Czech University of Life Sciences in Prague

Department of Soil Science and Soil Protection

Faculty of Environmental Sciences

EFFECT OF CARBONATE CONTENT ON SOIL SPECTRAL FEATURES

Diploma Thesis

Author: Ganzorig Khurelbaatar

Supervisor:

Prof. Dr. Ing. Luboš Borůvka   /……………………………./

Co-supervisor:

Ing. Aleš Klement   /……………………………./

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ABSTRACT

The main aim of the present study is using visible-near infrared Vis-NIR diffuse reflectance spectroscopy (DRS) to characterize and predict the effect of carbonate content on soil spectral features diffuse reflectance (Vis-NIR) spectroscopy is a fast, non-destructive technique well suited for analyses of some of the essential constituents of the soil. In this study focused on the evaluation of the effect of soil carbonate content on the empirical (in the laboratory) Vis-NIR diffuse reflectance spectroscopy for soil carbonate content. The experiments were focused on 3 locations with different soil-climatic conditions in the Czech Republic. In this study, in two types of soils with up addition of $CaCO_3$, another one soil type has naturally measured by Vis-NIR spectra (350-2500 nm). Soil is fundamental natural resource which people rely on for the production of food, fiber, and energy.

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CHAPTER 1

INTRODUCTION

Introduction

Soil is an important part of biosphere in our planet and the upper layer of lithosphere. Generally soil is a complex matrix that consists of minerals, air, water, and organic matter the countless micro organisms and the decaying remains of once living things. Soil is fundamental natural resource which people rely on for the production of food, fiber, and energy. The research of earth resources and environment by remote sensing methods are directly or indirectly related to soil spectral characteristics because soil is one of the most exposed earth media.

Soil is a heterogeneous mixture of various chemical compounds. Most methods for soil analysis are based on wet chemistry. A fast and convenient soil analytical technique is needed for soil quality assessment and precision soil management (Chang et al., 2002).

Therefore, the study on soil spectral reflectance features is a physical basis for proximal soil sensing (PSS). PSS provides soil scientists with an effective approach to learn more about soil. Over the last few decades a large number of attempts have been made to predict soil properties **with Visible and Near Infrared spectroscopy (Vis-NIRS, 350-2500nm) Diffuse Reflectance Spectroscopy (DRS).** This technique was used more than 30 years ago for rapid moisture analysis of grain and several soil spectral libraries have been created using a wide array of soils considering their physicochemical and biological properties (Ben-Dor et al., 1999; Malley et al., 2000; Chang et al., 2001). Vis-NIR spectroscopy has been used successfully by chemists and physicists to resolve structural arrangement of organic and inorganic substances. Several studies soil VIS-NIR measurements have been reported in scientific literature, however, only a few studies have been reported on Vis-NIR DRS for soil carbonate content.

In present thesis focused on determination of soil carbonate content on Vis-NIR (350 – 2500 nm) regions. Vis-NIR reflectance spectra for most primary and secondary minerals have been well-described, though quartz and feldspars have weak to non-existent absorptions in the Vis-NIR range (Hunt, 1977, 1982; Clark, 1999; Clark et al., 2003). Carbonates of alkali-earth elements have well-defined absorption bands in near infrared (NIR) range (Bendor & Banin, 1990).

Carbonate minerals, such as calcite ($CaCO_3$), aragonite and dolomite ($CaCO_3$, $MgCO_3$), are considered to be the main sources of neutralizing potential (NP) in soil, tailings and waste rock. Carbonate content of soil depends on parent material or results of neo-formation (secondary carbonates). Various primary and secondary carbonates are found in soil (Doner & Lynn, 1989), it is difficult to distinguish them in the natural soil field. Description of the carbonate content is interesting for extra-terrestrial exploration, because carbonates are typically formed by processes such as deposition from water which could indicate a history of an environment that supported life.

In generally, calcium carbonate content is a basic soil property widely used by soil scientist and surveyors and it is also interacting with other chemical and physical properties. For example: soil texture, morphology, organic matter, pH and ion exchange capacity etc. Soil pH is an important environmental factor which can influence plant growth (Reeuwijk et al., 2002). The carbonate minerals, due to their relatively high solubility, reactivity and alkaline character, act as pH buffers that mean pH values of most calcareous soils are within the range of 7.5 to 8.5. Therefore these soil properties, specially carbonate content, play an important role in Pedogenesis, Chemical and Rhizosphere processes in the soil.

This thesis intended to analyze the relationship between soil reflectance data and soil carbonate content. The following thesis is organized into two additional chapters. Chapter two is a review of literature concernig Vis- NIR, Diffuse Reflectance Spectroscopy. Chapter three meets the spectral analysis in two different soil sample sets from local scale, and where analysis in natural soil samples from regional scale.

Hypothesis

Vis-NIR diffuse reflectance spectroscopy is directly influenced by combinations and overtones of fundamental vibrations of soil properties such as: organic matter, moisture, pH, particle size, heavy metals and mineralogy. I hypothesize that soil carbonate concentration can effect soil spectral features in Vis-NIR regions which can predict carbonate contents of different soil types. It can be reasonably predicted from results of soil diffuse reflectance spectra.

Objective of study

The main aim of the present study is using Vis-NIR diffuse reflectance spectroscopy to characterize and predict the effect of carbonate content on soil spectral features. In other words the aim is to examine relationship between soil diffuse reflectance spectra and carbonate content of several types of soils in selected regional agricultural areas of the Czech Republic. Other way of aim is to evaluate the ability of Vis-NIR diffuse reflectance spectroscopy to predict diverse soil properties.

The following study is organized around the key question: **What is the role of Carbonate content in soil properties and which is how to effect in soil spectral features?** To answer the questions: several specific objectives are approached.

- o To determine soil pH properties different horizontal of soil profile.
- o To determine soil pH properties of two different soil types in selected regions
- o To assess the possibility of carbonate content prediction in natural soils.
- o To describe the effect of carbonate content on soil spectral features: based on Visible to Near Infrared Diffuse Reflectance Spectroscopy.

Chapter 2

LITERATURE REVIEW

2.1 Fundamentals of Visible to Near Infrared - Diffuse Reflectance Spectroscopy (DRS) Proximal Soil Sensing – Optical Soil Reflectance

Historically, scientists and surveyors understanding of the soil and soil assessment, its quality and function had been gained through routine soil chemical and physical laboratory analysis. The conventional laboratory analyses are still working well, but they can be expensive, complex, time- consuming and some are working with toxic substances. Proximal Soil Sensing (PSS) is a set of technologies developed to measure the physical, chemical and biological properties of soil when placing the sensor in contact with, or at proximal distance (less than 2 mm) to the soil being characterized (Viscarra Rossel et al., 2011). PSS is more cost and time effective than conventional laboratory analyses, which will be easy to carrying, faster and also can be used in-situ (field) like while landscape. PSS instruments allow for a relatively large number of measurements to be obtained rapidly and at a relatively low cost. Currently developed sensing systems may be categorized by the manner in which they operate. They may be static or mobile, invasive or non-invasive, active or passive, and direct or indirect.

Optical soil reflectance is one of the PSS techniques which are based on measuring the soil's ability to reflect and emit energy in different part of electromagnetic spectrum (EM). Especially Visible to Near Infrared Spectroscopy (Vis-NIRS) is widely used in science, industry, and commercial applications to identify and quantify chemical components. In past times a large number of attempts have been made to predict soil properties with Vis-NIR. Spectroscopy is rapid, timely, less expensive, non-destructive, straightforward and sometimes more accurate than conventional analysis. There is a global thrust towards the development of more time- and cost efficient methodologies for soil analysis as there is a great demand for larger amounts of good quality, inexpensive soil data to be used in environmental monitoring, modeling and precision agriculture. Diffuse reflectance spectroscopy provides a good alternative that may be used to enhance or replace conventional methods of soil analysis, as it overcomes some of their limitations.

Principle

Spectroscopy is the study of the interaction between light (including the non-visible wavelengths) and matter (solid, liquid, gas). Light beams enter to the matter that can be dispersed into the matter and emitted, reflected, or scattered by particle component of matter (molecule, atom) (Springsteen, 1998). Light can be measured in units of frequency or wavelength according to the equation

$$\lambda * \nu = c \qquad (1)$$

Where λ is wavelength (m), ν is frequency (Hz, s^{-1}) and c is the speed of light, $2.998 \cdot 10^8$ m s^{-1}. With c as a constant, frequency can also be described as the reciprocal of Wave length or wave number ($\acute{\nu}$)

$$\lambda^{-1} = \acute{\nu} \qquad (2)$$

This unit of measurement is analogous to wavelength and is used particularly in the mid infrared region. Light travels in "packets" of energy, or photons, and each photon carries a specific amount of energy related to the frequency or wavelength of the light according to this equation:

$$E = h * \nu \qquad (3)$$

Where E is energy (J), h is Planck's constant ($6.626 \cdot 10^{-34}$ J $\cdot$ s). This equation summarizes the qualitative impact of light – higher frequency results in higher energy and lower wavelength gives lower energy. Low-energy waves have long wavelengths, and high-energy light waves have short wave lengths. This relationship can be viewed in Fig. 2.1, a diagram of the electromagnetic spectrum. The regions focused on here will be the visible (Vis, 350-700 nm) and IR regions divided into the near infrared (NIR, 700-2500 nm), the mid infrared (MIR, 2500-25000 nm) and the far infrared (FIR, 25000-100000 nm) (Osborne, 2000).

ENERGY ⟵

| 25.000 | 14.286 | 4.000 | 400 | wavenumber (cm^{-1}) |

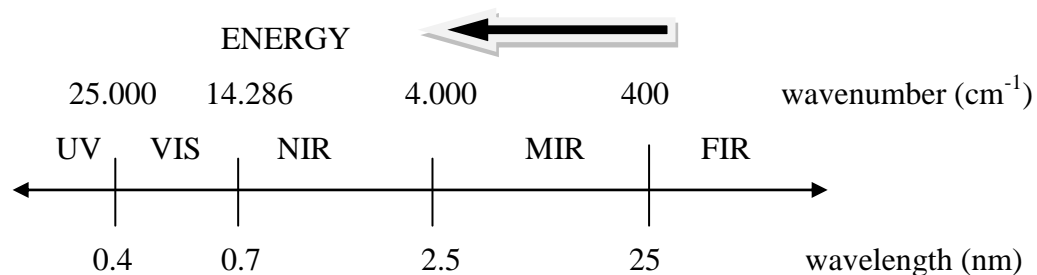| UV | VIS | NIR | MIR | FIR |

| 0.4 | 0.7 | 2.5 | 25 | wavelength (nm) |

Figure 2.1: Diagram of electromagnetic spectrum

Photons in the Ultraviolet/Visible spectral range have enough energy to excite or ionize materials by raising the energy level of bound electrons. Near Infrared radiation has

less energy (photons) but it does excite molecular vibrations. Vibration spectroscopy in the Vis-NIR range used for process monitoring and quality (concentration) control.

Spectral range is important to cover enough diagnostic spectral absorption to solve desired problems. Table 1.1 shows ranges of electromagnetic spectrum which are used in this thesis.

Table 2.1 Electromagnetic spectrum

Type of Radiation	Frequency Range (Hz)	Wavelength Range (nm)	Type of Transition
Visible	$4\text{-}7.5\text{x}10^{14}$	750 -350	outer electron
Near-infrared	$1\text{x}10^{14}\text{-}4\text{x}10^{14}$	2500 -750	outer electron molecular vibrations

As mentioned, Vis-NIR spectroscopy measures and records the interaction of radiation (in the form of light) with a material across the visible and near-infrared ranges of the electromagnetic spectrum. When light strikes a material it can react in one or a combination of different ways. Three of the major ways that light can react with a material are reflectance, transmittance, or absorbance (fig. 2.2). Those reactions can be qualified and quantified by spectroscopy.

