Centre for Geo-Information

Thesis Report GIRS-2014-11

MEASURING SOIL REFLECTANCE

The influence of different measuring setups on soil reflectance spectra

and estimated soil properties

Georgiana Alexandra Maxim

10.04.2014

II

Measuring soil reflectance

*The influence of different measuring setups on soil reflectance spectra
and estimated soil properties*

Georgiana Alexandra Maxim

Registration number 90 01 03 548 110

Supervisors:

Harm Bartholomeus

A thesis submitted in partial fulfilment of the degree of Master of Science

at Wageningen University and Research Centre,

The Netherlands.

Date 10.04.2014

Wageningen, The Netherlands

Thesis code number: GRS-80436
Thesis Report: GIRS-2014 -11
Wageningen University and Research Centre
Laboratory of Geo-Information Science and Remote Sensing

FOREWORD

I discovered how many applications soil spectroscopy has after choosing to write an assignment concerning the influence of soil mineralogy on the reflectance anisotropy for an advanced remote sensing course. At the same time I also discovered how much there is still to be researched and improve in order to get good results for estimating soil characteristics and assessing different methods of measuring in soil spectroscopy. That is what lead to my decision of choosing a subject that researches how soil spectra are acquired and how the differences between the different measuring techniques influence the estimation of soil characteristics. Of course, this could be a broad research, but I tried to bring a small contribution to it.

I would like to thank my supervisor, Harm Bartholomeus, for providing me with all the materials I needed to complete the research, and also for helping me out every time I needed a new perspective.

ABSTRACT

Soil spectroscopy has nowadays a large number of applications in fields like precision agriculture and soil mapping, because it provides cheap, fast and non-destructive methods of estimating soil characteristics. This has led to a large amount of research and, as a consequence, a large number of published articles. The main problem that arises is how different the soil spectra measured with different measuring setups are and what is the influence that these differences have on estimating soil characteristics. Another issue generated by the research done until now is the fact that very often the term "diffuse reflectance" is used regardless of its actual definition and also regardless of the equipment that should be used for measuring it. This research had two objectives: 1) to provide a short overview of how soil spectral measurements were performed until now and to analyse how often the term "diffuse reflectance" is used without considering its definition and to check if there is actually any difference between reflectance measured with specially designed equipment and other types of equipment (based on spectra comparison); and 2) to analyse the differences between soil spectra measured with different accessories and what influence the differences have on predicting soil characteristics (clay content, organic matter content and quartz content). The results show that the term "diffuse reflectance" is often used without any consideration for its definition and the equipment that should be used for measuring it, and it is confirmed from spectral comparison that spectra measured with a diffuse reflectance measuring accessory (e.g. integrating sphere) differ from spectra measured with other accessories. Also, spectral analysis showed that spectra measured with different accessories present considerable differences which influence the outcome of multivariate analysis for predicting soil characteristics. This has implications on the development of soil spectroscopy, for example on the project of building a global spectral library using measurements collected from different sources.

Table of Contents

1. Introduction

Soil spectroscopy has proven to be very valuable for a large number of fields, for example agriculture and soil science. It has developed considerably during the past two decades because of the large number of applications in which it can be utilized, and mostly because of the advantages for estimating soil characteristics when comparing to traditional methods. This rapid development can be seen in the exponential increase in the number of papers published in the soil and agricultural sciences literature (Guerrero et al., 2010). Until present day, numerous instruments and methods to measure soil reflectance and to estimate soil characteristics have been used. This is due to a number of causes from which we can mention the large amount of information that can be derived from the spectra and the advances in computation, instrument manufacturing, developments in multivariate statistics and the great number of potential applications in agriculture and soil science. The information about organic matter, mineralogy and water content in the soil, as well as particle size and colour can be estimated with visible, near-infrared and mid-infrared reflectance spectroscopy techniques, whether diffuse reflectance is measured or other type of reflectance (e.g. bi-conical reflectance) (Bartholomeus et al., 2011; Chang et al., 2001; Pirie et al., 2005; Stevens et al., 2008; Viscarra Rossel et al., 2006a). The techniques used in soil spectroscopy have important advantages over conventional soil analysis: they are non-destructive, highly reproducible, rapid, cheap when many measurements are needed, relatively easy to use, small quantities of sample are needed for analysis, they require minimal sample preparation, and do not need environmentally harmful extractants (Guerrero et al., 2010).

In the published articles it can be seen that a very large amount of research has been done in order to determine the best way of estimating soil characteristics and to prove that soil spectroscopy can actually be used to accurately determine the necessary information for the different applications, like precision agriculture and soil mapping.

Looking into the previously done researches, the methods of measuring soil spectra can divided by two criteria: 1) the region of the electromagnetic spectrum in which the measurements are done and 2) the type of reflectance that is measured. For each of those, the research has been done for determining a large number of soil characteristics like inorganic carbon (Chang et al., 2001; McCarty et al., 2002), total carbon (McCarty et al., 2002; Reeves III et al., 1999), biomass (Reeves Iii and McCarty, 2001; Reeves III et al., 1999), cation exchange capacity (Ben-Dor and Banin, 1995; Janik et al., 1998), Fe content (Chang et al., 2001; Cozzolino and Moron, 2003; Islam et al., 2003), but also different minerals like K (Cozzolino and Moron, 2003; Islam et al., 2003; Janik et al., 1998) and Mg (Chang et al., 2001; Cozzolino and Moron, 2003; Islam et al., 2003), clay, sand, silt, N content (Ben-Dor and Banin, 1995; Cozzolino and Moron, 2003; Islam et al., 2003; Janik et al., 1998) and organic matter content (Masserschmidt et al., 1999). There are also specific applications such as identifying earthworm's organic matter signatures (Huerta et al., 2013), spectral reflectance variability in oil contaminated soils (Chakraborty et al., 2012), analysis of petroleum-contaminated soils (Okparanma et al., 2014) or monitoring potentially toxic elements in the agricultural soils (Song et al., 2012). As we can see, the list of applications for soil spectroscopy is very large.

Considering the first criterion of dividing the measuring, there are two regions of the electromagnetic spectrum in which the research is done, consisting of similar equipment and measurement settings. One of the regions is in the interval 350-2500 nm, which covers the ultraviolet – visible – near-infrared spectrum, while the other region covers the mid-infrared spectrum, in the interval of 2500-25000 nm. Of course, different research has been done in variations of these intervals in order to check which region performs better in estimating certain soil characteristics. The range of the intervals also depends on the spectrometer that is used. For example, the spectrometer can measure between 400-2500 nm instead of the 350-2500 nm interval in the VIS-NIR region (Chang et al., 2001) or it can measure more in the UV part from 250-2500 nm which would actually be the UV-VIS-NIR region (Islam et al., 2003). The considered interval is also very often in the NIR between 1100-2500 (2498) nm for determining certain soil characteristics which perform better in this region (McCarty and Reeves, 2001; McCarty et al., 2002; Reeves III et al., 1999).

Considering the type of reflectance that is measured, there are two main types: diffuse reflectance and "regular reflectance". What can be noticed is that in the articles in which the "regular" reflectance is measured, it is usually not explained what type of reflectance that is. According to the paper of Nicodemus (Nicodemus, 1970), there are nine kinds of reflectance corresponding to nine geometries. They are combinations of directional, conical and hemispherical incident and reflected beam geometry and they are presented in Table 1.

Table 1. Types of reflectance

Incoming radiation / Reflected radiation	Directional	Conical	Hemispherical
Directional	Bidirectional	Directional-Conical	Directional–hemispherical
Conical	Conical – directional	Biconical	Conical – hemispherical
Hemispherical	Hemisph.–directional	Hemisph.–conical	Bihemispherical

There are two things that are most striking when browsing through the articles that use soil spectroscopy for their research: one is the variety of spectrometers and accessories used to measure soil spectra, and the other one is that in a large number of articles it is mentioned that diffuse reflectance is measured but not all of them are using diffuse reflectance measuring accessories. For example, there are articles that use a spectrometer with a diffuse reflectance integrating sphere (Islam et al., 2003; Viscarra Rossel et al., 2006a), while others use a fibre-optic and average two spectra taken with 90° rotation of the sample (Brown et al., 2005), or a contact probe (Nocita et al., 2013).

The question is if these "wrong" descriptions are actually a problem. Do these differences actually influence the outcome of using the data for deriving different soil characteristics?

Considering this information, the objective of this thesis is to analyse what the influence of the different settings for acquiring the soil spectra is on a) the derived soil spectra and b) on deriving the soil properties. The research is divided in four research questions:

1. What are the methods, measurement settings and equipment used until now in soil spectroscopy?
2. How is it said that diffuse reflectance is measured in the research done is soil spectroscopy? Is the terminology properly used in the articles in which the research is published?
3. What are the differences between soil spectra measured with different accessories and settings?
4. How much do the different settings influence the estimation of certain soil characteristics with multivariate analysis?

2. Methodology

2.1 Research questions 1 and 2: overview of soil spectra measuring setups and ways of measuring diffuse reflectance

Research questions 1 and 2 were answered by doing literature research.

For research question 1, three articles were used as base for the literature research, part of the cited articles being studied. These articles provide overviews over the advances in soil spectroscopy (Reeves Iii et al., 2012), visible and near infrared spectroscopy in soil science (Stenberg et al., 2010) and methods for NIR and MIR soil spectroscopy (Reeves Iii, 2010). The articles were analysed to get the following information:

- What is the information regarding spectral measurements that can usually be found in the articles describing research done in soil spectroscopy
  - Instruments and accessories used for measurements
  - The spectral region in which the measurements are performed
  - If there is any description of the sample preparation
  - How detailed the measuring settings are described

The results from the second research question were added to the results coming from studying references from the three above mentioned articles.

Research question 2 was answered with a query that was made on sciencedirect.com to find articles with the keywords "diffuse reflectance" and "soil", in the title, abstract and keywords, written in the period between 2011 and 2013. The articles were analysed in order to see which are the instruments, accessories and methods used for measuring what was called in the articles "diffuse reflectance". The articles that used specially designed accessories for measuring diffuse reflectance were considered to have used correctly the term "diffuse reflectance", while the articles that used other types of accessories were considered to have used the term erroneously.

2.2 Research question 3: assessments of the differences between soil spectra measured with different accessories and settings

2.2.1 Spectral measurements

In order to answer research questions 3 and 4, soil spectral measurements were done. Measurements were performed on 57 soil samples, consisting of measurements for bi-conical reflectance and measurements for diffuse reflectance. The soil samples originate from the North of Morocco, and have a large variation in texture and mineralogy. Sample preparation consisted of drying and sieving them in order to get a particle size smaller than 2 mm (Mulder et al., 2013). To minimize the influence of the surface roughness, the sample surface was flattened before measuring the reflectance. Spectra were collected with five different settings, using five different accessories.

The measurement settings were the following:

- Spectrometer mounted on a robotic arm (robot-based goniometer)
- Spectrometer with muglight
- Spectrometer with contact probe
- Spectrometer with an integrating sphere
- Spectrometer with illumination from an external lamp and 90° rotation of the sample between collecting two spectra

The measurements from the first two experiments were done before the start of this research, while the last three were done during this research.

Measurements with external lamp illumination

For the measurements of the samples using external lamp illumination, an Analytical Spectral Devices (ASD) Fieldspec Pro FR spectrometer was used with an external ASD lamp for illumination. The lamp was positioned at a 45° zenith angle. Petri dishes were used for the soil samples, and the fibre optic with a 25° view angle was positioned at 10 cm above the sample, so the field of view could cover the entire surface of the petri dish, but not include the edges. A spectralon panel was used for calibrating the spectrometer, and the calibration was done after measuring each 10 soil samples.

The measured spectra consisted of 25 averaged spectral measurements. With these settings, two spectra with 90° rotation of the petri dish were recorded for each soil sample. The final spectrum for each sample was obtained from averaging the two spectra.

Measurements using a contact probe

The ASD Fieldspec Pro FR spectrometer was equipped with an ASD High Intensity Contact Probe. For each sample five spectra were measured, each measured spectrum consisting of an average of 25 internal spectral measurements. A spectralon panel was used for calibration and the calibration was done after measuring each 10 soil samples.

The five spectra measured for each soil sample were averaged in order to obtain the final spectrum.

Integrating sphere measurements

The integrating sphere measurements were performed using the ASD Fieldspec Pro FR spectrometer equipped with an ASD integrating sphere. The sphere has openings through which light can enter, and ports for mounting samples and standards, and placing the appropriate detectors. The integrating sphere's original light source's lamp (collimated light source assembly) was broken so the lamp from the contact probe was used. For getting the best results, the calibration was done before measuring each soil sample, because of the differences between the soil samples and the small amount of radiation that reached the contact probe. The calibration was done using a 99% uncalibrated reference standard (white plug).

Stray light was measured before each session of measurements using the light trap accessory. The stray light values were used for correcting the soil sample spectra by excluding the specular reflectance.

For each soil sample three spectra were collected and each spectrum was obtained by averaging 200 measurements. The final spectrum was obtained by correcting the three measured spectra using the stray light correction and averaging them.

Goniometer measurements

The goniometer measurements were conducted as described in the paper of Bartholomeus et al. (2013). The measurements were performed with a robot-based goniometer system that had an ASD Fieldspec 3 spectrometer mounted on the robotic arm. A 1° fore-optic accessory was used for constraining the viewing angle. The reflectance was collected at 92 different angles, in the wavelength range of 350-2500 nm. The light source was a collimated solar illuminator positioned at 30° zenith angle (Bartholomeus et al., 2013).

