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Hyperspectroscopic and microtopographic analyses of salt crust forms on arid, silty clay loam desert soils

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Abstract
This paper describes simultaneous uses of field sampling and hyperspectroscopic approaches to understand the distributions of salt crusts and factors affecting them under field conditions. Samples of salt affected soils and associated salt crusts that represented a range of soil salinities, slope, and moisture contents were gathered from the banks of the Rio Grande. The samples were studied for salt identification by optical microscopy and using a high-resolution spectrometer, GER 3700, and for salinity level, and moisture content by the wet chemistry method. The study identified two main groups of salt crusts, contaminated halite and gypsum crusts. Reflectivity was correlated negatively with moisture content and positively with slope value, electrical conductivity and salt quantity. Reflectivity of halite-dominated crusts was higher than those of gypsum. Halite occurred over a greater range and higher slope values of soils than gypsum; however, a positive correlation between the slope and mean reflectivity of both salt crusts was reported. Although reflectivity of salt crusts varied according to changes in moisture content, and the salinity of the soil, moisture content can drastically reduce the reflectance more effectively than the other factors. The data reported indicate the possibility of assessing the type of salt crust by estimation of the ratio of slope and reflectivity to the other variables.

Keywords: Spectra, halite, gypsum, Rio Grande, soil, GER 3700

1. INTRODUCTION
Agricultural soil worldwide is seriously vulnerable to production losses due to the accumulation of salt. The impact of salts from the agricultural water return flow and capillary rise from the high-water table in some locations, increases the variable concentration of sulphate and chloride salts in agricultural fields through space and time. Despite the general understanding of factors controlling salt distribution it remains difficult to extrapolate their spatial patterns on a large scale in the field. Thus, spatial tools and techniques are needed to set background conditions and verify variations in salt distribution and their impacting factors. However, the presence of additional mineral phases on the surface of the crusts might affect the reflectance spectrum of the crusts. The present study was conducted using field crust samples to evaluate the factors affecting their spectra and distribution.

Earlier studies reveal that soil characteristics and salt minerals can be identified by examining absorption features using semantic and computational approaches (HOWARI et al., 2002; DRAKE, 1995; CLARK, 1999; ZHANG et al., 2013; ARAUJO et al., 2014; SORIANO-DISLA JOSE et al., 2014; LAPOTRE et al., 2017; ROBERTSON et al., 2016; ARAUJO et al., 2014; WANG et al., 2018). The absorption of the visible part of the electromagnetic spectrum happens when anionic groups, such as sulphate and carbonate, interact with surficial contamination with other salts or minerals such as clay minerals or quartz. When an uncontaminated crust is developed as a result of evaporation of saline solutions, salt minerals with low solubility form first, and the surface of the crust is likely to be composed of salt minerals with the greatest solubility or in their sequence of their arrival at saturation (HOWARI, 2004). This hypothesis, solubility-controlled system, was previously tested under controlled conditions (HOWARI et al., 2000b, 2002; HOWARI et al., 2002). The purpose of the present study was to examine the factors controlling the distributions of the different types of salt crusts. This presents an opportunity to couple such hyperspectroscopic methods and databases with new airborne sensor technologies to deal with soil quality problems and enhance the quality of the soil mapping process.

2. SOIL CHARACTERSTCS
Salt crust samples were gathered from the upper 3–4 cm of the soil from the Rio Grande banks, three replicates were taken at each location for better representing the spatial variability of the samples from Hungary, specifically from the Carpathian Basin. They used a statistical approach in conjunction with a stepwise principal component band identification method to distinguish thirteen groups of soil salinity. They documented the significance of hyperspectroscopy techniques as a function of band width. The recognition accuracy decreased from 91 to 88% as the bandwidth decreased from 10–40 nanometers. The same study reported a positive correlation between the spectral pattern and the following parameters: clay fraction (0.85), organic matter (0.78), pH (0.75), salt fraction (0.73), and organic carbon (0.60).

