CRANFIELD UNIVERSITY

Boyan Kuang

On-line Measurement of Some Selected Soil Properties for Controlled Input Crop Management Systems

School of Applied Sciences

PhD
Academic Year: 2008- 2012

Supervisor: Dr. Abdul Mounen Mouazen
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ABSTRACT

The evaluation of the soil spatial variability using a fast, robust and cheap tool is one of the key steps towards the implementation of Precision Agriculture (PA) successfully. Soil organic carbon (OC), soil total nitrogen (TN) and soil moisture content (MC) are needed to be monitored for both agriculture and environmental applications. The literature has proven that visible and near infrared (vis-NIR) spectroscopy to be a quick, cheap and robust tool to acquire information about key soil properties simultaneously with relatively high accuracy. The on-line vis-NIR measurement accuracy depends largely on the quality of calibration models. In order to establish robust calibration models for OC, TN and MC valid for few selected European farms, several factors affecting model accuracy have been studied. Nonlinear calibration techniques, e.g. artificial neural network (ANN) combined with partial least squares regression (PLSR) has provided better calibration accuracy than the linear PLSR or principal component regression analysis (PCR) alone. It was also found that effects of sample concentration statistics, including the range or standard derivation and the number of samples used for model calibration are substantial, which should be taking into account carefully. Soil MC, texture and their interaction effects are other principle factors affecting the *in situ* and on-line vis-NIR measurement accuracy. This study confirmed that MC is the main negative effect, whereas soil clay content plays a positive role. The general calibration models developed for soil OC, TN and MC for farms in European were validated using a previously developed vis-NIR on-line measurement system equipped with a wider vis-NIR spectrophotometer (305 – 2200 nm) than the previous version. The validation results showed this wider range on-line vis-NIR system can acquire larger than 1500 data point per ha with a very good measurement accuracy for TN and OC and excellent accuracy for MC. The validation also showed that spiking few target field samples into the general calibration models is an effective and efficient approach for upgrading the implementation of the on-line vis-NIR sensor for measurement in new fields in the selected European farms.

Keywords:

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
ANN	Artificial neural network
BPNN	Back-propagation neural network
CEC	Cation-exchange capacity
DGPS	Differential global positioning system
EC	Electrical conductivity
MIR	Mid infrared
K	Potassium
LV	Latent variable
MC	Moisture content
MLR	Multiple linear regression
Mg	Magnesium
NO_3	Nitrate
Na	sodium
NIR	Near infrared
OC	Organic carbon
PA	Precision agriculture
R^2	Coefficient of determination
r	Coefficient of correlation
P	Phosphorous
PCA	Principle component analysis
PCR	Principle component regression
PLSR	Partial least square regression
RMSECV	Root mean square error of cross-validation
RMSEP	Root mean square error of prediction
RPD	Ratio of prediction to deviation
P_2O_5	Phosphate
IP	Insulation protection
SD	Standard deviation
SEP	Standard error of prediction
SECV	Standard error of cross-validation
SOM	Soil organic matter
TN	Total nitrogen
TC	Total carbon

vis   Visible

1 General introduction

1.1 Introduction

Soil organic carbon (OC) is not only a key soil property for plant growth, but it is also essential for maintaining terrestrial ecosystems and for the overall environment, as OC reserves a large part of global carbon stock. It is the major component of soil organic matter, which is important in all soil processes. Shortages in OC result in decline of soil quality and crop production over the field. Soil OC is also an important component for evaluating soil resistivity to wind and water erosion (Morgan, 2005). Arable farming results in nitrogen loss from the soil-plant-system to the environment (Olfs, 2009). When the nitrogen inputs are surplus, nitrogen can be lost from land through runoff into surface water, denitrification and volatilization into the atmosphere, and leaching into groundwater (Miller and Wolfe, 1978). Leaching and denitrification are the two main processes through which nitrate lost is from soil to water environment and atmosphere (Addiscott, 2005). Nitrate in aquatic system may come from different sources, with only a small portion may be from nitrogen fertiliser. The rest may come from mineralization in soil, grazing animals or utilization of manures, ploughing old grassland as well as nitrogen deposition from the atmosphere (Addiscott, 2005). Nitrate leaching from land to ground water and stream water causes depletion of soil minerals, acidifying soils, affecting downstream water system and coastal marine ecosystems (Vitousek et al., 1997). Although plant uses mineral nitrogen, total nitrogen is important fraction as part of TN becomes mineral by a process called mineralisation (Addiscott, 2005). Soil moisture content (MC) is another critical soil property for regulation of plant growth and soil biology. Moreover, it regulates important soil processes such as soil nitrification/denitrification and hydrological such as leaching and erosion (Stenberg et al. 2010a). The spatial distribution variability of these three properties can be huge, even in a small field. This is the reason why this study focuses on the on-line measurement of these key soil properties, namely, OC, TN and MC.

The urgent need for doubling farm production over the next 25 years on less land and water resources through further intensification would inevitably involve substantial social, economic, and environmental cost. One of the strategies to minimize such costs through enhanced productivity and economic profits while simultaneously conserving the environment is precision agriculture (PA). PA can be defined as a historic and environmentally friendly strategy, in which farmers can vary input use and cultivation methods including application of seeds, fertilizers, pesticides, and water, variety selection, planting, tillage, harvesting to match varying soil and crop conditions across a field (Srinivasan, 2006). There are three fundamental elements in PA, namely describing variability, variable rate technology, and the decision support systems. Among these three components, the task of describing variability is the most important and should be done prior to the implementation of PA. In particular, it is based on variation within each field and should be understood in at least three aspects: spatial, temporal and predictive. Conventional description methods of soil spatial variability usually involve manual soil sampling, sample pre-treatment, laboratory chemical, physical analysis and mapping. Those procedures are very expensive, time-consuming and unaffordable by the farmers adopting site specific applications in PA, where high spatial sampling resolution is essential. Therefore, the development of a fast, cost effective and environmentally friendly soil spatial variability detection method is a preliminary task for the implementation of PA.

Visible and near infrared (vis-NIR) spectroscopy has become increasingly applied in soil analysis. The early stages of the implementation of the vis-NIR spectroscopy for soil analysis was along with multiple linear regression (MLR) calibration technique to determine key soil properties, such as soil MC, soil organic matter (SOM) or OC, TN and pH. With the emergence of commercial NIR spectrophotometers and multivariate calibration software packages, vis-NIR spectroscopy has been adopted much widely for the analysis of soil. Numerous researchers have extended the vis-NIR spectroscopy applications from the measurement of key soil properties (e.g. MC, pH, SOM, TN and OC) to almost all other soil micro and macro elements, such as phosphorous (P),

Potassium (K), sodium (Na), Calcium (Ca), Fe, cation exchange capacity (CEC), clay and magnesium (Mg). The analysis of soil with this technique was also extended to soil biological, physical and engineering properties. Multivariate calibration techniques made it possible to perform simultaneous measurements of several soil properties under consideration.

On-line sensors for real-time measurement of soil parameters can be particularly useful tools for implementing sensor-based and map-based variable rate application of different input, because these sensors can lead to reduced labour, time and cost of soil sampling/analysis and allow for high spatial resolution of soil sampling. With the progress achieved in information technology, the differential global position system (DGPS) has been introduced into the on-line soil measurement system. The DGPS can be used to locate and navigate agriculture machines within a field and have the capacity to determine the geographic coordinate (latitude and longitude). Moreover, high-accuracy DGPS receivers can measure the altitude and the data can be used to calculate slope, aspect and other parameters relevant to the landscape. When a DGPS receiver and a data logger are used to record the position of each soil sample or measurement, a map based the on-line collected data can be generated and processed along with other layers of spatially variable information. Currently, DGPS has been integrated into current on-line soil sensing systems. One example of DGPS equipped on-line soil sensors are those based on vis-NIR spectroscopy.

Compared to many non-mobile vis-NIR spectral measurements on dried or fresh soil samples, relatively few applications were found using the on-line vis-NIR spectroscopy measurement of soil constituents. This is attributed to the difficulties in designing and building on-line measurement systems (Mouazen et al., 2007). Inserting the illumination and detection units within the soil while driving with the tractor makes the delicate and fragile optical instrumentation to be prone to breakage, especially when the trial is to be carried out in fields with stubble and stones (Mouazen et al. 2007). A review on the state-of-the-art of on-line vis-NIR measurement systems (Kuang et al., 2012a) reveals that there are only three systems available today, with only one

system (e.g. Veris technologies, KS, the USA) commercially available. Shibusawa et al. (1999) developed an on-line vis-NIR (400-1700 nm) sensor to predict soil moisture, pH, electric conductivity (EC), SOM and NO_3-N. The sensor system composed of three main sub-systems, namely, a soil-penetrating chisel with the housing for micro optical devices, an optical unit of illumination supply and spectrometer, and a control and data logging system (personal computer). They correlated spectral reflectance data at four single wavelengths to MC, pH, EC, and SOM, reporting R^2 values of 0.68, 0.61, 0.64 and 0.87, respectively. Christy et al. (2003) developed a prototype soil reflectance mapping unit equipped with a vis-NIR spectrophotometer (900–1700 nm), which became latter commercial system, sold today for research purposes by Veris Technologies, The USA. It consisted of a tractor driven steel shank dug soil to 10 cm depth and a quartz tungsten bulb mounted within the shank to illuminate the soil while optical fibres were used to transmit the reflected light to the spectrophotometer mounted above the shank. Results of a pilot study using data from a single field in central Iowa showed that locally weighted principal component regression (PCR) was capable of predicting MC, TC, TN, and pH with R^2 values of 0.82, 0.87, 0.86, and 0.72, respectively. This system was further developed and the best one-field-out validation results were obtained for SOM (R^2 = 0.67 and RMSE = 0.52 %) (Christy et al. 2008). Integrating the vis-NIR spectroscopy sensor of Veris with a Landsat enhanced thematic mapper (ETM) and a DGPS, Huang et al. (2007) configured, an on-line soil sensor for TC mapping in a 50 ha glacial till soils in Michigan, the USA. They claimed that r values between measured and predicted carbon values were equal to 0.81 and 0.62, using NIRS data and ETM imagery, respectively. Further application of this system, however, could not even provide semi-quantitative accuracy for soil OC and clay content with RPD=1.8 (Bricklemyer et al. 2010). Later research using the same sensor achieved better results for OC with R^2 = 0.66 (Munoz et al. 2011) and RPD = 0.19 for OC (Knadel et al. 2011). However, the on-line system of Veris is equipped with a sapphire glass, which is susceptible to breakage due to the direct contact with soil containing stones.

A much simpler and robust design to that of Shibusawa et al. (2001) without sapphire window optical configuration was designed and developed by Mouazen (2006a). In this

thesis this on-line measurement will be used (Fig. 1.1). It consists of a subsoiler, which penetrates the soil to the required depth, making a trench, whose bottom is smoothened by the downwards forces acting on the subsoiler. The optical probe is housed in a steel lens holder. This is attached to the backside of the subsoiler chisel in order to acquire soil spectral reflectance data from the smooth bottom of the trench. The subsoiler is retrofitted with the optical unit and attached to a frame by means of the three point linkage of the tractor (Mouazen et al., 2005a). A mobile, fibre type, vis-NIR spectrophotometer (AgroSpec, Tec5, Germany) is used to measure soil spectra in diffuse reflectance mode. The spectrometer is an IP 66 model, protected for harsh working environments. A DGPS (EZ-Guide 250, Trimble, USA) is used to record the position of on-line measured spectra with sub-meter accuracy. A Panasonic semi-rugged laptop is used for data logging and communication. The spectrometer system, laptop and DGPS were powered by the tractor battery.
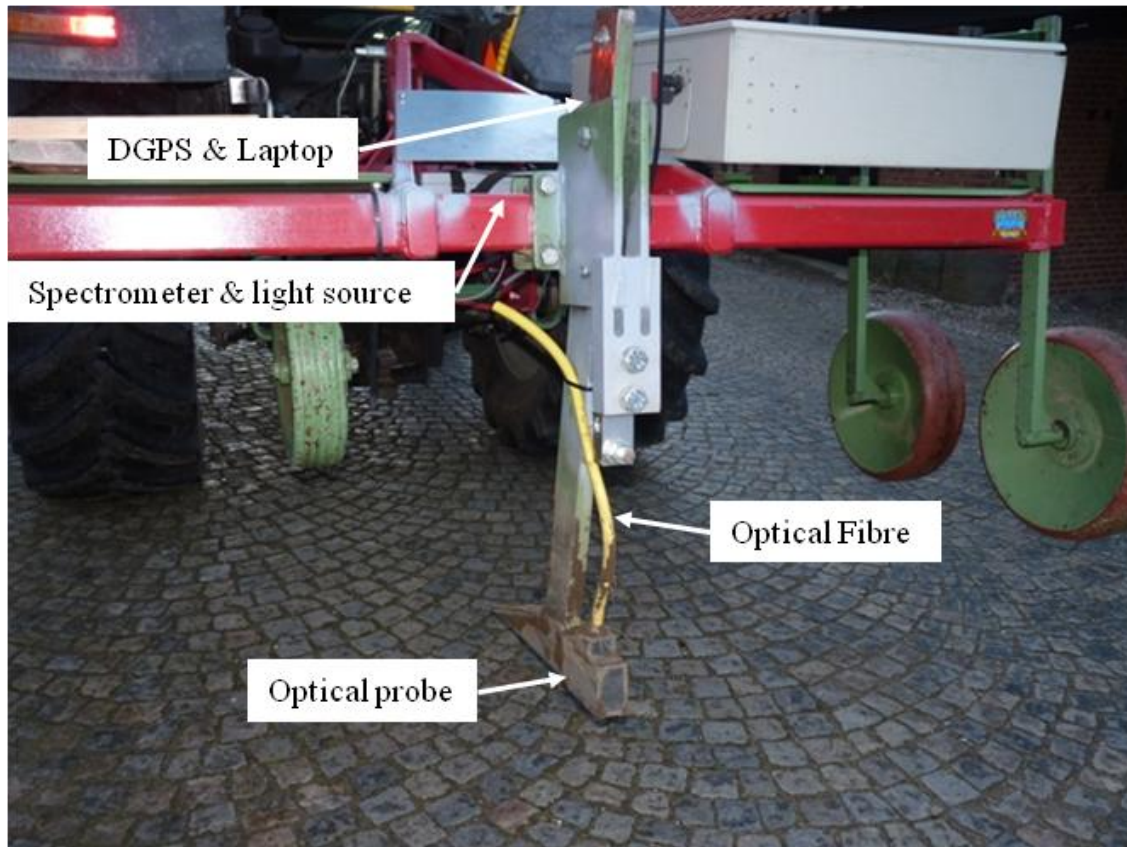
Figure 1-1 The on-line visible and near infrared (vis-NIR) spectroscopy-based soil sensor developed by Mouazen (2006a)

Adopting this on-line sensor, Mouazen et al. (2005) reported on on-line measurement of soil MC with a Zeiss Corona vis-NIR spectrophotometer (Zeiss, Jana, Germany) with a spectral range of 306.5–1710.9 nm. The spectrophotometer–optical unit system was calibrated for MC under stationary laboratory conditions on samples collected from an Arenic Cambisol field with different soil textures. The on-line field MC measurement showed a root mean square error of prediction (RMSEP) of 0.025 kgkg-1 and r value of 0.75. A further development of the sensor application was reported by Mouazen et al. (2007) for the measurement of soil TC, MC, pH and available P in a 7000 m^2 silt field in Belgium, obtaining a mean error values of 5.97, 0.37, 27.8 and 5.10 %, respectively, as compared to the laboratory reference methods. In a later published work, Mouazen et al. (2009) showed relatively high accuracy of prediction of extractable P with RMSE=1.07mg/100g^{-1} and RPD=1.42 based on national calibration model of P-ext

developed for the Flamish part of Belgium. From the results achieved so far by using the on-line sensor of Mouazen (2006a), it can be concluded that accuracy achieved so far for the measurement of key soil properties is not satisfactorily to claim robust and stable measurement system. Therefore, in this thesis a wider wavelength range AgroSpec spectrometer (Tec5 Technology for Spectroscopy, Germany) with a larger spectral range of 350 – 2200 nm will be considered to enhance the performance of on-line prediction of key soil properties (TN, OC, MC), as the NIR wavelength range larger than 1700 nm proven to be critical for measurement of OC and TN in particular. The performance of the system with the new spectrophotometer for the measurement of soil OC, TN and MC will be evaluated at farm scale, considering four European farms in Denmark, Germany, Czech Republic and the UK. This chapter is a guide to all aspects of the research considered in this dissertation towards understanding the system and affecting factors and towards the optimisation of the system utilisation for the best performance.

1.2 Calibration models for on-line measurement

Although vis-NIR spectroscopy allows for rapid, cost effective and intensive sampling, researchers admit some shortcoming associated with instrumentation instability to ambient conditions (e.g. light, temperature, etc), transferability of calibration curves between different instruments, model scale (global, continental, regional, country, local, field) vs accuracy and others. Under *in situ* field measurement conditions with non-mobile or mobile instrumentation, additional challenges associated with the influences of soil MC, texture, colour, temperature, harsh field conditions, dust, contaminates like stones and excessive residues, and surface roughness are all affect the accuracy of measurement with vis-NIR spectroscopy (Mouazen et al., 2007; Waise et al., 2007). To compensate or overcome one or many of these difficulties, some solutions were suggested and implemented by researchers. These includes, among other methods, the selection of a proper instrumentation e.g. spectrophotometer, optical accessories and optical probe design (Mouazen, et al., 2009), improved spectra

filtering and pre-processing, better control of ambient conditions and the selection of the multivariate statistical analysis method (Stenberg et al., 2010a).

Probably one of the most successful solutions to enhance the accuracy of vis-NIR measurement of soil attributes is the successful development of calibration models. However, it is still a challenge to develop accurate and robust calibration models for on-line measurement systems. Although some researchers suggested that the field scale models are of higher prediction accuracy (e.g. Christy, 2003) than larger geographic scale models, these are of limited practical values, as separate models should be developed for each particular field with the potential of increasing the cost. At least, farm scale or regional scale models have to be considered to take full advantage of the speed and cost effective acquisition of data with the vis-NIR spectroscopy-based on-line sensors.

In order to enhance modelling of soil spectra for best performance of the vis-NIR on-line sensor of OC, TN and MC (Mouazen et al. 2007) at farm scale, this thesis will study the effect of the following factors on accuracy:

- Multivariate calibration techniques,
- Sample statistics,
- Sample number,
- Soil MC, texture and their interaction on laboratory, *in situ* and on-line measurement conditions, and
- Spiking strategy and spiked sample size on on-line measurement.

Each of these five factors will be presented as one separate chapter, with brief content described below. It is worth noting that among the above mentioned four factors, the effect of calibration technique only will be evaluated using country scale data (e.g. Belgium and Northern France).

1.2.1 Calibration technique

Though PLSR (Viscarra Rossel, et al. 2006) has become a standard multivariate calibration method, there are situations where the response is non-linear, which requires non-linear modelling techniques, such as artificial neural network (ANN) (Mouazen, et al. 2007) and support vector machine (SVM) (Viscarra Rossel, et al. 2010). Since the linear PCR and PLSR analyses are the most common techniques for spectral calibration and prediction (Viscarra Rossel, et al., 2006a), with PLSR being the most accurate, other nonlinear techniques e.g. ANN and SVM methods have got much less attention and were rarely explored for the vis-NIR analysis of soil attributes. SVM study was not considered in this study as there is no commercial software available. Among those few studies utilising ANN, Fidêncio, et al. (2002) employed radial basis function networks (RBFN) in the NIR region (1000-2500 nm) and Daniel, et al. (2003) used ANN in the vis–NIR region (400–1100 nm). No literature is available about combining PLS with ANN.

Chapter 3 compares the performances of two linear (PCR and PLSR) and one non-linear back propagation neural network (BPNN) multivariate statistical analyses for the prediction of spectrally active (OC) and inactive (K, Mg, Na and P) soil attributes using vis-NIR diffuse reflectance spectra of soil samples collected from Belgium and Northern France. It also aims at the evaluation of the prediction accuracy of combined BPNN-PLSR, as compared to that of individual PCR, PLSR and BPNN analyses. This will inform of whether or not PLS will be efficient method to model soil spectra for on-line measurements.

1.2.2 Sample statistics

The statistics of soil samples including concentration range and standard deviation (SD) is another critical aspect affecting calibration. However, little research was found on this field, particularly at farm scale modelling. Stevens *et al*. (2010) reported improved results with local calibrations stratified by soil type and agro-geological region than with global calibrations. Spiking the local (target site) soil samples into the global or regional models has also proved to be an efficient way to improve the prediction

accuracy of target field for some soil constituents (Shepherd & Walsh, 2002; Brown, 2007, Viscarra Rossel *et al*., 2008, Guerrero *et al*., 2010). Guerrero *et al*. (2010) observed that the number of samples in the calibration set could be also an important factor controlling the adaptability of calibrations to target sites and, thus, small-size models performed better than large-size model. We believe that the different model performance caused by different sample size is mainly attributed to sample statistics, including the variation in concentration range and SD. However, there is limited literature on the effect of sample statistics of calibration set on the prediction accuracy, particularly for *in situ* measurement conditions at the farm scale. Furthermore, the performance of multi-farm (general) models in predicting key soil properties compared with the corresponding models for individual farms with different sample number and statistics has not been explored so far. One of the obligations of this study is to investigate the relationship between the calibration accuracy of the studies soil properties and the variation range or SD of soil samples using data of three farms in Europe. It is hoped that results reported in chapter 4 to be useful for informing the best strategy of selecting the range of concentration in the calibration sample set used for the development of calibration models of OC, TN and MC.

1.2.3 Sample number

Sample number is a sensitive factor affecting calibration, as chemical analysis of soil samples with laboratory reference methods are required during the model calibration procedure. The more the samples analysed with reference methods the higher is the cost for running vis-NIR spectroscopy analysis, although this does not always provide better accuracy. Hence, the sample number used for model calibration should be taking into account and optimised towards establishing a compromise strategy between cost and model accuracy. No previous researcher has shown the relationship between RMSEP, representing model performance (accuracy) and the sample number for farm scale modelling. Therefore, it will be interesting to establish how the number

of samples affects the farm-scale model accuracy when the range of properties is kept constant. Guerrero *et al*. (2010) observed that the number of samples in the calibration set could be also an important factor controlling the adaptability of calibrations to target sites and, thus, small-size models performed better than large-size model. Although some work has been reported about the effect of sample number on prediction accuracy, to our knowledge there is no report on the influence of the number of soil samples used for farm-scale calibration on the prediction error of models developed for the same range of variation in concentration of a soil property. This chapter will investigate the effects of the number of soil samples with the same concentration range on the prediction error of farm-scale calibration models of TN, OC and MC, developed using fresh soil samples collected from four farms in the Czech Republic, Germany, Denmark and the UK. This was important to evaluate, since a smaller number of sample needed for modelling means a reduction in cost of analysis with the vis-NIR spectroscopy. Furthermore, optimising the number of samples for appreciable accuracy at the lowest possible cost will be valuable information for researchers working on farm scale modelling of vis-NIR spectra and hence to guide the sampling strategy of on-line measurement adopted in this thesis.

1.2.4 Influences of moisture content and texture

Soil moisture content has for long been the main negative factor effecting field applications of vis-NIR spectroscopy for soil analysis. Absorption peaks of water that can be significant (e.g. at 1950 nm) mask wavebands associated with other soil attributes and thus deteriorate model performance and accuracy of these properties (e.g. OC, clay, etc) (Mouazen et al., 2005). Although drying of soil sample can remove soil moisture content, models established with spectra of dried samples is of little use for *in situ* and on-line applications. Apart from soil MC, soil texture is the other main factor to affect accuracy of vis-NIR spectroscopy (Mouazen et al., 2006b). Researchers concluded that small particle size can attribute to a better model performance (Fontán et al. 2010). Predictions of OC were most inaccurate for soils with a high sand content

(Stenberg, 2010b). Most literature considered the single effect of MC or texture on the prediction accuracy of SOM or OC. The interaction effect of both MC and texture (e.g. MC × clay; MC × silt; MC × sand) on *in situ* and on-line measurement of OC and TN at farm scale has not been studied so far. This chapter concerns about understanding and quantifying the individual and interaction effects of MC and soil texture on the performance of vis-NIR calibration models for *in situ* and on-line measurement of soil OC and TN. This will be considered to improve the measurement performance at farm scale vis-NIR spectroscopy. The ultimate target is to inform the best time (from MC point of view) for carrying out on-line measurement at different soil texture types.

1.2.5 Spiking strategy and spiked sample size on on-line measurement

After results achieved in the four Chapters discussed above are completed, it is hoped to learn about the best techniques and methods for optimal performance of the on-line soil sensor at farm scale. In addition, this chapter aims also to optimise the modelling procedure of on-line sensor, including spiking technique and spiked sample size using a general dataset collected from the four European farms. Some studies suggested spiking local samples into the general calibration models can improve prediction accuracy under laboratory (Sanky et al. 2008) or *in situ* measurement conditions (Minasny et al. 2009; Viscarra Rossel et al. 2009; Waiser et al. 2007; Wetterlind and Stenberg, 2010). However, literature suggests that as yet, no general calibration procedure that included spiking strategy have been reported for on-line measurement, which has led to stable performance of on-line sensors, at the lowest production cost of establishing and upgrading the existed calibration models.

1.3 Aim, objectives and outline of this study

1.3.1 Aim and objectives:

The main aim of this work is to perform in-depth analyses of the influence of key factors affecting farm scale, vis-NIR calibration for *in situ* and on-line measurements. The ultimate aim is to utilise knowledge gained from the in-depth analyses to inform the best strategies and methods that should be followed during on-line measurement of OC, TN and MC, to guarantee robust and stable sensor performance, with appreciable accuracies. The on-line soil sensor used in this project is the one designed and developed by Mouazen (2006a). .

To fulfil the project aim, the following objectives have to be addressed:

1. To explore and eventually develop new calibration techniques to improve the accuracy of vis-NIR spectroscopy models of OC, TN and MC. Although, the focus of this project was on farm scale calibration, a country scale modelling will be considered only for this particular objective using soil samples collected from Belgium and Northern France.

2. To develop and validate calibration models valid for each experimental farm in the four countries as well as a global calibration models valid for all four farms considered.

3. To study the effect of sample statistics including the concentration range and standard deviation on prediction accuracy of studied soil properties. Fresh soil samples collected from the four farms will be considered.

4. To study the effect of sample number used in the calibration set on prediction accuracy. This objective will be evaluated by using fresh soil samples.

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5. To quantify the individual as well as the interaction effects of MC and texture on model performance, evaluated on laboratory, *in situ* and on-line modelling scenarios.

6. To evaluate the effect of spiking strategy (method) and spiked sample size in the general dataset on on-line measurement accuracy of studied soil properties.

7. To evaluate the performance of a previously developed on-line soil sensing system (Mouazen, 2006a), for measurement of OC, TN and MC across four different countries in Europe, namely, Germany, the UK, Holland, Czech Republic and Demark.

1.3.2 Thesis structure:

This thesis will be consisted of the following nine Chapters

- Chapter 1 is the introduction and the aim and objectives,
- Chapter 2 gives a comprehensive literature review on soil vis-NIR spectroscopy. The content of this chapter is part of a book chapter published in Advances in Agronomy (Kuang et al., 2012a).
- Chapter 3 discusses the performance of various multivariate calibration techniques for modelling vis-NIR spectroscopic data for the prediction of soil properties. In particular, the performance of typical linear calibration methods will be compared with non-linear methods including ANN. The content of this chapter is part of a paper published in Geoderma (Mouazen et al., 2010).
- Chapter 4 investigates the effect of sample statistics, e.g. concentration range and SD on the prediction accuracy. It will inform the sample statistics that should be taken into consideration for model calibration. The content of this chapter is part of a paper published in European Journal of Soil Sciences (Kuang and Mouazen, 2011).
- Chapter 5 discusses how the sample number affects the model accuracy, aiming at concluding on the appropriate number of samples to be suggested for farm scale modelling. The content of this chapter is part of a paper accepted in European Journal of Soil Sciences (Kuang and Mouazen, 2012b).
- In chapter 6, discusses the individual and interaction effects of soil MC and texture on *in-situ* and on-line vis-NIR spectroscopy measurement of studied soil properties. The content of this chapter is part of a paper under review in European Journal of Soil Sciences (Kuang and Mouazen, 2012c).
- Chapter 7 discusses and evaluates on-line measurement of soil OC, TN and MC in three fields in three European farms. The content of this chapter is part of a paper under review in Soil & Tillage Research (Kuang and Mouazen, 2012d).

- Finally, chapter 8 provides conclusions for the whole work done in this study and outlook and guideline for future work are suggested.

2 Literature review

2.1 Introduction

For vis-NIR spectroscopy, to generate a soil spectrum, radiation containing all relevant frequencies in the particular range is directed to the sample. Depending on the constituents present in the soil the radiation will cause individual molecular bonds to vibrate, either by bending or stretching. These vibrations lead to absorption of light, to various degrees, with a specific energy quantum corresponding to the difference between two energy levels. As the energy quantum is directly related to frequency, the resulting absorption spectrum produces a characteristic shape that can be used for analytical purposes (Stenberg et al., 2010a). The fundamental frequency component from these vibrations in the mid-infrared (MIR) region result in overtones and/or combinations in the near infrared (NIR) region. In the visible (vis) range (400–780 nm), absorption bands related to soil colour is due to electron excitations, which assist the measurement of soil SOM and MC. However, in the NIR range, the overtones of OH and overtones and/or combinations of C-H + C-H, C-H + C-C, OH^+ minerals and N-H are important for the detection of SOM, MC, clay minerals and nitrogen (Mouazen *et al.*, 2010).

During the early stage of implementing this technique for soil analysis, the vis-NIR (400-2500 nm) spectroscopy, along with multiple linear regression (MLR) calibration technique, was used to determine some soil properties, such as soil MC, SOM, total carbon (TC), inorganic carbon (C_{-in}), organic carbon (OC), pH, cation exchange capacity (CEC) and total nitrogen (TN). As early as from 1965, Bowers *et al.*, (1965) used a NIR spectrophotometer to evaluate the influences of MC, SOM, and particle size on energy reflectance.

With the emerging of commercial NIR spectrophotometers and multivariate calibration software packages, the vis-NIR spectroscopy has been adopted much widely for soil analysis. Numerous researchers have extended the vis-NIR spectroscopy applications from the measurement of key soil properties (MC, pH, SOM, TN and OC)

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with high accuracy to almost all other micro and macro elements with less accuracy. The analysis of soil with this technique was also extended to soil biological, physical and engineering properties. Multivariate calibration techniques allowed for simultaneous measurements of several soil properties under consideration.

