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# Measuring soluble salts in soils via portable x-ray fluorescence spectrometry

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MEASURING SOLUBLE SALTS IN SOILS VIA PORTABLE X-RAY
FLUORESCENCE SPECTROMETRY

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The School of Plant, Environmental, and Soil Sciences

by
Samantha Lynn Swanhart
B.S., University of Florida, 2012
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"I can do all things through Christ who strengthens me." Philippians 4:13

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# ABSTRACT

For certain soil salinity characteristics, it would be desirable to know the individual concentrations of the major solutes in the soil water over the range of water contents that occur in the field and to obtain this information in the field, without the taking of soil samples and the carrying out of laboratory analyses. No practical methods are available at present to permit such detailed determinations….
–J.D. Rhoades, U.S. Salinity Laboratory, Riverside, California

Soil scientists have been using the same quantification methods for soluble salts for decades. Yet they have long struggled with an effective method for quantifying gypsum content, because current methods are fraught with problems. Saline soil has been historically defined as soil containing salts more soluble than gypsum (e.g., various combinations of $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $K^+$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$ and $CO_3^{2-}$) to the extent that soil fertility is severely reduced across a wide array of climates and geological settings. Since salinity is not germane to specific soil characteristics such as texture or parent material, it can be challenging to predict salt concentrations within a profile. Given the success of previous studies using portable x-ray fluorescence (PXRF) as a tool for measuring soil characteristics, the evaluation of soluble salts in soil with PXRF seems timely. Not only does this newer technology offer more accurate, quantifiable data to investigators, it produces results in-situ, in seconds. Recent enhancements to PXRF spectrometers have provided better detection limits especially for lighter elements such as S and Cl, a key component of gypsum and other salts. Thus, this research aimed to test the effectiveness of PXRF as a means of directly quantifying gypsum and salinity in soils. A total of 102 soil samples containing a wide variety of gypsum (~2–95%) and 122 samples with various salt concentrations were subjected to both traditional laboratory analysis (thermogravimetry and electrical conductivity, respectively) and elemental analysis via PXRF. Simple and multiple linear regression were used to establish the relationship between the two datasets. Log transformation of some datasets was necessary to normalize the data. Using simple linear

regression between laboratory and PXRF data, an $R^2$ of 0.88 was produced for the gypsum data, and an $R^2$ of 0.839 was produced for salinity data. Similarly, simple linear regression for laboratory-quantified gypsum vs. PXRF S produced an $R^2$ of 0.91. Multiple linear regression of laboratory quantified gypsum vs. both PXRF S and Ca produced an $R^2$ of 0.91, and 0.8669 for laboratory determined EC (dS m$^{-1}$) vs. PXRF Cl, S, Ca, and K. No significant differences were observed between model generation and validation datasets. Overall, PXRF shows great promise for the direct quantification of soluble salts in soils.

# CHAPTER 1: INTRODUCTION

## Soluble Salts: Gypsum and Salinity

Gypsiferous soils can contain both gypsum ($CaSO_4 \cdot 2H_2O$) as well as anhydrite compounds containing Ca. The interest of studying gypsum in semiarid regions is due to its solubility (Porta, 1988). With relatively little to no rainfall in these regions, gypsum can be dissolved and its ions translocated within the soil profile. Pervasive secondary accumulations of Ca in soils can occur as gypsum precipitates in the substratum or is inherited from parent materials (Figure 1.1) (Soil Survey Staff, 1993). Field identification of gypsum is possible, but must be undertaken carefully so as not to confuse gypsum with other salts. Gypsum can have several morphological expressions from transparent/translucent blocks or lenticular spires/platelets to white sand-sized soil deeper in the profile (Figure 1.2).



Figure 1.1. Highly gypsic in West Texas (Photo: Weindorf).
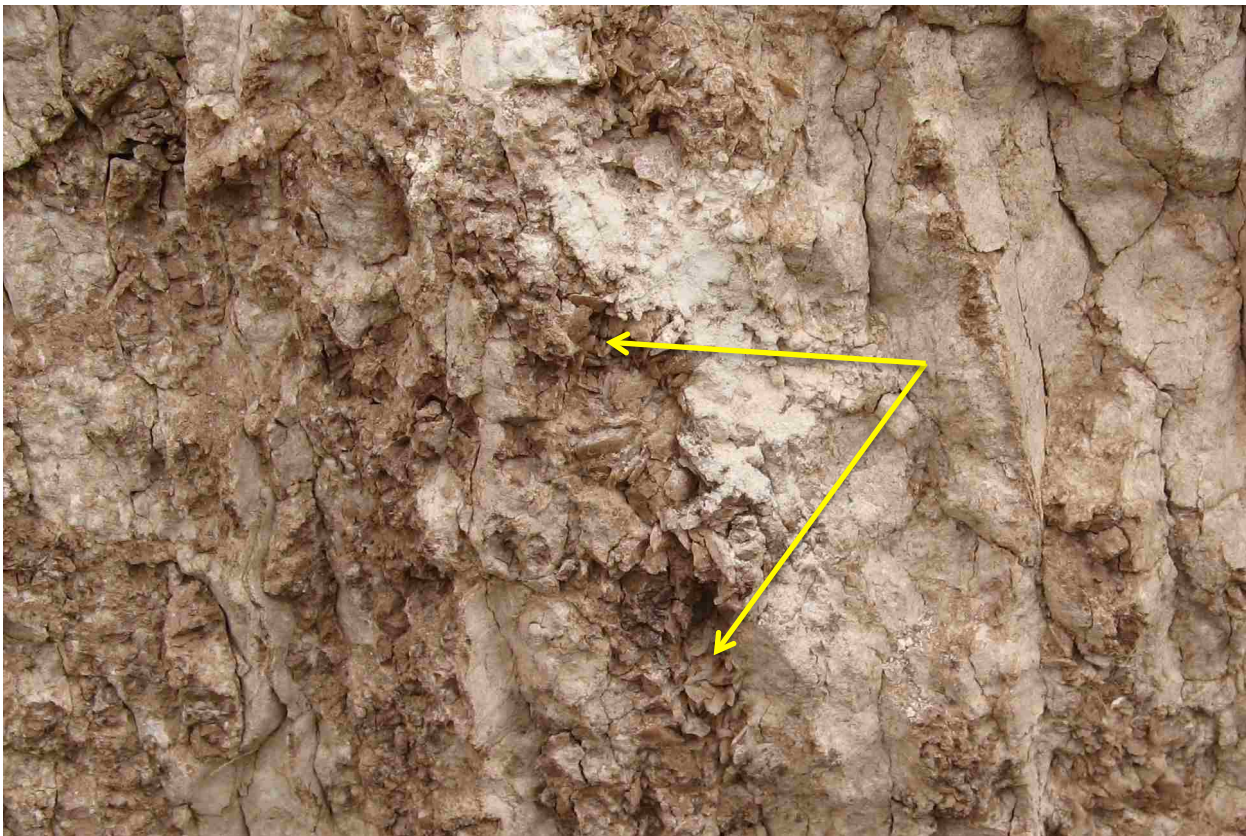
Figure 1.2. Lenticular gypsum in a soil profile from West Texas (Photo: Weindorf).

The term 'salinity' more generally describes the presence of dissolved soluble salts (e.g., various combinations of $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $K^+$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$ and $CO_3^{2-}$) in soil to the extent that soil fertility is severely reduced, including naturally occurring salt weathered from primary materials from the earth's crust, coastal regions with influence from ocean currents and tides, arid to semi-arid regions, or others of anthropogenic origin (Wang et al., 2007; Benito et al., 1995; Merrill et al., 1980; Hao and Chang, 2003; Saadi et al., 2007). Salt accumulation disturbs the normal metabolism, water quality, and nutrient uptake for plants and biota (Qadir and Oster, 2004). Salt affected soils have lower osmotic potential for plants to absorb water, causing the protoplasmic lining in plants to shrink; an action termed plasmolysis (Liu and Hellebust, 1976; Gardolinski et al., 2003; Childs and Hanks, 1975; Hasagawa et al., 2000). Accumulation of soluble salts in soils can occur across a wide variety of climate and geological settings, even impacting irrigated land used for agronomic production. Saline conditions are primarily found in

semiarid to arid regions; however, they can occur in humid regions. For example, soils in coastal areas can be subjected to sea water from storm surges (Salinity Staff, 1954). In arid regions, the rate of evaporation exceeds annual rainfall (300-350 mm $y^{-1}$) and further concentrates salts in soils and surface water. In Louisiana, the humid climate and excessive rainfall (>170 cm $y^{-1}$) from extreme weather patterns have impacted the coastal region in the Mississippi River delta. The majority of coastal Louisiana is below sea level (maximum 2.5 m), accelerating the rate of saltwater intrusion from the Gulf of Mexico.

**Gypsum Quantification**

A study by Porta (1998) reviews methodologies and techniques of characterizing gypsum in soils, each with limitations. In the field, it is only possible to detect gypsum by identifying $SO_4^{2-}$ ions using $1M$ $BaCl_2$ to a mixture of soil and water, and observing turbidity. The $Ba^{2+}$ ion replace $Ca^{2+}$ ions in the gypsum structure which becomes insoluble and causes the turbidity. For further investigation, samples can be subjected to laboratory analysis. However, when gypsiferous soil is heated to 105°C, part of the crystal water of gypsum ($CaSO_4 \cdot 2H_2O$) is lost, which is 20.91% of its weight, and can result in false quantification. To prevent this loss, samples should not be heated to more than 50°C. Alternately, a method that does not require drying the samples may be utilized (Artieda et al., 2006). When all the gypsum of a sample has been dissolved, it is possible to calculate both $SO_4^{2-}$ and $Ca^{2+}$ simultaneously. However, interference often comes from other sources of $Ca^{2+}$ not associated with gypsum (e.g., calcium carbonate). After dissolving gypsum in water, it is possible to precipitate a fraction of the gypsum, specifically the $Ca^{2+}$ ions, by adding acetone. A hot dissolution of gypsum in concentrated HCl will precipitate the $SO_4^{2-}$ ions, even if the sample is coated by $CaCO_3$. There are more sensitive methods for determining $SO_4^{2-}$ ions in gypsum, but they require lengthy

analysis by determining organic and inorganic forms of S, and multiple extractions to calculate a difference. A rapid conductance method precipitates the Ca specifically within $CaCO_3$ by adding acetone. The Ca precipitate is dissolved in water, and measured by electrical conductivity (EC) meter. The EC of $CaSO_4$ is 2.2 dS m$^{-1}$, when in a saturated aqueous solution. In salt-affected soils, a commonality in semiarid regions, there can be interference from various salts in electroconductometric measurements as salts often co-precipitate in various forms. Porta (1998) also examined an x-ray diffraction technique for qualitative identification of bulk mineralogy. This method requires multiple replicates and is substandard for quantitative determination because of the orientation of gypsum crystallites. For this research, the samples had relatively high gypsum contents (Appendix A). Thus, gypsum was quantified using thermogravimetric analysis (Artieda et al., 2006) (Appendix A). This method is based on the loss of weight when a sample is heated, due to dehydration of gypsum.

**Electrical Conductivity (EC)**

A variety of indicators exist for locating areas of high salt accumulation in soils. When water from the soil profile starts to evaporate, the dissolved salts are carried to the soil surface and deposited, leaving a visible salt crust on the surface (Figure 1.3). This salt crust can readily dissolve during episodes of rainfall or irrigation, subsequently infiltrating again into the rooting zone of plants. Vegetative communities are highly impacted in saline systems. Wilting or entire plant mortality is common in species unable to survive in such harsh conditions. Traditional methods of measuring salinity have used electrical conductance measurements to estimate total soluble salts in soils. The probe passes electrical currents through the soil/soil solution to quantify the conductance. This technique is termed 'electrical conductivity' (EC), and is used in the laboratory to determine soil salinity (Rhoades et al., 1987; Corwin and Lesch, 2001). Soil

Figure 1.3. Salt crusts and halophytic vegetation in coastal Louisiana soils.

samples are ground and mixed with distilled water to form a *saturated paste*, then allowed 24 h to equilibrate. While it is desirable to measure the soil saturation extract to measure the conductance of only the salt dissolved in water, there is a dilution effect with certain textures. Finer textures or organic materials have a much higher saturation percentage than coarser textures, which can give a false reading of true conductance. When prepared properly, electrical conductance in soil/soil solution shows a strong relationship to the amount of salts more soluble than gypsum, which readily dissolve in water. However, EC does not provide any information on the type of salts present.

**Portable X-ray Fluorescence Spectrometry**

Recently, the use of portable X-ray fluorescence (PXRF) spectrometry has been shown effective at quantifying a number of elemental concentrations in soils via a non-invasive and non-destructive scanning in situ. Previous studies using PXRF to determine soil characteristics include soil texture (Zhu et al., 2001), gypsum quantification (Weindorf et al., 2009, 2013),

heavy metal pollution (Weindorf et al., 2013, Clark et. al., 1999) and elemental analysis in

compost (McWhirt et al., 2012).

When a beam of x-rays strike matter, the energy produced ejects electrons from the inner

levels of the atoms of the targeted material (Jones, 1982). Next, outer shell electrons quickly

replace the voids in the inner shells, but in order to do so, they must release energy, termed

*fluorescence*. The fluorescent energy released is specific to each element. While previous

experiments have been successful in determining certain soil characteristics, the instrument does

have limitations. The instrument is not able to detect compounds present in the sample, only

individual elements (e.g., $K^+$ and $Cl^-$ are quantified separately, not KCl). The instrument is

unable to quantify elements with an atomic weight lighter than Mg, given their stable electron

shells and small fluorescent energy release. Zhu et al. (2011) examined moisture interferences

with the instrument, and confirmed moisture contents >20% can denude PXRF elemental

accuracy. Homogeneity of samples is also important to alleviate any matrix interferences within

the sample. Such limitations can often be overcome with standard laboratory preparation such as

air-drying samples and grinding them to pass a 2mm sieve.

