

Building a Geographic Soil VisNIR and XRF Spectral Library: Methods and Data Overview

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Abstract. *Laboratory methods for soil analysis need to cope with the increasing demand for expedited and widespread georeferenced soil data to support decisions in digital agriculture, digital soil mapping and natural resources monitoring and conservation. A soil visible-near-infrared (VisNIR) and X-ray fluorescence (XRF) spectral library containing data from different Brazilian states is under construction that will (1) support the development of green soil analysis methods, (2) produce data to populate soil geodatabases, and (3) allow fast and accurate soil monitoring. The methods used to build the spectral library and an overview of the current data are presented.*

1. Introduction

The increasing global demand for spatial soil data (McBratney et al., 2003; Minasny and McBratney, 2016) to calibrate soil prediction models (Collard et al., 2014), support digital soil mapping in regions lacking soil maps (Coelho et al., 2021) and other applications requires developing methods to produce fast and accurate soil data. Visible-near-infrared (VisNIR) and X-ray fluorescence (XRF) spectroscopy can be used to predict various soil chemical and physical properties both fast and accurately (Nocita et al., 2012; Silva et al., 2021). Other advantages of these approaches include non-destructiveness, multi-element capability, ease of use, minimal sample preparation and portability (Viscarra Rossel et al., 2006; Weindorf et al., 2012).

In combination, VisNIR and XRF spectroscopy may expedite soil analysis and boost up projects and studies that demand data to assess soil composition, monitor soil changes, guide agricultural practices, and address environmental issues. For instance, these methods were combined to estimate soil Cr content and complemented each other overcoming their individual limitations (Xu et al., 2019). Alos, soil VisNIR and XRF spectroscopy were successfully combined to predict soil nutrient (Ca, Mg and others) contents in basalt-derived tropical soils (Santos et al., 2023).

This paper presents the methods used to develop a geographic soil VisNIR and XRF spectral library including georeferenced soil property data coupled with soil

VisNIR and XRF spectral curves. An overview of the data currently available in the library from the Mato Grosso do Sul state, Brazil, is also provided.

2. Material and Methods

2.1. VisNIR spectral curves

To generate a soil VisNIR diffuse reflectance spectral curve, halogen light is directed to the sample and causes the molecular bonds of the soil sample to vibrate, absorbing light to various degrees according to the wavelength. A soil VisNIR curve is produced by measuring the amount of reflected light from the sample at each wavelength in the VisNIR range (~350-2500 nm) and plotting them against the wavelengths.

The resulting soil spectral curve has a characteristic shape that depends on the soil constituents, and thus, it can be used for analytical purposes. For instance, soil minerals, organic matter and water, control the shape and intensity of soil VisNIR reflectance as well as many soil chemical and physical properties that can, in turn, be estimated from the VisNIR spectral curves (Terra et al., 2015).

Soil VisNIR spectral curves were acquired from 508 samples (165 sampling sites) from the Mato Grosso do Sul state, Brazil. The samples were ground, sieved (2 mm), and dried at 45 °C overnight for 15 hours to harmonize the water content in the sample. Then, the samples were placed in a 10 cm Petri dish on an ASD Turntable (Malvern Panalytical, Malvern, United Kingdom) rotating at 22 RPM and illuminated by a 20W halogen bulb. The soil VisNIR curves were acquired using an ASD FieldSpec 4 spectroradiometer (Malvern Panalytical, Malvern, United Kingdom), averaging 100 repetitions per sample. Spectralon® (Labsphere, North Sutton, USA) was used as white reference (100% reflectance) and acquired before every block of 10 readings.

2.2. XRF spectral curves and elemental analysis

To generate a soil XRF spectral curve, an X-ray pulse is directed to the sample and causes electronic transitions from core states to vacant states, emitting secondary X-rays referred to as fluorescence. Each element emits XRF at specific energy levels, and thus, the amount of emitted XRF varies according to the sample elemental contents. A soil XRF spectral curve is produced by plotting the amount of emitted XRF at each energy level against the energy level. Elemental identification and quantification can be done from curve and peak shapes and intensities (Kaniu et al., 2012).

