QUANTIFICATION OF SOIL ORGANIC CARBON USING MID- AND

NEAR-DRIFT SPECTROSCOPY

A Thesis

by

MISUN KANG

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2002

Major Subject: Geology

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Approved as to style and content by:

Bruce E. Herbert (Chair of Committee)	Hongbin Zhan (Member)
John W. Morse (Member)	Richard H. Loeppert (Member)
Andrew Hajash (Department Head)	

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ABSTRACT

Quantification of Soil Organic Carbon Using Mid- and

Near-DRIFT Spectroscopy. (August 2002)

Misun Kang, B.S., Korea University

Chair of Advisory Committee: Dr. Bruce Herbert

New, rapid techniques to quantify the different pools of soil organic matter (SOM) are needed to improve our understanding of the dynamics and spatio-temporal variability of SOM in terrestrial ecosystems. In this study, total organic carbon (TOC) and oxidizable organic-carbon (OC_{WB}) fraction were calibrated and predicted by mid- and near-DRIFT spectroscopy in combination with partial least squares (PLS) regression method. PLS regression is a multivariate calibration method that can decompose spectral data (X) and soil property data (Y) into a new smaller set of latent variables and their scores that best describe all the variance in the data. Oxidizable organic-carbon content was measured by a modified Walkley-Black method, and total organic carbon was measured by the carbon analyzer.

The floodplain and Blackland Prairie soils in Texas were used for prediction of TOC and OC_{WB} using mid- and near-DRIFT spectroscopy. Floodplain soil is mainly composed of quartz and kaolinite, whereas Blackland Prairie soils contain high concentrations of smectitic clays and low to high concentrations of carbonate minerals. The total organic carbon of 68 soil samples from two Texas sites varied between 0.19

and 4.36 wt.% C, and the oxidizable organic carbon of 26 samples from floodplain soils was in the range of 0.05 to 1.33 wt.% C.

TOC and OC_{WB} of soil were successfully calibrated and predicted by the PLS regression method using mid- and near-DRIFT spectroscopy. The correlation using mid-IR spectra for TOC (r = 0.96, RMSEV = 0.32 for calibration; r = 0.93, RMSEP = 0.44 for prediction) was about the same as the near-IR result (r = 0.95, RMSEV = 0.37; r = 0.93, RMSEP = 0.42). Therefore, we can also use mid-infrared region for quantification of total organic carbon in soils. The PLS1 regression model (r = 0.92) for prediction of OC_{WB} using mid-IR spectra was more accurate than the PLS2 regression model (r = 0.90). PLS models showed better correlation with spectral data than the univariate least square regression method(r = 0.83) with TOC measured by the carbon analyzer.

This study shows that the partial least squares (PLS1) method using mid-and near-IR spectra of neat soil samples can be used to predict both total organic carbon and oxidizable organic-carbon fraction as a fast and routine quantitative method.

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Thanks to my committee, Dr. Hongbin Zhan, Dr. John Morse, and Dr. Richard Loeppert, for providing valuable insight into my work. Special appreciation is expressed to Steve Sweet (GERG) and Robert Blaisdell (Department of Rangeland Ecology and Management) who analyzed TOC of the soil samples studied, and to Dr. Jonathan Phillips (Kentucky University) and Robert Blaisdell for providing soil samples. Mineralogical study of floodplain soil samples was done in soil mineralogy class, which was offered by Dr. Joe Dixon and Dr. Norman White. I also want to express my appreciation to Lai Man Lee and Dr. Andreas Kronenberg who taught me to use instruments necessary for this study.

This work was done with the guidance and support of my graduate advisor, so I would like to thank my graduate advisor, Dr. Bruce Herbert.

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CHAPTER I

INTRODUCTION

Soil organic matter consists of a mixture of plant and animal residues in various stages of decomposition, of substances synthesized microbially or chemically from the breakdown products, of exudates from plant root systems, and of the remains, and living bodies of soil microorganisms (Schnitzer et al., 1991). Soil organic matter has a great influence on the physical (soil structure and porosity), chemical (complexing agent, sorbent), and biological (source of nutrients to plant and microorganisms) properties of soils. Soil organic carbon also plays an important role of the global C cycle (Schlesinger, 1990).

Soil organic carbon can be roughly divided into labile or active organic carbon and recalcitrant organic carbon fractions. The first model of soil organic matter dynamics divided soil C into three pools that have different turnover times including active (1 yr.), slow (30 yr.) and passive (1500 yr.) pools (Jenkinson and Rayners, 1977). The most recalcitrant portion of soil organic carbon is black carbon. Black carbon (BC) is produced by incomplete combustion of plants, woods, and fossil fuels where oxygen supply is limited at the temperature between 200°C and 500°C. Black carbon is widely distributed in the environment, including aerosols, sediments, and soils. It has been shown that BC is a substantial fraction of total organic carbon in some soils (Skjemstad

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This thesis follows the style of Journal of Environmental Quality.

et al., 1996).

Black carbon is chemically very resistant to weathering, can persist in soils for centuries, or millennia. Seiler and Crutzen (1980) suggested that only limited degradation of charcoal would take place with time through microbial or chemical degradation. Its chemical inertness at low temperatures, light-absorbing, and surface sorptive properties can be important in geological, ecological, and environmental disciplines. Black carbon distribution in the sedimentary record has been used as a record of forest fires and fossil fuel emissions (Griffin and Goldberg, 1983; Herring, 1985), and past atmospheric oxygen content (Cope and Chaloner, 1980). Black carbon strongly sorbs organic contaminants in natural environmental systems (Gustaffson et al., 1997). Consequently, the distribution of black carbon in surface sediments significantly affects the distribution, speciation, and bioavailability of polycyclic aromatic hydrocarbons (PAHs) and other nonionic organic contaminants.

Humic substances (HA), including fulvic acid, humic acid, and humin are usually considered as a refractory part of natural organic matter. Fillip and Berthelin (2001), however, showed that humic acids readily undergo microbial utilization as carbon and nitrogen sources, especially when easily utilizable nutrients are limited. Only small portions of HA were found to resist microbial degradation in the short-term experiment.

The labile organic C pool does not correspond to any single physical or chemical fraction of soil organic matter, but refers to a readily metabolized soil organic matter (SOM) component. The biologically active carbon pool is considered to be a key to soil

productivity and a major soil nutrient reservoir (Wander et al., 1994). Decomposition of SOM is characterized by gradual changes in C functional groups. Mineralization of important inorganic nutrient elements also occurs as SOM decomposes.

Considerable work has been done in characterizing and classifying different fractions of SOM in soils because understanding the dynamics of soil organic carbon is important in the characterization of soil quality and terrestrial ecosystems. Because of the complexity of SOM, fractions or pools of soil carbon are operationally defined. Most quantification techniques are laborious an expensive. New, rapid techniques to quantify the different pools of SOM are needed to improve our understanding of the dynamics and spatio-temporal variability of SOM in terrestrial ecosystems.

PREVIOUS WORK

Several different techniques have been used to quantify SOM. Total soil organic matter has been estimated following the mass change with a loss-on-ignition method. Soil organic matter has also been quantified as total organic C as determined by Walkley-Black method or dry combustion methods. Walkley and Black (1934) obtained average recovery rate of 76% of total soil organic carbon using dichromate oxidation, equivalent to a correction factor of 1.32. Several researchers found high correlations between the Walkley-Black and dry combustion methods. Recovery rate, however, is known to vary with soil depth and with the amount of more resistant organic matter in soil (Walkley, 1947; Certini et al., 2002). The automatic carbon analyzer has been widely used to measure soil carbon quantities.

Methods for the most recalcitrant carbon fraction (black carbon) determination have been based on distinguishable optical, chemical, and thermal properties of black carbon compared to other carbon forms. Lim and Cachier (1996) extracted black carbon from sediment using dichromate oxidation. Infrared spectroscopy has been used for qualitative characterization of coal, charcoal, and pure soot-BC (Bustin and Guo, 1999; Akhter et al., 1985a), but the technique has not been widely used to quantify BC in sediment and soils. Smith et al. (1975) measured black carbon by integrating the absorption from 1670 to 1400 cm^{-1} using transmission IR spectroscopy after removal of organic matter (KOH and hydrogen peroxide), inorganic carbon (HCl) and minerals (HF) in the sediments. Black carbon in soil fractions can be mistakenly determined as part of the colloidal organic carbon by conventional methods in soil organic matter analysis. This black carbon can be considered a serious source of contamination in the study of organic carbon in soils. Due to the heterogeneity and complexity of BC, there is no generally accepted analytical technique, and only limited progress has been made to quantifying the black carbon content in sediment and soils.

A number of methods have been used to assess labile soil carbon pools including physical fractionation techniques, chemical extractions, and procedures based on soil biological activity (Ellert and Gregorich, 1995). Physical fractionation of soil organic matter based upon density or size has been achieved using different liquids of densities between 1.6 and 2.2 g/cm^{-3} or sieving and sedimentation. These techniques can provide useful information on the labile soil C pool, but there is still no accord on the specific techniques for separating labile soil carbon. Among the chemical methods used for

measuring labile soil carbon, oxidation, acid hydrolysis, and water extraction are the common techniques. Most of these methods may not always be useful to assess labile soil carbon fraction. Biological fractionation is determined by microbial biomass or root biomass. Recently, spectral studies were successfully used for the investigation of decomposition processes of forest litter layers (Haberhauer and Gerzabek, 1999).

Near-infrared (NIR) spectroscopy has become well established in food and agricultural products industries (Wetzel, 1983). Over the past 30 years, NIR-spectroscopic techniques have been developed as a major quantitative tool for the simultaneous prediction of the moisture, organic carbon, and total N contents of soils (Dalal and Henry, 1986; Morra et al., 1991; Reeves et al., 1999; Salgó et al., 1998). Recently, Mid-infrared spectroscopy also has been investigated as a technique to quantify total organic carbon of bulk soil samples (Janik and Skjemstad, 1995; McCarty et al., 2002). Multivariate statistical methods such as multiple linear-regression (MLR), principal components regression (PCR), and partial least squares (PLS) has been applied to all spectroscopic studies with variable degrees of success.

CHEMOMETRICS

Quantitative infrared analysis was historically based on the height or the area of an isolated band. This univariate calibration method works reasonably well when the relationship between absorbance and concentration obeyed Beer's law at a selected wavelength, or when a standard calibration curve can be constructed.

The near-infrared spectral region initially appears to be a poor choice for

quantitative analysis. Because the highly overlapped overtone and combination bands of associated with C-H, N-H, and O-H bonds results in a spectral complexity that virtually defies the univariate calibration method using a selected peak. However, the extraction of useful information contained in optical spectra can be done using chemometric techniques such as multiple linear-regression (MLR) or other multivariate calibration methods such as principal component regression (PCR), and partial least squares (PLS) regression.

Multiple linear-regression (MLR) was developed by Bengera and Norris (1968a and 1968b) to determine moisture content in soybeans using NIR spectra. Multiple linear-regression handles nonlinearity by adding more terms to the equation. The added terms are chosen and scaled so that the nonlinearities cancel while a net linear sum is maintained.

$$C = e_0 + b_1 * A_1 + b_2 * A_2 + \ldots + b_n * A_n$$

where C is concentration, A_n is absorbance at wavelength n, e_0 is correction factor for interfering absorbances, b_n is coefficient. This implicit compensation allowed Norris to use diffuse reflectance on ground grain and oil seeds, providing simplicity of sample preparation and presentation that is a singularly important reason for the wide acceptance of NIR analysis.

The multiple linear-regression methods depend on selection of a limited set of analytical wavelengths and determination of suitable calibration coefficients to be applied to the data at these points. Alternative approaches, such as principal component analysis and partial-least-squares regression utilize all or large portions of the spectrum.

Principal components regression (PCR) is a two-stage process. First, it minimizes the number of independent components required to describe the variations across the entire spectrum and between spectra. This technique enables several thousand spectral points to be reduced to a few principal components (PCs), where the PCs describe the spectral variance across all the samples. Second, these PCs are regressed against known property data (measured concentration), and then calibration models constructed. These models are validated using separate independent and well-characterized samples to ensure they are robust enough to be used to predict property data from spectral information (Brereton, 1990).

Partial least squares (PLS) regression is a bilinear regression process developed by Wold and coworkers (Wold et al., 1989). It is similar to principal components regression (PCR) except that PLS regression uses both the spectral and known property data simultaneously during the calculation of the principal components. The spectral and known property data are projected onto a latent variable, and a second orthogonal variable is derived from the residuals. This process is repeated until the model is complete. The method has advantages in reducing noise, detecting unknown samples that are not represented by the calibration model, and obviating the need for wavelength selection.

In this work, PLS regression is used to interpret the IR spectral data following the construction of appropriate regression models.

RESEARCH OBJECTIVE

The objective of this study is to develop infrared spectroscopic methods that can predict total organic carbon and the oxidizable organic-carbon fraction using mid-DRIFT and near-DRIFT spectroscopy in combination with the PLS regression method. The labile or active organic carbon fraction is important in controlling many important ecological processes in soils.

In this study experimental objectives were as follows:

i) to investigate mineralogical composition of soils,

ii) to quantify TOC and oxidizable organic-carbon content in soils using the carbon analyzer and Walkley-Black methods, respectively,

iii) to analyze mid- and near-infrared spectra of neat soil samples using DRIFT spectroscopy ,

iv) to calibrate and predict TOC and oxidizable organic carbon combined with spectral data using the PLS regression method.

Oxidizable organic-carbon content was measured by a modified Walkley-Black method, and total organic carbon (TOC) was measured by the carbon analyzer. Mid- and near-DRIFT spectroscopic techniques were used to characterize soil components and to predict soil organic-carbon content.

CHAPTER II

QUANTIFICATION OF SOIL ORGANIC CARBON USING MID- AND NEAR-

DRIFT SPECTROSCOPY

INTRODUCTION

Soil is a heterogeneous combination of minerals, organic constituents, living organisms, liquids, and gases. Soil organic matter, an important constituent of soil, controls many physio-chemical characteristics of soils, affect important terrestrial ecological processes and acts as a dynamic carbon reservoir in the global carbon cycle (Schlesinger, 1990). Because of its extreme biochemical heterogeneity, soil organic matter is often fractionated into operationally defined fractions related to specific biogeochemical processes of interest (Herbert and Bertsch, 1995). This need has sparked a long history of research focused on the development of effective methods to fractionate, characterize, and quantify soil organic matter and its fractions.

Diffuse reflectance infrared Fourier-transform (DRIFT) spectrometry, which has been applied to investigate various solid materials because of simpler sample preparation, better resolution, and reduced interference from water in comparison to the transmission FT-IR technique, has been used to characterize and quantify natural soil organic matter (Baes and Bloom, 1989; Gressel et al., 1995). Organic matter absorbs the infrared (IR) light across the wide wavenumbers in the near- (4000 to 8000 cm^{-1}) and mid-IR (400-4000 cm^{-1}) regions due to heterogeneity of the structure with several functional groups. The strong absorption of IR light by soil minerals in the same regions can interfere in the IR-spectra of soil organic matter. Therefore, soil organic matter is

often characterized by minor peaks or by subtle changes to the infrared spectra of soil, such as peak broadening, frequency shifts, and intensity changes. The complexity of IR spectra of soil organic matter and highly overlapping bands with other mineral components in soil virtually defies the simple univariate calibration with a single selected peak. However, with development of chemometrics and spectroscopic techniques it is possible to construct a reliable calibration model to predict chemical and physical properties in soil.

Multivariate calibration techniques have been used successfully to extract information related to soil physical properties, organic matter and mineralogy from IR spectra of soils. Over the decades, near infrared spectroscopy has been extensively used for quantitative studies of various soil properties, such as moisture, total N, and total C (Chang and Laird, 2002; Dalal and Henry, 1986; Morra et al., 1991; Reeves et al., 1999; Salgó et al., 1998).

Recently, researchers have investigated the quantification of total organic carbon of bulk soil samples using mid-DRIFT spectroscopy. Janik and Skjemstad (1995) suggested that mid-infrared spectra of soils could be used to accurately predict a range of soil properties including total C, CEC, and pH. Previous studies quantifying soil organic matter by mid–infrared spectroscopy diluted samples with KBr to reduce distortion of reflectance spectra at high concentration of a certain component. Recent work has demonstrated that good quantitative measurements of total organic carbon across various soil types are possible in the mid-IR region with neat soil samples (McCarty et al., 2002).

Understanding the spatial and temporal dynamics of ecosystem processes in soils require rapid and accurate methods to quantify total organic carbon and specific fractions of organic matter, especially the more labile, reactive fractions. Current wet oxidation techniques, such as the Walkley-Black method (Walkley and Black, 1934) are toxic and expensive. It was hypothesized that both mid- and near-infrared spectra can be used for quantification of total organic carbon and oxidizable organic carbon. This experiment compared wet-oxidation and spectroscopic techniques to quantify TOC and oxidizable organic carbon in sets of soils from two areas in Texas.

Experimental objectives were i) to investigate mineralogical composition of soils, ii) to quantify TOC and oxidizable organic-carbon content in soils using the carbon analyzer and Walkley-Black method, respectively, iii) to analyze mid- and near-IR spectra of neat soil samples using DRIFT spectroscopy, iv) to calibrate and predict TOC and oxidizable organic carbon in combination with spectral data using PLS regression method.

MATERIALS AND METHODS

Soil samples

Two different soil sets were taken for this study, floodplain and Blackland Prairie soils having different soil properties. Floodplain soil samples (n = 26) were all collected on an alluvial floodplain on Loco Bayou in Nacogdoches county, Texas (Fig.1.). Loco Bayou is a tributary of the Angelina River in east Texas. Soil samples were collected from five different sites (LBL1, LBL2, LBL3, LBL4, and LBL5) as a function of depth

(Appendix I). X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were employed to identify mineral composition of LBL3 soil sample. The soil pH was measured by pH electrode with 1:1 soil to water ratio (Appendix II).