Under field conditions, several factors affect the spectral profiles of salt crusts: the texture of the background soil, moisture content, and surficial contamination with other salts or minerals such as clay minerals or quartz. When an uncontaminated crust is developed as a result of evaporation of saline solutions, salt minerals with low solubility form first, and the surface of the crust is likely to be composed of salt minerals with the greatest solubility or in their sequence of their arrival at saturation (HOWARI, 2004). This hypothesis, solubility-controlled system, was previously tested under controlled conditions (HOWARI et al., 2000b, 2002; HOWARI et al., 2002). The purpose of the present study was to examine the factors controlling the distributions of the different types of salt crusts. This presents an opportunity to couple such hyperspectroscopic methods and databases with new airborne sensor technologies to deal with soil quality problems and enhance the quality of the soil mapping process.
sites in the vicinity of El Paso, Texas (Figure 1). Relative topographic slopes in the investigated area varied from 1.3 to 17.5%. The general geology of the studied area is shown in Figure 2. The soil is generally composed of arid, silty clay loam desert soils without definite horizons, and very low organic matter. Visual observations in the field showed spotty salt crusts present in many areas around the sampled locations. Some of the soils appeared leached and in the wetter areas, dark colored, cracked silty clay soils were present. Areas along the bank and bed consist of alluvial or valley bottom very fine sand silty clay loams. The land surrounding the Valley is mostly soils developed from surrounding igneous geology, and fine-grained alluvial materials of the Rio Grande sediment system, which include quartz and clay minerals.

The bedrock of the study area is largely composed of limestone and dolomite. Caliche is formed when ground water rich in dissolved calcium carbonate from these source rocks leaches up into the soil, then evaporates or retreats, leaving the calcium carbonate behind. Over time, these soils are weathered by wind and rain, some soil is removed leaving only the hard cement-like caliche behind. This is why it is sometimes referred to as hard pan, because of the hard-impenetrable surface of exposed caliche in the soil. The major soils are mostly deep, brown or gray alkaline clays and loams. Some are saline. Most of the soils are used for rangeland to support grazing. Other part, the soil is used to grow irrigated grain sorghums and vegetables are grown along the Rio Grande (Figures 1 and 2).

Figure 1. Location map of the study area.

Figure 2. Main geological features of the Rio Grande valley showing (after VIL-LARRREAL-FUENTES et al., 2016).

Figure 3. Salt crust as appear under optical microscope (A, and B; 100x) and under binocular microscope (C to G; 20x).
3. METHODOLOGY

Soil samples (n=25) beneath the crusts were selected randomly from a salinized flood plain area tested for salinity by measuring electrical conductivity (EC) of a saturation extract, through a saturated soil paste made by gently dripping deionized H$_2$O onto about 150 g of soil until the mixture became thick (e.g. WANG et al., 2018). The thick paste was left for 2 hours before it was filtered by suction. The EC was measured on the filtrate using an EC-meter and reported as dS/m. Measurement of soil moisture, and salt contents were determined by gravimetric methods. Clinometers were used to measure the gradient of the soil surface. The salt crusts were tested using microscopic techniques with a Nikon-Eclipse ME600L, and Olympus microscopes. Testing was accomplished under transmitted light at magnification up to 600 x for crystal characterization and to determine optical attributes. The salt crust was also investigated under cross polarized light for pleochroism, interference colors and birefringence of anisotropic crystals as well as under plane polarized light for crystal habit and relief.

Before taking the spectral reading, the water content in the soil samples was standardized by drying in an oven at 40°C for 24 hours to prevent chemical alteration and therefore changes in soil sample compositions. Soon after, the soil samples were inserted in a desiccator for at least 24 hours until the spectral readings were taken. The spectral reflectance reading from salt crusts was taken with a high-resolution spectroradiometer (MODEL GER 3700) in a wavelength range from 500 to 2500 nm. This treatment was performed on a fraction of the collected samples in order to identify the minerals, another spectral run were performed on the bulk samples to study the impact of moisture content on the reflectance signatures. However, before starting the spectral reading, the instrument was calibrated by fixing it on a stand to measure the reflectance of its special white calibration panel. More details on spectral measurements are reported in HOWARI et al. (2002).