In this chapter, a comprehensive literature review about applications of the vis-NIR spectroscopy of soil analyses under laboratory (non-mobile scanning is undertaken from dried and sieved soil samples in the laboratory), *in situ* (non-mobile scanning is undertaken from fresh unprocessed soil samples in the laboratory or in the field) and on-line (mobile scanning is undertaken from fresh prepared soil surface in the field) measurement conditions will be introduced. The main factors affecting performance on the vis-NIR spectroscopy for soil analysis will be also discussed.

2.2 Laboratory visible and near infrared spectroscopy

Laboratory vis-NIR measurement needs minimal sample pre-treatments and is subjected to minimum outside interferences. A typical procedure in a laboratory includes soil sampling, samples treatments (drying, grinding and sieving), optical scanning, data pre-processing, calibration and validation. Drying and grinding of soil samples can minimize the negative effects of MC and structure on the accuracy of prediction.

2.2.1 Soil properties with direct spectral responses in near infrared range

Since carbon and nitrogen have both direct spectral responses in the NIR region, which can be attributed to overtones and combinations of N-H, C-H + C-H and C-H + C-C, successful measurement of these two properties with NIR is expected. However, C and N have different forms in the soil, e.g. mineral, organic and inorganic, which have an influence on the accuracy. Summary of measurement accuracy of C and N with vis-NIR

spectroscopy is provided in Table 2-1. In summary, the prediction of soil C and N with NIR depends upon the form to be measured and the most successful measurement is reported for the organic, inorganic and total forms (Table 2-1). Due to the obvious absorbance peaks in the NIR range at the 1st, 2nd and 3rd overtone regions, literature proves MC to be the most accurately measured property with NIR with excellent accuracy (Chang *et al*., 2001; Mouazen *et al*., 2006b). Clay content was also reported to be accurately measured with NIR, which is attributed to the direct spectral response of clay minerals around 2300 nm (Viscarra Rossel *et al*., 2006b).

Table 2-1 Summary of measurement accuracy of soil fundamental properties by laboratory visible and near infrared (vis-NIR) Spectroscopy

Soil properties	R^2 *	RMSEP	RPD	Accuracy	Key references
OC	0.46-0.98	0.06-2.90 (%)	1.30-9.70	A**	Dalal and Henry (1986); Chang *et al*. (2001); Shepherd and Walsh (2002); Viscarra Rossel *et al*., (2010)
C$_{inorg}$	0.53-0.96	0.17-0.56 (%)	4.01-4.99	A	Krishnan *et al*., (1980); Cohen *et al*., (2005); Brown *et al*., (2006); Fontan *et al*., (2010).
TN	0.04-0.99	0.0004-0.08 (%)	0.34-6.80	A	Couteaux *et al,*. (2003); Dalal and Henry (1986); Vagen *et al*., (2006); Guerrero *et al*., (2010)
pH	0.50-0.97	0.04-1.43	0.57-2.39	B-C	Shepherd and Walsh (2002); Cohen *et al*., (2005); Mouazen *et al*., (2006c); Viscarra Rossel *et al*., (2010)
Ca	0.07-0.95	0.66-52.90 (cmol kg^{-1})	0.60-2.75	B	Cozzolino and Moron (2003); Cohen *et al*., (2005); Mouazen *et al*., (2006c); Zornoza *et al*., (2008)
CEC	0.13-0.90	1.22-10.43 (cmol kg^{-1})	0.55-2.51	B	Ben-Dor and Banin (1995); Chang *et al*., (2001); Mouazen *et al*., (2006a); Brown *et al*., (2007); Awiti *et al*., (2008)
Clay content	0.15-0.91	0.79-6.10 (%)	1.70-3.10	A	Ben-Dor and Banin (1995); Chang *et al*., (2001); Brown (2007); Awiti *et al*., (2008)
Sand content	0.59-0.92	1.91-11.93 (%)	0.87-3.40	C	Ben-Dor and Banin (1995); Chang *et al*., (2001); Cozzolino and Moron (2003); Awiti *et al*., (2008)
Silt content	0.41-0.84	1.79-9.51 (%)	1.09-3.07	C	Ben-Dor and Banin (1995); Chang *et al*., (2001); Cozzolino and Moron (2003); Awiti *et al*., (2008)
MC	0.84-0.98	0.50-4.88 (%)	2.36-5.26	A	Chang *et al*., (2001); Chang *et al*., (2005); Dalal and Henry (1986); Mouazen *et al*., (2006b); Slaughter *et al*., (2001)
Total P	0.01-0.93	1.35-24.6 (100 mg kg^{-1})	0.10-3.80	C	Bogrekci and Lee (2005a); Mouazen *et al*., (2010); Wetterlind *et al*., (2010)
P$_{avl}$	0.68-0.95	0.01-19.79 (100 mg kg^{-1})	1.70-4.54	C	Bogrekci and Lee (2005a); Cohen *et al.,* (2005); Ludwig *et al*., (2002)
P$_{ext}$	0.32-0.77	1.70-3.89 (100 mg kg^{-1})	0.40-2.07	C	Chang *et al*., (2001); Cohen *et al*., (2005); Udelhoven *et al*., (2003)
Mg	0.53-0.91	0.03-38.36 (cmol kg^{-1})	0.48-2.54	B	Cozzolino and Moron (2003); Groenigen *et al*., (2003); Udelhoven *et al*., (2003); Wetterlind *et al*., (2010)
K	0.11-0.85	0.05-1.84 (cmol kg^{-1})	0.52-5.13	D	Cozzolino and Moron (2003); Groenigen *et al*., (2003); Mouazen *et al*., (2006c)
Na	0.09-0.68	2.3-25 (cmol kg^{-1})	0.92-1.94	E	Chang *et al*., (2001); Mouazen et al., (2006c); Mouazen *et al*., (2010)

* Values of R^2, RMEEP and RPD do not just represent the particular studies enlisted in adjacent column, but they are also based on other studies not listed in this table.

** Classification of accuracy into A, B, C, D and E were based on maximum number of publications confirming an accuracy category for a soil property. R^2: coefficient of determination, RMEEP: root square mean error of prediction, RPD: residual

prediction deviation (SD/RMSEP), A: excellent (RPD > 3.0 and R^2 > 0.90; B: good (RPD = 2.5~3.0 and R^2 = 0.82~0.90), C: approximate quantitative prediction (RPD = 2.0~2.5 and R^2 = 0.66~0.81), D: distinguish between high and low (RPD = 1.5~2.0 and R^2 = 0.50~0.65) and E: not usable (RPD < 1.5 and R^2 < 0.5) (Chang *et al.*, 2001).

2.2.2 Soil properties without direct spectral responses in near infrared range

Stenberg *et al.*, (2010a) concluded that occasionally successful reports for the measurement of soil properties without direct spectral response in the NIR range is due to co-variation through other properties that have direct spectral responses in the NIR, e.g. carbon, nitrogen and clay. Literature illustrates that only few successful reports on P determination by vis-NIR spectroscopy are available (Table 2-1). To date, the most significant reports on successful measurement of P are those of Bogrekci & Lee (2005a and 2005b).Bogrekci and Lee (2005a) obtained probably the best R^2 value of 0.92 between P concentrations and spectral absorbance using a vis-NIR spectroscopy in a fine sand soil type in Lake Okeechobee, in Florida. When they collected a larger amount of samples (150 - 345 samples) from more sites (3 - 10 sites), they reported a better prediction result (Bogrekci and Lee, 2005b). Literature (e.g. Chang *et al.*, 2001 and Mouazen *et al.*, 2006c) proves that the worst properties to be measured with NIR are K and Na (Table 2-1). Measurement of pH, Ca and Mg were reported to be more successful as compared to K and Na, but underperformed those properties with direct spectral response in NIR. Therefore, further research is recommended to understand and probably improve the calibration accuracy of soil properties without direct spectral responses in the NIR range.

2.2.3 Soil heavy metals

Literature demonstrates the potential of the vis-NIR spectroscopy for the measurement of soil microelements with acceptable accuracy (Table 2-2). Moron and Cozzolino (2003) explored the use of NIR reflectance spectroscopy to study

microelements in surface soils from 332 sites across Uruguay. They claimed that R^2 of the calibration and standard error of cross-validation (SECV) were respectively for Cu 0.87 and 0.7, Fe 0.92 and 21.7, Mn 0.72 and 83.0 and Zn 0.72 and 1.2 on mg kg^{-1} dry matter. Siebielec et al., (2004) employed the NIR spectroscopy to measure soil metal content from natural background levels to high contents indicative of industrial contamination region and they claimed successful measurement of Fe, Cu, Ni and Zn (R^2 = 0.87, 0.61, 0.84 and 0.67, respectively). From Table 2-2, it can be concluded that Fe, Cu and Zn can be measured with acceptable accuracy using the vis-NIR, which can be attributed to co-variation with other soil properties with direct spectral responses in NIR. Stenberg et al. (2010a) explained that heavy metals can be detected because they can be complex with SOM, associated with hydroxides, sulphides, carbonates or oxides that are detectable in the vis–NIR, or adsorbed to clay minerals. However, Al is the worst property to be measured followed by Mn.

Table 2-2 Summary of measurement accuracy of soil microelements by laboratory visible and near infrared (vis-NIR) Spectroscopy

Soil properties	R^2*	RMSEP (mgkg^{-1})	RPD	Accuracy	Key references
Fe	0.64-0.94	3.7-23.60	1.35-3.30	A-B **	Malley and Williams (1997); Moron and Cozzolino (2003); Cohen et al., (2005)
Cu	0.25-0.84	0.8-6.01	0.92-4.00	B	Malley and Williams (1997); Chang et al., (2001); Siebielec et al., (2004); Wu et al., (2007)
Mn	0.65-0.92	56.4-190	1.79-3.66	C	Malley and Williams (1997); Chang et al., (2001); Moron and Cozzolino (2003)
Zn	0.44-0.95	1.4-299	1.07-3.80	B	Malley and Williams (1997); Kooistra et al., (2001); Cohen et al., (2005); Viscarra Rossel et al., (2006a)
Al	0.61-0.68	0.88-506.7	0.5-1.97	D	Siebielec et al., (2004); Cohen et al., (2005)

* Values R^2, RMEEP and RPD do not just represent the particular studies enlisted in adjacent column, but they are also based on other studies not listed in this table.

** Classification of accuracy into A, B, C, D and E were based on maximum number of publications confirming an accuracy category for a soil property. R^2: coefficient of determination, RMEEP: root square mean error of prediction, RPD: residual prediction deviation (SD/RMSEP), A: excellent (RPD > 3.0 and R^2 > 0.90; B: good (RPD = 2.5~3.0 and R^2 = 0.82~0.90), C: approximate quantitative prediction (RPD = 2.0~2.5 and R^2 = 0.66~0.81), D: distinguish between high and low (RPD = 1.5~2.0 and R^2 = 0.50~0.65) and E: not usable (RPD < 1.5 and R^2 < 0.5) (Chang et al., 2001).

2.3 Non-mobile (*in situ*) field visible and near infrared spectroscopy

Although the application of the vis-NIR spectroscopy has considerably reduced the labour and time for the analysis, soil sample preparation for laboratory analysis including drying, grinding and sieving is still tedious. For *in situ* and on-line measurement with vis-NIR, calibration models developed from dried, ground and sieved samples cannot be utilised, since measurement is performed with fresh soil samples. As early as more than two decades ago, using an integrating cylinder and two narrow band interference filters, Barrett *et al*. (2002) developed a spectrophotometric colour measurement for *in situ* well drained sandy soils, reporting a moderately strong correlation. Fystro *et al*. (2002) confirmed the ability of vis-NIR spectroscopy for measurement of OC, TN and their potential mineralization in grassland soil samples, arriving at a moderate accuracy (R^2 > 0.7 and RPD > 1.5). Udelhoven *et al*., (2003) evaluated the ability of NIR spectroscopy to estimate soil Fe, Mn, Ca, Mg, K and they found that only Ca and Mg (R^2 = 0.67 and 0.69, respectively) were predictable under *in situ* conditions. Chang *et al*., (2005) attempted to predict TC, OC, TN, CEC, pH, texture, MC and potential mineralisable N and indicated that NIR was able to measure these soil attributes with reasonable accuracy using fresh soils (R^2 > 0.74).

Maleki *et al*., (2006) developed a calibration model of available P (P_{avl}) with acceptable prediction accuracy (R^2 > 0.73) based on fresh soil samples with the intention to be used for on-line variable rate P_2O_5 application system. Combining vis-NIR spectroscopy and laser induced breakdown spectroscopy (LIBS), Bricklemyer *et al*., (2005) reported moderate prediction accuracy (R^2 = 0.70) of TC and C_{-inorg} under *in situ* conditions. Meledenz-Pastor *et al*., (2008) identified optimal spectral bands to assess soil properties with vis-NIR radiometry in a semi-arid area and estimated SOM with worse accuracy (R^2 = 0.73, RPD = 1.92 and RMSEP = 0.52%) than generally reported under laboratory condition. Viscarra Rossel *et al*. (2009) found there is higher prediction accracy for *in situ* soil caly content using field sacn spectra (RMSE = 7.9%)

than using Lab scanned spectra (RMSE = 8.3%). A summary of prediction performance of *in situ* vis-NIR spectroscopy measurement of soil properties is reported in Table 2-3. A comparison between Table 2.1 and Table 2.3 reveals that laboratory vis-NIR methods (Table 2-1) provide better accuracy than *in situ* field measurement, which can be attributed to the influence of MC and structure that were eliminated under laboratory conditions by drying, grinding and sieving.

Table 2-3 Summary of measurement accuracy of fundamental soil properties by *in situ* visible and near infrared (vis-NIR) spectroscopy

Soil properties	R^2 *	RMSEP	RPD	Accuracy	Key references
OC	0.51-0.96	0.29-1.40 (%)	1.30-4.95	B-C **	Fystro *et al.*, (2002); Udelhoven *et al.*, (2003); Mouazen *et al.*, (2010); Kuang & Mouazen (2011)
TN	0.80-0.93	0.02-0.06 (%)	2.1-3.88	B	Chang *et al.* (2005); Fystro *et al.*, (2002); Mouazen *et al.*, (2006c)
pH	0.66-0.74	0.39-0.72	1.55-2.14	C	Chang *et al.*, (2005); Mouazen *et al.*, (2006c); Mouazen *et al.*, (2007)
Ca	0.77-0.86	1.63-1.68 (cmol/kg^{-1})	2.10-2.19	C	Chang *et al.*, (2005); Udelhoven *et al.*, (2003); Mouazen *et al.*, (2006c)
CEC	0.78-0.89	1.77-3.57 (cmol$_c$/kg^{-1})	2.31-2.33	C	Chang *et al.*, (2005); Mouazen *et al.*, (2006c)
Clay	0.76-0.83	5.25-7.9 (%)	1.45-2.36	C	Chang *et al.*, (2005); Waiser *et al.*, (2007); Bricklemyer *et al.*, (2010)
Sand	0.49	12.44 (%)	0.87	E	Chang *et al.*, (2005)
Silt	0.13	6.04 (%)	0.80	E	Chang *et al.*, (2005)
MC	0.4-0.98	1.0-6.4 (%)	1.98-5.74	A	Ben-Dor *et al.*, (2008); Mouazen *et al.*, (2005); Slaughter *et al.*, (2001)
Total P & P$_{avl}$	0.09-0.80	2.3-25 (mg100g^{-1})	1.45-2.24	C	Bogrekci and Lee, (2005a); Maleki *et al.*, (2006c); Mouazen *et al.*, (2007)
Mg	0.49-0.84	0.30-0.30 (cmol$_c$/kg^{-1})	1.39-1.56	D	Udelhoven *et al.*, (2003); Chang *et al.*, (2005); Mouazen *et al.*, (2006c)
K	0.33-0.87	0.21-3.90 (cmol$_c$/kg^{-1})	1.21-2.80	D	Udelhoven *et al.*, (2003); Zornaza *et al.*, (2008); Mouazen *et al.*, (2010); Wetterlind *et al.*, (2010)
Na	0.13-0.77	0.025-0.129 (cmol$_c$/kg^{-1})	1.29-1.98	E	Mouazen *et al.*, (2006); Zornaza *et al.*, (2008); Mouazen *et al.*, (2010)

** Classification of accuracy into A, B, C, D and E were based on maximum number of publications confirming an accuracy category for a soil property. R^2: coefficient of determination, RMEEP: root square mean error of prediction, RPD: residual prediction deviation (SD/RMSEP), A: excellent (RPD > 3.0 and R^2 > 0.90; B: good (RPD = 2.5~3.0 and R^2 = 0.82~0.90), C: approximate quantitative prediction (RPD = 2.0~2.5 and R^2 = 0.66~0.81), D: distinguish between high and low (RPD = 1.5~2.0 and R^2 = 0.50~0.65) and E: not usable (RPD < 1.5 and R^2 < 0.5) (Chang *et al.*, 2001).

2.4 Mobile (on-line) field vis-NIR sensors

Precision farming requires development of on-line sensors for real-time measurement of soil properties, because these sensors can lead to reducing labour and time cost of soil sampling and analysis. Compared to the non-mobile analysis, relatively less literature is available on the mobile vis-NIR spectroscopy analysis of soil properties. A review on the current status of on-line vis-NIR measurement systems confirms that only three on-line vis-NIR measurement systems are available (Shibusawa *et al.*, 2001; Mouazen *et al.*, 2005; Christy *et al.*, 2008).

The beginning of these systems dates back to 1991, when Shonk *et al.* (1991) developed a system to measure SOM and MC, which utilised a single wavelength (660 nm) of light (Table 3-4). Shibusawa *et al.* (2001) developed an on-line vis-NIR (400 – 1700 nm) sensor to predict MC, pH, SOM and NO_3-N. Although this system is highly technically instrumented, it is rather expensive. Christy *et al.* (2008) developed a prototype soil reflectance mapping unit equipped with a vis-NIR spectrophotometer, which is commercially available in the market. The sapphire glass of the optical probe makes direct contact with soil and stones. A simpler design to the one of Shibusawa *et al.* (2001) without sapphire window optical configuration was developed by Mouazen *et al.* (2005). The system was successfully calibrated for MC, TN, TC, pH and available P in different soils in Belgium and northern France (Mouazen *et al.*, 2005; Mouazen *et al.*, 2007; Mouazen *et al.*, 2009). More recently, employing the on-line system developed by Christy et al. (2008), Bricklemyer et al. (2010) reported on the on-line measurement for soil OC without achieving even semi-quantitative accuracy and clay content with a standard error of prediction (SEP) of 3.4 g kg^{-1} and a RPD value of 1.4,

respectively. Using the same system, coupled with topography and aerial photograph data, Munoz et al. (2011) reported low to moderate accuracy of soil OC measurement with R^2 and RMSEP ranged from 0.44 to 0.66 and from 1.41 to 1.51 g kg^{-1}, respectively. Applying this vis-NIR system in combination with electrical conductivity (EC) and temperature sensors in a Danish field, Knadel et al. (2011) obtained moderate prediction accuracy (RMSEP = 59.4 gkg^{-1} and RPD = 2.3) for soil OC. However, the vis-NIR sensor alone only achieved a relatively low accuracy (RMSEP = 59.8 gkg^{-1}, RPD = 1.9). This review shows that on-line sensors still do not provide sufficiently accurate data for their use in the site specific application of different inputs. The variable degrees of performance of on-line sensors currently available might be attributed to the fluctuation in model performance, with the majority of them established for field-scale analysis (e.g. Christy et al., 2008; Mouazen et al., 2005; Munoz et al., 2011) Shibusawa et al., 2001; or for regional- and country-scale analysis (e.g. Mouazen et al., 2007; Mouazen et al., 2009). Some studies suggested spiking local samples into the general calibration models can improve prediction accuracy under lab (Sanky et al. 2008) or *in situ* conditions (Minasny et al. 2009; Viscarra Rossel et al. 2009; Waiser et al. 2007; Wetterlind and Stenberg, 2010).

Table 2-4 Summary of measurement accuracy of soil properties by on-line visible and near infrared (vis-NIR) spectroscopy

Spectral range	nm	Results	Literatures
Single wavelength	660	SOM (r = 0.71)	Shonk *et al.*, (1991)
vis-NIR spectrum	300-1700	MC, pH, SOM and NO_3-N (R^2 = 0.68, 0.61, 0.64 and 0.19, respectively)	Shibusawa *et al.*, (2001)
NIR spectrum	1603-2598	SOM and MC (R^2 = 0.79 7 0.89, RPD = 2.17 & 2.86, respectively)	Hummel *et al.*, (2001)
NIR spectrum	900-1700	MC, TC, TN, pH (R^2 = 0.82, 0.87, 0.86 and 0.72, respectively)	Christy *et al.*, (2008)
vis-NIR spectrum	300-1700	Similarity of OC, TC, MC, pH, P$_{-avl}$ and P$_{-ext}$ maps	Mouazen *et al.*, (2007)
vis-NIR spectrum	350-2224	OC (SEP = 0.34) and clay content (RPD = 1.4, SEP = 6.94 %)	Bricklemyer *et al.*, (2010)

Comparing to Tables 2-2 and 2-3 with Table 2-4 reveals that both the laboratory and *in situ* non-mobile vis-NIR methods provide better accuracy than the on-line method, which might be attributed to other factors influencing the latter method. These factors include among others noise associated with tractor vibration, sensor-to-soil distance variation (Mouazen *et al.*, 2009) stones and plant roots and difficulties of matching the position of soil samples collected for validation with corresponding spectra collected from the same position.

There are some challenges that hinder a stable, accurate and robust on-line measurement system from emerging for soil OC, TN and MC measurement. First of all, a robust spectrometer system with wide enough measurement wavelength range that covers significant absorbance bands for C and N (up to 2200 nm). For early on-line sensors, the wavelength ranges were as large as up to 1700 nm (Shibusawa et al. 2001; Mouazen et al., 2005; Christy, 2008). Some of relatively high measurement accuracy of SOM or OC with these sensors might be attributed to the high correlation with soil colour. For soil TN, there was only one successful case reported by Christy (2008), whose calibration was valid for a field scale. However, soil MC was the most successful measured properties, as there are significant O-H absorbance peaks in the NIR region (Mouazen et al., 2005). Secondly, a delicate design for the sensor probe holder, which should ensure constant sensor-to-soil distance and smooth soil surface where scanning takes place. Using under field condition has proven that having a glass window between the soil surface and optical probe is not ideal, as the fragile glass might be broken, affecting the robustness of the system. Finally, even stable and high quality soil vis-NIR spectra can be acquired successfully during on-line measurement the overall accuracy depends largely on the calibration models. Though the field scale model can provide a relatively high accuracy (Christy 2008), it is rather costly, hence negatively affects adopting the on-line vis-NIR sensors for precision farming applications. Therefore, general calibration models for farm scale should be established for soil OC, TN and MC. This has to be accompanied with a spiking strategy and spiking rate that would assist improving the on-line prediction accuracy at relatively lower cost.

2.5 Factors affecting prediction accuracy of vis-NIR spectroscopy

In addition to extended application of vis-NIR spectroscopy for the simultaneous determination of many properties of soil, numerous researchers attempted to find new approaches to improve the vis-NIR prediction accuracy. It is well known that, soil MC and soil particle size are the main factors influencing the measurement accuracy in addition to soil colour. Hence, quantification of the effects of these properties might be useful for the improvement of calibration models developed for both laboratory and *in situ* measurements. Other factors including spectra pre-processing, sample preparation, size of calibration area (local, national or global), spectrophotometer wavelength range and type of detectors and calibration methods also affect calibration accuracy. Scientists investigated and introduced new spectral pre-treatment methods, including non-linear calibration techniques and/or predictive indicator to obtain more accurate results. Others used spectra classification methods to classify soils into different MC or texture classes; for each class they suggested a separate calibration models (Mouazen et al., 2005 and Mouazen et al., 2006b). The effects of the following factors are discussed in view of acquiring information for improving performance of on-line sensors.

2.5.1 Effect of calibration method

In the early stage, some multi-linear regression calibration methods, such as stepwise multiple linear regression (e.g. Shibusawa et al. 2001), multivariate adaptive regression splines (Shepherd and Walsh, 2002), PCR (e.g. Chang et al., 2001) were accepted for vis-NIR spectroscopy modelling. The PLSR has also been used as standard calibration technique for most researchers (McCarty et al., 2002). Although the linear PCR and PLSR analyses are the most common techniques for spectral calibration and prediction (Viscarra Rossel et al., 2006a), with PLSR being the most accurate, other nonlinear

techniques e.g. artificial neural networks (ANN) have got much less attention and were rarely explored for the spectral analysis in soil sciences. Du and Zhou (2007) and Du et al. (2007; 2008) have successfully implemented ANN based on principal components (PCs) obtained from principal component analysis (PCA) on mid infrared (MIR) and photoacoustic MIR soil spectra. Only two examples on the use of ANN-PCs technique for soil analysis with NIR spectroscopy could be found in literature. Fidêncio et al. (2002) have implemented the radial basis function networks (RBFN) in the NIR region (1000-2500 nm) and Daniel et al. (2003) have used ANN in the vis–NIR region (400–1100 nm). Other nonlinear calibration methods have been tested such as regression trees (RT) (Brown et al., 2006; Vasques et al., 2008; Viscarra Rossel and Behrens, 2010), multivariate adaptive regression splines (Shepherd and Walsh, 2002; Viscarra Rossel and Behrens, 2010), support vector machine regression (SVMR) (Stevens et al., 2010; Viscarra Rossel and Behrens, 2010), and penalized-spline signal regression (Stevens et al., 2010). Though regression tree sometimes can provide better accuracy, it is far too complicated for soil analysis. Generally, the nonlinear calibration techniques have their potential of being much powerful calibration tools for vis-NIR spectroscopy. However, there is still a long way for them to be main stream analysis technique due to lack of a uniform software platform on which the nonlinear algorithms can be evaluated fairly.

2.5.2 Effect of sample statistics (range and SD)

Sample concentration range or SD is other essential factor to influence the model accuracy but has not attracted much attention. It is essential to indicate that the range of the calibration set should be equal or larger than the prediction set. However, larger range or SD will introduce higher root mean square of prediction (RMSEP) (Stenberg, et al.2010a). This issue needs more in depth analysis.

2.5.3 Effect of moisture content

Literature shows that MC probably has the most influencing factor on the prediction of soil MC. Therefore, researchers attempt to understand and exclude this effect for effective application of field spectroscopy including *in situ* and on-line measurements. Mouazen et al. (2006b) tried to exclude the MC contribution to vis-NIR spectra by classifying (using factorial discriminate analysis, FDA) soil spectra into different MC groups and found that, for the single-field sample set, spectra were classified into six MC groups with correct classification (CC) of 94.1% and 95.6% for the calibration and validation sets, respectively. The corresponding data for multi-field sample set was three groups with CC of 88.1% and 79.7% for the calibration and validation sets, respectively. Adoption of an external parameter orthogonalisation (EPO) algorithm to remove the soil moisture effect on vis-NIR spectral, Minasny, et al. (2011) found better prediction accuracy for OC. This finding could be also potentially valuable for on-line prediction of soil properties, when scanned spectra can be pre-treaded automatically using suggested algorithm. In short, MC plays principally a negative role on field soil vis-NIR spectroscopy and there is still a research gap to be bridged in this study.

2.5.4 Effect of soil texture

Apart from soil MC, soil texture is the other main factor to affect accuracy of the vis-NIR spectroscopy. Soil classification and evaluation has become a critical tool to monitor the soil development or degradation. Usually, SOM, total iron, silt, sand and mineralogy (quartz, magnetite, kaolinite and smectite) were the most important attributes influencing reflectance intensity and spectral features and allowed characterization and discrimination of soils. Fontán et al. (2010) concluded that particle size has a significant effect on the accuracy and precision of models developed for analysing C content in Mediterranean dry land Vertisols. Their results were improved for a small particle size soils (i.e. after grinding and sieving with 2 mm sieve),

as compared to untreated soils with clods. Using processed soil sample in the laboratory, Stenberg (2010b) concluded that predictions of OC were most inaccurate for soils with a high sand content. Along with principle component analysis (PCA) or FDA clustering techniques, Mouazen et al. (2006b) suggested classifying soil texture into different texture classes. For each class, authors suggested to establish calibration models for other soil properties, which they expect to result in improved prediction accuracy. How soil texture fractions (sand, clay and silt) affect (positively or negatively) the vis-NIR measurement of other soil properties is still unclear and more research is needed. Furthermore, the interaction effect of MC and texture has not been studied so far, although this might be the most influencing on the performance of on-line sensors.

2.5.5 Effect of soil colours

Historically, soil colour is a key feature used for the identification and classification of soils. Soil reflectance has a direct relationship with soil colour, as well as with other parameters such as texture, soil moisture and organic matter. Quantitative soil colour analysis is not easy for colour papers. Mouazen et al. (2006b) focused on the potential of vis-NIR spectroscopy accompanied with PCA and FDA to derive colour groups utilising the Munsell soil colour charts. The intention was to establish groups of calibration models, each valid for one colour class. The results suggested that the vis-NIR spectroscopy combined with chemometric tools has the potential of identifying different soil colour groups for a large geographical area. Moranon et al. (2007) established models between L* (lightness) of CIELAB colour model and MC. The results indicate that predictions of the dryness condition, presence of plant-available water and wetness near to field capacity, but not the specific water content, can be made with reasonable confidence in any soil by using the models calibrated in other soil of similar colour. Similar research had been done by Viscarra Rossel *et al*., (2009). From this brief literature review it can be concluded that colour has positive effect on vis-NIR spectroscopy measurement of other soil properties (e.g. OC), which suggests that no need to consider more research about this factor.

2.5.6 Effect of sample pre-treatment

The effect of sample preparation such as grinding and drying and replication has not been addressed extensively. Barthes et al. (2006) conducted a research to assess how sample preparation affects NIR prediction of TN and total C. They concluded that the most accurate predictions (R^2>0.907, RPD>3.37 and R^2>0.936, RPD>3.37 for total C and total N, respectively) were obtained with oven-dried finely ground samples, with limited response to sample replication. In their application of NIR spectroscopy to determine OC in 10 farms in Uruguay, Cozzolino and Moron (2006) achieved determination coefficient (R^2_{CAL}) and standard errors in cross validation (SECV) of 0.90 and 0.6 for coarse-sand C, 0.92 and 0.4 for fine-sand C, and 0.96 and 2.1 for clay + silt C, respectively. Calibrations were poor for C/N ratio (R^2_{CAL}< 0.65). Those two publications confirmed that grinding and drying played a positive role in Vis-NIR measurements of soil properties. No research on this factor will be considered in this thesis, since on-line measurement does not require sample pre-treatment including drying and sieving.