The second set of soil samples (n = 42) were collected in the Blackland Prairie in Texas (Fig.1). The Texas Blackland Prairie is part of the prairie system that stretches from southern Manitoba, Canada to the Gulf of Mexico. The main belt of the prairie runs in a north-south direction beginning as a narrow strip near San Antonio and widening for about 400 miles northward to the Red River. The three dominant soil orders in the Blackland Prairie are Vertisols (abundant smectitic clays with low to moderate carbonate), Mollisols (organic rich and high carbonate), and Alfisols (high in sands and low carbonate, not sampled). Information for soil classification is given in Appendix C. Only surface soil samples were collected for this study. FTIR was used for mineralogical study of Blackland Prairie soil samples.

Mineralogical study of the LBL3 soil sample from floodplain

The LBL3 soil sample from floodplain was selected for detailed mineralogical analysis. All procedures followed the lab manual written by Dixon and White (1997). The bulk soil samples was air-dried, ground, and sieved (<2 mm). The sand (2mm-50μm) fraction was initially sieved out using 270-mesh sieve after removal of carbonates and organic matter by sodium acetate and hydrogen peroxide, respectively.

B: BLACKLAND PRAIRIE
C: COASTAL SAND PLAIN
E: EDWARDS PLATEAU
G: GULF COAST PRAIRES & MARSHES
H: HIGH PLAINS
L: LAND UPLIFT
O: OAK WOODS & PRARIES
P: PINEY WOODS
R: ROLLING PLAINS
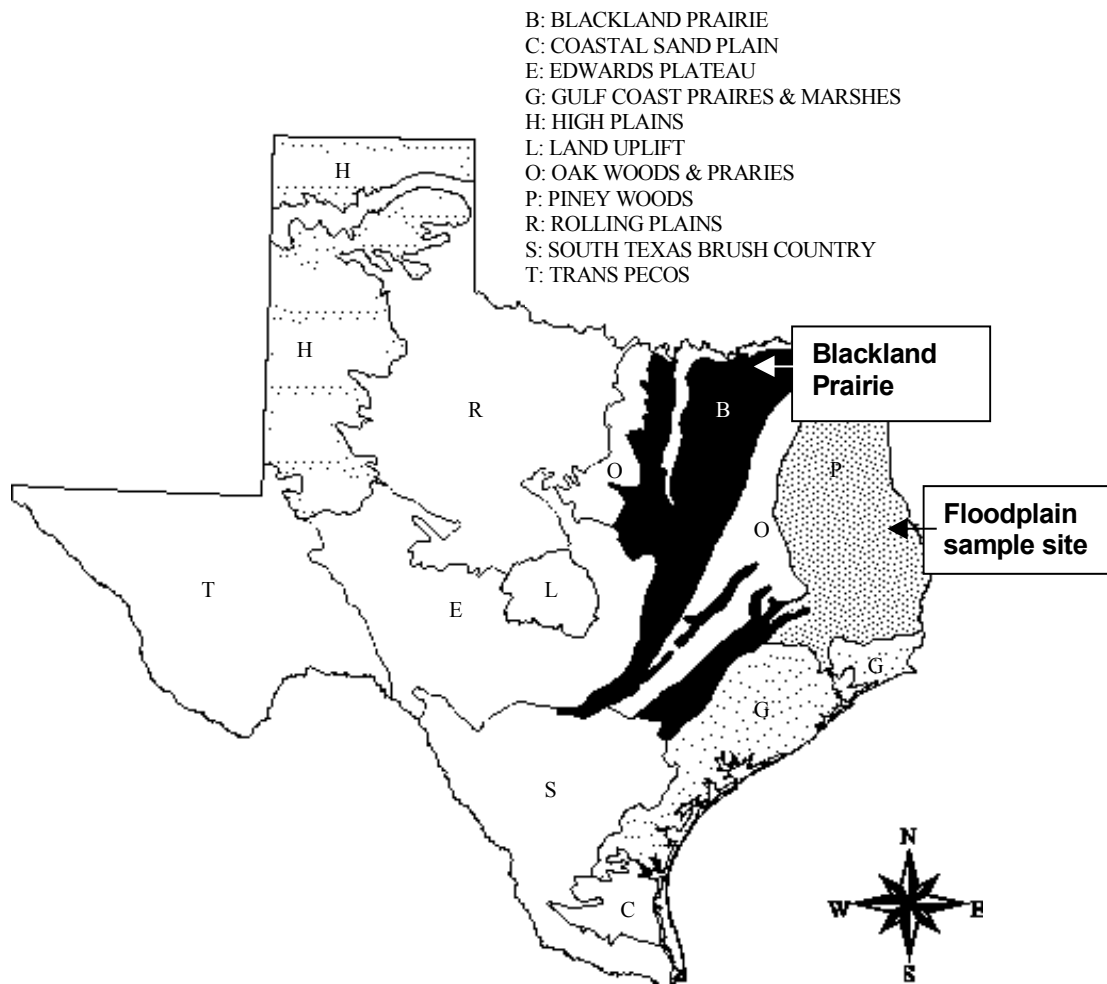S: SOUTH TEXAS BRUSH COUNTRY
T: TRANS PECOS

Figure 1a. Map of Texas showing the location of the Blackland Prairie and floodplain

sampling sites. Modified from Checklist of the vascular plants of Texas
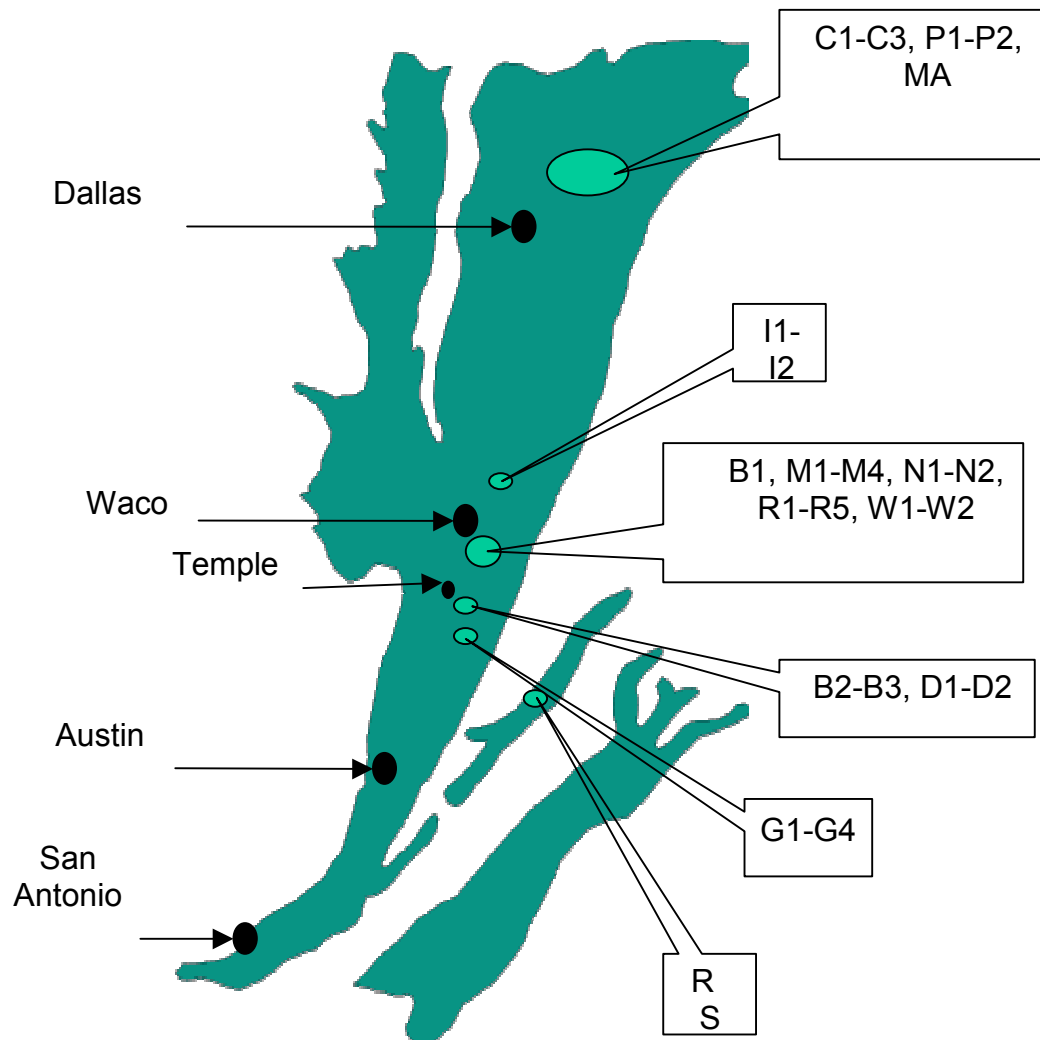
(Hatch et al., 1990).

Figure 1b. Map of Blackland Prairie showing site locations. Site codes are indexed in

the appendix III for detailed descriptions

The silt (50-2μm) and coarse clay (2-0.2μm) fractions were separated by centrifugation. The sand, silt, and coarse clay fractions were oven-dried and weighed. The fine clay (< 0.2μm) fraction was flocculated with NaCl, dialyzed, and freeze-dried. The recovery rate was calculated based on oven-dried weight.

X-ray diffraction (XRD) was used for the investigation of bulk soil, sand, silt, coarse clay, and fine clay fractions. Bulk soil, sand, and silt fractions were packed in the cavity of the aluminum plate holder and were scanned to 65° 2θ using graphite monochromated Cu Kα radiation for X-ray diffraction. The coarse clay and fine clay fractions were saturated with Mg and K before mounting on the slides. 150mg of each coarse clay and fine clay fraction were washed several times with 1N $MgCl_2$ and 1N KCl for the cation saturation. The Mg-saturated samples and K-saturated samples were then dried at room temperature on petrographic microscope slides and Vicor slides, respectively, and were investigated with X-ray diffraction. Additional aliquots of the Mg-saturated samples were reacted with glycerol. Heat treatments of the K-saturated slides were performed at 300 °C and 550°C. The samples of the silt fraction were resolved by a JEOL 6400 SEM and their chemical composition determined by concurrent energy-dispersive X-ray spectrometry (EDS). Grains of the silt fraction were mounted and coated with gold for scanning electron microscopy study. Coarse clay sample for TEM was prepared by diluting a well dispersed suspension in water until it was only slightly turbid. A drop of this diluted solution was placed on a copper-metal grid coated with a holey carbon film. The specimen was dried and investigated under a

JEOL 2010 TEM operated at 200kV. DRIFT spectroscopy in mid-IR region was examined for the coarse clay and fine clay fractions diluted with KBr.

TOC and OC$_{WB}$ analysis

The soil samples were oven-dried and sieved (<2mm) to remove plant debris and large root matter. Floodplain soil samples were thoroughly ground using an agate mortar and pestle and homogenized to reduce variability between replicates. Samples were weighed (about 3mg) in crucibles and in-situ acidified with 1M HCl to remove inorganic carbon and oven dried overnight. Total organic carbon (TOC) of oven dried samples were determined using a Leco carbon analyzer (LECO Model 521, Horiba PIR2000, and HP model 3390A Integrator). Total organic carbon of Black Prairie soil samples (about 10mg) was determined by a Carlo Erba NA 1500 Elemental Analyzer after removing inorganic carbon by acidification with 1M HCl. Before analysis, Blackland Prairie soils were dried for 2 weeks at 65º C and then pulverized using an Angiostrom model TE 250 ring pulverizer to make sure the sample is homogenous.

The oxidizable organic carbon was measured by a modified Walkely-Black method (Schulte, 1988) for 26 floodplain soil samples. Ten ml of 0.167M $K_2Cr_2O_7$ and 20mL H_2SO_4 (96%) were added to one gram of soil. After standing 30 minutes, the solution was diluted with 150ml water. Ten ml of 85% H_3PO_4 and 0.2g of NaF were added to the solution to complex Fe^{3+}, which would interfere with the titration endpoint. The solution was titrated with 0.5M Fe^{2+} after adding ferroin indicator. Reagent blanks without soil were run for each set of 6 titrations following the above procedure. The

concentrations of oxidizable organic carbon were calculated from the difference between titrant volume of a reagent blank and titrant volume of a sample. Duplicate was measured and averaged.

Mid- and near-DRIFT spectroscopy

All soil samples were sieved (<2mm) and ground with an agate mortar and pestle to reduce the particle size effect of reflectance spectra. Sample variation such as particle size and packing density can change the near-infrared spectra. The soil samples were oven-dried overnight at 65°C to reduce the moisture level in soil, which shows strong peaks in both the mid-IR and near-IR range. The stainless steel sample cup was filled with neat soil sample without dilution with KBr, and the sample surface was leveled with a flat spatula. The mid-IR spectra were collected by Nicolet 560 equipped with DTGS-KBr detector. The spectra were recorded from 4000 to 400 cm^{-1} by 100 scans at 8 cm^{-1} resolution. The near-IR spectra were collected by Nicolet 560 with white light source and PbS detector. The spectra were recorded in the range of 3800 to 7800 cm^{-1} (1351 to 2632 nm) with 100 scans and 8 cm^{-1} resolution. All spectra were corrected against the spectrum with ambient air as background.

The spectra of the main mineral components of soil such as silica gel, kaolinite and smectite, which are main interference of the quantification using univariate or multivariate analysis of organic matter of soils, were also collected.

Calibration method

The multivariate analysis was done by The UNSCRAMBLER[TM] version 7.6 (CAMO AS, U.S.A). Partial least squares (PLS) regression was employed to quantify organic carbon content of soil (both total organic carbon and oxidizable organic carbon) from mid-IR and near-IR spectra. PLS regression is a multivariate calibration method that can decompose spectral data (X) and soil property data (Y) into a new smaller set of latent variables and their scores that best describe all the variance in the data (Haaland and Thomas, 1988; Wold et al. 2001). Spectral data were pretreated using various transformation techniques such as baseline correction, normalization, and derivatives to correct undesirable spectral distortion due to scattering and other environmental factors and to select the best calibration model. The spectral data pre-processing using these transformation techniques made a limited improvement in the regression results. Therefore, no-pretreated data was used to make the calibration model using PLS1 and PLS2 with entire wavelengths taken by DRIFT spectroscopy. PLS1 method performs calibration and prediction analyses of one component at a time, whereas PLS2 method can calibrate and predict two or more components simultaneously.

Full cross-validation (leave-one-out approach) and mean centering were performed for both PLS1 and PLS2 regression to verify the calibration model. In full cross-validation, one sample from all n samples within a data set is consecutively kept out during the calibration and n-1 samples were utilized to build the regression model. Based on this calibration model, the concentration of the sample that was not used in developing the calibration model was predicted. This procedure was repeated until

concentrations of all n samples have been predicted (Haaland and Thomas, 1988). Optimum number of PLS factors (principle components) was determined by full cross-validation. The accuracy of the calibration model is described by the correlation coefficient (r), the root mean square error of calibration (RMSEC), and root mean square error of prediction (RMSEP). RMSEC and RMSEP represent the average difference between predicted and measured response values at calibration and validation stage, respectively.

RESULTS AND DISCUSSION

Characteristics of soils

LBL3 soil has a loam texture (34% sand, 49% silt, 7% coarse clay, and 10% fine clay) (Table 1). The mineral composition of LBL3 soil is mainly composed with quartz and kaolinite with small amounts of mica, K-feldspar, zircon, smectite, and goethite. Quartz was the most abundant mineral in the sand (2mm-50μm) and silt (50-2μm) fractions. Mica, K-feldspar, zircon, anatase, opal, and quartz in the silt fraction were identified with SEM/EDS. The XRD, TEM, and FTIR of the coarse clay fraction showed that smectite, mica, kaolinite, goethite, and quartz were present in the coarse clay fraction (2–0.2μm). The presence of smectite, mica, kaolinite, and goethite in the fine clay fraction (<0.2μm) was confirmed with XRD and FTIR (Appendix V). Mineralogy of the LBL3 soil sample is summarized in Table 1. The Blackland Prairie soil samples have clay texture and are dominated by smectitic clay minerals, and have low to high carbonates content. Figure 2 shows that the IR absorption intensities at 2513 cm^{-1} and 1796 cm^{-1}

Table 1. Mineralogy of the LBL3 soil sample from floodplain.