The measurements taken from all the angles were averaged for each soil sample in order to obtain a spherical coverage, which could be considered close to what some authors are doing when measuring diffuse reflectance by averaging spectra measured with sample rotation by different angles.

Measurements with mug light illumination

As the measurements done with a spectrometer mounted on a goniometer, the measurements done with the mug lamp illumination were performed before this research was started. This measurements were performed on powdered samples. The settings are described in the paper of Mulder et al. (2013). The spectral measurements were performed using an Analytical Spectral Devices (ASD) Fieldspec 3 spectroradiometer. The spectroradiometer measured the spectra in the 350–2500 nm wavelength region. The samples were measured using an ASD High Intensity Muglight (4 W quartz tungsten halogen lamp) to minimise measurement errors associated with stray light and specular reflection. The samples were placed in pure quartz

sample holders to avoid scattering from the sample holder. As mentioned before, the difference between this measuring experiment and the other mentioned before is that the samples were grounded to a powder (<68μm). All sample holders were calibrated against a non-reflecting reference standard prior to sample measurements (Mulder et al., 2013).

For each soil sample five spectra consisting of an average of 25 measurements were measured and then averaged to obtain the final result.

An overview of the geometrical properties of the five measuring experiments is presented in Table 2.

Table 2. Overview of the geometrical properties of the five measuring experiments

Spectrometer	Illumination Accessory	Illumination zenith angle [^{o}]	Sensing accesory	FOV [^{o}]	Viewing zenith angle [^{o}]
ASD Fieldspec 3	High Intensity Muglight	35	High Intensity Muglight	25	12
ASD Fieldspec 3 mounted on goniometer	Collimated solar illuminator	30	Fibre optic with 1° foreoptic	1	Different angles
ASD Fieldspec Pro	ASD lamp	45	Bare fibre	25	0
ASD Fieldspec Pro	Lamp in contact probe	12	Fibre optic in contact probe	25	35
ASD Fieldspec Pro	Lamp in integrating sphere	Hemispherical	Fibre optic in integrating sphere		Hemispherical

2.2.2 Spectra comparison

The third research question was answered based on the spectra comparison. The comparison was done in three ways:

1. Visual comparison:

The general aspect of the five spectra obtained for each soil sample was assessed in order to see how much they differ visually and if there is any trend in how the spectra differ (e.g. if one of the experiments gives constantly higher or lower values than the others).

2. The spectra obtained using the High Intensity Contact Probe were considered as reference spectra because the contact probe is, as its name already sais, a contact accessory, which does not allow interference with radiation from the outside environment and the spectra showed less noise than in the case of the integrating sphere. The muglight is also a contact accessory, but since the measurements were not

performed during this research and the soil samples were powdered, the spectra obtained with it was not chosen as reference data. The RMSE was obtained by calculating the average of the squared differences between the contact probe spectra and each other spectra, and then taking its squared root; this shows how much the spectra differ in value, regardless of the shape:

The RMSE shows how much the soil samples differ in reflectance values (Dennison et al., 2004). If the illumination on a sample is higher with one accessory than with another one (e.g. it is higher with the external lamp illumination than with the integrating sphere), the RMSE would still have a big value, even though the spectra are similar in shape.

3. Spectral angle mapper (SAM) was used to determine how big the differences between the shape of the contact probe reference spectra and the other spectra are, regardless of the differences in their reflectance values:

The Spectral Angle Mapper is a tool for image classification, whose algorithm determines the spectral similarity between two spectra by calculating the angle between them, treating them as vectors in a n-dimensional data space. The measure of similarity is not influenced by the differences in the quantity of reflectance, because the angle between the spectra considered as vectors is not influenced by the length of the vectors, so what is actually estimated is how similar the spectra's shape are (Kruse et al., 1993). The SAM value is an angle expressed in radians and it represents the similarity between the spectra. The smaller the angle is, the higher the similarity between the spectra. The value can be expressed also as the value of the angle's cosine, in this case a value close to one showing high similarity between the spectra (De Carvalho and Meneses, 2000).

2.3   Research question 4: the influence of different measuring setups on estimating soil characteristics

The last research question was answered by modelling the obtained data for estimating three characteristics of the soil: clay content, organic matter content and quartz content. For this, four experiments were conducted, using Partial Least Squares Regression (PLSR). The experiments are presented in Table 3.

The experiments consisted of first using data without pre-processing and then pre-processed data. The pre-processing of the spectra consisted of applying the Savitzky-Golay filter for noise removal (Savitzky and Golay, 1964) and calculating the 1st derivatives for removing the additive and multiplicative effects in the spectra (Rinnan et al., 2009).
The same experiments were conducted for both pre-processed data and processed data:
1) The PLSR model was calibrated using data from each measurement setting and validated using the leave-one-out (LOO) cross-validation
2) The PLSR model was calibrated using the data obtained with the contact probe and validated using the other four sets of data. The results of the LOO cross-validation were used for determining the number of factors used for modelling.
The spectra manipulation and the modelling were done using the chemometrics software ParLeS 3.1 (Viscarra Rossel, 2008).

The software calculates statistics for each validation, and for this research three of the statistics were analyzes: root mean square error (RMSE), relative percent deviation (RPD), and R^2 (Viscarra Rossel, 2008). For satisfactory results, the RMSE should be very low, while the R^2 and RPD values can be classified in three categories: category A - RPD values higher than 2 and R^2 between 0.8 and 1, category B – RPD values between 1.4 and 2 and R^2 between 0.5 and 0.8, and category C – RPD <1.4 and R^2 <0.5 (Chang et al., 2001).

3. Results

3.1 Overview of instruments and measuring experiments in soil spectroscopy

Due to the fact that soil spectroscopy has started developing in the 60's and 70's, with a more modern use of laboratory spectrometers starting in the 80's and getting popular during the 90's, there is currently a large variety of instruments and accessories used for measuring soil spectra (Reeves Iii, 2010). The instruments are divided mainly in two categories, accordingly to the spectral range in which they are measuring: instruments that measure in the VIS-NIR part of the electromagnetic spectrum (350-2500 nm) and instruments that measure in the MIR part of the spectrum (2500-11000 nm). The VIS-NIR spectroscopy was the first part of soil spectroscopy that started to develop, research about soil application using this part of the electromagnetic spectrum being done since the 60's and 70's as mentioned before. The research using MIR spectroscopy started to be applied for the analysis of agricultural products and soils in the 90's. Because of this, the choice of instruments that measure in the VIS-NIR is much larger than the one of instruments measuring in the MIR part of the spectrum (Reeves Iii, 2010).

The research done in the MIR part of the spectrum consists mostly in measuring diffuse reflectance – diffuse reflectance infrared fourier transform spectroscopy (DRIFTS). The instruments used for MIR spectroscopy are Fourier Transform spectrometers equipped most often with diffuse reflectance accessories (Azuaje et al., 2012; Ben-Dor and Banin, 1995; Davinic et al., 2012; Jindaluang et al., 2013; McDowell et al., 2012; Rasche et al., 2013; Ryals et al., 2014; Song et al., 2012), or without accessories (McBratney et al., 2006; Viscarra Rossel et al., 2006b).

As mentioned before, for the VIS-NIR spectroscopy there is a larger variety of instruments and accessories that can be used. This is due, as presented, to the fact that research in this part of the spectrum started earlier than for MIR, but also to the fact that VIS-NIR instruments are cheaper and present some advantages, like portability for in-situ measurements (Reeves Iii, 2010). The instruments used until now in research are: a) spectrometers, though referred to with different terms in different articles - spectrometers (Barthès et al., 2008; Bogner et al., 2011; McDowell et al., 2012; Rawlins et al., 2011; Stevens et al., 2008; Viscarra Rossel et al., 2006a; Viscarra Rossel et al., 2006b), spectroradiometers (Brown et al., 2005; Brown et al., 2006; Chakraborty et al., 2012; Nocita

et al., 2013; Xie et al., 2012), and spectrophotometers (Ben-Dor and Banin, 1995; Chang and Laird, 2002; Ge et al., 2011; Islam et al., 2003; Jordanova et al., 2013; Minasny et al., 2011; Nocita et al., 2014; Okparanma et al., 2014; Song et al., 2012) and b) scanning monochromators (Chang et al., 2001; Cozzolino and Morón, 2006; Siebielec et al., 2004). Although it is not encountered very often, there are also fourier transform instruments used for the NIR spectroscopy (Ben-Dor and Banin, 1995).

An overview of the accessories that are used for the VIS-NIR instruments is provided below, in Table 3. The type of reflectance presented in the table is classified accordingly to the paper of Nicodemus (1970), although in some of the articles it is mentioned that diffuse reflectance is measured (e.g. (Brodský et al., 2013; Okparanma et al., 2014; Siebielec et al., 2004)).

The settings of the measurements are usually not described in detail. What can most often be found in the articles cited in this research is:

- a short description of the instrument and accessories used;
- the spectral range in which the spectra are measured;
- the description of the preparation of the samples (e.g. samples are dried, sieved and placed in petri dishes);
- the number of spectra and internal measurements for the spectra that are averaged in order to obtain the final spectrum: they are never chosen based on a rule, being different for the different articles, e.g. two averaged spectra (Viscarra Rossel et al., 2006a), 64 averaged spectra (Siebielec et al., 2004), 15 internal measurements (Ge et al., 2011), 25 internal measurements (Chang et al., 2001);
- a short description of the settings for the measurements (e.g. the inclination angle of the external lamp, if the sample was illuminated from above or from below, or if the sample was rotated between collecting the spectra).

Due to the fact that for this research MIR instruments were not easily available and also because most research in articles is done with NIR spectroscopy or VIS-NIR spectroscopy, I chose to do the last three parts of the research based only on NIR and VIS-NIR spectroscopy.

Table 3. Overview of the used accessories for the VIS-NIR instruments.

Instruments	Accessory	Type of reflectance	Citations
Spectrometer	Contact probe	Bi-conical	(Brodský et al., 2013; Minasny et al., 2011; Nocita et al., 2013; Okparanma et al., 2014; Rossel and Chen, 2011; Stevens et al., 2008)
	Integrating sphere	Diffuse	(Islam et al., 2003; Viscarra Rossel et al., 2006a; Viscarra Rossel et al., 2006b)
	Praying mantis attachment	Diffuse	(Ben-Dor and Banin, 1995)
	Mug light	Bi-conical	(Brown et al., 2005; Brown et al., 2006; Chakraborty et al., 2012; Ge et al., 2011; Rawlins et al., 2011)
	External lamp	Bi-conical	(Nocita et al., 2014) (Ge et al., 2011; McDowell et al., 2012; Sarkhot et al., 2011);
Scanning monochromator	Rotating cup	Bi-conical	(Siebielec et al., 2004)

3.2 "Diffuse" reflectance measurements

As mentioned before, the second problem arising after the literature research is that often it is mentioned that diffuse reflectance spectroscopy is used to determine different soil characteristics, but what is said to be "diffuse reflectance" is measured in many different ways. In some articles it is said that diffuse reflectance is measured although the measurements are done with accessories that can only measure bi-conical reflectance (which is actually what is used in the researches that use bi-conical reflectance). As mentioned before, the difference between the two types of measured soil reflectance, namely bi-conical reflectance and diffuse (bi-hemispherical reflectance or conical-hemispherical reflectance) is

the quantity of radiation that reaches the sample, is reflected by it and then is collected by the spectrometer.

In general, diffuse reflectance measurements are made using an instrument (e.g. spectrometer) equipped with a diffuse reflectance accessory (e.g. integrating sphere). An integrating sphere is a hollow sphere, coated on the inside with a white material of diffuse reflectance close to one. The radiation that is reflected by the sample is completely collected by the fibre optic, since there is almost no radiation absorption in the sphere's walls, which makes this diffuse reflectance, or bi-hemispherical reflectance (Torrent and Barrón, 2008).

In laboratory spectroscopy, what is usually measured as "regular" reflectance is the bi-conical reflectance, while the diffuse reflectance is the bi-hemispherical reflectance, if one wants to be strict about it. Some authors mention that they measure diffuse reflectance in conditions in which strictly speaking they measure bi-conical reflectance or hemispherical-conical at most (cases in which the sample is illuminated from multiple directions with lamps, which could simulate hemispherical illumination, but the reflectance is measured with a fibre optic with a certain field of view). The bidirectional reflectance cannot really be measured since it is the reflectance corresponding to an infinitely small ray of radiation illuminating the sample and the infinitely small reflectance measured with an infinitely small field of view (FOV) (Nicodemus, 1970). Therefore, the reflectance that is measured is the bi-conical reflectance: the reflectance corresponding to a conical incident beam (e.g. from a lamp) and a conical reflected beam (e.g. measured with a fibre optic with a certain FOV). The diffuse reflectance is actually the bi-hemispherical reflectance, since it is usually measured with instruments equipped with diffuse reflectance accessories (e.g. integrating sphere) (Torrent and Barrón, 2008).

However, as it can be seen in the literature and partly exemplified below, many authors say that they use diffuse reflectance, but the spectral measurements are done with a lot of different other accessories that are not specifically designed for measuring diffuse reflectance.

The search resulted in 44 articles among which 23 are using spectra measured in the UV-VIS-NIR region, two are not relevant to the research (they are not using diffuse reflectance for soil applications) (Nicolini et al., 2011; Uchimiya et al., 2013), two are overviews of the use of diffuse reflectance measurements in soil science and soil applications (Hapke and Lindon, 2010; Reeves Iii et al., 2012), one is using satellite remotely sensed data (Kodikara et al., 2012) and the rest of 17 articles are measuring diffuse reflectance in the MIR region of the electromagnetic spectrum.

