



Chemometric soil analysis on the determination of specific bands for the detection of magnesium and potassium by spectroscopy



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ABSTRACT

The laboratory soil analysis is traditionally used to establish elements, such as those related with fertility. It is costly and time consuming, which insures issues for future of precision agriculture, which is stagnated in some countries. Reflectance spectroscopy has recently emerged as a potential tool to reduce these issues. However, chemical elements are usually only underlined with spectra by a “coincidentally” statistics and doesn't provide real detection. This study aims to investigate to interaction of K^+ and Mg^{2+} with electromagnetic energy for decrease the demand of soil analysis and rationalize the use of fertilizers. The experiment was carried out using three major soil classes with different textures from tropical environment in Brazil. To reach K^+ and Mg^{2+} saturation in different levels, the soils were saturated with concentrated solutions of KCl and $MgCl_2$ in vertical columns and then washed with distilled and deionized water to extract the residual elements. A second experiment was made by incubation of these elements in soils during four days in room temperature around 30 °C. Laboratory spectral sensing was carried out in the VIS-NIR-SWIR regions (350–2500 nm). Spectra were processed by the Continuum Removal, the Principal Components Analysis (PCA) and Partial Least Squares regression. The PCA showed a high degree of association between spectral and chemical variations. There was no alteration on mineralogy, texture, organic matter, moisture and effective cation exchange capacity (CEC) after the experiment occurs. On the other hand, differences on spectral, mainly where occurs CEC around 2200 nm, did change. Thus, the incident energy interacts with K^+ and Mg^{2+} which promoted these alterations, mostly for Arenosol and Ferrasol. In Cambisol (2:1 mineralogy) we had a double effect due to effective CEC and cations alteration. Were encountered specific bands which altered features due to K^+ and Mg^{2+} content mainly in 2186, 2189 and 2200 nm. Based on the results, the identified bands (related to K^+ and Mg^{2+} contents in the soil) were extracted from the spectral data of soil samples obtained from a Brazilian soil spectral library. Indeed calibrations of K^+ and Mg^{2+} models allowed to quantify these elements with 0.66 R^2 for the selected bands and 0.64 for the entire spectrum. Thus, the results indicate that it is possible to detect chemical elements, such K^+ and Mg^{2+} in VIS-NIR-SWIR, looking forward on to assist soil analysis and all inherent approaches.

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1. Introduction

World population corresponds to 7.207.456 people and is expected to 8.612.262 in 2050 (FAO, 2013). To attend this increase of population, the production of food is the most important goal, and thus, soils have to be managed to reach higher productivities. One of the most important strategies is closing the yield gap, which requires mainly a good land use planning for the existent fields and also the upcoming ones (Godfray, 2010). Thus, soil analysis is the most important information

to help farmers on increasing productivity. In Brazil, Raji et al. (2001) observed about one million soil fertility analyses in one year. An example of this huge increase in agriculture is the growth of soybean in developing countries, mainly in Brazil and Argentina. Soybean is expected to continue been one of the most dynamic crops, bringing by 2050 a production over 70% (Brazil, Argentina, China and India) accounting for 90% of total production in developing countries (Bruinsma, 2009).

With the objective to increase productivity, the Precision Agriculture (PA) system started in the 90's with the necessity of one sample per ha, and today is working with about one per four ha (Demattê et al., 2014a), in the case of sugar cane and soybean in Brazil. According to the authors, if on one hand this system uploaded the productivity, in another made greater the cost in soil analyses. The strong and fast agriculture advances in countries such as Brazil, and now in Africa, takes the necessity for new

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methods on soil analysis that can deal with a so large scale areas to work. Despite of this, the commercial laboratories use several types of chemical products that even when correctly disposed, can rely on environment issues (Nocita et al., 2015).

Thus, the necessity for a more quick and cost effective method on soil analysis has been the focus of community on chemometrics. Basically this subject deals with the electromagnetic energy that interacts with matter and shows several elements in a soil sample. Looking towards the main goal on determining soil attributes by spectroscopy, several works have been performed such as Nanni and Demattê (2006), Viscarra Rossel et al. (2009), Viscarra Rossel et al. (2010), Kuang et al. (2012) or can be widely observed in a review by Soriano-Disla et al. (2014) and Demattê et al. (2016). These works indicate strong evidences for soil properties quantification, i.e., organic matter, clay and mineralogical composition. These elements present a great background about their physical and chemistry relationship with the electromagnetic energy, justifying these findings. On the other hand, other elements, such as exchangeable cations and soil chemical composite, are less studied with variable results until the present. In fact, Stenberg et al. (2010) indicate that there is difficulty on the detection of exchangeable cations due to its non-relationship with absorption features. Thus, spectral models for estimating chemical attributes haven't yet reached optimal levels of accuracy compared to conventional methods, as also observed by Soriano-Disla et al. (2014). The diversity of mineral composition and organic matter (OM) content makes soil properties a challenge through NIR (Fernandez-Pierna and Dardenne, 2008). Thus, research focused on the improvement of the accuracy of estimation must be developed.