Fraction	Recovery rate (%)	Mineralogy [a]
Sand (2 mm–50 μm)	34	Q, K, M, F
Silt (50 μm–2 μm)	49	Q, K, M, F, A, O, Z
Coarse Clay (2μm–0.2μm)	7	Q, K, M, S, G
Fine Clay (< 2 μm)	10	K, M, S, G

[a] Q: quartz, K: kaolinite, M: mica, F: feldspar, S: smectite, A: anatase,

O: opal, G: goethite, Z: zircon

Table 2. Characteristics of all soil samples studied

Property	# sample	Mean	Standard deviation	Range
TOC[a], wt.%	68	1.73	1.17	0.19 - 4.36
OC_{WB}[b], wt.%	26	0.43	0.32	0.05 - 1.33

[a] organic carbon wt.% measured by the carbon analyzer

[b] organic carbon wt.% by a modified Walkley Black method
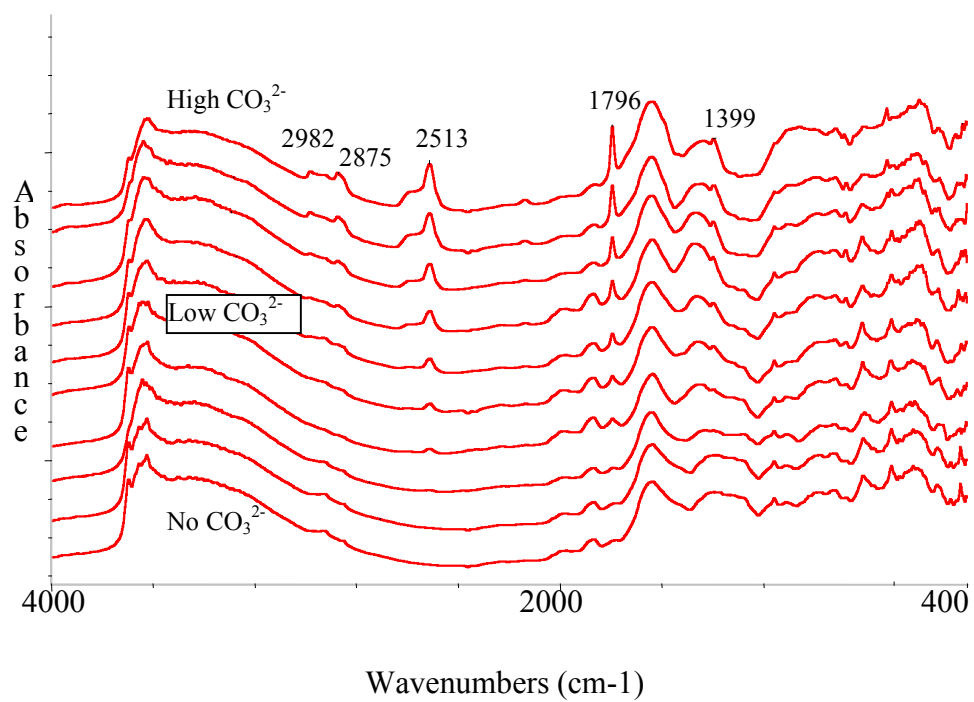
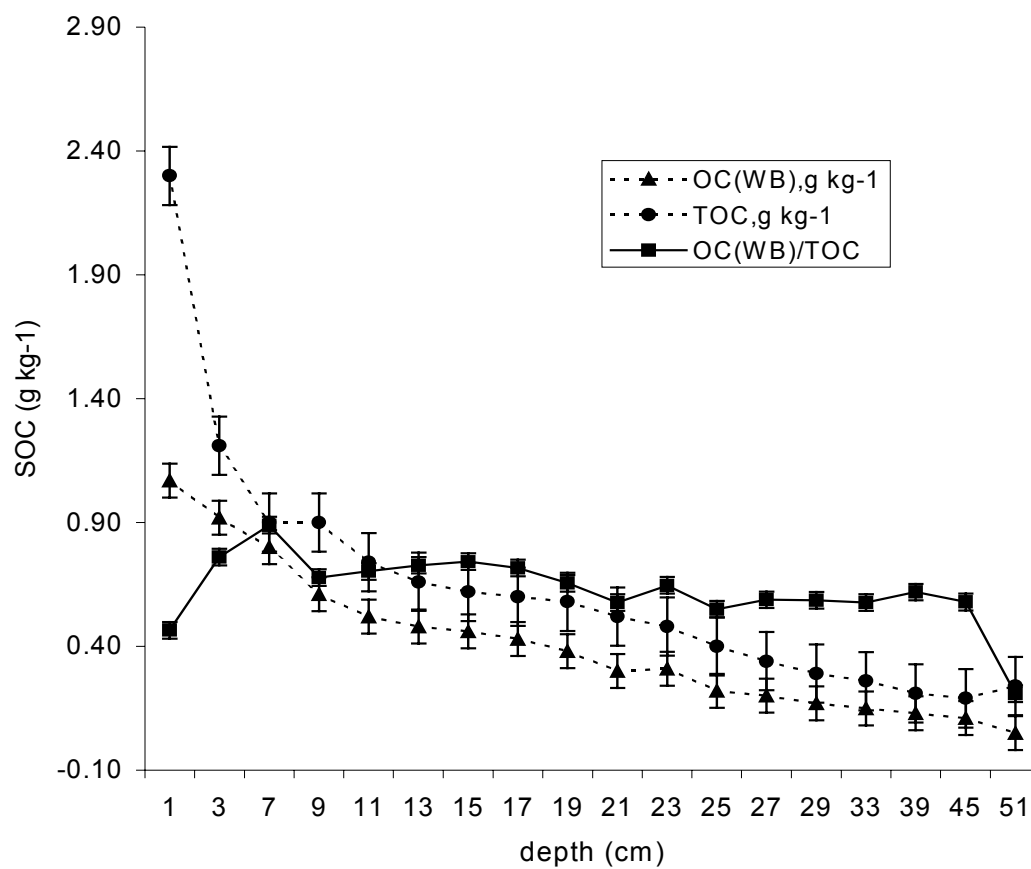Figure 2. Blackland Prairie soils containing low to high concentrations of calcium carbonates

Figure 3. Total organic carbon (TOC), oxidizable organic carbon (OC$_{WB}$), and OC$_{WB}$ to

TOC ratio with depth (cm) at the site LBL3 from floodplain.

peak increase as carbonate content increases. This peak can be used to detect the presence of carbonate minerals in soil, or to confirm the complete carbonate removal with acid before TOC analysis. As shown in Table2, the total organic carbon of 68 soil samples from both floodplain and Blackland Prairie varied between 0.19 and 4.36 wt.% C, and the oxidizable organic carbon (OC_{WB}) of 26 samples from the floodplain ranged from 0.05 to 1.33 wt.% C. Individual TOC and OC_{WB} values of all samples are given in Appendix II (floodplain soils) and III (Blackland Prairie soils). Figure 3 shows that total soil organic-carbon and oxidizable organic-carbon contents of the LBL3 of floodplain soils decreased with depth. The oxidizable organic carbon to total organic carbon ratio of the LBL3 floodplain soil increased with depth to 7cm, is nearly constant to depth 45cm, and then decreased. These trends might be caused by more abundant plant residues in the upper layers leading to high TOC values and an accumulation of fulvic acids having lower molecular weights in deeper layers (Bornemisza et al., 1979) or exudates of roots of plants in the root zone (rhizosphere).

Mid-IR and near-IR spectra

Mid- and near- IR spectra were dominated by the relatively strong intensities representing main constituent minerals, such as quartz, kaolinite (floodplain soils), and smectite (Blackland Prairie soils). Mid-IR spectra of floodplain (LBL3-1) and two Blackland Prairie surface soils (W1-1F-1 and P2-6F-2) showed obvious differences (Fig. 4). One of Black Prairie soil samples (W1-1F-1) shows strong absorption at 2513 cm^{-1}, 1796 cm^{-1} and 1455 cm^{-1}due to carbonate minerals and broad peaks in the 3600 cm^{-1} and
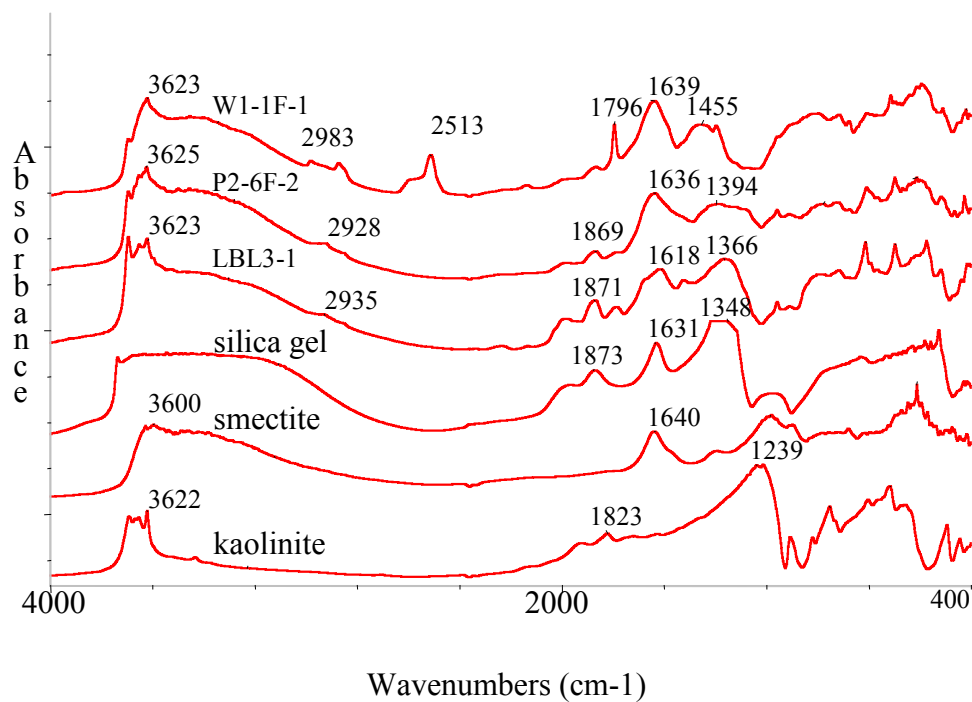
Figure 4. Mid-IR spectra of 2 Blackland Prairie surface samples (W1-1F-1, P2-6F-2), 1

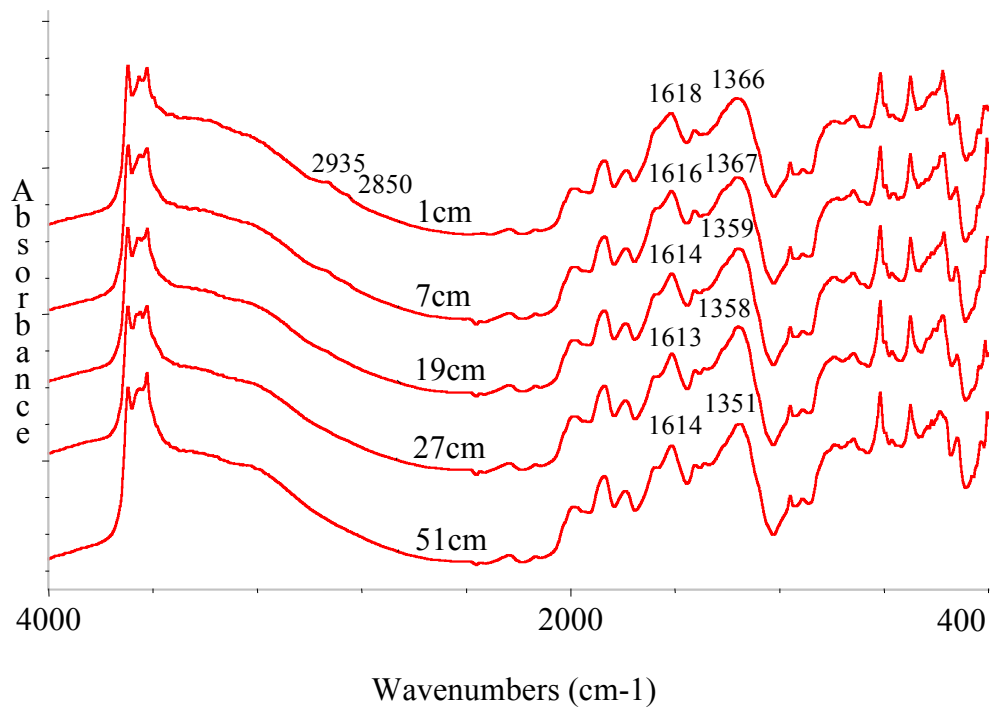floodplain surface sample (LBL3-1), and reference minerals.

Figure 5. Mid-IR spectra of the LBL3 soil samples with selected depths.

1640 cm^{-1} region due to the high smectitic clay mineral content, whereas the P2-6F-2 Blackland Prairie sample lacks peaks at 2513 cm^{-1} and 1796 cm^{-1} peaks, indicating limited carbonates in these samples. The floodplain soil shows sharp peaks at 3697, 3654, and 3623 cm^{-1} (O-H stretching vibration) due to kaolinite, strong absorption at 1366 cm^{-1} (O-Si-O vibration) due to quartz, and no absorption at 2513cm^{-1} indicating no carbonate minerals.

Organic matter absorbed the IR light over a wide range of frequencies due to heterogeneity of structure with several functional groups. Stevenson (1994) reported that the main absorption bands of humic substances extracted from soil are in the region 3400-3300 cm^{-1} (O-H stretching), 2940-2900 cm^{-1} (aliphatic CH_3, CH_2 stretching), 1725-1720 cm^{-1} (C=O stretching of COOH), 1660-1630 cm^{-1} (C=O stretching of amide groups), 1620-1600 cm^{-1} (aromatic C=C), 1590-1517 cm^{-1} (COO-symmetric stretching, N-H deformation, C=N stretching), 1460-1450 cm^{-1} (aliphatic C-H), 1400-1390 cm^{-1} (OH deformation and C-O stretching of phenolic OH, C-H deformation of CH_2 and CH_3), 1280-1200 cm^{-1} (C-O stretching and OH deformation of COOH), and 1170-950 cm^{-1} (C- O stretching of polysaccharide). Figure 4 shows distinct absorption in the region 2940-2800 cm^{-1} (aliphatic CH_3, CH_2 stretching), but other absorption peaks in the 2000 to 1000 cm^{-1} of OM were overlapped by main mineral absorption. In this range, OM only contributed to small changes to infrared spectra such as frequency shift, intensity changes, and peak broadening. The LBL3 infrared spectra (Fig. 5) obviously show decreasing absorption intensities at 2935 and 2850 cm^{-1} (aliphatic CH_3 and CH_2 stretching) as a function of depth consistent with the decreasing TOC and OC trend with

depth in Figure 3. Slight frequency shifting and intensity changes can be noticed in the range 2000 to 1000 cm^{-1}. It might be caused by increasing aromatic C=C vibration, decreasing carboxyl C=O stretching vibration or slight mineralogical composition changes. Near-IR spectra of both soils (Fig. 6) show very similar peak features having three major peaks at 1414, 1910 and 2208 nm and a few small peaks between 2300 and 2600 nm. However, Blackland Prairie soil shows higher intensity of the peak at 1911 nm mainly due to high content of semetitic clay mineral present. One of black prairie soil (W1-1F-1) shows carbonate peaks at 2346 and 2538 nm. Soil organic matter and carbonates have very different NIR spectra. Chang and Laird (2002) reported that pure carbonate shows two prominent absorption peaks near 2340 and 2500 nm and three small but distinct absorption peaks near 1870, 2000, and 2160 nm due to overtones and combinations of fundamental mid-IR vibrations for the planar CO_3^{2-} ion. Other absorption peaks related with water are at 1400, 1900, and 2200 nm.

Humic acid has absorption peaks around 1850, 2310, and 2350 nm and small peaks around 1700 and 2150 nm. Prediction of organic carbon with multivariate liner regression using NIR peaks in this region has been successful. Dalal and Henry (1986) chose 1744, 1870, and 2052 nm to predict organic C concentration (R = 0.92), and Morra et al. (1991) used 1736, 1766, and 2032 nm to calibrate organic carbon concentration (R^2 = 0.93) using multivariate linear-regression (MLS). However, it is difficult to unambiguously assign these peaks to predict various components in soils due to the highly overlapped NIR spectra.
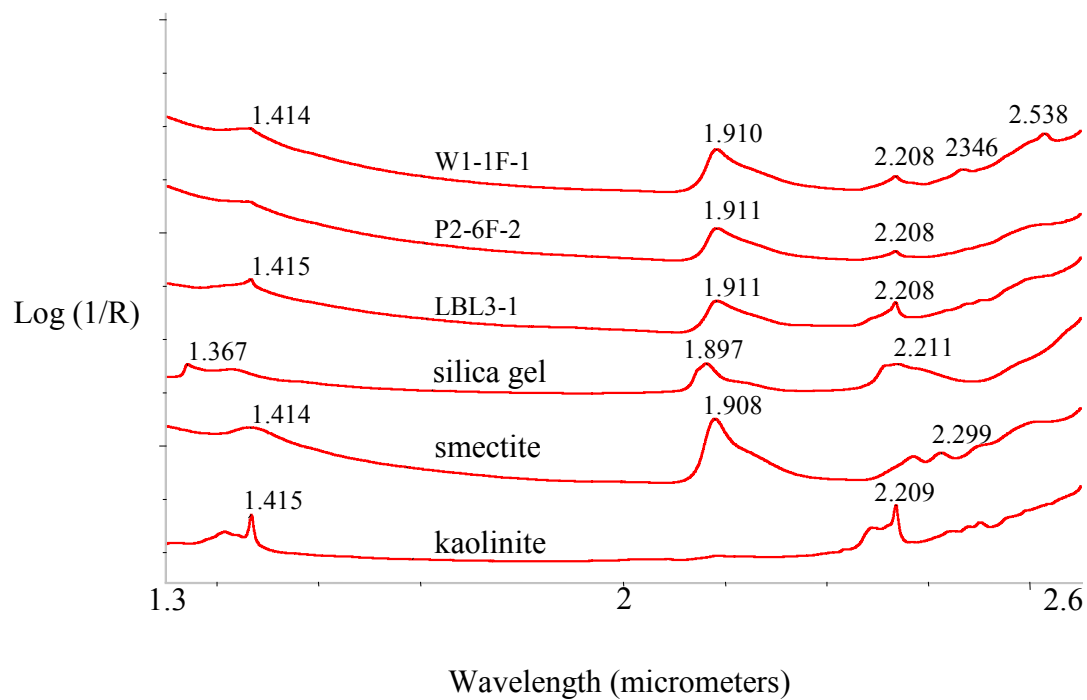
Figure 6. Near-IR spectra of 2 Blackland Prairie surface soils (W1-1F-1, P2-6F-2),

1 floodplain surface sample (LBL3-1), and reference minerals.