In the 23 articles about research using the VIS-NIR part of the spectrum, the instruments used are spectrometers and it is said that diffuse reflectance is measured with different accessories, or with an external lamp or a muglight together with the rotation of the sample. Below is a list with the articles and the accessories or techniques used for measuring diffuse reflectance:

- Using a contact probe: five articles (Brodský et al., 2013; Minasny et al., 2011; Nocita et al., 2013; Okparanma et al., 2014; Rossel and Chen, 2011);

- Using rotation of the sample and illumination from a lamp: four articles – sample scanned twice in both directions (Nocita et al., 2014); averaging of three spectra with the sample cup rotated 20° between each measurement (McDowell et al., 2012); two scans obtained by rotating the petri dish 90° between (Ge et al., 2011); four scans from each of the four quadrants of a petri dish by rotating the sample 90° (Sarkhot et al., 2011);

- Using the rotation of the sample and illumination from a muglight: three articles – four spectra scanned with a 90° rotation between successive scans (Chakraborty et al., 2012); two spectra collected with a 90° rotation of the sample (Rawlins et al., 2011); four scans from the four quadrants of the petri dish by rotating it 90° (Ge et al., 2011);

- Using fibre optic and illumination from a lamp: five articles (Bábek et al., 2011; Ge et al., 2011; Myers et al., 2011; Song et al., 2012; Xie et al., 2012)

- Using diffuse reflectance measuring accessories: two articles – integrating sphere (Jordanova et al., 2013), and a cricket accessory (Bogner et al., 2011);

- One article mentions that diffuse reflectance is measured with a spectrometer in diffuse reflectance mode, without any other specifications (Marín-González et al., 2013)

- Three articles do not mention any accessory, they only specify that the measurements are done with a spectrometer (Balsam et al., 2011; Kuang and Mouazen, 2013; Kweon and Maxton, 2013)

3.3   Comparison between spectra measured with different accessories

The spectra measured with the integrating sphere were very noisy in certain wavelength ranges (Fig. 1). Therefore, the spectra were compared between 600 and 1700 nm.
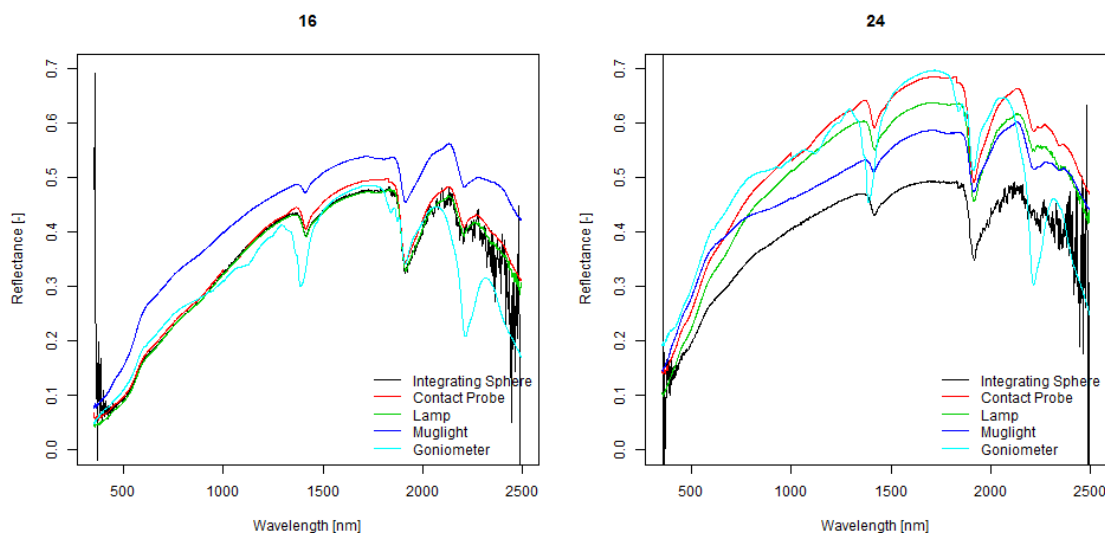

Fig. 1. Example spectra between 350 – 2500 nm for two soil samples. Noise is clearly visible for the integrating sphere spectra in the regions below 600 nm and above 1700 nm.

In Fig. 2, spectra from six soil samples are presented, with the spectral range between 600 – 1700 nm. From the visual comparison, the first thing that can be noticed is that for each

sample, the spectra measured with the different accessories have similar shapes, except for the spectrum measured with the goniometer. However, it is clear that for most samples, the reflectance values measured in the different experiments are quite different, although there is not a clear pattern for all the samples of which spectrum has the highest values and which has the lowest values.

What can be seen for all soil samples is that the reflectance measured with the mug light illumination has much higher values than the other measured spectra. This is the result of the different texture of the samples, since in this case the samples are powdered. Also, as mentioned before, the spectrum measured with the goniometer has a considerably different shape than the other four spectra: it has a much deeper absorption peak around 1400 nm, and also other absorption features along the spectrum. This may be due to the fact that, during the measurements, the fibre optic was further away from the soil samples than the receiving sensor was for the other experiments.

For most of the soil samples, the spectrum measured with the integrating sphere has the lowest values, while the spectra measured with the contact probe and the external lamp illumination have mostly close values, although there is no pattern on which has the highest values (for some samples the reflectance measured with the contact probe has higher values than the one measured with the external lamp illumination, and for other samples this is the other way around). There are also samples for which the spectrum measured with the integrating sphere has higher values than the spectrum measured with the contact probe and external lamp, and samples for which all three spectra are very close together. The main cause of this variation is probably the soil texture. Although the soil samples have grains smaller than 2 mm, some of the samples are very sandy and have a fine texture, while other samples have bigger, individual grains and look very coarse. For the coarse samples, the values of the integrating sphere measurements are much lower.

This observation is based only on a few examples that were recorded during the measurements sessions, since there is no information about the soil samples texture, and all the samples were sieved to have particle sizes smaller than 2 mm. Because of the shading, not a lot of radiation is reflected to the fibre optic. As it can be seen from the spectra measured with the muglight for the powdered samples, the texture has great influence on the reflectance intensity, fact that could confirm the presented theory.
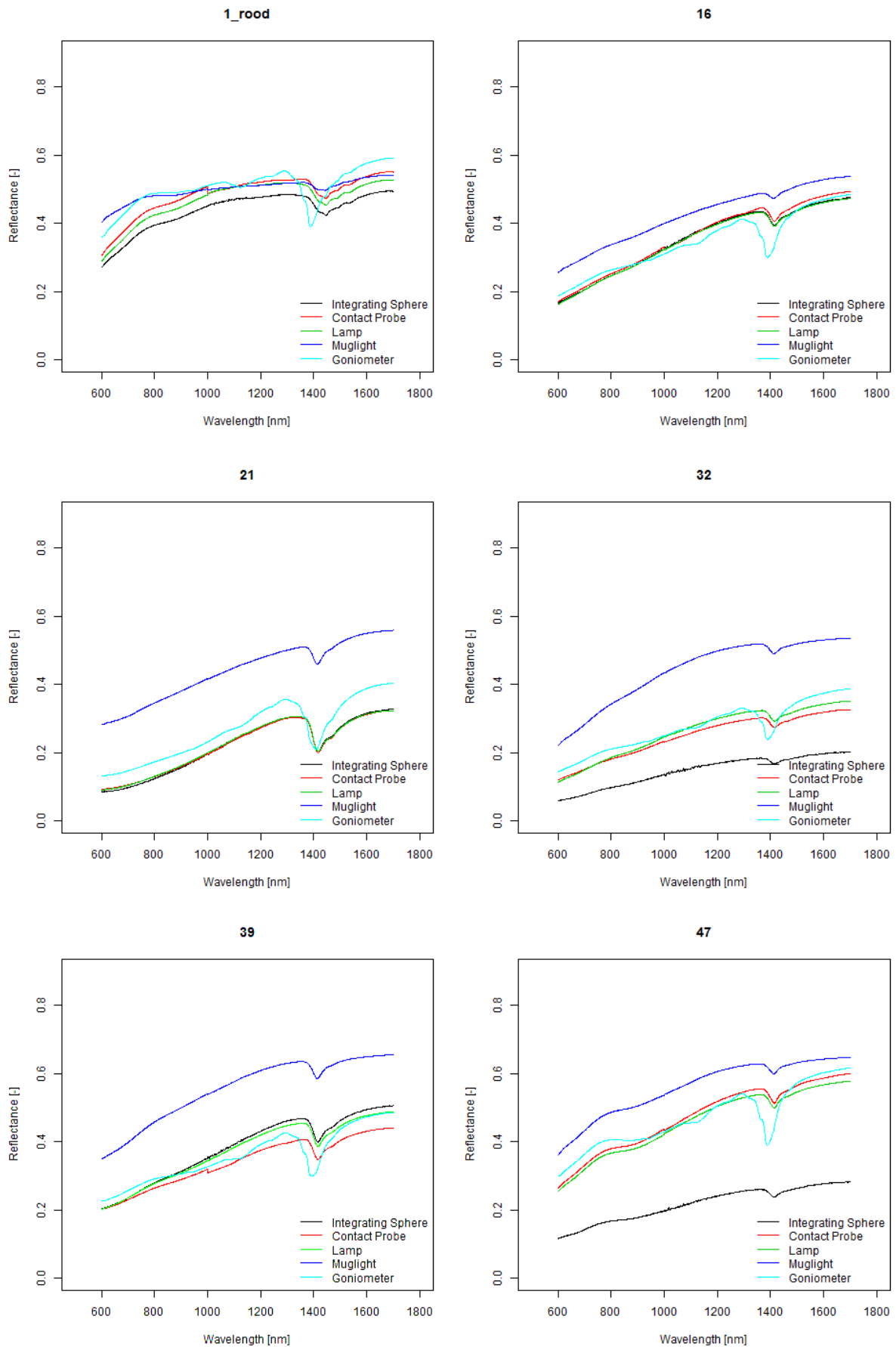
Fig. 2. Soil sample spectra in the 600 – 1700 nm spectral range.

Table 4. The average RMSE value of the differences between the reference spectrum and the other spectra

RMSE [%]	Integrating sphere	External lamp	Mug light	Goniometer
Contact probe	5.7	2.1	19.4	4.1

Table 4 shows the values for RMSE. As expected from the visual comparison, the highest RMSE is for the differences between the spectra measured with the contact probe and the ones measured with the mug light, showing a difference of 19.4% in reflectance intensity. This was already expected because for all the samples, the values for the reflectance measured with the mug light were much higher than all the others. The smallest value is for the RMSE for the external lamp measurements (difference in reflectance intensity of only 2.1%), which could also be seen in the visual assessment. The values between the spectra obtained with the contact probe and the external lamp were the closest for almost all the samples. The goniometer measurements have also a high RMSE (4.1%), because although the differences in reflectance were not very high (not as high as the ones from the mug light), the spectra still presented deeper absorption peaks and also more absorption features.

Since the RMSE cannot show if the contact probe spectra have higher or lower values than the other datasets and if there is any trend in which measuring experiment gives higher or lower values, going back to the visual assessment we can see how many samples have the contact probe measurements lower than the other, which samples have them similar to the lamp measurements, and which samples have all the spectra with very small distance in between (all the spectra are almost completely overlaying, which are showed in the graph as the value "All spectra similar") (this analysis excludes the mug light measurements, since it was mentioned before that all the samples except for one give the highest reflectance values when measuring with this accessory). In Fig. 3 is presented the number of samples for the sample groups presented before.
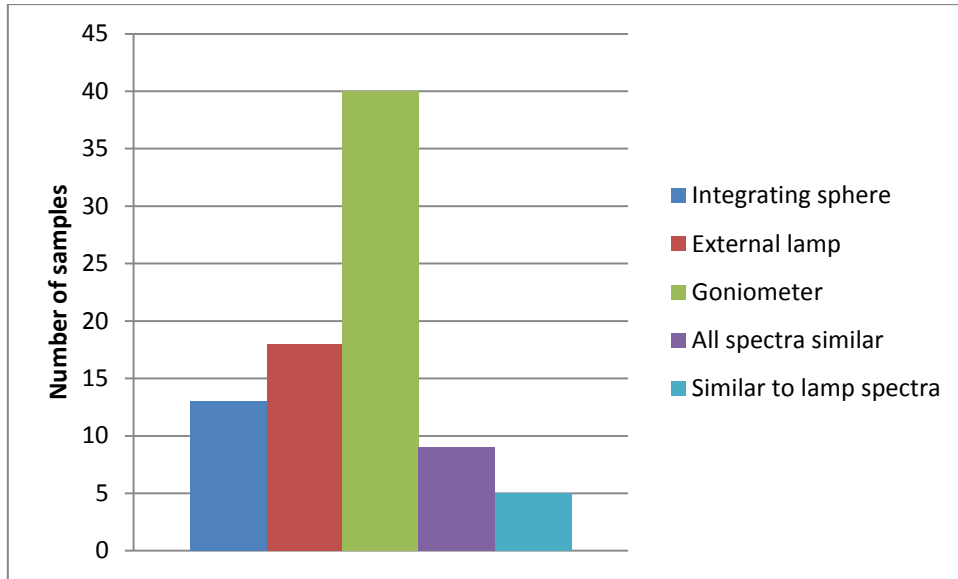
Figure 3. Comparison of reflectance intensities between the contact probe spectra and the other spectra. The graph shows the number of samples that have higher reflectance for the mentioned accessories when compared to the contact probe measured reflectance.