The spectral profiles were studied by computerized peak picking techniques using a spectral software package (Specview). Comparison between the groups and subgroups of samples involved use of Analyses of Variance (ANOVA) One Way Layout
design. Principal Component Analyses (PCA) and the F-test using Excel and JMP/SAS software packages (SALL & ANN, 1996). Processed data were compared with the spectral data from NASA and USGS spectral libraries, and the spectral profiles and findings reported by CROWELY (1991), DRAKE (1995), and HOWARI et al. (2000 a, b and 2002). The data was firstly summarized and then the spectra were presented in terms of the mean plus and minus the standard deviation. Then the emphasis was placed on evaluating which factors govern the greater variability of reflectance and crust formation.

4. RESULTS AND DISCUSSION

Halite crusts have a glassy, transparent appearance with white to colorless, cubic to euhedral crystals (Fig. 3a). The surfaces of halite crusts were contaminated with quartz grains, and a clay-like surface cover (Fig. 3c). Gypsum crusts appeared as white, transparent to translucent, and had prism-like to monoclinical shapes, with earthy to vitreous lustre. Lamellae of successive zones of halite and gypsum crusts were observed in cross-sections prepared for crust collection (Fig. 3).

The shape of the spectral profile as well as the shape and location of the of the absorption band are significant in identifying and interpreting the spectral properties of salt crusts. The outlook of a spectral profile can be identified by the continuum slope and the intensity distribution, and the albedo. Although albedo is the main source of variability, absorption characteristics have an important role in relation to certain chemical properties. In the tested soil samples, the highest reflectance value ranged from 25% to 45% (Table 1). There are five regions of the mean spectra that demonstrate unique absorption properties and high differences among the tested soil spectra. These are located around 1000, 1400, 1900, 2200, 2300 nm (Fig. 4).

A crust with a certain grain size will have a particular reflectance, as when grain size changes, reflectance changes accordingly. It may increase or decreases as a function of the transparency and opacity of the material. Halite, which cannot induce absorption bands in the visible and near thermal infrared (HUNT et al., 1971 a, b; MOUGENOT et al., 1993) had visible absorption features due to moisture and fluid inclusions or due to contamination and was placed at 1500, 1884, and 2245 nm (Fig. 4).

The surface of halite crusts is contaminated with materials from the surrounding soils which have plenty of quartz grains, and clay minerals (Fig. 3). Quartz is translucent, therefore, when its proportion in the soil or soil crust increases, light will more easily be transmitted through the crust, strengthening the detected band strength of absorbance properties in the reflectance spectra of halite crusts contaminated with quartz. The study observed a minor absorption feature present at 2310 nm. Although not very visible, this absorption is related to the combination of -OH stretching mode with Mg-O-H bending mode, and it is present in triocahedral clays as described by PIETERS & ENGLERT (1993) and EL-RADAIDEH et al. (2017).

The spectra shown in Figure 3b had strong absorption features at 1024, 1226, 1780, and 2337 nm, and even stronger ones at 1458, 1866, and 1989 nm. Those absorption features are known for gypsum. In gypsum the overtones or combination tones from fundamental vibrations of the water molecules produced a series of bands affecting the infrared spectrum between 1000 and 2500 nm, e.g. 1464, 1550, 1750, 1978 and 2300 nm (CLARK, 1999 and HOWARI et al., 2002). These can be detected in the spectra of gypsum crusts (Fig. 4a). However, the most dominant absorption features occurred at 1464, 1750 and 1978 nm.