Figure 2.2 The light beam affected by matter
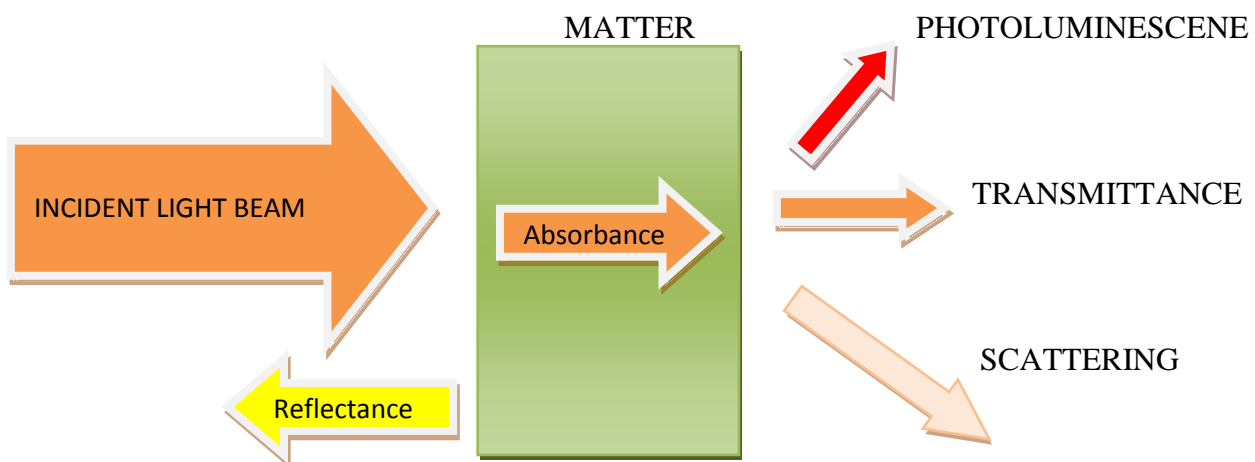
Basic discussion about each reaction will achieve more comprehensive understanding of methodology behind Vis-NIR spectroscopy. The first concern principle of this study is how light reflected off by sample surface.

Reflectance

One of the primary reactions incident light has with a material is reflectance. In almost all cases a portion of incident light is reflected off of the surface or near surface of a matter. Reflectance can be divided into two forms: specular, and diffuse reflectance. Specular reflection is light that has been defined as the angle of reflection equaling the angle of incidence. This type of reflection is mirror like in nature and is typically inconvenient in reflectance spectroscopy. Specular reflection refers to a surface effect that reflects nears all of to the entire incident light. It means that it can be used to determine physical characteristics such as roughness and grain size (soil texture, clay content) of matter surface but it is not explored as a viable method in this study.

Diffuse reflectance is light that has been redirected over a range of angles after entering and passing through the sample (Stewart, 1998). It can be defined as the opposite of specular reflectance. Diffuse reflectance measurements are used to solid and granular samples (Penner, 1994). A common misconception is that this type of reflectance is purely a surfacing phenomenon (Hubbard 2006). The degree to which photons penetrate a matter surface and remerge allows reflectance spectroscopy methods to be a practical means of matter identification. A photon enters a material to a certain depth where it may undergo variable refractions before being absorbed or reemerge as diffused light (Hubbard 2006). This reaction of light is often called diffuse reflectance and can be used to make assumptions regarding the presence of various absorption features (Hubbard 2005).

Figure: 2.3: Schematic diagram of Vis-NIR diffuse reflectance spectroscopy
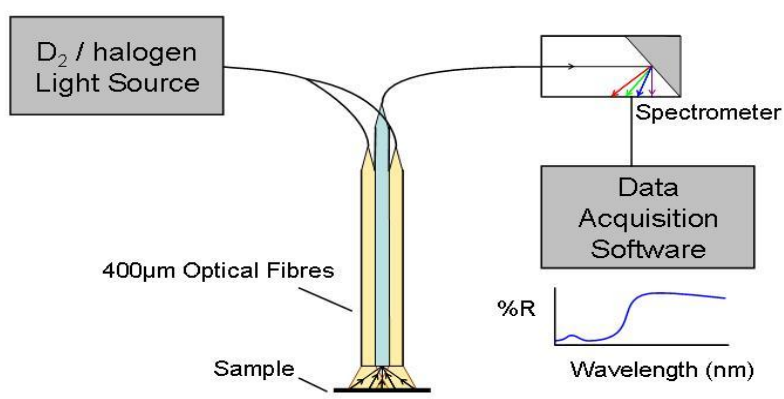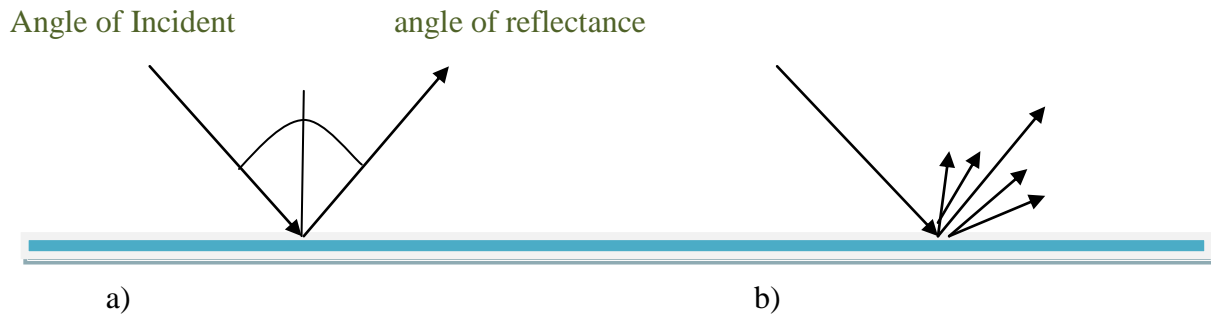
Figure 2.4: The type of surface reflectance process, a) specular, b) diffuse

Angle of Incident   angle of reflectance

a)   b)

Transmittance

A second interaction incident light may have with a material is that it may be transmitted. Transmitted light is defined as incident light that passes through the entire width of the material. The incident light may be reflected or refracted from one grain to the next as its travel path through the material is rarely direct. Transmission spectroscopy is based upon the relationship known as Beer's Law, a quantitative interpretation as to how photons are attenuated in relation to an intervening medium (Clark, 1999).

When used in transmission spectroscopy, Beer's Law is stated as

$$I = I_0 * e^{-acl} \tag{4}$$

Where I is the output intensity at a specific wavelength, Io is the original intensity at the same wavelength, a is the wavelength and material specific absorbance, c is the concentration of the substance and e is the optical path length. This law only applies when the substance is diluted in a non-absorbing matrix such as KBr. The equation leads to a derivation of the linear relationship between absorbance and concentration (Duckworth, 1998)

$$A = \log(1/T) = a * c * l \tag{5}$$

Where A is absorbance and T is transmittance or I/Io.

Similarly, the Kubelka-Munk function is a linear relationship between substance concentration and reflectance for diffuse reflectance spectroscopy –

$$f(R\infty) = \frac{(1 - R\infty)^{\wedge}2}{2R\infty} = \frac{K}{S} \tag{6}$$

Where R∞ is the reflectance after penetration and scattering throughout a non-absorbing matrix of infinite depth, K is molar absorption coefficient, C is concentration and S is scattering coefficient (Coates. J. 1998). This relationship only applies to samples diluted in a non-absorbing matrix.

Absorbance

The third interaction, covered in this study, that incident light has with a material is absorbance. When incident light strikes a material it can be absorbed by that material or the chemical or elemental composition of the material. The amount of light absorbed is wavelength dependent and is graphically expressed as either a Lorentzian, Gaussian, or ixed Lorentzian/Gaussian curve (Mark and Workman 2003). Therefore, the amount of photons absorbed by the material can be plotted graphically in relation to the wavelengths at which this interaction takes place. The absorption coefficient is a function of wavelength (Clark 1995). Researchers quantify how much light is being absorbed by a material using Beers Law. (Equation №5) There are many factors that dictate the amount of light that is absorbed by a material and for a more comprehensive discussion refer to Hunt and Salisbury (1970, 1971); Hunt et al. (1971); Hunt (1977); and Clark (1999). This study firstly focused on two processes that determine the amount of incident light that is absorbed by a matter. According to Clark (1999), there are two processes of absorption: Electronic transition and vibrational.

Electronic transition process

At the atomic level atoms and ions exist at a certain energy state (Clark 1999). When photons are continuously absorbed by an atom the predefined energy state increases exponentially. Conversely, when a photon is released from an atom, the energy state of that atom decreases. However, this release of energy rarely occurs at the same wavelength. The resulting spectrum reveals information about the chemical composition of the material. The most common information revealed by this process is the presence or absence of certain transitional elements. Some of these transition elements include Ni, Cr, Co, and Fe (Clark 1999). These elements are missing one or more electrons in their outer shell causing their energy level to split within a crystal field. A photon is then acquired to balance out the electrons energy level states.

Iron is the most common transitional element in minerals (Clark 1999). Iron is also common in most soil types and minerals to a degree that its absorption spectral feature can be readily identified. Iron ions split in various ways depending upon the crystal fields present in a mineral and this directly alters the size of the absorption feature. This makes it possible to identify specific mineral composition as in the case study previously mentioned (De Souza 2004).

A second electronic transition process that causes distinctive absorption bands is called charge transfers. In a charge transfer interaction an element absorbs an incoming

photon, which causes one of its electrons to jump to another element. The red color of iron oxides is primarily caused by this phenomenon (Morris et al. 1985). By studying the spectral response of a mineral undergoing charge transfer, one may be able to identify its mineral composition. The final electronic processes covered in this study are absorption bands caused by color centers. Color centers are a function of an imperfect crystal, which is illuminated by solar radiation (Clark 1999).

Vibrational stretching and bending process

The creation of absorption features is brought about by internal vibrations and their subsequent overtones. These features occur in the infrared part of the electromagnetic spectrum ranges from 1200nm to 40,000nm. Clark (1999) describes the molecular bonds or crystal lattice of a mineral as springs with weights attached. When incident light interacts with these types of bonds the transferring of electrons triggers a vibration.

Vibrational absorption is a result of molecular bonds. Bonds between atoms of a molecule with a dipole moment vibrate at a specific frequency due to symmetric stretching, asymmetric stretching and bending (Umland and Bellama, 1986). In minerals some of the most common of vibrational absorption features are caused by the presence of water molecules. The spectral features produced by water occur at 1400, 1900, and 2400 nm. The atomic composition of some minerals contributes to the amount of this spectral response. The OH bonding in water, called hydroxyl bonding, causes these vibrations when irradiated with photons. In this manner the careful analysis of spectral data can give the researcher information about the chemical bonding of the mineral being studied.
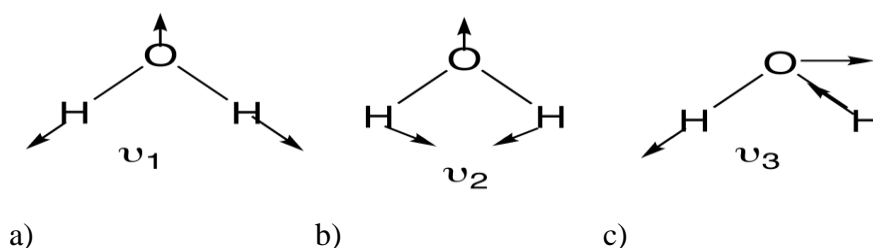

Figure 2.5 In liquid water nonlinear molecules stretch vibrations. a) Symmetric stretch is denoted v_1 , b) Asymmetric stretch is denoted v_2 , c) bending motions are v_3.

The Vis-NIR region holds first overtones of C-H, O-H and N-H bond vibrations (Weyer and Lo, 2002) because of the close proximity of the relative fundamentals within the MIR region. For example, water fundamentals are found at 6269, 2738, and 2662 nm with

overtones of the OH stretch at about 1400 nm and the combination of the H-O-H bend with the OH stretch found near 1900 nm (Clark, 1999). Although fundamental absorptions are stronger than overtones and combinations, overtones are specific to each component and are more sensitive to changes in the chemical composition of the absorbing molecule leaving both regions (Wetzel, 1983).

Carbonates of alkali-earth elements have well-defined absorption bands in near infrared (NIR) range (Bendor and Banin, 1990). This may be especially interesting when studying soil carbonate content due to the variable amounts of carbonate ions present in some soil types. An absorption feature caused by the presence of various carbonates might be diagnostic of certain soil. Simply, it is absorption measurement of Vis-NIR frequencies by sample positioned in the path of the Vis-NIR beam. The main goal of the Vis-NIR spectroscopic analysis is to determine the chemical functional groups in the samples and which different functional groups absorb characteristic frequencies of Vis-NIR radiation.