Calibration and prediction of TOC

A predictive model for total and oxidizable organic carbon in the two Texas soils was developed using multivariate regression of the mid- and near-IR spectra of the soils and TOC and oxidizable organic carbon, as measured by the carbon analyzer and the Walkley-Black method, respectively.

Table 3 summarizes the calibration and validation (prediction) results for total organic carbon of 68 samples by mid-IR and near-IR spectra. The correlation using Mid-IR spectra (r = 0.96, RMSEV = 0.32 for calibration; r = 0.93, RMSEP = 0.44for prediction) (Fig.7a) is about the same as the near-IR result (r = 0.95, RMSEV = 0.37; r = 0.93, RMSEP = 0.42) (Fig. 7b). Therefore, we can also use mid-IR region for quantification of organic carbon in soils. The score plot of the first two principal components is shown in Figure 8a. In this score plot, first principal component (PC1) described 56% of variations of the TOC data, and 14% of the information in the TOC data was explained by second principal component (PC2). The regression coefficient plot of PC1 is shown in Figure 8b. The score plot of PC1 and PC2 indicates that samples (n = 68) can be divided into two groups, floodplain soils and Blackland Prairie soils. The floodplain soil samples are close to each other along the horizontal axis (PC1), but far from Blackland Prairie soil samples with respect to PC1. The score plot can be used for dentification of sample differences and similarities. All other score plots and regression coefficient plots of PCs are in Appendix IV.

Table 3. Calibration and prediction of TOC using mid-IR and near-IR spectra in combination with PLS1 based on TOC (wt.%) by carbon analyzer (n = 68).

Parameters	Mid-IR		Near- IR	
	Calibration	Prediction	Calibration	Prediction
# Factor	6	6	6	6
Slope	0.92	0.88	0.90	0.88
Offset	0.13	0.22	0.17	0.20
Correlation (r)	0.96	0.93	0.95	0.93
Root mean square error (RMSE)	0.32	0.44	0.37	0.42
S.E.	0.33	0.45	0.37	0.42
Bias	0	2.3 e-3	0	-3.3 e-3
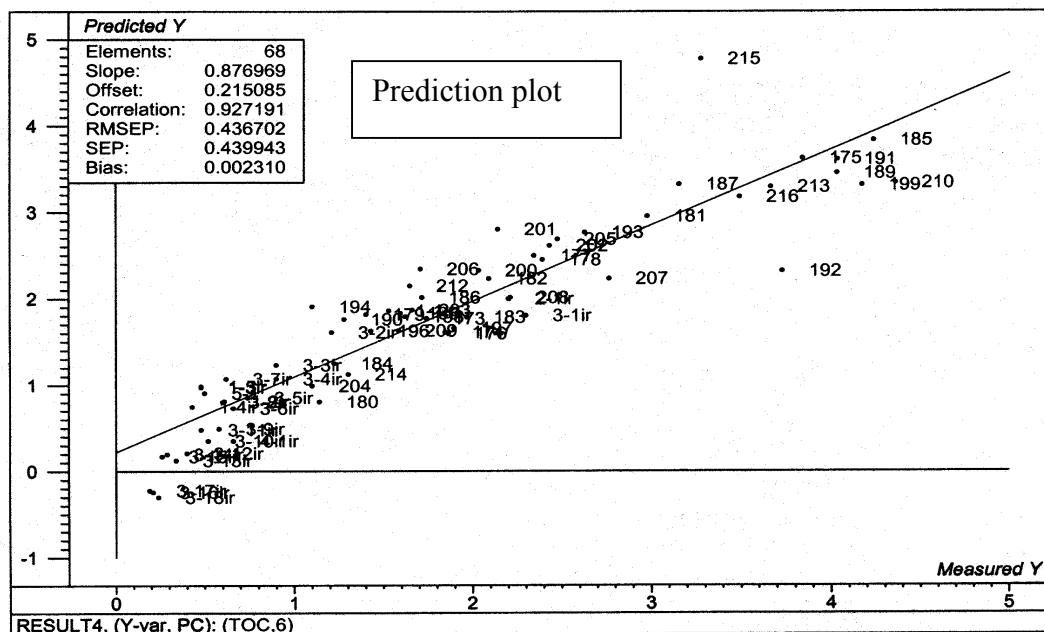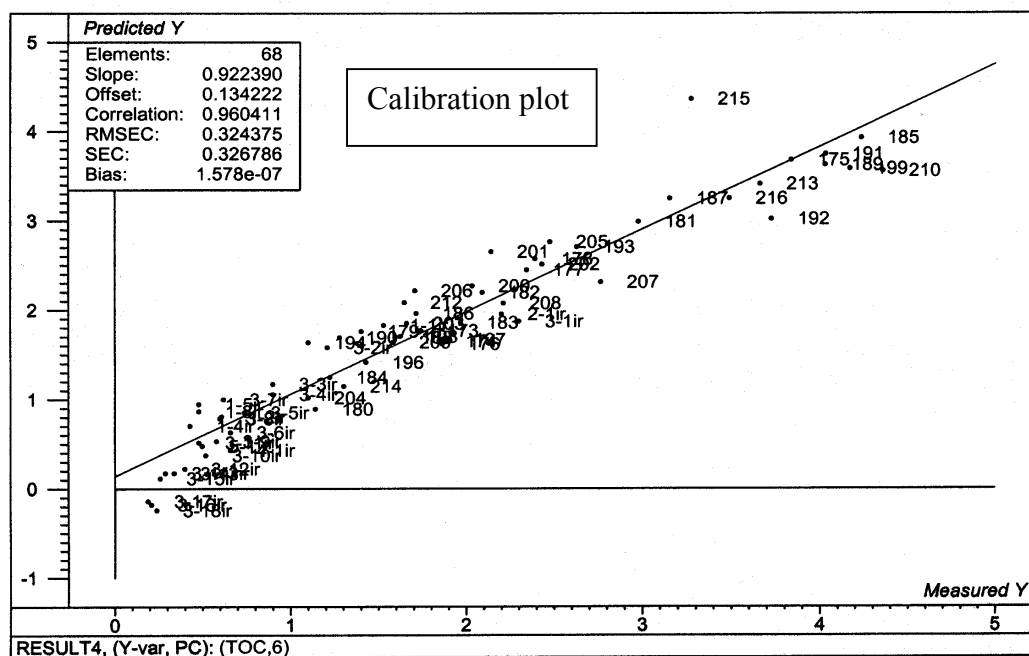
Figure 7.a. Calibration and prediction plot for mid-IR spectra based on TOC using

PLS1. (Measured Y: TOC (wt. %) measured by carbon analyzer; Predicted

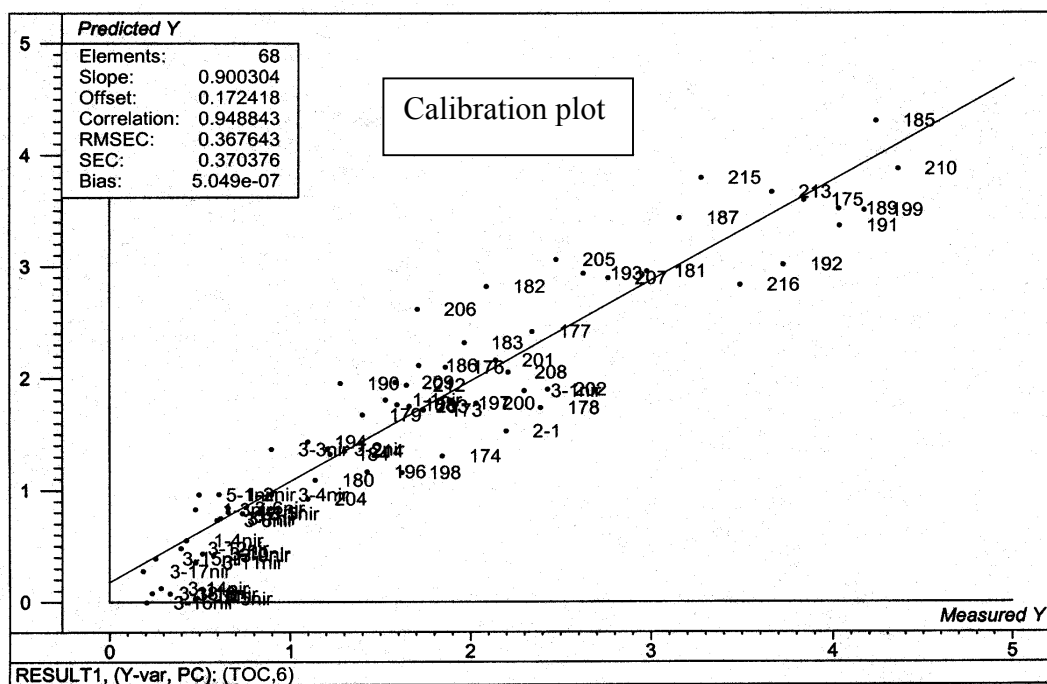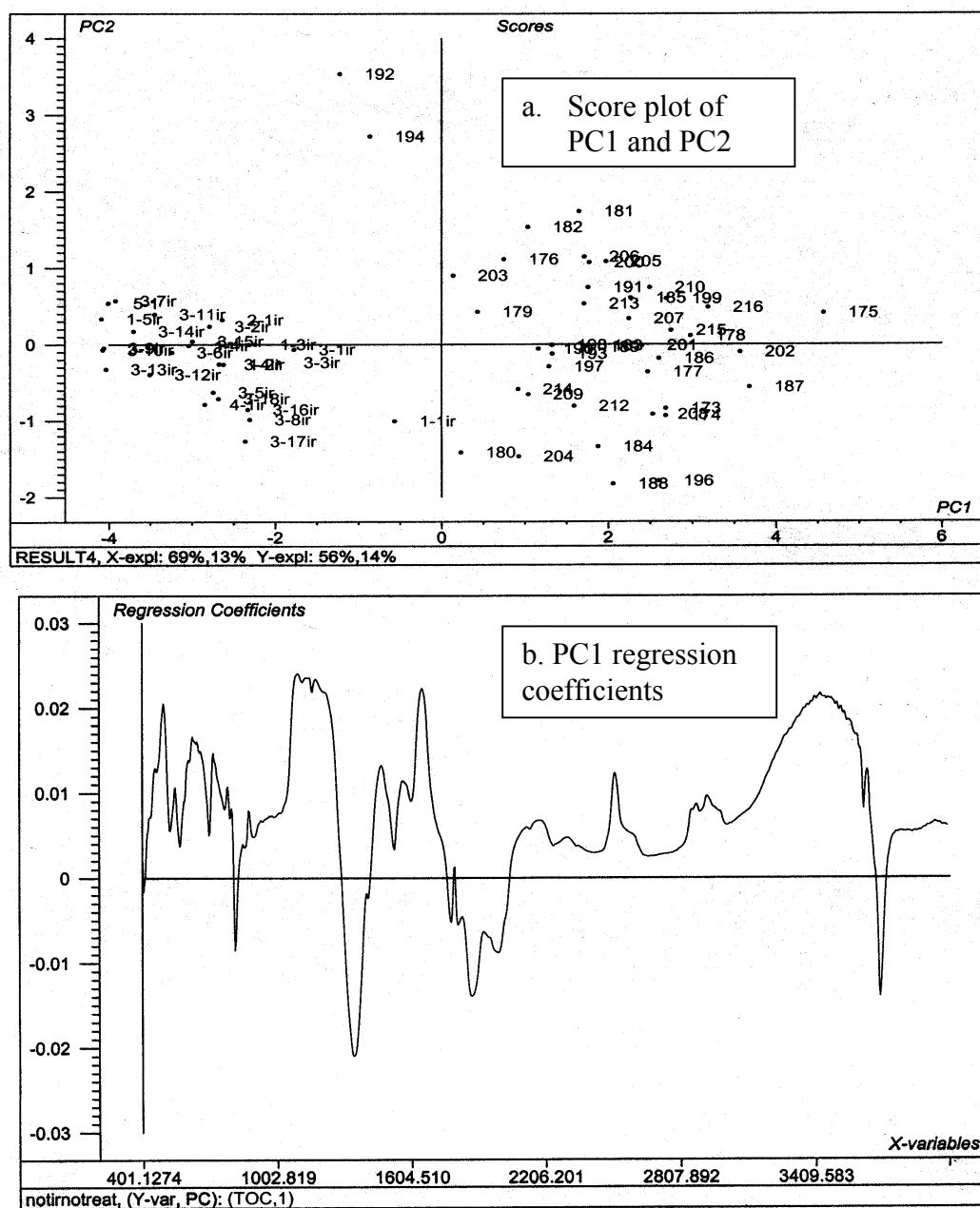Y: TOC (wt.%) predicted by PLS1 using mid-IR spectra.
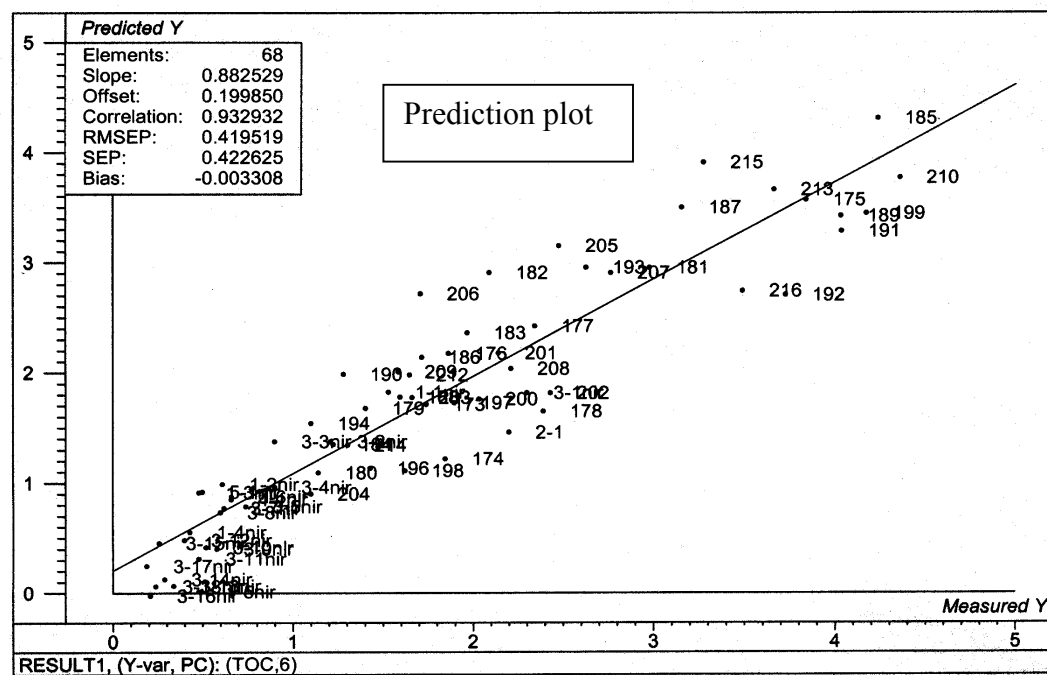
Figure 7.b. Calibration and prediction plot for near-IR spectra based on TOC using

PLS1. (Measured Y: TOC (wt. %) measured by carbon analyzer; Predicted

Y: TOC (wt.%) predicted by PLS1 using near-IR spectra.)

Figure 8. Sore and a regression coefficient plots. a. Score plot of PC1 for TOC using mid-IR spectra in combination with PLS1 (n = 68) . b. Regression Coefficients of PC1 for TOC using mid-IR spectra in combination with PLS1 (X-variables: wavenumbers(cm^{-1})).

Calibration and prediction of OC$_{WB}$

The calibration and validation results for oxidizable organic carbon (OC$_{WB}$) of 26 soil samples are summarized in Table 4. The PLS1 regression model with mid-IR region (r =0.97, RMSEV = 0.08; r = 0.92, RMSEP = 0.12) (Fig. 9a) was slightly better than the result with the near-IR region spectra (r = 0.95, RMSEV = 0.10; r = 0.90, RMSEP = 0.14) (Fig. 9.b). The PLS2 regression model (mid-IR spectra: r = 0.96, RMSEV = 0.10; r = 0.90, RMSEP = 0.14; near-IR spectra: r = 0.95, RMSEV = 0.10; r = 0.87, RMSEP = 0.16), which uses two y-variables at the same time, yields slightly less accurate results than PLS1 to predict oxidizable organic carbon (Fig. 10a and Fig. 10b). The linear regression model using TOC (Fig. 11) shows the lowest correlation coefficient value (r = 0.83, RMSEP = 0.18). The variations at the high concentrations in Figure 11 are larger than the variations at the low concentrations, because the high amount of plant debris on the surface soils led to high concentration of TOC, and resulted in low oxidizable organic carbon to total organic carbon ratio. The concentration of oxidizable organic carbon by Walkley-Black method varies with soil depth and depends on the magnitude of the recalcitrant carbon pool in the soil sample (Certini et al. 2002).

The oxidizable organic-carbon content (OC$_{WB}$) can be predicted more accurately using PLS regression model combined with spectral data than by the univariate least-square technique with the total organic carbon concentration measured by the carbon analyzer.