Soil XRF spectral curves were acquired from the same prepared (ground, sieved and dried) 508 samples from Mato Grosso do Sul. The soil XRF readings were taken using a Innov-X Delta Premium 6000 spectrometer (Olympus, Waltham, USA). The instrument has two acquisition modes: Geochem and Soil. In Geochem mode, two X-ray beams are directed to the sample, each beam measuring specific element sets: Beam 1 (40 kV) – V, Cr, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Ta, W, Hg, Pb, Bi, Th and U; and Beam 2 (10 kV) – Mg, Al, Si, P, S, K, Ca, Ti and Mn. In Soil mode, the instrument shoots three beams, which measure: Beam 1 (40 kV) – Sr, Zr, Mo, Ag, Cd, Sn and Sb; Beam 2 (40 kV) – Fe, Co, Ni, Cu, Zn, As, Se, Rb, Hg and Pb; and Beam 3 (15 kV) – P, S, Cl, K, Ca, Ti, Cr, Mn and Ba.

The prepared soil samples were placed in a 2 cm wide dish and scanned in both Geochem and Soil modes for 30 s for each beam, totaling 60 s in Geochem and 90 s in

Soil mode, respectively. Instrument calibration checks were carried out by scanning a certified 316 stainless steel reference coin before every block of 10 readings.

The soil XRF curves derived from the 2 Geochem and 3 Soil mode beams were exported, along with the elemental contents measured by the two modes. Descriptive statistics of selected elements measured in Geochem (Mg, Al, Si, K, Ca, Mn, Cu, Zn, Zr and Mo) and Soil (P, S, K, Ca, Mn, Fe, Cu, Zn, Zr and Mo) modes were calculated.

3. Results and Discussion

Currently there are 508 samples from 165 sampling sites in Mato Grosso do Sul in the geographic spectral library. Another 2000+ samples from the same state with both geographic coordinates and soil chemical and/or physical property data are under analysis or in the queue waiting for analysis (Figure 1) to be included in the library.

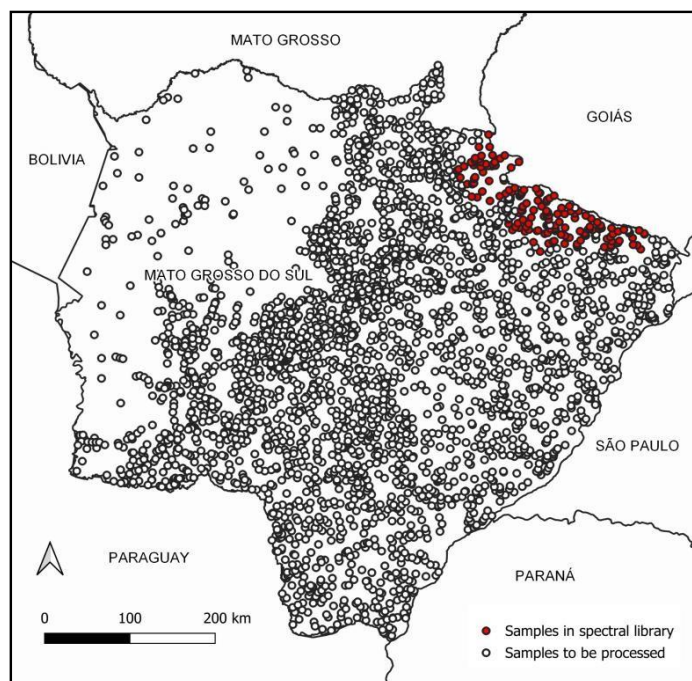


Figure 1. Samples from Mato Grosso do Sul in the spectral library (red circles) or under analysis or in the queue waiting for analysis (white circles).