<u>Application of reflectance spectroscopy</u>

Vis-NIR reflectance spectroscopy is one of the proximal soil sensing techniques that has been in use in science and industry for over fifty years. The speed and non-destructive nature of the sensor are advantages that have contributed valuable data to a number of scientific fields. Vis-NIR spectroscopy is currently applied in the chemical, pharmaceutical, food and beverage, petrochemical, pulp and paper, textile, paint, and tobacco industries as well as in many other fields (Hatchel 1999).

In soil science Vis-NIR spectroscopy sensing data could provide good quality soil information more efficiently than laboratory methods of soil analysis, which can be expensive and time consuming. Due to different principles of inter action between light and matter, not only can chemical composition be measured, but layer thickness and surface properties as well. Especially NIR spectroscopy is an important tool that can be used to simultaneously optimize process control and product quality, delivering an improved product to the market. One other advantage is the potential adaptability of the techniques for on-the-go field use (Viscarra Rossel and McBratney, 1998b). These are particularly important advantages now that there is an increasing global need for larger amounts of good quality inexpensive spatial soil data to be used in environmental monitoring, modelling and precision agriculture.

Advantages and Disadvantages of Vis-NIR DRS

There are many reasons for the interest in Vis–NIR. For example, sample preparation involves only drying and crushing, the sample is not affected by the analysis in any way, no (hazardous) chemicals are required, measurement takes a few seconds, several soil properties can be estimated from a single scan, and the technique can be used both in the laboratory and in situ (Viscarra Rossel et al., 2006c). Spectral reflectance in the Visible and near infrared (0.35 to 2.55 micrometer) offer a rapid, inexpensive, nondestructive technique for determining the mineralogy and obtaining some information on the minor element chemistry of the hard to discriminate carbonate minerals, and it can in one step, provide information previously obtainable only by the combined application of two or more analytical techniques (Gaffey, 1986), well suited in soil mineral analysis. Generally it means that sampling, handling and pretreatment of samples and calibration procedures including reference analysis should be kept to minimum.

The rapid nature of data collection is also a benefit to the researcher who wishes to analyze large numbers of samples. Even allowing for thirty minute equipment set up and initializing time period, the technique is remarkably fast, capable of analyzing over a hundred samples in an hour. The device gathers a full spectrum of reflectance data in 0.1 seconds, therefore, the most time consuming process is simply arranging the sample under the probe (Hatchel 1999). No sample preparation is necessary other than the standard cleaning and drying of the material prior to analysis unless more destructive techniques are desired.

Vis-NIR DRS are influenced by sample moisture and particle. Moisture content of samples is of particular interest as moisture interference in spectral readings has been noted in many studies (Morgan et al. 2009; Stevens et al. 2006; Van der Meer and De Jong 2000). The use of Vis-NIR DRS has been more extensive in fields related to compost: agriculture and waste management. The technology has been shown in these fields to identify different soil properties by several scientists.

Quantitative analysis of spectroscopy

Over the past several years, several studies of soil VIS-NIR measurements have been reported in scientific literatures. These have been with fixed base spectrometers, either in a lab or field setting. These have laid the groundwork for on-the-go VIS-NIR sensing by studying the relationships between VIS-NIR and various soil properties. The Vis-NIR

spectroscopy was generally considered to be able to provide qualitative and quantitative analysis of common samples, especially when spectral data were acquired using conventional laboratory methods. However development of reliable Vis-NIR spectroscopy instrumentation and strong computerized data processing capable to have greatly improved performance of the quantitative Vis-NIR analysis. The quantitative analysis is using to express the large amount of spectral data into form which can be reliably identified.

Diffuse reflectance spectra of soil in the Vis–NIR are nonspecific due to the overlapping absorption of soil components. This characteristic lack of specificity is compounded by scatter effects caused by soil structure or specific components. All of these factors result in complex absorption patterns that need to be mathematically extracted from the spectra and correlated with soil properties (Viscarra Rossel et al., 2006). Hence, the analyses of soil diffuse reflectance spectra require the use of multivariate calibrations (Martens and Naes, 1989). Multivariate calibration is a very useful tool for extracting chemical information from spectroscopic signals. It has been applied to various analytical techniques, but its importance has been manifested in near-infrared (NIR) spectroscopy (Feudale et al. 2002).

The analytical information contained in the typically broad, extensively overlapped bands of NIR spectra is hardly selective and is influenced by a number of physical, chemical and structural variables. In addition, differences between samples may cause very slight spectral differences that are difficult to distinguish with the naked eye. However, the powerful Vis-NIR instruments currently available quickly provide vast amounts of data that require speedy, efficient processing if it is to yield useful analytical information. For these reasons, Vis-NIR spectroscopy requires chemometrics to extract as much relevant information as possible from the analytical data.

Chemometrics:

Chemometric is the process through which we will obtain chemical information about an "unknown" material using chemical data from a reference material. In spectroscopy, chemometric process refers to utilizing spectral data to predict related chemical data (Duckworth, 1998). Chemometrics is the bridge between connecting the state of a chemical system to the measurements of the system. Spectroscopists need to use the following methods within a chemometric tools used to construct the model.

    • Principal Component Analysis (PCA)

• Regression (PLS, PCR and MLR) and Prediction (Dongsheng Bu, dPhD, Principal Scientist, CAMO).

Principal component analysis of the chemometric methods is not discussed here.

Regression methods:

Regression is used as a prediction method though one of the key problems in spectroscopy is the set of highly correlated predictor variables (spectral data).The Beer-Lambert law is easiest way of constructing regression line (Adams, 1995). The most common prediction methods for soil applications are based on linear regressions, namely multiple linear regressions (MLR) (Ben-Dor and Banin, 1995a; Dalal and Henry, 1986), principal component regression (PCR) (e.g. Chang et al., 2001), and partial least squares regression (PLSR) (e.g. McCarty et al., 2002). This predictive approach is insensitive to input errors because of the weighting procedure, requires no variable transformations, handles large amounts of data in a relatively short period of time. It is a new application to the world of spectroscopy that has thus far only been applied within global spectroscopic analysis of soils (Brown et al., 2006). However PCR and PLSR are the most common techniques for spectral calibration and prediction (Viscarra Rossel et al., 2006). Some most common regression methods are described here. But in this study deals with MLR that is rapid analysis, can handle co-linear data, and can provide useful qualitative information.

Multi-Linear Regression:

The Multi-linear regression (MLR) is the oldest of the presented methods and is less and less used in applications due to the improvement of computation power. This regression allows establishing a link between a reduced number of wavelengths (or wavenumber) and a property of the samples. The prediction yj of the search property can then be described with the formula:

$$y(j) = b(0) + \sum_{i=1}^{k} b(i)x(i) + e(i,j)$$

where $b(i)$ is the computed coefficient, $x(i)$ the absorbances at each considered wavelength and $e(i,j)$ is the error. Each wavelength is studied one after the other and correlated with the studied property. The selection is based on the predictive ability of the wavelength. The three modes of selection are: forward, backward, and stepwise. When the correlation reaches a value fixed by the operator it is kept as a part of the model calibration wavelengths. The

model is then computed between this set of calibration wavelengths and the reference values of the studied property (Yves Roggo et al., 2007).

Principal Component Regression:

The purpose of principal component regression (PCR) is to estimate the values of response variables at the selected principal components of the explanatory variables. The PCR divided into two steps. First the spectral data are treated with a PCA. Then a MLR is performed on the scores as predictive variables. The prediction equation is written **Y** (sampling) =**T** (sampling) *****b.** Where **T** is the new dimensional coordinates, **Y** is the reference values and **b** is the coefficient vector.

Partial Least Squares Regression:

Statistical analysis module performs model construction and prediction of activity/property using the **Partial Least Squares (PLS) regression** technique. It is based on linear transition from a large number of original descriptors to a small number of orthogonal factors. PLS regression is one of the more effective and commonly used prediction methods in spectroscopy (viscarra Rossel et al., 2006) and is widely used in reflectance spectroscopy data analysis. The basis of this technique is decomposition of the spectral data into a set of eigenvectors and scores while using the concentration data from a set of "known values" (Duckworth, 1998). PLS regression method, a chemometric technique is similar to PCR in that both X and Y variables are used to build vectors with the greatest predictive power, correlating new X variables with provided Y data (Wold et al., 2001). In PLS method the regressions are computed with least squares algorithms. The goal of the PLS is to establish a linear link between two matrices, the spectral data **X** and the reference values **Y**. This technique is modelling both **X** and **Y** in order to find out the variables in **X** matrix that will best to describe the **Y** matrix. This can be explained by the representation of the spectra in the space of wavelengths in order to show directions that will be linear combinations of wavelengths called factors which describe best the studied property (Adams, 1995).

2.2 Vis-NIR DRS used to measure soil properties

The past two decades, research on the use Visible (400-700nm) –Near Infrared (700-2500nm) diffuse reflectance spectroscopy in soil science has increased rapidly (Ben-Dor and Banin, 1995a; Brown et al., 2006; Shepherd and Walsh, 2002; Stenberg et al., 1995; Sudduth

et al., 1989; Viscarra Rossel et al, 1998). The soil scientists currently use Vis-NIR spectroscopy to identify soil properties in the laboratory and in the field (in-situ). The utility of VNIR-DRS for soil property determination is based on the following facts: (1) a soil is a complex mixture composed of various components with varying spectral properties such as primary minerals, clay minerals, organic matter, salts, and water; and (2) each spectral component has unique electronic transitions (caused by its atoms) and vibrational stretching and bending (caused by structural groups of atoms) leading to its distinct spectral signatures at some critical wavelengths.

Soil spectra in the Vis-NIR region are most influenced by absorption bands of iron oxides (870 and 1000 nm), overtones of water (1200, 1450, 1770 and 1950 nm) and hydroxyl stretching (1400 nm) and a metal-OH stretch combination (2200-2300 nm). The Vis-NIR region contains useful information on the organic and inorganic content in the soil and both clay minerals and soil organic matter (SOM), both of which are essential constituents of the soil, have well recognized absorptions features in this region (Viscarra Rossel et al, 2013). Both clay and SOM content are important for the soil structure and thereby soil aeration and water holding capacity which are factors strongly affecting plant growth. However, plant nutrient salts are by themselves not expected to absorb in the vis–NIR region and correlations found to vis–NIR are often weak (Stenberg et al., 2010).

Organic matter has been more difficult to characterize in the Vis-NIR region as it only holds overtones of CH, OH and NH fundamental absorptions found at low wavelengths of the MIR region. Workman (1998) assigned absorptions in the NIR to organics including 1700-1900 and 1100-1300 nm to C-H first and second overtones, respectively, and 1450-1550 nm as the N-H first overtone. Chang et al. (2002) and Workman (1998) both assigned a distinct stretch from 2300-2350 nm to humic acid. The most of the organic absorption features would likely be overlapped by stronger absorptions of water and carbonates, explaining the difficulty in interpretation of Vis-NIR soil spectra. Water has strong absorption features in the Vis–NIR spectra of soils, most visibly near 1400 nm and 1900 nm, but there are weaker overtone bands elsewhere (Clark et al., 1990). Most of soil properties measured by Vis-NIR spectrum and results of absorption and reflection features are possible to identify interested soil property. Here are some band assignments for fundamental Vis-NIR absorptions of soil constituents and their overtone and combinations. Show by below table 2.2.

Table 2.2 Some band assignments for fundamental Vis-NIR absorptions of soil constituents and their overtone and combinations (Viscarra Rossel et al., 2010), (Clark et al., 1990).

Soil constituents	Fundamental (cm^{-1})	Vis-NIR wavelength (nm)	Vis-NIR mode
Fe oxides			
Goethite		434, 480, 650, 920.	Electronic transition
Haematite		404, 444, 529, 650, 884.	Electronic transition
Water	$\nu 1$ O–H 3278 cm^{-1}	1915	$\nu 2+\nu 3$
	$\nu 2$ H–O–H 1645 cm^{-1}	1455	$2\nu 2+\nu 3$
	$\nu 3$ O–H 3484 cm^{-1}	1380, 1135, 940.	$\nu 1+\nu 3$, $\nu 1+\nu 2+\nu 3$, $2\nu 1+\nu 3$.
Clay minerals			
Carbonate	$\nu 3$ CO3^{-2} 1415 cm^{-1}	2336	$3\nu 3$
Organics			
Aromatics	$\nu 1$ C–H 3030 cm^{-1}	1650, 1100, 825.	$2\nu 1$, $3\nu 1$, $4\nu 1$.
Amine	δ N–H 1610 cm^{-1} $\nu 1$ N–H 3330 cm^{-1}	2060, 1500, 1000, 751.	$\nu 1+\delta$ $2\nu 1$, $3\nu 1$, $4\nu 1$
Carboxylic acid	$\nu 1$ C;O 1725 cm^{-1}	1930, 1449.	$3\nu 1$, $4\nu 1$
Methyls	$\nu 1$ C–H 1445–1350 cm^{-1}	2307–2469, 1730–1852.	$3\nu 1$, $4\nu 1$
Carbohydrates	$\nu 1$ C–O 1050 cm^{-1}	2381	$4\nu 1$

Interpretation of soil Vis-NIR spectra can be difficult but particularly soil properties being studied. It will be summarize such as absorption features in the 400 – 1000 nm are mostly due to the Fe- oxides and 1000 – 2500 nm can be due to water, clay minerals and organic matter.