Table 4. Calibration and prediction results for OC_{WB} by least squares regression, PLS1, and PLS2 (n = 26)

Regression	X-variable	Model	# Factor	Correlation (r)	Root mean square error (RMSE)	S.E.
Linear	TOC	Calibration	1	0.88	0.15	0.15
		Prediction	1	0.83	0.18	0.19
PLS1	Mid-IR	Calibration	4	0.97	0.08	0.08
		Prediction	4	0.92	0.12	0.13
	Near-IR	Calibration	5	0.95	0.10	0.10
		Prediction	5	0.90	0.14	0.14
PLS2	Mid-IR	Calibration	5	0.96	0.09	0.09
		Prediction	5	0.90	0.14	0.14
	Near-IR	Calibration	5	0.94	0.10	0.11
		Prediction	5	0.87	0.16	0.16
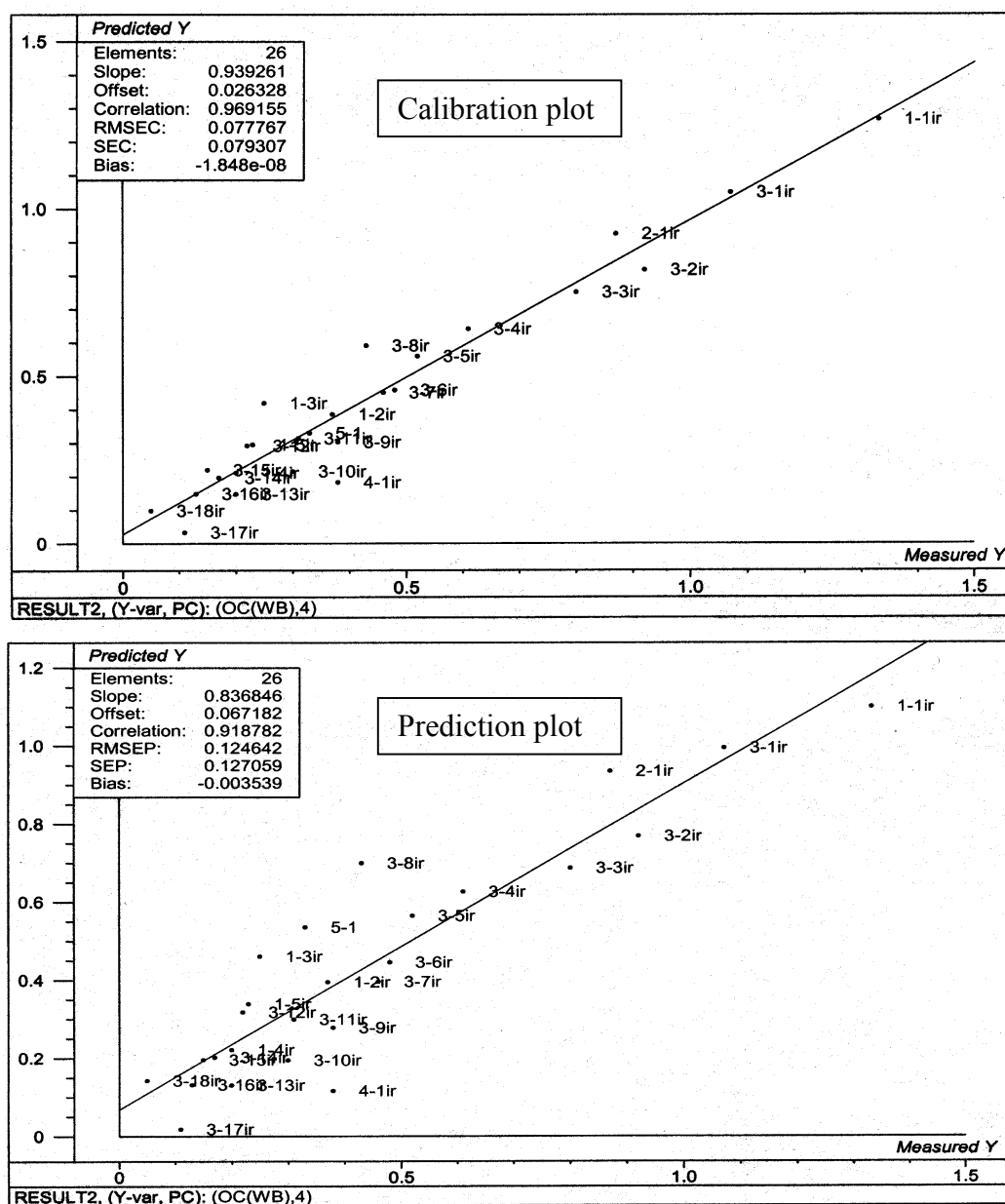
Figure 9.a. Calibration and prediction plot for mid-IR spectra based on OC_{WB} measured

by Walkley-Black method using PLS1. (Measured Y: OC_{WB} measured by

Walkley- Black method; Predicted Y: OC_{WB} predicted by PLS1 using mid-
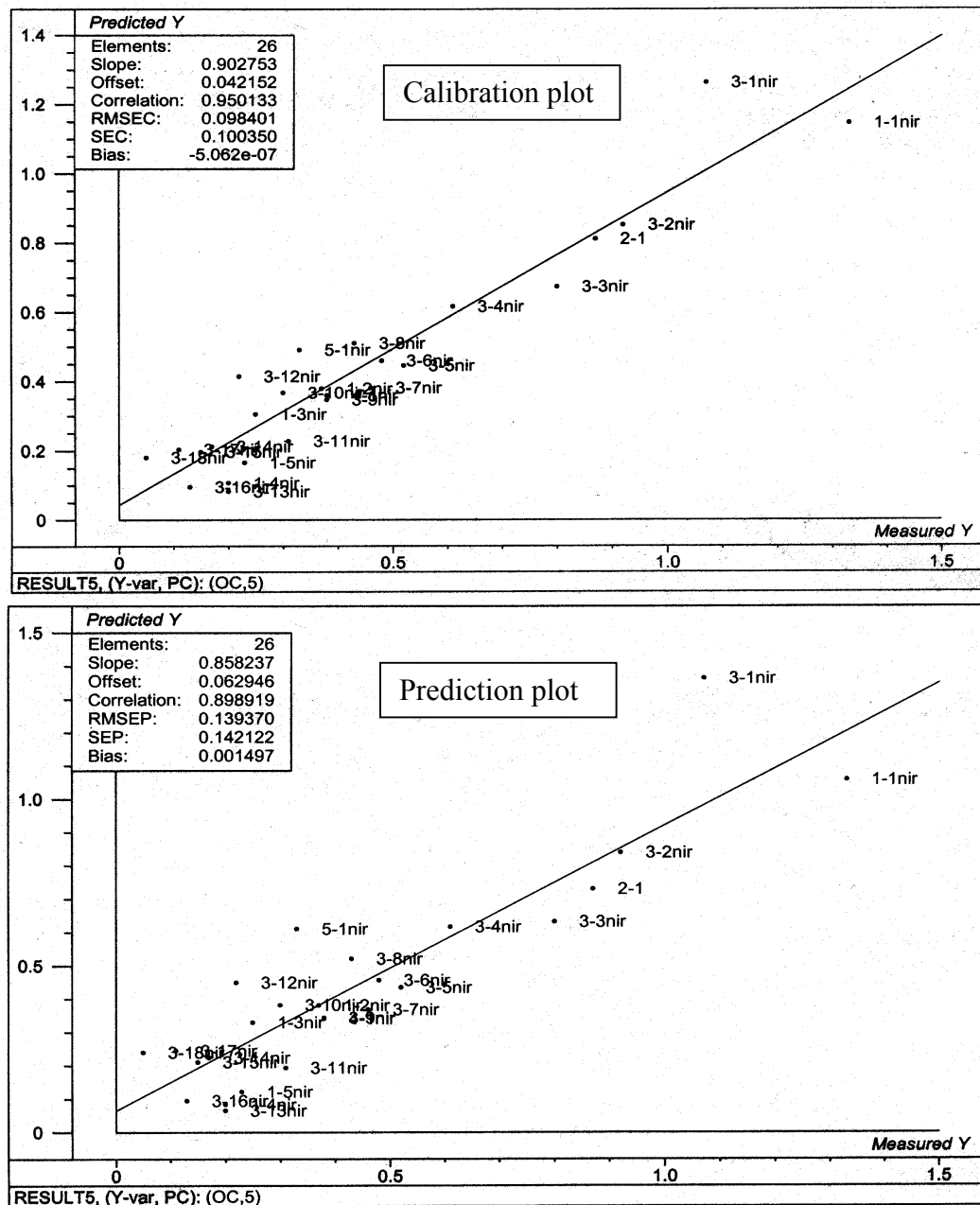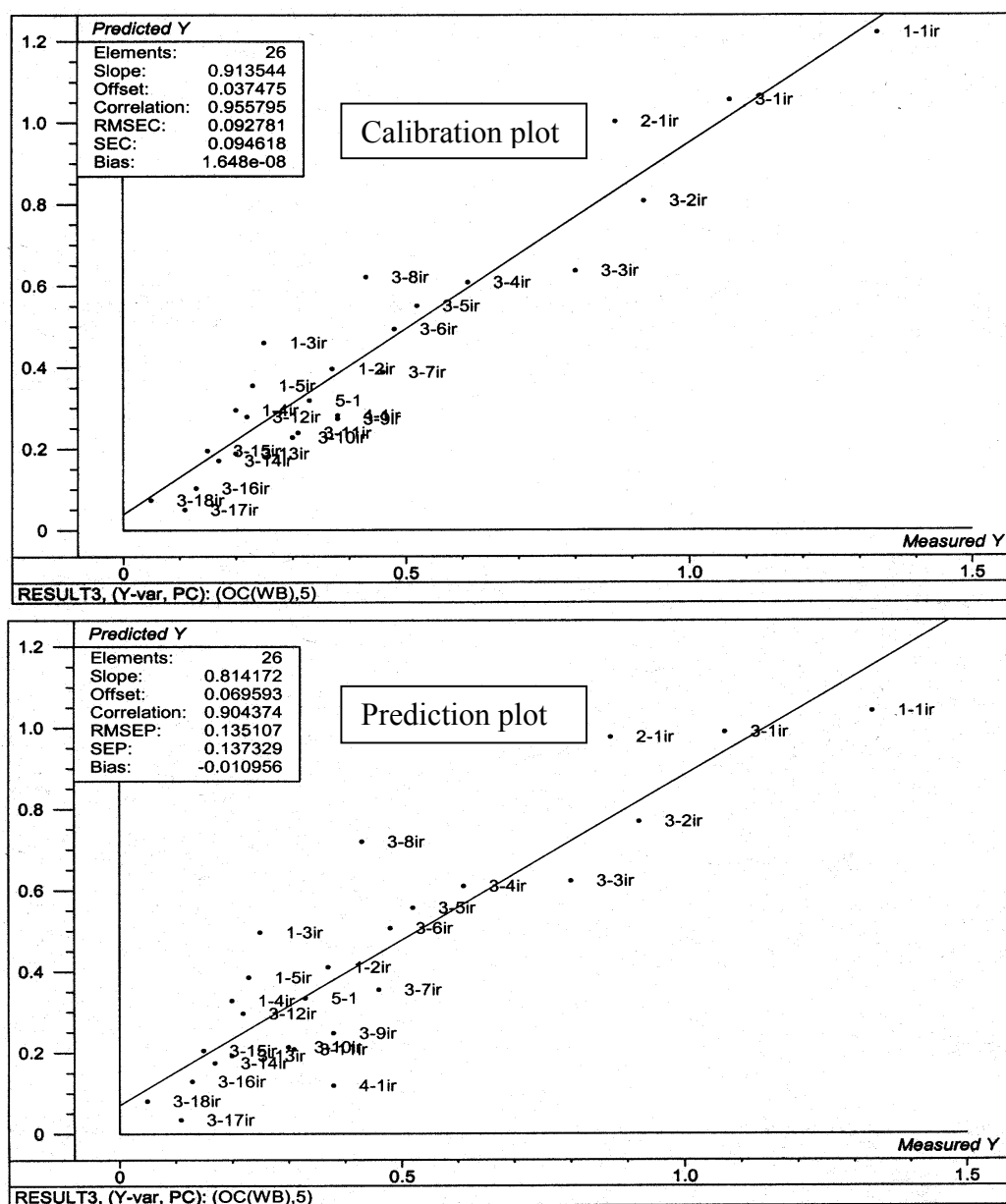
IR spectra.)

Figure 9.b. Calibration and prediction plot for near-IR spectra based on OC_{WB} measured by Walkley-Black method using PLS1. (Measured Y: OC_{WB} measured by Walkley- Black method; Predicted Y: OC_{WB} predicted by PLS1 using near-IR spectra.)

Figure 10.a. Calibration and prediction plot for mid-IR spectra based on OC$_{WB}$ measured by Walkley-Black method using PLS2 (n = 26). (Measured Y: OC$_{WB}$ (wt. %) measured by Walkley-Black method; Predicted Y: OC$_{WB}$ (wt.%) predicted by PLS2.)
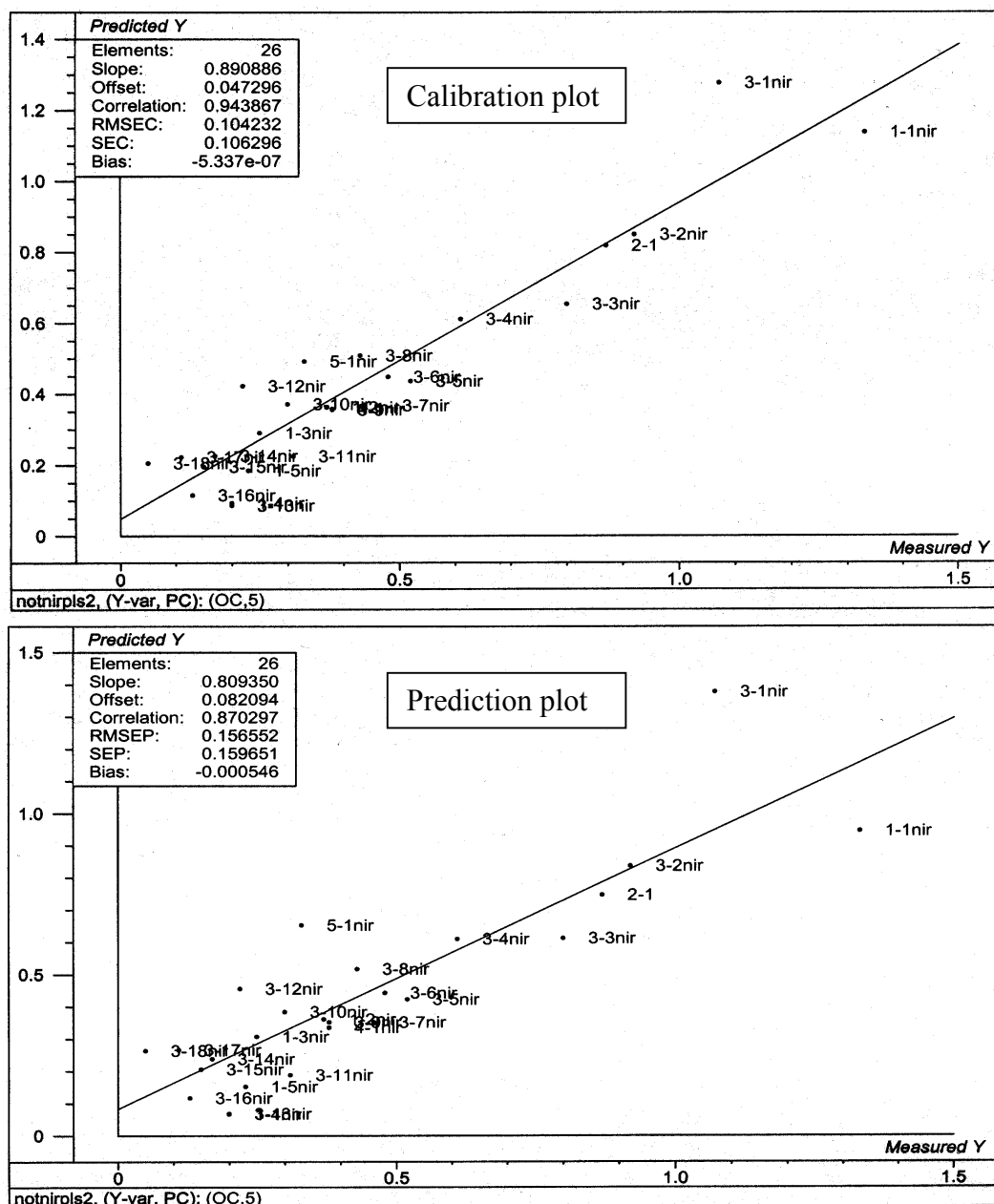
Figure 10.b. Calibration and prediction plot for near-IR spectra based on OC_{WB}

measured by Walkley-Black method using PLS2 (n = 26). Measured Y:

