Mineralogy, Pedology and Remote Sensing: A Multi-scaled Approach to Potassium Deficiency Risk in California Vineyards

Michael L. Whiting¹*, Susan L. Ustin¹, and Leroy O. Garciano¹

Objectives

Site specific application of fertilizer is critical in potassium (K) sensitive crops. The relationship between mineral type and K fixation may be determined through reflectance spectroscopy analysis of the soil clay fraction when combined with the geomorphology, to provide the necessary high spatial resolution.

1. Identify the mineral types of the laboratory soil samples, their band centers and band depths using a portable field spectrometer.
2. Correlate the results of mineral identification using spectroscopy to the x-ray diffraction analysis;
3. Increase the prediction of K-fixation using spectral reflectance data through a landscape model.

Introduction

The soils from the Lodi region form an east to west gradient from the Sierra Nevada foothills to the Sacramento San Joaquin Delta. Major river systems such as the Sacramento, Cosumnes, and Mokelumne, and their tributaries deliver sediment from contrasting geologic parent materials. These complex sediment sources further differentiate the soil properties.

Fig 1 Map of topsoil textures for Lodi-Woodbridge Winegrape District, from USDA-NRCS San Joaquin County SSURGO database (O’Geen et al. 2006).

¹Center for Spatial Technologies and Remote Sensing, LAWR, University of California, Davis
*Principal Investigator
For more information contact Dr. Michael Whiting (mwhiting@ucdavis.edu).
controlling K fixation and tendency for K leaching - mainly a function of degree of soil development, soil texture, and soil mineralogy. The Lodi-Woodbridge winegrape district on the east side of the Central Valley, which supports more than 750 growers and 75,000 acres of diverse production, has identified a potassium deficiency in their soils. High K fertilizer rates (400 lb K₂O/acre or more) are often required to satisfy the K fixation capacity. Studies by UC Davis researchers on Central Valley soils on tomato (Hartz et al. 2002) and on cotton (Murashkina et al. 2004) found K fixation capacity measured in the laboratory ranged from negative (i.e., the soil releases K into solution) to 600 ppm – equivalent to fixation of ~2400 lb K₂O/acre within a one-ft depth of soil. In grapes, K deficiency reduces vine growth and causes premature leaf drop, resulting in yield loss (Christensen et al., 1978). However, excessive K uptake by grapes leads to an increase in juice pH (Boulton, 2001) and lower yeast-assimilation of nitrogen and ammonia in the fruit (Wehmeier, 2002). Both conditions are undesirable from the wine-making perspective. Excess K in the wine may precipitate as potassium tartrate during cold stabilization, requiring that the winery purchase acid for pH adjustment to avoid losing an important sensory component (astringency) in the wine (T. Prichard, personal communication). Greater spatial resolution than available soil survey mapping is needed to develop K fertilizer prescriptions that will lead to improved management operations (Sadler et al., 1998).

In K fixation, vermiculite (a layer silicate mineral resulting from the weathering of mica) actually removes K from solution by trapping it on sorption sites within the mineral layers. A portion of K fixed in this manner serves as a very slow-releasing source for plants, but most of the K is not available during times of high K demand, such as berry formation. Soils high in vermiculite that are known to fix K are found on the east side of the Central Valley, especially on landscapes with soils that are weakly to moderately weathered. Soils formed on more highly weathered landscapes may not fix as much K due to the dominance of non-K-fixing smectitic or kaolinitic mineralogy. Hartz et al. (2002) observed strong K fixation in fine-textured soils in the Sacramento Valley. Murashkina et al. (unpublished) showed that K-fixing capacity in some San Joaquin Valley soils occurs mostly in the silt and fine-sand size fraction and not in the clay-sized material. Mineralogical assemblages, hence K supply characteristics, are governed by the nature of parent material and degree of pedogenesis. The natural distribution has been changed by overland flow and deposition, and farming practices, such as land-leveling, which have mixed the mineral surface and subsurface on the landforms, and within fields. The existing soil landscapes will serve as the initial template to detect differences in soil mineralogy and additional details will be provided by point measurements and image spectroscopy.