2.5.7 Effect of spectrophotometer and measurement range

In their work to choose a suitable wavelength range instrument for on-line soil sensor, Mouazen et al. (2006c) compared the prediction ability of short wavelength range (SWR) of 300-1700 nm and a full wavelength range (FWR) of 350-2500 nm using both dried and fresh soil samples. They suggested that a larger wavelength range than 1700 nm was not useful for improving the measurement accuracy of soil properties (except N and C) with vis-NIR spectroscopy when measurement was to be conducted in field under wet conditions. Also the same research team has studied the measurement accuracy of MC of four spectrophotometers differing in wavelength range and type of detector, namely, a diode array (DA), a combination of diode array and scanning

monochrometer (DASM), a Fourier transform (FT) and a scanning monochrometer (SM) (Mouazen et al., 2006c). They found that the four instruments provided good predictions for soil MC with largest R^2 values between 0.84-0.86 and the RPD values ranged from 2.53 to 2.75. Generally, a wider wavelength range instrument results in a higher measurement accuracy for most soil properties. This is the reason why at the start of this project, it was decided to replace the previously used Zeiss Corona spectrophotometer (Mouazen et al., 2005) by a wider spectral range AgroSpec spectrophotometer (tec5 Technology of Spectroscopy, Germany) with a spectral range of 305 – 2200 nm.

2.5.8 Effect of scale and spiking

Most studies on soil vis-NIR spectroscopic applications are limited to modelling within field scale or homogenous soil type area, although researchers tend to expand applications to national, continental or even global libraries. However, soil constituent models developed from large scale geographic area with diverse soil samples often completely fail or provide unacceptable prediction accuracy. Mouazen et al. (2006b) found a higher accuracy of MC quantitative prediction using a single-field sample set than for a multi-field samples set. When they applied the PLSR on the 1st derivative vis-NIR reflectance spectra using soil samples obtained from six sites with similar soils across three counties in north central Montana, Brown et al. (2005) got relatively accurate prediction for OC and inorganic C (RPD>2) and demonstrate that 'pseudo-independent' validation (random selection of non-independent test samples) can overestimate predictive accuracy relative to independent validation. To date, only few global models are reported (e.g. Brown et al. 2006; Viscarra Rossel et al., 2009). Brown et al. (2006) selected 3768 samples from all 50 U.S. states and two tropical territories and an additional 416 samples from 36 different countries in Africa (125), Asia (104), the Americas (75) and Europe (112), and obtained validation root mean squared deviation (RMSD) estimates of 54 g kg-1 for clay, 7.9 g kg^{-1} for OC, and 5.6 g kg^{-1} for inorganic C. Also, they found that combining global soil-spectral libraries with local

calibration samples has the potential to provide improved vis-NIR spectroscopy soil characterization predictions than with either global or local calibrations alone (Brown et al. 2007). Stevens *et al*. (2010b) reported improved results with local calibrations stratified by soil type and agro-geological region than with global calibrations. Spiking (refer to the procedure that add some samples to a general data set, then produce a new data set) the local (target site) soil samples into the global or regional models has also proved to be an efficient way to improve the prediction accuracy of target field for some soil constituents (Shepherd & Walsh, 2002; Brown, 2007, Viscarra Rossel *et al*., 2008, Guerrero *et al*., 2010). Guerrero *et al*. (2010) observed that the number of samples in the calibration set could be also an important factor controlling the adaptability of calibrations to target sites and, thus, small-size models performed better than large-size model. However, further research is needed as general calibration model has huge economical advantage over field scale models for on-line soil vis-NIR measurement. This should aim at optimising the number of samples, spiking strategy and spiking rate to be used for farm scale modelling for *in situ* and on-line measurements.

2.6 Conclusions

The soil analysis with vis-NIR spectroscopy in the laboratory has relatively higher measurement accuracy, as compared to those for *in situ* and on-line measurements using fresh (wet) soil conditions. The laboratory analysis requires sample pre-treatment and is subjected to minimum environmental interferes. However, the degree of accuracy depends on soil attribute to be measured, calibration geographical scale, sample statistics and sample size, type of spectrophotometer used and wavelength range, and soil type diversities. Generally, vis-NIR spectroscopy has proven to be a good tool for the prediction of soil MC, OC, SOM, TN and clay content (R^2>0.8 and RPD>2.0) and to provide moderate or acceptable prediction accuracy for pH, Ca, CEC, P and Mg (R^2>0.6 and RPD>1.5). However, literature suggests that it is quite difficult to measure K and Na (R^2<0.6 and RPD<1.5) using the vis-NIR spectroscopy.

However, many of previous and current soil vis-NIR spectroscopic applications are limited to small geographic area e.g. field scale or homogenous soil type area. The larger scale modelling procedures with diverse soil type often results in less accurate model performance, or even complete failure might occurs. There are few successful calibrations using farm, regional or global soil spectral libraries, where spiking might offer potential solutions for enhancing model performance.

In comparison to laboratory application, *in situ* measurement of soil properties is shown to provide lower accuracy due to the influence of soil moisture, plant debris, and variable particle size. Quantifying the effect of these factors is needed to understand and probably improve measurement accuracy of *in situ* and on-line measurements.

The vis-NIR on-line soil sensors are rapid, non-destructive and compact and provide high spatial resolution with cost effective data. Although there are three on-line sensors with several successful applications, there is only one commercially available sensing system from Veris (Veris Technologies, KS, the USA). However, practical applications proved this sensor to be sensitive to breakage due to the sapphire optical window, which is in direct contact with soil and potential presence of solid objects like stones. The vis-NIR on-line sensor designed by Mouazen (2006a) and available at Cranfield University for further development proved to be simple, robust and does not have sapphire window sensitive to breakage.

In comparison with electrical and electromagnetic sensors which are being widely used in PA today, the vis-NIR on-line sensors provide quantitative measurement of many soil attributes simultaneously. This character is essential for site specific application of different input in PA, which needs detailed (quantitative) information about the spatial variations in soil properties collected at low acquisition cost. Development of reliable and efficient methods of on-line measurement of soil properties using available hardware will be the direction of future research to be considered in this thesis.

3 Effect of multivariate calibration technique

3.1 Introduction

The vis and NIR diffuse reflectance spectroscopy has become increasingly attracting to researchers (*e.g.* Ben-Dor and Banin, 1995; Chang et al., 2001; Reeves and McCarty; 2001; Shepherd and Walsh, 2002; Brown et al., 2006; Mouazen et al., 2007; Zornoza et al., 2008), due to well recognised advantages of this technique as compared to the laboratory reference methods of soil analysis. Although vis-NIR spectroscopy allows for rapid, cost effective and intensive sampling, researchers admit shortcomings associated with instrumentation instability to ambient conditions (*e.g.* light, temperature, etc), transferability of calibration between different instruments, difficulties associated with model scale (global, continental, regional, country, local and field) vs accuracy and others. Under *in situ* measurement conditions with non-mobile or mobile instrumentation, additional challenges associated with diverse soil moisture content, texture, colour, harsh field conditions, dust, stones and excessive residues and surface roughness all affect the accuracy of measurement with vis-NIR spectroscopy (Mouazen et al., 2007; Waiser et al., 2007). To compensate or overcome one or more of these difficulties, some solutions were suggested and implemented by researchers. This includes, among other methods, the selection of proper instrumentation *e.g.* spectrophotometer, optical accessories and optical probe design (Mouazen et al., 2009), improved spectra filtering and pre-processing (Maleki et al., 2008), better control of ambient conditions (Mouazen et al., 2007; Waiser et al., 2007) and the successful selection of the multivariate statistical analysis.

Probably one of the most recommended solutions to enhance the accuracy of vis-NIR measurement of soil properties is the successful development of calibration models. A comprehensive review of literature on calibration methods on diffuse reflectance spectroscopy and on comparison of predictions of soil properties using the most

common calibration techniques was provided by Viscarra Rossel et al. (2006a). These calibration methods include multiple linear regression analysis (e.g. Dalal and Henry, 1986) and a stepwise multiple linear regression (e.g. Shibusawa et al. 2001), multivariate adaptive regression splines (Shepherd and Walsh, 2002), PCR (e.g. Chang et al., 2001), PLSR (e.g. McCarty et al., 2002) and boosted regression trees (Brown et al., 2006). Five multivariate techniques, namely, SMLR, PCR, PLSR, regression tree and committee trees were compared by Vasques et al., (2008) with the aim of identifying the best combination of multivariate statistics and spectra pre-processing to predict soil carbon. They concluded that PLSR performed the best as compared to other techniques tested. Although the linear PCR and PLSR analyses are the most common techniques for spectral calibration and prediction (Viscarra Rossel et al., 2006a), with PLSR being the most accurate, other nonlinear techniques e.g. ANN have got much less attention and were rarely explored for the spectral analysis in soil sciences. Du and Zhou (2007) and Du et al. (2007; 2008) have successfully implement ANN based on principal components (PCs) obtained from PCA on MIR and photoacoustic MIR soil spectra. Only two examples on using ANN-PCs technique for soil analysis with NIR spectroscopy could be found in literature. Fidêncio et al. (2002) have implemented the RBFN in the NIR region (1000-2500 nm) and Daniel et al. (2003) have used ANN in the vis–NIR region (400–1100 nm). No literature is available about combining PLSR with ANN for the analysis of soil properties with full range vis-NIR spectroscopy (350-2500 nm) has been explored so far.

The scope of this chapter is to compare the performances of linear PCR and PLSR and non-linear BPNN analyses for the prediction accuracy of spectrally active (OC) and inactive (K, Mg, Na and P) soil properties using vis-NIR diffuse reflectance spectroscopy. The BPNN analyses will be based on latent variables (LVs) obtained from PLSR (BPNN-LVs) and PCs obtained from PCA (BPNN-PCs) (Martens and Naes, 1989).

3.2 Material and method

3.2.1 Collection of soil samples

A total of 168 samples were obtained from the Soil Service of Belgium (Heverlee, Belgium). They were collected in the spring and summer of 2004 from many fields in Belgium and northern France. These fields represent a wide range of soil textures and colours. Collecting the samples during a relatively long period of time (5 months) resulted in samples with different moisture contents. Each sample was mixed and divided into two parts; the major amount of the soil was used for the laboratory chemical analyses, whereas the remaining part was used for optical measurement. Samples were stored in plastic bags at 4°C from the time of sampling until the time of analysis.

3.2.2 Laboratory analyses of soil properties

Laboratory analyses for OC and extractable forms of K, Mg, Na and P were performed by the Soil Service of Belgium (Heverlee, Belgium) using their official methods (Vanden Auweele, et al., 2000). Soil OC expressed in percentage of carbon weight to the total weight of dry soil was determined by the Walkley-Black method (Hesse, 1971). The air-dried soil (1 g) was extracted with 20 mL ammonium lactate (0.1 N ammonium lactate and 0.4 N acetic acid; pH 3.75) to determine K, Mg and Na contents with atomic absorption spectrometry (AAS) (Egner et al., 1960). Phosphorus was determined by colorimetry (445 nm) on the same extract after addition of a mixture of ammonium vanadate, nitric acid and ammonium molybdate (Teicher, 1967; Csato and Kadar, 1992).

3.2.3 Description of vis-NIR spectrophotometer and optical measurement

A mobile spectrophotometer (LabSpec[@]Pro Near Infrared Analyzer, Analytical Spectral Devices, Inc, USA) was used. It is with one Si array (350-1000 nm) and two Peltier cooled InGaAs detectors (1000-1800 nm and 1800-2500 nm). The sampling interval of the instrument was 1 nm. However, the spectral resolution was 3 nm at 700 nm and 10

nm at 1400 and 2100 nm. A high intensity probe with a light source built in was used. A quartz-halogen bulb of 3000 K° light source and a detection fibre are gathered in the high intensity probe enclosing a 35° angle.

Optical scanning was carried out on fresh soil samples to build calibration models that can be used for *in situ* or on-the-go measurement. Only large plant residues and stones were removed from these fresh samples. Different amounts of non-sieved soil according to different textures were packed in Petri dishes of a 1.0 cm height by 3.6 cm in diameter. Soil in a Petri dish was shaken and a gentle pressure was applied on the surface before levelling with a spatula. This resulted in a smooth soil surface that ensured a maximum diffuse reflection and thus a good signal-to-noise ratio. Dark (7% reflectance) and white (75% reflection) reference measurements were taken before measurement of soil samples. One reading was collected from each soil sample. Each reading was an average of 15 successive measurements at 1.5 s, and this was used for spectra pre-processing and model establishment.

3.2.4 Pre-processing of spectra

The same pre-processing was used for all properties and for all analyses. Soil spectra were first reduced to 453-2448 nm, to eliminate noise at edges of each spectrum. After noise cut, spectra were reduced by averaging 5 successive wavelengths. Maximum normalisation was followed, which is typically used to get all data to approximately the same scale, or to get a more even distribution of the variances and the average values. The maximum normalisation is a normalisation that "polarizes" the spectra. The peaks of all spectra with positive values scale to +1, while spectra with negative values scale to -1. Since all soil spectra in this study have positive values, the peaks of these spectra scaled to +1 (Mouazen et al., 2005). The maximum normalisation led to better results for all elements as compared to other pre-processing options tested. Spectra were then subjected to Savitzky-Golay first derivation (Martens and Naes, 1989). This method enables to compute the first or higher-order derivatives, including a smoothing factor, which determines how many

adjacent variables will be used to estimate the polynomial approximation used for derivatives. A second order polynomial approximation was selected. A 2:2 smoothing was carried out after the first derivative to decrease noise from the measured spectra. All pre-processing steps were carried out using MatLab software V. 7.1 (The Math Works, Natick, MA, USA).

3.2.5 Establishment of calibration models

Three different calibration techniques were used, namely, PCR, PLSR and BPNN. The PCR and PLSR were adopted for relating the variations in one response variable (OC, K, Mg, Na and P) to the variations of several predictors (wavelengths), using a TOMCAT, a MATLAB multivariate calibration toolbox (Daszykowski et al., 2007). Both PCR and PLSR model validation procedure was based on the leave-one-out cross validation method. The number of PCs of PCR and LVs of PLSR for a model was determined by examining a plot of leave-one-out cross validation residual variance against the number of loadings or latent variables obtained from PCR and PLSR, respectively (Martens and Naes, 1989). For example, the number of latent variable of the first minimum value of residual variance was selected (Brown et al., 2005). Outliers were detected by subjecting the pre-processed spectra to PCA. The scores plot of the first two PCs provides two-dimensional maps showing the relation between data. Data points lying outside the 95% confidence ellipse (Hotelling T^2) were considered as strong outliers (Figure 3-1) and were eliminated from the matrix (Constantinou et al., 2004).
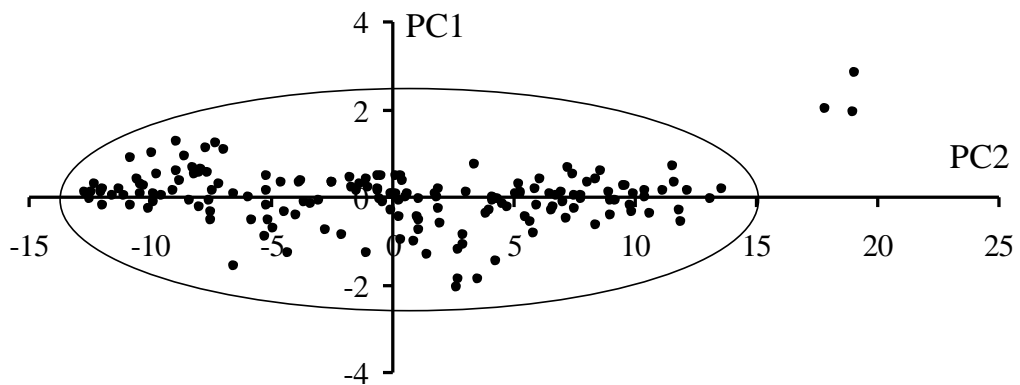
Figure 3- 1 Detection of outliers after principal component analysis (PCA)

The most popular neural network is BPNN (Bishop, 1995), which has been used for many applications. It can be used as calibration method for its supervised learning ability providing good results (Liu et al., 2008). Back propagation is the generalization of the Widrow-Hoff learning rule to Multiple-layer networks and nonlinear differentiable transfer functions (MatLab Neural Network Toolbox™ 6 User's Guide). Input vectors and the corresponding target vectors are used to train a network until it can approximate a function, associate input vectors with specific output vectors, or classify input vectors in an appropriate way. Networks with biases, a sigmoid layer, and a linear output layer are capable to approximate any function with a finite number of discontinuities (MatLab Neural Network Toolbox™ 6 User's Guide). Figure 3-2 illustrates the architecture of the network that is most commonly used with the back propagation algorithm—the multilayer feed forward network.

Extreme long training time and over-fitting are two main difficulties of ANN calibration when using raw infrared spectral data points as inputs. The detailed network training procedure could be found in the 'MatLab Neural Network Toolbox™ 6 User's Guide'. The input of BPNN might be either PCs obtained from PCA, or LVs obtained from PLSR (PLSR-vectors), and output will be the chemical values of the properties, some the input dimensions will be number of samples by PCs or LVs. Adopting PCs or LVs as input for BPNN is an effective way of reducing computation resources and improving the robustness of ANN calibration (Janik et al., 2007). In this study the two possibilities were tested, namely BPNN-PCs and BPNN-LVs. The number of PCs chosen as input for BPNN was based on the cumulative percentage of explained data variance. The first 5 PCs were considered as input in this study, since experience show that they can explain nearly 100 % of variance. The number of LVs considered as input for BPNN was the optimal number obtained at the first minimum value of residual variance, as explained by Brown et al. (2005). The selection of different numbers of PCs and LVs during the PCA and PLS, respectively, can be attributed to the fact that this procedure provided

the best results. Furthermore, this selection was also based on experience and review of literature.

A standard three-layer feed-forward network composed of one input layer (PCs or LVs), one hidden layer (initially ten nodes) and one output layer (one node) was used. Each node in ANN, which represents a "neuron", is associated with a transfer (activation) function that sums up the outputs from that node and passes them to the next layer in the network. This function was found achieved best accuracy for prediction. The tan-sigmoid function and a linear function were adopted in the hidden and in the output layers, respectively. The momentum set as 0.6, the least learning rate as 0.2, the threshold residual error as 0.5×10^{-5} and the training times as 2000, as suggested by He et al. 2008. During the training, 2 node configuration mehods were tested. After training, the number of nodes of the hidden layer was adjusted (12) so that to achieve the best results. To avoid over-fitting, the cross validation option was adopted. More details on the mathematical background of the ANN approach can be found in literature (e.g. Cheng and Titterington, 1994; Basheer and Hajmeer, 2000).
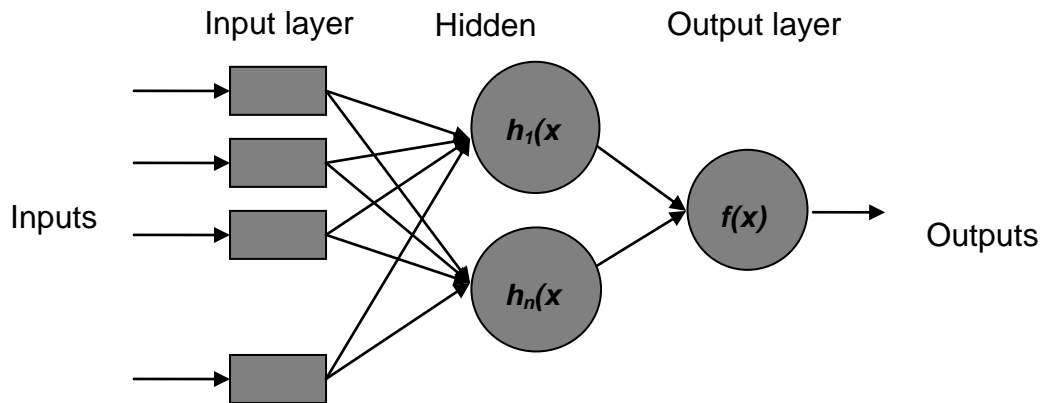
Figure 3-2 Illustration of a feed-forward back propagation neural network (BPNN) containing input, hidden (with "n" neurons) and output layer

Due to the relatively small number of soil spectra covering a large geographical area, the total number of spectra (168) was randomly divided into two sets of 90 % and 10 %. We need around 150 soil samples to build up calibration models to obtain

stable model performance, that's why we divided the dataset to 90%:10%. The former set was the calibration set (cross-validation set) and was used to establish the calibration models based on leave-one-out cross-validation technique, which calculate the best model by using mean root mean square of prediction. The latter set was the validation set (prediction set) and was used for independent validation of the established models. This division of cross-validation (90%) and prediction (10%) sets was replicated three times and all four analyses (PCR, PLSR, BPNN-PCs and BPNN-LVs) were carried out on the three replicates. This was done in order to examine the robustness of calibration models developed for the prediction of five soil properties investigated. The sample statistics for the cross-validation and prediction sets for the three replicates are given in Table 3-1.

Table 3-1 Sample statistics of cross-validation and prediction data sets of the three divisions (replicates) of sample sets

Property		Number of samples	Minimum	Maximum	Mean	Standard deviation
Cross-validation set						
OC, %						
	Set1	133	0.7	6.0	1.7	1.0
	Set2	133	0.8	5.6	1.6	1.0
	Set3	133	1.0	5.7	1.7	1.0
P, mg 100 g^{-1}						
	Set1	150	4.0	103.0	30.0	24.5
	Set2	150	5.0	100.0	37.2	24.4
	Set3	150	9.0	86.0	38.2	23.8
Na, mg 100 g^{-1}						
	Set1	140	0.8	10.0	3.3	3.1
	Set2	140	1.3	9.9	3.7	3.2
	Set3	140	0.9	8.3	3.3	3.0
K, mg 100 g^{-1}						
	Set1	139	7.0	78.0	24.6	18.3
	Set2	139	9.0	76.0	25.4	18.2
	Set3	139	8.0	73.0	24.8	17.8
Mg, mg 100 g^{-1}						
	Set1	148	3.0	60.0	19.0	14.6
	Set2	148	6.0	51.0	18.7	14.3
	Set3	148	6.0	60.0	19.2	14.6
Prediction set						
OC, %						
	Set1	15	0.8	5.7	3.0	1.8
	Set2	15	0.9	5.7	2.9	1.7
	Set3	15	1.0	6.0	2.9	1.7
P, mg 100 g^{-1}						
	Set1	15	4.0	100.0	43.3	27.8
	Set2	15	9.0	86.0	40.5	26.4
	Set3	15	6.0	85.0	41.8	26.9
Na, mg 100 g^{-1}						
	Set1	16	1.5	9.0	4.6	3.8
	Set2	16	1.3	7.9	4.4	3.5
	Set3	16	1.4	8.5	4.5	3.8
K, mg 100 g^{-1}						
	Set1	16	2.0	73.0	49.1	24.3
	Set2	16	10.0	77.0	51.4	24.1
	Set3	16	10.0	74.0	52.1	24.3
Mg, mg 100 g^{-1}						
	Set1	15	3.0	54.0	23.7	14.1
	Set2	15	4.0	47.0	22.6	13.9
	Set3	15	5.0	46.0	23.2	13.6

3.2.6 Statistical indicators used to assess the accuracy of calibration models developed

To compare between different calibrations methods established, the root mean square error of prediction of the independent prediction set was considered. The accuracy of each calibration was evaluated based on the residual prediction deviation (RPD=SD/RMSEP), which is the ratio of standard deviation of the laboratory measured values to RMSEP of the independent prediction set (Williams, 1987). The formula to calculate RMSEP is $\sqrt[2]{average\ (a1-a2)^\wedge 2}$ .It is the factor, by which the prediction accuracy has been increased, compared to the mean composition for all samples. Viscarra Rossel et al. (2006b) classified RPD values as follows: RPD<1.0 indicates very poor model/predictions and their use is not recommended; RPD between 1.0 and 1.4 indicates poor model/predictions where only high and low values are distinguishable; RPD between 1.4 and 1.8 indicates fair model/predictions which may be used for assessment and correlation; RPD values between 1.8 and 2.0 indicates good model/predictions where quantitative predictions are possible; RPD between 2.0 and 2.5 indicates very good, quantitative model/predictions, and RPD>2.5 indicates excellent model/predictions. This classification system was adopted in this study.

3.3 Results and discussion

3.3.1 Prediction accuracy obtained with different calibration methods

The calibration methods considered in this study provide different prediction accuracy of the studied soil properties. Figure 3-3 and Figure 3-4 summarise predictions of OC and extractable forms of K, Mg, Na and P obtained in the three

replicates. Among soil properties studied, OC is the most accurately measured with BPNN-LVs (average values of the three replicates of R^2_{pre} (coefficient of determination) = 0.84, RMSEP = 0.68% and RPD = 2.54). This prediction accuracy is classified to be excellent. One of the highest reported accuracy of OC measurement with a vis-NIR spectroscopy is that of Fidêncio et al. (2002), accounting for only two soils (Oxisols and Ultisols) in Brazil. Fidêncio et al. (2002) arrived at R^2_{pre} (coefficient of determination) value of 0.91 and RMSEP of 0.25 %, by conducting BPNN-PCs analysis on spectra of dry soil samples. By comparing this result with that of the current study, one can conclude that BPNN-LVs modeling is a better choice than BPNN-PCs, since the sample set used in the latter study was collected from large geographical area (Belgium and Northern France) including many soil types, and that optical scanning occurred under variable moisture content of soil samples. Similarly, results obtained with BPNN-LVs for Mg is also classified to be excellent, although the prediction accuracy is slightly lower than that of OC (average values of the three replicates of R^2_{pre} = 0.82, RMSEP = 5.46 mg 100 g^{-1} and RPD = 2.54). In spite of the fact that Mg does not possess direct spectral response in vis-NIR range, it is most likely to be measured throughout other properties as explained section 3.2. Both PLSR and PCR do not confirm Mg to be the second best property to be predicted after OC (Figure 4-4). Literature supports a high accuracy (R^2_{val} = 0.82) for Mg measurement with NIR spectroscopy (van Groenigen et al., 2003), which was better measured than Ca, K and available P.
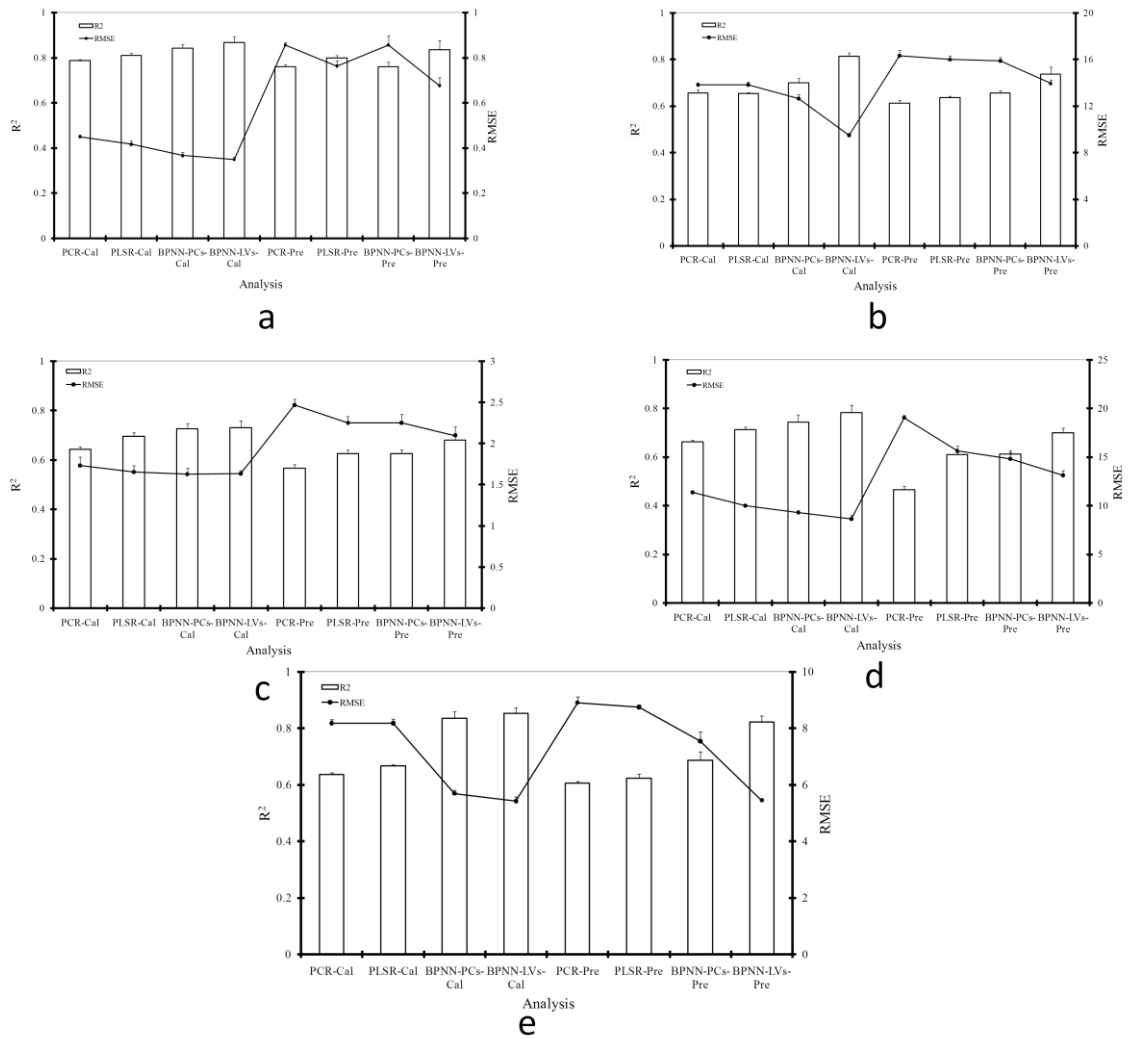
Figure 3-3 Mean values (average of three replicates) and standard deviation (error bar) of R2 and root mean square error (RMSE) obtained from principal component regression (PCR), partial least squares regression (PLSR), back propagation neural network-principal components (BPNN-PCs) and back propagation neural network-latent variables (BPNN-LVs) analyses for cross-validation (Cal) and prediction (Pre) data sets for: (a) organic carbon (OC), (b) extractable phosphorous (P), (c) extractable sodium (Na), (d) extractable potassium (K) and (e) extractable magnesium (Mg)