Figure 2.6: typical soil spectrum in the A) visible, B) near infrared, and C) mid infrared portions of the electromagnetic spectrum. (Viscarra Rossel et al., 2011, pp247.)
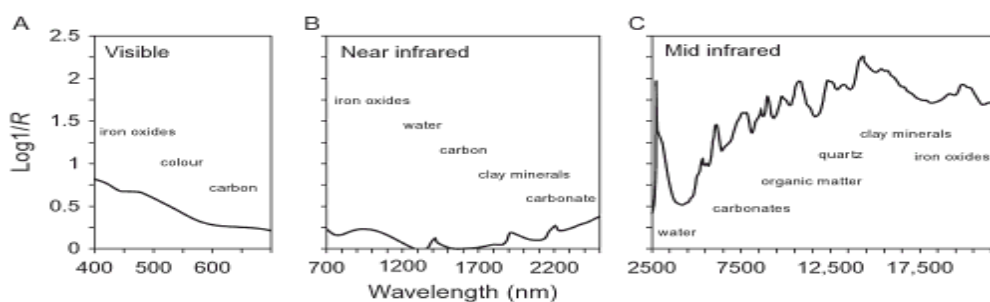
Soil Carbonate:

A functional group that contains the grouping carbonates (CO_3^{-2}). In organic carbonates, there are carbon atoms attached to three of the oxygen molecule which has (CO_3^{-2}) grouping has a (-2) negative two charges (anion), and is ionically bonded to two positive ions, usually metal ions (cation).

Figure 2.7: Chemical structure of carbonate ion, trigonal planar
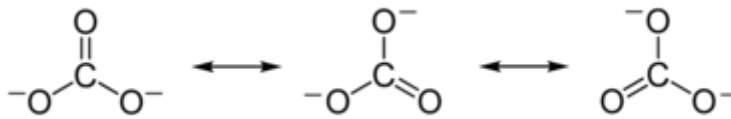
The carbonate content such as mineral a dominating influence on soils in which they are present because of their relatively high solubility. Inorganic carbonate in soil occurs predominantly as the sparingly soluble alkaline-earth carbonates, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Calcite is usually the dominant form in active pedogenetic environments (Doner & Lynn, 1977; Nelson, 1982). In this subtopic focus on Carbonate content in soil and find answer of question: What soil properties are affected by carbonate content variables? In particularly, Clay and calcium carbonate ($CaCO_3$) contents are soil data widely used by soil surveyors to describe soil types, and are also pertinent properties used to quantify vulnerability to erosion (Gomez et al., 2008). Soils developed on sedimentary rocks in arid zones usually contain carbonate minerals such as calcite and dolomite. Also soil carbonates play a role in soil respiration positively or negatively depending on the soil type, the weather conditions, soil texture, soil pH etc. The soil respiration is a biological process mainly contributed by soil microbes and plant roots.

Carbonate is indicating two characterize in soil reason by source, are in soils either residues of the parent material (primary carbonate) or neo-formation (secondary carbonate). In many soils, it's difficult to distinguish in the field between primary and secondary carbonates. Soils are formed through pedogenetic processes from weathering of geological substrate and accumulation of organic material. In generally soil minerals are clay minerals, carbonate and bedrock minerals which included Fe, Mn, Al (oxide, Hydroxide). Primary minerals originated from bedrocks, Secondary minerals originated from primary minerals by geological weathering. The forms of secondary carbonates in soils are diverse and are

considered to be informative for diagnostics of soil genesis (Guidelines for soil description, 2006). Water in the soil may dissolve the carbonates, changing them into bicarbonates (HCO_3^-) which will be carried through the soil and then may precipitate, producing accumulations of carbonates. These are generally composed of calcite.

Prediction of soil attributes in unknown soils can be achieved by deriving models from the reference laboratory data and corresponding spectra. Some attributes (e.g., carbonates, SOM, and Fe oxides) can be predicted directly based on the presence of characteristic chemical bonds or molecules that absorb at specific wavelengths (Jose, 2014). Combination and overtone bands of the CO_3^{-2} fundamentals occur in the near IR. Carbonaceous soils show overtone features at 2500 and 2300-2350 nm and weaker combinations near 2120-2160, 1970-2000 and 1850-1870 nm (Clark, 1999), 2335 nm – (Soriano-Disla et al., 2014). For $CaCO_3$, an absorption peak is expected around 2348 nm, corresponding to CO_3 overtone vibrations (Hunt and Salisbury, 1971).

CHAPTER 3

EXPERIMENTS

3.1 Introduction:

In this study, focused on the evaluation of the effect of soil carbonate content on the empirical (in the laboratory) Vis-NIR diffuse reflectance spectroscopy for soil carbonate content. The experiments were focused on 3 locations with different soil-climatic conditions in the Czech Republic. The whole experiment was carried out in the laboratory of the Department of Soil Science and Soil Protection of the Czech University of Life Science Prague during spring of 2013.

The overview of experimental part is following three groups of analysis.

Group 1: Two different types of natural soil samples, Haplic Cambisol (Humpolec town) and Haplic Luvisol (Hnevceves Town) from local scale. These soils with no natural carbonate content were thoroughly mixed with pure calcium carbonate at different rate (from 0 to 50 %).

Group 2: Measurement natural carbonate contents of natural soil samples from Haplic Chernozem (Praha, Suchdol).

Group3: Determination of basic soil properties in all soil samples: Soil pH, soil carbonate content and assessment of their relationship to spectral data in the Vis-NIR range.

3.2 Study areas and soil sampling:

The study areas consist of three locations in selected regional agricultural areas of the Czech Republic with three different types of soils. The first soil sample was collected from an agricultural field of crop research institute in Hněvčeves. Studied soil was Haplic Luvisol (loess parent material). The second place is Humpolec that is town of northwestern edge of the Bohemian-Moravian Highlands. The studied soil was Haplic Cambisol (orthogniess parent material). Third place is Suchdol in Praha, Czech University and Life Science, study field area. The studied soil was Haplic Chernozem (loess parent material).The Position of selected areas is shown below on figure 3.1.

Figure 3.1 The map of the Czech Republic including selected three study areas. (Identified by point symbol and labeled with names)
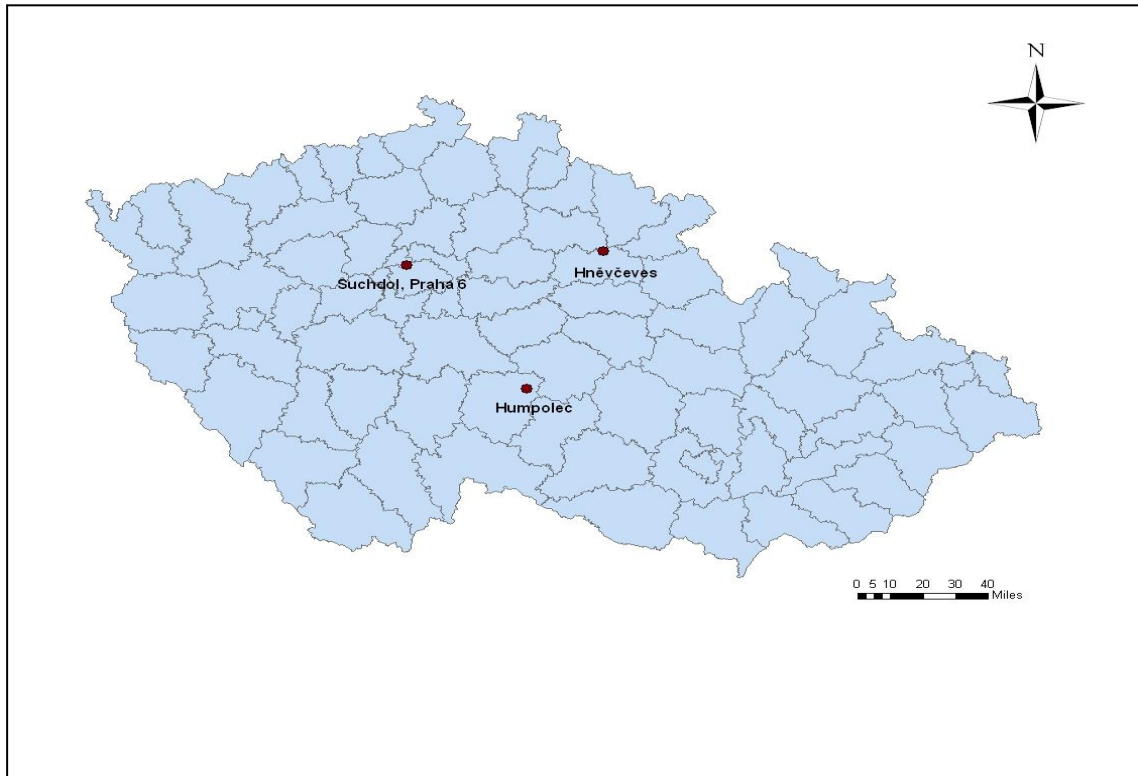
Picture 3.1 The Haplic Luvisol soil from Hněvčeves　　　　　**Picture 3.2 The Haplic Cambisol soil from Humpolec**
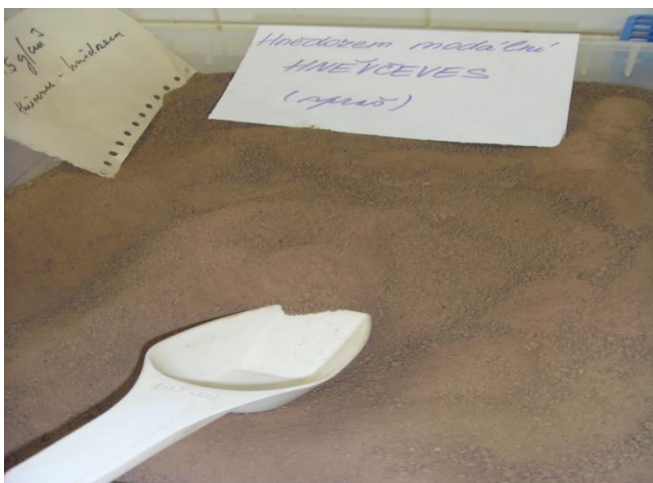
Table 3.1 The general parameters of study areas and soil samples characteristics. Source of data: Environmental soil science course- lecture material, 2011-2012. Refference number 20.

Set	Soil type	Parent material	Soil profile	Carbonate content	Location	Altitude (m.a.s.l)	Collected samples number
I	Haplic Chernozem	Loess	A, B, C three horizontal points/ In depth each 10 cm	Different cultural crops	Praha-6 Suchdol	260	42 samples (natural)
II	Haplic Luvisol	Loess (no carbonate in upper part)	Top and sub soil mixed	Grass	Hněvčeves	272	14 samples with different rate of CaCO$_3$
III	Haplic Cambisol	Orthogneiss	Top and sub soil mixed	Grass	Humpolec	527	14 samples with different rate of CaCO$_3$

Picture 3.3 The Haplic chernozem soil core in Suchdol Prague-6

Picture 3.4 The pure calcium carbonate

Soil sample preparation

The Haplic Chernozem soil samples collected by three horizontal points A, B, C. at each point took 14 samples were collected from soil layers 10cm thick, that is to the total depth of 140cm. The haplic Luvisol and haplic Cambisol soil samples were prepared by mixing top and subsurface soil samples together.