The Lodi preliminary investigations have identified four soilscapes with multiple topsoil constituents (Fig 1): 1) undulating volcanic terrain in the east, 2) well-developed soils on old dissected terraces, 3) young mica-rich soils on flood plains and stream terraces, and 4) smectitic soils along basin rims and poorly drained valleys. Sandy soils with high mica content (and likely high K-fixation potential, especially in the silt and sand fractions) tend to occur in the Lodi area. Well developed soils such as the San Joaquin series and like soils found east of Highway 99 have hardpans but due to advanced weathering probably do not strongly fix K because the weathering processes have altered primary minerals to secondary minerals that do not fix K.
To add detail within map units, the surface soil can be characterized by quantifying the mineral types and texture contents using field and image spectrometers. Early work on terrestrial soil reflectance studies have been conducted to demonstrate a better understanding of how soil reflectance data and certain soil properties that correspond to well-known relationships with soil color (Stoner et al. 1981; Baumgardner et al. 1985; Irons et al. 1989; Ben-Dor et al. 2008). Field full-range spectrometers and airborne hyperspectral imagers have an effective range from 400 to 2500 nm wavelengths that can be used to identify and determine the abundance of minerals, when calibrated with local soil sampling and analysis (Whiting et al., 2005). Several spectroscopic techniques are successful in determining the abundance of the mineral by the derivative, shape, depth and area of the various regions of the solar spectrum that is absorbed by the minerals (Ben-Dor et al. 1995; Ben-Dor et al. 1999; Sunshine et al. 1993; Mustard and Sunshine, 1999).

These models along with experimental approaches were used to demonstrate meaningful correlations between the spectra and mineralogical properties of soils. Studies made on the spectral absorption features in the SWIR region (1.100 – 2.500 nm) of minerals have demonstrated that these absorption band centers are sensitive indicators of mineralogy (Burns, 1970, Adams 1975). The fundamental modes of vibration of most of these geologic materials are usually beyond our instruments in the near-infrared and mid-infrared regions of the electromagnetic spectrum. When these fundamental modes are excited by two or more quanta of energy, an overtone occurs producing a band center at (or near) twice (or some multiple integral of the value) of the fundamental frequency (Hunt 1977). Mostly the overtones are in the near-infrared while the fundamental frequencies are in the mid-infrared. One of the most well-defined absorption features of soils in the infra-red region is the OH-group.

The light absorption features near 1400 and 1900 nm band centers assigned to OH- are due to free water molecules, absorbed water on the crystal lattice surface itself and adsorbed water between clay platelets. The hydrogen-oxygen stretch may also be coupled with bending vibrations in the molecular structure to create combination band features. These combination

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**Table 1. Diagnostic band centers for minerals in Figure 2.**

<table>
<thead>
<tr>
<th>Mineral Species</th>
<th>Absorption Center (µm)</th>
<th>Primary</th>
<th>Secondary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>Flat Line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>2.200</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>2.200</td>
<td>2.180</td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td>2.230</td>
<td>2.320</td>
<td></td>
</tr>
<tr>
<td>Vermiculite</td>
<td>2.320</td>
<td>NA</td>
<td></td>
</tr>
</tbody>
</table>

**Fig 2.** Continuum removed mineral spectra illustrating the separation between known minerals in the study areas (data from the Jet Propulsion Laboratory spectral library).
bands attributed to OH-bearing minerals within the octahedral positions near 2000 to 2500 nm region. The wavelength, depth and shape provide unique spectral fingerprint of the minerals. The bending of Al-OH bonds coupled with stretching produces combination bands near 2200 nm which are due to secondary clay minerals (Hunt 1980), and the combination vibrations are due to magnesium-hydroxyl (MgOH) near 2300 nm, but other absorptions in this region are due to carbonate (CaCO₃) double bonds (Ben-Dor et al. 2008).

Spectra of weathered materials show evidence of the presence of both iron and oxygen. The higher concentration of iron indicates the degree of pedogenesis or advanced weathering stages of the soil, while low abundance of iron content implies early crust evolution (Pieters et al., 1996). The abundance of iron is detected with spectroscopy in the visible range near 550 nm for Fe₂O₃ (ferric oxide) in soils (Ben-Dor et al. 2008). For soils that have undergone oxidation-reduction, the resulting chemical reaction of the ferric ion with oxygen transforms it into FeO (ferrous oxide) having reduce oxygen content resulting in a black colored texture, whose band center is near 650 nm.