Table 5. The average SAM angle values between the reference spectrum and the other spectra

SAM [radian]	Integrating sphere	External lamp	Mug light	Goniometer
Contact probe	0.00211	0.0133	0.0703	0.0700

As mentioned before, the SAM value does not take into account the illumination and shading (Table 5). It can now be seen that the smallest angle is between the contact probe spectrum and the integrating sphere spectrum, although the integrating sphere spectrum was for most of the samples the one with the lowest values. This means that, although the radiation that reached the fibre optic in the integrating sphere was lower than the radiation that reached the contact probe or the fibre optic with the other accessories, the shape of the spectra collected with the integrating sphere and the contact probe present the highest similarity in shape. The biggest differences are found when compared to the spectra collected with the mug light and the goniometer. Although from the visual comparison one would expect to get a higher difference between the shape of the contact probe spectra and the goniometer spectra, since the goniometer spectra have the absorbance features, the highest difference is actually found when compared to the mug light spectra. However, the difference between the SAM value when compared to the goniometer measurements and to the mug light measurements is very low, the values being almost equal.

3.4 Effects of the different measuring settings on estimating soil characteristics

The question that arises from the already mentioned results is if the differences between spectra can be eliminated by pre-processing. The differences in intensities should be eliminated by calculating the 1st derivatives of the spectra (Rinnan et al., 2009), which should lead to better result for modelling. However, the shape of the spectra will still influence the model's outcome, and the question is how important will the differences between the spectra be.

The clay content of the samples is between 5% and 47.5%, the organic matter content between 0.27% and 9.33%, and the quartz content between 12.6% and 83% (considering the mineralogical content). Although the organic matter content is not very high in the measured soil samples, the model performs the best for it, giving the lowest values for the RMSE. Because the organic matter content has values lower and higher than 5%, the plots for the observed and predicted values showed a non-linear relation (Figure 4), which lead to the decision of transforming the organic matter values in the logarithm values. In this situation, the organic matter values for the samples are between -0.57 log% and 0.97 log%.
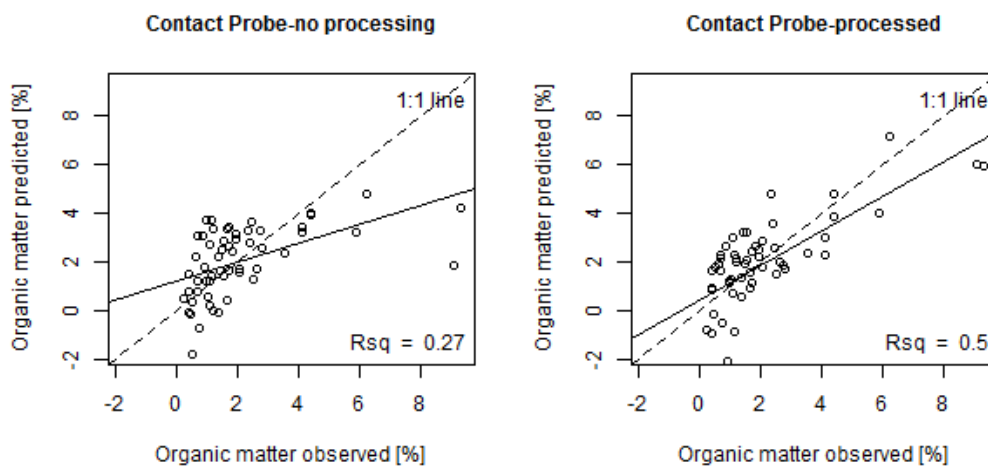

Figure 4. Non-linear relation when plotting the organic matter observed values against the predicted values (example for the contact probe measurements, but comparable for all measurements).

In Figures 6 and 8 it can be seen that the relation becomes linear when using the logarithm values.

As it can be seen in Tables 6, 7 and 8, the statistics for the leave-one-out cross validation of the PLSR models calibrated on each different dataset are not very satisfactory.

Table 6. Statistics for the LOO cross-validation for clay content

Data pre-processing	RMSE [%]		R^2		RPD		No. of latent variables	
	No	Yes	No	Yes	No	Yes	No	Yes
Contact probe	8.699	8.771	0.265	0.245	1.10	1.05	6	3
Integrating sphere	9.931	8.400	0.198	0.289	0.96	1.14	6	6
Lamp	9.853	10.652	0.200	0.138	0.97	0.90	6	3
Muglight	9.140	9.334	0.222	0.231	1.05	1.02	4	3
Goniometer	8.382	8.381	0.308	0.297	1.14	1.14	6	6

The best values are for the models estimating organic matter, where the RMSE values for using no pre-processing techniques are between 0.213 log% for the lamp measurements and 0.249 log% for the muglight measurements. This is also a result of the low range that the soil samples have in organic matter content, also considering that the logarithm values of the organic matter content were used. However, the R^2 values are very low, the models explaining only between 48.1% (for the muglight measurements) and 62.1% (for the lamp measurements) of the variability of the data. When using the pre-processed data, the results are different for the different datasets: for the contact probe, muglight and goniometer measurements the RMSE values are improving, although not by much taking into consideration the RMSE values, the maximum being a decrease of 1.531 % for the integrating sphere measurements in the case of clay predictions and 4% for quartz predictions. For the integrating sphere and lamp measurements, the RMSE values are increasing, which means that the model is getting worse. The same change can be seen in the R^2 values and the RPD values, but still the values that improve are not good enough.

Table 7. Statistics for the LOO cross-validation for organic matter content

Data pre-processing	RMSE [log%]		R^2		RPD		No. of latent variables	
	No	Yes	No	Yes	No	Yes	No	Yes
Contact probe	0.238	0.254	0.522	0.458	1.45	1.36	4	3
Integrating sphere	0.226	0.244	0.578	0.496	1.53	1.42	6	3
Lamp	0.213	0.224	0.621	0.584	1.62	1.55	6	5
Muglight	0.249	0.227	0.481	0.593	1.39	1.53	7	
Goniometer	0.230	0.229	0.563	0.576	1.50	1.51	6	6

Table 8. Statistics for the LOO cross-validation for quartz content

Data	RMSE [%]		R^2		RPD		No. of latent variables	
Pre-processing	No	Yes	No	Yes	No	Yes	No	Yes
Contact probe	16.755	16.296	0.302	0.337	1.08	1.11	4	4
Integrating sphere	20.163	16.278	0.164	0.250	0.90	1.12	6	8
Lamp	17.218	19.069	0.284	0.223	1.05	0.95	6	4
Muglight	16.367	17.379	0.284	0.255	1.11	1.04	6	4
Goniometer	15.073	16.554	0.378	0.296	1.20	1.10	5	4

When looking at the statistics for all three contents estimations, the RPD values for clay and quartz content do not go higher than 1.20, while a good value for the RPD should be at least higher than 1.4, considering the categories presented in the methodology. This happens for the organic matter estimations, using the logarithm values, where the RPD is between 1.39 and 1.62 when using spectra without pre-processing, and 1.36 and 1.55, when using the pre-processed spectra.

For the clay and quartz predictions the values of the statistics are worse, the values for the RMSE being the highest for quartz, since quartz content has the highest range (between 12.6% and 83%). The integrating sphere measurements give the highest RMSE values for both minerals: 9.931% for clay and 20.163% for quartz. However, these are the values that improve when using pre-processed spectra, the value for clay decreasing with 1.531% and the value for quartz with almost 4%. There is no actual trend in the way the RMSE values increase or decrease after spectra pre-processing, the value for the lamp measurements being the only one that increases for all three soil characteristics. The R^2 and RPD values present a similar behaviour, for some of the datasets the values improve, while for other datasets the values worsen.

When looking at the plots of the observed values against the predicted values for the leave-one-out cross validation (Figures 5, 6 and Appendix A), it can be observed that the regression lines in all the plots present an offset, for some higher and for some lower. For each of the three soil characteristics, the offset is in the same range of values for the spectra collected with the five different accessories. For the clay content (Figure 4), the offset for using raw and pre-processed data has values around 10, while the distribution of the values is scattered, with values that go far away from the 1:1 line, and with values clustered mostly near the first half of the line. However, the values are evenly distributed on both sides of the line.

For the organic matter content (Figure 6), the points are closer to the 1:1 line, which could have been expected from the better statistics obtained in this case. The offset of the regression line here is smaller than in the case of the clay content, with negative values between -0.5 and 0. In the quartz content plots (Appendix A), the values are farther away from the 1:1 line than

in the previously mentioned cases, with more values above the line. The offsets of the regression lines have the highest values from the three soil characteristics, the values being around 20.

The use of pre-processed data does not change considerably the aspect of the plots. What can be noticed for the clay content plots is that the farthest away values come closer to the 1:1 regression line, but the values that were already clustered close to the line get more dispersed, so, although the most extreme values come closer to the line, the overall dispersion gets higher. For the organic matter content, the clusters of points around the origin of the line get more compact, while in the quartz content plots it can be seen that the points get farther away from the 1:1 line, the dispersion being increased.
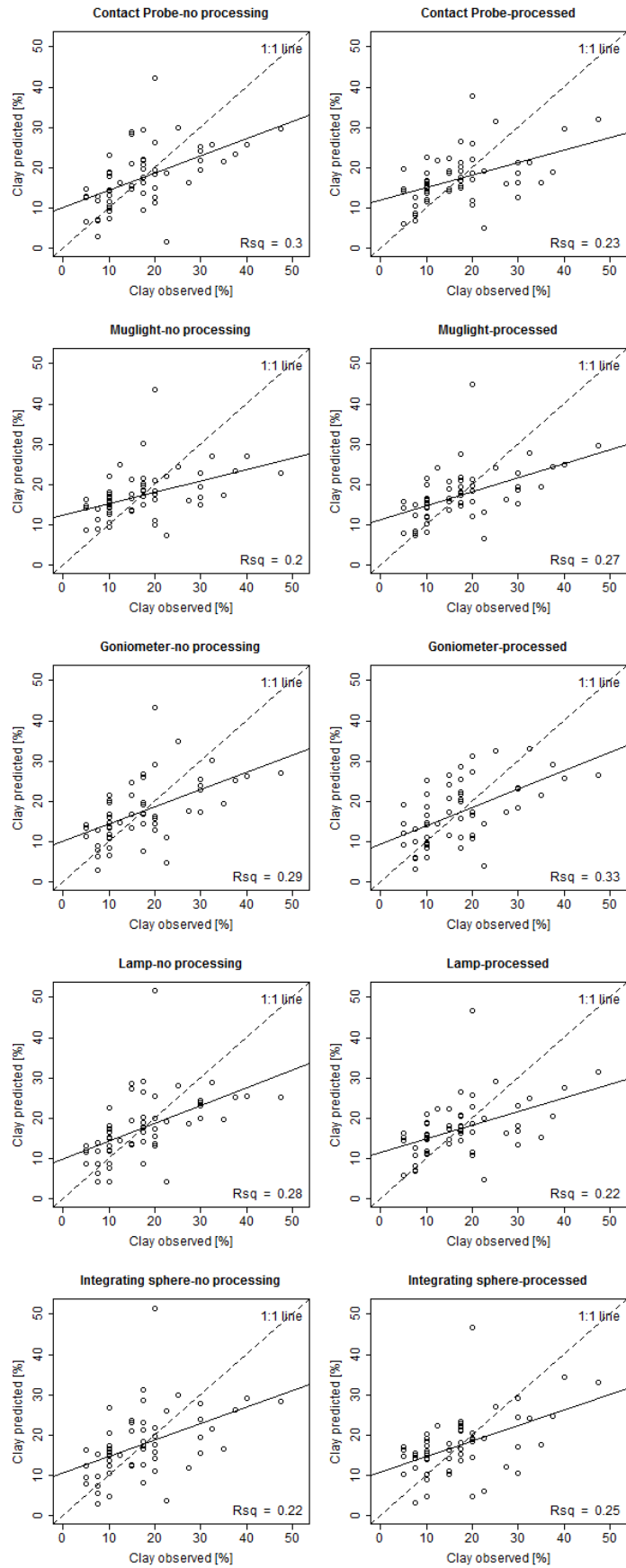
Figure 5. Observed vs. predicted values plots for the LOO cross-validation for clay content.
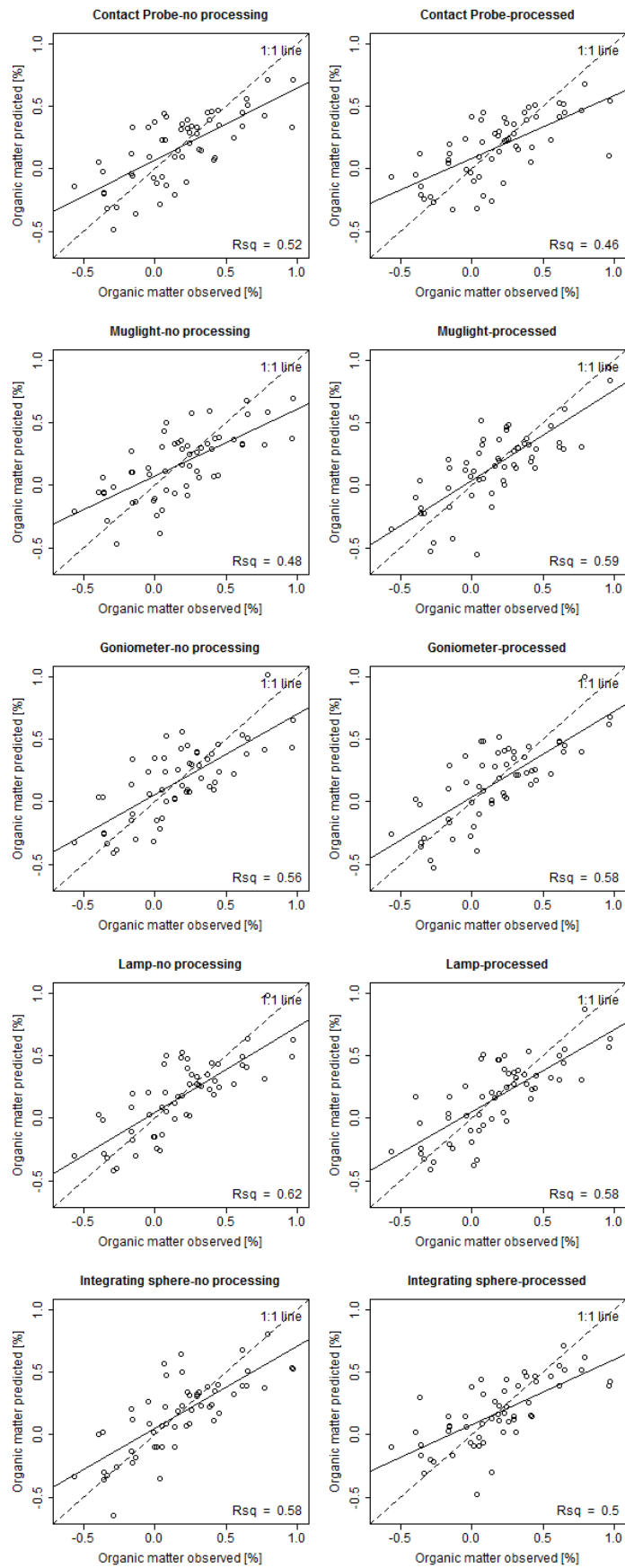
Figure 6. Observed vs. predicted values plots for the LOO cross-validation
for organic matter content.