**Method Development**

Dr. Juan Herrero of the Estacion Experimental de Aula Dei, Consejo Superior de

Investigaciones Cientificas used the thermogravimetric method for gypsum quantification, and

HCl digestion for total Ca concentrations (Appendix A). These methods were compared to

prediction models from PXRF (Appendix A). Weindorf et al. (2009) completed a preliminary

study using PXRF to predict gypsum concentrations in soil. The PXRF used (Innov-X PXRF

Alpha) in their study featured a Si-PIN diode detector with limited S detection. Thus, Ca was

used as a proxy for gypsum content. The newer PXRF (Olympus/Innov-X Delta PXRF) used in

the present study has much greater sensitivity for S; a result of the newly integrated silicon drift detector (Appendix A). Simple and multiple linear regression models were used to compare the laboratory methods of quantifying Ca and gypsum with PXRF Ca and S as a proxy for direct soil quantification of gypsum *in situ* (Appendix A).

This research examines PXRF's ability to determine specific salt concentrations regardless of other physicochemical interferences often included with conductance. While EC is an accurate method, which has been used for decades, its inability to detect elements present can be overcome with use of PXRF. One key limitation of PXRF is that it cannot presently detect Na; a key constituent of NaCl, a common salt. Consequently, the salinity models developed used Cl concentration as a proxy to measure salinity concentrations *in situ*. Simple and multiple linear regression models compared EC values to PXRF concentrations of common salt ions, specifically Cl, S, K, and Ca.

**The Future of Soil Testing**

Field pedologists currently use rudimentary testing (e.g., acid effervescence, slake testing, colorimetric tests for qualitative nutrient value) to make simple determinations of soil properties. Many determinations are based primarily on field observations combined with ancillary information such as climate, vegetation, and topography. Yet the future of classifying and mapping soils include evolutionary improvements in technology and available data. Where surveyors once relied on paper maps and a compass, contemporary surveyors utilize geographic information systems (GIS), the global positioning system (GPS), and remotely sensed data (via satellites or aerial views) to improve the consistency and accuracy of mapping soils. Thus, the enhancement of older, simplistic techniques such as EC determination of soluble salts with newer, advanced technologies such as PXRF spectrometry seems timely. Not only do such newer

technologies offer more accurate, quantifiable data to investigators, they produce results in-situ, in seconds.

The objectives of this research were to: 1) collect samples containing gypsum and salts more soluble than gypsum, 2) quantify concentrations of soluble salts and gypsum using traditional laboratory methods, 3) use PXRF to quantify elemental concentrations in the collected samples, and 4) compare results of both methods using regression models to determine if PXRF can be used as a tool for in situ measurement of soluble salts and/or gypsum.

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# CHAPTER 2: MEASURING SOIL SALINITY VIA PORTABLE X-RAY FLUORESCENCE SPECTROMETRY

**Abstract**

Saline soil has historically been defined as a soil containing salts more soluble than gypsum (e.g., various combinations of $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $K^+$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$ and $CO_3^{2-}$) to the extent that soil fertility is severely reduced across a wide array of climates and geological settings. Thus, it is not related to specific soil characteristics, such as texture or parent material. As technology has advanced, so has soil testing and evaluation for optimal soil characterization. Traditional methods of measuring soil salinity, while accurate, are labor intensive and require laboratory analysis. Given the success of previous studies using PXRF as a tool for measuring soil characteristics, the evaluation of soil salinity with PXRF spectrometry is worth examination. Not only does this newer offer more accurate, quantifiable data to investigators, it produces results in-situ, in seconds. For this study, 122 soil samples were collected from salt impacted soils of coastal Louisiana, USA. Samples were collected from the soil surface (0-15 cm), sealed in plastic bags, and returned to Louisiana State University for laboratory analysis. Standard soil characterization included loss on ignition (LOI) organic matter, particle size analysis, electrical conductivity, and elemental quantification via PXRF. Regression models were developed to correlate elemental concentrations from PXRF to EC results using statistical analysis software (SAS Institute, 2011). Both simple and multiple linear regressions were employed in this study. In order to meet the assumptions for simple and multiple linear regressions, logarithmic transformation was used to normalize the variables to obtain a normal distribution for the error term (residual, $e_i$). While both models resulted in similar acceptable $R^2$ (0.839, and 0.8669, respectively), simple linear regression is recommended per the law of parsimony.

**Introduction**

<u>Soil Salinity</u>

Saline soil is defined as a soil containing salts more soluble than gypsum (e.g., various combinations of $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $K^+$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$ and $CO_3^{2-}$) to the extent that soil fertility is severely reduced (US Soil Salinity Laboratory Staff, 1954). Globally, >20% of irrigated land has been negatively impacted by salinization. Salinity effectively lowers the osmotic potential of water, making it difficult for plants to absorb or causes the protoplasmic lining of cells to shrink; an action called plasmolysis (Childs and Hanks, 1975; Hasagawa et al., 2000; Liu and Hellebust, 1976; Gardolinski et al., 2003; Qadir and Oster, 2004).

Soil salinity can appear across a wide range of climates and geological settings. Thus, it is not related to specific soil characteristics, such as texture or parent material (Caballero et al., 2001; Biggs and Jiang, 2009; Zeng and Shannon, 2000). Saline conditions in soil can occur in areas at or near coastal regions, arid to semi-arid regions where evaporation exceeds precipitation, and in areas of anthropogenic impact (e.g., oil production wells pumping brine to the surface where it is contained within artificial ponds; Figure 2.1) (Wang et al., 2007; Benito et al., 1995; Merrill et al., 1980; Hao and Chang, 2003; Saadi et al., 2007). In areas of pervasive salinity, native vegetative species have been replaced by salt-tolerant halophytes (Figure 2.2).



Figure 2.1. Salt-impacted soil at an old petroleum production site in Southern Louisiana (Photo: Weindorf).

Figure 2.2. Salt-affected organic marshland with halophytes in Grand Isle, Louisiana.

Land management practices have sought to maintain soil productivity through evaluation of morphological, physical, chemical, and biological soil properties; often used as differentia for evaluating the overall quality of soils (e.g., one soil series to another or even within a given profile) (Hudson, 1991; McBratney et al., 2000; Wilson et al., 2008; Bouma et al., 2007). As technology has advanced, so has testing and evaluation for optimal soil characterization (Soil Survey Staff, 1993). Traditional methods of measuring soil characteristics, while accurate, often require laboratory analysis and are labor intensive.

Electrical Conductivity

Older methods of measuring salinity in soil utilized an electrode probe (e.g., Solubridge), which passed electrical currents through the soil/soil solution to measure electrical conductivity through the solution. Higher salt concentrations were found to generally be proportional to electrical conductance. Hence, the term 'electrical conductivity' (EC) and became synonymous with soil salinity quantification (Rhoades et al., 1987; Corwin and Lesch, 2001). To facilitate

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complete salt dissolution, soil samples are ground and mixed with distilled water to form a

saturated paste, then allowed equilibrate for 24 h (US Soil Salinity Laboratory Staff, 1954).

Uniform preparation of the saturated paste is critical. However, the amount of water required to

saturate the soil varies considerably with soil texture (e.g., sands require less water than clays to

reach saturation). Adding too much water could cause a dilution effect and render atypically low

EC values (Hogg and Henry, 1984; Sudduth et al., 2005; Saxton and Rawls, 2006). Thus, the

consistent preparation of the soil paste requires considerable skill. Rhoades et al. (1989) explored

the effect of soil-water slurry dilutions (e.g., 1:1, 1:2, or 1:5 v/v) using the aforementioned probe,

and found that larger volumes of water resulted in lower EC values. While the established EC

techniques have been widely used for a number of years, they are not able to differentiate

specific elements associated with salinity.

In coastal Louisiana, salt accumulation in tidal marsh soils are highest where inputs (tide)

and output (drainage and diffusion) begin to balance, or when high and low tides occur in

proximity to each other or frequently. Seawater is rife with dissolved salts, many of which are

comprised of the anion Cl including $NaCl$, $MgCl_2$, and $CaCl_2$. Chloride is an essential plant

nutrient, and is highly soluble and leachable in a soil profile (Frankenberger et al., 1996).

Chloride's solubility and variability in concentration (few to several hundred milligrams per

kilogram) within a soil profile makes it an accurate tracer for salt and water movement.

Portable X-ray Fluorescence Spectrometry

Recently, portable X-ray fluorescence (PXRF) spectrometry has been shown effective at

quantifying elemental concentrations to determine soil characteristics, including soil texture (Zhu

et al., 2001), pedon horizonation (Weindorf et al., 2011) and gypsum content (Weindorf et al.,

2009, Weindorf et al., 2013). X-ray fluorescence is a technique utilizing X-rays generated from a

Ta/Au (or other) X-ray tube, which strike the soil. When x-rays strike matter, it causes inner shell electrons to be ejected (Jones, 1982). Subsequently, outer shell electrons cascade down to fill the inner electron shell void. In doing so, they must relinquish energy which is emitted as fluorescence. The wavelength of emitted radiation is specific to each element, while the intensity quantifies to elemental abundance. Piorek et al. (1998) outline techniques to decrease the counting error including sample homogenization, multiple scans per sample, and increasing x-ray beam exposure time to ensure an optimal quantification of x-ray photons (e.g., shorter measurements (<60 s for initial screening of specific elemental detection, or longer measurements (up to 300 s) for a precise and accurate measurement). Given the success of previous studies using PXRF as a tool for measuring soil characteristics, the evaluation of soil salinity with PXRF spectrometry seems timely. Not only does PXRF offer accurate, quantifiable data to investigators, it does so in-situ, in seconds.

Field pedologists currently use rudimentary testing (e.g., acid effervescence, slake testing, colorimetric tests for qualitative nutrient value) and field observations (climate, vegetation, topography) to make determinations of soil properties. Yet the future of classifying and mapping soils must embrace evolutionary improvements in technology and available data. Where surveyors once relied on paper maps and a compass, contemporary surveyors utilize geographic information systems (GIS), the global positioning system (GPS), and remotely sensed data (via satellites or aerial views) to improve the consistency and accuracy of mapping soils. Thus, the enhancement of older, simplistic techniques such as electrical conductivity determination of soluble salts with newer, advanced technologies such as PXRF is beneficial.

The objectives of this research were to: 1) collect salt-impacted soil samples from areas of coastal Louisiana, 2) examine soil salinity properties through traditional laboratory methods

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and PXRF, and 3) determine the relationship between soluble elements and their electrical conductivity. If PXRF proves a reliable method for quantification and differentiation of salts in soils, it could be used to quickly assess salinity in various regions worldwide.

**Materials and Methods**

Soil Sampling

A total of 122 samples were collected in Jefferson, Plaquemine, and Cameron Parishes to represent Louisiana's organic and mineral marshland in 2012 and 2013. Soil series collected included: Scatlake (Very-fine, smectitic, nonacid, hyperthermic Sodic Hydraquent), Felicity (Mixed, hyperthermic Aquic Udipsamment), Hackberry (Sandy, mixed, hyperthermic Aeric Endoaquepts), Peveto (Mixed, thermic Typic Udipsamments), Creole (Fine, smectitic, nonacid, hyperthermic Typic Hydraquents), Convent (Coarse-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts), and Commerce (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts) (Soil Survey Staff, 1995; Soil Survey Staff, 1983; Soil Survey Staff, 2000). Samples were collected from the surface (0-15 cm), sealed in plastic bags, and returned to Louisiana State University for laboratory analysis.

Standard Laboratory Testing

Samples were air-dried and passed through a 2 mm sieve prior to additional analysis. Standard soil characterization included loss on ignition (LOI) organic matter, particle size analysis, electrical conductivity, and elemental quantification. Soils featuring appreciable organic contents were tested first, then thoroughly oxidized with $H_2O_2$ prior to conducting particle size analysis. Particle size analysis was via the pipette method per Gee and Bauder (1986). Sands were determined via wet sieving with a 53 $\mu$m sieve. Loss on ignition (LOI) organic matter was determined per Ben-Dor and Banin (1989). Samples were combusted for 8-16 h at 400°C such

that maximum weight loss (ashing) of all organic matter occurred with minimal dehydroxylation of clay minerals (Ben-Dor and Banin, 1989). Soil electrical conductivity (EC) was determined for each sample via saturated paste. Deionized water was added to approximately 20-30 g of soil until it reached complete saturation (US Salinity Laboratory Staff, 1954). Samples were allowed to equilibrate for 24 h. A model 4063CC digital salinity bridge (Traceable Calibration Control Company, Friendswood, TX) was then inserted to the sample and allowed to equilibrate for 60-90 s before a conductivity reading was made and reported in dS m$^{-1}$.

Portable X-ray Fluorescence Spectrometry

A Delta Premium portable x-ray fluorescence spectrometer (Olympus Innov-X, Woburn, MA) was used to facilitate total elemental characterization. Samples were subjected to PXRF scanning both in-situ and in the laboratory; the former for initial screening to ensure saline soil conditions, and the latter for the development of regression models for this research. The PXRF features a Ta/Au x-ray tube operated at 10-40 kV and a 2 cm aperture for sample scanning. Prior to scanning, the instrument was calibrated with a "316" metal alloy clip, tightly secured to the aperture. The PXRF was operated in a proprietary configuration known as *soil mode* with the light elements analysis program (LEAP) engaged. Optimal Cl quantification (the element of interest for a large portion of the current study) was enhanced by longer scanning time and averages of multiple scans. The Delta PXRF uses three beam sequential scanning for elemental analysis. For this study, each beam was set to scan for 30 s. Thus, one complete scan took 90 s. The instrument was then repositioned and the sample scanned a second time such that an average between scans was obtained.