The predictions of K, Na and P are also best achieved with BPNN-LVs models (Figure 3-3 and Figure 3-4). These predictions are classified as good model predictions (average values of the three replicates for R^2_{pre} = 0.68 − 0.74, RMSEP = 2.10 − 13.94 mg 100 g^{-1} and RPD = 1.77 − 1.94). Here, these models were considered to provide possible quantitative predictions. However, Figure 3-4 confirms P to be the best measured as compared to K and Na. Shepherd and Walsh (2002) reached high prediction qualities

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for exchangeable Mg, medium prediction quality for exchangeable K and poor prediction quality for P, whereas Mouazen et al. (2006c) reached medium prediction quality for exchangeable Mg and P and poor prediction quality for exchangeable K. Others reported high prediction accuracy for P (Bogrekci and Lee 2005a). It can be concluded that Mg and P can be measured with higher accuracy that Na and K, which is in line with results achieved in this study using BPNN-LVs analysis (Figure 3-3 and Figure 3-4).
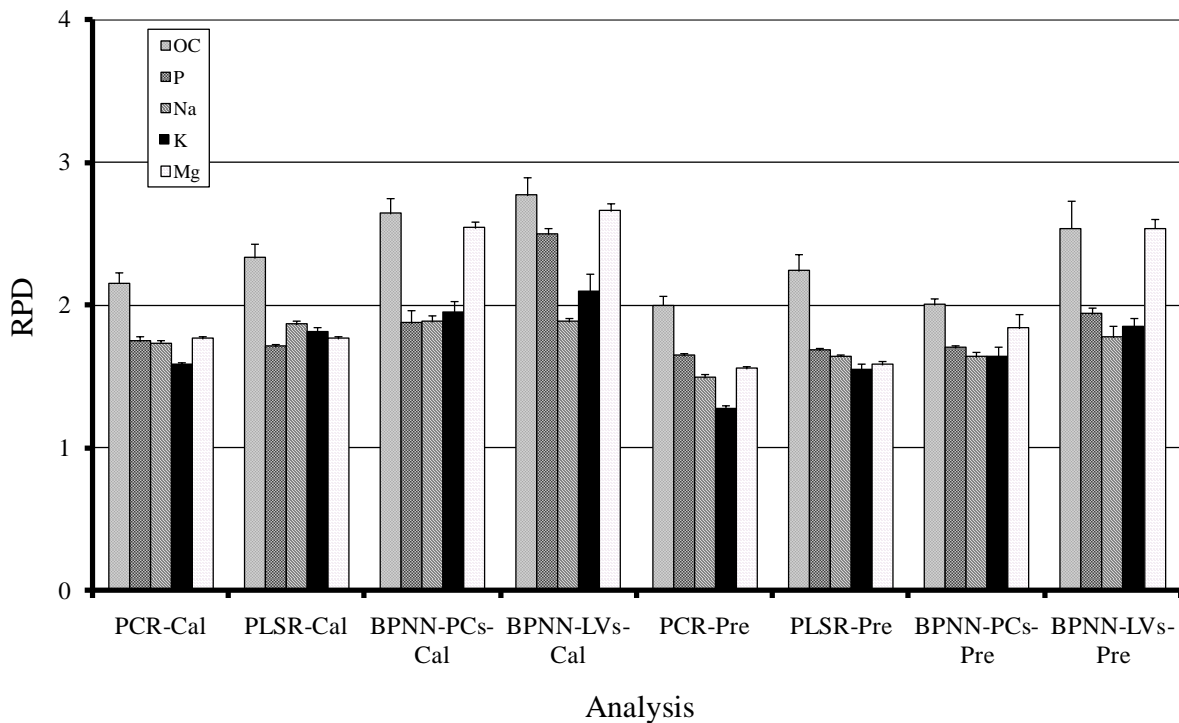
Figure 3-4 Mean values (average of three replicates) and standard deviation (error bar) of residual prediction deviation (RPD) obtained from principal component regression (PCR), partial least squares regression (PLSR), back propagation neural network-principal components (BPNN-PCs) and back propagation neural network-latent variables (BPNN-LVs) analyses for cross-validation (Cal) and prediction (Pre) data sets for: organic carbon (OC), extractable phosphorous (P), extractable sodium (Na), extractable potassium (K) and extractable magnesium (Mg)

versus vis-NIR measured soil properties, including three replicates, is shown in Figure 3-5), as an example. Since OC is the only spectrally active property, it is accepted that

All four analyses result in the highest prediction accuracy for OC, as compared to the other four soil properties. Both the leave-one-out cross validation and prediction results showed that all BPNN-LVs models outperformed PCR, PLSR and BPNN-PCs

models (Figure 3-3 and Figure 3-4). Janik et al. (2009) reported similar results for the prediction of selected soil chemical and physical properties using mid infrared spectroscopy. Furthermore, PLSR provided smaller accuracy than BPNN-LVs but showed better performance than PCR (Figure 3-3. and Figure 3-4). Compared to PLSR, BPNN-PCs provided a slight improvement of prediction accuracy of all properties studies except OC (Figure 3-3 and Figure 3-4).
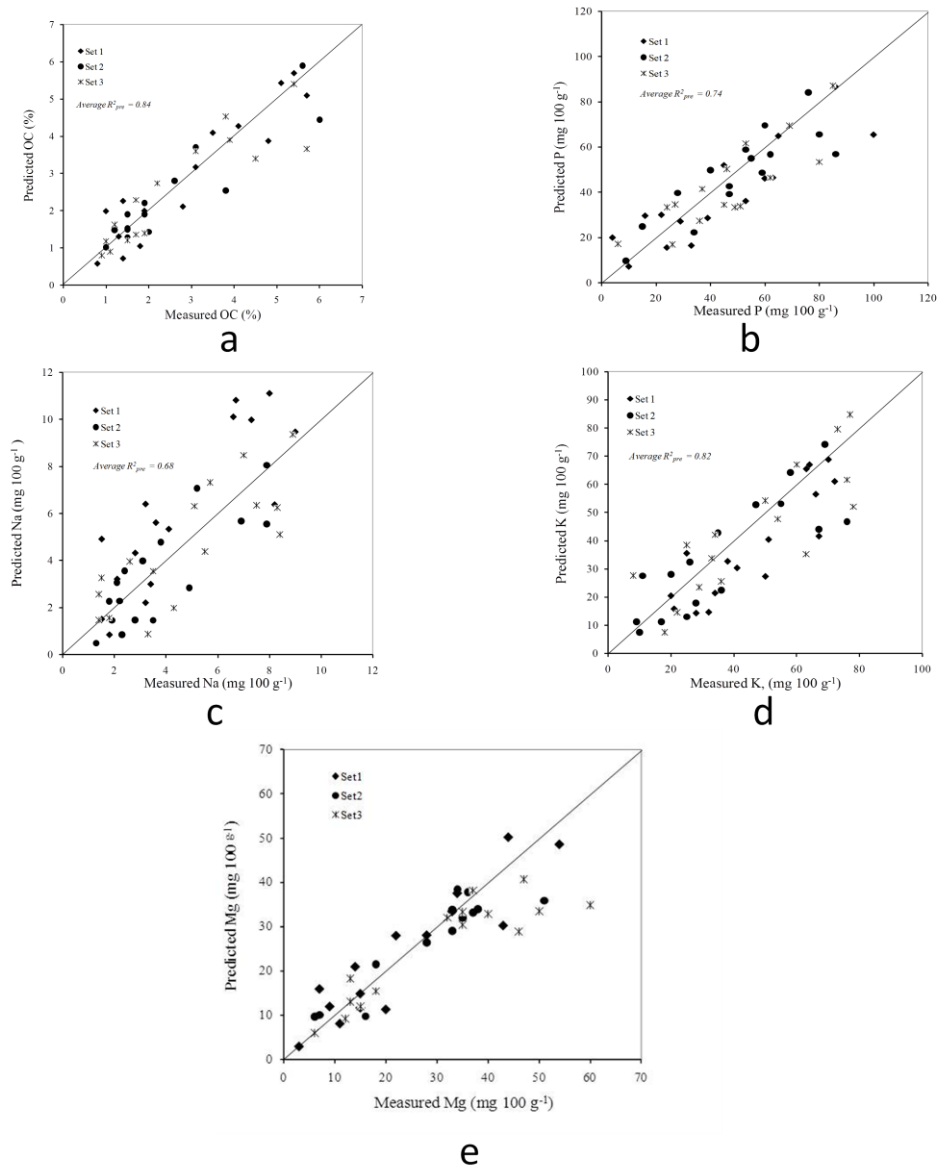
Figure 3- 5Scatter plot of laboratory measured versus visible (vis) and near infrared (NIR) predicted soil properties using back propagation neural network-latent variables (BPNN-LVs) models developed for the three prediction sets (Table 4-1) for: (a) organic carbon, (b) phosphorous, (c) sodium, (d) potassium and (e) magnesium.

3.3.2 Regression coefficients and prediction

The regression coefficients distribution over the entire wavelength range (453 – 2448 nm) shows distinguished few wavelength bands for almost all soil properties considered (Figure 3-6). These bands are in vis and NIR regions and might be attributed to energy absorption due to colour, water, organic constituents and clay minerals in the soil. Two peaks in vis range at about 490 and 640 are associated with the blue region around 450 nm and the red region around 680 nm. It was reported that the absorption band at 450 nm could be also caused by paired and single Fe^{3+} electron transitions to a higher energy state (Sherman and Waite 1985). These two peaks are remarkably similar for all properties except for K. This leads to the conclusion that colour contributes similarly to the prediction accuracy of all studied elements except K. In NIR region between 750 – 1800, only two distinguished peaks can be seen for all properties. These two peaks associate with the water absorption bands in the third overtone region (960 nm) and in the second overtone region (1450 nm). However, these peaks are more evident with OC, P, Na and K, as compared to Mg. It is clearly demonstrated that the most active spectral region is between 1800 and 2450 nm, where more distinguished bands can be seen. These bands associate with the water absorption band in the first overtone region (1950 nm), clay minerals around 2300 nm and C-H + C-H, C-H + C-C and N-H combinations (Figure 3-6). Of all chemical properties studied, only OC possesses direct spectral response (overtones or combinations) in NIR region, whereas all other properties (K, Mg, Na and P) do not have direct spectral responses. Therefore, the prediction of these properties (K, Mg, Na and P) may be attributed to locally present co-variation to spectrally active constituents (organic matter, carbonates, clays, etc). Such co-variations may of course vary between data sets. It is worth indicating that this paper reports on the measurement of the extractable fraction of K, Mg, Na and P, which makes the interpretation of the regression coefficients curve very complicated. In fact, what fraction of these properties can be correlated with NIR spectroscopy is still unknown and needs further investigation. For example, it is possible that the excellent prediction of extractable Mg (Figure 3-3. and Figure 3-4) is due to the high correlation between NIR and total Mg (indirectly captured by NIR through spectrally active compounds and minerals), which

is mediated through the relationship between the total and extractable Mg. Reeves and Smith (2009) have reported good results for the prediction of Mg with NIR considering soils from a geochemical survey of North America. They attributed this good prediction to Mg correlations with carbonate content and factors influencing cation exchange capacity, such as organic matter content (Malley et al., 2004). Miller (2001) realised that it is often not possible to confidently isolate relevant effects in the NIR spectrum based on knowledge of the sample's chemistry and spectroscopy only. Therefore, further study is needed to understand why these properties are measurable with excellent (Mg) and acceptable accuracy (K, P and Na) using NIR spectroscopy.
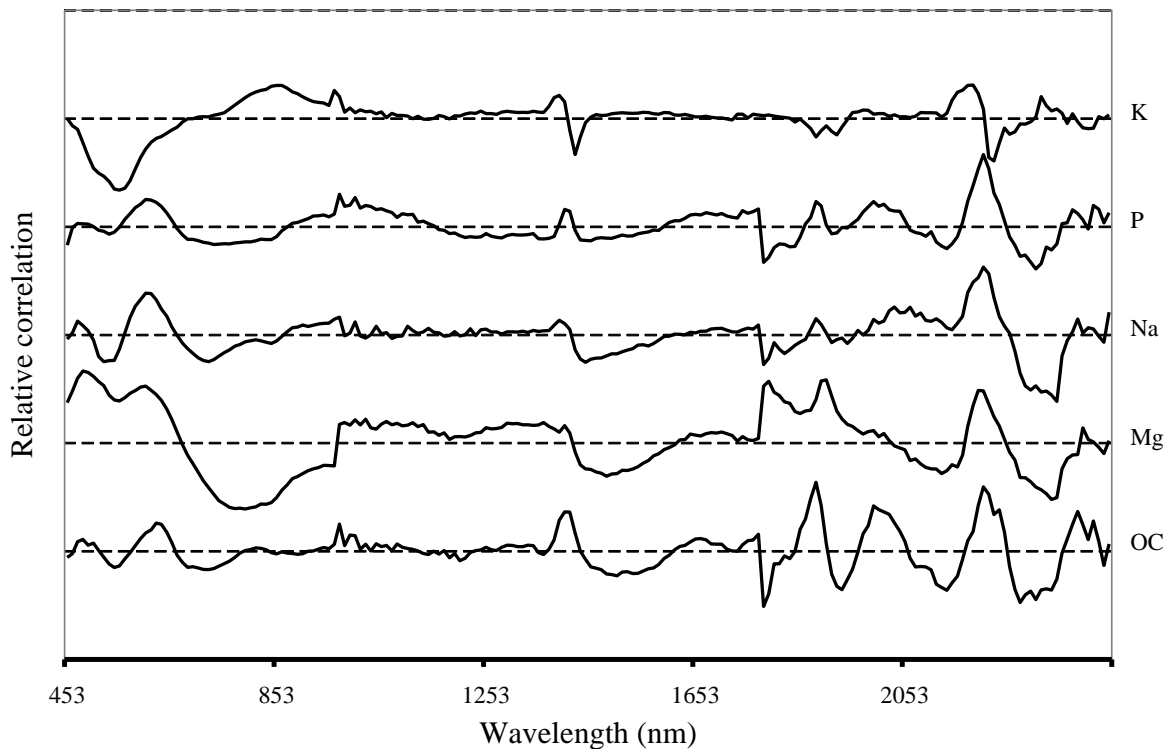
Figure 3- 6 Regression coefficients distribution over the entire wavelength obtained from partial least squares regression (PLSR). Dotted lines representing zero correlation are separated by equal factor of 1.5 for clarity of presentation

3.4 Conclusions

The comparison among PCR, PLSR and BPNN methods for the prediction accuracy of OC, extractable forms of K, Na, Mg and P using vis and near infrared NIR diffuse reflectance spectroscopy allowed the following conclusions to be drawn:

1. BPNN-LVs models outperformed PCR, PLSR and BPNN-PCs models for all soil properties.

2. The best prediction accuracy obtained with BPNN-LVs model was for OC, which is the only property that possesses spectral response in the NIR region. However, comparable results to OC were obtained for Mg with BPNN-LVs models.

3. Soil mineral nutrients, namely, K, Mg, Na and P were found measurable with different degree of accuracy using vis-NIR spectroscopy, which was attributed to co-variation to spectrally active constituents.

Based on results achieved in this study, it is recommended to adopt BPNN-LVs analysis as the best modelling method to predict soil properties (OC, K, Mg, Na and P). However, further studies are needed to provide in depth interpretation of the successful measurement of soil properties that do not possess direct spectral response in NIR region.

4 Effect of sample range or standard deviation on model accuracy

4.1 Introduction

The evaluation of the soil spatial variability using a fast, robust and cheap tool is one of the key steps towards the successful implementation of the precision agriculture (Srinivasan, 2006). During the last two decades, vis-NIR spectroscopy has been proved to be a fast, cost effective and a relative accurate alternative method to the laboratory analyses of soil physical, chemical and biological properties (Shepherd & Walsh, 2002; Brown *et al.*, 2006; Mouazen *et al.*, 2006a; Wetterlind *et al.*, 2008). However, the successful application of the Vis-NIR spectroscopy depends largely on the development of accurate and robust calibration models, which is particularly crucial for *in situ* and on-line measurement conditions. This is because, under field-measurement conditions, the influence of environmental factors, namely, ambient light, soil moisture content, texture, colour, temperature, harsh field conditions, dust, stoniness and surface roughness are possible sources of error (Waiser *et al.*, 2007). Thus, numerous researchers have explored new modelling approaches to improve vis-NIR calibration accuracy.

Most studies on soil Vis-NIR spectroscopic applications are limited to within-field scales (Huang *et al.*, 2007; Mouazen *et al.*, 2005; Wijaya *et a.l*, 2001), or to homogenous soil-type areas, although researchers tend to expand applications to regional or national (Mouazen *et al.*, 2006c), continental or even global (Brown, 2007) scales. It was reported by Stenberg *et al.* (2010a) that the calibration scale affects the accuracy of the models developed, and that field-scale modelling provides the greatest accuracy. Models developed for large geographical areas based on diverse soil samples may provide unacceptable prediction accuracy or even fail, largely because of the large variability of texture type, colour, moisture content and origin of soil. However, spectral libraries for global calibration models should include sufficient number of soil samples, which can illustrate the soil variability in the new target site where the prediction will be carried out (Viscarra Rossel *et al.*, 2008; Guerrero *et al.*, 2010). However, the large sample number may increase the prediction error. Therefore,

before deciding on the scale of calibration, a decision on the degree of precision required has to be made. Cost evaluation for building calibration models has to be also considered.

Mouazen *et al.* (2006b) reported greater accuracy of prediction (R^2 = 0.98; RMSEP = 1.6%; RPD = 5.22) of the soil moisture content of a local calibration developed for one field of about 7-ha, compared with a general calibration developed for several fields distributed in Belgium and Northern France (R^2 = 0.88; RMSEP = 2.5%; RPD = 2.88). Similar results were found by the same research group for extractable phosphorous (P) (Mouazen *et al*., 2009). Stevens *et al*. (2010) reported improved results with local calibrations stratified by soil type and agro-geological region than with global calibrations. Spiking the local (target site) soil samples into the global or regional models has also proved to be an efficient way to improve the prediction accuracy of target field for some soil constituents (Shepherd & Walsh, 2002; Brown, 2007, Viscarra Rossel *et al*., 2008, Guerrero *et al*., 2010). Guerrero *et al*. (2010) observed that the number of samples in the calibration set could be also an important factor controlling the adaptability of calibrations to target sites and, thus, small-size models performed better than large-size model. We believe that the different model performance caused by different sample size is attributed to sample statistics, including the variation (concentration) range and SD. However, there is limited literature on the effect of sample statistics of calibration set on the prediction accuracy, particularly for *in situ* measurement conditions at the farm scale. Furthermore, the performance of multi-farm (general) models in predicting key soil properties compared with the corresponding models for individual farms with different sample number and statistics has not been explored so far.

The aim of the present paper is to investigate the relationship between the calibration accuracy and the variation range or SD of soil samples using data of three farms in Europe. The paper also compares the results of individual farm models with that of a multi-farm model using samples from three farms across three European countries.

4.2 Material and methods

4.2.1 Soil samples

A total of 408 soil samples were used in this study. They were collected from three different farms in Europe, namely, Mespol Medlov, A.S. (Czech Republic; http://farmsubsidy.org/CZ), Wimex (Germany; http://www.wimex-online.de), Bramstrup Estate (Denmark; http://www.bramstrup.dk). Bulked samples from 16 cores were collected from the upper soil layer (0 – 30 cm) in the spring of 2008 (Czech Republic and Germany) and in the spring of 2009 (Denmark), covering a large landscape and soil diversity. A total of 205 and 70 soil samples were, respectively, collected from six fields in the Czech Republic and five fields in Denmark. The remaining 128 soil samples were collected from four sub-areas belong to Wimex farm in Germany, with four samples from two fields at Reppichau, 50 samples from nine fields at RAG, 20 samples from ten fields at Aken and 54 samples from 15 fields at the Wulfen farm. About 200 g of each sample was stored at -18º C. Half of each sample was sent to the Leibniz Centre for Agricultural Landscape Research (ZALF) in Germany for soil chemical analyses and the remaining samples were to Cranfield University for optical measurements and data analysis.

4.2.2 Chemical analysis

Laboratory analyses of total carbon (TC), organic carbon (OC), total nitrogen (TN), extractable phosphorous (P) and pH were carried out by ZALF using standard procedures described here. The calcium acetate lactate method was used for preparing an extraction, in which P was measured by a colorimetric method. Soil TC, OC and TN were measured by a TrusSpecCNS spectrometer (LECO Corporation, St. Joseph, MI, USA) using the Dumas combustion method (Dumas, 1963). Soil pH was measured by a glass electrode in a 1:5 (volume basis) suspension of soil in a solution of

1 M KCl after shaking on a side-to-side shaker (set at 300 rpm per minute) for 60 minutes.

4.2.3 Optical measurement

Each soil sample was placed in a glass container and mixed well. Big stones and plant residues were excluded. Then each soil sample was placed into three Petri dishes, which were 2 cm in depth and 2 cm in diameter. The soil in the Petri dish was shaken and pressed gently before levelling with a spatula to ensure a smooth soil surface and therefore maximum light reflection and a large signal to noise ratio (Mouazen *et al.*, 2005).

Soil samples were scanned by a fibre Vis-NIR spectrophotometer (LabSpec@Pro Near Infrared Analyzer, Analytical Spectral Devices, Inc, Boulder, Co, USA): this had one Si array (350 – 1000 nm) and two Petier cooled InGaAs detectors (1000 – 1800 nm and 1800 – 2500 nm). The sampling interval of the instrument was 1 nm. However, the spectral resolution was 3 nm at 700 nm and 10 nm at 1400 and 2100 nm and this data pre treatment can reduce the noise effectively without losing the spectral information. A high-intensity probe with a quartz-halogen bulb of 3000 K built-in was used. The light source and detection fibre were gathered in the high-intensity probe enclosing a 35° angle. A 100% white reference was used before scanning. A total of three scans were collected from each replicate, and these were averaged into one spectrum for each sample.

4.2.4 Data pre-treatment

The same pre-treatment of spectral data was carried out for all soil properties investigated by using the Unscrambler 7.8 software (Camo Inc.; Oslo, Norway). The spectra were first reduced to 450 – 2450 nm, to eliminate the noise at both edges of each spectrum. After noise was removed, spectra were reduced by averaging 5

successive wavelengths. Maximum normalization was followed, which is typically used to get all data to approximately the same scale, or to get a more even distribution of the variances and the average values. The maximum normalisation 'polarizes' the spectra. The peaks of all spectra with positive values are scaled to +1, while spectra with negative values are scaled to -1. Since all soil spectra in this study had positive values, the peaks of these spectra were scaled to +1 (Mouazen *et al.*, 2005). The maximum normalization led to improved results for all the investigated properties as compared with other pre-treatments tested. Spectra were then subjected to Savitzky-Golay first derivation (Martens & Naes, 1989). This method enables the computation of the first- or higher-order derivatives, including a smoothing factor, which determines how many adjacent variables to be used to estimate the polynomial approximation used for derivatives. A second-order polynomial approximation was selected. A 2:2 Savitzky-Golay smoothing was carried out after the first derivative to remove noise from spectra.

4.2.5 Establishment of calibration models

The pre-treated spectra and the results of laboratory chemical analyses were used to develop the calibration models for the different soil properties listed in Table 4-1. Soil spectra were divided into either calibration (70%) or independent validation (30%) sets. The calibration spectra were subjected to a PLSR with leave-one-out cross validation using the Unscrambler 7.8 software (Camo Inc.; Oslo, Norway). The number of latent variables for a model was determined by examining a plot of leave-one-out cross validation residual variance against the number of latent variables obtained from PLSR. The latent variable of the first minimum value of residual variance was selected (Brown *et al.*, 2005). Outliers were detected by using the residual sample variance plot after the PLSR. Samples located individually far from the zero line of residual variance were considered to be outliers and were excluded from the analysis.

Table 4-1 Sample statistics of laboratory results of samples collected from Bramstrump Estate farm in Denmark (70 samples), Wimex farm in Germany (128 samples) and Mespol Medlov farm in Czech Republic (205 samples)

Property	Nr of samples	Calibration set				Independent validation set			
		Min	Max	Mean	SD	Min	Max	Mean	SD
1- Bramstrup Estate	70								
Total carbon (TC) / %		0.75	18.02	1.84	3.0	1.00	13.11	2.46	3.47
Organic carbon (OC) / %		0.74	14.43	1.74	2.5	0.99	11.89	2.37	3.22
Total nitrogen (TN) / %		0.07	1.22	0.17	0.2	0.10	0.947	0.21	0.25
Phosphorous (P) / mg 100g^{-1}		3.34	13.01	6.46	2.1	3.69	11.13	6.17	2.24
pH		6.67	8.22	7.19	0.5	6.89	8.16	7.37	0.34
2- Wimex	128								
Total carbon (TC) / %		0.72	7.61	1.65	1.2	0.83	7.44	1.89	1.40
Organic carbon (OC) / %		0.70	3.51	1.38	0.7	0.82	3.49	1.57	0.60
Total nitrogen (TN) / %		0.06	0.38	0.13	0.1	0.08	0.38	0.16	0.06
Phosphorous (P) / mg 100g^{-1}		2.78	12.92	7.02	1.9	2.67	53.27	10.65	11.62
pH		6.01	7.59	6.78	0.4	4.92	7.70	6.65	0.71
3- Mespol Medlov	205								
Total carbon (TC) / %		1.07	2.28	1.53	0.2	1.05	2.04	1.41	0.21
Organic carbon (OC) / %		1.06	2.16	1.48	0.2	1.04	2.03	1.39	0.21
Total nitrogen (TN) / %		0.11	0.24	0.17	0.0	0.11	0.21	0.16	0.03
Phosphorous (P) / mg 100g^{-1}		2.37	37.51	9.36	5.3	2.16	25.3	7.90	3.94
pH		5.87	7.87	6.96	0.6	5.62	7.60	6.39	0.39
4- General models	403								
Total carbon (TC) / %		0.72	18.03	1.63	1.5	0.83	13.11	1.73	1.68
Organic carbon (OC) / %		0.70	14.43	1.50	1.2	0.82	11.89	1.61	1.34
Total nitrogen (TN) / %		0.06	1.22	0.16	0.1	0.08	0.95	0.16	0.11
Phosphorous (P) / mg 100g^{-1}		2.37	37.51	8.08	4.2	2.16	53.27	8.55	7.47
pH		5.87	8.22	6.94	0.5	4.92	8.16	6.63	0.62

Calibration models were developed for each farm separately using samples from each farm, whereas general calibration models using samples from all three farms were

developed. Tables 4-2 and 4-3 summarize the results of cross validation and independent validation, respectively.

4.3 Results and discussion

Both R^2 and RPD were used to compare the prediction accuracy of different models for different properties, whereas RMSEP was used to evaluate the accuracy of measurement as compared with the standard chemical analysis.

4.3.1 Farm individual models

Examining results in Tables 4-2 and 4-3 reveals that the accuracy of prediction differed among the different farms. The best results were obtained for Bramstrup Estate farm, followed by those for Wimex farm (Germany), with R^2 = 0.85 – 0.93 and RPD = 2.61 – 3.96 for the cross-validation set, and R^2 = 0.74 – 0.96 and RPD = 2.00 – 4.95 for the independent validation set obtained for both farms. These results are in line with those achieved by others (Chang *et al.*, 2001; Reeves & McCarty, 2001; Brown *et al.*, 2005; Cohen *et al.*, 2005; Guerrero *et al.*, 2010) for the same soil properties. However, fresh soil samples were scanned in the present study to simulate *in-situ* measurement conditions, whereas the former studies used dried and sieved samples. The poorest results were obtained for the Mespol Medlov, A.S. farm for all the soil properties investigated. Although TC, OC and TN had direct spectral responses in the NIR region that should normally result in successful measurement, the poor accuracy of prediction of Mespol Medlov, A.S. models can be attributed mainly to the narrow range of concentrations of those properties in the soil samples (Table 4-1). For those soil properties without direct spectral responses in the NIR range (such as pH and P), the results are relatively poor (Tables 4-2 and 4-3).

Table 4-2 Validation results of partial least squares regression (PLSR)-cross validation models on calibration data set. Soil samples were collected from three European Farms, namely, Bramstrump Estate farm in Denmark (49 samples), Wimex farm in Germany (128 samples) and Mespol Medlov farm in Czech Republic (205 samples)

Property	LV[a]	R^{2}[b]	Slope	Intercept	RMSEP[c]	RPD[d]
1- Bramstrup Estate						
Total carbon (TC) / %	6	0.90	0.79	0.29	0.90	3.29
Organic carbon (OC) / %	6	0.93	0.81	0.27	0.63	3.96
Total Nitrogen (TN) / %	5	0.90	0.75	0.03	0.06	3.38
pH	1	0.15	0.16	6.04	0.41	0.94
Phosphorous (P) / mg 100g^{-1}	2	0.21	0.24	4.82	1.86	1.12
2- Wimex						
Total carbon (TC) / %	7	0.85	0.87	0.20	0.47	2.61
Organic carbon (OC) / %	3	0.87	0.87	0.17	0.24	2.75
Total Nitrogen (TN) / %	4	0.87	0.87	0.02	0.02	2.91
pH	1	0.64	0.64	2.38	0.26	1.68
Phosphorous (P) / mg 100g^{-1}	1	0.00	0.00	1.72	1.95	0.99
3- Mespol Medlov, A.S.						
Total carbon (TC) / %	8	0.56	0.63	0.55	0.16	1.55
Organic carbon (OC) / %	9	0.66	0.70	0.43	0.13	1.72
Total Nitrogen (TN) / %	8	0.65	0.68	0.05	0.02	1.67
pH	9	0.76	0.78	1.50	0.30	1.99
Phosphorous (P) / mg 100g^{-1}	9	0.51	0.57	3.97	3.75	1.42
4- General models						
Total carbon (TC) / %	9	0.70	0.68	0.50	0.80	1.83
Organic carbon (OC) / %	9	0.74	0.64	0.51	0.59	1.95
Total Nitrogen (TN) / %	15	0.74	0.68	0.05	0.049	1.99
pH	12	0.66	0.72	1.92	0.32	1.69
Phosphorous (P) / mg 100g^{-1}	9	0.26	0.33	5.68	3.86	1.09

[a] latent variables.

[b] determination coefficient.

[c] root mean square error of prediction.