Tables 9, 10 and 11 present the calculated statistics for validating the PLSR model calibrated with the measurements obtained by using the contact probe with the other four datasets.

For all three cases, the RPD values when using pre-processed spectra decrease considerably to values below 0.9 for the organic matter, below 0.4 for quartz content predictions and below 0.8 for clay content predictions.

Table 9. Statistics for contact probe model's validation with the other datasets for clay content

Contact probe to	RMSE [%]		R^2		RPD	
	No pre-processing	Pre-processing	No pre-processing	Pre-processing	No pre-processing	Pre-processing
Integrating sphere	7.783	15.711	0.429	0.010	1.23	0.61
Lamp	6.839	15.224	0.499	0.020	1.40	0.63
Muglight	18.054	13.070	0.275	0.069	0.53	0.73
Goniometer	31.813	14.683	0.214	0.005	0.30	0.65

Table 10. Statistics for contact probe model's validation with the other datasets for organic matter content

Contact probe to	RMSE [log%]		R^2		RPD	
	No pre-processing	Pre-processing	No pre-processing	Pre-processing	No pre-processing	Pre-processing
Integrating sphere	0.228	0.392	0.588	0.159	1.52	0.88
Lamp	0.225	0.393	0.607	0.246	1.53	0.88
Muglight	0.639	0.405	0.292	0.327	0.54	0.85
Goniometer	0.590	0.398	0.594	0.203	0.59	0.87

Table 11. Statistics for contact probe model's validation with the other datasets for quartz content

Contact probe to	RMSE [%]		R^2		RPD	
	No pre-processing	Pre-processing	No pre-processing	Pre-processing	No pre-processing	Pre-processing
Integrating sphere	14.704	48.953	0.385	0.061	1.23	0.37
Lamp	12.375	49.320	0.533	0.058	1.47	0.37
Muglight	16.208	51.343	0.367	0.190	1.12	0.35
Goniometer	13.969	49.949	0.572	0.037	1.30	0.36

As it can be seen at first, the best prediction statistics are calculated for the organic matter content, which was also the case for the models validated with the leave-one-out cross validation. When using data without pre-processing, the RMSE values for the organic matter content estimation are between 0.225 log% for the validation with the lamp measurements and 0.639 log% for the validation with the muglight measurements. The raw spectra obtained

by using the integrating sphere and lamp perform the best in the case of the organic matter content estimation. The same can be seen for the clay content, but for the quartz content the situation changes, the best statistics being calculated for the lamp and goniometer measurements. However, the RMSE has the highest values for the clay content estimation by using the muglight and goniometer measurements (with the highest value for the goniometer measurements – 31.813%) and for the estimation of the quartz content, with values between 12.375% (lamp measurements) and 16.208% (muglight measurements). The R^2 and RPD values are overall very low. The highest value for R^2 is 0.572 and it corresponds to the use of goniometer measurements for the quartz content predictions, explaining 57.2% of the data variation. This is surprising, considering the high differences between the spectra obtained with the contact probe and the ones obtained with the goniometer, which makes it actually a coincidence. Although the RMSE values are high for the quartz content predictions, it appears that the R^2 has on the average the best values, between 36.7% for the muglight measurements and, as mentioned above, 57.2% for the goniometer measurements. Considering all four validations, the lowest values are for the organic matter content predictions, with values between 14.0% for the muglight measurements and 45.8% for the lamp measurements. The RPD values are between 0.30 for the clay content estimation using the goniometer measurements and 1.47 for the quartz content predictions using the lamp measurements. The lowest RPD values are for the validations with the muglight and goniometer measurements in the cases of the clay content and organic content predictions, and for the validations with the integrating sphere and muglight measurements in the case of the quartz content estimation.

The values for the statistics become worse when validating the model with the pre-processed data. The lowest RMSE values are still for the organic matter content (between 4.585% for the integrating sphere measurements and 7.985% for the muglight measurements) and the highest for the quartz content predictions (between 48.953% for the integrating sphere measurements and 51.343% for the muglight measurements). A high jump in RMSE values can be noticed for the quartz content, from an average of 14.314% (for all four validations of the model) to an average of 49.851%. The values become almost four times higher. The same thing can be noticed also for the organic matter content and clay content predictions, with two exceptions: for the clay content predictions, when validating the model with the pre-processed data obtained with the muglight and goniometer measurements the RMSE values decrease from 18.054% to 13.070% and from 31.813% to 14.683% respectively. This are the only two situations in which the quality of the model shows an improvement after pre-processing the spectra. Also, these are the only two exceptions in which the model perform better on the muglight and goniometer spectra.

Besides the already mentioned two exceptions and the case of validating the model for quartz content estimation with the integrating sphere spectra without pre-processing, all the other situations give the lowest RMSE values for the integrating sphere and lamp measurements. The integrating sphere and lamp measurements also give the lowest SAM values when compared to the contact probe spectra, although in the case of the RMSE for spectra comparison, the integrating sphere measurements give the third lowest value, the goniometer measurements having a lower RMSE.

Taking into consideration the poor results obtained when using pre-processed data, it is obvious that it should definitely not be used. Regarding the results using the spectra without pre-processing: for the clay content estimations, the best results are given by the integrating sphere and lamp measurements and the worst by the goniometer measurements, for organic matter the best are given again by the integrating sphere and lamp measurements while the worst is given by the muglight measurements. For the quartz content estimations, the best results are given by the lamp measurements and goniometer measurements, and the worst by the muglight measurements.

Figures 7, 8 and Appendix B present the graphs obtained by plotting the observed values against the predicted values for contact probe model's validation with the other datasets for clay, organic matter and quartz content respectively. Looking at all three figures, it can be noticed at once that using pre-processed data leads to very poor estimation results. The predicted values are very low, always below the 1:1 line, while the regression line fit through the points is almost horizontal, with a slope close to zero. This shows even better the bad results, confirming the fact that using pre-processed data does not lead to correct estimations.

The plots for the clay content estimation using data without pre-processing (Figure 7) show a slight grouping of most of the points around the origin of the regression line for the lamp and integrating sphere measurements, with more points above or respectively below the 1:1 line. For the goniometer and muglight measurements the points are very dispersed, with almost all points above the 1:1 line for the muglight measurements and all points at a considerable distance above the 1:1 line for the goniometer measurements. However, the majority of the values are dispersed away from the line, the goniometer and muglight measurements presenting the highest dispersion. The regression lines also present offsets with values around 5 for the integrating sphere and lamp measurements, around 20 for the muglight measurements, and around 40 for the goniometer measurements. When using pre-processed data, the slopes of the regression lines get close to zero (the lines appear almost horizontal), while the points get farther away from the lines.

For the organic matter content predictions (Figure 8), the plots present a similar clustering of the points around the regression lines, with the difference that the clusters are more compact and the clustering point is around the middle of the line. However, the points are closer to the 1:1 line for the lamp and integrating sphere measurements, while for the muglight measurements they are almost completely above and for the goniometer completely below. Here the offset values are smaller than the previous case, with negative values. When using pre-processed spectra the plots change their aspect considerably, as in the other two cases.

In the case of the quartz content predictions (Appendix B), the points are dispersed along the 1:1 regression lines, the majority being away from the lines, the highest dispersion can be seen for the integrating sphere measurements and for the muglight measurements. The points are mostly above the 1:1 line for the muglight and lamp measurements, and mostly below for the goniometer and integrating sphere measurements. The offset values are around 20 for the integrating sphere, lamp and muglight measurements, and around 10 for the goniometer measurements.
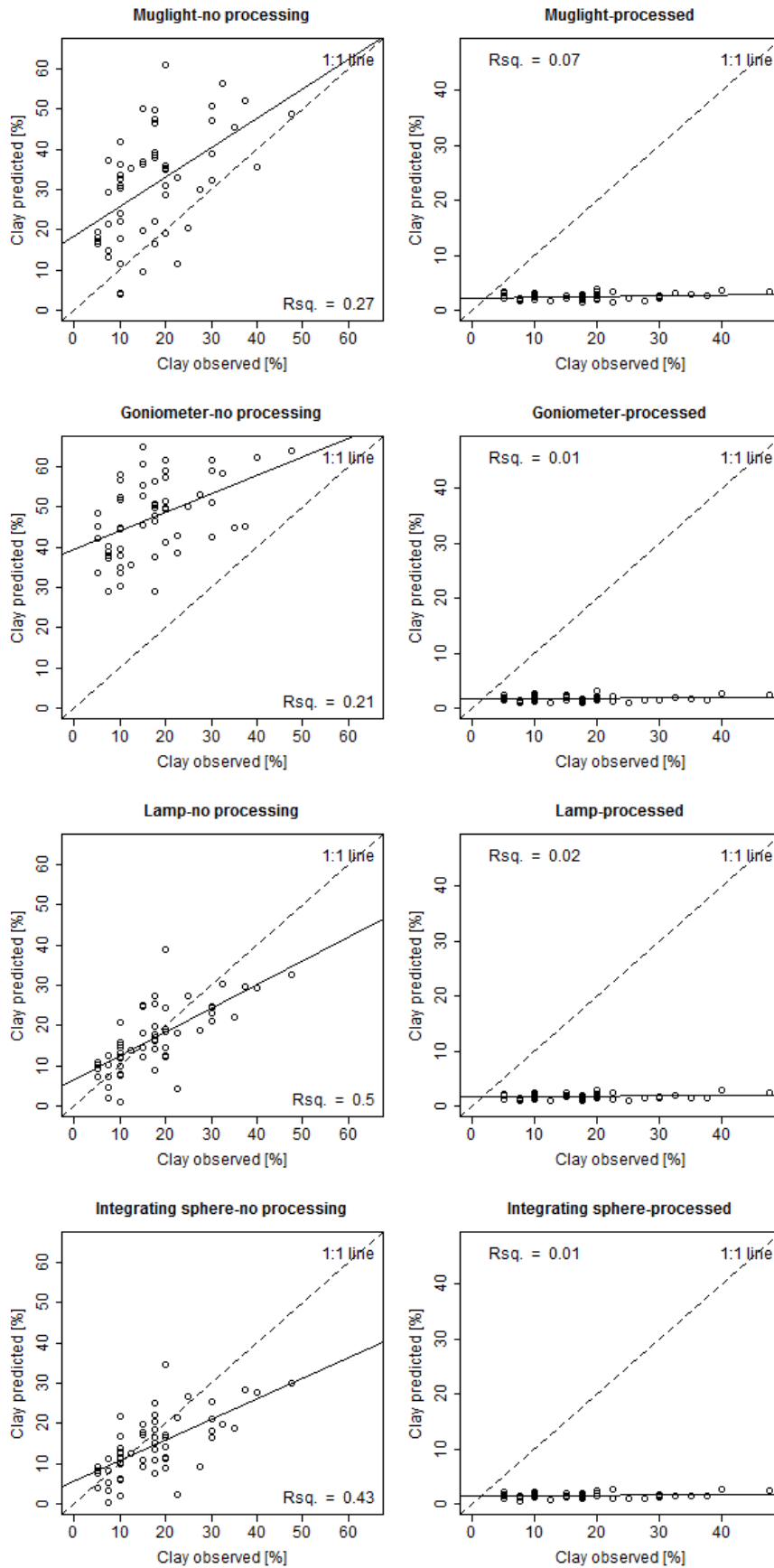
31