OC_{WB} (wt. %) measured by Walkley-Black method; Predicted Y: OC_{WB}
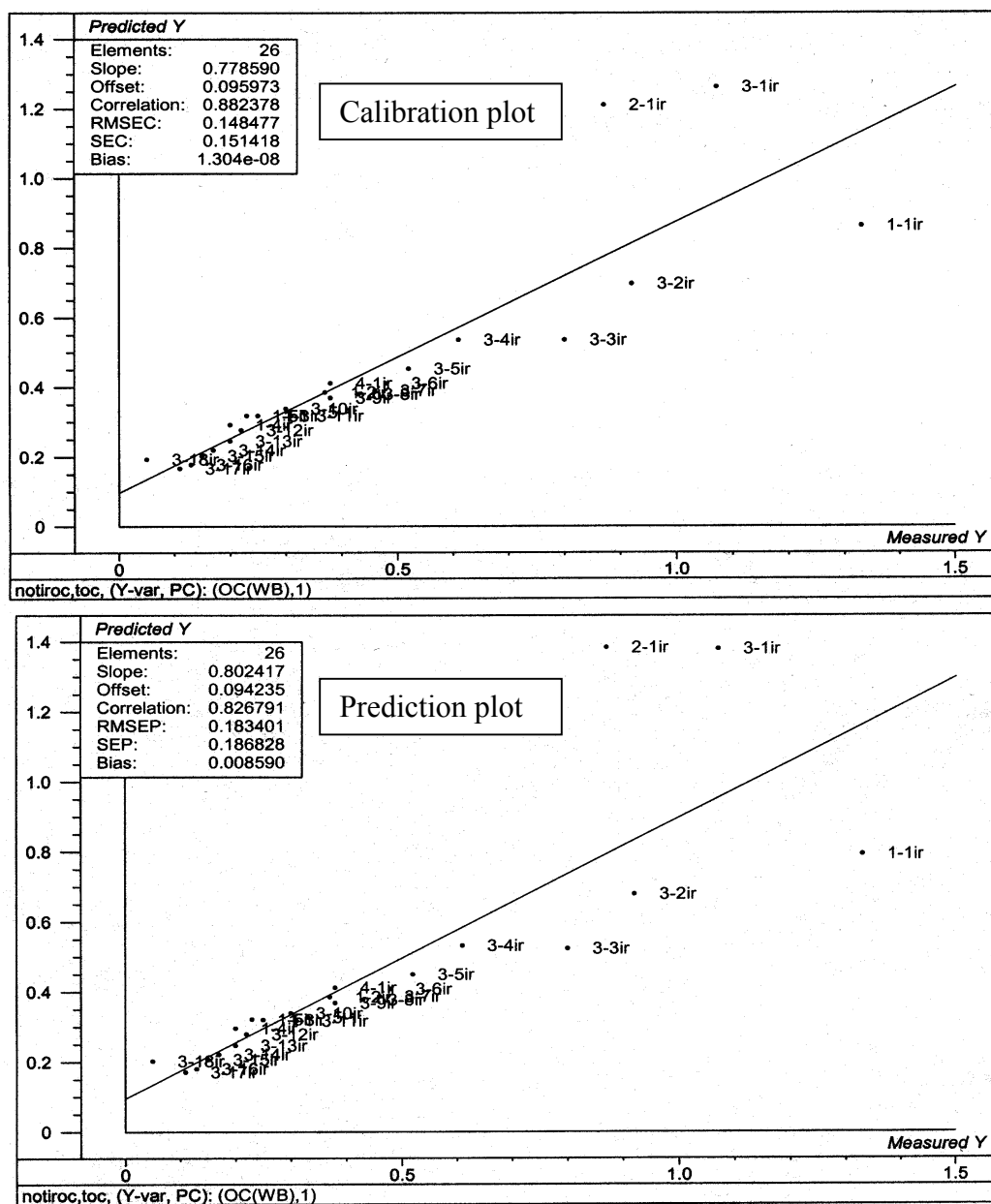
(wt.%) predicted by PLS2.)

Figure 11. Calibration and prediction plot of OC_{WB} using TOC with least squares

regression. (Measured Y: OC_{WB} (wt. %) measured by Walkley-Black

method; Predicted Y: OC_{WB} (wt. %) predicted by least squares regression

using TOC measured by carbon analyzer).

IMPLICATIONS

In this study, both mid-and near-DRIFT spectroscopy in combination with the PLS regression model successfully estimated total organic carbon (TOC) and oxidizable organic-carbon (OC_{WB}) concentrations in two soil sets having different properties. In future studies, the calibration model constructed in this study may be used to predict total organic carbon (TOC) and oxidizable organic-carbon fraction (OC_{WB}) of unknown samples. Therefore, mid-and near-DRIFT spectroscopic methods could reduce time-consuming laboratory work and harmful chemicals, especially when dealing with many soil samples.

We might also estimate the recalcitrant organic carbon fraction by subtraction of the oxidizable organic-carbon fraction from total organic carbon (TOC). However, these results should be interpreted with caution because of errors in determination of the oxidizable organic-carbon fraction. Further studies should be done to construct reliable calibration model to predict concentration of different fractions of soil organic matter using mid-and near- spectroscopy.

CHAPTER III

SUMMARY AND CONCLUSIONS

The floodplain and Blackland Prairie soils having different soil properties were used for prediction of TOC and OC_{WB} using mid- and near-DRIFT spectroscopy. Floodplain soils are mainly composed of quartz and kaolinite, with no carbonate mineral, whereas Blackland Prairie soils contain high concentrations of smectitic clays with low to high concentrations of carbonate minerals. The total organic carbon of 68 soil samples from both Blackland Prairie and floodplain varied between 0.19 and 4.36 wt.% C and the oxidizable organic-carbon contents of 26 samples from floodplain soils were in the range of 0.05 to 1.33 wt.% C.

Mid- and near-IR spectra were dominated by the relatively strong intensities representing the main constituent minerals, such as quartz, kaolinite (floodplain soils), and smectite (Blackland Prairie soils). Mid-IR spectra of floodplain (LBL3-1) and two Blackland Prairie surface soils (W1-F-1 and P2-6F-2) show obvious differences. One of Blackland Prairie soil sample (W1-F-1) shows strong absorption at 2513, 1796, and 1455 cm^{-1} due to carbonate mineral and broad peaks at 3600 cm^{-1} and 1640 cm^{-1} region due to high smectitic clay mineral contents, whereas the P2-6F-2 Blackland Prairie sample lacked peaks at 2513 cm^{-1} and 1796 cm^{-1} peaks indicating limited carbonates in these samples. The floodplain soils showed sharp peaks at 3697, 3654, and 3623 cm^{-1} (O-H stretching vibration) due to kaolinite, strong absorption at 1366 cm^{-1} (O-Si-O vibration) due to quartz, and no absorption at 2513cm^{-1} indicating no carbonate minerals.

Near-IR spectra of both soils showed very similar peak features having three major peaks at 1414, 1910, and 2208 nm, and a few small peaks between 2300 and 2600 nm. Organic matter was only characterized by minor peaks or by small changes in mid- and near-IR spectra such as peak broadening, frequency shifts, and intensity changes.

TOC and OC_{WB} of soil were successfully calibrated and predicted by PLS regression method using mid- and near-DRIFT spectroscopy. The correlation using mid-IR spectra for TOC (r = 0.96, RMSEV = 0.32 for calibration; r = 0.93, RMSEP = 0.44 for prediction) was about the same as near-IR result (r = 0.95, RMSEV = 0.37; r = 0.93, RMSEP = 0.42). Therefore, mid-infrared region may be also useful to quantify total organic carbon. PLS1 regression model for quantification of oxidizable organic carbon with mid-IR region (r =0.97, RMSEV = 0.08; r = 0.92, RMSEP = 0.12) was slightly better than the result with near-IR region spectra (r = 0.95, RMSEV = 0.10; r = 0.90, RMSEP = 0.14). PLS2 regression model (mid-IR spectra: r = 0.96, RMSEV = 0.10; r = 0.90, RMSEP = 0.14; near-IR spectra: r = 0.95, RMSEV = 0.10; r = 0.87, RMSEP = 0.16) yielded slightly less accurate results than the PLS1 model to predict oxidizable organic carbon. The linear regression model using TOC (r = 0.83, RMSEP = 0.18) showed a lower correlation coefficient value.

The partial least square (PLS) method using mid-IR and near-IR spectra of neat soil samples can be used to predict both the total organic carbon and oxidizable organic-carbon contents as a fast and routine quantitative method.

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APPENDIX I

DESCRIPTION OF FLOODPLAIN SAMPLE SITES

Site	Description
LBL1	The upper floodplain, left (east) bank, coordinates N 31º 32.1023`, W 94º 46.3787`. Sampled 0-7.5, 7.5^{-1}5, 16-31 cm, 31-46 cm, and 46-61 cm (5samples)
LBL2	The middle floodplain, left (east) bank, along the previously *surveyed transect line. There is one surface (0-3 cm) sample.
LBL3	The right (west) floodplain, 11.4m from the stream bank along the previously surveyed transect line. Sampling was at 2 cm increments to 30 cm, and 6 cm increments from 30 to 54 cm (19 samples)
LBL4	The right (west) floodplain, at the edge of the forested slough on the surveyed transects line. Material from two crawfish towers. Single surface sample (0-3 cm)
LBL5	The right (west) bank levee top on the surveyed transect line. Single surface sample (0-3 cm)

* The " surveyed transect" referred to crosses the floodplain normal to the stream

channel.

APPENDIX II
FLOODPLAIN SAMPLE PROPERTIES

Sample site	Mean Depth(cm)	pH	OC_{WB}, wt.%	TOC, wt.%	OC_{WB}/TOC
LBL1-1	3.75	5.15	1.33	1.53	0.87
LBL1-2	11.25	5.02	0.37	0.61	0.61
LBL1-3	23	4.75	0.25	0.48	0.52
LBL1-4	38.5	4.46	0.20	0.43	0.47
LBL1-5	53.5	4.33	0.23	0.48	0.48
LBL2-1	1.5	5.43	0.87	2.2	0.40
LBL3-1	1	5.45	1.07	2.3	0.47
LBL3-2	3	5.35	0.92	1.21	0.76
LBL3-3	7	5.61	0.80	0.9	0.89
LBL3-4	9	5.80	0.61	0.9	0.68
LBL3-5	11	5.93	0.52	0.74	0.70
LBL3-6	13	6.00	0.48	0.66	0.73
LBL3-7	15	6.01	0.46	0.62	0.74
LBL3-8	17	5.83	0.43	0.6	0.72
LBL3-9	19	5.87	0.38	0.58	0.66
LBL3-10	21	5.73	0.30	0.52	0.58
LBL3-11	23	5.50	0.31	0.48	0.65
LBL3-12	25	5.29	0.22	0.4	0.55
LBL3-13	27	5.06	0.20	0.34	0.59
LBL3-14	29	4.94	0.17	0.29	0.59
LBL3-15	33	4.88	0.15	0.26	0.58
LBL3-16	39	4.85	0.13	0.21	0.62
LBL3-17	45	4.87	0.11	0.19	0.58
LBL3-18	51	4.90	0.05	0.24	0.21
LBL4-1	1.5	4.78	0.38	0.66	0.58
LBL5-1	1.5	5.04	0.33	0.5	0.66

APPENDIX III

BLACKLAND PAIRIE SOIL SAMPLE PROPERTIES

Sample #	Site	TOC[a], %	Texture	Subgroup
172	B1-4F-1	1.4115	Clay	Udic Haplusterts
173	B2-4F-1	1.7410	Clay	Udic Pellusterts
174	B-3-1F-1	1.8458	Silty clay	Typic calciustolls
175	C1-5F-1	3.8369	Clay	Udic Chromusterts
176	D1-6F-1	1.8629	Clay	Tipic Hapllustolls
177	D2-7F-1	2.3433	Clay	Tipic Hapllustolls
178	G1-3F-1	2.3904	Silty clay	Udic Pellusterts
179	G2-7F-1	1.4034	Clay	Udic Pellusterts
180	G4-7F-1	1.1425	Clay	Udic Pellusterts
181	HI-3F-1	2.9764	Clay	Udic Chromusterts
182	H2-5F-1	2.0902	Clay	Udic Chromusterts
183	M1-2F-1	1.9672	Clay	Udic Chromusterts
184	M2-4F-1	1.2239	Clay	Udic Chromusterts
185	M3-4F-1	4.2336	Clay	Udic Chromusterts
186	M4-3F-1	1.7151	Clay	Udic Chromusterts
187	MA-6F-1	3.1541	Clay	Udic Pellusterts
188	N1-6F-1	1.5948	Clay	Udic Chromusterts
189	N2-7F-1	4.0290	Silty clay	Entic Haplustolls
190	P1-7F-1	1.2804	Clay	Udic Pellusterts
191	P2-3F-1	4.0319	Clay	Udic Chromusterts
192	R1-4F-1	3.7244	Clay	Udic Pellusterts
193	R4-1F-1	2.6272	Silty clay	Entic Haplustolls
194	W1-1F-1	1.1017	Clay	Udic Pellusterts
196	B1-3F-2	1.4291	Clay	Udic Haplusterts
197	B2-3F-2	1.8957	Clay	Udic Pellusterts
198	B3-4F-2	1.6219	Clay	Typic calciustolls
199	C1-1F-2	4.1696	Clay	Udic Chromusterts
200	D1-1F-2	2.0333	Clay	Tipic Hapllustolls
201	D2-1F-2	2.1407	Clay	Tipic Hapllustolls
202	G1-2F-2	2.4300	Clay	Udic Pellusterts
203	G2-8F-2	1.6612	Clay	Udic Pellusterts
204	G4-4F-2	1.1016	Clay	Udic Pellusterts
205	H1-4F-2	2.4751	Clay	Udic Chromusterts
206	H2-6F-2	1.7077	Clay	Udic Chromusterts
207	MA-1F-2	2.7633	Clay	Udic Pellusterts
208	M1-3F-2	2.2107	Clay	Udic Chromusterts
209	M2-3F-2	1.5842	Clay	Udic Chromusterts

APPENDIX III continued.

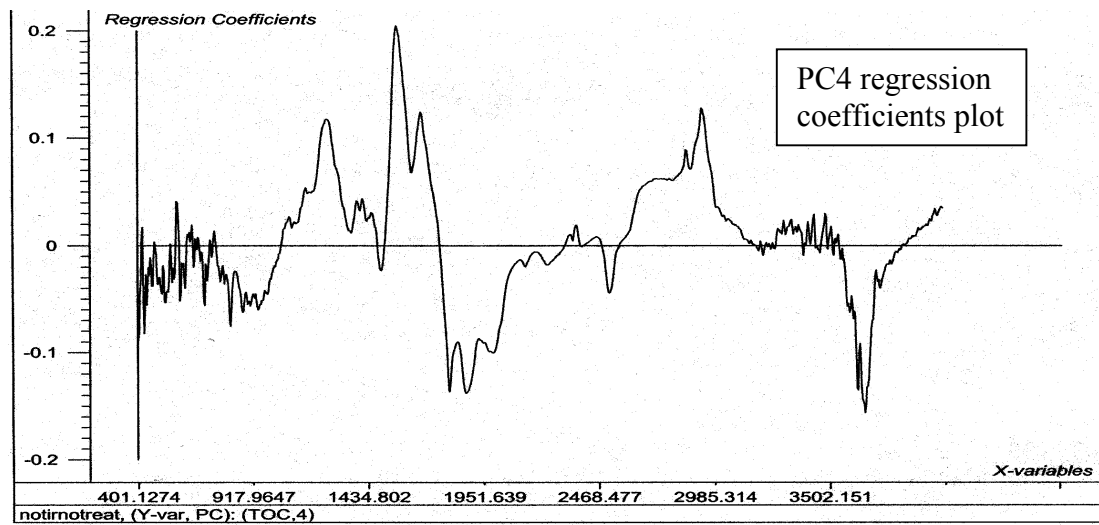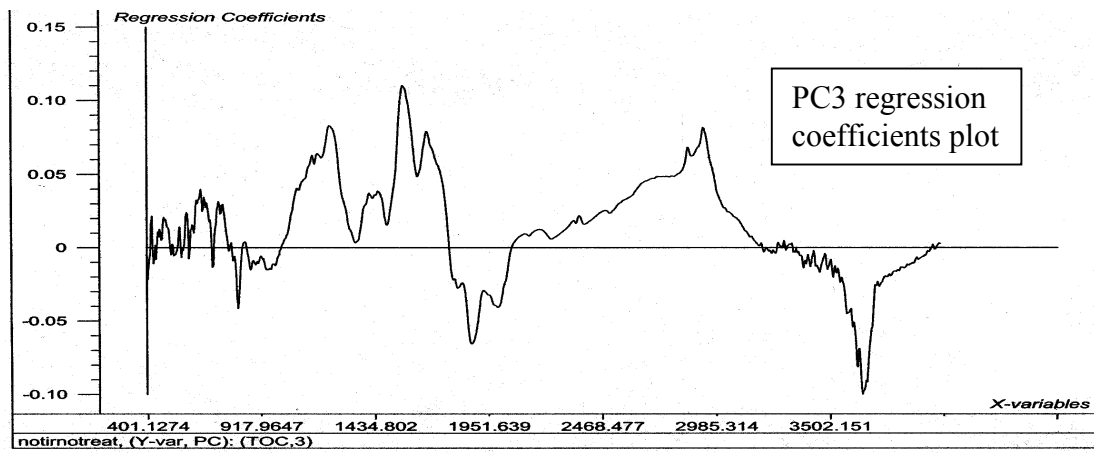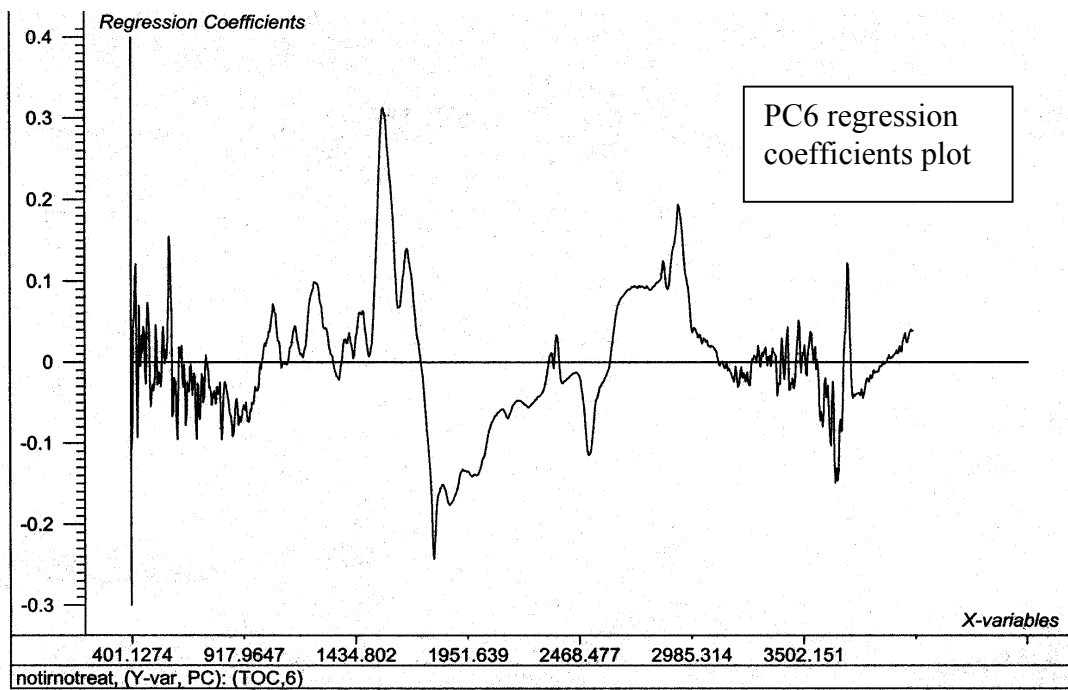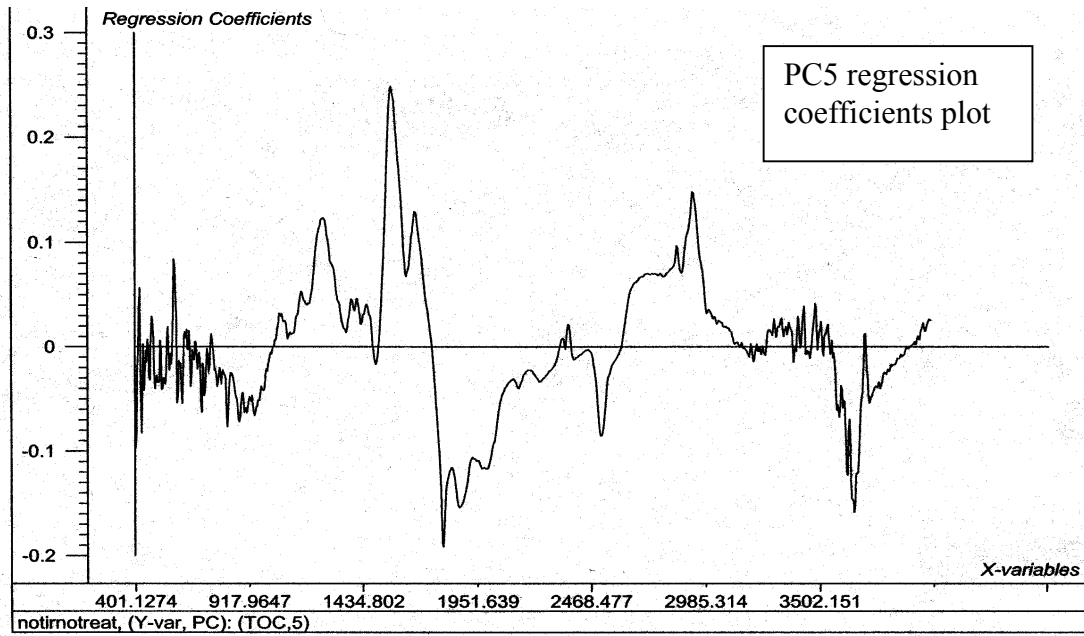| 210	M3-6F-2	4.3568	Clay	Udic Chromusterts
212	N1-2F-2	1.6472	Clay	Udic Chromusterts
213	N2-5F-2	3.6613	Clay	Entic Haplustolls
214	P1-4F-2	1.3040	Clay	Udic Pellusterts
215	P2-6F-2	3.2736	Clay	Udic Chromusterts
216	R1-3F-2	3.4882	Clay	Udic Pellusterts