A few sources of error must also be considered with PXRF: 1) moisture, 2) sample homogeneity, and 3) inter-elemental interferences. Zhu et al. (2011) noted that excessive (>20%)

soil moisture degraded the accuracy of PXRF data. Specifically, when only dry sample scans were considered, the correlation between PXRF readings and laboratory measurements improved substantially. Another disadvantage of in-situ measurements is the degree of uncertainty caused by sample heterogeneity (Argyraki et al., 1997; Zhu et al., 2011). Jones (1982) noted that sample homogeneity is promoted when soils are dried and ground to pass a 2mm sieve; practices followed as part of this study. Finally, with respect to salinity assessment, current PXRF equipment not able to quantify Na, given it small, stable electron cloud. Nonetheless, many Na based salts associate with Cl, which can accurately be quantified by PXRF.

Statistical Analysis

Regression models were developed to correlate PXRF elemental concentrations with EC results using statistical analysis software (SAS Institute, 2011). Both simple and multiple linear regressions were employed in this study. In order to meet assumptions for simple and multiple linear regressions, logarithmic transformation was used to normalize the variables to obtain a normal distribution for the error term (residual, $e_i$). To normalize the data, the command term "LOG" was used with each variable to validate the regression models. PROC REG was used for regression analysis based on the method of least squares, and is capable of tests of linear hypothesis, producing co-linearity diagnostics, residuals, and predicated values among other output statistics (Cody and Smith, 2006). PROC UNIVARIATE was used to test the performance of the regression. Variables included in regression analysis included results from various physiochemical analysis results, including particle size, organic matter, elemental concentration via PXRF, and EC. All statistical analyses were conducted at a significance level of $\alpha=0.05$. Regression models were validated by randomly selecting 22 (~20%) of the total (122) scanned soil samples. Different statistical analyses were applied to quantify significant

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differences and the correlation between laboratory measured values and predicted values from the regression models for Cl and salinity. Tukey's test was used to identify significant differences of least squares means between the two datasets. The *null* hypothesis for the validation analysis was "there are no significant differences between the measured observations and the predictions from each model."

**Results and Discussions**

Elemental concentrations of Cl, S, K, and Ca were determined via PXRF and used to predict EC values. In addition to overall models inclusive of all samples, additional models were parsed based on specific physicochemical properties per characteristics outlined in the Soil Survey Manual (Soil Survey Staff, 1993) such as sand percentage, clay percentage, and organic matter.

<u>Simple Linear Regression</u>

Saline soils were split into 5 classes based on their respective EC value: Class 0, Non saline (0-2 dS m$^{-1}$), Class 1, Very slightly saline (2-4 dS m$^{-1}$), Class 2, Slightly saline (4-8 dS m$^{-1}$), Class 3, Moderately saline (8-16 dS m$^{-1}$), and Class 4, Strongly saline (>16 dS m$^{-1}$). Table 2.1 describes the average EC and Cl concentration from experimental analysis. To determine the validity of the model, residual normality was tested. For the prediction model of EC based on PXRF Cl readings, the residual term for simple linear regression was not normally distributed ($P > 0.05$). In order to obtain normal distribution, a log-transformation was applied to normalize the error term (Weindorf et al., 2013). For consistency, log-transformation was applied to both the Y (EC) and X (PXRF Cl) variables. Samples with EC >2 dS m$^{-1}$ had Cl concentrations ranging 701-23,142 mg kg$^{-1}$ (0.07-2.30% Cl). Samples with EC of 0-2 dS m$^{-1}$ averaged Cl concentrations of 0.39 mg kg$^{-1}$ (0.000039 % Cl). As the latter class was below the detection limit for PXRF (60-

100 mg kg^{-1}), those samples were excluded from simple linear regression analysis (excluded

samples n=33) (Papachristadoulou et al., 2006). Furthermore, EC values in the range of 0-2 dS

m[-1] are not considered saline (Soil Survey Staff, 1993; Hoppin et al., 1995). In Figure 2.3, the

PXRF Ln Cl concentrations were compared with Ln EC readings based on the constructed

models. The residual normality test for the log-transformed data passed ($P > 0.05$) (Table 2.2).

Table 2.1. Average Cl concentrations and EC (dS m^{-1}) for all samples (n=122) from Louisiana,
USA.

| Salinity Class | EC range (dS m^{-1}) | Avg. EC (dS m^{-1}) | Avg. Cl (mg kg^{-1}) |
| --- | --- | --- | --- |
| 0 | 0-2 | 0.39 | 36.09 |
| 1 | 2-4 | 3.05 | 804.19 |
| 2 | 4-8 | 6.24 | 1265.64 |
| 3 | 8-16 | 11.08 | 2362.16 |
| 4 | >16 | 37.52 | 6676.92 |
| Total | 0≥16 | 13.92 | 2564.24 |

With all samples in the modeling dataset considered (n=67), each model's validity was

determined by residual normality after log transformation. The correlation between Ln Cl and Ln

EC was 0.8397 (n=67) (Figure 2.3 (a)). The validation dataset (n=22) showed different trends

with $R^2$ between Ln Cl and Ln EC of 0.7688 (Figure 2.3 (b)). Finally, the validation data (n=22)

was applied to the developed modeling equation to test its predictive accuracy against actual lab

quantified EC. The correlation coefficient ("R") showed a strong relationship with lab measured

EC and predicted EC from simple linear regressions (R=0.827).

a) SLR Ln EC and Ln Cl
n=67

R² = 0.83969

b) SLR Ln EC and Ln Cl
n=22

R² = 0.76877
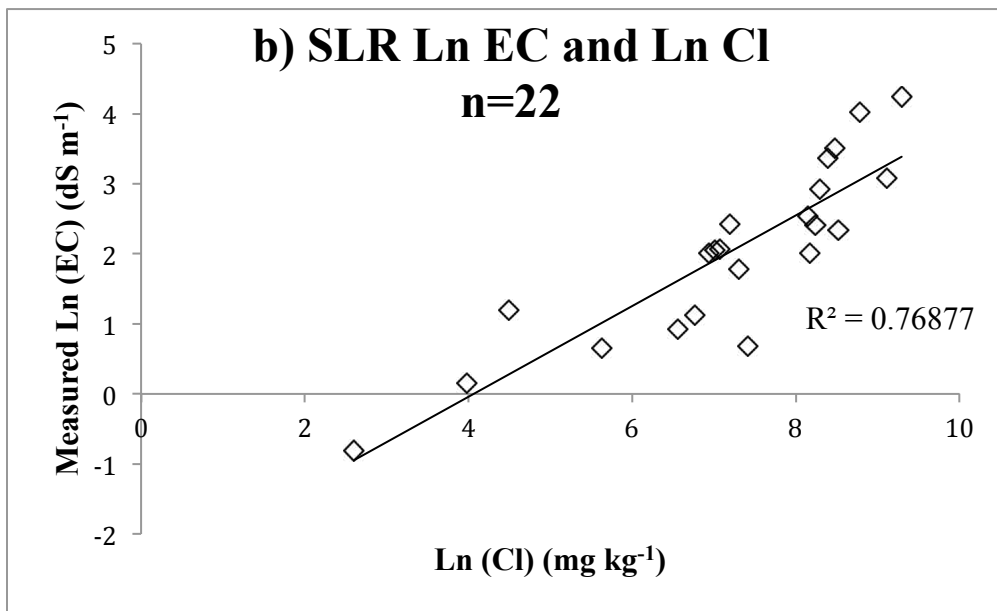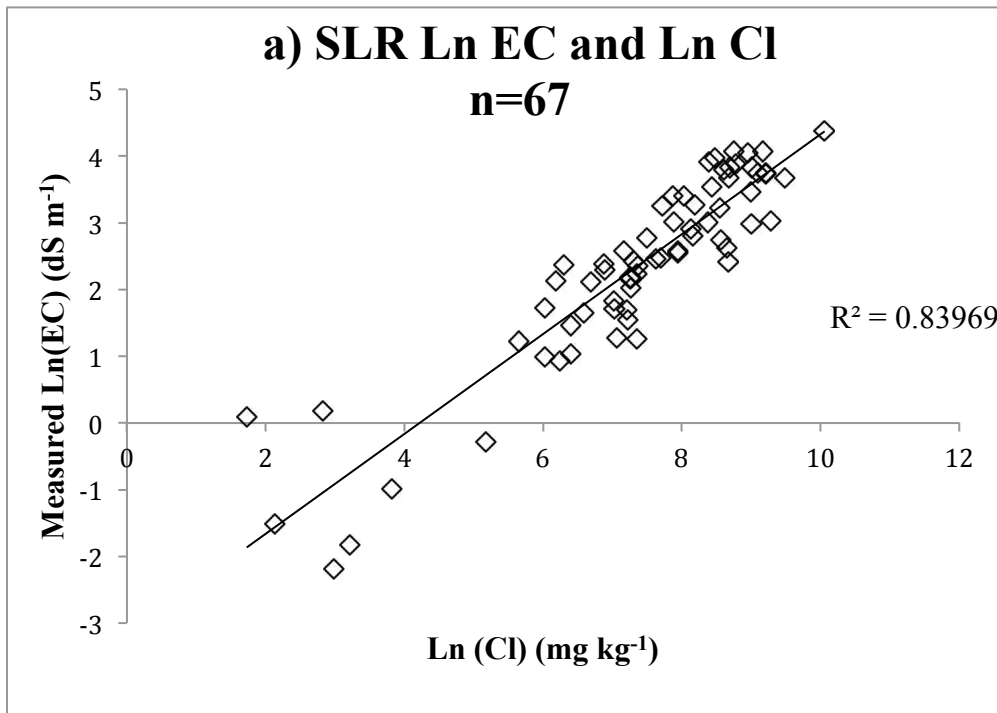
Figure 2.3. a. Simple linear regression between Ln EC and Ln Cl via portable X-ray fluorescence (PXRF) with 95% confidence for modeling data(n=67) b. Simple linear regression between Ln EC and Ln Cl via PXRF with 95% confidence for validation data (n=22) with saline soils in Louisiana, USA.

Table 2.2. Parameters of fitting lines between PXRF Cl and EC (dS m$^{-1}$), and PXRF Cl, S, K, Ca and EC (dS m$^{-1}$) under different linear regression models for soil samples from Louisiana, USA.

| SLR and MLR Models | Model Parameter | Untransformed Variables | Log transformed X and Y variable |
|---|---|---|---|
| SLR Cl and EC | Intercept | 2.761 | -3.305 |
| | Slope | 0.0041 | 0.755 |
| | $R^2$ | 0.731 | 0.839 |
| | RMSE (Antilog) | 9.524 (-) | 0.5691 (1.766) |
| | Normality test[ǂ] (p) | Failed (<0.0001) | Passed (0.5867) |
| | Significance[ψ] (p) | Passed (<0.0001) | Passed (<0.0001) |
| MLR Cl, S, K, Ca and EC | Intercept | -0.72509 | -3.651 |
| | Slope (Cl) | 0.00424 | 0.6759 |
| | Slope (S) | -0.00126 | -0.0859 |
| | Slope (K) | 0.000794 | 0.1646 |
| | Slope (Ca) | -0.00001014 | -0.0054 |
| | $R^2$ | 0.758 | 0.8669 |
| | RMSE (Antilog) | 9.165 (-) | 0.6692 (2.012) |
| | Normality test[ǂ] (p) | Failed (<0.0001) | Passed (0.4884) |
| | Significance | Passed (<0.0001) | Passed (<0.0001) |

[ǂ]= The normality test for the error term or residual ($e_i$) was achieved based on the Shapiro–Wilk test in which the *p* value should be greater than the significance level of 0.05.

[ψ] = The statistical significance test was achieved based on the one way ANOVA test which the *p* value should be less than the significance level of 0.0001.

Variability in physical field conditions was examined with respect to EC and Cl. To test influence of physical properties, additional regression models were created based on organic matter (LOI%), sand content, and clay content. Models created were restricted to criteria outlined in the Soil Survey Manual (Soil Survey Staff, 1993) (Table 2.3). Evaluated parameters included: non-organic (LOI 0-2%), moderate-highly organic (LOI >2%), predominately sand (sand content >80%), and those with appreciable clay (clay content >20%). Each model's validity was determined by residual normality after log transformation. Moderately high organic soils showed

the highest average EC (20.33 dS m$^{-1}$), followed by clayey soils (13.42 dS m$^{-1}$), non-organic

soils (10.36 dS m$^{-1}$), and sandy soils (5.82 dS m$^{-1}$). PXRF Cl readings showed an identical

pattern with moderately high organic soils, clayey soils, non-organic soils, and sandy soils

having Cl readings of 3,437, 2,586, 2,111, and 1,639 mg kg$^{-1}$, respectively. Interestingly, the

sandy and non-organic soils had the strongest correlations between EC and PXRF Cl with R$^2$ of

0.93 and 0.90, respectively. While systems that offer electrostatic attraction to free cations in soil

solution may effectively bind them to the exchange complex of clays or integrate them into the

molecular structure of complex organics, anions such as Cl would still be freely available as like

charges repel each other. However, clays and organics may exchange/contribute cations to soil

salinity, which would be reflected in higher overall soil EC, but not reflected by higher PXRF Cl

readings, and not captured by simple linear regression with Cl as the single element of analysis.

This is likely the rationale behind lower EC/PXRF correlations with regard to more clayey and

more organic soils.

One limitation of using single element analysis (e.g., Cl) via PXRF is the potential for

matrix interference from other elements with higher concentrations. However, such limitations

can be managed with extended scanning time, sample homogenization, correction via NIST

standards, and consideration of multiple scans (Anderson and Olin, 1990).

Multiple Linear Regressions

In consideration of the possibility of more diverse types of salt contributing soil salinity,

multiple linear regression was used to compare EC readings with concentrations of Cl, K, S, and

Ca. Another model was created including K, S, Ca, and Cl salts from PXRF as constituent

elements of common salt compounds. Similar to the procedure described with simple linear

regression, residual normality was tested and log transformation was applied. After log

transformations, the residual normality data passed ($P > 0.05$) with an acceptable $R^2$ of 0.8669 (Table 2.2).