[d] residual prediction deviation (Standard deviation/root mean square error of prediction)

Table 4-3 Validation results of partial least squares regression (PLSR)-cross validation technique models on independent validation data set. Soil samples were collected from three European Farms, namely, Bramstrump Estate farm in Denmark (21 samples), Wimex farm in Germany (128 samples) and Mespol Medlov farm in Czech Republic (205 samples)

Property	R^2	Slope	Intercept	RMSEP	RPD
1- Bramstrup Estate					
Total carbon (TC) / %	0.89	1.24	0.09	1.10	3.15
Organic carbon (OC) / %	0.96	1.10	0.01	0.62	4.95
Total Nitrogen (TN) / %	0.93	1.17	0.01	0.06	3.88
pH	0.08	0.16	6.21	0.33	1.10
Phosphorous (P) / mg 100g^{-1}	0.37	0.28	4.15	1.72	1.40
2- Wimex					
Total carbon (TC) / %	0.74	0.84	0.42	0.70	2.00
Organic carbon (OC) / %	0.75	0.83	0.23	0.30	2.00
Total Nitrogen (TN) / %	0.75	0.79	0.03	0.03	2.10
pH	0.16	0.22	5.40	0.63	1.13
Phosphorous (P) / mg 100g^{-1}	0.16	0.07	7.15	12.02	0.97
3- Mespol Medlov, A.S.					
Total carbon (TC) / %	0.14	0.35	0.97	0.22	0.95
Organic carbon (OC) / %	0.12	0.53	0.58	0.19	1.07
Total Nitrogen (TN) / %	0.09	0.21	0.11	0.03	0.81
pH	0.30	0.38	0.93	0.30	1.31
Phosphorous (P) / mg 100g^{-1}	0.50	0.82	-1.47	4.41	0.88
4- General models					
Total carbon (TC) / %	0.83	0.98	0.28	0.66	2.45
Organic carbon (OC) / %	0.83	0.96	0.11	0.54	2.49
Total Nitrogen (TN) / %	0.79	0.99	0.01	0.05	2.21
pH	0.03	0.12	5.71	0.70	0.90
Phosphorous (P) / mg 100g^{-1}	0.01	0.07	8.57	8.36	0.92

[b] determination coefficient.
[c] root mean square error of prediction.
[d] residual prediction deviation (Standard deviation/root mean square error of prediction)

Soil P is a crucial soil nutrient for plant growth and yield and in this study its measurement with Vis-NIR spectroscopy was unsuccessful ($R^2 \leq 0.51$; RPD ≤ 1.42), which is also in line with most studies reporting on the use of this technique for soil analysis. To date, the most significant reports on successful measurement of P are those of Maleki *et al*. (2006) and Bogrekci & Lee (2005a). This underlines the need for further investigation to understand and improve the calibration accuracy of soil properties without direct spectral responses in the NIR range for soil components such as P.

4.3.2 General models

In a similar way to the farm individual models, the accuracies (R^2 and RPD) of the general calibration models for TC, OC and TN were good, emphasising the influence of the direct spectral responses of these properties in the NIR range (Tables 4-2 and 4-3). Furthermore, poor calibration results were obtained for properties without direct spectral responses such as pH and P (Tables 4-2 and 4-3). The accuracies of prediction of the general models in the independent validation (Table 4-3) were considerably larger (R^2 = 0.79 − 0.83 and RPD = 2.21 − 2.49 in the independent validation set) than those for Mespol Medlov, A.S. (R^2 = 0.09 − 0.14 and RPD = 0.81 − 1.07) and Wimex (R^2 = 0.74 − 0.75 and RPD = 2.0 − 2.1) farms only, but poorer than those of the individual models for the Bramstrup Estate farm. In spite of the fact that the mixed sample models were developed with a larger number of soil samples (403), they performed better than those of Mespol Medlov A.S. and Wimex farms, using a smaller number of soil samples of 205 and 128, respectively, which is a contradictory result to that reported by Guerrero *et al*. (2010). The larger sources of error caused by the larger variability in colour, texture and moisture content in the general models might explain the less successful output compared with the individual models for the Bramstrup Estate farm.

4.3.3 Prediction accuracy versus variation sample concentration

To investigate the reason for the different quality of results obtained with different models, we plotted RPD against the range and R^2 and RMSEP against SD of sample concentration obtained with the standard laboratory chemical analyses. Figures 4-1a, 4-1b and 4-1c show RPD variation with range for the three properties with direct spectral response (TC, OC and TN). A positive linear correlation of RPD with the concentration range (R^2 >0.97) was found for individual models of the three farms. The clear increase in RPD with the range explains the descending order of successful results obtained successively with models for Mespol Medlov, A.S., Wimex and Bramstrup Estate farms. In spite of the fact that general models have larger sample concentration ranges and SDs than all other individual farms, the greater soil variability (for example of colour, moisture content, soil texture, land management, parent material, etc) of the mixed sample set has resulted in deterioration of RPD and R^2 values. These results prove clearly that farms with small variations in concentrations of a particular property will lead to poor model accuracy. However, RMSEP increased with SD (Figures 4-2a, 4-2b and 4-2c), which demonstrates that, with increasing variability of sample concentration, the prediction error as compared with the chemical analysis (Saeys *et al*., 2005) also increases. Stenberg et al. (2010b) also discussed how the variation in soil organic matter (SOM) influences the prediction accuracy considered as RMSEP, and suggested that less soil variation expected at field scale would result in better calibrations than more general ones over larger geographic scales. Although R^2 and RPD values (Tables 4-2 and 4-3) indicate that the prediction of TC, OC and TN for Bramstrup Estate farm models was more successful than for other individual farms and general models because of the larger range of sample chemical concentration in both the calibration and validation sets (Table 4-1), the errors (RMSEP) expected from Bramstrup models are much larger. An opposite relationship between RPD and range to those for TC, OC and TN was found for pH (Figure 4-1d), and no clear relationship between RPD and the range was found for P (Figure 4-1e). A similar trend for the relationship between RPD and sample concentration range were obtained for the relationship between R^2 and SD for both groups with and without direct spectral

responses (Figure 4-2). As was the case of the Mespol Medlov A.S. model, the prediction of pH and P was poor for the Bramstrup Estate and Wimex farms, regardless of the concentration range and SD. This suggests that the variation of soil properties (both the range and SD), does not affect the prediction those without spectral responses, but does affect those properties with direct spectral responses.
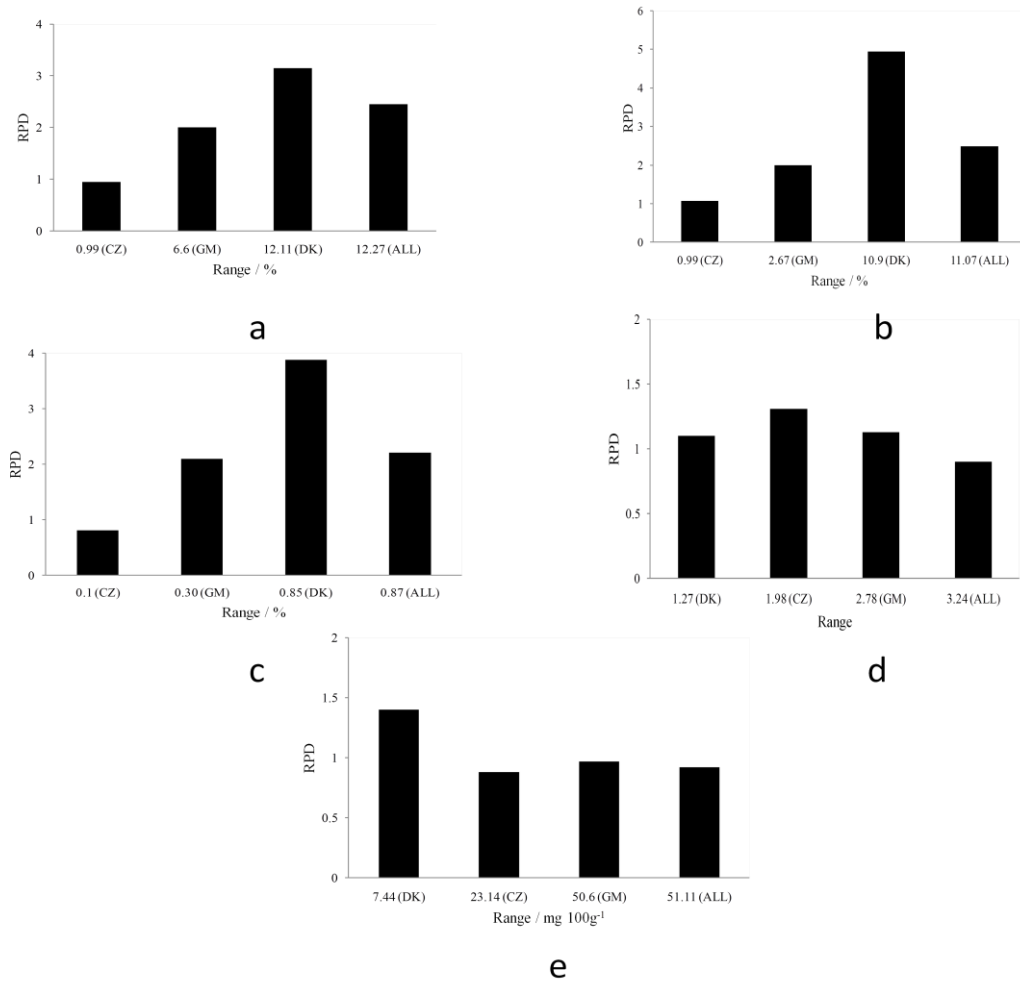
Figure 4-1 Variation of the residual prediction deviation (RPD) as a function of the sample concentration range in the validation set for (a) total carbon (TC), (b) organic carbon (OC), (c) total nitrogen (TN), (d) pH and (e) extractable phosphorous (P). Soil samples were collected from three European Farms, namely, Bramstrump Estate farm in Denmark (21 samples), Wimex farm in Germany (38 samples) and Mespol Medlov farm in Czech Republic (61 samples).

4.3.4 Analysis of prediction with different models

To explain the various measurements regarding different soil properties, we plotted the regression coefficients for TC, OC, TN, P and pH resulted from the general model. The distribution of regression coefficients over the entire wavelength range (450 – 2450 nm) studied shows distinguishable wavelength bands for almost all soil properties considered (Figure 5-3). These bands are in the Vis and NIR regions and might be attributed to energy absorption caused by colour, water, organic constituents and clay minerals in the soil. Two peaks in the Vis range at about 490 and 640 nm reflect the blue band around 450 nm and the red band around 680 nm.
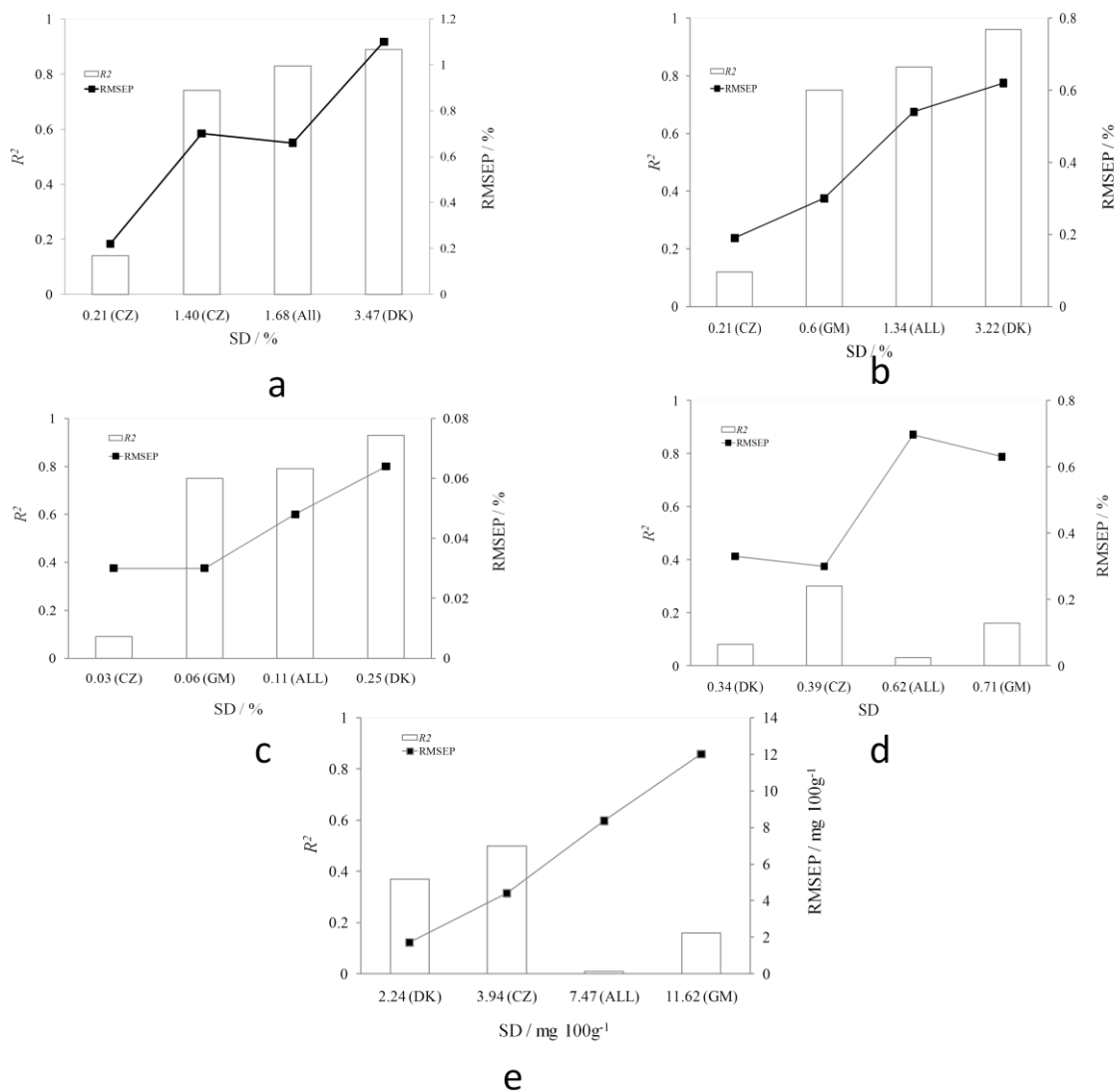
Figure 4-2 Variation of root mean square error of prediction (RMSEP) and R2 as a function of the sample standard deviation (SD) in the validation sets for (a) total carbon (TC), (b) organic carbon (OC), (c) total nitrogen (TN), (d) pH and (e) phosphorous (P). Soil samples were collected from three European Farms, namely, Bramstrump Estate farm in Denmark (21 samples), Wimex farm in Germany (38 samples) and Mespol Medlov farm in Czech Republic (61 samples)

It has been reported that the absorption band at 450 nm can be also caused by paired and single Fe^{3+} electron transitions to a higher energy state (Sherman & Waite, 1985). Another two peaks could be seen in Figure 4-3, which result from the water absorption bands in the third (960 nm) and second (1450 nm) overtone regions. However, the peak at 1450 nm was more evident with TC, OC, TN and P than with pH. It is clearly

demonstrated that the most active spectral region is that between 1800 and 2450 nm, where several distinct bands can be seen. These bands associate with the water absorption band in the first overtone region (1950 nm), clay minerals around 2300 nm, C-H + C-H, C-H + C-C, OH + minerals and N-H combinations (Mouazen *et al*., 2010). These peaks are much more evident with TC, OC and TN, than with pH and P. The regression coefficients of TC, OC and TN have similar trend and clearly defined peaks in both the Vis and NIR region. However, stronger peaks were found in the NIR region for TC, OC than for TN. Fewer and weaker peaks could be found in the Vis and NIR regions for P, and there was a 'flat' relationship for pH (Figure 4-3), both of which explain the unsuccessful measurement of these two properties.
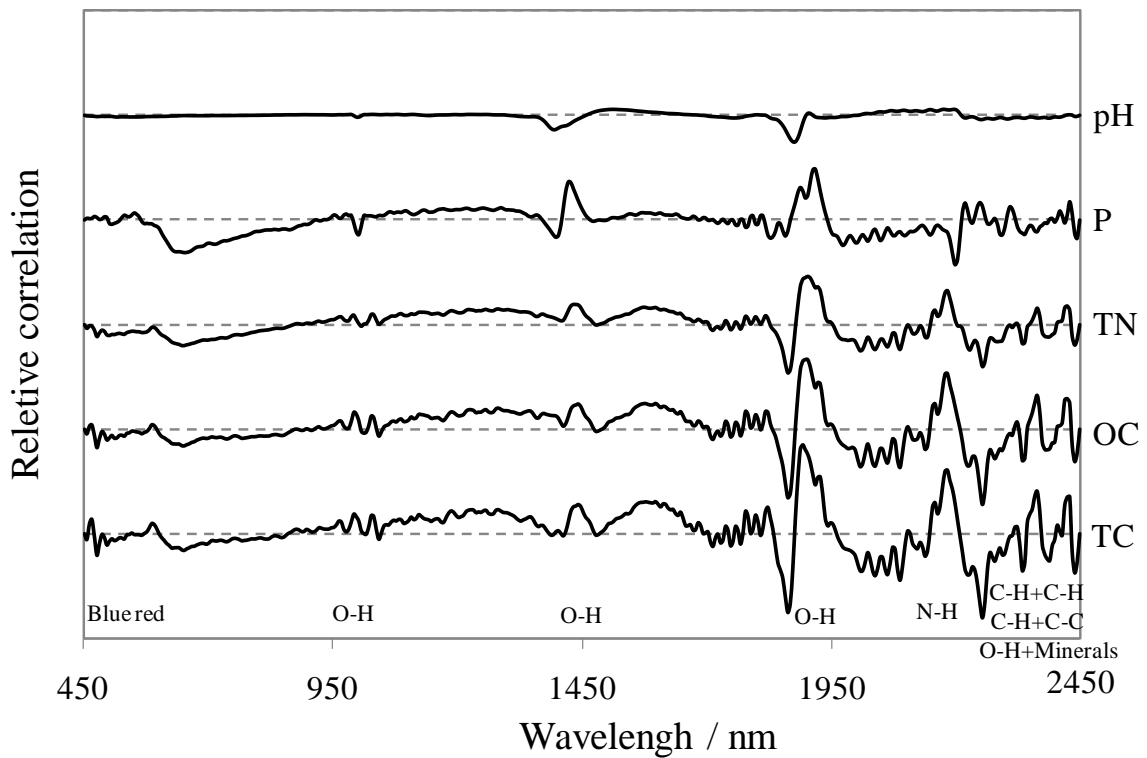
Figure 4-3 Regression coefficients distribution for total carbon (TC), organic carbon (OC), total nitrogen (TN), phosphorous (P) and pH over the entire wavelength obtained from the partial least squares regression (PLSR). Dotted lines representing zero correlation are separated by an equal factor of 1.5 for clarity of presentation

Table 4-4 shows the cross-linear correlations between all five soil properties studied on the basis of the chemical analysis values of the general calibration set (408 samples). Good correlations ($R^2 \geq 0.92$) between TC, OC and TN can be seen, whereas there were poor correlations between P and pH on the one hand and the spectrally active group of properties on the other hand.

Table 4-4 Pearson correlations (R2 value) between chemical analysis value of total carbon (TC), organic carbon (OC), total nitrogen (TN), phosphorous (P) and pH for all soil samples collected from Bramstrump Estate farm in Denmark (70 samples), Wimex farm in Germany (128 samples) and Mespol Medlov farm in Czech Republic (205 samples)

	TC	OC	TN	P	pH
TC	1				
OC	0.93	1			
TN	0.92	0.97	1		
P	0.01	0.01	0.02	1	
pH	0.01	0.05	0.06	0.13	1

The good correlation between TC and OC might be attributed to the extremely small contents of inorganic materials in the samples. The strong correlations between TC and TN, and that between OC and TN are because the N content in soil is almost entirely dependent on the organic matter content, and the overall TN: OC ratio is 1:10 (Martin *et al*., 2002).

4.4 Conclusions

Using four groups of soil sample sets collected from three European farms as experimental materials, Vis-NIR calibration models for TC, OC, TN, P and pH have been

developed and the calibration accuracy was assessed. On the basis of the results obtained, the following conclusions can be drawn.

First, except for one farm (Czech Republic), the calibration and validation of TC, TN and OC of individual farm models were successful. Results ranged as R^2 = 0.85-0.93 and 0.74-0.96 and RPD = 2.61-3.96 and 2.00-4.95, for the cross validation and independent validation, respectively. The poor prediction of pH and P was attributed to the fact that these two properties do not have direct spectral responses in the NIR range.

Second, independent farm-scale or field-scale models are not always the best performed models, because general calibration models covering several farms provide larger accuracy than individual farm calibration models developed with narrow range and SD of sample concentration.

Third, the SD and range of concentration of soil samples that explain the variability in the sample set are the determinant factors influencing the accuracy of calibration models. A larger SD and wider range of the calibration data set has resulted in larger R^2 and RPD values, but also larger RMSEP values. However, properties without direct spectral response showed inconsistent relationships and therefore they are independent of SD and range of sample concentration.

Finally, a small range of variation in sample concentrations will not result in successful calibration, as shown with the results from the farm in Czech Republic). Therefore, to build a multi-farm calibration models with farms of different European countries, a large variation range should be selected that does not lead to unacceptable accuracy because of large RMSEP values. In fact, a compromise solution should be sought during the selection of calibration sample set so that to cover a wide concentration range without increasing the measurement error above a desired threshold.

5 Effect of number of samples on prediction error

5.1 Introduction

The urgent need to double farm production over the next 25 years using smaller land and water resources, through further intensification of agriculture will inevitably involve substantial social, economical and environmental cost. One of the strategies to increase productivity and economic profits while conserving the environment is PA. PA is an environmental friendly strategy, in which farmers can vary input use and cultivation methods including application of seed, fertilizers, pesticides, water, planting and tillage to respond to variable soil and crop conditions across a field (Srinivasan, 2006). Conventional measurement of soil spatial variability needed for the implementation of PA usually involves manual soil sampling, sample pre-treatment, laboratory chemical and physical analyses and mapping. This procedure is very expensive and time consuming because the implementation of PA needs analysis of numerous soil samples to characterise the soil spatial variability in the field. Therefore, the development of fast, cost effective and environmental friendly methods for the measurement of soil spatial variability is a preliminary task for the implementation of PA.

The vis-NIR spectroscopy recently became a proven technique for a fast, inexpensive and relatively accurate alternative method to the laboratory analyses of soil properties (Viscarra Rossel & McBratney, 1998; Shepherd & Walsh, 2002; Mouazen *et al*, 2010; Stenberg *et al.*, 2010b). Today, intensive research is being carried out to establish new approaches, improve existing methods and combine several techniques of modelling to enhance the calibration accuracy of vis-NIR spectroscopy. Research indicates that

there is a debate on the optimal size of sample set to be used to build calibration models with the largest possible accuracy. This requires careful consideration, as recent reports showed this to affect the robustness and accuracy of the calibration models developed (Kuang & Mouazen, 2011). Although a large number of soil samples might be a better option to characterise the soil variability than a small sample set, the cost of analysing a larger number of samples would be significantly higher. In general, the spectral libraries need to include sufficient soil samples to account for the soil variability in the new target site, where the prediction will be carried out (Viscarra Rossel *et al.*, 2008; Guerrero *et al.*, 2010). However, this requirement is not always fulfilled due to the large number of soil samples needed (Shepherd and Walsh, 2002; Brown *et al.*, 2006). Spiking the local (target site) soil samples into the global or regional models proved to be an efficient way to improve the prediction accuracy of target field for some soil constituents (Shepherd & Walsh, 2002; Janik *et al.*, 2007, Viscarra Rossel *et al.*, 2008, Guerrero *et al.*, 2010). However, these studies did not compare the error resulting from calibration models established with a large number of samples with that of significantly smaller number of samples for *in situ* measurement conditions using fresh soil samples. Considering dried soil samples collected from one area in Spain, Guerrero *et al.* (2010) claimed that spiking could increase the prediction accuracy. The authors observed the important influence of the number of samples in the calibration set, which controls the adaptability of calibrations to target sites. They observed that a small-size model provided a better prediction accuracy of TN than large-size model. This conclusion is disputable because the authors did not use the same range of variation of soil properties for both the large-size and small-size models. Comparing the accuracy of general calibration models based on samples collected from three farms across Europe with that of farm specific calibration models for TC, TN and OC, pH and P, Kuang & Mouazen (2011) found that larger SD and wider variation ranges resulted in larger R^2 values and RPD, but also larger RMSEP. Authors did not test the effect of sample number on the calibration accuracy of these properties for farm-scale modelling. Therefore, it will be interesting to establish how the number of samples affects the farm-scale model accuracy when

the range of properties is kept constant. To our knowledge there is no report on the influence of the number of soil samples used for farm-scale calibration on the prediction error of models developed for the same range of variation of a soil property.

The aim of this study was to investigate the effects of the number of soil samples on the prediction error of farm-scale calibration models of TN, OC and MC developed using fresh soil samples collected from four farms in the Czech Republic, Germany, Denmark and the UK. This was important to evaluate, since a smaller number of sample needed for modelling would mean a reduction in cost of analysis with vis-NIR spectroscopy.

5.2 Material and methods

5.2.1 Soil samples

A total of 399 soil samples were used in this study. They were collected from four different farms in Europe, namely Mespol Medlov, A.S. (Czech Republic, http://farmsubsidy.org/CZ), Wimex (Germany, http://www.wimex-online.de), Bramstrup Estate (Denmark, http://www.bramstrup.dk) (Kuang & Mouazen, 2011) and Silsoe Farm (the UK). Bulked samples from 16 cores were collected from the upper soil layer (0-30 cm) in the spring of 2008 (Czech Republic and Germany), spring of 2009 (Denmark) and summer of 2009 (UK) and represented a diverse range of soil conditions. A total of 111, 70 ,128 soil samples were, respectively, collected from six fields in Mespol Medlov, A.S. farm in Czech Republic, five fields in Bramstrup Estate farm in Denmark, five fields in Silsoe farm in the UK and 36 fields at the Wimex farm in Germany. The number of samples taken from each field was depending on the field size and was collected randomly within the field with the aim of covering the whole field area. Table 5-1 provides information about the samples collected from different farms of this study.

About 200 g of soil was collected randomly for each sample and kept deep frozen (-18 °C) until analysis. After careful mixing, half of each of the samples from the Czech Republic, Germany and Denmark was sent to Leibniz Centre for Agricultural Landscape Research (ZALF) in Germany for soil chemical analyses for TN and OC and the second half was sent to Cranfield University for optical measurement and data analysis. Samples collected from the UK were subjected to both optical and chemical measurement at the National Soil Resources Institute (NSRI), Cranfield University.

Table 5-1 Sample information for four studied farms

Country	Nr of samples	Nr of Fields	Soil type	Farm size / ha	Sampling time
Czech Republic	111	6	Sandy, Clay, silt clay loam	2200	2008
Germany	128	36	Sandy, clay, silt loam	7000	2008
Denmark	70	5	Sandy loam, clay loam	300	2009
UK	90	5	Sandy loam, clay loam, clay	120	2009

5.2.2 Chemical analysis

The measurements of OC and TN were done by a TrusSpecCNS spectrometer (LECO Corporation, St. Joseph, MI, USA) using the Dumas combustion method. The MC was measured by oven drying the samples at 105°C for 24 hour.

5.2.3 Optical measurement

Each soil sample was placed in a glass container and mixed well, after big stones and plant residues were removed. Then each soil sample was placed into three Petri dishes, which were 2 cm deep and 2 cm in radius. The soil in the Petri dish was shaken and pressed gently before levelling with a spatula. A smooth soil surface ensures maximum light reflection and high signal-to-noise ratio (Mouazen *et al.*, 2005).

The soil samples were scanned in diffuse reflectance mode by an AgroSpec mobile, fibre type, vis-NIR spectrophotometer (tec5 Technology for Spectroscopy, Germany), with a measurement range of 305-2200 nm. Although this spectrophotometer does not cover the entire wavelength range in the NIR region, it was selected in this study as it uses diode array detectors, which proved to be stable under on-line measurement conditions (Mouazen *et al.*, 2009). A 20 watt halogen lamp was used as a light source. A 100 % white reference was used before scanning, which was repeated every 30 minutes. Three replicates were considered for each sample and a total of 10 scans were collected from each replicate.

5.2.4 Data pre-treatment and establishment of calibration models

The triplicate raw spectra were averaged to one spectrum, followed by noise cut on both sides arriving at a wavelength range of 371 - 2150 nm. A three-point (wavelength) average was applied in the visible range and 10-point average was applied in the NIR range. This was followed successively by maximum normalisation, Savitzky-Golay (S-G) first derivative and S-G smoothing. Normalisation is typically used to get all data to approximately the same scale, or to get a more even distribution of the variances and the average values. The maximum normalisation method is a normalisation that "polarizes" the spectra. The peaks of all spectra with positive values scale to +1, while spectra with values negative values scale to -1. Since all the soil spectra in this study had positive values, the peaks of these spectra scaled to +1 (Mouazen *et al.*, 2005). Spectra were then subjected to the S-G first derivative (Martens and Naes, 1989). This method enables computing the first or higher-order derivatives, including a smoothing factor, which determines how many adjacent variables will be used to estimate the

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polynomial approximation used for derivatives. A second order polynomial approximation was selected. A 2:2 smoothing was carried out after the first derivative to remove noise from the measured spectra. The same pre-treatment was used for all properties, using Unscrambler 7.8 software (Camo Inc.; Oslo, Norway).