[a] organic carbon % determined by carbon analyzer

APPENDIX IV

SCORE AND REGRESSION COEFFICIENTS PLOTS OF EACH PRINCIPAL

COMPONENT OF MID-FTIR SPECTRA TO PREDICT TOC BY PLS1

Score plot of PC3 and PC4

Score plot of PC5 and PC6

APPENDIX IV continued.

PC 2 regression coefficients plot

notirnotreat, (Y-var, PC): (TOC,2)

PC3 regression coefficients plot

notirnotreat, (Y-var, PC): (TOC,3)

PC4 regression coefficients plot

notirnotreat, (Y-var, PC): (TOC,4)
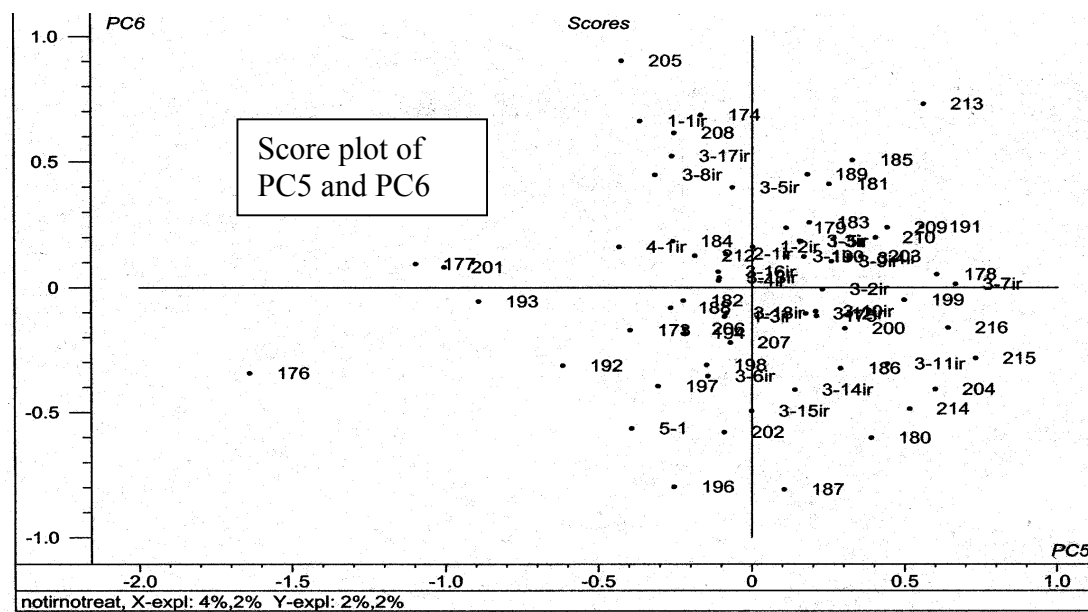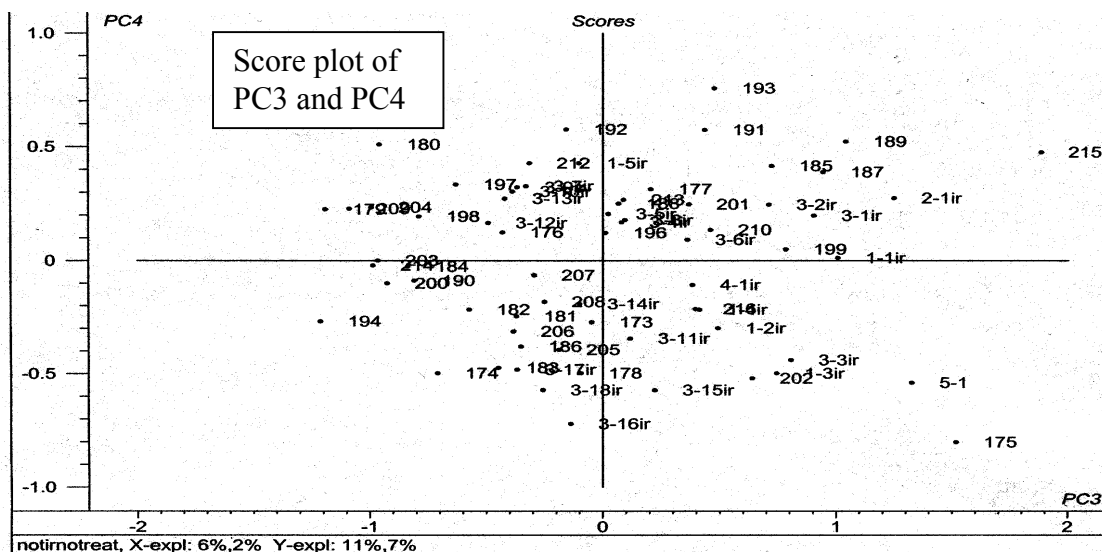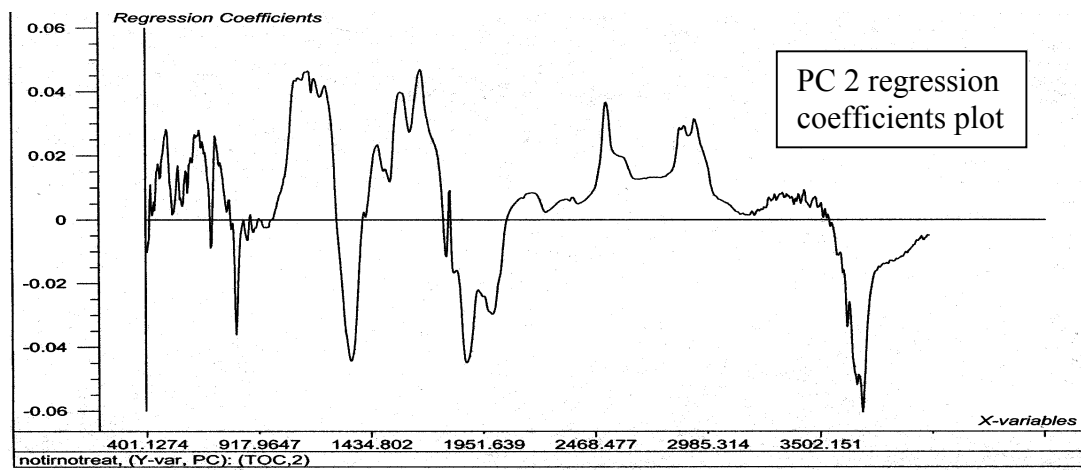
APPENDIX IV continued.

APPENDIX V

XRD, SEM, TEM AND FTIR DATA OF LBL3 SOIL SAMPLE FROM FLOODPLAIN

Bulk soil XRD

Q: quartz

Sand fraction XRD

Silt fraction XRD

APPENDIX V continued.