3.1. VisNIR spectral curves

The mean soil VisNIR spectral curve of the 508 Mato Grosso do Sul samples along with the spectral curves from 30 randomly chosen samples from the library are shown in Figure 2. The absorption peaks of O-H at around 1400 and 1900 nm, and of C-H groups at around 2200 nm (Vasques et al., 2008) appear in the spectral curves from all samples.

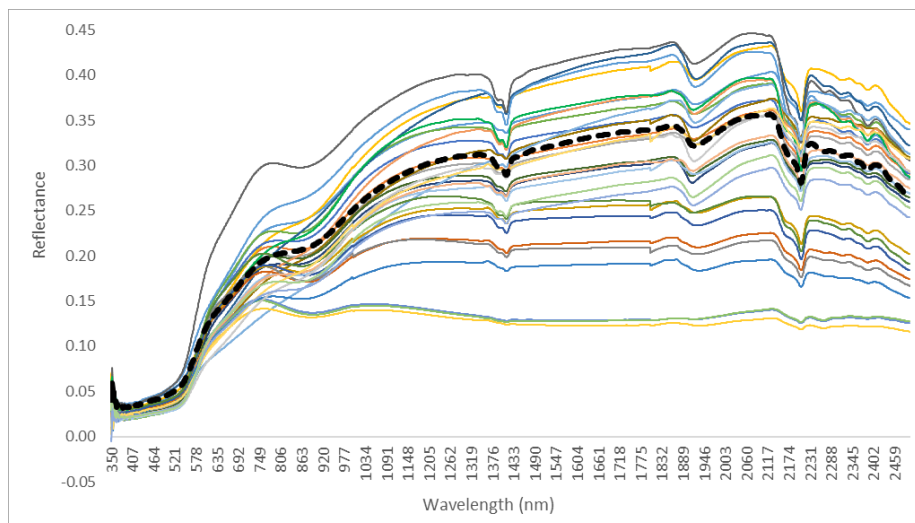


Figure 2. Mean soil VisNIR spectral curve of the 508 Mato Grosso do Sul samples (black dashed line) and spectral curves from 30 randomly chosen samples from the spectral library (colored lines).

3.2. XRF spectral curves and elemental contents

The mean soil XRF spectral curves of the 508 Mato Grosso do Sul samples scanned in Geochem and Soil modes are shown in Figure 3. Among the elements selected for the study, XRF emission peaks of Mn (~6 keV), Cu (~7.5 keV), Zr (~16 keV) and Mo (~17.5 keV) are visible in the curve from Geochem beam 1. Geochem beam 2 shows XRF emission peaks of Al (~1.5 keV), S (~2.5 keV) and Mn (~6.5 keV). In Soil mode, XRF emission peaks include: Fe (~6.5 keV), Cu (~7.5 keV), Zr (~17.5 keV) and Mo (~19 keV) for beam 1; Cu (~7.5 keV), Zr (~18 keV) and Mo (~19 keV) for beam 2; and P (~1.5 keV), S (~2.5 keV), K (~3.5 keV), Mn (~6.5 keV) and Fe (~7 keV) for beam 3.