| Variable by Variable | Correlation Count Signif Prob |
|----------------------|-----------------------------|
| Reflectance Slope    | 0.1744 25 0.4044            |
| EC Slope             | 0.2735 25 0.1858            |
| EC Reflectance       | 0.3526 25 0.0839            |
| Moisture Slope       | -0.3827 25 0.0590           |
| Moisture Reflectance | -0.1709 25 0.4139           |
| Moisture EC          | -0.5094 25 0.0093           |
| Quantity Slope       | -0.2633 25 0.2035           |
| Quantity Reflectance | -0.2422 25 0.2434           |
| Quantity EC          | -0.1560 25 0.4564           |
| Quantity Moisture    | 0.3115 25 0.1296            |
| Quantity Slope       | -0.2633 25 0.2035           |
| Quantity Reflectance | -0.2422 25 0.2434           |
| Quantity EC          | -0.1560 25 0.4564           |
| Quantity Moisture    | 0.3115 25 0.1296            |
| Quantity g/cm²       | 1.0000 25 0.0000            |
Comparison of a group of variable differences obtained from gypsum and halite crusts is shown in Figure 5, and Table 2. A tool called a “diamond plot” was used to visualize the variability and results are shown in Figure 4. It condensed essential information, group means, grand sample mean (the horizontal line in Figure 5), confidence interval (CI), and raw data. A horizontal dotted line represents the grand sample mean. The diamond is the confidence interval for each group and the horizontal line within each diamond is the group means. The flatter the diamond, the tighter the CI. The groups of variables for halite concentrate...
Table 2. Descriptive statistics of the studied soil samples.

| Parameter         | Reflectivity (%) | Slope (%) | EC   | Salt Quantity (g/cm²) | Moisture (%) |
|-------------------|------------------|-----------|------|-----------------------|--------------|
| Minimum           | 25               | 1.32      | 6    | 1.36                  | 3.86         |
| Maximum           | 45               | 17.55     | 19   | 7.67                  | 11.86        |
| Mean              | 32.91            | 3.61      | 13.36| 7.03                  | 7.03         |
| Standard error    | 0.8663           | 0.72      | 0.82 | 0.38                  | 0.39         |
| Median            | 32.5             | 2.13      | 14.4 | 3.97                  | 6.63         |
| Standard deviation| 4.23             | 3.56      | 4.06 | 1.89                  | 1.93         |
| Sample variance   | 17.9             | 13.68     | 16.5 | 3.58                  | 3.75         |

Figure 8. Ratio of the surface slope and reflectivity to other soil characteristics.

Table 3. Principal component analyses among the studied variables.

| Principal Components | PC1   | PC2   | PC3   | PC4   | PC5   |
|----------------------|-------|-------|-------|-------|-------|
| EigenValue           | 2.6656| 1.3282| 0.892 | 0.7005| 0.4137|
| Percent              | 44.4272| 22.1362| 14.8662| 11.6751| 6.8954|
| CumPercent           | 44.4272| 66.5633| 81.4295| 93.1046| 100   |
| Slope                | -0.34024| 0.24565| -0.45603| 0.77205| 0.14093|
| Reflectance          | -0.2967| 0.21914| 0.8078 | 0.33429| -0.31568|
| EC                   | -0.33737| 0.55637| 0.13165| -0.3669| 0.65168|
| Moisture             | 0.4026 | -0.36501| 0.34914| 0.37881| 0.66279|
| Quantity             | 0.51005| 0.47374| -0.0114| 0.0839 | -0.09087|

5. CONCLUSION

Although different interlinked factors were found to affect the reflectivity of gypsum and halite, their spectra remained recognizable. The reflectivity of salt crusts varied according to changes in moisture content, and the salinity of the soil drastically reduced the reflection much more than other factors. Halite occurred at high soil slope value than gypsum; however, positive correlation
between the slope and reflectivity of both salt crusts was reported. It was difficult to assess the order of factors controlling the reflectivity and formation of salt crusts and their alternation in the following suggesting orders, for halite: salt quantity > slope > moisture content; and for gypsum: moisture content > salt quantity > slope. The present results are encouraging for assessing the type of salt crust by estimating the ratio of slope and reflectivity to the other variables.

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