. These soil samples were air-dried for one week. After it they were crushed ground, sieved to 2mm (< 2mm) and prepared for soil analytical methods which are soil pH and carbonate content determination. But haplic Luvisol and haplic Cambisol soil samples were mixed with pure calcite ($CaCO_3$) at different amount rate. (0%-50% on the weight basis; see table 3.2). In total 70 soil samples were used (42 samples collected from Chernozem, 14 samples of Cambisol and Luvisol each after amending with $CaCO_3$.

Table 3.2. Calcite ($CaCO_3$) at different amount rate - 0%-50% on the weight basis.

mass [CaCO3] g	0	0.15	0.3	0.45	0.6	0.75	1.125	1.5	2.25	3	3.75	7.5	15	37.5
soil sample (g)	75	74.85	74.7	74.55	74.4	74.25	73.88	73.5	72.8	72	71.3	67.5	60	37.5

The pretreatment of soil sample before Vis-NIR analysis in the laboratory is drying and sieving, as well as for most other soil analytical methods. Stones (>2mm) and course plants remmants which could affect the spectra were removed.

Picture 3.5 Sieving process of soil   **Picture 3.6 The soil sample collection from core.**

3.3 Conventional laboratory analyses

The main soil physical and chemical properties are determined by soil pH, Organic carbon, carbonate content, texture (clay, silt, sand), and cation exchange capacity (CEC). In this laboratory experiment we measured and determined only two of them.

Soil pH

The acidity or alkalinity properties of soil can influence plant growth significantly. The soil pH was measured using an Inolab Level 1 pH-meter and all soil samples measured by suspensions solution of distilled water and potassium chloride (KCl). That suspension soil: liquid ratio was equal to 1:2. In each sample using 10g soil and 20 ml distilled water or potassium chloride /1M/ (KCl) mixed into 50 ml plastic bottles. That was helped to shaken for 60 minutes on the shaker and then placed into centrifuge for 5 minutes. That measurement was done in three repetitions for each soil sample at room temperature.

Picture 3.7 Weighting of soil sample

Picture 3.8 Soil pH measurement in lab

Carbonate content:

The determination of carbonate content was based on the volumetric calcimeter analysis (Loopert et al., 1996) of carbon dioxide (CO_2), which was release during the certain application of 10% hydrochloric acid (HCl) solution added into 20g soil. But in this situation we used 5g soil and then result will be multipliedly by 4. Only haplic Chernozem soil was measured by this method. The chemical processes are following reaction:

$$(CaCO_3 + MgCO_3) + 4HCl \rightarrow (CaCl_2 + MgCl_2) + 2H_2O + 2CO_2 \uparrow$$
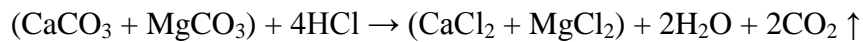
During the application of the acid into the soil sample a characteristic foaming is observed, evidence of carbon dioxide's emission and the existence of carbonate minerals consequently. If liquid level of the tube is stopped, we can write down mark number of tube. That is percent value of soil carbonate content.

In this analysis applied chemical and physical properties of Haplic Chernozem soil (Appendix 1, marked properties). It was used to evaluate relationships between carbonate contents and organic matter in soil profile.

Picture 3.9 Volumetric calcimeter method
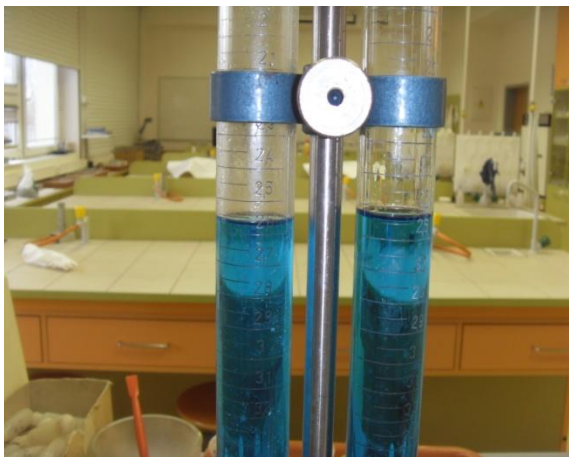
Picture 3.10 Volumetric calcimeter method

3.4. Laboratory reflectance measurements

Soil sample preparation

- In total, 70 soil samples collected or mixed from selected three areas. In this study we collected three types of soil.
- Hold into plastic Petri dishes of 60 mm in diameter and 5 mm in depth.
- The upper surface of the sample was fixed and smoothed.

Picture 3.11 FieldSpec-3 instrument	Picture 3.12 Soil sample of spectral measurement

Picture 3.11 FieldSpec-3 instrument

Picture 3.12 Soil sample of spectral measurement

Spectral measurements

The soil samples were measured in the visible and near-infrared (wavelength range of 350-2500 nm) spectroscopy in the laboratory with the ASD High Intensity Contact Probe and FieldSpec-3 instrument. That was designed for contact measurement of solid raw material. The contact probe used is equipped with a halogen bulb light source (6.5 W, with color temperature 2901 ±10% K). Diameter of contact probe's spot size is 22 mm. The instrument has spectral resolution 3 nm at 350-700nm and 10 nm at 1400-2100 nm, while the spectral sampling intervals varies between 1.4 nm at 350-1050 nm and 2 nm at 1000-2500 nm wavelength (Brodsky et al., 2011). The Vis–NIR spectra were recorded as percent reflectance (R%) at room temperature. Each sample was measured at three repetitions.

Data pretreatment

All spectral data recorded as original percent reflectance (%R) and transformed to absorption (A) through A=Log(1/R). Average spectra of repeated Vis-NIR scans on the same soil sample due to repeated data are almost similar. Data analyses were done on Microsoft Excel XLSTAT software tool. A correlation coefficient (r) was calculated between the various

reflectance data at each wavelength and chemically measured $CaCO_3$ content of the soils. A correlation matrix of all transformed spectra was generated using Pearson's product moment correlation coefficient.

$$r = (\Sigma(X- \mu x)(Y- \mu y))/(N^*x^*y)$$

(Where r = Pearson product-moment correlation coefficient, X and Y = random variables, x and y = definitive data points, N = total number of data points.)

The data for the 10 wavelengths giving the highest coefficient of correlation were used to calculate calibration model equation by a multivariate regression procedure. When the calibration models are established, new samples only need to be measured using Vis-NIR and the calibration models are used to predict the targeted soil properties.

Regression method

There are many different algorithms that can be used to calibrate soil Vis–NIR spectra to predict soil properties. We used the Multivariate Linear Regression (MLR) which is one of the linear calibration and prediction methods. A scheme of the main steps in the procedure to prediction is presented in Figure 3.2.

MLR procedure between the concentration of carbonate in soil and spectral response (Reflectance, R) of every band was run. Carbonate bands corresponding wavelength providing highest correlation of coefficient were further selected for examination under MLR procedure. The result, multi linear regression equation was used to determine the concentration of carbonate.

Figure 3.2 The data processing of Vis-NIR spectral measurements.
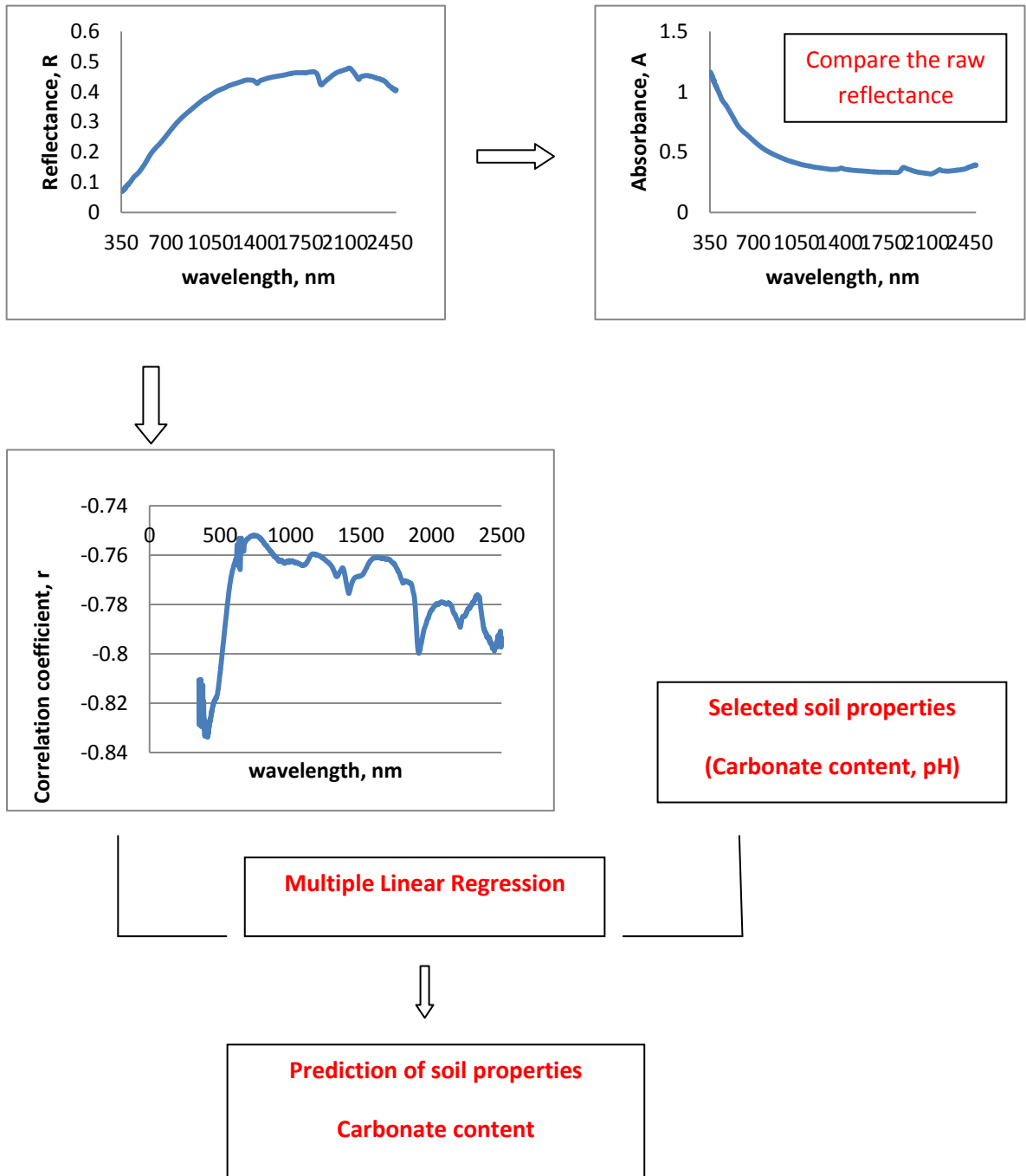
CHAPTER 4

RESULTS

4.1. Conventional laboratory methods

We have studied two conventional laboratory analyses (soil pH, carbonate content) in all soil samples. Three different types of soils are collected from three different locations. On the basis of these measurements we selected the following sets of soils for measure:

> Set I. The Haplic Cambisol- this set of soils containing 14 samples prepared with $CaCO_3$, which was added in the range of concentrations from 0% to 50%.

> Set II. The Haplic Luvisol - this set of soils containing 14 samples prepared with $CaCO_3$, which added was in the range of concentrations from 0% to 50%.

> Set III. The Haplic Chernozem – this set of soils containing 42 samples collected from three points (A, B, C), distance between points was 0.3m. Each of the points was collected 14 samples in every 0.1m following soil profile.

Table 4.1 The average values of observations for conventional laboratory analysis.