Table 2.3. Parameters of restricted SLR models of EC (dS m$^{-1}$) and Cl (mg kg$^{-1}$) for physical and chemical characteristics of soils from Louisiana, USA: Non-organic (LOI 0-2%); Moderate-High Organic (LOI >2%); Sand fraction >80%; and Clay fraction >20%.

| | Non-Organic (0-2% LOI) | Moderate-High Organic (>2% LOI) | Sand >80% | Clay >20% |
|---|---|---|---|---|
| Avg. EC (dS m$^{-1}$) | 10.356 | 20.334 | 5.822 | 13.423 |
| Avg. Cl (mg kg$^{-1}$) | 2111.478 | 3436.829 | 1638.759 | 2586.445 |
| Avg. %$^{\dagger}$ | 0.779 | 5.566 | 92.904 | 36.142 |
| $R^2$ | 0.9 | 0.78 | 0.93 | 0.56 |
| Significant (P<0.001) | Yes | Yes | Yes | Yes |
| n | 45 | 43 | 29 | 22 |
| Normality (p) | Yes | Yes | Yes | No (0.0049) |

$^{\dagger}$Average of physicochemical parameter for each column; LOI, LOI, sand %, and clay %, respectively.

With all samples in the modeling dataset considered (n=67), the correlation between Ln Cl/S/K/Ca and Ln EC was 0.8669. The validation dataset (n=22) showed different trends with $R^2$ between Ln Cl/S/K/Ca and Ln EC of 0.6644. Since the $R^2$ of simple and multi linear regressions (n=67) had similar acceptable results, the former is recommended with deference to the law of parsimony (Figure 2.3 (a) and (b)). Though the simple linear regression model was slightly less accurate, the multi linear model has greater complexity (Table 2.4). Figure 2.4 applied the validation data (n=22) to respective modeling equations to test its predictive accuracy against actual lab quantified EC. The correlation coefficient ("R") showed similar trends for simple and

multiple linear regressions (0.827 and 0.823, respectively). For research of specific salts, the use of multiple linear regression models may be preferable. Both models provide options for future studies, but for most applications the use of simple linear regression as a predictor of EC is recommended.
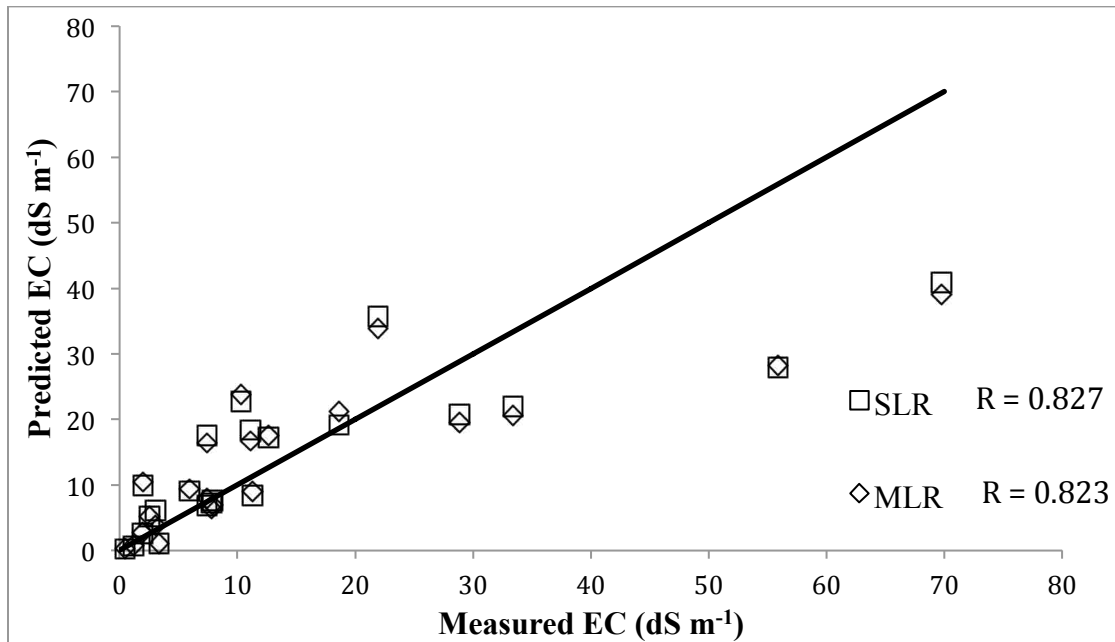


Figure 2.4. Prediction model created using laboratory measured EC (dS m-1) and Cl via PXRF for SLR, and Cl, S, K, and Ca via PXRF for MLR using validation set (n=22) for saline soil samples in Louisiana, USA.

Table 2.4. Prediction equations for Ln EC produced from modeling dataset (n=67) of PXRF Ln Cl and PXRF Ln Cl, S, K, Ca under simple and multiple linear regression models, respectively, in saline samples in Louisiana.

| Prediction | Regression Model | Regression Equation | $R^2$ |
|---|---|---|---|
| Cl | Simple | Ln EC = -3.305 + (0.755 $X$ Ln (Cl PXRF)) | 0.839 |
| Cl, S, K, Ca | Multiple | Ln EC = -3.651 + (0.6759 $X$ Ln (Cl PXRF)) + (-0.0859 $X$ Ln (S PXRF)) + (0.1646 $X$ Ln (K PXRF)) + (-0.0054 $X$ Ln (Ca PXRF)) | 0.8669 |

**Conclusions**

Previous studies using PXRF to measure physical, chemical, and morphological

properties in soil have been proven successful. For decades, the technique for measuring salinity

in soils used an electrode to measure the electrical conductance of soil solution, which has been

directly correlated to total salts present in soil. This research sought to develop a method of using

PXRF to enhance measuring salinity in soils by elemental quantification, as a corollary to

measurements such as EC. Salt impacted soil samples were collected from Louisiana coastal

parishes, representing a wide variety of soil organic matter, texture, and salinity. Samples were

subjected to traditional methods of measuring physical and chemical properties, with subsequent

elemental quantification via PXRF. Simple and multiple linear regression models were created to

relate EC to PXRF data as an accurate method of measuring salinity in situ. While both models

resulted in similar acceptable $R^2$ (0.839, and 0.8669, respectively), simple linear regression is

recommended given its simplicity and practicality for field use.

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# CHAPTER 3: CONCLUSIONS

Determining soluble salt concentration *in situ* is possible, but the identification of specific types of salts and their constituent elements is not possible with current field methods. Visual indicators can guide pedologists to areas of suspected salinity, but the question still remains as to the concentration of salt, and what specific salt is present. To answer these questions, samples with broad ranges of gypsum and salts were examined with PXRF for elemental quantification (Appendix A). For gypsum, samples were treated for carbonate digestion before thermogravimetric gypsum quantification (Appendix A). For salinity, samples were dried and sieved for uniform representation of the sample. The PXRF scanned each sample for 90 s, with replications to generate an average. Prior to scanning, the instrument was calibrated with a "316" alloy clip and validated using an NIST reference standard.

Simple and multiple linear regression models were used to compare laboratory analysis (thermogravimetry and EC) and elemental analysis via PXRF. Simple linear regression and multiple linear regressions were used to establish the relationship between the two datasets. To predict gypsum, simple linear regressions using Ca, laboratory data, and PXRF Ca data produced an $R^2$ of 0.8794 (Appendix A). Similarly, simple linear regression for laboratory-quantified gypsum versus PXRF S produced an $R^2$ of 0.9120 (Appendix A). Multiple linear regression of laboratory quantified gypsum versus both PXRF S and Ca produced an $R^2$ of 0.9127 (Appendix A). To predict salinity, simple linear regression using EC data and PXRF Cl data produced an $R^2$ of 0.839. Multiple linear regressions of EC data versus PXRF Cl, S, Ca, and K produced an $R^2$ of 0.8669. Since the $R^2$ values of multiple and simple linear regressions are very similar, it is recommended to only require PXRF Cl concentrations to predict salinity values. Overall, PXRF shows great promise for the direct quantification of soluble salts in soils.

In order to use PXRF in the field as a tool for determining various soluble salts, interference considerations must be addressed. PXRF can also be used in the laboratory following previously mentioned pre-treatments for specific salts, because of its increased efficiency of detection when samples are homogenized, thus minimizing the risk of interference. A pedologist can use PXRF in the field as a reliable tool for sampling by detecting "hot spots," or areas of high elemental concentration to prevent over-sampling, thus increasing research efficiency by only collecting samples with known salinity/gypsum. This technology can enhance the previously mentioned laboratory techniques by providing elemental concentrations of the soil. Summarily, PXRF shows excellent promise for providing salinity and/or gypsum quantification from elemental concentrations in soil.

# APPENDIX A: DIRECT SOIL GYPSUM QUANTIFICATION VIA PORTABLE X-RAY FLUORESCENCE SPECTROMETRY

## Abstract

Soil scientists have long struggled with an effective method for quantifying gypsum content in soils. Several methods exist, but each is fraught with problems. Recent enhancements to portable X-ray fluorescence (PXRF) spectrometers have provided better detection limits especially for lighter elements such as S, a key component of gypsum. Thus, this research aimed to test the effectiveness of PXRF as a means of directly quantifying gypsum in soils. A total of 102 soil samples containing a wide variety of gypsum (~2–95%) were subjected to both traditional laboratory analysis (thermogravimetry) and elemental analysis via PXRF. Simple linear regression and multiple linear regression were used to establish the relationship between the two datasets. Log transformation of some datasets was necessary to normalize the data. Using simple linear regression for Ca, laboratory data and PXRF Ca data produced an $R^2$ of 0.8794. Similarly, simple linear regression for laboratory-quantified gypsum vs. PXRF S produced an $R^2$ of 0.9120. Multiple linear regression of laboratory quantified gypsum vs. both PXRF S and Ca produced an $R^2$ of 0.9127. No significant differences were observed between model generation and validation datasets. Overall, PXRF shows great promise for the direct quantification of gypsum in soils.

## Introduction

Soils with high gypsum contents are commonplace in many arid and semiarid regions of the world (e.g., Syria, Libya, Tunisia, New Mexico, Spain, and western Texas). The direct determination of gypsum ($CaSO_4 \bullet 2H_2O$) in soils is difficult since there are inherent drawbacks involved with the extraction of this mineral with water. The factors that influence the extracted Ca and sulfate from gypsiferous soils involve the solubility of gypsum, other sources of Ca and

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sulfate, and exchange reactions between soluble Ca and other cations, such as Na and Mg (Bashour and Sayegh, 2007). Frequent errors associated with other methodologies were reviewed by Herrero et al. (2009). Morphologically, the Soil Survey Staff (2010) indicates that the "suffix yy is used when the horizon has such an abundance of gypsum (generally 50% or more, by volume) that pedogenic and/or lithologic features are obscured or disrupted by growth of gypsum crystals." But how much gypsum is present in a given horizon? How can a field pedologist reliably distinguish between a horizon of 40–45% gypsum and one of >50% gypsum when both can appear as nondescript, white, powdery soil?

Field pedologists have struggled with these questions for years. Qualitative field estimates are possible but imprecise. Several methods have attempted to provide quantitative data on gypsum content, but require laboratory processing and are fraught with problems (Herrero et al., 2009). Among them are acetone precipitation (Soil Survey Staff, 2004) and loss of the structural water of the gypsum (Nelson et al., 1978; Artieda et al., 2006; Lebron et al., 2009). Zhu and Weindorf (2009) and Weindorf et al. (2009) used PXRF spectrometry to quantify Ca and then gypsum, respectively. Laboratory calibration used a polynomial fit to associate PXRF Ca content with reagent grade gypsum at different concentrations, achieving an $R^2$ of 0.986. Field application of the technique proved more challenging. The procedure involved first calculating total Ca in the soil. As soil horizons often contain both gypsum and $CaCO_3$, the latter was quantified using a pressure calcimeter. The Ca associated with calcite was then subtracted from total Ca obtained by PXRF. The remaining Ca was assumed to be associated with gypsum and estimates made. Strong, significant correlations of PXRF data to acetone precipitation ($R = 0.85$) and quantitative X-ray diffraction ($R = 0.96$) were observed (Weindorf et al., 2009). Yet the necessity of backing out the Ca associated with calcite made this method cumbersome when

mixed calcite/gypsum horizons were observed. The elegant solution to this challenge was to use S as a proxy for gypsum rather than Ca. However, earlier versions of the PXRF instrument lacked sufficient sensitivity for S detection to provide meaningful results.

Four years later, newer versions of the PXRF instrument have greatly increased the sensitivity for S detection and quantification making direct calculation of gypsum from S data possible. The published limits of detection of S for the Innov-X PXRF Alpha (older) and Olympus/Innov-X Delta (newer) are 10,000–50,000 mg kg$^{-1}$ and <200 mg kg$^{-1}$, respectively. The key advantage of the newer PXRF (Delta) is three beam sequential scanning and an ultra-high resolution silicon drift detector. Notably, other manufacturers (e.g., Oxford Instruments, Niton) also produce PXRF equipment with similar features, though those instruments were not tested as part of this study.

X-ray fluorescence is a technique whereby X-rays are generated from a Ta/Au (or other) X-ray tube for sample bombardment. Upon striking the soil, electrons from the inner shell (k and l orbitals) are ejected, causing outer shell electrons to cascade down to fill the inner shells. In doing so, they must relinquish energy, which is the *fluorescence* emitted by each element. The wavelength of fluoresced radiation is characteristic of each element, while the intensity gives an indication of the elemental abundance. Use of portable X-ray fluorescence for elemental determination in soils and sediment is sanctioned by the EPA per method 6200 (USEPA, 2007). An excellent overview of X-ray fluorescence operational theory is given by Potts and West (2008). In recent years, PXRF has quickly gained popularity for in situ environmental (Gutiérrez-Ginés et al., 2013; Gardner et al., 2013; Scott et al., 2013, Weindorf et al., 2012a), pedological (Zhu et al., 2011; Weindorf et al., 2012b; Weindorf et al., 2012c; McLaren et al.,

2012b), and agronomic applications (McLaren et al., 2012a; Paltridge et al., 2012a; Paltridge et al., 2012b).