The pre-treated spectra and the laboratory measurement were used to develop calibration models for the three soil properties, namely, OC, TN and MC. To study the effect of the number of samples of the calibration set on the prediction error, two types of calibration models were developed, namely large-size and small-size dataset models. For the former models, two-thirds of soil samples from each farm were randomly selected. From these two-third sample sets, 25 samples were randomly selected to develop the small-size dataset models. Particular attention was paid to ensure that the selection of 25 samples was carefully done to cover the full range of variation in soil properties on a farm. To eliminate the effect of different ranges of concentration of a property on the prediction error, the ranges were kept identical in both the calibration and prediction sets for both the large-size and small-size dataset models. The selection of calibration-prediction samples and the validation of PLS regression models were performed in the following sequences (Figure 5-1):
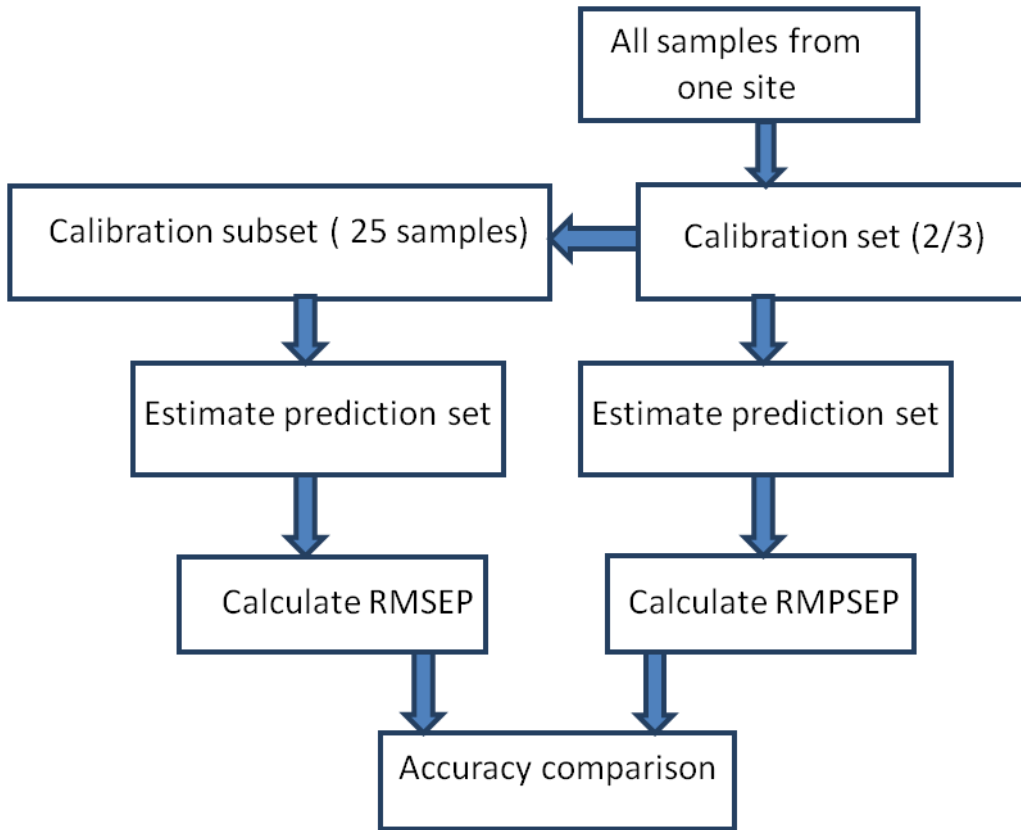
Figure 5- 1 Flow chart of steps considered during the model calibration and prediction set for the small-
and large-size dataset models

Table 5-2 Sample statistics of laboratory results of both large- and small-size calibration sets of samples collected from Mespol Medlov farm in Czech Republic (111 samples), Wimex farm in Germany (128 samples, Bramstrump Estate farm in Denmark (70 samples) and Silsoe farm in the UK (90 samples)

Property	Farm	Sample number	Calibration set				
			Min	Max	Mean	Range	SD
TN / g kg^{-1}	CZ	74	1.34	2.09	1.60	0.75	0.24
	CZ	25	1.34	2.09	1.66	0.75	0.25
	GM	84	0.35	4.84	1.51	4.45	0.78
	GM	25	0.35	4.80	1.51	4.45	0.79
	DK	46	0.72	1.64	1.28	0.92	0.20
	DK	25	0.72	1.64	1.28	0.92	0.22
	UK	62	0.92	3.07	1.80	2.15	0.50
	UK	25	0.92	3.07	1.90	2.15	0.60
OC / g kg^{-1}	CZ	74	10.65	22.78	14.90	12.13	2.60
	CZ	25	10.65	22.78	15.40	12.13	3.00
	GM	84	4.58	76.10	18.00	71.52	15.00
	GM	25	4.58	76.10	20.22	71.52	16.80
	DK	46	7.50	16.79	12.60	9.29	2.20
	DK	25	7.50	16.79	12.90	9.29	2.40
	UK	62	8.51	29.42	18.00	20.91	4.90
	UK	25	8.51	29.42	18.30	20.91	5.70
MC / g kg^{-1}	CZ	74	92.30	216.00	148.80	123.70	27.50
	CZ	25	92.30	216.00	148.80	123.70	34.60
	GM	84	55.10	330.50	157.20	275.40	45.30
	GM	25	55.10	330.50	158.40	275.40	54.90
	DK	46	82.40	131.00	101.10	48.60	12.20
	DK	25	83.10	131.00	102.00	48.60	12.90
	UK	62	86.48	268.80	165.19	182.38	44.30
	UK	25	86.48	268.80	171.60	182.38	48.50

The accuracy of models developed was evaluated by comparing values of the root mean square error of cross validation (RMSECV), RMSEP and bias in prediction. Bias was also considered to evaluate whether differences in RMSEP is due to bias or to the number of samples used in the calibration set.

1- The entire soil spectra for each farm were divided into calibration (two-third) and prediction (one-third) sets. The sample statistics for these two sets are provided in Tables 5-2 and 5-3, respectively.

2- A subset was selected from calibration samples, which was used as the small-size calibration set.

Table 5-3 Sample statistics of laboratory results of prediction set with samples collected from Mespol Medlov farm in Czech Republic, Wimex farm in Germany, Bramstrump Estate farm in Denmark, and Silsoe farm in the UK

Property	Farm	Sample number	Prediction set				
			Min	Max	Mean	Range	SD
TN / g kg^{-1}	CZ	36	1.3	2.1	1.6	0.8	0.2
	GM	44	0.6	3.1	1.5	2.5	0.6
	DK	24	1.0	1.6	1.3	0.6	0.2
	UK	28	1.3	3.1	2.1	1.8	0.6
OC / g kg^{-1}	CZ	36	12.0	19.8	14.5	7.8	1.8
	GM	44	7.2	71.5	18.1	64.2	11.9
	DK	24	9.7	17.2	12.9	7.5	1.8
	UK	28	12.2	30.2	20.3	18.1	5.4
MC / g kg^{-1}	CZ	36	96.9	197.0	150.1	100.1	25.8
	GM	44	95.4	280.9	160.0	185.5	42.3
	DK	24	85.8	128.6	104.6	42.8	14.6
	UK	28	112.2	276.6	187.8	164.4	58.4

3- The calibration spectra of the large-size and small-size datasets were subjected to a partial least squares regression (PLSR) with leave-one-out cross validation using an Unscrambler 7.8 software (Camo Inc.; Oslo, Norway).

4- Both the small-size and large-size dataset models were validated on the same prediction set, extracted in step 1.

Further analysis was considered to evaluate the effect of different-size datasets of the calibration set models on prediction accuracy. This was done for the Wimex farm only, which was considered as an example. The number of samples in the calibration set was

25, 50, 75, and 100. Those 4 different-size dataset models were validated using the same 28 samples used as prediction set.

5.3 Results and discussion

5.3.1 Prediction accuracy of models developed with large-size datasets

Table 5-4 summarises values of R^2, RPD, RMSEPCV and RMSEP, resulted from the large- and small-size dataset models for the prediction of TN, OC and MC. The accuracy of calibration and prediction varies from property to property and farm to farm.

Examining values of R^2 and RPD, which is the standard deviation divided by RMSEP obtained from the large-size dataset models in all four farms, reveals that the prediction of soil MC is the most successful, as compared to OC and TN with R^2 = 0.80-0.96 and RPD = 1.98-4.69 for the calibration set and R^2 = 0.74-0.92 and RPD = 1.63-4.57 for the prediction set. The accuracy of predicting OC (R^2 = 0.58-0.90 and RPD = 1.30-3.08 for the calibration set and R^2 = 0.47-0.90 and RPD = 0.97-3.28 in the prediction set) is similar to that of TN (R^2 = 0.61-0.88, RPD = 1.27-3.33 for the calibration set and R^2 = 0.54-0.90, RPD = 1.19-3.33 in the prediction set), because OC and TN are strongly correlated (Table 5-5). Using crushed and air-dried soils samples, Brunet et al. 2007 reported farm scale calibration models accuracy for TN with square error of prediction (SEP) = 0.03-0.39 g kg^{-1}, which is comparable or higher than the majority of RMSEP values in this study (Table 6-4) even when fresh soil samples are used. Similarly, Moron and Cozzolino (2002) have built a farm scale organic carbon calibration model with RMSEP =5 g kg^{-1}, which is higher than most of farm scale models' RMSEP values reported in this study. The values of the RMSECV and RMSEP reported in Table 5-4 for MC are smaller than those reported by other researchers with similar scale of calibration (Dalal *et al.*, 1986; Slaughter *et al*. 2001; Mouazen et al. 2005).

Table 5-4 Comparison of root mean square error of prediction in cross-validation (RMSEP-cv) and in prediction set (RMSEP), ration of prediction deviation (RPD) and R2 of total nitrogen (TN), organic

carbon (OC) and moisture content (MC) between large and small dataset-size models in Mespol Medlov farm in Czech Republic (CZ), Wimex farm in Germany (GM), Bramstrump Estate farm in Denmark (DK) and Silsoe farm in the UK

Property	Farm	Sample number	Calibration set					Prediction set		
			LVs	R^2_{CV}	RPD$_{-CV}$	RMSEP-cv / g kg^{-1}	R^2_{Pre}	RPD$_{-Pre}$	RMSEP, / g kg^{-1}	Bias
	CZ	74	3	0.63	1.41	0.17	0.61	1.27	0.15	-0.002
	CZ	25	2	0.57	1.32	0.19	0.54	1.19	0.16	0.002
	GM	84	3	0.85	2.69	0.29	0.74	1.91	0.32	-0.003
TN	GM	25	3	0.86	2.32	0.34	0.67	1.42	0.43	0.003
	DK	46	9	0.81	2.40	0.05	0.68	1.60	0.10	-0.004
	DK	25	2	0.66	1.47	0.15	0.69	1.45	0.11	-0.004
	UK	62	5	0.83	3.13	0.16	0.88	3.33	0.18	0.006
	UK	25	4	0.90	3.33	0.18	0.88	2.61	0.23	-0.001
	CZ	74	5	0.65	1.44	1.80	0.58	1.35	1.33	-0.022
	CZ	25	1	0.63	1.30	2.30	0.47	0.97	1.85	0.083
	GM	84	5	0.85	2.94	5.10	0.77	1.86	6.40	-0.165
OC	GM	25	7	0.87	2.63	6.40	0.71	1.59	7.50	0.070
	DK	46	6	0.86	2.82	0.78	0.61	1.58	1.14	-0.051
	DK	25	4	0.86	2.18	1.10	0.66	1.49	1.21	0.008
	UK	62	4	0.90	3.08	1.59	0.82	2.66	2.03	0.038
	UK	25	3	0.90	3.28	1.74	0.82	2.35	2.30	-0.001
	CZ	74	1	0.88	2.75	10.01	0.87	2.55	10.11	0.105
	CZ	25	1	0.85	2.37	14.60	0.79	1.82	14.20	0.800
	GM	84	4	0.90	3.04	14.90	0.80	1.97	21.50	-0.480
MC	GM	25	3	0.88	2.92	18.80	0.76	1.83	23.10	-0.390
	DK	46	3	0.96	4.69	2.60	0.84	2.23	6.55	-0.260
	DK	25	1	0.80	1.98	6.50	0.75	1.63	8.95	-0.390
	UK	62	5	0.96	4.57	9.70	0.93	4.49	13.00	-0.057
	UK	25	4	0.92	3.54	13.70	0.92	3.82	15.30	-0.179

All calibration models developed provide small RMSE, not only in the calibration set, but also in the prediction set (Table 5-4). The lowest prediction error (the smallest RMSEP) for the three properties studied, in both the calibration and prediction sets is for the farm in Denmark (Table 5-4), which is successively followed by the results for the Czech Republic, UK and German farms. These results confirm the conclusion obtained from a previous study (Kuang and Mouazen, 2011) that a larger range in

concentration range or a larger SD of samples in the calibration set result not only in higher R^2 and RPD, but also in higher RMSEP values. The smaller variation ranges of the three properties (Tables 5-2 and 5-3) reported for the Denmark farm is the reason explaining why this farm had the smallest RMSEP, as compared to the other three farms. For a successful calibration, it is recommended to cover the widest possible variation range in soil properties, so that the prediction is feasible for any new field or farm with any concentration range that falls within the range of concentration of the calibration model. However, when the range of concentration of a property has to be decided in advance, the most meaningful criteria is RMSEP, as end users are interested to work with the smallest errors. A compromise selection of the range of variation should be made to cover a wide range of variation while preserving low RMSEP. Because the range of variation of soil properties was kept identical between the small-size dataset and the large-size dataset models in the calibration and prediction sets for all four farms, the only criterion that could be used to assess accuracy was the RMSEP.

5.3.2 Comparison between large- and small-size dataset models

Comparing the accuracy of the large-size dataset models with corresponding small-size dataset (25 samples) models, estimated as R^2 values, provide mixed results for all four farms in both the calibration and prediction, although the former results in a higher accuracy in majority of farms. Regarding RPD, large-size models provided higher RPD values than the small-size models in both the calibration and prediction sets. Also, since the range was kept identical in the calibration and prediction sets, the RMSEP is the most valuable parameter to consider, as this reflects the error. Figure 5-2a, 5-2b and 5-2c show the RMSEP values calculated for TN, OC and MC, respectively, to be lower for the large-size dataset models than for the small samples-size models (in both the calibration and validation sets). However, the error differences between the two sets vary from farm to farm. Comparing the number of latent variables (LVs) used during PLS in both the large- and small-size dataset calibration sets (Table 5-4), slight increases in the number of LVs for the former, as compared to the latter set can be observed. In some cases, the same LVs are used for both cases, whereas in another

case a larger number of LVs is used to develop the small-size dataset model (e.g. for OC model in the German farm). Furthermore, a similar conclusion can be drawn if values of the bias of the two modelling procedures are compared (Table 5-4). The absolute values of bias are relatively very small compared to RMSEP, thus the influence of bias is not important.

Furthermore, examining the scatter plot of the measured versus predicted values, no samples can be observed as outliers that might explain the higher RMSEP values of small-size datasets. The scatter plots for measured and predicted TN, OC and MC in both calibration and prediction sets obtained for Silsoe farm are shown, respectively, in Figures 5-3, 5-4 and 5-5, as an example. Therefore, it can be concluded that differences in RMSEP values resulted from the two-size dataset models can be barely attributed to the number of LVs, present of outliers in the data sets or bias, which confirms that these differences are mainly due to different the number of samples considered during the development of calibration models for MC, OC and TN. There are two subgroups of soil samples in the data set, which are because the physical and chemical values of MC, OC and TN in one farm are significantly higher than that of other farms.
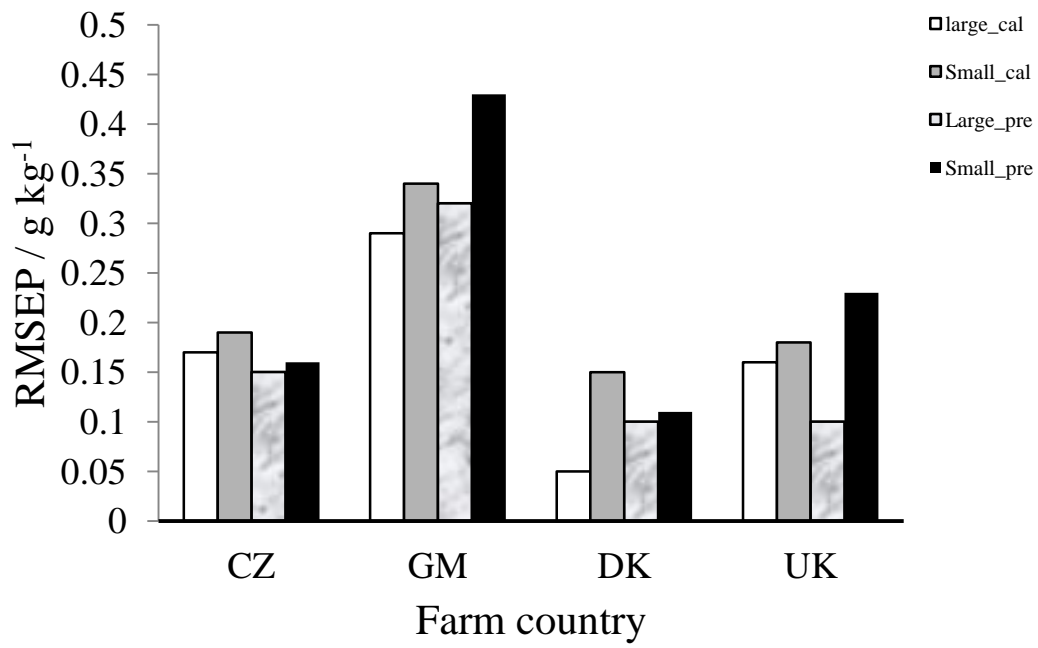
(a)
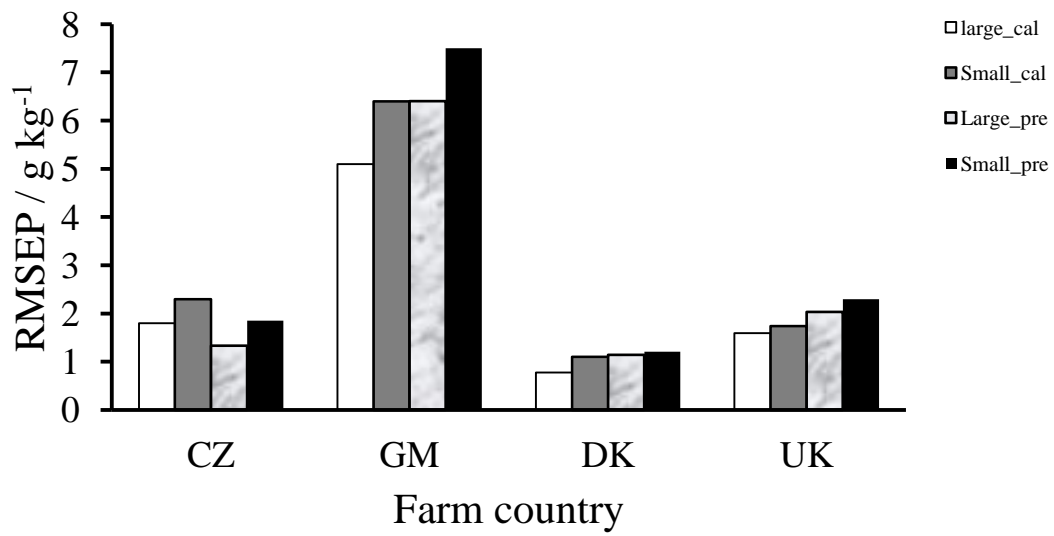
(b)
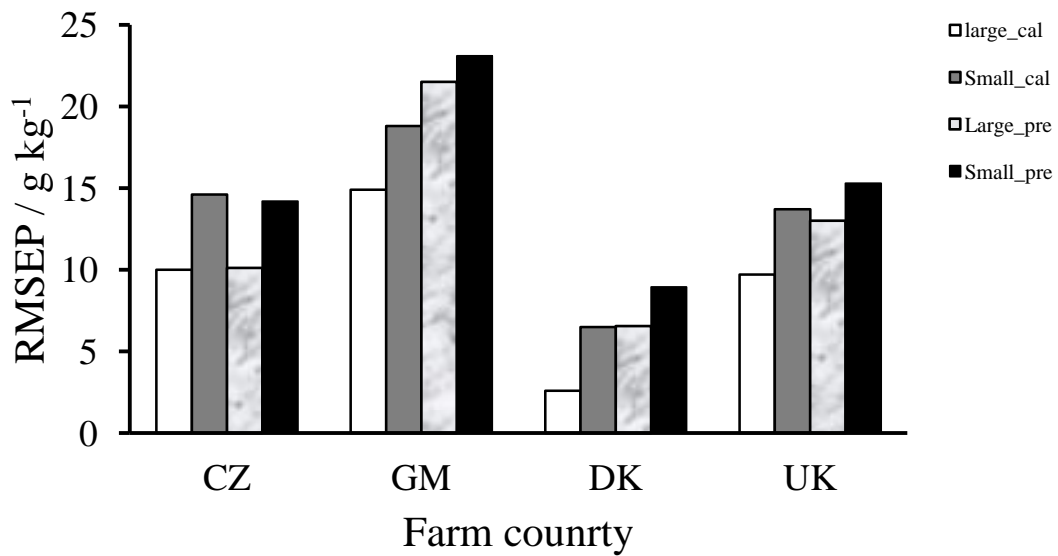
(c)

Figure 5-2 Comparison of root mean square error of prediction (RMSEP) in prediction set of (a) total nitrogen (TN), (b) organic carbon (OC) and (c) moisture content (MC) between large- and small-size sample models

For global and local calibration schemes using dry soil samples, Shepherd and Walsh (2002) reported a decrease in R^2 and an increase in RMSEP values with the reduction in the number of soil samples used for calibration, which is in line with the results obtained in this study for farm-scale modelling under *in situ* measurement conditions. Guerrero *et al*. (2010) achieved more accurate calibration (higher R^2 and lower RMSEP) for local, small-size dataset models, after spiking with a few local samples, than models derived from very large libraries. This was attributed to the fact that, among the large number of samples in the very large library, there were only few soil samples that could describe the variability of the target fields. Since Guerrero *et al*. (2010) did not consider the same range of variation when comparing the performance of the small sample model with the large sample model, the lower RMSEP of the former model, as compared to that of the latter model, might result from the narrow range of concentration (Kuang and Mouazen, 2011). Wetterlind *et al.* (2008) reported a successful farm scale calibration model for soil organic matter using 25 soil samples only, but with a relatively high RMSEP of 3.2 gkg[-1], high R^2 of 0.89 and RPD of 3.0.
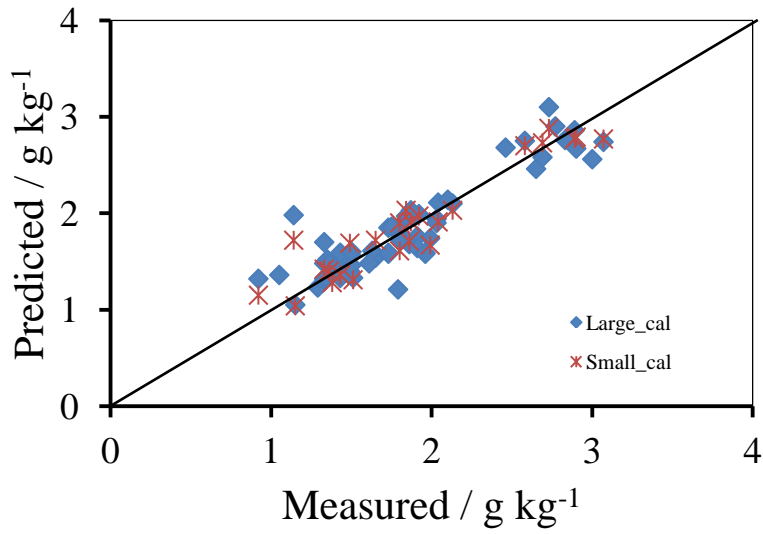
(a)
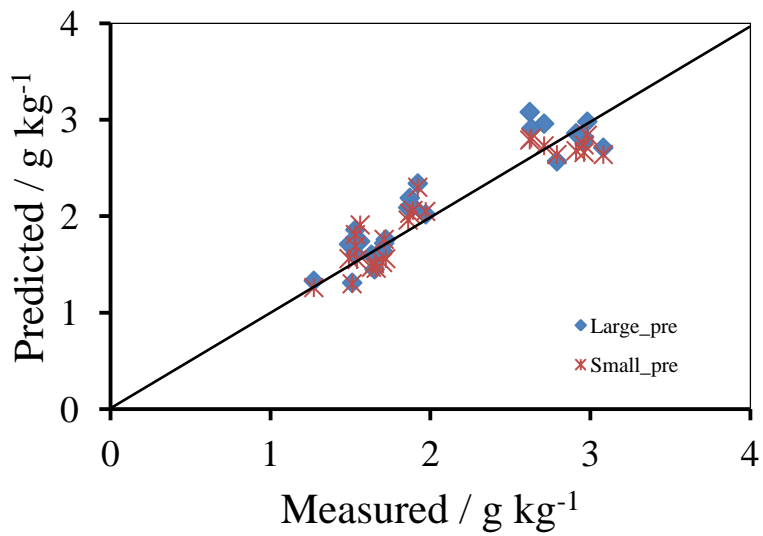
(b)

Figure 5- 3Scatter plots of predicted versus measured moisture content (MC) shown for Silsoe Farm in the UK, as an example for (a) large- and small-size dataset models in cross-validation, (b) large- and small-size dataset models in prediction set

Authors did not make it explicitly clear whether or not RMSEP could be improved by increasing the number of soil samples used for model development.
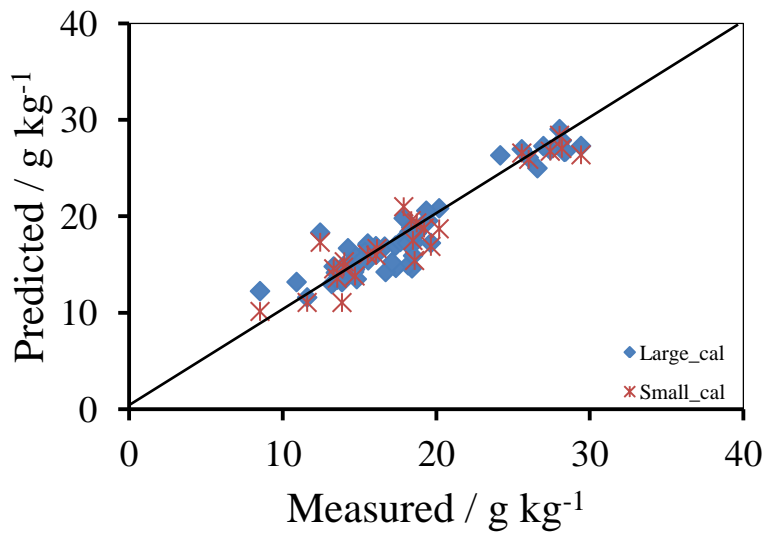
(a)
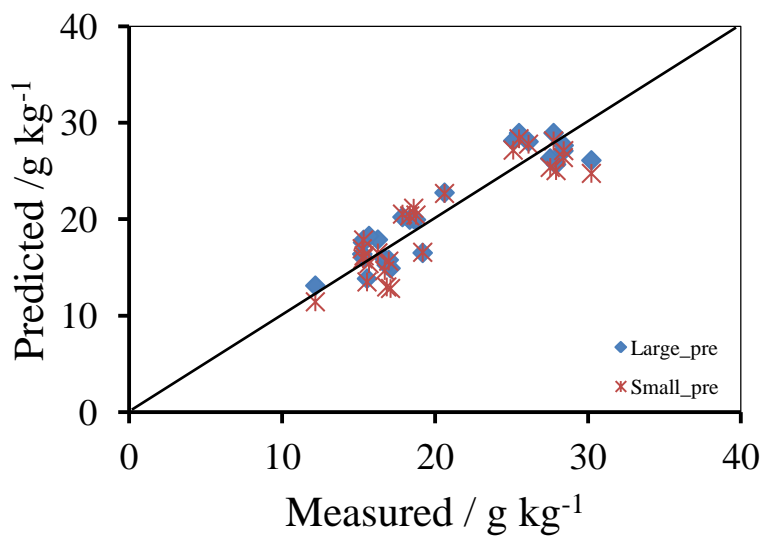
(b)

Figure 5- 4 Scatter plots of predicted versus measured organic carbon (OC) shown for Silsoe Farm in the UK, as an example for (a) large- and small-size dataset models in cross-validation, (b) large- and small-size dataset models in prediction set
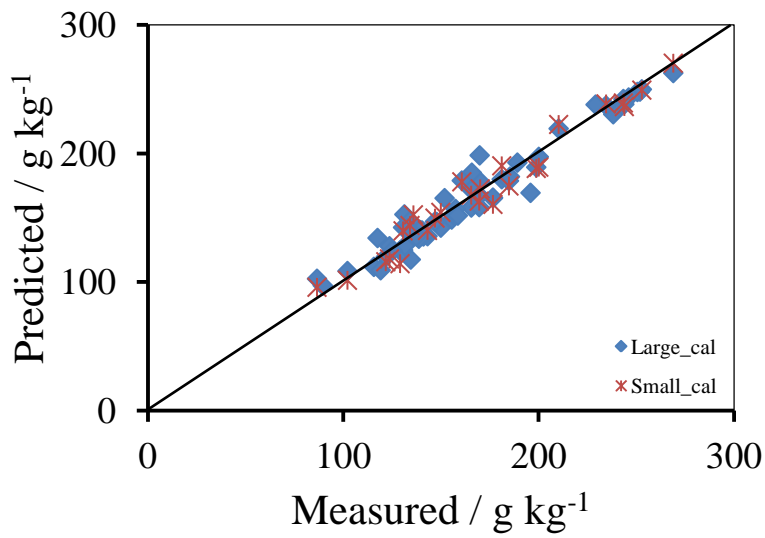
(a)
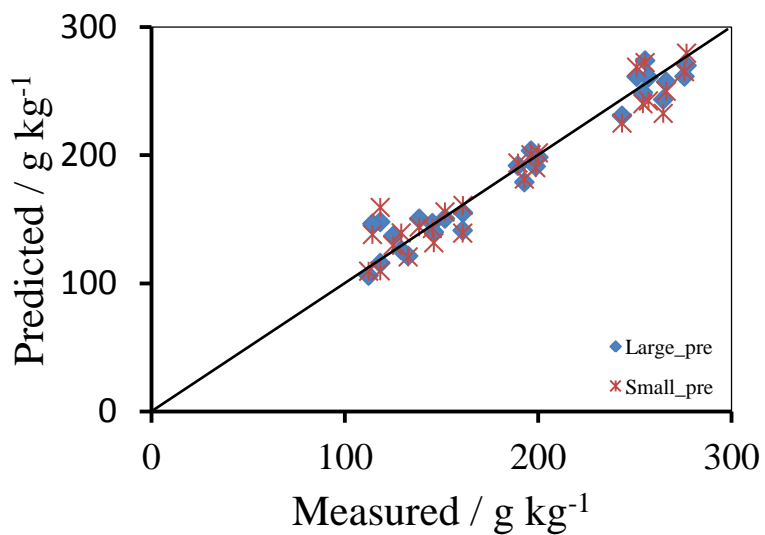
(b)

Figure 5- 5 Scatter plots of predicted versus measured moisture content (MC) shown for Silsoe Farm in the UK, as an example for (a) large- and small-size dataset models in cross-validation, (b) large- and small-size dataset models in prediction set

Compared to other reports, the current study proves that large-size dataset models (> 25 samples) for TN, OC and MC result in smaller RMSEP values, compared to small-size

dataset models of 25 samples, when the same concentration range is considered in both calibration sets.