Soil types	Set 1-Cambisol			Set 2-Luvisol			Set 3-Chernozem			
Selected soil properties	pH water	pH KCl	$CaCO_3$ (%)	pH water	pH KCl	$CaCO_3$ (%)	Depth (m)	pH water	pH KCl	$CaCO_3$ (%)
1.	5.44	4.61	0	6.53	5.92	0	0.1	7.44	6.87	2.68
2.	6.12	6.06	0.2	6.82	6.69	0.2	0.2	7.68	6.91	3.3
3.	6.37	6.31	0.4	6.86	6.7	0.4	0.3	7.76	6.99	4.66
4.	6.44	6.35	0.6	6.97	6.73	0.6	0.4	7.86	7.18	11.7
5.	6.49	6.37	0.8	6.99	6.75	0.8	0.5	7.94	7.27	19.2
6.	6.49	6.4	1	7.02	6.77	1	0.6	8.03	7.33	17.9
7.	6.51	6.41	1.5	6.95	6.77	1.5	0.7	8.07	7.29	17
8.	6.50	6.42	2	6.97	6.78	2	0.8	8.11	7.31	16.4
9.	6.47	6.43	3	7.01	6.80	3	0.9	8.12	7.31	15.4
10.	6.53	6.45	4	7.04	6.81	4	1.0	8.19	7.30	14
11.	6.59	6.45	5	7.02	6.81	5	1.1	8.20	7.23	10.7
12.	6.61	6.51	10	7.07	6.85	10	1.2	8.16	7.25	8
13.	6.66	6.5	20	7.14	6.92	20	1.3	8.16	7.26	4.8
14.	6.85	6.85	50	7.37	7.17	50	1.4	8.10	7.25	3

Soil pH

The pH is the activity of [H$^+$] ion of measurement acidity or alkalinity in water and KCl (potassium chloride) solutions. A neutral solution has a pH of 7. Solutions with a lower pH are termed acidic and solutions with a higher pH are termed alkaline. We obtained summary assumptions of measurements described by average values of pH measurements of three repetitions.

Figure 4.1.Soil pH values correlated with soil carbonate contents.
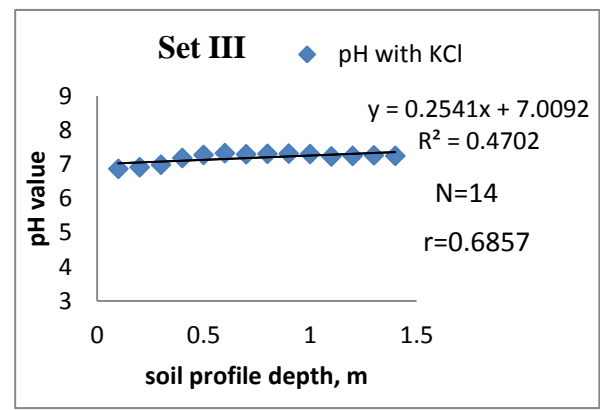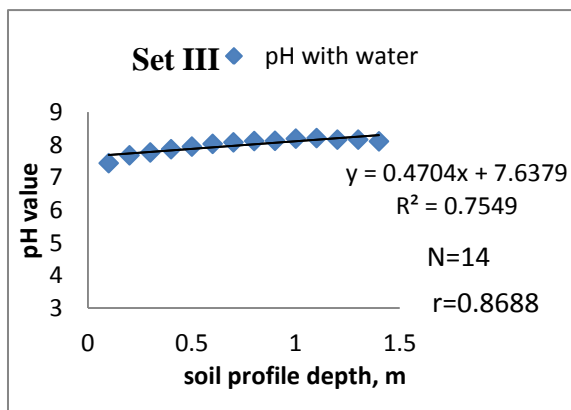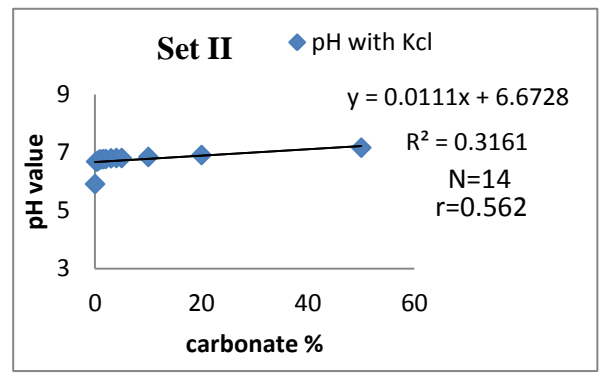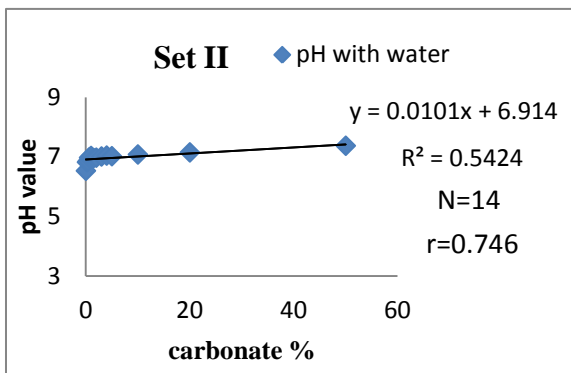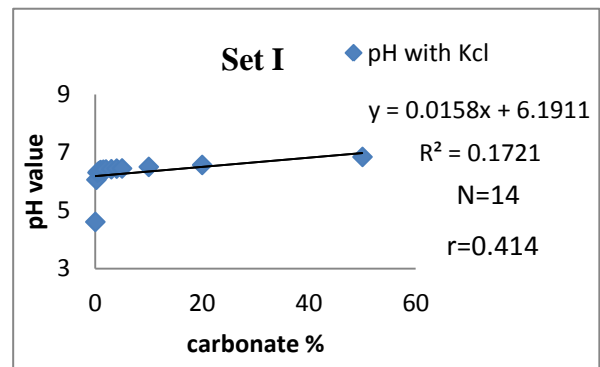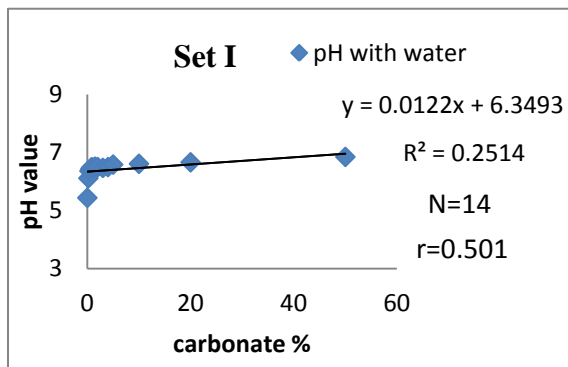
The soil pH values were around 5 to 8, but most of them greater than 7. It particularly presented in figure 4.1.Values of soil pH determined in water versus those determined in KCl solution are closely correlated and r values (correlation coefficient) ranging from 0.501 to 0.414 (fig 4.1 Set I). For the soils set III studied, the pH measured in KCl is approximately one unit lower than is the pH water. The differences in pH as measured in KCl and pH in water tends to increasing through soil profile, minimum pH values in top soil horizons, and to reach a maximum pH values in lower subsoil horizons. See the figure 4.1.

Carbonate content

Soil carbonate content was measured only for set III (haplic Chernozem) soil samples (Table 3.1). Because the set III soil samples prepared by natural soil, no mixed with any chemical substances. But other soil sets I, II mixed with different rate of pure $CaCO_3$. Each of the samples has measured for three repetitions and laboratory analysis then used average values of carbonate contents. See the figure 4.2. The observations of measured carbonate concentrations are changing through soil profile, maximum concentrations in middle horizon of soil profile and minimum in top and lower soils horizons.

Figure 4.2 Carbonate contents of the set III soil samples. Each of the soils corresponds to a different soil horizon and is classified according system of soil classification.

Carbonate contents

$y = 0.2084x + 10.508$
$R^2 = 0.0002$
N=14
r = 0.0142

- C horizon
- B horizon
- Ah horizon
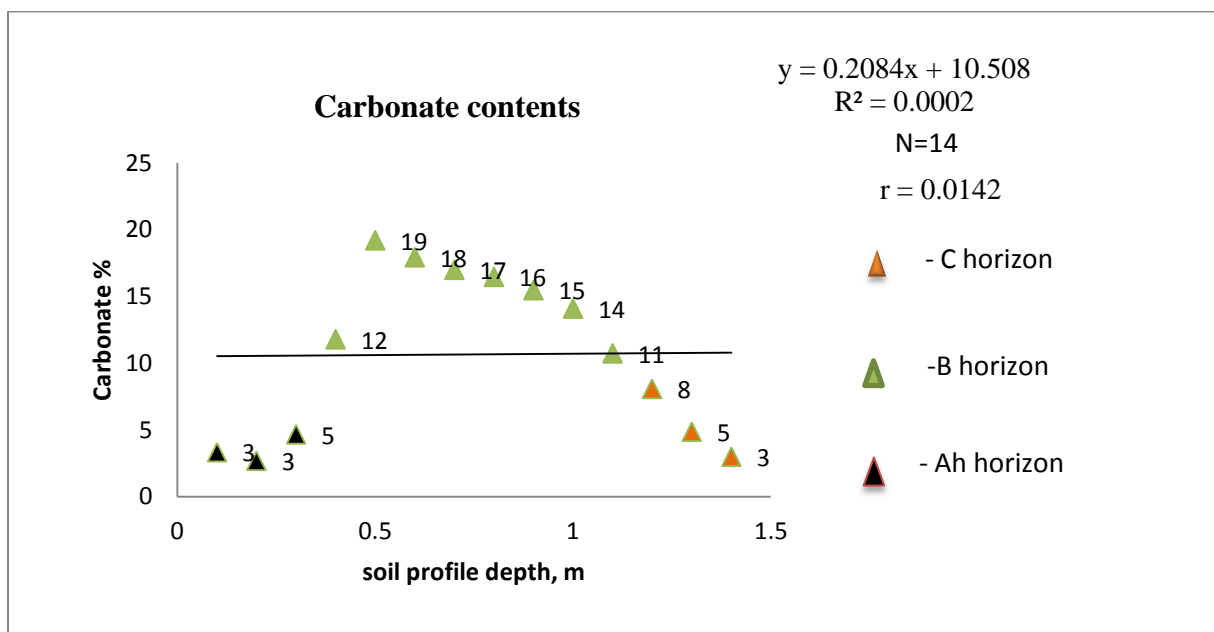
Determination of soil horizons in Set III soil:

- Ah – horizon, near the soil surface characterized by organic matter and humus. Enrichment with organic matter and dark colored horizon. This is usually most fertile part of soil profile. Range 0 - 0.3 m.
- B – horizon, is mineral horizon characterized by enrichment of clay and carbonate minerals with yellow and red color. Range 0.4- 0.11 m.
- C- horizon, precipitated horizon and parent material of soil forming process A, B horizons. Grey colored. Range 0.11 – 0.14 m.

The soil carbonate content is most influenced by soil pH and organic matter, determination of carbonate contents is correlated with organic matters (Appendix 1).

Picture 4.1 The Haplic Chernozem soil profile.

4.2 Vis-NIR DRS measurements

<u>Spectral data</u>

There was large variation of data collected from spectral measurements. In total 70 samples of three sets soil, and each sample was reflected three times. That mean 70*3=210 soil sample reflectance data measured by Vis-NIR (350 – 2500 nm) spectroscopy and spectral data were recorded as percent reflectance (R%). Figure 4.2 provides raw reflectance spectral data evaluated by FieldSpec-3 instrument. The original reflectance consisting

Figure 4.3 The Vis-NIR spectra of the all soil samples.
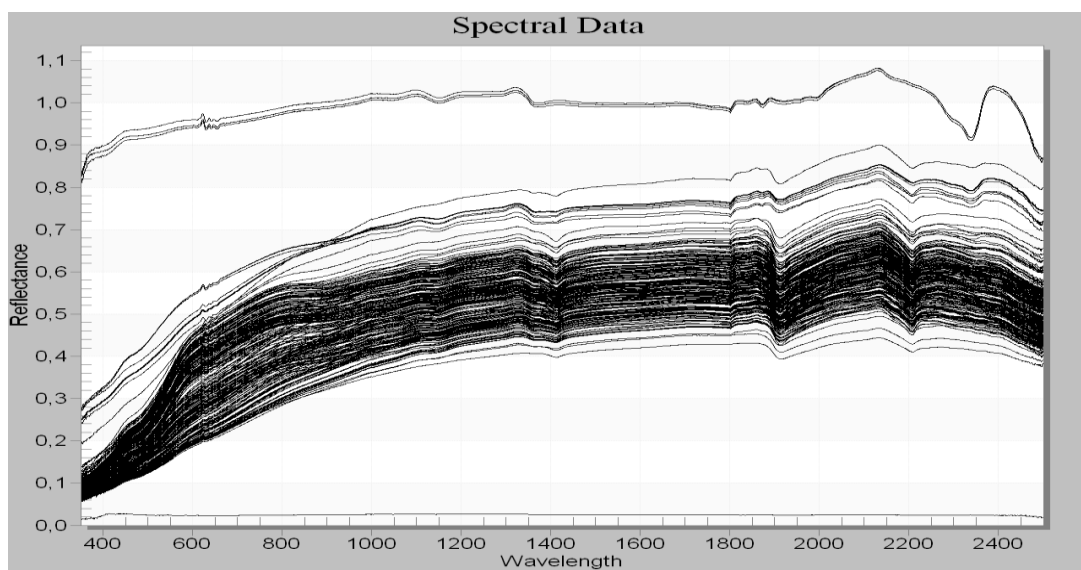
The original reflectance (R) transformed to the absorption (A) through equation A=log (1/R).