S: smectite; M: mica; K: kaolinite; Q: quartz; G: goethite
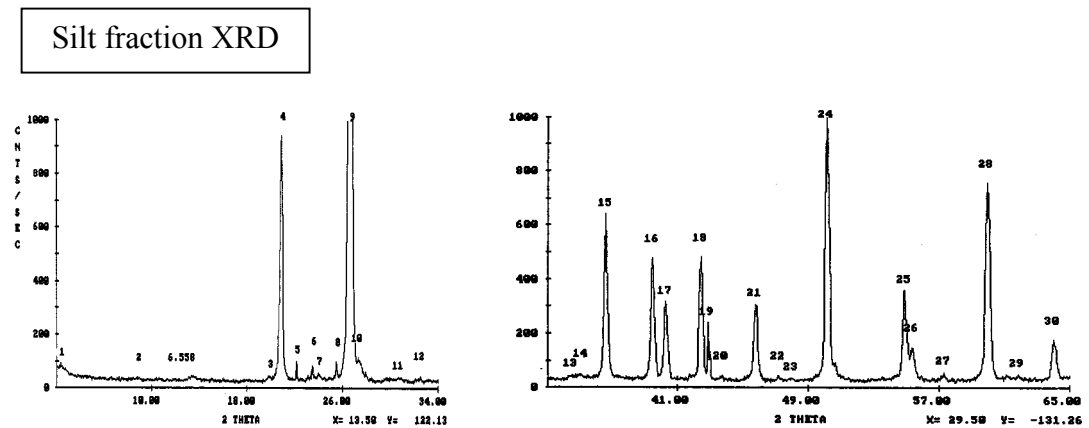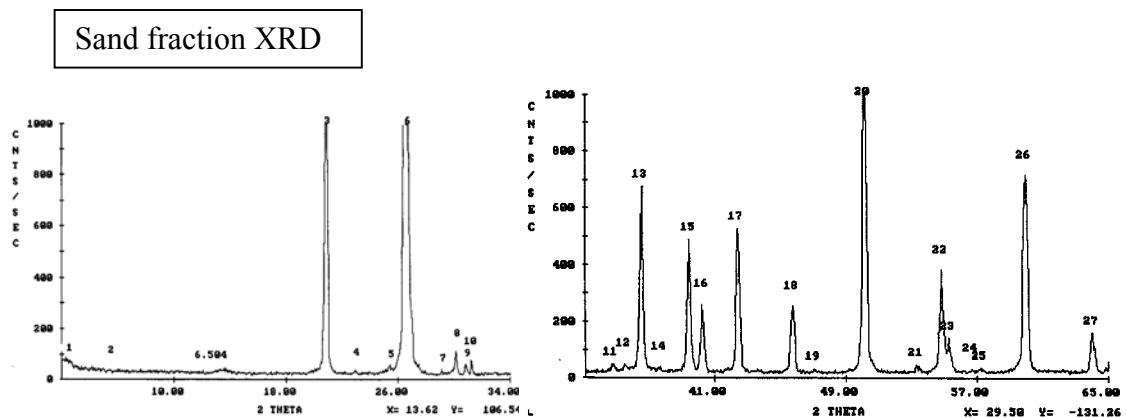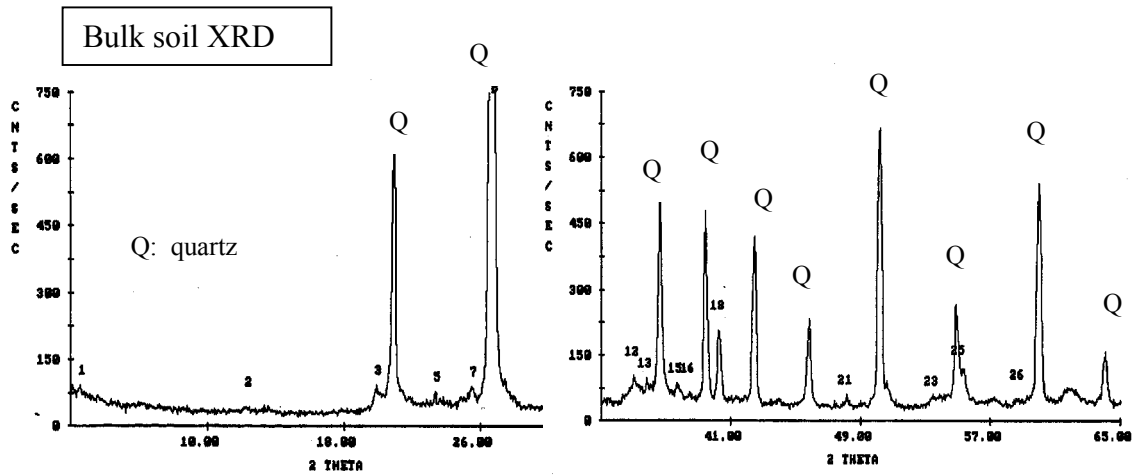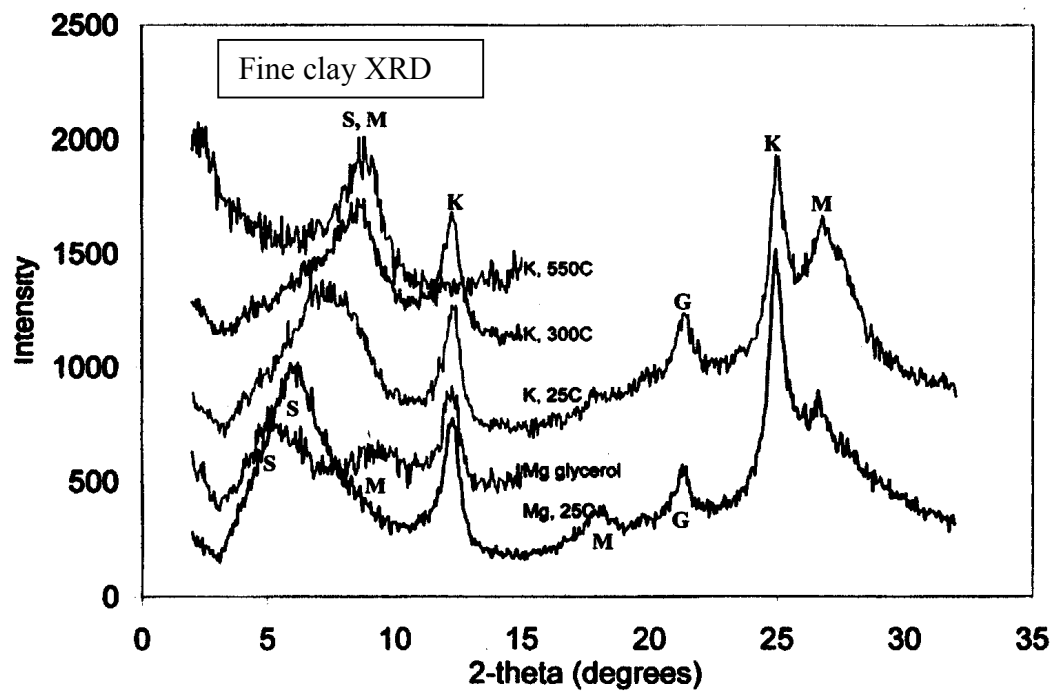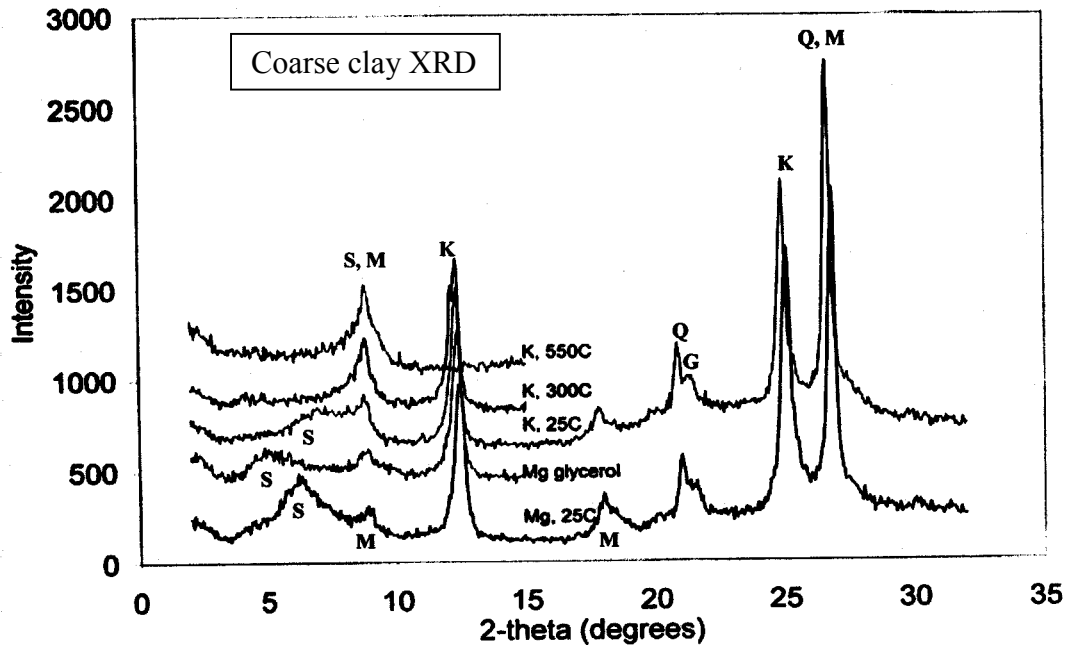
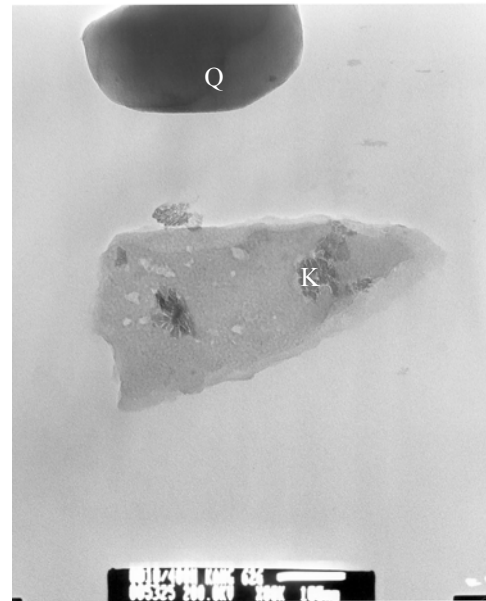APPENDIX V continued.
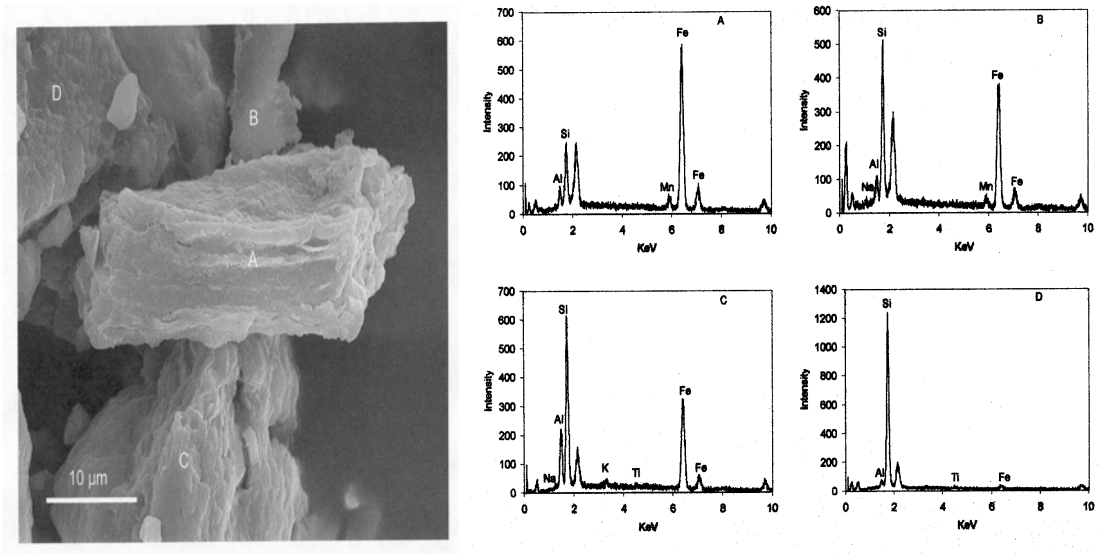
SEM: A.Goethite
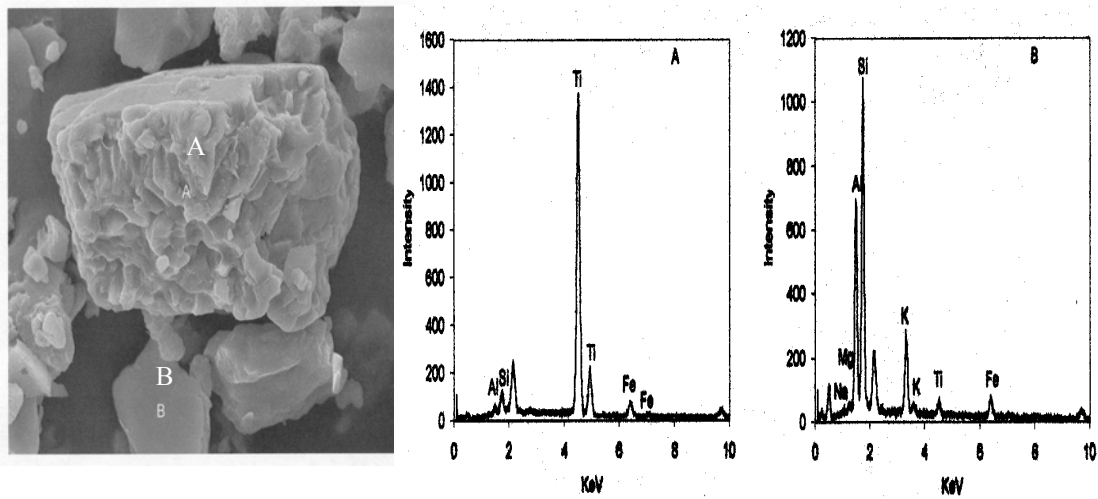
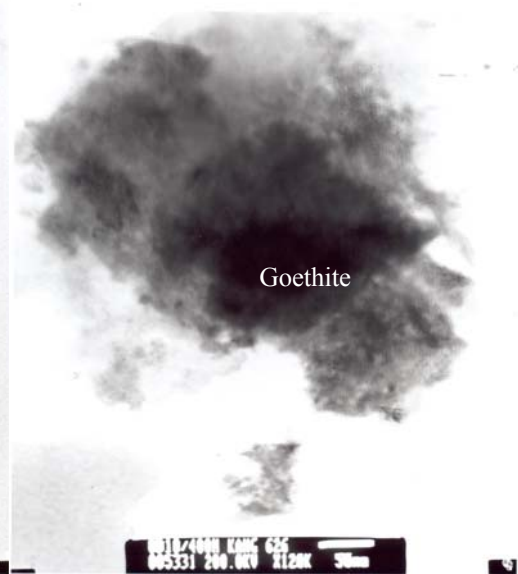

SEM: A. Anatase, B. Mica
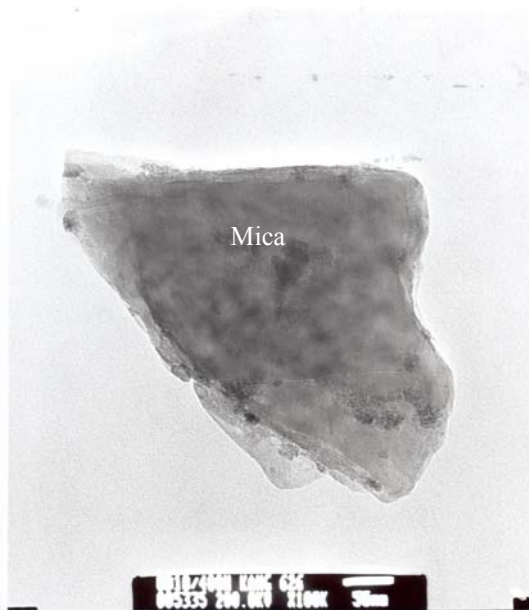
APPENDIX V continued.
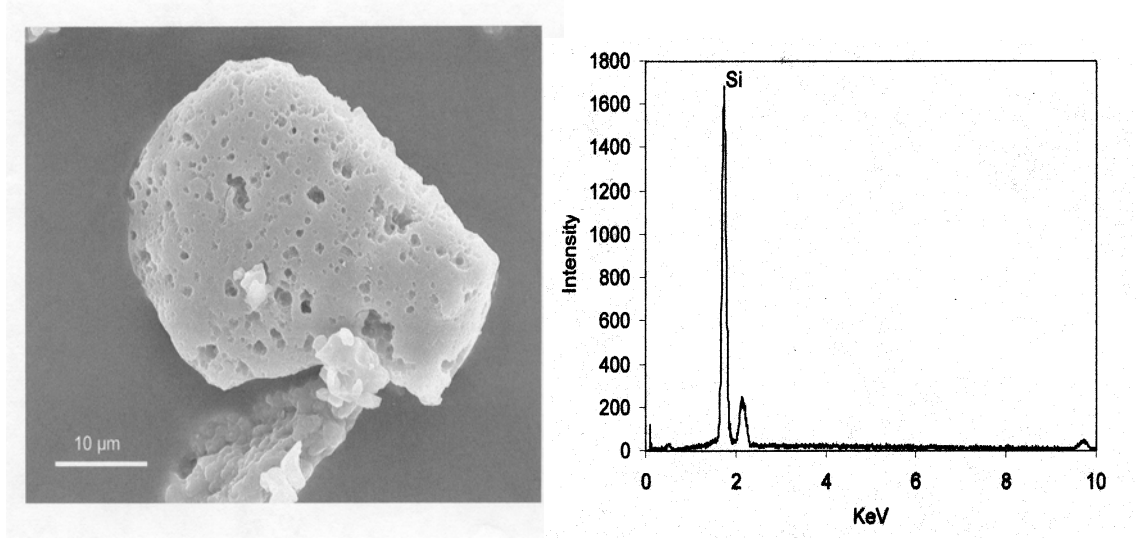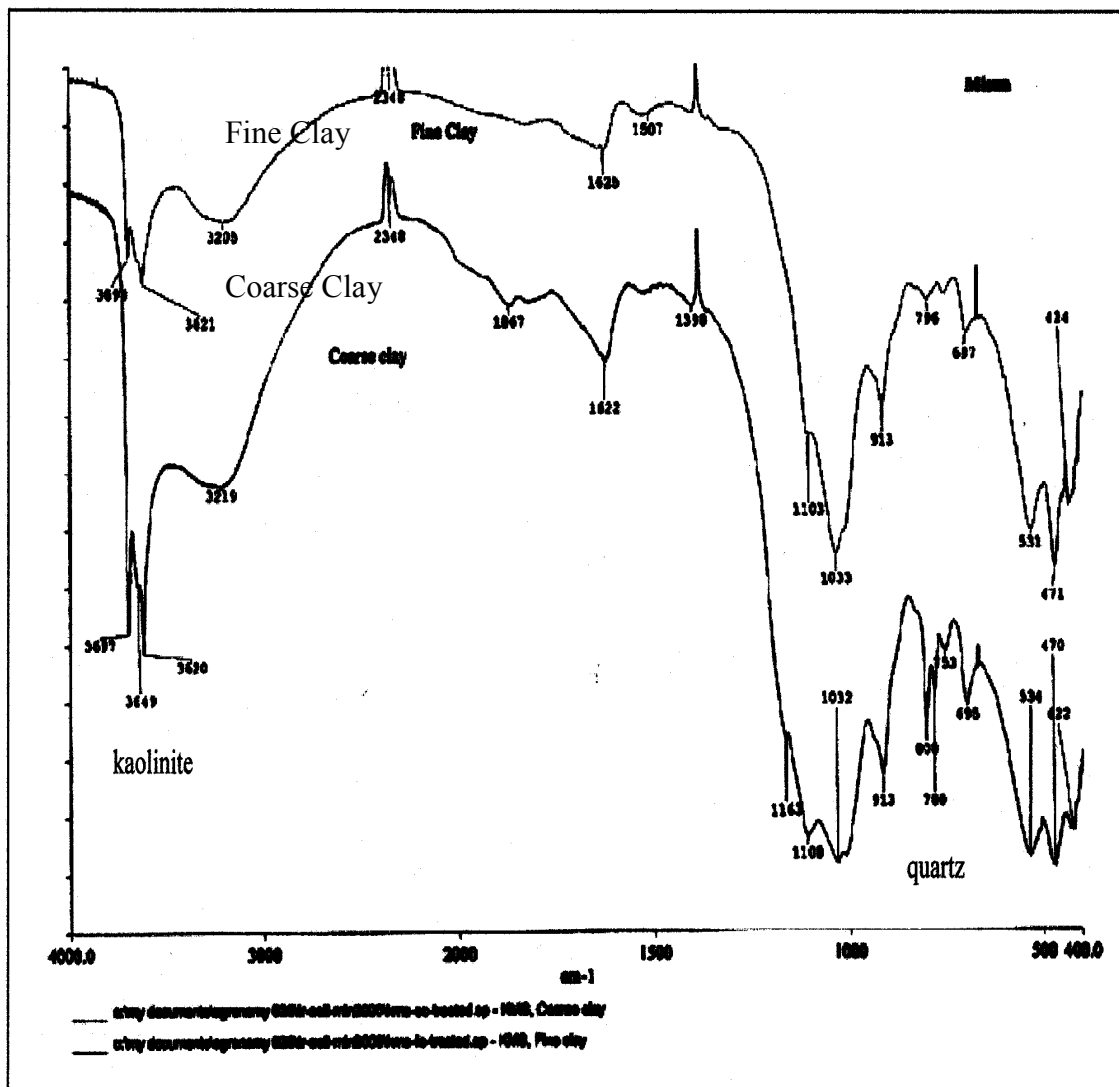

SEM: Opal
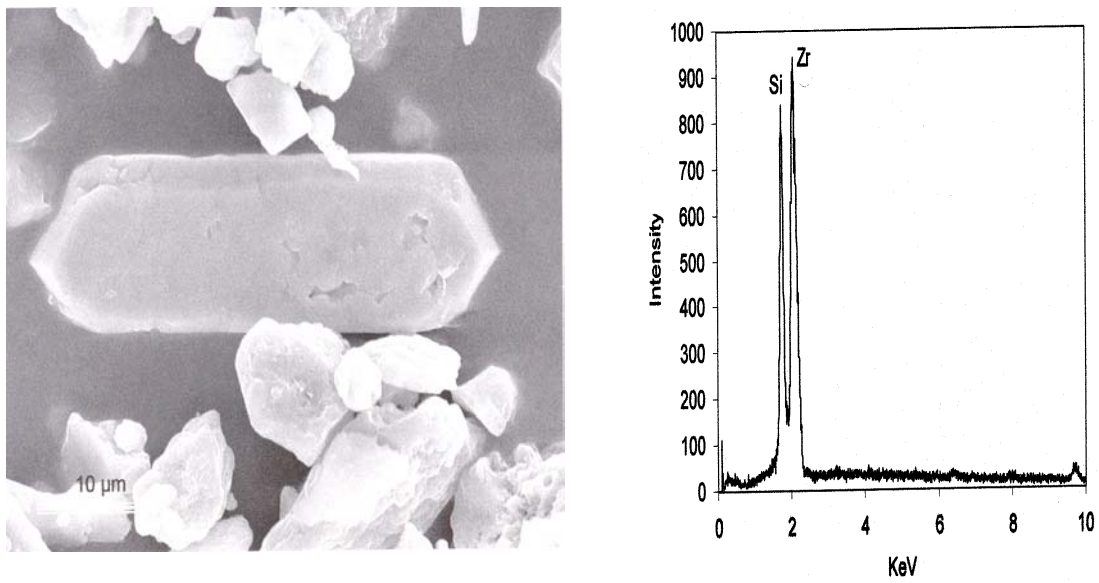
SEM: Zircon

TEM: S: smectite; K: kaolinite; Q: quartz

APPENDIX V continued.

Diffuse reflectance Fourier transform IR spectroscopy: Fine and coarse clay fraction

mid-IR spectra diluted with KBr

VITA

Misun Kang graduated from Korea University in the department of chemistry in 1993. She came to the U.S.A. in 1998 with her husband, Seung-Yong Jung, who has been studying in the chemistry department at Texas A&M University. She was interested in environmental geochemistry, so she started work toward a M.S. degree in the department of geology at Texas A&M University in the fall semester, 2000. She learned knowledge and the way of thinking as a scientist from many great teachers during her graduate studies. She graduated in August 2002.

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