The spectra of the minerals expected to have the greatest influence on the soil reflectance and K-fixation are shown in Figure 2. These spectra are from the Jet Propulsion Laboratory (JPL) library (jpl1.sli; http://asterweb.jpl.nasa.gov/speclib/). Distinct absorption centers and doublets are shown normalized on the spectrum’s upper continuum (continuum removed, Clark and Roush, 1984). The spectral range is divided into visible and near-infrared (400 - 1000 nm, VNIR), shortwave-infrared (1000 - 1800 nm, SWIR-1 and 1800 - 2500 nm, SWIR-2). These measurements demonstrate that both the 1 nm field spectrometers and 10 nm airborne imaging spectrometers have sufficient spectral resolution for mineral identification. Table 1 lists the band centers of OH bearing minerals in the study site. Field spectrometer measurements, calibrated to local minerals and conditions, provided rapid point measurements extendable by landform, and from future hyperspectral imagery.
Approach and Procedures

Soil sampling at the study site and laboratory analysis

The soil sampling was stratified by five landscape categories shown in Tables 2 and 3 with soil series, pedon sampling and sampling types (data from collaborators Hideome Minoshima, Antony O’Geen, Stuart Pettygrove and Randy Southard). The sites were selected for the various soil geomorphology characteristics of the region. Points 1, 2, 6, and 7 represents the young fine and coarse soils, while the 4, 5, 8, 9 and 10 are old lower and higher terrace, as well as, volcanic parent material. The soils were sampled at the surface and each horizon or at specific depths in the vineyard soils. The map of the Lodi-Woodbridge Winegrape District study site in Figure 3 is marked with sample point locations of the 2006 and 2007 seasons.

Table 2. Soilscapes, soil series, pedon sampling and type of sampling of the 2006 data

<table>
<thead>
<tr>
<th>Region</th>
<th>Soil Series</th>
<th>Sampling Pits</th>
<th>Sample ID</th>
<th>Sampling type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – Young, fine texture</td>
<td>Stockton</td>
<td>1, 2, 3</td>
<td>3-1,3-2, 3-3, 3-4</td>
<td>Horizon</td>
</tr>
<tr>
<td>2 – Young, coarse texture</td>
<td>Kingdom Tokay Tujunga</td>
<td>4, 5, 6, 7, 8, 9</td>
<td>6-1, 6-2, 6-3, 6-4, 6-5-6-6</td>
<td>Horizon</td>
</tr>
<tr>
<td>3 – Old lower terrace</td>
<td>Bruella San Joaquin (SJ) Intermediate of Bruella and SJ</td>
<td>17, 18, 19, 20, 21</td>
<td>17-1, 18-1, 19-20-1, 21-1</td>
<td>Horizon</td>
</tr>
<tr>
<td>4 – Old higher terrace</td>
<td>Redding</td>
<td>10, 11, 12</td>
<td>11-1,11-2, 11-3, 11-4, 11-5,11-6, 11-7</td>
<td>Horizon</td>
</tr>
<tr>
<td>5 – Volcanic parent material</td>
<td>Pentz Ramoth/Alamo/Madera</td>
<td>13, 14, 15, 16</td>
<td>13-1,13-2, 13-3,13-4, 13-5</td>
<td>Horizon</td>
</tr>
</tbody>
</table>

Table 3. Soilscapes, soil series, pit sampling and type of sampling of the 2007 data