Figure 4.4 The effect of spectral transformations on Reflectance (R) and absorbance (A) spectra
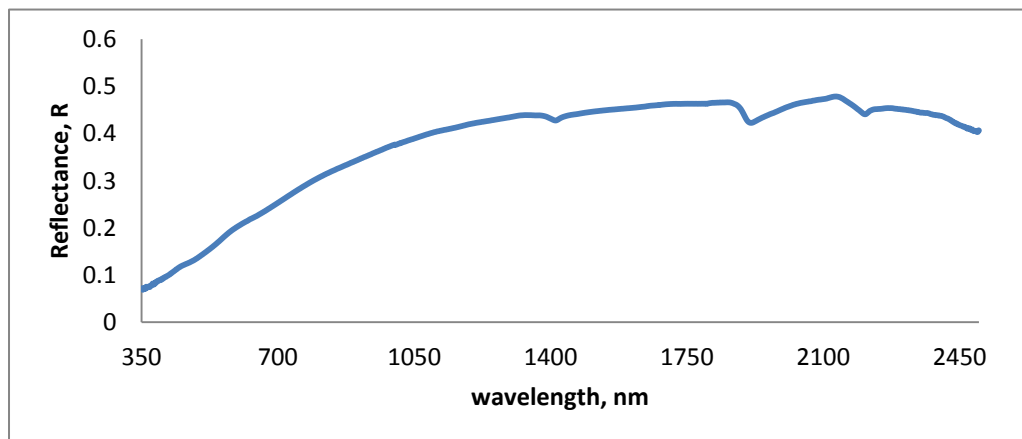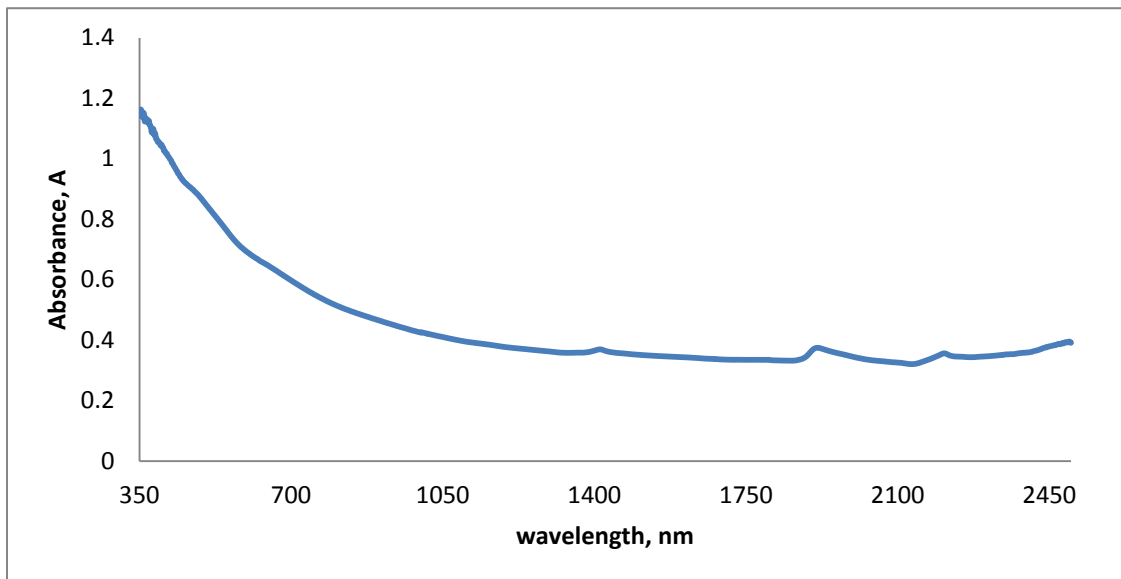
Soil properties and Reflectance spectra

This is results of data pretreatment process, It used conventional laoboratoy measurement results of soil pH and soil carbonate contents. See table 4.1 we tested each repeation reflectance and soil properties values, but all soil tested in this study had similar visible and near infrared reflectance spectra. Therefore we used average values of soil properties and reflectance spectral data.

Reflectance variable and soil characterization properties determined by correlation coefficients. The calculation of correlation coefficient (r) on the Microsoft excel that using pH values, carbonate contents and specrtral data of each wavelength. It is possible to identify regions of the Vis-NIR spectrum that show reflection due to carbonate content and pH value in soil sets. the main processes are incident light reflected by soil components such as carbonate content. That all provided figue 4.5 and figure 4.6. All soil sets tested in this study had similar visible and near infrared reflectance spectra, they had high optical reflection in visible region:

Set I: 366, 403, 642 nm; Set II: 366, 409. 642 nm; Set III : 352, 369, 382, 640 nm.

In near infrared region:

Set I: 1328, 1409, 1802, 1908, 2205, 2436, 2448 nm; Set II: 1328, 1415, 1801, 1914, 2206, 2436, 2497 nm; Set III: 1415, 1801, 1914, 2206, 2438, 2450 nm.

Figure 4.5 Soil pH values correlated with reflectance spectra.
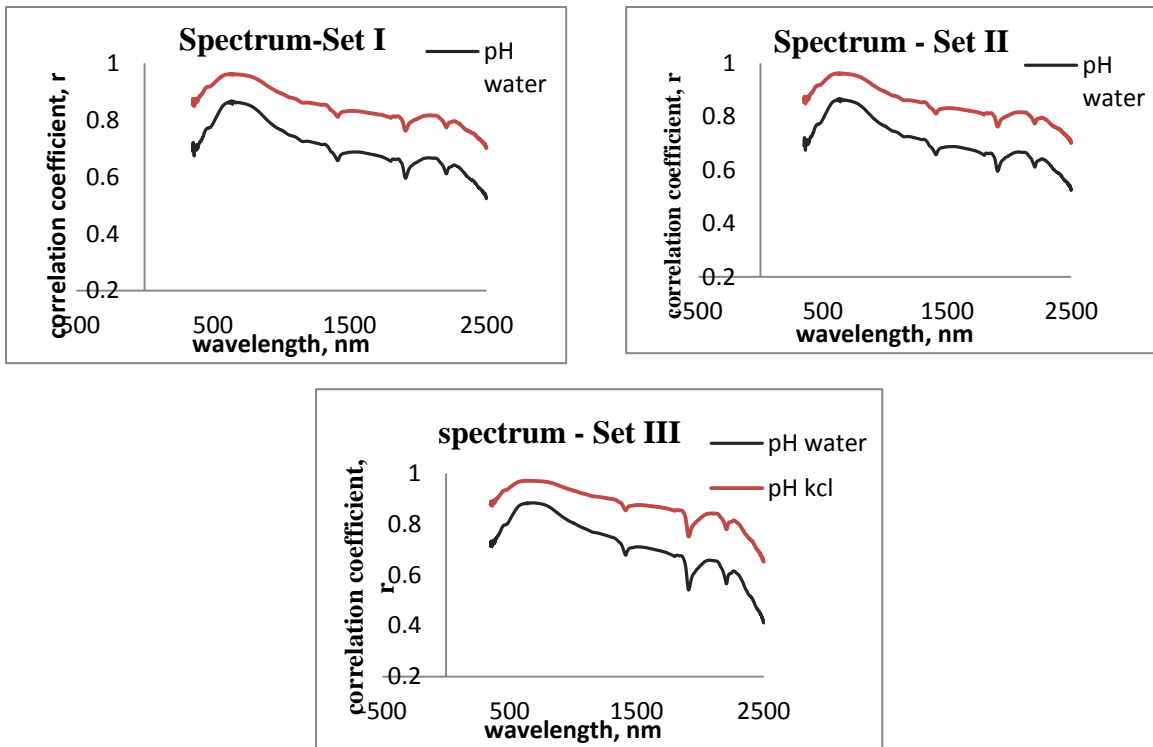
Figure 4.6 Soil carbonate content correlated with reflectance spectra.
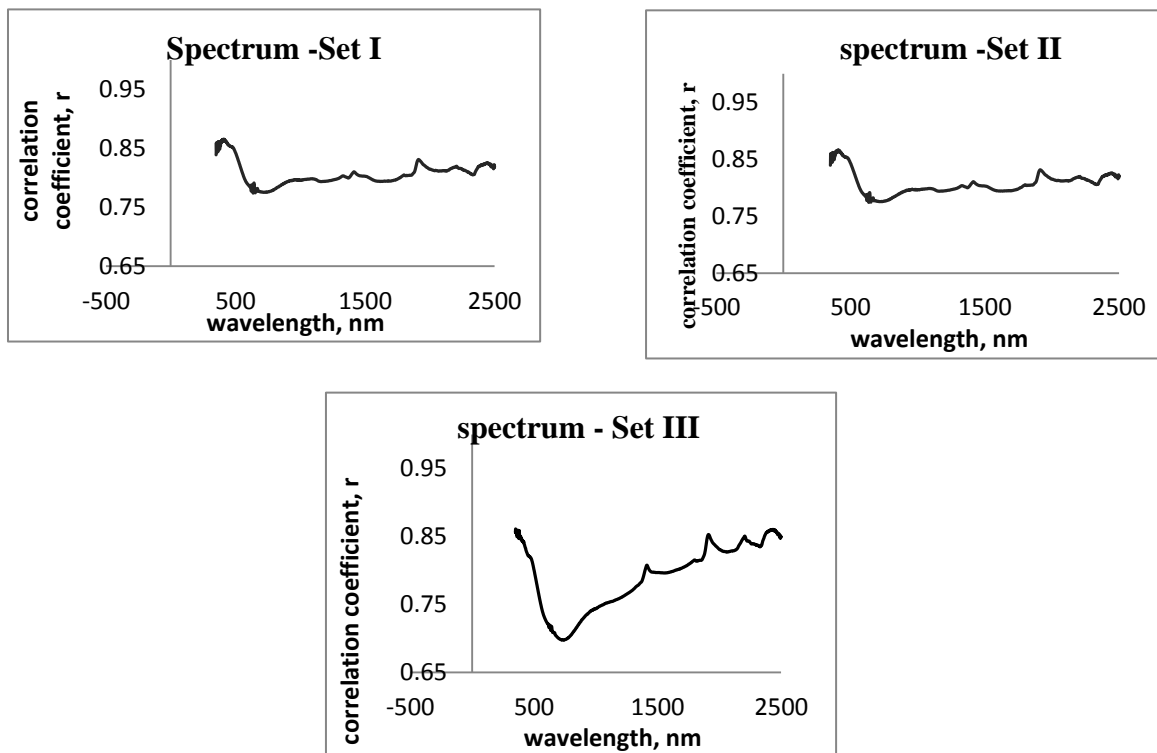
Regression analysis

In this analysis, Multiple Linear Regression (MLR) was tested on selected highest optical reflections of carbonate bands. They could be used directly in MLR without any numerical methods. The MLR procedure selected a best multiple correlation equation between carbonate concentration Cp in a given sample and the selected spectral parameters as follows:

$$Cp = b_0 + b_1L_1 + b_2L_2 + b_3L_3 + \ldots.. b_\lambda L_\lambda$$

Where b_0 is an intercept, b_1, b_2… b_λ are weighting factors for spectra readings in various selected wavelengths 1 to n. L_1, L_2, L_3 are the values of spectral parameters (reflectance) at wavelengths 350 -2500 nm.

Table 4.2 Comparison of carbonate prediction model parameter of MLR estimation.