Chemical elements such as K^+ and Mg^{2+} are important for agriculture because are widely used as fertilizers and are basic for plant growing, which account for 95% of global potassium chemical production (Greenwood and Earnshaw, 1997). They originate from natural resources and it are leached during pedogenesis, reducing or even running out, necessitating its correct and optimal use. Despite of this, they come from natural resources, and thus can decrease until finish, what makes necessary its correct and optimized use (Prud'homme and Krukowski, 2006). The best system to use fertilizers with less waste is certainly the PA, but as exposed before, this technology still didn't grow due to several issues. The most important issue indicated by farmers are the time consuming on collecting soil samples and the high costs of soil analysis. Moreover, users have to wait for the laboratory results, which can take days. A strategy to make this task less cost-effective in to quantify soils elements in situ was proposed by Kodaira and Shibusawa (2013), although these works shows few statistical results. The implementation on the use of spectroscopy on a commercial scale as a technique to quantify soil attributes must have strong evidences of physical and chemical relationship among the elements we want to determine.

Although the spectral regions of the entire VIS (350–800 nm), NIR (800–1100 nm), SWIR (1100–2500 nm) may be used to calibrate models for quantification, most of the undesired regions that do not contain relevant information related to the attribute of interest can generate noise in the models and increase computational processing. Theoretical considerations (Xu and Schechter, 1996; Spiegelman et al., 1998) indicate that a careful selection of spectral regions for models calibration using the Partial Least Squares (PLS) method can result in a higher performance of prediction models (Vaidyanathan et al., 2001; Jiang et al., 2002; Hemmateenejad et al., 2006; Xiaobo et al., 2007). On the other hand, how can we isolate all factors to indentify the cations influence on spectra?

When the first findings of mineralogical elements were done, laboratory experiments were performed to understand the relationship between elements and electromagnetic energy (Bowers and Hanks, 1965; Hunt et al., 1971). Most methodologies have been developed in different areas of soil science and a few in cations experiments. One of the first was done by Schreier (1977) to quantify K^+ , but did not explain

its bands. It's likely that the current available algorithms do not solve the whole identification problem of bands suitable for the improvement of K^+ and Mg^{2+} estimation. After this is solved, statistics analysis could be done with more secure. Therefore, it is necessary to use the experimental design (ideal in soils) needed to eliminate sources of interference for the identification of bands to understand the system. There is a lack between the papers that show high R^2 for exchangeable cation and the description of why they are or not related with spectra. Until now, there are few works with a chemical focus of K^+ and Mg^{2+} in tropical soils. All literature indicates that energy reaches O—H and cause adsorption, but what happens to the elements (cations) that fill the exchange sites? Did energy reach before interacting to CEC charges? Energy does not interact with a charge, but with an element filling the exchange sites.

Thus this work considered that: a) the soil is a very complex mixture; b) spectral models commonly calibrated for exchangeable K^+ and Mg^{2+} in the soil do not present a desirable prediction performance, because they do not have any background to explain why this; c) literature indicates that the identification of spectral bands may improve the performance of spectral models; d) few studies have evaluated individually the reflectance of cations in soils; and e) the soil characteristics mostly researched by reflectance spectroscopy techniques are organic carbon, clay and iron content.

Our hypothesis is that the incident energy can be altered by different cation ionic radius and hydration levels. Remember that the energy reaches O—H of the mineral, but before pass through the cations and can modify spectra. Since the literature already agrees that the cation exchange capacity is related with electromagnetic energy, it is plausible that the same energy can be changed by the elements in the charge sites.

Thus, this paper aimed to identify the specific spectral responses of K^+ and Mg^{2+} in the soil and, therefore, improve the prediction performance of quantification models.

2. Material and methods

2.1. Soils selected for the experiment and preliminary analysis

Soil samples were collected considering three different textures: sandy, clayey and heavy clayey, in three distinct regions of São Paulo state, Brazil, at 0.6 m depth (to avoid the influence of organic matter). The soil classes were Ferralsol (LV), Cambisol (CX) and Arenosol (RQ) (WRB, 2014) and they were chosen due to differences on texture and mineralogy which will interfere on the cations behavior. Soil samples were submitted to chemical and particle size analyses (Raij et al., 2001), comprising the determination of the pH ($CaCl_2$); exchangeable cations (Ca^{2+} , Mg^{2+} , K^+); organic matter (OM), H + Al and Al^{3+} ; with the result of these analyses was calculated sum of cations ($SB = Ca + Mg + K$) and cation exchange capacity (effective CEC = $K + Mg + Ca + Al$ and CEC pH 7 = $K + Mg + Ca + Al + H$). Particle size analysis were carried out by the densimetric method (Camargo et al., 1987) using hexametaphosphate calcium 0.1 N and 0.1 N sodium hydroxide as dispersing agents in order to separate and quantify the fractions: sand (>0.02 mm), silt (0.002 to 0.02 mm) and clay (<0.002 mm). Appropriate amounts of all collected soils were dried, ground and sieved (2 mm mesh) to be used in two experiments, described as follows.

2.2. Saturation with K^+ and Mg^{2+}

Columns were built with rigid PVC pipes rings (diameter 0.15 m), closed at the bottom with a reducing glove of 0.10 m diameter and a hole at its base to attach a hose. Silica was deposited up to a height of 0.07 m from the column base and a plastic filter screen was placed on its top.

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