<table>
<thead>
<tr>
<th>Region</th>
<th>Soil Series</th>
<th>Vineyard Owner</th>
<th>Sample Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – Young, fine texture</td>
<td>Galt</td>
<td>KTR</td>
<td>Depth</td>
</tr>
<tr>
<td>2 – Young, coarse texture</td>
<td>Sailboat/Columbia</td>
<td>KTR</td>
<td>Horizon depth</td>
</tr>
<tr>
<td>4 – Old higher terrace</td>
<td>Redding and Cometa/Montperier</td>
<td>CM</td>
<td>Horizon depth</td>
</tr>
<tr>
<td>5 – Volcanic parent material</td>
<td>Pentz/Alamo/Madera Pentz/Hicksville Pentz/Bellota</td>
<td>BH</td>
<td>Depth</td>
</tr>
</tbody>
</table>
In 2006, 13 different soil series were sampled using the horizon and depth method with a total of 16 pits and 115 soil samples, and in 2007, 71 sites were sampled. In this report, only the analyzed 2006 data and some 2007 data are provided, which includes 29 representative soil samples from the five regions. These samples were coded such as 3-1, 6-1 and 13-4, where the first one or two digits represents the soil type or soil series and the digits after the hyphen represents sequence in depths sampled.

**Laboratory soil spectral measurement**

A 50 g subsample of the air dried soil was lightly ground and sieved to a size fraction of less than 2 mm. Spectral reflectance was measured in the lab with an ASD FieldSpec Pro spectrometer (Analytic Spectral Devices Inc., Boulder, CO) with a spectral range 350 to 2500 nm at 1 nm data interval output. The accessory portable self-contained light probe was used for consistent incident light.

**X-ray diffraction (XRD) of soil samples**

To corroborate the diagnostic absorption strength to mineral abundance, x-ray diffraction analysis of the laboratory soil samples (clay fraction only) was conducted by collaborator Minoshima. In the x-ray diffraction analysis, samples were prepared by drying the soils at room temperature, then processing using the standard techniques of sieving, orienting on glass slides and measured through a series of Mg and K ion saturations with glycerol and heating. X-ray diffraction analyses was made with a Diano XRD 8000 diffractometer (Diano Corporation, Woburn, MA) employing CuKα radiation fitted with a Ni filter and curved graphite monochromator.

**Modified Gaussian Model (MGM) and Soil Moisture Gaussian Model (SMGM)**

The MGM is a quantitative method of de-convolving individual absorptions within mineral spectra (Sunshine et al., 1990). Through an iterative process all absorptions within the spectrum are fitted simultaneously using multiple Gaussian functions. Each function shape reduces the absorption to three terms: band center, band depth and bandwidth (distance to the point of inflection). The area within the curve is also calculated (Whiting et al. 2004). Iteratively, the differences between the simulated curve and the actual spectrum is compared, and in the end reported as the root mean square error (RMSE). The MGM neither relies on a library of spectra that may or may not reproduce all permutations and combinations of absorption bands (Pieters et al. 1996).

The relationship of water content on soil spectra was modeled by Whiting et al. (2004) using the Gaussian function on the fundamental water absorption in soil spectra at 2800 nm as the Soil Moisture Gaussian Model (SMGM). This position was inserted in the MGM fitting algorithm as the SWIR continuum. In the ultraviolet region, the strong water absorption at 200 nm was inserted. The spectra were normalized and separated into two parts using the point of maximum reflectance. This addition of modeling the absorptions beyond the range of the instruments is a new technique in the MGM.

An example of the fitting results to Kaolinite (CM9) at unknown water content from the USGS library using the MGM/SMGM are shown in Figure 4. These results of fitting this pure mineral show the Gaussian curves departure from the straight line at the top of the natural log
reflectance (1.0 reflectance). The modeled spectrum is superimposed on the actual spectrum with an RMSE of 0.020 and 0.0034 reflectance.

**Results**

Figure 5 a) shows a stack plots of XRD analysis of the clay fraction of soil sample 3-3. The prominent intensities were from the minerals kaolinite, vermiculite and smectite in size fractions treated with Mg saturated with glycerol. Mica was observed in K-saturated samples at 25 °C. Mica and some remaining amount of kaolinite were observed at K-saturated sample at 325 °C and only the mica mineral remained at K 550 °C. The intensity measurement of the XRD analysis allows comparison of the identified minerals abundance. To proceed with the analysis, the curve from the Mg saturated in glycerol step was normalized, then the continuum was removed, and the noise was removed using a Savitzky-Golay filter. In Figure 5 b) the smoothed intensity values of kaolinite, smectite and vermiculite minerals were superimposed on the noisy data.