Given promising results from earlier applications of PXRF for gypsum quantification, coupled with increased sensitivity of contemporary PXRF instruments, the study of PXRF for direct quantification of gypsum using S as a proxy seems timely. As such, the objective of this research was to evaluate the use of contemporary PXRF for direct quantification of gypsum. The authors theorize that PXRF will provide robust data for on-site gypsum quantification minimizing the need for laboratory analysis.

**Materials and Methods**

A total of 102 soil samples were collected near Zaragoza, Spain in 2007 and 2010. The parent material of these soils is a horizontal stratum of Miocene rocks or derived sediments, all of them with considerable gypsum content (~2–95%). The soils were mostly Typic Calcigypsids, Typic Haplocalcids, Typic Haplogypsids, and Gypsic Aquisalids (Soil Survey Staff, 2010). Samples were ground to pass a 2-mm sieve and subjected to gypsum quantification per thermogravimetry (Artieda et al., 2006). For carbonate determination, HCl was used to produce $CO_2$, which was then measured with a Bernard calcimeter to calculate $CaCO_3$ equivalent (CCE) percentage (Sherrod et al., 2002).

The molecular weight of gypsum is 172.171, that of $CaCO_3$ is 100.087, and the atomic weight of Ca is 40.078, so the total concentration of Ca content measured in the laboratory can be calculated as follows:

$$\text{Total Ca}_{\text{lab}}\left(\%\right) = 0.2328 * \text{gypsum} + 0.4004 * \text{CCE}$$

where *total* $Ca_{lab}$ is the calculated Ca from laboratory results of CCE and gypsum and reported as a percentage. The results from this equation were compared to the total Ca concentration from

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PXRF to produce the best model for describing the data set. Determinations of S were made directly via PXRF.

**PXRF Scanning**

A subsample of each soil was sent to Louisiana State University for characterization by PXRF. A Delta Premium PXRF (Olympus Innov-X, Waltham, MA) featuring a Ta/Au X-ray tube was operated at 15–40 KeV for sample analysis. Before sample analysis, the PXRF was standardized using a "316" alloy clip (containing 16.130% Cr, 1.780% Mn, 68.760% Fe, 10.420% Ni, 0.200% Cu, and 2.100% Mo) tightly fitted over the aperture. Fluorescent radiation detection was accomplished via ultra-high resolution (<165 eV) silicon drift detector. Scanning was conducted using a proprietary Olympus software configuration known as *Soil Mode* with the light elements analysis program (LEAP) engaged. Samples were scanned directly through sealed plastic bags, ensuring excellent contact between the PXRF aperture and sample to be scanned. Sequential scanning was conducted for 30 s per beam (three-beam operation), such that total scanning time was 90 s per sample. Each sample was scanned in duplicate, with data subsequently averaged for analysis. The Delta Premium PXRF limits of detection (LOD) for Ca and S are <50 and <200 mg kg$^{-1}$, respectively. These LODs are considerably lower than the older version Alpha PXRF that was previously used by Weindorf et al. (2009).

Results of PXRF scans produced total elemental concentrations of Ca and S reported as milligrams per kilogram. As the concentrations of those elements were high in the evaluated soil samples, the final concentrations were expressed as g kg$^{-1}$. When measured Ca and S exceeded 10,000 mg kg$^{-1}$ the PXRF instrument reported them as percentages (10,000 mg kg$^{-1}$ = 1%). Percentages were transformed for expression as g kg$^{-1}$ so that all measurements used the same unit.

**Statistical Analysis**

The results of 82 soil samples were utilized to construct different regression models; the remaining 20 samples (randomly selected) were used for model validation. Specifically, the PXRF readings for Ca were used to create simple linear and nonlinear regression models. Additionally, PXRF readings for S were used to construct simple regression models to quantify gypsum content. Furthermore, PXRF readings for both Ca and S were utilized to produce multiple linear regression models to estimate gypsum content.

Logarithmic transformation was used in this study to normalize the variables to obtain a normal distribution for the error term (residual, $e_i$), an established assumption when producing simple and multiple linear regression models. Using logarithmic transformation of the $Y$ variable (exponential relationships) or $X$ and $Y$ variables (power relationships) in simple and multiple regressions is one of the most frequently used methods of fitting various quantitative data in environmental studies (Newman, 1993). The PROC REG statement in SAS® 9.3 software (SAS Institute, 2011) was employed to construct the regression models and ANOVA table, and produce the correlation plots based on the log-transformed variables. All statistical analysis was conducted at a significance level of $\alpha = 0.05$.

Model validation was used to determine if model predictions were in agreement with measured observations. The regression models were validated by randomly selecting 20 (20%) of the total (102) scanned soil samples. The PROC BOXPLOT statement was used to statistically describe the differences between the measured and predicted data for the validation samples. Different statistical analyses were applied to quantify significant differences and the correlation between laboratory measured values and predicted values from the regression models for Ca and gypsum. Tukey's test was used to identify significant differences of least squares means between

the two datasets. The *null* hypothesis for the validation analysis was "there are no significant differences between the measured observations and the predictions from each model." Additionally, PROC CORR was used to produce the Pearson correlation coefficient. All the validation analyses were conducted at a significance level of $\alpha = 0.05$.

**Results and Discussion**

Total elemental concentrations of Ca and S were acquired from PXRF readings. These readings were used to fit the required models to predict the respective values for total $Ca_{lab}$ (CCE + gypsum) and gypsum. The statistical parameters for the 82 soil samples that were used to produce the regression models are shown in Table A.1.

Shacklette and Boerngen (1984) provided a comprehensive study of 50 element concentrations in soil samples that covered the entire United States. In their project, they established averages and ranges of those 50 elements including total Ca and S, which were compared to the measured Ca and PXRF readings for Ca and S in the current study samples (Table A.1). Additionally, the averages of soil samples of the current study were compared to the average of total Ca and S concentrations of Vinogradov (1959). These averages were calculated based on worldwide samples (Table A.1). The averages of measured Ca and PXRF Ca readings of targeted soil samples (144.5 and 114 g kg$^{-1}$) were higher compared to averages of Shacklette and Boerngen (1984) and Vinogradov (1959) but likely related to the high gypsum contents of the studied soils.

Table A.1. Descriptive statistical parameters of gypsum (laboratory measured), Total Ca$_{lab}$ (calculated based on Ca from CaCO$_3$ equivalent (CCE) and gypsum), and the portable X-ray fluorescence (PXRF) readings for Ca and S for gypsiferous soils from Spain.

| Parameter | Laboratory Measured | | PXRF Reading | |
| | CaSO$_4$.2H$_2$O | Total Ca$_{lab}$† | Ca | S |
| --- | --- | --- | --- | --- |
| | | ——— g kg$^{-1}$——— | | |
| N | 82 | 82 | 82 | 82 |
| Mean | 180.528 | 144.543 | 114.007 | 30.055 |
| Median | 126.850 | 133.851 | 99.019 | 18.722 |
| Minimum | 21.600 | 102.113 | 66.104 | 4.023 |
| Maximum | 947.000 | 256.057 | 244.217 | 176.373 |
| Standard Deviation | 169.517 | 35.251 | 43.425 | 37.617 |
| Kurtosis | 7.232 | 1.928 | 1.033 | 9.917 |
| Skewness | 2.499 | 1.539 | 1.336 | 2.950 |
| Shacklette and Boerngen (1984) (Average, Range) | – | (24, 0.1–320) | | (1.6, 0.8–48) |
| Vinogradov (1959) (Average) | – | (20) | | (0.85) |

† Total Ca$_{lab}$ = CaCO$_3$ equivalent + Ca in gypsum.

The statistical parameters presented in Table A.1 indicate that PXRF readings of Ca were reasonably related to the total Ca$_{lab}$ calculated based on the Ca content in CCE and gypsum, as the parameters had close values. The positive values of skewness indicate that the data was not perfectly normal, but it skewed to the right. For measured gypsum and PXRF S readings, the higher values of kurtosis (7 and 10) and skewness (2.5 and 3), compared to total Ca$_{lab}$ or PXRF Ca readings, indicate that the data was not normally distributed and it was more skewed.

**Modeling of Ca**

To examine the validity of the regression model, the residual normality was tested. For the modeling of Ca based on the PXRF Ca readings and the total Ca$_{lab}$, the residual term for the simple linear regression model was not normally distributed using the untransformed dataset ($P < 0.05$) (Table A.2). Consequently, log-transformation was needed to normalize the error term and validate the regression model. In SAS, the function "LOG" was used to produce the natural

log of the data. Two simple linear regression models were created using the transformed dataset. The first model was created by log-transforming only the $Y$ variable (total $Ca_{lab}$) and used the untransformed $X$ variable (PXRF Ca readings). The second model was produced by log-transforming both variables ($X$ and $Y$). The PXRF Ca readings (g kg$^{-1}$) were matched with the Ln total $Ca_{lab}$ (g kg$^{-1}$) based on the constructed models (Figure A.1). As the residual normality test for the log-transformed dataset of only the $Y$ variable (total $Ca_{lab}$) passed (Table A.2), this regression model was used as a valid relation between Ln total $Ca_{lab}$ and PXRF Ca data with an acceptable $R^2$ of 0.88 (Table A.2 and Figure A.1). The simple linear relationship shown in Table 2.3 explains the correlation between Ln total $Ca_{lab}$ and the PXRF Ca reading. Poor regressions were obtained between total $Ca_{lab}$ and CCE and between CCE and PXRF Ca readings, especially with a higher content of gypsum. These results were consistent with the findings of Weindorf et al. (2009). Validation samples were used to examine the appropriateness and efficiency of the constructed model. Correlation between the total Ca, produced by the regression model based on PXRF Ca readings, and total $Ca_{lab}$, based on the calculations of (CCE + gypsum), was examined. Figure 2.2 shows the boxplot for both groups: total $Ca_{lab}$, as a measured group, and predicted total Ca from a regression model, as a predicted group. The boxplot indicated that both groups are reasonably matched with no significant differences between measured and predicted values. This result was confirmed by Tukey's test with no significant differences in the least square means between the two groups, with $P$ value $> 0.05$ ($P = 0.7843$). Additionally, a good correlation coefficient ($R = 0.938$) was achieved between the measured and predicted values based on Pearson Correlation, which indicated a high positive correlation between the measured total Ca (CCE + gypsum) and the total Ca content obtained by the regression model based on the PXRF Ca readings (Figure A.3).

Table A.2. Parameters of fitting lines between total $Ca_{lab}$ and measured gypsum and portable X-ray fluorescence (PXRF) Ca and S readings under different linear regression models for gypsiferous soils from Spain.

| Linear regression model | | Model parameter | Untransformed variables | Log-transformation | |
|---|---|---|---|---|---|
| | | | | *Y* variable | *Y* and *X* variables |
| Ca — Simple | | Intercept | 57.5216 | 4.4148 | 2.1285 |
| | | Slope | 0.7633 | 0.00468 | 0.6031 |
| | | $R^2$ | 0.8842 | 0.8794 | 0.8757 |
| | | *RMSE (Antilog)* | 12.073 (-) | 0.0758 (1.0787) | 0.0769 (1.0799) |
| | | *Normality test (p)†* | Failed (0.0016) | Passed (0.5978) | Failed (0.0066) |
| Gypsum (S) — Simple | | Intercept | 49.9627 | 4.3605 | 3.0014 |
| | | Slope | 4.3443 | 0.0171 | 0.6653 |
| | | $R^2$ | 0.9293 | 0.6412 | 0.9120 |
| | | *RMSE (Antilog)* | 45.346 (-) | 0.4842 (1.6229) | 0.2398 (1.2710) |
| | | *Normality test (p)* | Failed (<0.0001) | Failed (<0.0001) | Passed (0.3893) |
| Gypsum (S) — Multiple | | Intercept | 78.5998 | 5.0469 | 3.2986 |
| | | Slope (S PXRF) | 4.5578 | 0.0222 | 0.6694 |
| | | (Ca PXRF) | −0.3075 | −0.0073 | −0.0661 |
| | | $R^2$ | 0.9333 | 0.7425 | 0.9127 |
| | | *RMSE (Antilog)* | 44.3359 (-) | 0.4128 (1.5110) | 0.2404 (1.2718) |
| | | *Normality test (p)* | Failed (<0.0001) | Passed (0.4511) | Passed (0.7778) |

† The normality test for the error term or residual ($e_i$) was achieved based on the Shapiro–Wilk test in which the *p* value should be greater than the significance level of 0.05.
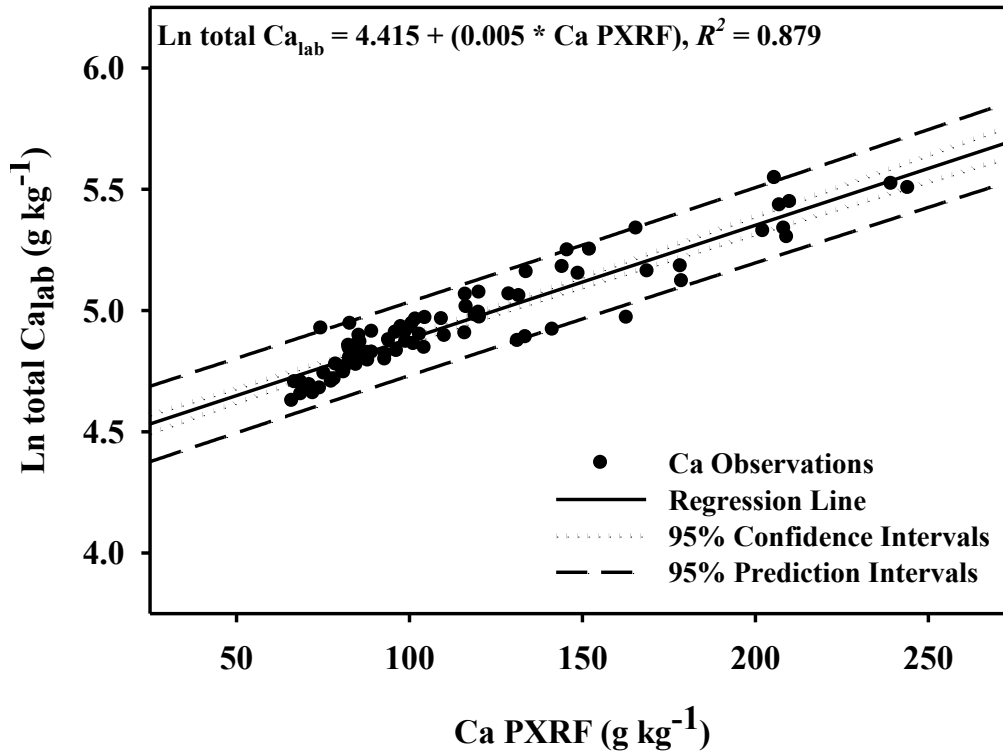
Figure A.1. Simple linear regression between the log-transformed *total Ca_lab* (*Ln total Ca_lab*) and PXRF Ca readings with 95% confidence and prediction intervals for gypsic soils from Spain.