Figure 7. Observed vs. predicted values plots for contact probe model's validation with the other datasets for clay content.
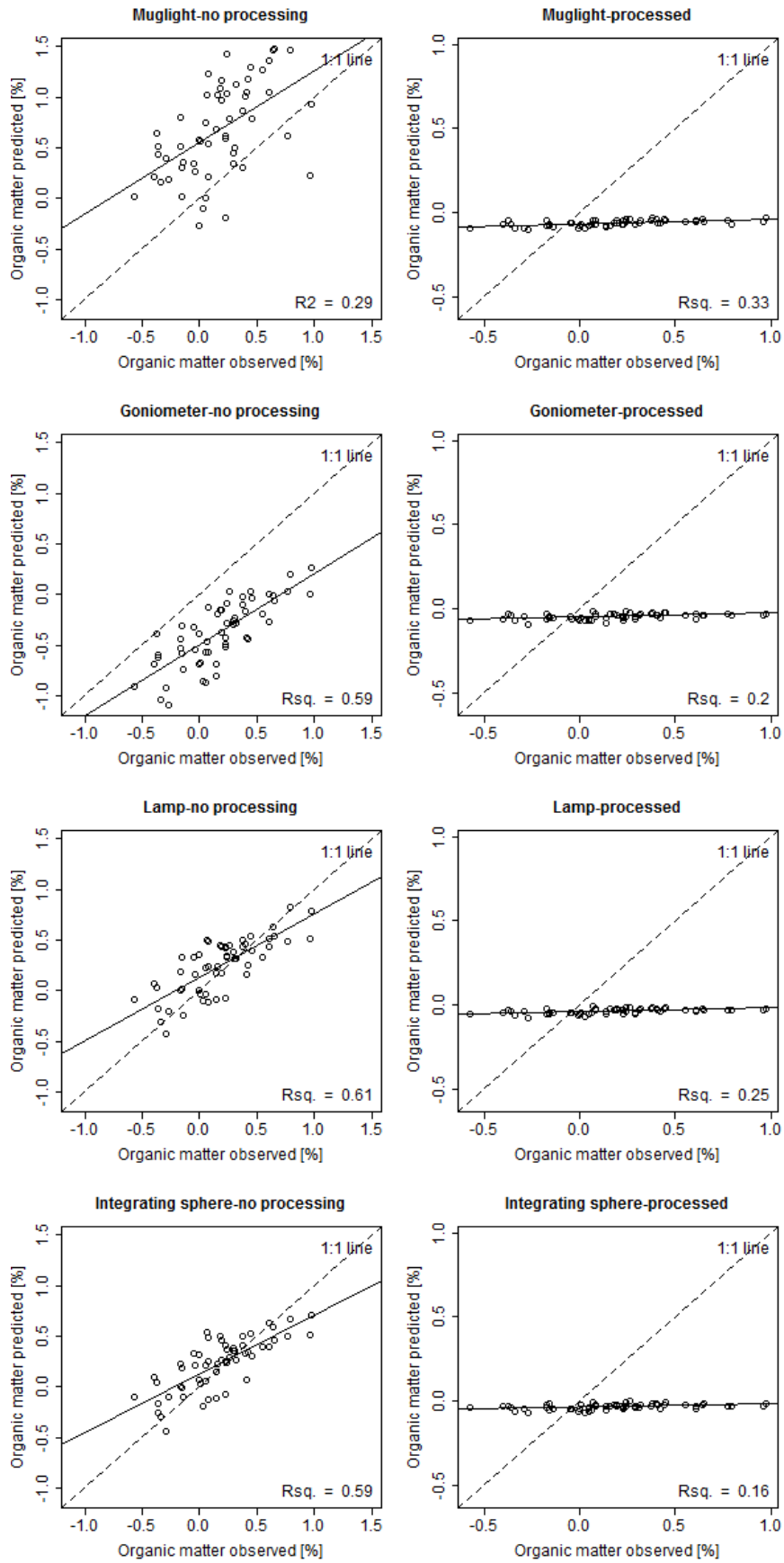
Figure 8. Observed vs. predicted values plots for contact probe model's validation with the other datasets for organic matter content.

4. Discussion

The results of the spectra comparison show considerable differences in the spectral measurements taken with the different accessories. However, there is no clear trend in how the spectra differ, since the intensity values change for the different accessories used. Besides the muglight, where the measured samples were powdered, there is no other accessory that constantly gives the highest or the lowest values for the spectra. The fact that the integrating sphere measurements give most often the lowest values can be attributed to the variation in the very short distance between the sample and the light source. Because of the very short distance, the small variations could have considerable influence. As mentioned in the results, the spectral values given by the integrating sphere are not always the lowest, but sometimes they are in between the lamp, goniometer and contact probe measurements, or even higher. This could come from the differences in the soil texture (Chang et al., 2001). Although the samples were prepared in the same way, and all of them had particle dimensions smaller than 2 mm, it could be observed during the measurements that some samples contained more sand and had a finer texture than other samples that were very coarse. This could have caused different shading on the samples, thus different reflectance intensities. Unfortunately, besides the few observations done during the measurements, there was no information about the texture of the samples for confirming the theory. That could be a subject for further research.

As expected, the measurements taken with the muglight gave the highest RMSE values compared to the measurements taken with the contact probe. This is the consequence of the fact that the muglight spectra had constantly much higher values than all the other spectra. The muglight is also a contact accessory, so one would expect that the measurements taken with the contact probe and muglight would give similar spectra in shape and reflectance, but as it can be seen from the RMSE and SAM values, the spectra resulted from the two contact accessories are the most different. This is mainly the result of the different texture of the measured samples.

Although the goniometer spectra show high similarity to the contact probe spectra in terms of intensity, the differences in shape seem to be more considerable. The SAM values show that the goniometer and muglight give the spectra with highest differences in shape when compared with the contact probe spectra. This result was expected for the goniometer measurements, since the goniometer obtained spectra show much deeper absorption features, but it seems like the muglight spectra also have considerable differences in shape, although not very noticeable on the visual assessment. This differences are probably the result in the different texture of the samples. The deeper absorption features in the goniometer spectra could also come from the fact that the sensor was farther away from the sample then in the other measuring experiments.

The external lamp and integrating sphere measurements gave the spectra with the smallest differences compared to the contact probe spectra. In intensity the external lamp gave the closest results, while in shape the closest spectra to the contact probe spectra came from the integrating sphere measurements. However, considering the results found from the second

research question, all spectra should be very similar in values and shape, since accordingly to the articles, they all measure the same quantity, namely "diffuse reflectance".

The applied PLSR to the obtained datasets to predict organic matter and quartz content performed better to predict organic matter content than to predict quartz content. The second best values are given for estimating the clay content, while the worst are for the quartz content predictions. A cause for the poor results might be the very wide variety in the soil mineralogy of the samples combined with the small number of samples used for modelling. For good results considering the high variety in mineralogy, the model should be applied on a much higher number of samples, although this contradicts the idea that using a small amount of samples could lead to over-predictions (Reeves Iii et al., 2012). Another explanation for the high RMSE values in the case of quartz content estimations could be the fact that this mineral has very few absorption features in the studied spectral region and its presence cannot be very easily noticeable (Mulder et al., 2013). However, the R^2 and RPD values are very low for all the cases, which shows the need for more samples: the model explains very little of the data variability.

The results do not improve very much after spectral processing, or they even get worse, which shows that in the case of the leave-one-out cross validation, the noise removal and calculating the derivatives do not influence the final outcome. The plots of the predicted and observed values also show an increase in the data dispersion, which confirms that pre-processing does not help improving the model.

The model calibrated with the contact probe measurements showed the same trend when validated with the other measurements as when validated with the leave-one-out cross validation: the statistics calculated for organic matter content predictions gave better values then for the clay and quartz content estimations. It should be taken into consideration that the samples used for the muglight measurements had a different texture than for the other measuring experiments, but the samples still had the same clay, organic matter and quartz content, which should be shown in the predictions (the prediction results should be similar). As expected after the spectra comparison, the validation done with the muglight and goniometer measurements give the highest values for the RMSE, which shows that the high differences in intensity and shape between the contact probe spectra and the other two sets of spectra have a high influence on the predictions. The results are poor also for the other two validations, although they gave overall the smallest RMSE values and the highest R^2 and RPD values. The fact that the mug light and the goniometer measurements give the poorest results from the four validating datasets could also be caused by the fact that they were performed with different spectrometers in different environments and the settings had a high influence on the outcome (Ge et al., 2011). The poor results using the spectra measured with the goniometer and the muglight were expected, considering the results of the spectra comparison, which showed that the muglight measurements had the highest difference in overall reflectance and also highest difference in shape, and that the goniometer measurements had a high difference in shape, with a SAM value close to the highest (the SAM value for the muglight measurements).

The pre-processed data makes the validation results worse, as in the case of the leave-one-out cross validation performed for the modelling of the individual datasets. The RMSE increases with high quantities, while the R^2 and RPD decrease to very low values (as showed in results). This shows that trying to correct the spectra for the differences in shape and intensity does not have the expected result of improving the model, but it actually makes the differences have higher influence on the prediction and it enhances their importance. The plots obtained when using processed data show extreme changes in predictions, the slope of the regression line being close to zero and the points being completely under the 1:1 line. This shows how important the shape of the spectra is when using first derivatives.

The plots of the observed and predicted values show that the points get more scattered when using data without pre-processing, which confirms the fact that pre-processing the data increases the influence of the differences between the spectra on the predicted soil characteristics.

The model performs differently for the not processed goniometer and muglight measurements when estimating the three contents. For the muglight measurements the explanation might be the highest difference in reflectance intensity when compared to the contact probe spectra, and apparently the intensity is an important parameter in the model, and it seems that the soil texture influences considerably the prediction outcome. The soil samples had the same characteristics excepting the texture, but apparently that cannot be seen when predicting them. In the case of the goniometer measurements, the reason could also the wavelengths that have the highest weights in the model (the variable importance for projection – VIP). As it can be seen in Figure 11, for clay and organic matter content estimations the wavelengths close to and including the absorption peaks seen in the spectra get much more weight in the model than in the case of the quartz content estimations. This leads to the model performing differently in the three different cases: it seems like the performance is much worse for clay, where the important wavelengths are around 1500 nm and also 1700 nm, than in the case of the organic matter content where after 1500 nm (where a peak can be seen) the wavelengths get low weights, or in the case of the quartz content estimations, where the weights are low overall. When estimating organic matter content and quartz content the reflectance intensity differences appear to be more important than the shape differences between the contact probe spectra and the other spectra, since the muglight measurements give lower results than the goniometer measurements.
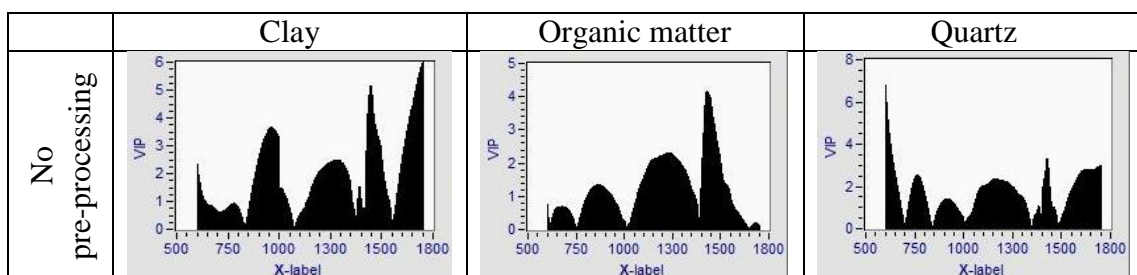

Figure 9. VIPs for the models used to estimate clay, organic matter and quartz content with spectra without pre-processing.

Although the statistics obtained for the leave-one-out cross validation of each model obtained based on each separate dataset are similar to the statistics obtained for validating the model constructed with the contact probe measurements with the other datasets, one cannot say that the prediction results are similar. The predicted values obtained using the other datasets on the contact probe model are very different than the predicted values with the leave-one-out cross validation, fact that can be seen in the plots (Figures 5-10). This confirms that spectra obtained with different accessories cannot be combined.

Another interesting observation is the fact that having the same soil sample with two different textures gives different results for predicting the characteristics, although in this research a clear differentiation cannot be made in order to see if the different results come from using different accessories for measuring (in this case contact probe and muglight) or from the different textures. Testing how measuring with the same accessory spectra for the same soil sample but with different textures would help make the differentiation, and could be a subject for further research.

Considering the results of the second research question, in which all the measuring accessories from this research were used for determining the "pseudo-diffuse" reflectance, validating the model constructed with the contact probe measurements with the other datasets should give satisfactory outcomes, since the measured quantities would define basically the same notion: diffuse reflectance. There was no article in which the measurements for "diffuse" reflectance were performed with a spectrometer mounted on a goniometer, but averaging the measurements taken from all the different angles would resemble averaging spectra taken when rotating the sample, where actually only the azimuth angle is varied (Ge et al., 2011; Nocita et al., 2014). As it can be seen, the spectra obtained with the different accessories give different results for the predictions.

These results have great implication when considering the idea of building a large soil spectral database, suggested in previous researches (Brown et al., 2006; Ge et al., 2011). The spectral database would consist of measurements performed with different instruments and accessories and as it can be seen from the results in this research, using spectral datasets from multiple sources does not give a good result when estimating soil characteristics. It has been previously shown that data obtained with different spectrometers should not be combined without carefully designed algorithms for the transfer of the calibration models (Ge et al., 2011), so a subject for future research could be designing an algorithm for combining datasets resulted from measuring with different accessories.