5.3.3 Effect of dataset size on prediction error

Although, the increase in the number of samples can improve the prediction accuracy in terms of RMSEP, analysing large number of samples results in a significant increase in the cost of model development.

Table 5-5 Pearson correlations (*r* value) between chemical analysis value of total nitrogen (TN), organic carbon (OC) and moisture content (MC) using soil samples collected from Mespol Medlov farm in Czech Republic, CZ (111 samples), Wimex farm in Germany, GM (128 samples), Bramstrump Estate farm in Demark, Dk (70 samples) and Silsoe Farm in the UK (90 samples)

Farm	Number of samples		TN	OC	MC
CZ	111	TN	1		
		OC	0.79	1	
		MC	0.10	0.05	1
GM	128	TN	1		
		OC	0.85	1	
		MC	0.91	0.81	1
DK	70	TN	1		
		OC	0.99	1	
		MC	0.97	0.98	1
UK	90	TN	1		
		OC	0.96	1	
		MC	0.85	0.84	1

To optimise the number of soil samples to be considered in the calibration set, so as to achieve accurate results at minimal cost, 25, 50, 75 and 100 soil samples from Wimex farm (Germany) were used to build four calibration models for MC, OC and TN. These models were validated on the same prediction set of 28 samples. Table 5-6 and Figure 6-6 illustrate the decrease in RMSEP with increase the size of sample set. However, the rate of decrease varies, with the largest decrease occurring between models of 25 and

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50 samples. This is particularly true for TN (Figure 5-6a) and OC (Figure 5-6b), whereas linear decrease is observed for MC.

Table 5-6 Comparison of root mean square error of prediction in cross-validation (RMSEP-cv) and in prediction set (RMSEP-pre) and bias in prediction set of total nitrogen (TN), organic carbon (OC) and moisture content (MC) for different dataset-sizes models in Wimex farm in Germany (GM)

Property	Sample number	Latent variables	RMSEP-cv / g kg^{-1}	RMSEP / g kg^{-1}	Bias$_{-pre}$
TN		10	0.21	0.28	-0.05
OC	100	6	4.20	6.40	-0.03
MC		2	14.10	19.80	-0.37
TN		11	0.24	0.28	-0.01
OC	75	8	4.60	6.80	-0.04
MC		2	15.30	20.90	0.54
TN		10	0.27	0.28	-0.06
OC	50	7	5.10	7.10	-0.02
MC		1	16.80	21.70	-0.34
TN		9	0.34	0.43	-0.01
OC	25	8	6.40	7.80	-0.36
MC		2	18.30	23.40	-0.22
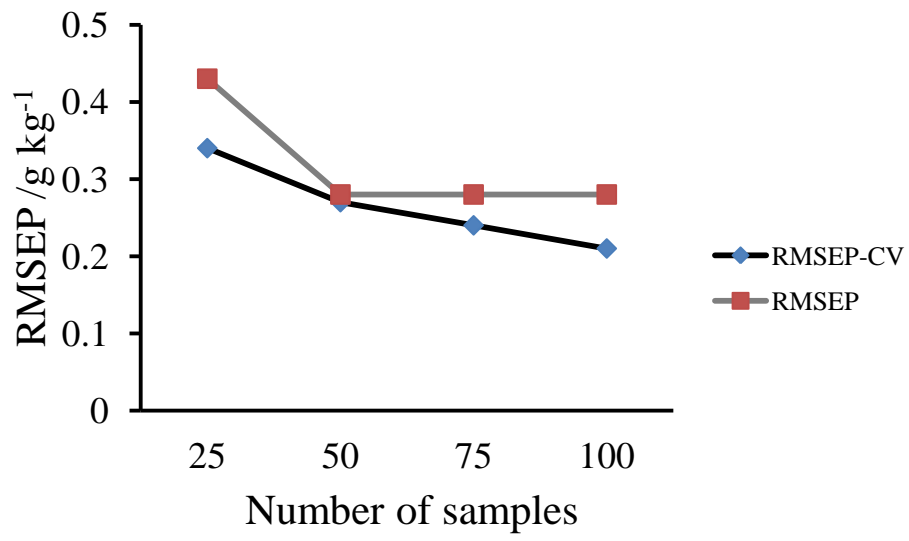
(6)
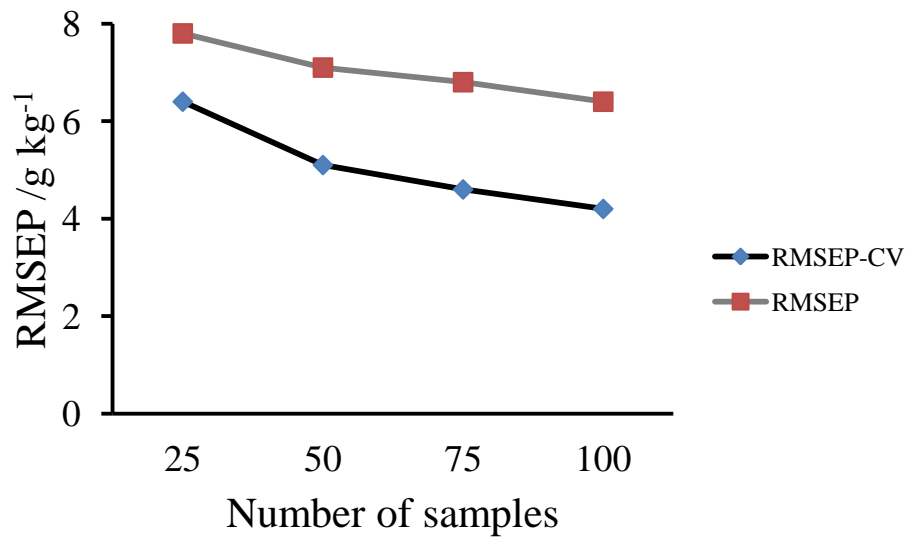
(6)
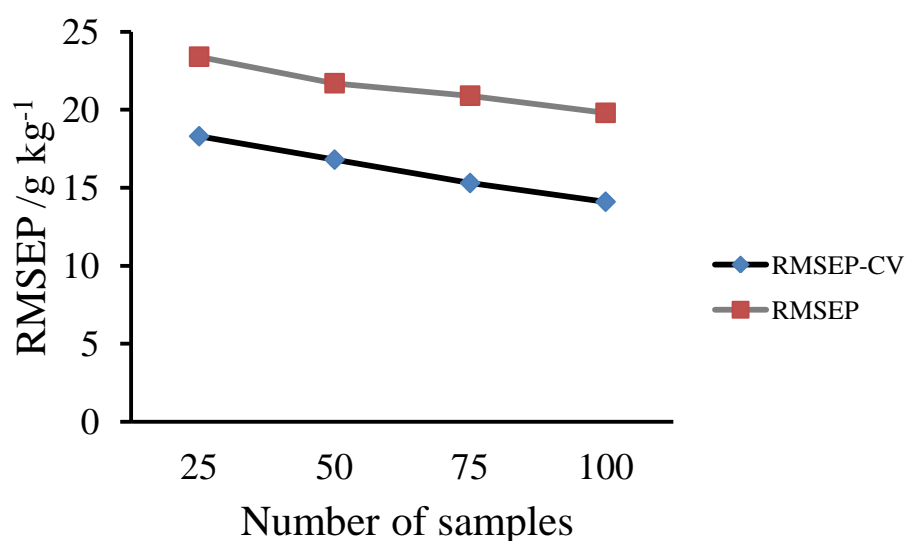
(6)

Figure 5- 6 Comparison of root mean square error of prediction obtained from calibration models developed with different sample number in both cross-validation (RMSEP-cv) and independent validation set (RMSEP) for Wimex farm in Germany for TN (6a), OC (6b) and MC (6c)

Although, no tipping point between sample number and RMSEP can be deducted, a minimum of 50 soil samples is recommended to obtain a reasonable accuracy at a minimal cost for farm-scale calibration of vis-NIR spectroscopy for MC, OC and TN. A balance between accuracy and cost has to be made to select the optimal number of samples in the calibration set, which will be governed by the degree of accuracy required for a given application of model output.

5.4 Conclusions

This study investigated the influence of the dataset size of the calibration set on prediction error of MC, OC and TN with the vis-NIR spectroscopy under *in situ* (using fresh samples) measurement conditions at farm-scale in four different European countries. The following conclusions can be drawn from the results:

1. Individual farm-scale models for the four European farms can be successfully established with good accuracy.

2. When the same range of variation of a given soil property was preserved, the RMSEP is the best indicator of accuracy; this is important because farmers and land managers are interested in the error of measurement of soil properties.

3. The large sample data set models produced lower RMSEP than the small sample data set models (25 soil samples), in both the calibration and prediction sets for the three soil properties studied.

4. The RMSEP decreases with sample number in linear fashion for MC, whereas for OC and TN the largest decrease occurred between models with 25 and 50 samples.

Overall, how many samples should be chosen for farm scale calibration models for MC, OC and TN depends on accuracy required. However, using around 50 soil samples to establish calibration models for MC, OC and TN at farm-scale modelling is considered appropriate, as it will result in smaller prediction errors than other models with smaller sample numbers. Increasing the number of samples beyond 50 samples would lead not only to increase accuracy but also to increase cost. In the future, field scale models might need to be developed to establish a quantitative relationship between number of samples and RMSEP.

6 Effect of soil moisture and texture on laboratory, *in situ* and on-line prediction

6.1 Introduction

Soil OC is a key property for soil functioning, soil quality maintenance, plant nutrition supply and soil moisture content holding (Flessa et al., 2000). It is the major component of soil organic matter, which is important in all soil processes. Shortages of OC result in decline of soil quality and crop production over the field. There is a continuous cycle of OC in soils that is not uniform and dependent on mostly land use and land management systems. Therefore, even small changes in OC stocks cause important CO_2 fluxes between terrestrial ecosystems and the atmosphere (Stevens et al., 2006). Soil OC is also important component to evaluate soil resistivity to wind and water erosion (Morgan, 2005). Nitrogen is another important nutrient for plant and sufficient N fertilizer application is critical for normal plant growth and development. It is in chlorophyll and therefore essential for photosynthesis and crop protein. However, over application of N fertilisers result not only in economical losses but ground water contamination is to be expected. Nitrate leaching from land to ground water and stream water causes depleting soil minerals, acidifying soils and affecting downstream water system and coastal marine ecosystems (Vitousek et al., 1997). PA is an environmental friendly strategy, in which farmers can vary input use and cultivation methods including application of seed, fertilizers, pesticides, water, planting and tillage to respond to variable soil and crop conditions across a field (Srinivasan, 2006). Hence, PA can increase the crop productivity while reduce fertiliser application and preserve the environment. Determination of within field variation in soil OC and TN at high resolution sampling is one of the prerequisites for the implementation of PA.

During the last two decades, vis-NIR spectroscopy has proved to be a fast, cost effective, non-destructive and a relative accurate alternative method to the traditional laboratory analytical methods of soil physical, chemical and biological properties

(Shepherd & Walsh, 2002; Brown *et al.*, 2006; Wetterlind et al., 2008; Mouazen et al., 2010). Although the application of vis-NIR spectroscopy has considerably reduced the labour and time for the analysis, soil sample preparation for laboratory analysis including drying, grinding and sieving is still tedious. For *in situ* and on-line measurements with vis-NIR, calibration models developed from dried, ground and sieved samples cannot be utilised, since these measurements are performed with fresh (unprocessed) soils (Mouazen et al., 2005). Although MC can be successfully measured with vis-NIR spectroscopy, it is considered as one of the most critical factors that negatively affect the accuracy of measurement of other soil properties (Bogrekci & Lee, 2006; Lobell & Asner, 2001; Minasny et al. 2011; Mouazen et al. 2006b; Sudduth & Hummel, 1993). Modifications for removing the influence of MC on the accuracy of vis-NIR measurement of soil properties have been considered by the classification of samples into different MC groups (Mouazen et al. 2006b), adoption of an external parameter orthogonalisation (EPO) algorithm (Minasny, et al. 2011), construction of dry soil spectra from wet spectra (Bogrekci & Lee, 2006) and drying of soil samples to remove MC (Ben-Dor & Banin, 1995; Chang et al., 2001). Most reports showed that the highest accuracy is to be expected when dried soil samples are used (Chang et al., 2005; Mouazen et al., 2006b; Tekin et al., 2011). Unfortunately, for *in situ* and on-line measurements, calibration models should be developed based on vis-NIR scanning of wet soils.

Apart from soil MC, soil texture is the other main factor to affect accuracy of the vis-NIR spectroscopy. Fontán et al. (2010) concluded that particle size has a significant effect on the accuracy and precision of models developed for analyzing C content in Mediterranean dry land Vertisols. Their results were improved for a small particle size soils (i.e. after grinding and sieving with 2 mm sieve), as compared to untreated soils with clods. Using processed soil sample in the laboratory, Stenberg (2010b) concluded that predictions of OC were most inaccurate for soils with a high sand content. Cozzolino & Moron (2006) found mixed results for different textures, with coefficients of determination in calibration and standard errors in cross validation of 0.90 and 0.6, 0.92 and 0.4 and 0.96 and 2.1 for coarse-sand C, fine-sand C and clay + silt C,

respectively. All above literature considered the single effect of MC or texture, on the prediction of soil organic matter or OC. The interaction effect of both MC and texture on prediction accuracy of OC and TN at farm scale has not been studied so far. Furthermore, to our knowledge, no reports studying these effects on models' performance using on-line collected spectra can be found in the literature.

The objective of this paper is to understand and quantify the individual and interaction effects of MC and soil texture on the performance of vis-NIR calibration models for *in situ* and on-line measurement of soil OC and TN. This will be considered to improve the measurement performance of the vis-NIR spectroscopy at farm scale modelling.

6.2 Material and methods

6.2.1 Soil samples

A total of 174 soil samples were used in this study. They were collected in summer 2009 from five fields in Silsoe Farm (Figure 6-1), the United Kingdom with variable soil texture and cropping condition (Table 6-1). The soil of those five fields is from the same mother material and subjected to nearly same farm management practices. Soil samples were collected from the surface layer from the bottom of 15 cm deep trench, opened by a tractor drawn subsoiler during on-line measurement. Around 200 g soil was taken from each soil sample and placed into a tightly sealed plastic bag to hold field moisture. The soil samples were then transferred to the soil laboratory in Cranfield University, where they were stored deep frozen (-18 °C) until analysis. After defrost and thoroughly mixed, each soil sample was divided into two parts equally. One part was used for MC measurement, where the soil was oven dried at 105°C for 24 hours. Before drying the fresh (wet) soil was scanned with the vis-NIR spectrophotometer. The other part of the soil was dried at 45°C, sieved with 2 mm sieve and used for vis-NIR scanning under dry conditions. This part was also used to determine soil OC, TN and particle size distribution.
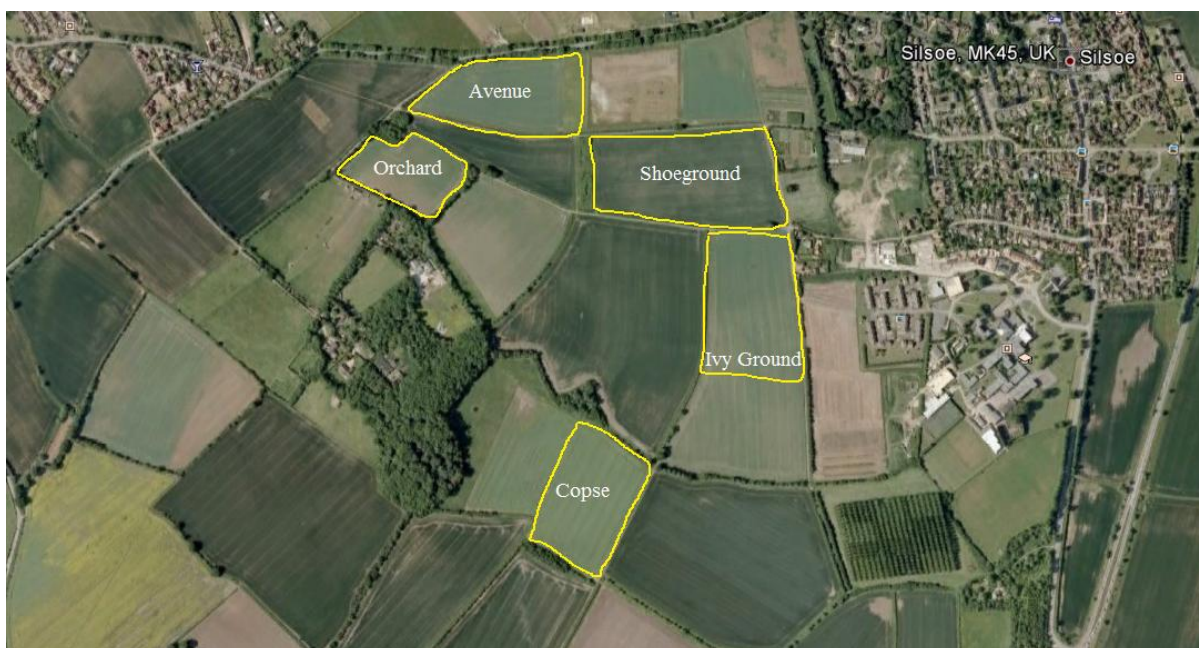
Figure 6-1 Location of five fields in Silsoe farm in the UK measured in summer 2009 with the on-line visible and near infrared (vis-NIR) sensor

Table 6-1 Information of 174 soil samples collected from 5 fields in Silsoe Farm, the UK

Field	Area, ha	Crop	Sample Nr	Sand / %	Silt / %	Clay / %	Texture	MC / %
Avenue field	3	wheat	28	61.87	20.06	18.07	Sandy loam	13.66
Orchard field	2	wheat	26	40.11	27.38	32.51	Clay loam	17.84
Ivy Ground	3	soybean	40	21.14	27.17	51.69	Clay	25.05
ShoeGround	4	wheat	40	64.98	20.93	14.09	Sandy loam	13.43
Copse field	3	wheat	40	14.55	27.84	57.61	Clay	26.88

6.2.2 Chemical analysis

The measurement of OC and TN were carried out in the soil laboratory in Cranfield University by a TrusSpecCNS spectrometer (LECO Corporation, St. Joseph, MI, USA) using the Dumas combustion method (Sweeney, 1989). The measurement of MC was carried out using the oven drying method for 24 hour in 105°C. Soil texture was measured with the sieving and sedimentation methods, according to BS 7755 Section 5.4 (BSI, 1998). The texture analysis results of the five fields are based on a mixed sample from each field. Soil texture type was determined according to the United State Department of Agriculture (USDA, 1983) classification system.

6.2.3 On-line measurement

The on-line measurement system designed and developed by Mouazen (2006a) was used (Figure 6-2) to measure soil spectra in five selected fields in Silsoe farm in summer 2009, after previous crop was harvested. It consists of a subsoiler that penetrates the soil to the required depth, making a trench, whose bottom is smoothened due to the downwards forces acting on the subsoiler (Mouazen et al., 2005). The optical probe, housed in a steel lens holder was attached to the backside of the subsoiler chisel to acquire soil spectra in reflectance mode from the smooth bottom of the trench. The subsoiler retrofitted with the optical unit was attached to a frame, which was mounted onto the three point hitch of the tractor (Mouazen et al., 2005). An AgroSpec mobile, fibre type, vis-NIR spectrophotometer (tec5 Technology for Spectroscopy, Germany) with a measurement range of 305-2200 nm was used to measure soil spectra in diffuse reflectance mode. The spectrometer was IP 66 protected for harsh working environments. Although this spectrophotometer does not cover the entire wavelength range in the NIR region, it was selected in this study as it uses diode array detectors, which proved to be stable under on-line measurement conditions (Mouazen et al., 2009). A 20 watt halogen lamp was used as a light source. A 100% white reference was used before scanning, which was repeated every 30 minutes. A deferential global positioning system (DGPS) (EZ-Guide 250, Trimble, USA) was used to record the position of on-line measured spectra with sub-meter accuracy.

A Panasonic semi-rugged laptop was used for data logging and communication. The spectrometer system, laptop and DGPS were powered by the tractor battery.

Figure 6-2 The on-line visible and near infrared (vis-NIR) spectroscopy-based sensor developed by Mouazen (2006a)

Five fields in Silsoe farm in the UK (Fig 6-1) were measured with the on-line sensor in summer 2009, namely, Avenue, Orchard, Ivy Ground, Shoeground and Copse fields. In each field, blocks of 150 m by 200 m, covering 3 ha of land were measured. Each measured line was 200 m long with 10 m intervals between adjacent transects. The travel speed of the tractor was around 2 km/hour and the measurement depth was set at 15 cm. During the measurement at each line, 2 or 3 soil samples were collected from the bottom of the trench and the sampling positions were carefully recorded. Each of those samples were equally divided into two halves, with one half used to carry out the laboratory reference measurements of soil OC, TN and texture and the

other half was used for optical scanning of fresh soil and for measurement of MC (see above).

6.2.4 Optical measurement

Scanning of soil samples took place under fresh (unprocessed) and oven-dried conditions. Samples were placed in glass containers and mixed well, with big stones and plant residues excluded. Then each soil sample was placed into three Petri dishes which were 2 cm deep and 2 cm in radius. The soil in the Petri cup was shaken and pressed gently before levelling with a spatula. A smooth soil surface ensures maximum light reflection and high signal to noise ratio (Mouazen et al., 2005). The soil samples were scanned in diffuse reflectance mode by the same vis-NIR spectrophotometer (AgroSpec from tec5 Technology for Spectroscopy, Germany). A total of 10 scans were collected from each replicate, and these were averaged in one spectrum.

6.2.5 Data pre-treatment and establishment of calibration models

The data set comprised of averaged spectra was subjected to noise cut to remove the noisy part of spectra on both sides, arriving at a wavelength range of 371 - 1900 nm. A 3-point (wavelength) average was applied in the visible wavelength range and 10-point average was applied in the infrared wavelength range to reduce the number of wavelengths and smooth the spectra. This reduced method had achieved best calibration accuracy. This was followed successively by first Savitzky-Golay (S-G) derivative, maximum normalisation and first S-G smoothing. A 2:2 smoothing was first carried out to remove noise from the measured spectra. Normalisation is typically used to get all data to approximately the same scale, or to get a more even distribution of the variances and the average values. The maximum normalisation method adopted in this study is a normalisation that "polarizes" the spectra. The peaks of all spectra with positive values scale to +1, while spectra with negative values scale to -1. Since all the

soil spectra in this study had positive values, the peaks of these spectra scaled to +1 (Mouazen, et al., 2006a). The maximum normalisation led to better results for the measurement of OC and TN, compared to the other pre-treatment options tested. Spectra were then subjected to Savitzky-Golay first derivative (Martens & Naes, 1989). This method enables to compute the first or higher-order derivatives, including a smoothing factor, which determines how many adjacent variables will be used to estimate the polynomial approximation used for derivatives. A second order polynomial approximation was selected. The same pre-treatment was used for both OC and TN models, which was carried out using Unscrambler 7.8 software (Camo Inc.; Oslo, Norway).

Table 6-2 Sample statistics for calibration set and validation set of individual field samples and of total 174 samples collected from 5 fields in Silsoe farm, the UK

	Field	OC / $g\ kg^{-1}$				TN / $g\ kg^{-1}$			
		Min	*Max*	*Mean*	*SD*	*Min*	*Max*	*Mean*	*SD*
Calibration set	Avenue	9.4	22	17	4.2	0.9	1.9	1.5	0.35
	Orchard	16	22	20	3.9	1.6	2.1	1.9	0.27
	Ivy	24	35	28	3.2	2.4	3.1	2.7	0.33
	Shoeground	12	20	15	4.4	1.1	1.9	1.4	0.25
	Copse field	22	29	25	2.8	2.2	2.7	2.5	0.34
	Overall	9.4	35	21	7.9	0.9	31	2	0.76
Validation set	Avenue	13	18	16	3.8	1.2	1.7	1.5	0.31
	Orchard	17	25	20	3.6	1.7	2.0	1.9	0.26
	Ivy	27	34	30	2.8	2.2	3.1	2.8	0.28
	Shoeground	12	20	16	4.3	1.2	1.9	1.5	0.27
	Copse field	20	30	26	2.6	1.9	2.6	2.4	0.31
	Overall	13	34	22	7.4	1.2	3.1	2.2	0.72

The pre-treated soil spectra of dried and fresh samples and the laboratory chemical measurement of OC and TN were used to develop calibration models of OC and TN. Out of the total number of samples of 174, 60 % (a total of 104 samples) of samples collected from each field were used for the development of calibration models,

whereas the remaining 40 % (a total of 70 samples) of samples from each field were used as prediction set (Table 6-2). The calibration spectra were subjected to a partial least squares regression (PLSR) with leave-one-out cross validation using the Unscrambler 7.8 software (Camo Inc.; Oslo, Norway). This was done in three repetitions, with samples randomly selected. The resulted accuracy of the three repetitions was averaged and reported in Table 6-3 for the *in situ* and on-line measurements and Table 6-4 for dry samples.

6.2.6 Statistical evaluation of model calibration and prediction

Both root mean square error of prediction (RMSEP) and residual prediction deviation (RPD), which is standard deviation of prediction set (S.D.) to RMSEP were used to compare the prediction accuracy of CO and TN models under dry, fresh (*in situ*) and on-line measurement conditions. Viscarra Rossel et al. (2006a) classified RPD values as follows: RPD<1.0 indicates very poor model/predictions and their use is not recommended; RPD between 1.0 and 1.4 indicates poor model/predictions where only high and low values are distinguishable; RPD between 1.4 and 1.8 indicates fair model/predictions which may be used for assessment and correlation; RPD values between 1.8 and 2.0 indicates good model/predictions where quantitative predictions are possible; RPD between 2.0 and 2.5 indicates very good, quantitative model/predictions, and RPD>2.5 indicates excellent model/predictions. This classification system was adopted in this study. Furthermore, to evaluate how significant are the separate and interaction effects of MC and texture fractions on the prediction accuracy of OC, two way univariate analysis of variance (ANOVA) of between-subjects effects test was carried out considering RPD and RMSEP obtained for the prediction set as accuracy indicators using Office 2007.

6.3 Results and discussion

6.3.1 Soil spectral analysis

To distinguish and group soil spectra from each field of the 5 fields considered in this study, principle component analysis (PCA) was carried out using soil spectra collected in the laboratory with fresh soil samples. The first two principal components (PCs) accounted for 97 % of total variance with the first PC accounted for 92 % of total variance (Figure 6-3). Three groups of soil samples can be observed, which are separated along principal component 1 (PC1), namely, sandy (Avenue and Shoeground), loam (Orchard) and clay (Ivy Ground and Copse) groups. However, separation between two fields (Avenue and Shoeground and Ivy Ground and Copse) of the same group can also be observed, with minimal overlapping of samples. These separations occur along PC2, which might be explained by the different MC in these fields. However, this might be due to the interaction effect of MC and texture. This implies that there is soil texture information in the vis-NIR soil spectra, which will potentially influence the soil vis-NIR measurement on soil properties.
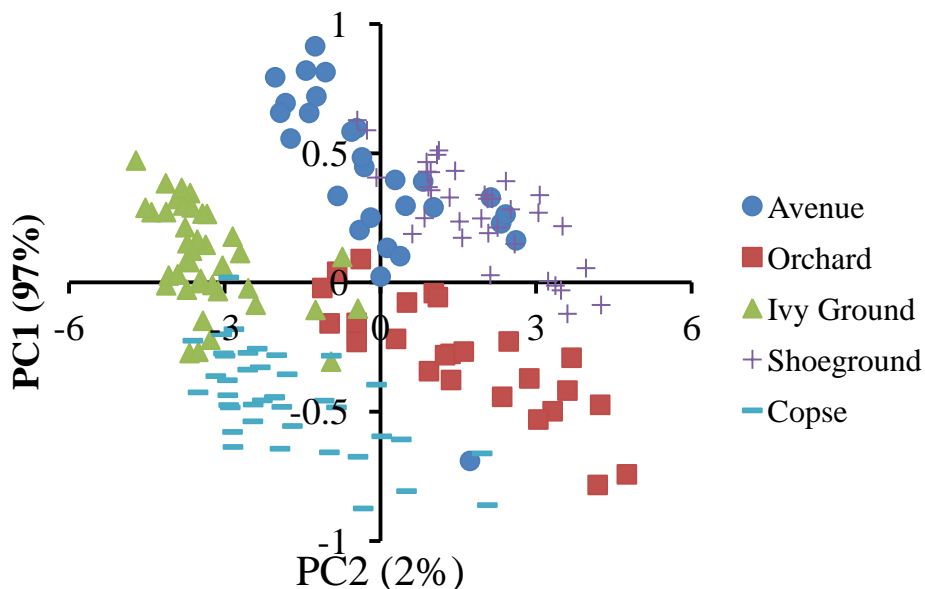
Figure 6-3 Principle component analysis (PCA) similarity maps for soil samples from Avenue (round), Orchard (square), Ivy Ground (triangle), Shoeground (cross) and Copse (dot) fields

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To analyse the soil moisture content and soil texture effects on the soil vis-NIR spectra, the average spectra of each field under wet and dry conditions are shown in Figure 6-4. This Figure explains differences in MC and texture of each field, which is reflected and in-line with PCA plot shown in Figure 6-3 too. It can be clearly observed that the dry soil absorbs less light (large reflectance), as compared to wet soils of the same field. Also clay soil samples of Ivy Ground and Copse fields have smaller reflectance (larger absorption) in the NIR spectral range than that of loamy soils (Orchard field) and sandy soils (Avenue and Shoeground fields). Due to the interaction effect of both MC and texture, average reflectance in the vis and in the NIR change when samples are dry as compared to wet soil samples.