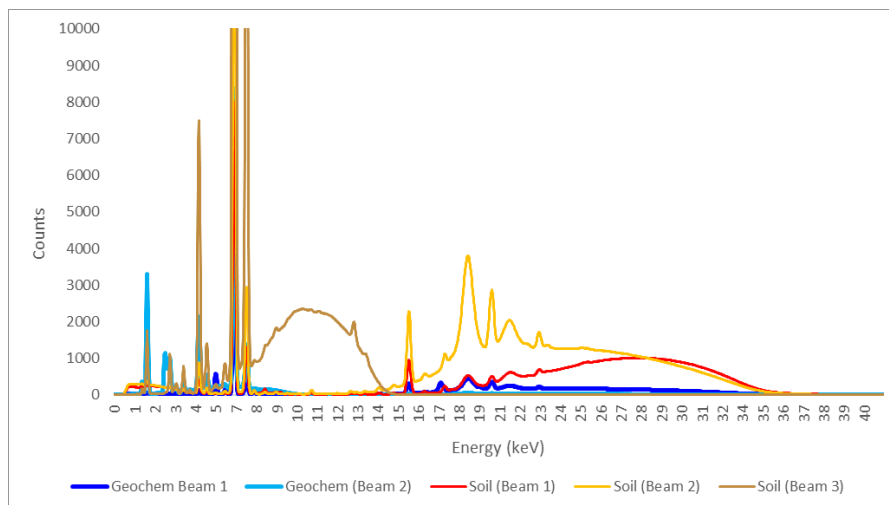


Figure 3. Mean soil XRF spectral curves from the 508 Mato Grosso do Sul samples in the spectral library scanned in Geochem (2 beams) and Soil (3 beams) modes.

The descriptive statistics of the elements measured by XRF spectroscopy in Geochem and Soil acquisition modes are presented in Tables 1 and 2, respectively. All elements selected are measured in both acquisition modes, except Al and Si, which are only measured in Geochem mode. Inconsistent Fe, and Mg values were produced in Geochem, and Soil modes, respectively, and were left out of the tables, whereas P and S contents fell below the limit of detection (LOD) in Geochem mode.

Table 1. Descriptive statistics of selected elements measured in Geochem mode.

Element	Mg	Al	Si	K	Ca	Mn	Cu	Zn	Zr	Mo
Nobs (> LOD)	63	503	503	25	9	270	18	96	336	10
Minimum (mg kg ⁻¹)	10500	18900	55400	262	332	77	23	11	24	9
Mean (mg kg ⁻¹)	14863	78515	189438	5665	1520	249	130	31	204	12
Median (mg kg ⁻¹)	14300	71200	208700	2123	961	183	118	24	153	12
Maximum (mg kg ⁻¹)	25600	193500	304200	36270	7190	1494	285	108	671	14
SD (mg kg ⁻¹)	2597	28982	59798	8690	2161	209	85	21	145	2

Nobs (> LOD), number of samples above the limit of detection; SD, standard deviation.

Table 2. Descriptive statistics of selected elements measured in Soil mode.

Element	P	S	K	Ca	Mn	Fe	Cu	Zn	Zr	Mo
Nobs (> LOD)	410	61	153	64	489	508	363	433	491	166
Minimum (mg kg ⁻¹)	410	61	55	57	7	508	1	3	38	2
Mean (mg kg ⁻¹)	7318	473	2399	1773	246	33710	14	10	284	4
Median (mg kg ⁻¹)	5346	397	731	836	144	13836	11	6	211	4
Maximum (mg kg ⁻¹)	96334	1904	24767	21466	9956	386629	66	47	930	10
SD (mg kg ⁻¹)	8315	280	4087	2970	511	55648	10	8	185	2

Nobs (> LOD), number of samples above the limit of detection; SD, standard deviation.

The mean K, Cu, Zn and Mo contents measured in Geochem mode were larger than those measured in Soil mode, whereas the Ca, Mn and Zr contents were similar between modes. Although the accuracy of XRF was not addressed in this study, previous studies (Zhu et al., 2011) have shown that the method is reasonably accurate for many elements. The means and ranges of element contents measured by XRF differed from those reported by Zhu et al. (2011) in Louisiana and New Mexico, USA.

4. Conclusions

The geographic soil VisNIR and XRF spectral library currently has 508 registered samples and is rapidly growing. The preliminary results show the potential of the approach to characterize the soil spectral features with minimum sample preparation, reduced analytical time and effort, and zero waste. Soil chemical and physical property data in the library include pH, exchangeable bases, organic carbon, sand, silt and clay contents, and others. The data is stored in Excel tables, which are extracted from instruments and are readily available. Subsequently, the analysis is executed through visually informative graphics, providing a comprehensive representation of the data. The programming language employed for this analytical process is R. The library will be expanded to further characterize the VisNIR and XRF spectral properties of Brazilian soils and estimate soil properties of interest.

5. References

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