5. Conclusions

There is a multitude of instruments and accessories used in soil spectroscopy, and also a multitude of different settings for the measuring experiments. The measuring settings are often not very well described, the description being resumed to mentioning the type of instrument and accessories used, the number of collected spectra and the sample preparation. However, all of these techniques have been used to measure spectra for estimating the same soil characteristics. Also, the same techniques have been used to measure both bi-conical reflectance and what is called in the articles "diffuse" reflectance without making any difference between the two notions. The different researches use for example a contact probe to measure "diffuse" reflectance, which by definition should then be equal to measuring diffuse reflectance with a diffuse reflectance measuring accessory (e.g. integrating sphere), therefore the two quantities should be equal and should give the same performance when modelling using them. It is clear that the term "diffuse reflectance" is used without any consideration for its actual definition and accessories that are needed to measure it.

Considering the results obtained by analysing the spectral data, it can be said that the quantities that are measured in the multitude of articles as "diffuse" reflectance are not actually diffuse reflectance by definition. If diffuse reflectance could have been measured with all the presented accessories, then the spectra obtained in this research should have been similar and the results of modelling it for clay, organic matter and quartz content would have been comparable.

Performing the spectra comparison by visual assessment, calculating the RMSE for the differences in reflectance intensity and determining the differences in shape by calculating the SAM values, showed considerable differences between the results of the five different measuring experiments.

Also, building multivariate models with the five different datasets in order to estimate the clay, organic matter and quartz content of the samples gave different results. This confirms that reflectance measured with an accessory specially designed for measuring diffuse reflectance is different than reflectance measured with an accessory that is not made for measuring diffuse reflectance (e.g. contact probe).

There are two main conclusions resulting from this research: 1) only the reflectance measured with diffuse reflectance measuring accessories is diffuse reflectance and only then the term "diffuse reflectance" should be used and 2) spectral data originated from different measuring setups should not be combined for estimating soil characteristics.

Appendix A. Observed vs. predicted values plots for the LOO cross-validation for quartz content.
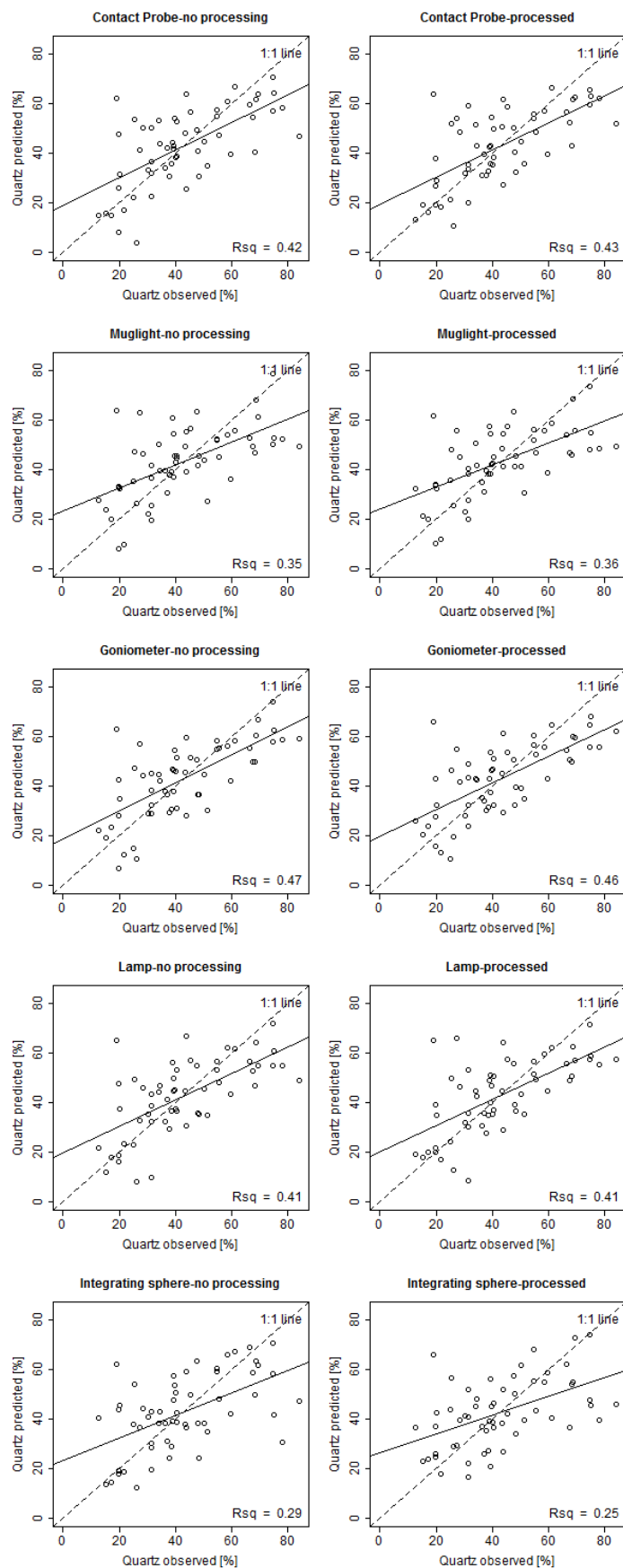
Appendix B. Observed vs. predicted values plots for contact probe model's validation with the other datasets for quartz content.
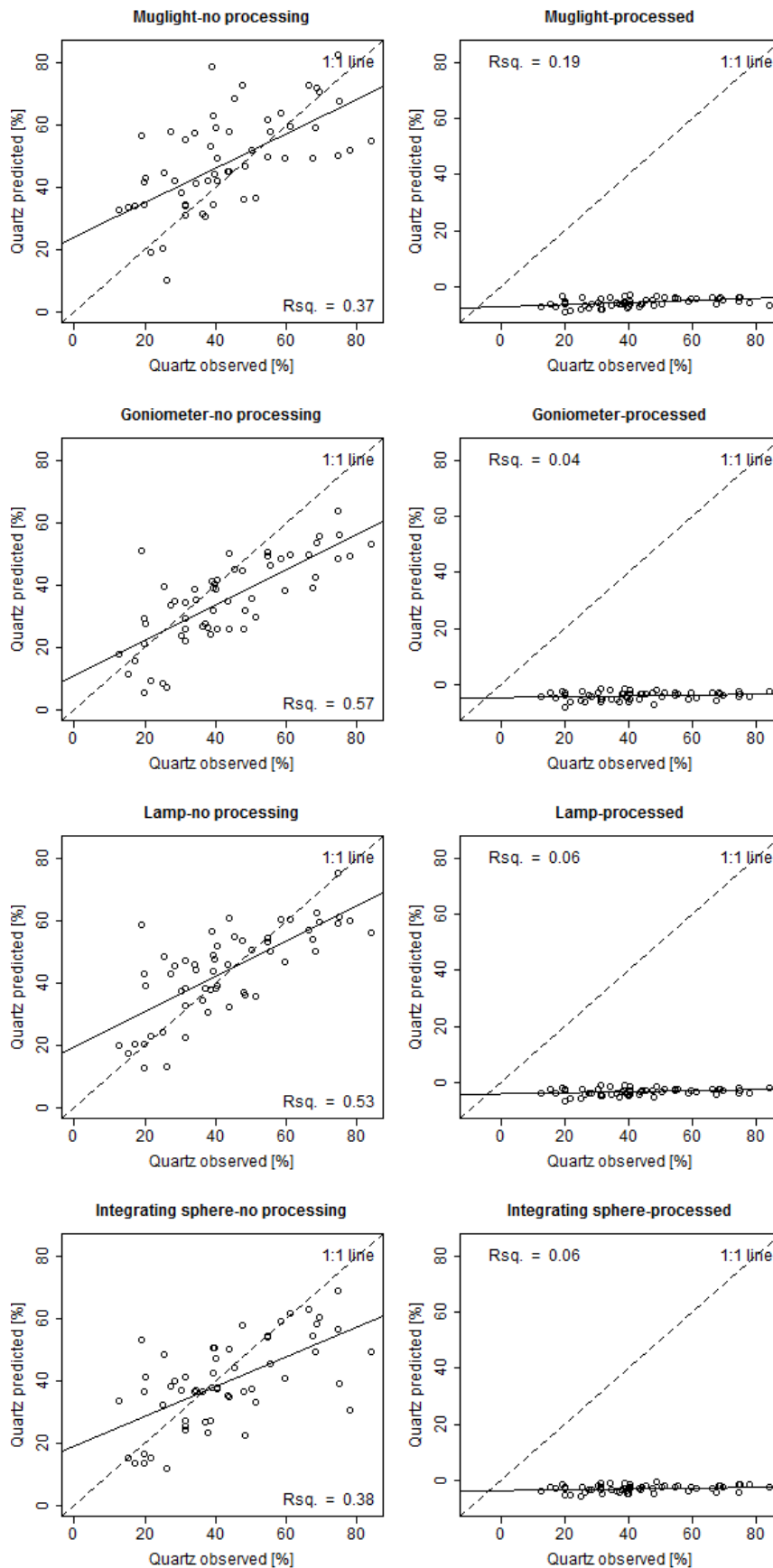
References

Azuaje, E. I., Comerford, N. B., Harris, W. G., Reeves Iii, J. B., and Grunwald, S., 2012, Loblolly and slash pine control organic carbon in soil aggregates and carbon mineralization: Forest Ecology and Management, v. 263, no. 0, p. 1-8.

Bábek, O., Chlachula, J., and Grygar, T. M., 2011, Non-magnetic indicators of pedogenesis related to loess magnetic enhancement and depletion: Examples from the Czech Republic and southern Siberia: Quaternary Science Reviews, v. 30, no. 7–8, p. 967-979.

Balsam, W. L., Ellwood, B. B., Ji, J., Williams, E. R., Long, X., and El Hassani, A., 2011, Magnetic susceptibility as a proxy for rainfall: Worldwide data from tropical and temperate climate: Quaternary Science Reviews, v. 30, no. 19–20, p. 2732-2744.

Barthès, B. G., Brunet, D., Hien, E., Enjalric, F., Conche, S., Freschet, G. T., d'Annunzio, R., and Toucet-Louri, J., 2008, Determining the distributions of soil carbon and nitrogen in particle size fractions using near-infrared reflectance spectrum of bulk soil samples: Soil Biology and Biochemistry, v. 40, no. 6, p. 1533-1537.

Bartholomeus, H., Kooistra, L., Stevens, A., van Leeuwen, M., van Wesemael, B., Ben-Dor, E., and Tychon, B., 2011, Soil Organic Carbon mapping of partially vegetated agricultural fields with imaging spectroscopy: International Journal of Applied Earth Observation and Geoinformation, v. 13, no. 1, p. 81-88.

Bartholomeus, H. M., Roosjen, P. P. J., Clevers, J. G. P. W., Suomalainen, J. M., Mulder, V. L., and Kooistra, L., Estimation of soil clay content using multidirectional laboratory spectroscopy measurements, *in* Proceedings 8th Earsel Imaging Spectroscopy Workshop, Nantes, France, 2013.

Ben-Dor, E., and Banin, A., 1995, Near-Infrared Analysis as a Rapid Method to Simultaneously Evaluate Several Soil Properties: Soil Sci. Soc. Am. J., v. 59, no. 2, p. 364-372.

Bogner, C., Schmiedinger, I., and Huwe, B., 2011, Rapid estimation of Brilliant Blue concentrations in soil by vis diffuse reflectance spectroscopy: Geoderma, v. 164, no. 1–2, p. 95-98.

Brodský, L., Vašát, R., Klement, A., Zádorová, T., and Jakšík, O., 2013, Uncertainty propagation in VNIR reflectance spectroscopy soil organic carbon mapping: Geoderma, v. 199, no. 0, p. 54-63.

Brown, D. J., Bricklemyer, R. S., and Miller, P. R., 2005, Validation requirements for diffuse reflectance soil characterization models with a case study of VNIR soil C prediction in Montana: Geoderma, v. 129, no. 3–4, p. 251-267.

Brown, D. J., Shepherd, K. D., Walsh, M. G., Dewayne Mays, M., and Reinsch, T. G., 2006, Global soil characterization with VNIR diffuse reflectance spectroscopy: Geoderma, v. 132, no. 3–4, p. 273-290.

Chakraborty, S., Weindorf, D. C., Zhu, Y., Li, B., Morgan, C. L. S., Ge, Y., and Galbraith, J., 2012, Spectral reflectance variability from soil physicochemical properties in oil contaminated soils: Geoderma, v. 177–178, no. 0, p. 80-89.

Chang, C.-W., and Laird, D. A., 2002, Near-Infrared Reflectance Spectroscopic Analysis of Soil C and N: Soil Science, v. 167, no. 2, p. 110-116.

Chang, C.-W., Laird, D. A., Mausbach, M. J., and Hurburgh, C. R., 2001, Near-Infrared Reflectance Spectroscopy–Principal Components Regression Analyses of Soil Properties Journal Paper no. J-18766 of the Iowa Agric. and Home Econ. Exp. Stn., Ames, IA: Soil Sci. Soc. Am. J., v. 65, no. 2, p. 480-490.

Cozzolino, D., and Moron, A., 2003, The potential of near-infrared reflectance spectroscopy to analyse soil chemical and physical characteristics: The Journal of Agricultural Science, v. 140, no. 01, p. 65-71.

Cozzolino, D., and Morón, A., 2006, Potential of near-infrared reflectance spectroscopy and chemometrics to predict soil organic carbon fractions: Soil and Tillage Research, v. 85, no. 1–2, p. 78-85.