Table A.3. The constructed regression models for Ca and gypsum prediction of the normalized variables for gypsiferous soils from Spain.

| Prediction | Regression model | Regression equation | $R^2$ |
|---|---|---|---|
| Ca | | Ln total $Ca_{lab}$ = 4.415 + (0.005 $X$ Ca PXRF) | 0.8794 |
| | Simple | Ln Measured Gypsum = 3.001 + (0.665 $X$ Ln S PXRF) | 0.9120 |
| Gypsum | | Ln Measured Gypsum = 5.047 + (0.022 $X$ S PXRF) − (0.007 $X$ Ca PXRF) | 0.7425 |
| | Multiple | Ln Measured Gypsum = 3.299 + (0.669 $X$ Ln S PXRF) − (0.066 $X$ Ln Ca PXRF) | 0.9127 |
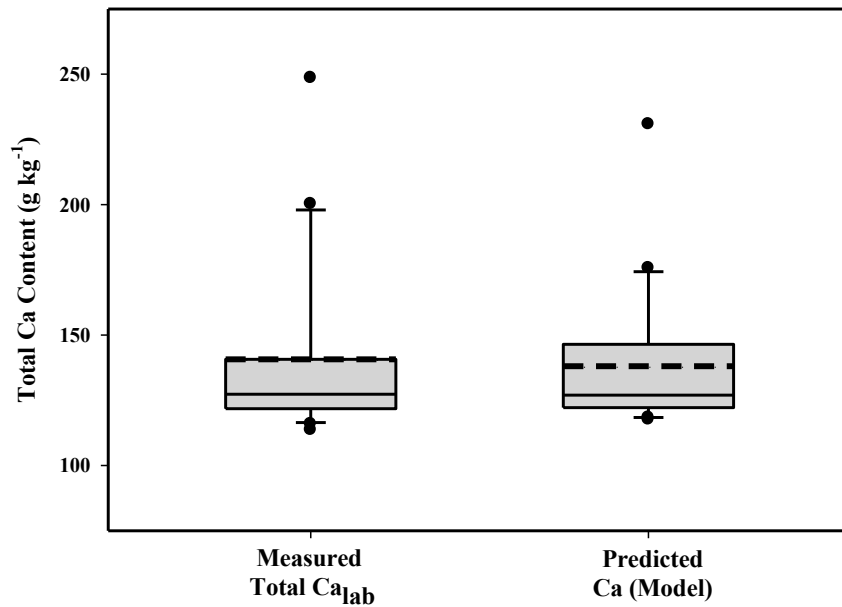
Figure A.2. Boxplot for the descriptive statistical parameters of the *total Ca_{lab}* as measured and total Ca from the regression model based on PXRF Ca readings as predicted for gypsic soils from Spain.
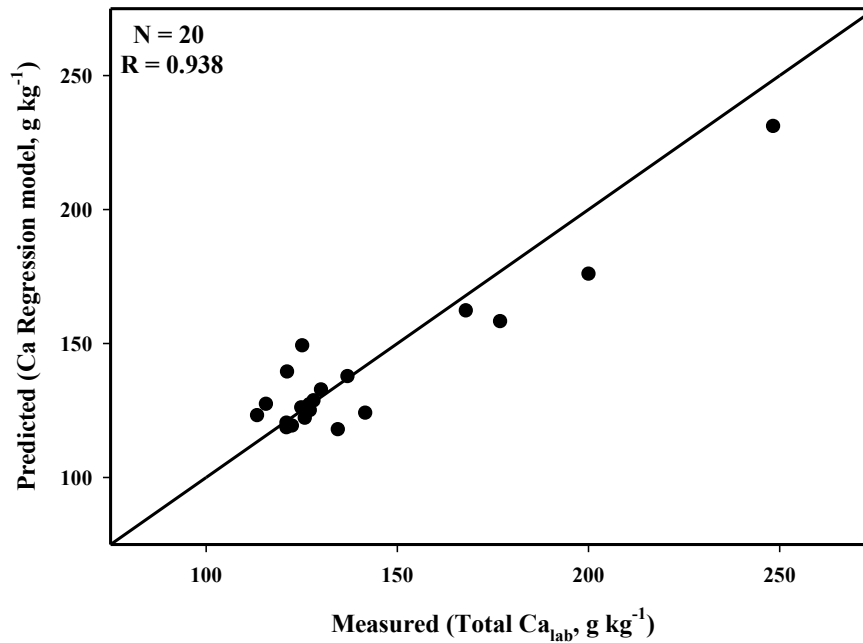


Figure A.3. Correlation between the *total Ca_{lab}* as measured and total Ca from the regression model based on PXRF Ca readings as predicted for the validation samples for gypsic soils from Spain. Circles represent the Ca observations, N represents number of observations, and R represents the correlation coefficient.

Based on the aforementioned discussion, a simple linear regression model is recommended for predicting the total Ca content using PXRF Ca readings. Supporting this conclusion, McLaren et al. (2012b) found a strong linear correlation between Ca measured by standard microwave aqua regia digestion and PXRF Ca readings in Vertisols from Australia. Additionally, the current study results were consistent with the findings from Weindorf et al. (2009) who reported a correlation coefficient ($R$) of 0.84 between measured Ca and PXRF Ca readings in soil samples from Texas and New Mexico.

**Modeling of Gypsum**

As there is no direct method for measuring gypsum by PXRF, elemental readings were used to develop regression models between PXRF S and Ca and thermogravimetrically measured gypsum. Similar to Ca modeling, the error term normality test was performed over the linear regression models. The residual normality test indicated that the simple linear regression models, based on untransformed data, or based on the log-transformed measured gypsum, were not valid as the error terms for both models were not normally distributed ($P < 0.05$) (Table A.2). However, the regression model based on the log-transformation of both measured gypsum and PXRF S readings was valid since the residual was normally distributed ($P > 0.05$) (Table A.2). As a result, the simple linear relationship between the log-transformed measured gypsum (Ln Measured Gypsum) and the log-transformed PXRF S readings (Ln S PXRF) was created and shown in Table A.3 and Figure A.4 (a). A very high $R^2$ of 0.91 was obtained from this relationship based on the provided dataset.

As gypsum is a compound that contains both Ca and S in its formulation, multiple regression models based on the PXRF readings of both S and Ca were examined. When the multiple linear regression model was constructed based on untransformed data, the model was

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not valid since the error term was not normally distributed ($P < 0.05$) (Table 2.2). Yet when measured gypsum data was log-transformed and when all variables (measured gypsum and PXRF S and Ca readings) were log-transformed, the error terms were normally distributed ($P > 0.05$) and the models were valid (Table A.2). The log-transformation for only the $Y$ variable (measured gypsum) produced a poor relationship with an $R^2$ of 0.74 compared to the higher $R^2$ of 0.91 for both simple and multiple linear regression models using the same dataset (Table A.3 and Figure A.4 (b) and (c)).

a)

Ln measured Gypsum = 3.001 + (0.665 * Ln S PXRF), $R^2$ = 0.912

- S Observations
- Regression Line
- 95% Confidence Intervals
- 95% Prediction Intervals

b)

Ln measured Gyps = 5.047 + (0.022 * S PXRF) - (0.007 * Ca PXRF)
$R^2$ = 0.742

- S Observations
- Ca Observations
- Multiple Regression Line
- 95% Confidence Intervals
- 95% Prediction Intervals

S & Ca PXRF (g kg$^{-1}$)

c)

Ln measured Gyps = 3.299 + (0.669 * Ln S XRF) - (0.066 * Ln Ca PXRF)
$R^2$ = 0.913

- S Observations
- Ca Observations
- Multiple Regression Line
- 95% Confidence Intervals
- 95% Prediction Intervals

Ln S & Ln Ca PXRF (g kg$^{-1}$)

Figure A.4. Different linear regression models; a) simple linear regression between log-transformed thermogravimetrically measured gypsum (Ln measured gypsum) and log-transformed PXRF S readings (Ln S PXRF), b) multiple linear regression between Ln measured gypsum and untransformed PXRF S and Ca readings, and c) multiple linear regression between Ln measured gypsum and Ln S and Ca PXRF readings. The 95% confidence and prediction intervals are provided for each regression model.

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Using the validation samples, strong agreements were found between the prediction model based on simple regression (Predicted S PXRF) and the prediction model based on multiple regression (Predicted Ln S&Ca PXRF$^{(2)}$). These two models were highly matched for measured gypsum of <400 g kg$^{-1}$. For higher gypsum content, lower estimations were observed using the two regression models (Figure A.5). Another multiple regression model (Predicted S&Ca PXRF$^{(1)}$) with the lowest $R^2$ of 0.74 was matched reasonably with the other two models when the gypsum content was >400 g kg$^{-1}$; however, with lower gypsum content, this model was not good enough to simulate the data. The result of Tukey's test indicated no significant differences in the least squares means between the three created models and the measured gypsum, with a very high $P$ value of 0.90. Additionally, a strong correlation coefficient of ($R >$ 0.95) was achieved between the measured and predicted values based on Pearson correlation (Table A.4 and Figure A.6), which indicated a high positive correlation between the measured gypsum and the predicted gypsum obtained by the regression models based on PXRF S&Ca readings (Figure A.6)
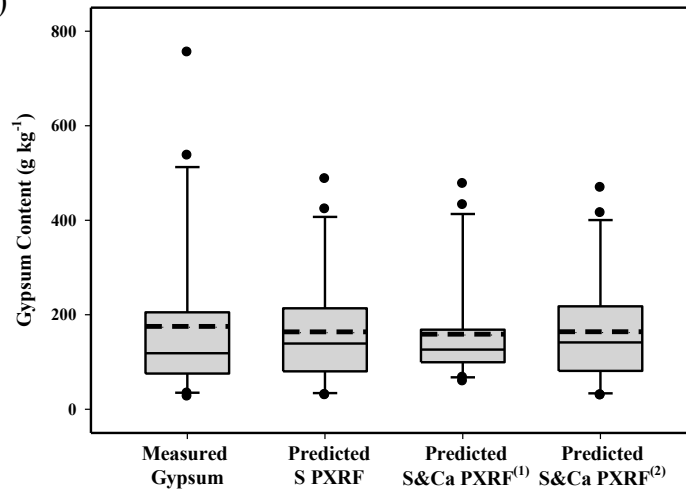


Figure A.5. Boxplot for the descriptive statistical parameters of the thermogravimetrically measured gypsum and predicted gypsum from; simple linear regression model based on PXRF S reading, multiple linear regression model based on the log-transformed gypsum and untransformed PXRF S and Ca readings (S&Ca PXRF$^{(1)}$), and multiple linear regression model based on the log-transformed gypsum and PXRF S and Ca readings (S&Ca PXRF$^{(2)}$) for the validation dataset for gypsic soils from Spain.

Table A.4. Pearson correlation matrix for the thermogravimetrically measured gypsum and the three created models to predict the gypsum content based on the validation dataset for gypsiferous soils from Spain.

| | Measured gypsum | Predicted S PXRF † | Predicted S&Ca PXRF[(1)] ‡ | Predicted S&Ca PXRF[(2)] § |
|---|---|---|---|---|
| Measured gypsum | 1.000 ¶ | | | |
| Predicted S PXRF | 0.961 | 1.000 | | |
| Predicted S&Ca PXRF[(1)] | 0.973 | 0.978 | 1.000 | |
| Predicted S&Ca PXRF[(2)] | 0.953 | 0.999 | 0.974 | 1.000 |

† Simple linear regression model based on portable X-ray fluorescence (PXRF) S reading.
‡ Multiple linear regression model based on the log-transformed gypsum data and untransformed PXRF S and Ca readings.
§ Multiple linear regression model based on the log-transformed gypsum data and PXRF S and Ca readings.
¶ Each pair(s) of variables with positive correlation coefficients and P values < 0.05.
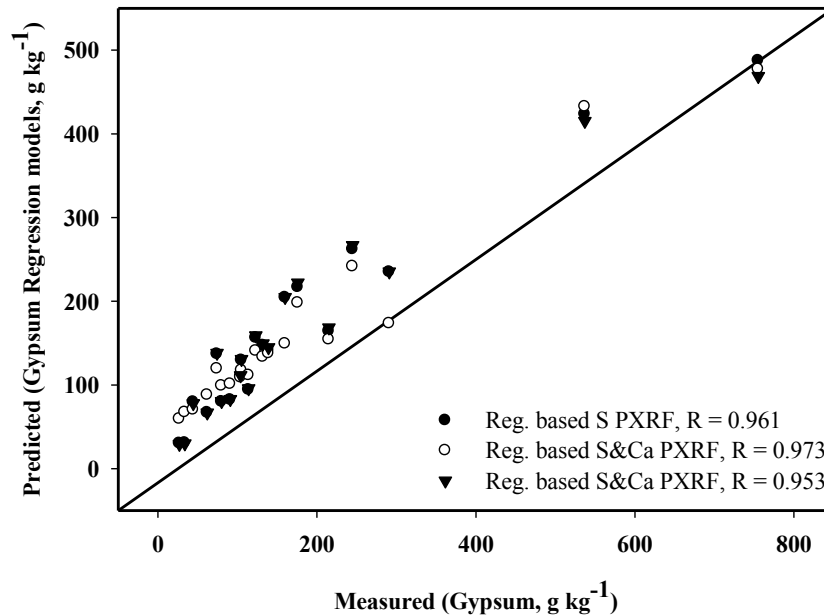


Figure A.6. Correlation between thermogravimetrically measured gypsum and the predicted gypsum from the three models; simple linear regression model based on PXRF S reading, multiple linear regression model based on the log-transformed gypsum and untransformed PXRF S and Ca readings (S&Ca PXRF[(1)]), and multiple linear regression model based on the log-transformed gypsum and PXRF S and Ca readings (S&Ca PXRF[(2)]) for the validation dataset for gypsic soils from Spain. R represents the correlation coefficient for each relationship.