Set I (10 explanatory variables)		Set II (9 explanatory variables)		Set III (10 explanatory variables)		Universe variables (10 explanatory variables)	
Source	Value	Source	Value	Source	Value	Source	Value
Intercept	-13.25	Intercept	-10.131	Intercept	-46.6	Intercept	-9.133
366	-327.2	366	-269.4	352	668.9	366	0.000
403	473.1	409	364.0	369	-68.3	382	0.000
642	88.4	642	112.3	382	-228.5	406	256.3
1328	-580.6	1328	-646.2	640	82.1	642	0.000
1409	181.1	1415	572.9	1415	-795.0	1328	0.000
1802	221.2	1801	0.000	1801	131.5	1415	0.000
1908	15.5	1915	-226.9	1914	-232.1	1801	0.000
2205	105.5			2206	839.9	1912	-98.7
2436	0.000	2436	255.9	2438	0.000	2206	68.1
2448	0.000	2497	0.000	2450	0.000	2436	0.000

Table 4.3 Prediction R^2(coefficient determination) and root mean square error(RMSE) for carbonate content estimation for MLR method.

Observations	Set I	Set II	Set III	Universe varialbes
R^2	0.902	0.907	0.961	0.900
RMSE	3.088	2.747	1.956	3.135

Figure 4.7 Regression lines comparison between predicted values to the observed values in all sets.
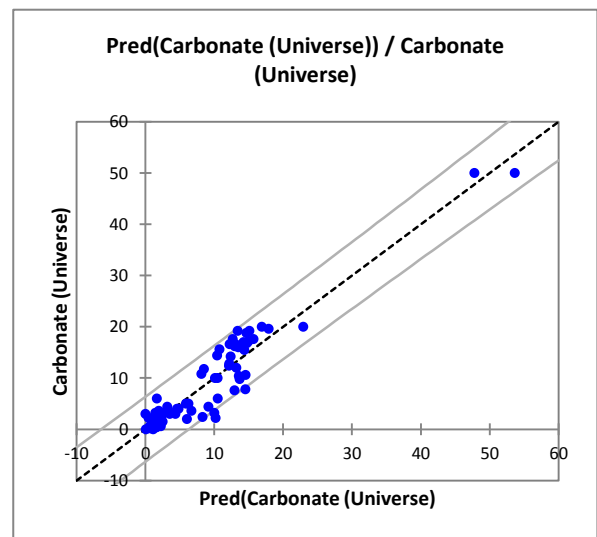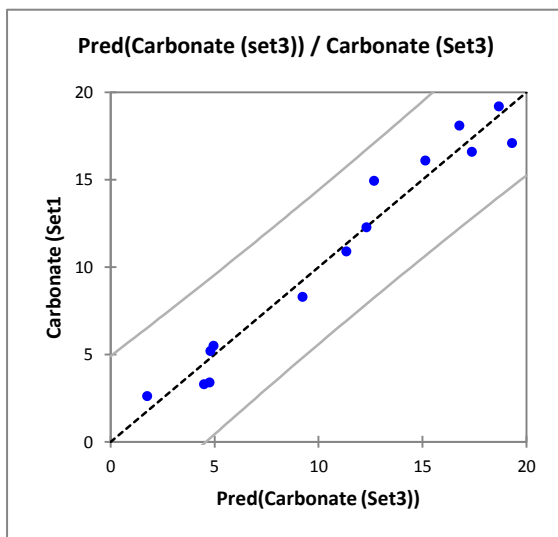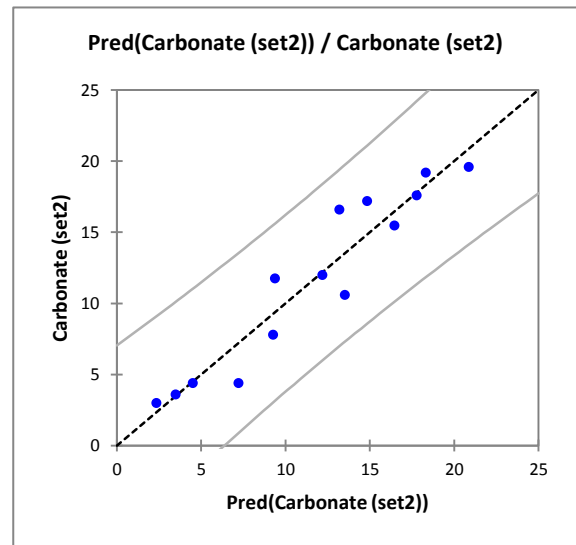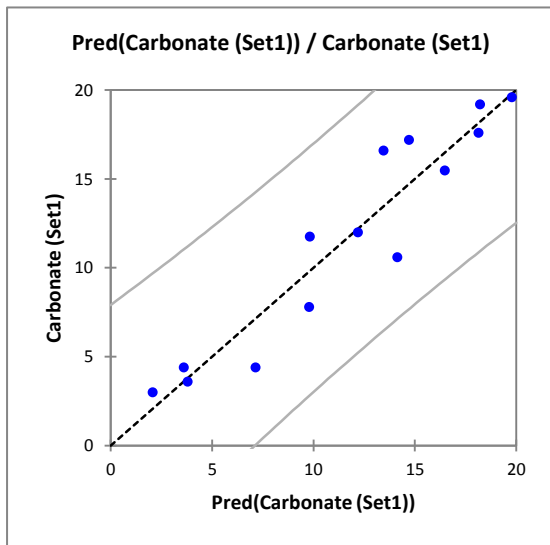
The regression line estimates the average value of y axis (carbonate) for each value of x axis (Pred.carbonate). These differences are prediction error or residuals.

CHAPTER 5

DISCUSSION

This study tried to define prediction of soil carbonate content effect to spectral measuring in the laboratory using Vis-NIR spectroscopy. Vis-NIR spectroscopic analysis is rapid method based on absorption of light by different materials in the visible (350-800) and near infrared regions of the electromagnetic spectrum. Recent research has suggested that proximal Vis-NIR diffuse reflectance spectroscopy (DRS) could provide inexpensive prediction of soil physical, chemical and biological properties (Brown et al., 2006). It is possible to analyze in soil science.

Soil pH

Soil pH is among the important environmental factors which can influence plant growth. Initially, each type of soil has a certain level of acidity and pH depending upon its composition, organic matter and precipitation, however various factors over time changes in soil pH. Soil pH value is strong affected by soil carbonate content. pH values measured with water and KCl (potassium chloride) solution. Therefore result was based on relationship between pH value and carbonate content. pH values measured with water and KCl solution. With KCl solution was more acidity pH values around 4-6, 7. Because KCl is slightly acidic, we used it for comparable with pH –water value. If we compare pH result of sample Set I and sample Set II, results were confident similar with yield of r (correlation coefficient) differences were less than 0.1. See the figure. The reason is carbonate concentrations are the same. Sample Set III was depends from   depth of soil profile, and then r values are near to 1. Top soil was more alkalinity than subsoil.

Soil carbonate:

The soil carbonate can have profound effect on many other properties and is considered one of the chemical properties in soil. Carbonate content of Set III was estimated by organic matter, which was in different soil horizons. See the picture 4.1. It could be explain by soil horizons. Carbonate content are obviously different on the soil depth: top soil is deep brown and black color, middle horizon (B) is whine yellow and lower sub soil horizon is grey colored. Also values of carbonate contents were very different amount of it.

Reflectance spectra and carbonate

Vis-NIR reflectance spectra of carbonate content results were informed in results part of thesis. Soil minerals are absorbed in all regions of electromagnetic spectrum. Carbonate minerals gave several absorptions in the NIR region, which are due to overtone and combination bands of the CO_3 fundamental that occurs in Mid-IR (middle-infrared) (Clark et al., 1990).

Spectral signatures of soil properties are defined by their reflectance R, or absorbance A as function wavelength. We measured reflectance spectra and transformed to absorbance through equation A=log (1/R). they are inverse variables. It can be express for plane waves: $A=1-|R|^2$.

The correlation in the wavelength space can be used to compare spectra (Yoon et al.,1999). Correlation coefficient r is calculated from variables of soil properties (pH and Carbonate) and wavelet data in each wavelength. Correlation coefficient used for build for effect of soil properties. See figure 4.5 and 4.6. This spectrum used for prediction method. It is possible to identify regions of the Vis-NIR spectrum that show reflection due to carbonate content and pH value in soil sets. The main processes are incident light reflected by soil components such as carbonate content. pH values of Sets of soils are affected to spectrum similar. We not concerned pH value in spectra any more. Set III soil samples were scanned more strong effective peaks than Set I and Set II.

Predicted Results

Interpretation of Vis- NIR spectra always requires mathematical processing due to their complexity. Prediction method was obtained using the reflectance data.

First, MLR built on Microsoft Excel XLSTAT for three soil sets (Set I, Set II and Set III) separately, and after built with inter variables of all three set soil variables. It called universe variables which were derived from predicted model parameters of soil sets. Model parameters of soil sets are merged and presented on table 4.2. In this regression process, to estimated only for carbonate content spectra. Because this MLR methods are not valid for each set soils. MLR for whole dataset(universe variables) are validated. See Table 4.2.

regression values are : 406 nm-256.3; 1912 nm –(-98,7); 2206 nm -68.1. Those significantly different. Also R^2 values near to 1.

The R² (coefficient of determination) indicates the % of variability of the dependent variables (carbonate contents) which is explained by the explanatory variables (selected highest optical reflections).

The RMSE (root mean square error) is measured typical blue points of data around regression line (Figure 4.7). The better model is small size of errors.

CHAPTER 6

CONCLUSION

The knowledge of spectral reflectance characteristics of earth materials is important in the development of proximal sensing technology, and in the analysis and interpretation of proximatly sensed data.Vis-NIR reflectance spectroscopy is simple and non- destructive analytical methods that can be used to predict several soil properties simultaneously.

Our results show that: 1) difference between three different types of soils properties (carbonate content and pH) were determined successfully, results were related for spectral reflectance measurements. 2) Hypothesis of thesis was proved that soil carbonate concentration can effect to soil spectral features in Vis-NIR regions which can predict carbonate contents of different soil types. 3) We used MLR method which was provided calibration process. Best prediction (lowest RMSE , and R^2 near to 1) is all three soil sets. It called universe set. In other words the aim is to examined relationship between soil diffuse reflectance spectra and carbonate content of several types of soils.

Further study and use of the NIRA approach in the soil science field is strongly recommended.

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List of abbreviations and symbols

DRS - Diffuse Reflectance Spectroscopy

CEC - Cation Exchange Capacity

FIR - Far Infrared

EM - Electromagnetic Spectrum

NP - Neutralizing Potential

MIR - Mid Infrared

MLR - Multiple Linear Regressions

PCA - Principal Component Analysis

PCR - Principal Component Regression

PLS - Partial Least Squares

PLSR - Partial Least Squares Regression

PSS - Proximal Soil Sensing

SOM - Soil Organic Matter

UV- Ultraviolet Visible

Vis-NIRS - Especially Visible to Near Infrared Spectroscopy

Vis - Visible and Near Infrared

λ - wavelength

ν - frequency

c - speed of light

$\acute{\upsilon}$ - wave length or wave number

E - energie

h - planck's constant

A - absorbance and

T - transmittance

R_∞ - reflectance

K - molar absorption coefficient

C - concentration

S - scattering coefficient

$b(i)$ - computed coefficient,

$x(i)$ - absorbances at each considered wavelength

$e(i,j)$ - error.

T - new dimensional coordinates

Y - reference values

b - coefficient vector

r - correlation coefficient

R^2 - coefficient of determination

RMSE - root mean square error

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Appendix 1

Basic chemical and physical soil properties of the experimental field CULS Prague

Soil Classification Haplic Chernozem (WRB)

pH_{KCl}, pH_{H2O}, exchange able acidity (EA), cation exchange capacity (CEC), basic cation saturation (BCS), sorption complex saturation (SCS), OM (organic matter content), $CaCO_3$ content, salinity, bulk density (ρz), sand, silt and clay content.

Soil Horizon	pH_{KCl} (-)	pH_{H2O} (-)	EA (mmol+kg^{-1})	CEC (mmol+kg^{-1})	BCS (mmol+kg^{-1})	SCS (%)	OM (%)	$CaCO_3$ (%)	Salinity (μScm^{-1})	ρz (gcm^{-3})	Sand (%)	Silt (%)	Clay (%)
Ah	7.21	7.69	0.72	263.8	259.6	98.4	3.47	7.8	43.7	2.52	24	56.3	19.3
C	7.4	8.14	0.99	241.3	238.28	98.7	0.76	11.6	7.7	2.53	24	51.8	24.5

Nutrients Status

87 ppm P, 203 ppm K, 197 ppm Mg, 8073 ppm Ca (Melich 3)

Source: Soil analysis of the experimental field CULS Prague, 2010, Department of Soil Science and Soil Protection.