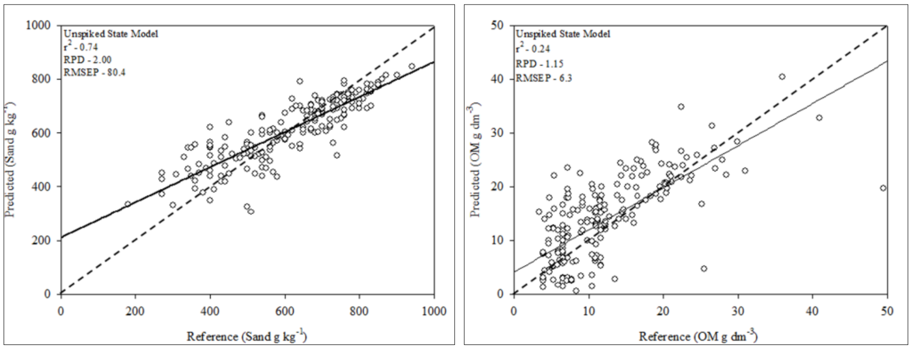


Figure 3. Spectral curves representative of the soil classes found at the target site.

The high spectral response was influenced mainly by sample sand content, with values close to 69.0%, in agreement with that described by Hunt and Salisbury (1971). On the other hand, the use of local models did not present values above the critical limit established by the T^2 Hotteling test, indicating that all values estimated for the samples are under statistical control (without any outliers). However, during soil attribute prediction, no satisfactory results were obtained, demonstrating high data dispersion as presented by scatter-plots (Figure 4), especially for organic matter.



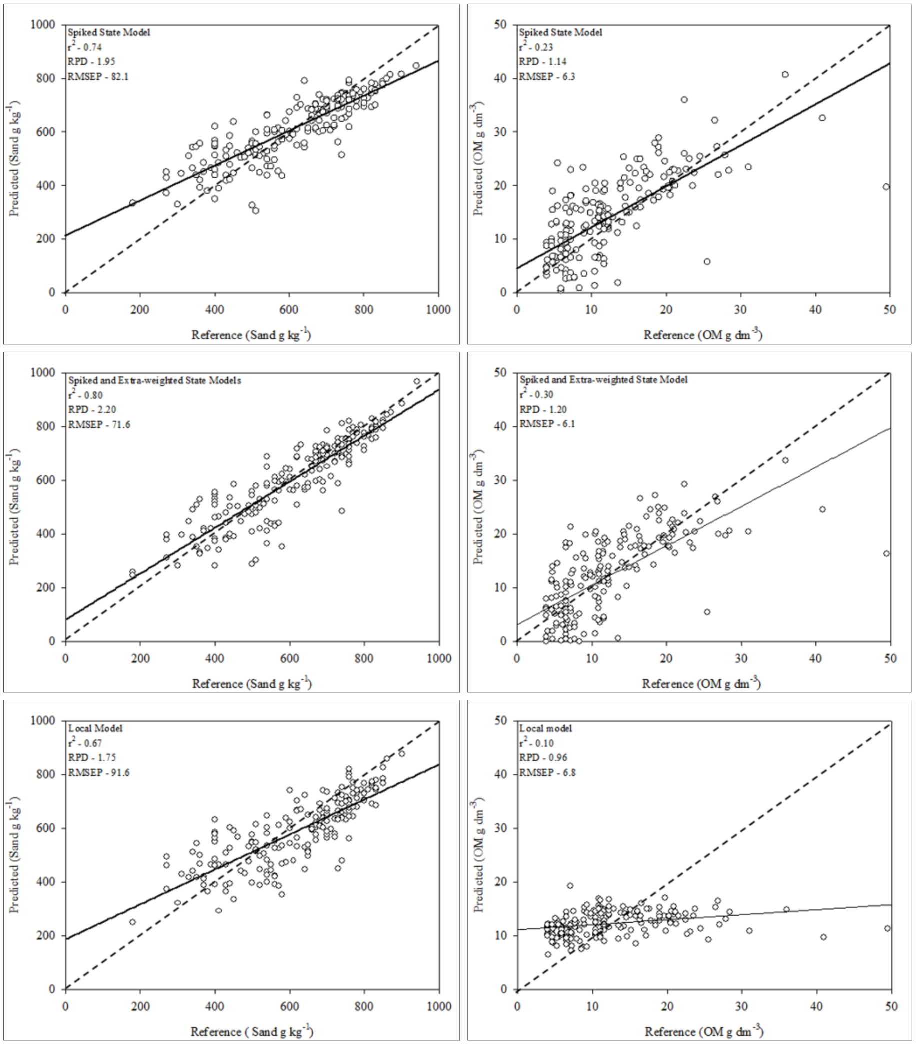


Figure 4. Scatter-plots obtained during the prediction phase. The unspiked state model, spiked state model, spiked and extra-weighted state model and local model are presented. Line 1:1 (dashed); regression line (solid line).

4. Conclusions

The spiked state model, as well as the spiked and extra-weighted state models, presented better sand and organic matter predictions compared to the local model.

Sample selection from the center of the spectral space, associate with extra-weight (mainly 10 copies), was shown to be more effective in sand prediction for the target site.

Selected subsets at the target site were not able to represent the entire the variability of the local samples regarding organic matter, damaging the expansion of the recalibrated state models and estimations for this attribute.

The results obtained in this specific study demonstrate that it is unnecessary to generate local models to estimate sand in the state of Paraná, and that recalibrated state models (spike) can be applied. However, it should be emphasized that new local models must be generated (in Brazilian conditions) from a larger number of samples to evaluate if the prediction results will be similar to those obtained herein.

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