Accordingly, simple and multiple regression models are recommended for soil gypsum prediction based on PXRF S and Ca readings with $R^2$ up to 0.91. As the PXRF is a relatively new application in soil science, there are few studies in the literature about using PXRF to predict gypsum content. However, Harris et al. (2011) performed a project in Texas in which a Niton XL3t handheld XRF analyzer was used as a predictor for S and, thus, sulfate content. Their results indicated that this device was not suitable for predicting low concentrations (<4500 mg $kg^{-1}$) of sulfate when using S as the predictor whereas the limits of detection of the device for Ca were more suitable. Notably, gypsiferous soils are rife with S, essentially eliminating this constraint. However, Berger et al. (2009) used a Niton XRF XLt 500He for detecting S concentrations in river sediment samples under different water contents. Their results indicated that samples with S varying from 0.3 to 2.0% were successfully measured with this instrument with an estimated quantitation limit of 237 mg $kg^{-1}$ S. In other PXRF studies on soil, moisture has been cited as a potential source of error, especially when soil moisture is >20% (Laiho and Perämäki, 2005). Laiho and Perämäki (2005) added 5–40% moisture (gravimetrically) to oven dried soils and then evaluated the performance of multiple PXRF instruments. They concluded that soil moisture of 5–15% caused nominal errors to PXRF elemental readings, supporting Piorek's (1998) finding that soil moisture of <20% had nominal effects on PXRF accuracy. Thus, applied to gypsiferous soils in arid environments, it likely that PXRF data would not be substantially compromised unless soils moisture levels exceeded 20%.

**Conclusions**

Soil samples from Spain with a broad range of gypsum content were evaluated via traditional laboratory analysis and compared with elemental (Ca and S) data obtained from a contemporary PXRF spectrometer. Previous versions of the PXRF lacked sufficient sensitivity

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for S, necessitating the use of Ca as a proxy for gypsum quantification. The newer model PXRF was able to produce quality Ca and S data, such that direct quantification of total soil Ca content as well as the direct prediction of gypsum content from S data is possible. For the former, simple linear regression was used and produced a valid relation between lab generated (total $Ca_{lab}$) and PXRF Ca data with an acceptable $R^2$ of 0.88. Notably, it was necessary to log transform some datasets to normalize the data. Similarly, regression of log-transformed lab-measured gypsum and log-transformed PXRF S data produced an $R^2$ of 0.91. Multiple regression approaches including both Ca and S for gypsum prediction were somewhat weaker. No significant differences were observed between modeling and validation datasets. Summarily, contemporary PXRF shows strong potential for directly predicting gypsum content in soil samples with minor gypsum contents as well as truly "gypsic" soils with much larger gypsum contents.

**Acknowledgements**

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# APPENDIX B: COMPREHENSIVE ANALYSIS RESULTS

*Via PXRF*

| Sample | EC | Cl | S | K | Ca | Sand | Clay | LOI |
|--------|------|--------|---------|---------|---------|------|------|------|
| | ---dS m$^{-1}$--- | --------------------mg kg$^{-1}$----------------- | | | | --------------%-------------- | | |
| P1 | 11.29 | 1498.0 | 1245.8 | 13410.6 | 9637.1 | 12.9 | 45.2 | 2.4 |
| P2 | 16.54 | 3457.3 | 1116.6 | 12172.5 | 9494.4 | 27.0 | 35.4 | 2.2 |
| P3 | 10.82 | 973.5 | 815.5 | 12944.4 | 10373.1 | 11.1 | 8.3 | 2.2 |
| P4 | 1.87 | -45.3 | 1586.2 | 9074.2 | 97009.0 | 55.1 | 19.6 | 6.3 |
| P5 | 1.30 | -74.8 | 373.2 | 10404.2 | 7165.0 | - | - | 3.5 |
| P6 | 12.65 | 3452.5 | 13328.3 | 11596.5 | 15314.4 | 2.7 | 35.9 | 16.1 |
| P7 | 1.10 | 5.7 | 741.2 | 8201.7 | 28377.7 | - | - | 3.3 |
| P8 | 19.87 | 8141.5 | 10620.0 | 9947.0 | 8785.7 | 5.6 | 16.0 | 24.5 |
| P9 | 21.90 | 9064.8 | 13291.0 | 10035.5 | 14963.3 | 6.6 | 19.3 | 24.1 |
| P10 | 13.75 | 5700.8 | 12152.5 | 9739.5 | 13618.0 | 1.9 | 23.2 | 22.5 |
| J1 | 11.72 | 2056.5 | 2380.0 | 8353.3 | 2870.1 | 71.2 | 2.6 | 1.1 |
| J2 | 7.41 | 3525.8 | 3179.6 | 8459.9 | 37392.6 | 93.9 | 4.8 | 0.5 |
| J3 | 20.80 | 10793.8 | 1560.8 | 8156.2 | 4738.2 | 97.8 | 1.8 | 0.4 |
| J4 | 3.52 | 1560.8 | 1274.7 | 6958.0 | 7987.5 | 95.1 | 3.4 | 0.4 |
| J5 | 10.31 | 4993.8 | 1650.5 | 9190.6 | 7491.1 | 89.1 | 5.7 | 0.6 |
| J6 | 11.11 | 5832.5 | 5571.3 | 9224.4 | 9034.0 | 92.1 | 2.1 | 1.6 |
| J7A | 4.70 | 1366.5 | 688.3 | 10847.5 | 4022.8 | 83.7 | 11.6 | 1.2 |
| J7B | 5.44 | 1350.0 | 1726.2 | 10199.3 | 3627.8 | 86.3 | 8.9 | 1.2 |
| C1 | 0.10 | -49.3 | 171.0 | 2053.3 | 4689.0 | 97.2 | 0.7 | 0.1 |
| C2 | 0.22 | -31.7 | 254.3 | 1699.5 | 115.0 | 95.4 | 0.29 | 0.1 |
| C3 | 0.12 | -25.0 | 77.5 | 1620.0 | -120.7 | 96.9 | 1.6 | 0.2 |
| C4 | 0.07 | -25.0 | 142.0 | 1574.3 | 46.0 | 98.9 | 0.32 | 0.1 |
| C5 | 0.14 | -15.7 | 233.7 | 2152.5 | 341.0 | 97.3 | 1.75 | 0.2 |
| C6 | 0.16 | -26.0 | 314.8 | 2057.0 | 1034.8 | 97.0 | 0.4 | 0.1 |
| C7 | 0.16 | -23.0 | 251.5 | 5040.5 | 8019.5 | 93.7 | 3.4 | 0.5 |
| C8 | 0.12 | -8.3 | 141.3 | 1241.8 | 127.0 | 98.9 | 5.1 | 0.3 |
| C9 | 0.09 | -20.0 | 130.3 | 1809.8 | 1158.5 | 98.5 | 4.7 | 0.2 |
| C10 | 0.10 | -19.7 | 221.8 | 2749.0 | 1273.5 | 98.3 | 6.4 | 0.2 |
| C11 | 0.11 | 19.8 | 402.3 | 1786.8 | 4134.3 | 97.0 | 2.0 | 0.3 |
| C12 | 2.52 | 514.8 | 1157.8 | 3332.5 | 5970.0 | 96.4 | 5.8 | 0.3 |
| C13 | 3.07 | 872.3 | 670.0 | 1540.4 | 119.8 | 62.4 | 3.8 | 0.2 |
| C15 | 0.37 | 45.5 | 494.8 | 1862.8 | 1862.8 | 93.5 | 3.7 | 0.2 |
| C16 | 3.61 | 1165.5 | 479.9 | 1240.5 | 113.0 | 97.0 | 2.0 | 0.2 |

| | | | | *Via PXRF* | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample | EC | Cl | S | K | Ca | Sand | Clay | LOI |
| | ---dS m⁻¹--- | | | -mg kg⁻¹- | | | -%- | |
| C17 | 0.11 | -18.0 | 156.0 | 2306.0 | 5703.0 | 94.1 | 3.8 | 0.3 |
| C18 | 0.13 | -17.3 | 164.7 | 3460.5 | 5571.3 | 83.2 | 5.9 | 0.4 |
| C19 | 0.11 | -18.0 | 36.5 | 2094.3 | 558.3 | 97.0 | 2.0 | 0.2 |
| C20D | 0.18 | -45.3 | 172.8 | 5948.8 | 14832.3 | 97.0 | 2.0 | 0.4 |
| C20L | 0.10 | -18.0 | 107.0 | 1363.5 | 133.5 | 97.0 | 2.0 | 0.1 |
| C21 | 0.17 | -19.7 | 298.3 | 5312.5 | 5594.0 | 97.0 | 2.0 | 0.3 |
| C22 | 0.16 | -27.3 | 194.3 | 5841.8 | 5312.8 | 97.0 | 2.0 | 0.5 |
| C23 | 0.16 | -52.0 | 83.0 | 6062.5 | 6806.5 | 97.0 | 2.0 | 0.3 |
| C24 | 0.18 | -18.0 | 271.8 | 5255.5 | 3724.0 | 97.0 | 2.0 | 0.2 |
| C25 | 0.26 | -88.3 | 200.3 | 5166.0 | 6384.0 | 97.0 | 2.0 | 0.3 |
| C26 | 0.20 | -57.3 | 277.7 | 6061.8 | 5475.0 | 97.0 | 2.0 | 0.3 |
| C27 | 0.16 | -49.0 | 203.3 | 5384.0 | 5048.0 | 97.0 | 2.0 | 0.3 |
| C28 | 0.16 | -20.7 | 95.3 | 6289.8 | 5620.0 | 97.0 | 2.0 | 0.3 |
| C29 | 0.20 | -61.0 | 75.3 | 5836.5 | 4364.8 | 97.0 | 2.0 | 0.4 |
| C30 | 0.44 | 13.5 | 134.3 | 5575.0 | 3265.3 | 97.0 | 2.0 | 0.3 |
| C31 | 0.15 | -25.0 | 165.7 | 5442.8 | 4061.8 | 97.0 | 2.0 | 0.3 |
| C32 | 0.16 | 24.7 | 114.3 | 4820.5 | 8165.3 | 97.0 | 2.0 | 0.6 |
| C33 | 0.22 | 8.5 | 275.0 | 4677.3 | 4483.5 | 97.0 | 2.0 | 0.3 |
| C34 | 0.19 | -75.3 | 419.5 | 6244.3 | 22184.8 | 97.0 | 2.0 | 0.4 |
| C35 | 7.90 | 1176.3 | 723.6 | 5412.3 | 6362.6 | 97.0 | 2.0 | 0.4 |
| C36 | 0.25 | -70.0 | 517.3 | 5695.5 | 43201.0 | 97.0 | 2.0 | 0.8 |
| C37 | 0.30 | -25.7 | 334.7 | 6040.0 | 35554.0 | 97.0 | 2.0 | 0.2 |
| C38 | 0.22 | -17.7 | 254.5 | 6008.8 | 4235.5 | 97.0 | 2.0 | 0.2 |
| C39 | 8.29 | 802.5 | 941.4 | 9618.1 | 3954.4 | 41.6 | 36.2 | 2.5 |
| C40 | 9.29 | 1552.5 | 2916.3 | 7866.5 | 15963.9 | 70.8 | 26.4 | 1.7 |
| C41 | 18.59 | 3978.5 | 529.8 | 9108.6 | 7938.4 | 31.6 | 48.6 | 2.7 |
| C42 | 10.51 | 1571.0 | 535.8 | 10668.3 | 15634.5 | 23.7 | 61.5 | 2.7 |
| C43 | 13.20 | 1293.3 | 1846.6 | 8079.8 | 5606.9 | 52.9 | 26.4 | 1.6 |
| C44 | 7.80 | 1108.3 | 1597.0 | 6228.8 | 21256.0 | 85.1 | 12.7 | 0.9 |
| C45 | 10.70 | 545.7 | 4334.3 | 8732.9 | 13192.4 | 56.1 | 30.3 | 2.9 |
| C46 | 2.70 | 413.2 | 4513.2 | 4983.2 | 14100.0 | - | - | 0.3 |
| C47 | 5.20 | 722.7 | 251.6 | 11655.2 | 7694.5 | 7.5 | 40.7 | 2.2 |
| C48 | 8.40 | 480.3 | 756.7 | 9839.2 | 7479.8 | - | - | 1.9 |
| C49 | 5.52 | 1130.0 | 1407.3 | 10404.8 | 29226.3 | 27.1 | 57.8 | 3.6 |