Davinic, M., Fultz, L. M., Acosta-Martinez, V., Calderón, F. J., Cox, S. B., Dowd, S. E., Allen, V. G., Zak, J. C., and Moore-Kucera, J., 2012, Pyrosequencing and mid-infrared spectroscopy reveal distinct aggregate stratification of soil bacterial communities and organic matter composition: Soil Biology and Biochemistry, v. 46, no. 0, p. 63-72.

De Carvalho, O., and Meneses, P. R., Spectral correlation mapper (SCM): an improvement on the spectral angle mapper (SAM), *in* Proceedings Summaries of the 9th JPL Airborne Earth Science Workshop, JPL Publication 00-182000, Volume 9, JPL Publication Pasadena, CA.

Dennison, P. E., Halligan, K. Q., and Roberts, D. A., 2004, A comparison of error metrics and constraints for multiple endmember spectral mixture analysis and spectral angle mapper: Remote Sensing of Environment, v. 93, no. 3, p. 359-367.

Ge, Y., Morgan, C. L. S., Grunwald, S., Brown, D. J., and Sarkhot, D. V., 2011, Comparison of soil reflectance spectra and calibration models obtained using multiple spectrometers: Geoderma, v. 161, no. 3–4, p. 202-211.

Guerrero, C., Rossel, R. A. V., and Mouazen, A. M., 2010, Special issue 'Diffuse reflectance spectroscopy in soil science and land resource assessment': Geoderma, v. 158, no. 1–2, p. 1-2.

Hapke, B., and Lindon, J. C., 2010, Reflectance Methods and Applications, Encyclopedia of Spectroscopy and Spectrometry (Second Edition): Oxford, Academic Press, p. 2420-2425.

Huerta, E., Brunet, D., Velazquez, E., and Lavelle, P., 2013, Identifying earthworm's organic matter signatures by near infrared spectroscopy in different land-use systems in Tabasco, Mexico: Applied Soil Ecology, v. 69, no. 0, p. 49-55.

Islam, K., Singh, B., and McBratney, A., 2003, Simultaneous estimation of several soil properties by ultra-violet, visible, and near-infrared reflectance spectroscopy: Soil Research, v. 41, no. 6, p. 1101-1114.

Janik, L. J., Merry, R. H., and Skjemstad, J. O., 1998, Can mid infrared diffuse reflectance analysis replace soil extractions?: Australian Journal of Experimental Agriculture, v. 38, no. 7, p. 681-696.

Jindaluang, W., Kheoruenromne, I., Suddhiprakarn, A., Singh, B. P., and Singh, B., 2013, Influence of soil texture and mineralogy on organic matter content and composition in physically separated fractions soils of Thailand: Geoderma, v. 195–196, no. 0, p. 207-219.

Jordanova, N., Jordanova, D., Liu, Q., Hu, P., Petrov, P., and Petrovský, E., 2013, Soil formation and mineralogy of a Rhodic Luvisol — insights from magnetic and geochemical studies: Global and Planetary Change, v. 110, Part C, no. 0, p. 397-413.

Kodikara, G. R. L., Woldai, T., van Ruitenbeek, F. J. A., Kuria, Z., van der Meer, F., Shepherd, K. D., and van Hummel, G. J., 2012, Hyperspectral remote sensing of evaporate minerals and associated sediments in Lake Magadi area, Kenya: International Journal of Applied Earth Observation and Geoinformation, v. 14, no. 1, p. 22-32.

Kruse, F. A., Lefkoff, A. B., Boardman, J. W., Heidebrecht, K. B., Shapiro, A. T., Barloon, P. J., and Goetz, A. F. H., 1993, The spectral image processing system (SIPS)—

interactive visualization and analysis of imaging spectrometer data: Remote Sensing of Environment, v. 44, no. 2–3, p. 145-163.

Kuang, B., and Mouazen, A. M., 2013, Effect of spiking strategy and ratio on calibration of on-line visible and near infrared soil sensor for measurement in European farms: Soil and Tillage Research, v. 128, no. 0, p. 125-136.

Kweon, G., and Maxton, C., 2013, Soil organic matter sensing with an on-the-go optical sensor: Biosystems Engineering, v. 115, no. 1, p. 66-81.

Marín-González, O., Kuang, B., Quraishi, M. Z., Munóz-García, M. Á., and Mouazen, A. M., 2013, On-line measurement of soil properties without direct spectral response in near infrared spectral range: Soil and Tillage Research, v. 132, no. 0, p. 21-29.

Masserschmidt, I., Cuelbas, C. J., Poppi, R. J., de Andrade, J. C., de Abreu, C. A., and Davanzo, C. U., 1999, Determination of organic matter in soils by FTIR/diffuse reflectance and multivariate calibration: Journal of Chemometrics, v. 13, no. 3-4, p. 265-273.

McBratney, A. B., Minasny, B., and Viscarra Rossel, R., 2006, Spectral soil analysis and inference systems: A powerful combination for solving the soil data crisis: Geoderma, v. 136, no. 1–2, p. 272-278.

McCarty, G. W., and Reeves, J. B., 2001, Development of rapid instrumental methods for measuring soil organic carbon", in Assessment Methods for Soil Carbon: Advances in Soil Science, Ed by R. Lal, J.M. Kimble, R.F. Follett and B.A. Stewart. CRCPress, Boca Raton, Florida, USA, p. 371.

McCarty, G. W., Reeves, J. B., Reeves, V. B., Follett, R. F., and Kimble, J. M., 2002, Mid-Infrared and Near-Infrared Diffuse Reflectance Spectroscopy for Soil Carbon Measurement: Soil Sci. Soc. Am. J., v. 66, no. 2, p. 640-646.

McDowell, M. L., Bruland, G. L., Deenik, J. L., Grunwald, S., and Knox, N. M., 2012, Soil total carbon analysis in Hawaiian soils with visible, near-infrared and mid-infrared diffuse reflectance spectroscopy: Geoderma, v. 189–190, no. 0, p. 312-320.

Minasny, B., McBratney, A. B., Bellon-Maurel, V., Roger, J.-M., Gobrecht, A., Ferrand, L., and Joalland, S., 2011, Removing the effect of soil moisture from NIR diffuse reflectance spectra for the prediction of soil organic carbon: Geoderma, v. 167–168, no. 0, p. 118-124.

Mulder, V. L., Plötze, M., de Bruin, S., Schaepman, M. E., Mavris, C., Kokaly, R. F., and Egli, M., 2013, Quantifying mineral abundances of complex mixtures by coupling spectral deconvolution of SWIR spectra (2.1–2.4 µm) and regression tree analysis: Geoderma, v. 207–208, no. 0, p. 279-290.

Myers, D. B., Kitchen, N. R., Sudduth, K. A., Miles, R. J., Sadler, E. J., and Grunwald, S., 2011, Peak functions for modeling high resolution soil profile data: Geoderma, v. 166, no. 1, p. 74-83.

Nicodemus, F. E., 1970, Reflectance nomenclature and directional reflectance and emissivity: Applied Optics, v. 9, no. 6, p. 1474-1475.

Nicolini, J., Pereira, B. F., Pillon, C. N., Machado, V. G., Lopes, W. A., de Andrade, J. B., and Mangrich, A. S., 2011, Characterization of Brazilian oil shale byproducts planned for use as soil conditioners for food and agro-energy production: Journal of Analytical and Applied Pyrolysis, v. 90, no. 2, p. 112-117.

Nocita, M., Stevens, A., Noon, C., and van Wesemael, B., 2013, Prediction of soil organic carbon for different levels of soil moisture using Vis-NIR spectroscopy: Geoderma, v. 199, no. 0, p. 37-42.

Nocita, M., Stevens, A., Toth, G., Panagos, P., van Wesemael, B., and Montanarella, L., 2014, Prediction of soil organic carbon content by diffuse reflectance spectroscopy

using a local partial least square regression approach: Soil Biology and Biochemistry, v. 68, no. 0, p. 337-347.

Okparanma, R. N., Coulon, F., and Mouazen, A. M., 2014, Analysis of petroleum-contaminated soils by diffuse reflectance spectroscopy and sequential ultrasonic solvent extraction–gas chromatography: Environmental Pollution, v. 184, no. 0, p. 298-305.

Pirie, A., Singh, B., and Islam, K., 2005, Ultra-violet, visible, near-infrared, and mid-infrared diffuse reflectance spectroscopic techniques to predict several soil properties: Soil Research, v. 43, no. 6, p. 713-721.

Rasche, F., Marhan, S., Berner, D., Keil, D., Kandeler, E., and Cadisch, G., 2013, midDRIFTS-based partial least square regression analysis allows predicting microbial biomass, enzyme activities and 16S rRNA gene abundance in soils of temperate grasslands: Soil Biology and Biochemistry, v. 57, no. 0, p. 504-512.

Rawlins, B. G., Kemp, S. J., and Milodowski, A. E., 2011, Relationships between particle size distribution and VNIR reflectance spectra are weaker for soils formed from bedrock compared to transported parent materials: Geoderma, v. 166, no. 1, p. 84-91.

Reeves Iii, J., and McCarty, G., 2001, Quantitative analysis of agricultural soils using near infrared reflectance spectroscopy and a fibre-optic probe: Journal of Near Infrared Spectroscopy, v. 9, p. 25.

Reeves III, J., McCarty, G., and Meisinger, J., 1999, Near infrared reflectance spectroscopy for the analysis of agricultural soils: Journal of Near Infrared Spectroscopy, v. 7, p. 179.

Reeves Iii, J. B., 2010, Near- versus mid-infrared diffuse reflectance spectroscopy for soil analysis emphasizing carbon and laboratory versus on-site analysis: Where are we and what needs to be done?: Geoderma, v. 158, no. 1-2, p. 3-14.

Reeves Iii, J. B., McCarty, G. W., Calderon, F., Hively, W. D., Liebig, M. A., Franzluebbers, A. J., and Follett, R. F., 2012, Chapter 20 - Advances in Spectroscopic Methods for Quantifying Soil Carbon, Managing Agricultural Greenhouse Gases: San Diego, Academic Press, p. 345-366.

Rinnan, Å., Berg, F. v. d., and Engelsen, S. B., 2009, Review of the most common pre-processing techniques for near-infrared spectra: TrAC Trends in Analytical Chemistry, v. 28, no. 10, p. 1201-1222.

Rossel, R. A. V., and Chen, C., 2011, Digitally mapping the information content of visible–near infrared spectra of surficial Australian soils: Remote Sensing of Environment, v. 115, no. 6, p. 1443-1455.

Ryals, R., Kaiser, M., Torn, M. S., Berhe, A. A., and Silver, W. L., 2014, Impacts of organic matter amendments on carbon and nitrogen dynamics in grassland soils: Soil Biology and Biochemistry, v. 68, no. 0, p. 52-61.

Sarkhot, D. V., Grunwald, S., Ge, Y., and Morgan, C. L. S., 2011, Comparison and detection of total and available soil carbon fractions using visible/near infrared diffuse reflectance spectroscopy: Geoderma, v. 164, no. 1–2, p. 22-32.

Savitzky, A., and Golay, M. J. E., 1964, Smoothing and Differentiation of Data by Simplified Least Squares Procedures: Analytical Chemistry, v. 36, no. 8, p. 1627-1639.

Siebielec, G., McCarty, G. W., Stuczynski, T. I., and Reeves, J. B., 2004, Near-and mid-infrared diffuse reflectance spectroscopy for measuring soil metal content: Journal of environmental quality, v. 33, no. 6, p. 2056-2069.

Song, Y., Li, F., Yang, Z., Ayoko, G. A., Frost, R. L., and Ji, J., 2012, Diffuse reflectance spectroscopy for monitoring potentially toxic elements in the agricultural soils of Changjiang River Delta, China: Applied Clay Science, v. 64, no. 0, p. 75-83.

Stenberg, B., Viscarra Rossel, R. A., Mouazen, A. M., and Wetterlind, J., 2010, Visible and Near Infrared Spectroscopy in Soil Science, Advances in Agronomy, Volume 107, p. 163-215.

Stevens, A., van Wesemael, B., Bartholomeus, H., Rosillon, D., Tychon, B., and Ben-Dor, E., 2008, Laboratory, field and airborne spectroscopy for monitoring organic carbon content in agricultural soils: Geoderma, v. 144, no. 1–2, p. 395-404.

Torrent, J., and Barrón, V., 2008, Diffuse reflectance spectroscopy: Methods of Soil Analysis. Part, v. 5, p. 367-387.

Uchimiya, M., Orlov, A., Ramakrishnan, G., and Sistani, K., 2013, In situ and ex situ spectroscopic monitoring of biochar's surface functional groups: Journal of Analytical and Applied Pyrolysis, v. 102, no. 0, p. 53-59.

Viscarra Rossel, R. A., 2008, ParLeS: Software for chemometric analysis of spectroscopic data: Chemometrics and Intelligent Laboratory Systems, v. 90, no. 1, p. 72-83.

Viscarra Rossel, R. A., McGlynn, R. N., and McBratney, A. B., 2006a, Determining the composition of mineral-organic mixes using UV–vis–NIR diffuse reflectance spectroscopy: Geoderma, v. 137, no. 1–2, p. 70-82.

Viscarra Rossel, R. A., Walvoort, D. J. J., McBratney, A. B., Janik, L. J., and Skjemstad, J. O., 2006b, Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties: Geoderma, v. 131, no. 1–2, p. 59-75.

Xie, X.-L., Pan, X.-Z., and Sun, B., 2012, Visible and Near-Infrared Diffuse Reflectance Spectroscopy for Prediction of Soil Properties near a Copper Smelter: Pedosphere, v. 22, no. 3, p. 351-366.