**Spectral de-convolution using the MGM**

Figure 6 a) shows the full spectrum of sample 3-3 which was normalized and presented in natural logarithm (ln) form. The red line falls at the point of maximum reflectance for the spectrum where the data was partitioned for an MGM analysis. The bold dashed line is the soil spectrum, and the red dashed line is the fitted reflectance. All spectra parameters from the MGM fitting were used in the statistical regression analysis to determine mineral content.

In Figure 6 b), absorption features near 550 and 650 nm are attributed to the presence of iron minerals. In Figure 6 c), the mixture of absorption features de-convolved by MGM/SMGM in the SWIR are due to the OH-bearing minerals in the soil and these combination bands. The O-H bands near 1914 nm were composed of three Gaussian curves related to water content. In addition, de-convolved components show the mineral components within the 2100 to 2500 nm region.
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**X-ray Diffraction analysis**

Fig. 5 a) X-ray diffractogram of the clay fraction of a soil sample (sample 3-3, sampled at 38-60 cm). b) Intensity curve smoothed and continuum removed for consistent base line. Peaks are identified by d-spacing in nm (Pettygrove et al. 2005).
Fig. 6 a) MGM/SMGM de-convoluted spectra of sample 3-3 showing all absorption features of the full spectra (Refl) and fitted (Fit), and the Gaussian distributions. b) Spectra in the visible, NIR and SWIR with continuum Gaussian centered at 200 nm, and c) spectra in the SWIR with continuum Gaussian centered at 2800 nm.
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**Functional relationship between K-fixation and soil chemical, pedogenesis, and mineralogy**

The response of soil to K-fixation potential is a complex interaction of the physico-chemical properties or chromophores (Ben-Dor et al. 2008), pedogenesis and soil mineralogy. In investigating the K-fixation potential in soils the following relationship is proposed as expressed in equation (1).

\[ k\text{-fixation} = f (\text{chemical characteristics, pedogenesis, soil mineralogy}) \quad (1) \]

In equation (1), the mineral charge characteristics are represented by CEC; pedogenesis is represented by the spectral absorption of iron near 550 nm, and soil mineralogy is represented by the band depth \((BD)\). The empirical model is presented in equation (2).

\[ M_k = a_0 + a_1 BD_{550} + a_2 BD_{2190} + a_3 BD_{2320} + a_4 \text{CEC} \quad (2) \]

where: \(M_k\) = predicted potassium fixation; \(a_0, a_1, a_2, a_3, a_4\) are the linear regression coefficients; and \(BD_{550}, BD_{2190}, \) and \(BD_{2320}\) are the band depths with subscripts for the diagnostic wavelengths for iron, smectite and vermiculite minerals, respectively. Figure 7 a) shows the results of equation (2) with a coefficient of determination \(R^2\) of 0.53. This suggests that the K-fixation potential in these soils is correlated to mineral types and charge characteristics.

To investigate the possibility of solely using spectroscopy to identify K-fixation potential in soils, the spectral parameters were evaluated, but yielded one significant \(BD\) near the diagnostic vermiculite 2320 nm as shown in equation (3).

\[ M_k = b_0 + b_1 BD_{2320} \quad (3) \]

The results of the model (3) are shown in Fig. 7 b). These results also indicate the complexity of the fixation is not solely due to mineral type. The relationship of CEC to clay type, while not correlated to the band centers and over fitting the model, did also improve the prediction model.

![Graph](image)

**Fig. 7.** a) K-fixation prediction with CEC and multiple band depths, b) predicted with the vermiculite band alone.
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Discussion

When combined with XRD and K-fixation chemical analysis, spectroscopy of soil samples was shown to be related to K-fixation, and future development of faster, more economical determination of the potassium deficiency risks of soils in California vineyards.

This new technique of simultaneously including the variation in water content into the MGM improved the parameterization of the mineral absorptions. The water absorptions at each end of the spectrum, based on the SMGM, significantly improved the Modified Gaussian Modeling (MGM) fitted curve.

The capability of spectroscopic analysis of soil minerals in the laboratory, and in the field, leads to a way of analyzing soil surfaces from airborne and satellite hyperspectral sensors. These images contain similar spectral measurements within each pixel. The spatial analysis of spectra, geomorphology and existing soil databases advances this Kearney Mission by adding scale information from detail surface to the landscape perspective.

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References

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