| Sample | EC | Cl | S | K | Ca | Sand | Clay | LOI |
|--------|-----|-----|-----|-----|-----|------|------|-----|
| | ---dS m$^{-1}$--- | --------------------mg kg$^{-1}$------------------- | | | | ----------------%--------------- | | |
| C50 | 9.90 | 976.8 | 336.4 | 9780.5 | 26863.3 | 33.4 | 3.9 | 3.1 |
| C51 | 8.83 | 1419.8 | 572.2 | 9577.0 | 75729.5 | 27.6 | 38.4 | 4.4 |
| C52 | 8.72 | 1419.8 | 280.8 | 11096.3 | 11617.5 | 29.8 | 46.9 | 2.1 |
| C53 | 7.40 | 1027.0 | 203.2 | 10311.5 | 65588.9 | 27.0 | 36.8 | 2.5 |
| C54 | 5.61 | 415.8 | 1224.8 | 8926.3 | 21446.7 | 31.3 | 30.4 | 2.6 |
| C55 | 12.81 | 2814.4 | 2186.0 | 6843.7 | 67463.5 | 76.7 | 10.4 | 2.8 |
| C56 | 4.30 | 599.8 | 1732.3 | 7076.8 | 22915.7 | 85.6 | 11.9 | 1.1 |
| C57 | 6.27 | 1112.3 | 2881.2 | 6986.5 | 48193.3 | 62.1 | 5.5 | 3.6 |
| C58 | 11.90 | 2198.5 | 2778.8 | 6851.0 | 37707.8 | 65.1 | 10.6 | 3.5 |
| C59 | 11.10 | 3777.3 | 717.0 | 6388.3 | 32868.0 | 98.6 | 1.3 | 0.7 |
| C60 | 18.42 | 3384.5 | 2985.2 | 7114.7 | 22787.7 | 81.2 | 10.1 | 1.3 |
| C61 | 3.39 | 285.0 | 1275.0 | 7134.8 | 60620.8 | 18.48 | 26.22 | 7.3 |
| C62 | 3.33 | 89.3 | 402.5 | 5809.2 | 11295.5 | 66.8 | 36.0 | 8.5 |
| C63 | 7.60 | 1426.0 | 878.0 | 11020.8 | 13722.7 | 17.7 | 50.4 | 6.6 |
| C64 | 2.80 | 603.5 | 3598.3 | 4765.0 | 100876.3 | 82.5 | 2.3 | 3.2 |
| G1 | 1.16 | 53.5 | 365.0 | 7469.0 | 2404.5 | 71.5 | 11.9 | 0.9 |
| G2 | 26.00 | 2250.5 | 722.5 | 7958.9 | 2637.3 | 66.4 | 15.1 | 1.3 |
| G3 | 1.20 | 16.8 | 1665.0 | 9503.5 | 10836.0 | 36.4 | 18.4 | 5.1 |
| G4 | 5.93 | 1493.1 | 1651.0 | 8996.8 | 16922.6 | 73.5 | 1.5 | 3.4 |
| G5 | 39.40 | 13292.4 | 1867.3 | 8031.9 | 14545.1 | 84.8 | 9.7 | 1.3 |
| G6 | 20.20 | 4335.6 | 1965.9 | 7117.1 | 16504.9 | 85.2 | 0.03 | 2.0 |
| G7 | 2.52 | 701.8 | 1182.4 | 7924.4 | 13194.1 | 86.8 | 3.6 | 2.6 |
| G8 | 13.14 | 2809.0 | 427.0 | 8345.6 | 15177.0 | 86.2 | 9.2 | 0.7 |
| G9 | 15.66 | 5213.2 | 1054.8 | 7365.6 | 18206.8 | 87.5 | 9.4 | 1.3 |
| G10 | 1.92 | 279.6 | 481.0 | 7681.1 | 8926.3 | 39.9 | 1.1 | 2.6 |
| G11 | 42.70 | 10059.5 | 410.9 | 7889.4 | 2583.4 | 79.1 | 12.3 | 1.9 |
| G12 | 32.00 | 8052.7 | 1034.8 | 8584.9 | 6700.8 | 87.8 | 6.7 | 1.3 |
| G13 | 55.90 | 6557.5 | 1519.0 | 8968.6 | 16899.1 | 63.8 | 18.7 | 1.7 |
| G14 | 58.40 | 6251.0 | 1929.9 | 8015.9 | 14537.0 | 43.4 | 0.21 | 1.8 |
| G15 | 16.01 | 1798.4 | 1977.6 | 7191.0 | 17084.4 | 66.3 | 6.6 | 1.3 |
| G16 | 34.50 | 4599.5 | 410.9 | 7889.4 | 2583.4 | 30.1 | 8.3 | 4.4 |
| G17 | 39.70 | 5849.8 | 1034.8 | 8584.9 | 6700.8 | 60.6 | 4.2 | 1.4 |
| G18 | 41.80 | 9961.4 | 1519.0 | 8968.6 | 16899.1 | 85.4 | 9.7 | 1.6 |
| G19 | 69.80 | 10858.8 | 1929.9 | 8015.9 | 14537.0 | 63.0 | 0.8 | 6.0 |

*Via PXRF*

| Sample | EC | Cl | S | K | Ca | Sand | Clay | LOI |
|---|---|---|---|---|---|---|---|---|
| | ---dS m$^{-1}$--- | --------------------mg kg$^{-1}$------------------ | | | | ----------------%---------------- | | |
| G20 | 79.70 | 23142.6 | 1977.6 | 7191.0 | 17084.4 | 6.8 | 5.5 | 11.1 |
| G21 | 46.00 | 5962.9 | 393.4 | 7947.9 | 2486.9 | 39.9 | 2.6 | 4.5 |
| G22 | 11.30 | 1330.0 | 692.3 | 8157.8 | 4649.3 | 73.7 | 1.0 | 1.6 |
| G23 | 44.50 | 5460.5 | 1637.8 | 9097.1 | 15081.6 | 60.7 | 17.7 | 3.6 |
| G24 | 42.20 | 8912.3 | 1804.2 | 8470.2 | 14919.3 | 85.9 | 0.6 | 1.4 |
| G25 | 28.90 | 4414.8 | 1962.2 | 7676.8 | 17107.5 | 75.8 | 1.2 | 1.3 |
| G26 | 25.30 | 5155.8 | 462.2 | 7526.7 | 2307.8 | 74.9 | 9.7 | 2.6 |
| G28 | 0.75 | 175.7 | 315.8 | 8288.8 | 2592.8 | 81.0 | 10.9 | 1.1 |
| G29 | 20.50 | 2661.5 | 617.2 | 7721.7 | 2607.0 | 62.1 | 17.1 | 4.2 |
| G30 | 30.20 | 3086.5 | 1754.5 | 9258.3 | 10903.3 | 30.1 | 10.5 | 2.3 |
| G31 | 30.10 | 2630.8 | 1249.2 | 9047.3 | 18867.0 | 24.7 | 15.0 | 4.3 |
| G32 | 49.70 | 4371.3 | 1996.5 | 8088.2 | 13558.2 | 72.7 | 2.2 | 5.1 |
| G33 | 58.70 | 9602.8 | 2249.7 | 7496.0 | 18089.8 | 63.4 | 0.02 | 3.4 |
| G34 | 57.70 | 7749.8 | 1517.0 | 6947.8 | 14941.7 | 70.5 | 4.5 | 2.3 |
| G35 | 33.40 | 4781.3 | 1472.5 | 7206.5 | 14621.8 | 66.6 | 0.7 | 2.7 |
| G36 | 53.40 | 4800.0 | 748.0 | 8455.2 | 10738.5 | 63.5 | 6.8 | 6.7 |
| G37 | 26.10 | 3592.3 | 361.0 | 7752.7 | 7083.0 | 33.1 | 3.7 | 0.9 |
| G38 | 1.98 | 1654.5 | 664.3 | 8988.2 | 23623.7 | 13.2 | 21.5 | 3.7 |
| G39 | 46.20 | 8172.0 | 892.8 | 7690.0 | 22863.7 | 76.1 | 23.8 | 1.8 |
| G40 | 48.20 | 6508.3 | 1071.5 | 6966.8 | 13482.3 | 76.1 | 23.8 | 2.8 |

# APPENDIX C: SAS CODE FOR SINGLE AND MULTI LINEAR REGRESSION

Simple Linear Regression, $Ca_{lab}$ and $Ca_{PXRF}$:

```
dm 'log;clear;output;clear';
options nodate nocenter pageno = 1 ls=78 ps=53;
data gypsum;
Input Sample $ Calab CaPXRF;
LCalab=log(Calab); cards;
proc print data=gypsum; run;
proc plot data=gypsum; plot LCalab*CaPXRF; run;
proc reg data=salinity; model LCalab=CaPXRF / clb cli clm influence;
OUTPUT out=outdata p=predicted r=resid cookd=cooksd dffits=diffits H=hat
student=student rstudent=rstudent lclm=lclm uclm=uclm lcl=ccl ucl=ucl; run;
proc print data=outdata; var LCalab predicted resid student rstudent; run;
proc plot data=outdata; plot resid*predicted; run;
proc univariate data=outdata normal plot; var resid; run;
```

Simple Linear Regression, $gypsum_{lab}$ and $S_{PXRF}$:

```
dm 'log;clear;output;clear';
options nodate nocenter pageno = 1 ls=78 ps=53;
data gypsum;
Input Sample $ gypsumlab SPXRF;
Lgypsum=log(gypsumlab); LSPXRF=log(SPXRF); cards;
proc print data=gypsum; run;
proc plot data=gypsum; plot Lgypsum*LSPXRF; run;
proc reg data=gypsum; model Lgypsum=LSPXRF / clb cli clm influence;
OUTPUT out=outdata p=predicted r=resid cookd=cooksd dffits=diffits H=hat
student=student rstudent=rstudent lclm=lclm uclm=uclm lcl=ccl ucl=ucl; run;
proc print data=outdata; var Lgypsum predicted resid student rstudent; run;
proc plot data=outdata; plot resid*predicted; run;
proc univariate data=outdata normal plot; var resid; run;
```

Multiple Linear Regression, $Gypsum_{lab}$ and $Ca_{PXRF} + S_{PXRF}$

```
dm 'log;clear;output;clear';
options nodate nocenter pageno = 1 ls=78 ps=53;
data gypsum;
Input Sample $ gypsum S Ca;
Lgypsum=log(gypsum); cards;
proc print data=gypsum; run;
proc plot data=gypsum;
plot Lgypsum*S;
plot Lgypsum*Ca; run;
proc reg data=gypsum; model Lgypsum=S Ca / clb cli clm influence;
```

OUTPUT out=outdata p=predicted r=resid cookd=cooksd dffits=diffits H=hat
student=student rstudent=rstudent lclm=lclm uclm=uclm lcl=ccl ucl=ucl; **run**;
**proc print** data=outdata; var Lgypsum predicted resid student rstudent; **run**;
**proc plot** data=outdata; plot resid*predicted; **run**;
**proc univariate** data=outdata normal plot; var resid; **run**;

Multiple Linear Regression, Gypsum$_{lab}$ and Ca$_{PXRF}$ + S$_{PXRF}$

dm 'log;clear;output;clear';
options nodate nocenter pageno = **1** ls=**78** ps=**53**;
**data** gypsum;
Input Sample $ gypsum S Ca;
Lgypsum=log(gypsum);
LCa=log(Ca); LS=log(S); cards;
**proc print** data=gypsum; **run**;
**proc plot** data=gypsum;
plot Lgypsum*LS;
plot Lgypsum*LCa; **run**;
**proc reg** data=gypsum; model Lgypsum=LS LCa / clb cli clm influence;
OUTPUT out=outdata p=predicted r=resid cookd=cooksd dffits=diffits H=hat
student=student rstudent=rstudent lclm=lclm uclm=uclm lcl=ccl ucl=ucl; **run**;
**proc print** data=outdata; var Lgypsum predicted resid student rstudent; **run**;
**proc plot** data=outdata; plot resid*predicted; **run**;
**proc univariate** data=outdata normal plot; var resid; **run**;

Simple Linear Regression, EC$_{lab}$ and Cl$_{PXRF}$:

```
dm 'log;clear;output;clear';
options nodate nocenter pageno = 1 ls=78 ps=53;
data salinity;
Input Sample $ EC Cl;
LEC=log(EC); LCl=log(Cl); cards;
proc print data=salinity; run;
proc plot data=salinity; plot LEC*LCl; run;
proc reg data=; model LEC=LCl / clb cli clm influence;
OUTPUT out=outdata p=predicted r=resid cookd=cooksd dffits=diffits H=hat
student=student rstudent=rstudent lclm=lclm uclm=uclm lcl=ccl ucl=ucl; run;
proc print data=outdata; var LEC predicted resid student rstudent; run;
proc plot data=outdata; plot resid*predicted; run;
proc univariate data=outdata normal plot; var resid; run;
```

Multiple Linear Regression, EC and Cl$_{PXRF}$ + S$_{PXRF}$+ K$_{PXRF}$+ Ca$_{PXRF}$

```
dm 'log;clear;output;clear';
options nodate nocenter pageno = 1 ls=78 ps=53;
data salinity;
Input Sample $ EC Cl K S Ca;
LEC=log(EC);
LCl=log(Cl); LS=log(S);
LK=log(K); LCa=log(Ca); cards;
proc print data=salinity; run;
proc plot data=salinity;
plot LEC*LCl; plot LEC*LS; plot LEC*LK; plot LEC*LCa; run;
proc reg data=salinity; model LEC=LCl LS LK LCa / clb cli clm influence;
OUTPUT out=outdata p=predicted r=resid cookd=cooksd dffits=diffits H=hat
student=student rstudent=rstudent lclm=lclm uclm=uclm lcl=ccl ucl=ucl; run;
proc print data=outdata; var LEC predicted resid student rstudent; run;
proc plot data=outdata; plot resid*predicted; run;
proc univariate data=outdata normal plot; var resid; run;
```

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## THE VITA

Samantha Swanhart was born and raised in Tampa, FL. She completed her B.S. in Agricultural Education at University of Florida in Gainesville, Florida with a minor in Soil and Water Science. Upon completion of a teaching internship, she immediately entered her master's program at Louisiana State University under Dr. David C. Weindorf in Plant, Environmental, and Soil Science. The title of her thesis is, "Measuring Soluble Salts in Soils via Portable X-ray Fluorescence Spectrometry." She is currently employed with Talbot, Carmouche & Marcello reviewing documents subpoenaed from oil companies including soil test data and geologic reviews, build maps with GIS software, and visit sites operated by defendant companies to assist environmental consultants.