6.3.2 In situ prediction accuracy of models with fresh soil samples

Tables 6-3 summarises the RMSEP and RPD values of PLS cross validation and PLS model prediction using *in situ* (wet soil) collected spectra of the prediction set for each field. According to RPD limits of accuracy proposed by Viscarra Rossel et al. (2006), the accuracy of the prediction OC in the prediction set is evaluated as very good with RPD values range of 2.11-2.34 in all five fields. The accuracy for TN prediction is evaluated to be good to excellent with larger range of RPD of 1.91-2.68.
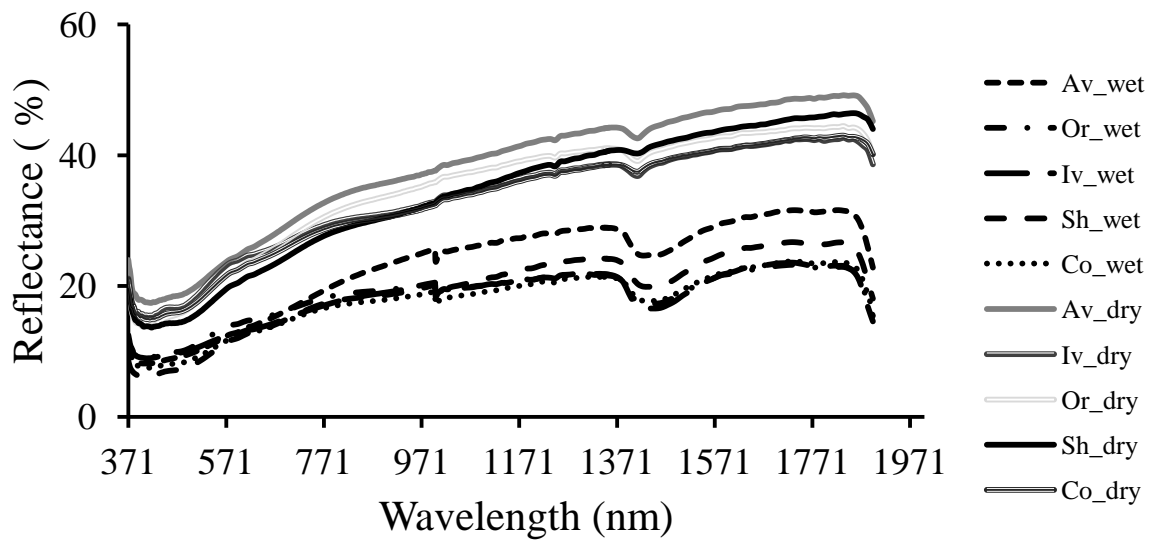
Figure 6- 4 The combined effect of moisture content (MC) and texture on soil spectra

Table 6-3 Validation results of partial least squares regression (PLS) in cross validation (model) and in prediction sets for the prediction of soil organic carbon (OC) and total nitrogen (TN) under fresh in situ and on-line measurement conditions

	Field	OC			TN		
		$RMSEP / g\ kg^{-1}$	RPD	SD	$RMSEP^{a} / g\ kg^{-1}$	RPD^{b}	SD
In situ validation	Avenue	1.69	2.24	3.8	0.11	2.64	0.31
	Orchard	1.66	2.16	3.6	0.11	2.45	0.26
	Ivy	1.30	2.15	2.8	0.11	2.17	0.28
	Shoeground	1.83	2.34	4.3	0.16	2.68	0.27
	Copse field	1.23	2.11	2.6	0.16	1.91	0.31
On-line validation	Avenue	1.74	2.18	3.8	0.12	2.51	0.31
	Orchard	1.75	2.05	3.6	0.11	2.36	0.26
	Ivy	1.4	2.03	2.8	0.13	2.08	0.28
	Shoeground	1.9	2.24	4.3	0.1	2.58	0.27
	Copse field	1.29	2.01	2.6	0.16	1.86	0.31
Model		3.34	2.36	7.9	0.28	2.71	0.76

[a] residual prediction deviation (Standard deviation/root mean square error of prediction)

[b] root mean square error of prediction.

6.3.3 On-line prediction accuracy of models with fresh soil samples

As the soil organic matter (SOM) or OC are essential for soil management and carbon sequestration, they were the main properties considered for on-line vis-NIR measurement (Shonk et al., 1991; Shibusawa et al., 2001; Hummel et al., 2001; Christy et al., 2008; Mouazen et al., 2007; Bricklemyer et al., 2010). Although there are some significant absorbance peaks for carbon in both vis and NIR spectral ranges, only few moderate successful cases for on-line measurement have been reported so far (Hummel et al., 2001; Christy et al., 2008). This might be attributed to the affecting factors during on-line measurement, including noise associated with tractor vibration, sensor-to-soil distance variation (Mouazen et al., 2009) stones and plant roots and difficulties of matching the position of soil samples collected for validation with corresponding spectra collected from the same position (Mouazen et al., 2007). Compared to the on-line sensing of SOM or OC, there is even fewer study on TN can be found in the literature (Mouazen et al., 2007; Christy et al., 2008). Only Christy et al., (2008) achieved high accuracy for TN (R^2 = 0.86) for a field scale calibration. This was not confirmed stable for different fields as it is reported in the current study where on-line validation is classified as good to very good in the five measured fields (Table 6-3). Actually, there is high correlation between OC and TN, because the N content in soil is almost entirely dependent on the organic matter content, and the overall TN:OC ratio is 1:10 (Martin et al., 2002).

6.3.4 Prediction accuracy with models of dry soil samples

Overall, after MC removal, the accuracy of OC and MC prediction has considerably improved comparing to that of the *in situ and on-line* prediction, not only in the cross-validation, but also in prediction sets of the five measured fields. Therefore, under dry soil condition, the measurement of OC and TN is classified as excellent accuracy (Table 6-4). This confirms that soil MC plays a negative role on the prediction of OC and TN with vis-NIR spectroscopy. The measurement of soil OC can be classified as excellent

for both cross-validation (RPD = 3.36) and prediction sets of 5 measured fields (RPD = 2.66 - 3.39, RMSEP = 0.76 − 1.61 gkg^{-1}), which is better accuracy as compared to previous studies (Dunn et al., 2002; Fidencio et al., 2002; Shepherd & Walsh. 2002; Chang et al., 2005; Brown et al., 2006). The measurement accuracy of TN was even better, which can also be classified as excellent for cross-validation (RPD = 3.84) and prediction sets of five measured fields (RPD = 2.85 - 3.45, RMSEP = 0.08 - 0.1gkg^{-1}), which is comparable to those obtained in previous studies (Couteaux et al,. 2003; Dalal & Henry, 1986; Vagen et al., 2006; Guerrero et al., 2010).

Table 6-4 Validation results of partial least squares regression (PLS) in cross validation (model) and in prediction data sets for the prediction of soil organic carbon (OC), total nitrogen (TN) using dry soil samples

	Field	OC			TN		
Prediction		RMSEP / g kg^{-1}	RPD	SD	RMSEP / g kg^{-1}	RPD	SD
	Avenue	1.32	2.86	3.8	0.1	2.96	0.31
	Orchard	1.16	3.08	3.6	0.08	3.15	0.26
	Ivy	0.88	3.17	2.8	0.08	3.27	0.28
	Shoeground	1.6	2.66	4.3	0.09	2.85	0.27
	Copse field	0.76	3.39	2.6	0.08	3.45	0.31
Model		2.04	3.36	7.9	0.19	3.84	0.76

6.3.5 Effect of soil moisture content and texture on prediction accuracy

Figures 6-5 and 6-6 illustrate the effect of soil MC and texture (in terms of soil clay content) on the measurement accuracy of soil OC and TN, respectively. Under wet soil condition, the increase of field clay content and MC results in decrease of measurement accuracy of OC and TN in terms of RPD. Although the influence of MC on decrease of prediction accuracy of OC and TN with vis-NIR spectroscopy is in line with

other studies (Chang et al., 2005; Mouazen et al., 2006b;Tekin et al., 2011), clay content used to contribute to the enhancement of measurement accuracy (Stenberg, 2010). However, results shown in Figure (6-5 & 6-6) give the illusion that clay fraction plays the same negative role as MC on prediction accuracy. When MC is removed by considering dry samples, it becomes clear that clay content plays a positive role on the accuracy of vis-NIR spectroscopy (Figures 6-5 & 6-6). The illusion that with increase in clay content, the prediction accuracy of OC and TN deteriorates when using wet soil samples, can be explained by the fact that clay can hold larger amount of water than sand due to the large water holding capacity and plasticity index of clay.
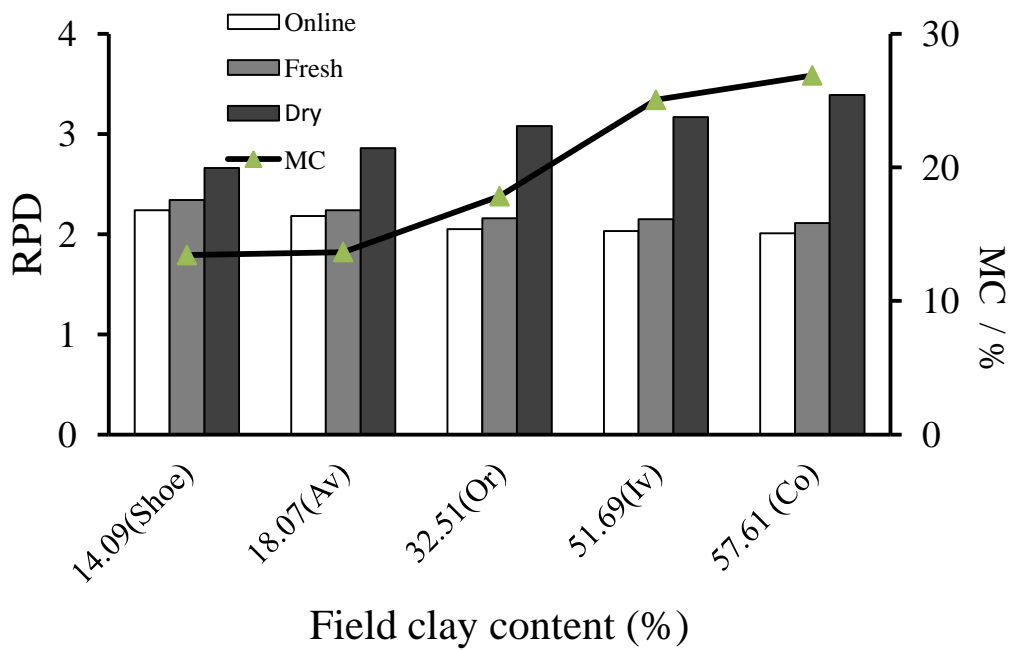
Figure 6-5 Mean values of three replicates of ratio of prediction deviation (RPD) obtained for prediction sets of five fields for on-line (white), in situ (grey), oven-dried (black) measurement for soil organic carbon (OC)
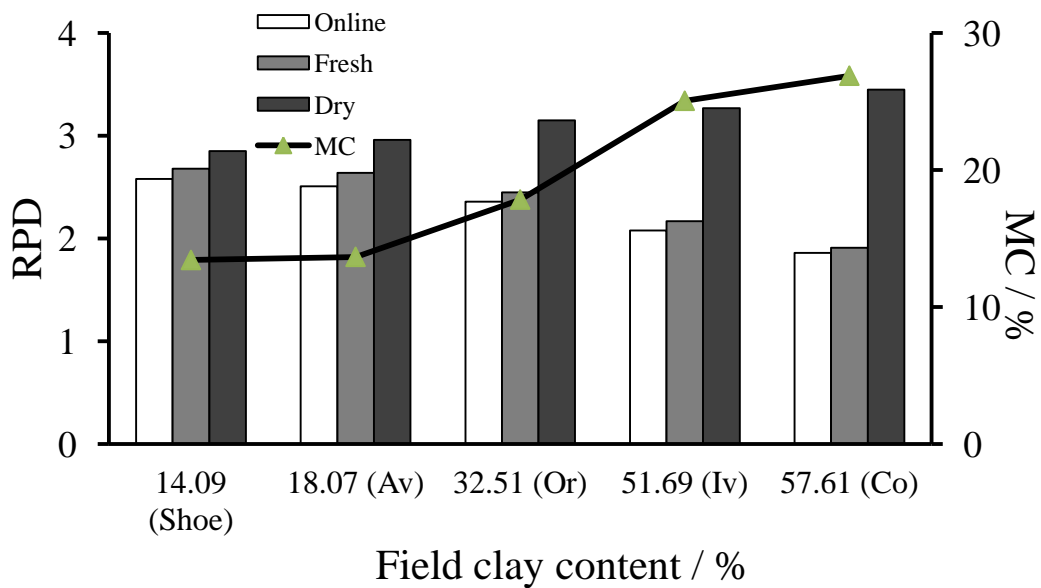
Figure 6- 6 Mean values of three replicates of ratio of prediction deviation (RPD) obtained for prediction sets of five fields for on-line (white), in situ (grey), oven-dried (black) measurement for soil total nitrogen (TN)

When dry soil samples were used the highest accuracy for OC and TN prediction, measured as RPD was obtained for field with the highest clay content (Copse field), whereas the lowest RPD values was obtained for field with the lowest clay content (Shoeground field). Moreover, as the soil clay content increase, the prediction of soil OC in the field improved. Stenberg (2010b) reported increase in prediction error of OC with sand, which was also attributed to the scattering effect of sand content, which is in line with the finding of this study.

Table 6-5 Results of univariate analyses of variance (ANOVA) performed on the independent validation set to evaluate separate effect of moisture content (MC) and texture and interaction effect of MC and texture on prediction accuracy of organic carbon (OC) and total nitrogen (TN) evaluated as ratio of prediction deviation (RPD), root mean square error of prediction (RMSEP) for in situ measurement using wet soil samples

		OC			TN		
	Source	MS	F-ratio	p-value	MS	F-ratio	p-value
RPD	MC	737.19	37.10	0.0002	722.67	36.28	0.0003
	Clay	2655.9	13.98	0.005	2163.83	8.455	0.027
	sand	3672.7	13.96	0.005	2628.28	13.83	0.005
	silt	1262.9	171.48	0.008	1243.89	167.78	0.009
Interaction	MC*Texture	1107.9	4.65	0.01	1098.59	4.6	0.01
R^2	MC	768.57	33.87	0.0002	894.36	43.74	0.0001
	Clay	2647.2	16.54	0.003	3251.32	16.23	0.006
	sand	3823.1	14.44	0.005	4675.2	15.22	0.004
	Silt	1325.9	180.93	0.008	1123.26	212.63	0.05
Interaction	MC*Texture	1124.7	4.34	0.01	1234.12	5.12	0.009
RMSEP	MC	794.77	39.94	0.0002	925.63	46.60	0.0001
	Clay	2764.2	14.54	0.005	3003.98	15.81	0.004
	sand	3800.1	14.44	0.005	4080.4	15.51	0.004
	Silt	1337.9	180.93	0.03	1506.26	204.63	0.05
Interaction	MC*Texture	1144.7	4.80	0.009	1226.69	5.15	0.007

Table 6-5 and Table 6-6 summarises the output of ANOVA, with the intention to evaluate how significant the effects on MC and soil texture fractions and the interaction between them on the prediction on OC and TN under both *in situ* (Table 6-5) and on-line (Table 6-6) measurement conditions. In terms of measurement accuracy evaluated as RPD, R^2 and RMSEP, MC, clay content, silt content and sand content all have significant effects on the prediction of OC ($p<0.05$), with MC has the most significant influence ($p = 0.0001$ regarding RPD).

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Table 6- 6Results of univariate analyses of variance (ANOVA) performed on the independent validation set to evaluate separate effect of moisture content (MC) and texture and interaction effect of MC and texture on prediction accuracy of organic carbon (OC) and total nitrogen (TN) evaluated as ratio of prediction deviation (RPD), root mean square error of prediction (RMSEP) for on-line measurement

		OC			TN		
	Source	MS	F -ratio	p-value	MS	F -ratio	p-value
RPD	MC	745.63	37.53	0.0003	730.51	36.69	0.0003
	Clay	2671.91	14.06	0.006	2643.2	13.91	0.005
	sand	3691.77	14.03	0.005	3658.0	13.90	0.006
	silt	1273.96	172.96	0.02	1254.1	169.34	0.05
Interaction	MC*Texture	1113.39	4.67	0.01	1103.6	4.63	0.01
R^2	MC	723.12	32.33	0.0001	834.23	43.74	0.0001
	Clay	2234.24	12.54	0.004	3654.1	16.21	0.003
	sand	3673.16	14.44	0.006	4945.2	15.67	0.006
	Silt	1123.95	183.93	0.009	1247.2	212.38	0.04
Interaction	MC*Texture	1865.7	4.34	0.01	1234.1	5.67	0.007
RMSEP	MC	788.18	39.61	0.0002	926.21	46.63	0.0001
	Clay	2751.9	14.48	0.005	3005.0	15.81	0.004
	sand	3785.74	14.39	0.005	4081.6	15.51	0.004
	Silt	1329.40	179.80	0.04	1507.0	204.73	0.01
Interaction	MC*Texture	1140.594	4.78	0.009	1140.5	4.78	0.009

Tekin et al. (2011) found the effect of MC on the prediction of soil OC to be significant when this was tested on a data set with mixed texture samples collected from the UK and Turkey, which supports the finding of the current study. Further analysis shows that the interaction effects between MC and texture are significant for all accuracy standards and both on-line and *in situ* conditions.

6.4 Conclusions

The signal effects of both soil MC and soil texture fractions and the interaction effects of MC and texture fractions on the prediction of OC and TN were investigated using soil samples collected from five fields of the same farm, with different field MC levels and soil textures. The investigation was carried out for dry, fresh and on-line collected vis-NIR spectral data. Results obtained allowed drawing the following conclusions:

1. Soil MC, sand and silt fractions have negative influence, whereas clay content has a positive effect. Soil MC, silt, clay and sand fractions play significant role in soil vis-NIR spectroscopy for the prediction of soil OC and TN, with MC has the most significant influence on both on-line and *in situ* measurement conditions for both OC and TN.

2. The interaction effects of MC with soil texture were found to be significant on both on-line and in situ conditions for both OC and TN; however, this was less significant than all individual effect.

3. A better accuracy of vis-NIR spectroscopy of soil OC and TN is expected in dry and clay ridden than in wet and sandy fields. When measurement is to be carried out under mobile (on-line) or non-mobile conditions, it is recommended to access the field as driest possible conditions, particularly in clay fields. Accessing clay fields under wet condition would result in the highest expected error, as water holding capacity of clay is high. Larger error is to be expected in this case as compared to that in fields with light soils.

7 Validation of on-line measurement

7.1 Introduction

One of the strategies used in PA is to minimize the production costs through enhanced efficiency, which can increase profits and conserve the environment. It is proved that PA is an environmental friendly strategy, in which farmers can vary the use of input to respond to variable soil and crop conditions within a field (Srinivasan, 2006). Conventional determination of soil spatial variability usually involves manual soil sampling, sample pre-treatment, laboratory reference analyses and mapping. This procedure is very expensive, time consuming and provides scattered measurement points. Therefore, the development of a fast, robust, cost effective and environmental friendly detecting method of the soil spatial variability is a preliminary task for the implementation of PA.

The vis-NIR spectroscopy is a recently proven technique for a fast, inexpensive and relatively accurate alternative method to the laboratory analyses of soil properties (Mouazen et al, 2010; Shepherd & Walsh, 2002; Stenberg et al., 2010; Viscarra Rossel & McBratney, 1998). In comparison to non-mobile analysis, there is considerably less literature available about on-line vis-NIR spectroscopy analysis of soil properties. Generally, both the laboratory and *in situ* non-mobile vis-NIR methods provide better accuracy than the on-line method (Kuang et al., 2012a). This might be attributed to other factors influencing the latter method only, such as noise associated with tractor vibration, sensor-to-soil distance variation (Mouazen et al., 2009), stones and plant debris and difficulties of matching the position of soil samples collected for validation with corresponding spectra collected from the same position (Mouazen et al., 2007). A review on the current status of on-line vis-NIR measurement systems confirms that only three systems are available today (Christy et al., 2008; Mouazen et al., 2005; Shibusawa et al., 2001). The beginning of these systems dates back to 1991, when Shonk et al., (1991) developed a system to measure SOM and MC, which utilised a

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single wavelength (660 nm) of light, reporting a R^2 of 0.83 for SOM. Shibusawa et al., (2001) developed an on-line vis-NIR (400 – 1700 nm) sensor to predict OC, MC, pH and NO3-N. Although this system is highly technically instrumented, it is rather expensive. Christy et al., (2008) developed a prototype soil reflectance mapping unit equipped with a vis-NIR spectrophotometer, which is commercially available in the market today. The sapphire glass of the optical probe makes direct contact with soil and stones. They have reported that OC can be successfully measured with a RMSEP of 3.0 gkg^{-1} in a high OC variability area (standard deviation = 5.1 gkg^{-1} and range = 3.0-26.3 gkg^{-1}). A simpler design to the one of Shibusawa et al., (2001) without sapphire window optical configuration was developed by Mouazen (2006a). So far, the system provided variable degrees of success for the measurement of MC, total nitrogen (TN), total carbon (TC), pH and available P in different soils in Belgium and northern France (Mouazen et al., 2005; Mouazen et al., 2007; Mouazen et al., 2009). More recently, employing the on-line system developed by Christy et al. (2008), Bricklemyer et al. (2010) reported on the on-line measurement for soil OC and clay content. Although authors did not report quantitative estimation of accuracy for OC, they calculated a standard error of prediction (SEP) of 3.4 gkg^{-1} and a RPD value of 1.4 for clay content. Using the same system, coupled with topography and aerial photograph data, Munoz et al. (2011) reported low to moderate accuracy of soil OC measurement with R^2 and RMSEP ranged from 0.44 to 0.66 and from 1.41 to 1.51 gkg^{-1}, respectively. Applying this vis-NIR system in combination with electrical conductivity (EC) and temperature sensors in a Danish field, Knadel et al. (2011) obtained moderate prediction accuracy (RMSEP = 59.4 gkg^{-1} and RPD = 2.3) for soil OC. However, the vis-NIR sensor alone only achieved a relatively low accuracy (RMSEP = 59.8 gkg^{-1}, RPD = 1.9). This brief review reveals that the existing on-line sensors do not provide sufficiently accuracy and stability to recommend them for site specific application of different inputs. The variable degrees of performance of on-line these sensors might be attributed to the fluctuation in model performance, with the majority of them established for field-scale analysis (e.g. Christy et al., 2008; Mouazen et al., 2005; Munoz et al., 2011 Shibusawa et al., 2001), or for regional- and country-scale analysis (e.g. Mouazen et al., 2007;

Mouazen et al., 2009). Some studies suggested spiking local samples into the general calibration models can improve prediction accuracy under laboratory (Sanky et al. 2008) or *in situ* measurement conditions (Minasny et al. 2009; Viscarra Rossel et al. 2009; Waiser et al. 2007; Wetterlind and Stenberg, 2010). As yet, no general calibration procedure that included spiking strategy have been reported for establishing calibration models of on-line sensors, which has led to stable performance of on-line sensors, at the lowest production cost.

This paper aims at reporting on a methodology for the calibration of a vis-NIR on-line measurement system (Mouazen, 2006), including spiking concept for automatic data collection of OC, TN and MC at farm scale in three European farms.

7.2 Material and methods

7.2.1 Soil sample

A total of 425 soil samples were used as the general dataset to be used to establish calibration models for the measurement of OC, TN and MC in European soils (Table 7-1). They were collected from four different farms in Europe, namely Mespol Medlov, A.S. (Czech Republic, http://farmsubsidy.org/CZ), Wimex (Germany, http://www.wimex-online.de), Bramstrup Estate (Denmark, http://www.bramstrup.dk) and Silsoe Farm (The UK). Bulked samples from 16 cores were collected from the upper soil layer (0-30 cm) in the spring of 2008 (Czech Republic and Germany), spring of 2009 (Denmark) and summer of 2009 (UK) and covered diverse soil conditions. A total of 128, 97 and 48 soil samples were, respectively, collected from seven fields in Mespol Medlov, A.S. farm, six fields in Bramstrup Estate farm and two fields in Silsoe farm. Further 152 soil samples were collected from four sub-areas belong to Wimex farm, with four samples from two fields at Reppichau, 50 samples from nine fields at RAG, 20 samples from ten fields at Aken and 54 samples from fifteen fields at the Wulfen farm.

Table 7-1 Soil samples used to establish general calibration models for organic carbon (OC), total nitrogen (TN) and moisture content (MC). Samples were collected from Mespol Medlov, A.S. farm in Czech Republic, Wimex farm in Germany, Bramstrup Estate farm in Denmark and Silsoe farm in the UK

Country	Number of samples	Nr of Fields	Sampling time
Czech Republic	128	7	2008
Germany	152	37	2008
Denmark	97	6	2009
UK	48	3	2009

Apart from these soil samples, another 113 soil samples were collected from three selected fields, where on-line measurement was carried out, namely, in Mespol Medlov, Bramstrump Estate and Silsoe farms (Table 7-2).

Table 7- 2Information about the three fields in Mespol Medlov, A.S. farm in Czech Republic, Bramstrup Estate farm in Denmark and Silsoe farm in the UK, where on-line measurement took place in 2010

Field	Area, ha	Crop	Sample Nr	Texture type	Sand, %	Silt, %	Clay, %
Czech republic	2	wheat	48	Silt clay loam	4.86	70.58	24.56
Denmark	2	wheat	37	Sandy loam	68.57	21.96	9.48
UK	2	wheat	28	Clay loam	40.11	27.38	32.51

These were considered as validation fields. They were collected during the on-line measurement from the bottom of trenches at a depth of 15 cm. Of these, 20 % were spiked into the general calibration dataset and the remaining 80% were used for the on-line validation purpose. The validation field in Silsoe farm is 500 m away from the nearest fields, where samples used for general data set were collected, whereas the validation fields in Mespol Medlov and Bramstrump Estate farms are 2.5 km and 3 km far from the nearest fields, respectively. A PCA, performed on 425 samples of general

calibration dataset and 113 validation data set show clear separation between validation samples from the general dataset samples (Figure 8-1).
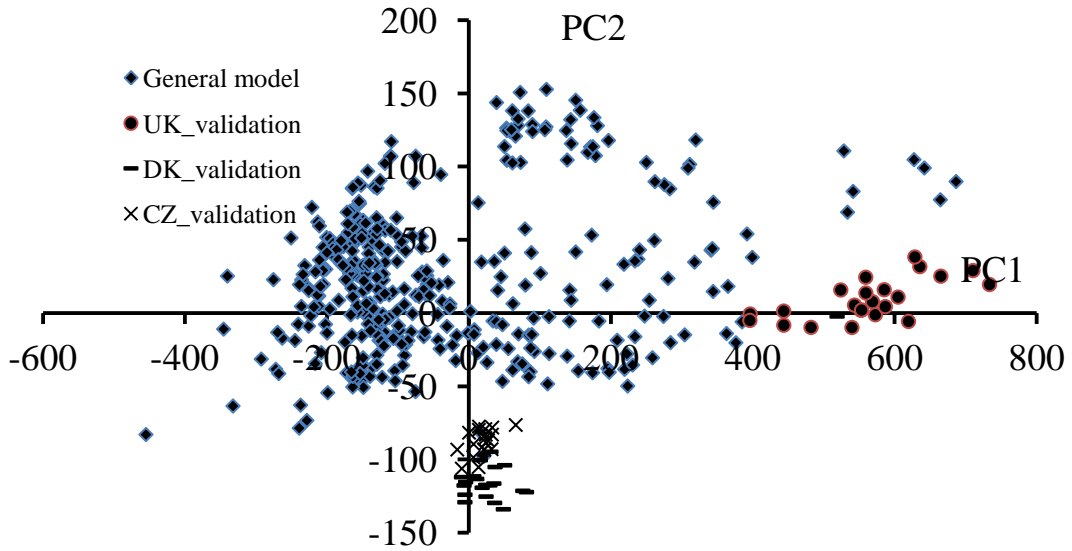
Figure 7-1 Principal component similarity map of principal component analysis (PCA) carried out on both 425 calibration and 113 validation datasets. Principal components 1 and 2 accounted for 91.5 % and 6.9 % of the total variance, respectively

Around 200 g of soil from each sample was kept deep frozen (-18 °C) until analysis. After careful mixing, half of each sample from Czech Republic, Germany and Denmark was sent to Leibniz Centre for Agricultural Landscape Research (ZALF) in Germany for soil chemical analyses for TN and OC and the second half was sent to Cranfield University for optical measurement and data analysis. Samples collected from the UK and 113 soil samples collected during the on-line measurement in 2010, were subjected to both optical and chemical measurement at Cranfield University. Sample statistics of laboratory reference measurements is summarised in Table 8-3 for the calibration and validation datasets.

Table 7-3 Sample statistic for general calibration model (425) and samples taken during online measurement (133) in three in European.

Model set	Sample Nr	Property, g kg^{-1}	Min	Max	Mean	SD
General calibration set	425	OC	4.5	34.8	15.1	6
		TN	0.56	3.08	1.51	0.6
		MC	77.3	292	156	95
Validation set	133	OC	10.9	20.6	15.5	4.38
		TN	1.09	2.13	1.62	0.39
		MC	105	219	192	36.8

7.2.2 On-line measurement

The on-line measurement system designed and developed by Mouazen (2006) was used (Figure 1-1) to measure three fields in the three European farms. It consists of a subsoiler, which penetrates the soil to the required depth, making a trench, whose bottom is smoothened by the downwards forces acting on the subsoiler. The optical probe is housed in a steel lens holder. This is attached to the backside of the subsoiler chisel in order to acquire soil spectral reflectance data from the smooth bottom of the trench. The subsoiler was retrofitted with the optical unit and attached to a frame. This was mounted onto the three point hitch of the tractor (Mouazen et al., 2005). An AgroSpec mobile, fibre type, vis-NIR spectrophotometer (Tec5 Technology for Spectroscopy, Germany) with a measurement range of 305-2200 nm was used to measure soil spectra in diffuse reflectance mode. The spectrometer was an IP 66 model, protected for harsh working environments. A deferential global positioning system (DGPS) (EZ-Guide 250, Trimble, USA) was used to record the position of on-line measured spectra with sub-meter accuracy. A Panasonic semi-rugged laptop was used for data logging and communication. The spectrometer system, laptop and DGPS were powered by the tractor battery.

Three fields were measured in summer 2010, namely, in Mespol Medlov, A.S. farm in Czech Republic, Bramstrup Estate farm in Denmark and Silsoe farm in the UK. In each field, blocks of 150 m by 150 m, covering about 2 ha of land were measured. Each measured line was 150 m long with 10 m intervals between adjacent transects (Figure 8-2). The travel speed of the tractor was around 2 km/h and the measurement depth was set at 15 cm. During the measurement at each line, 2 or 3 soil samples were collected from the bottom of the trench and the sampling positions were carefully recorded with a DGPS. Each of those samples was equally divided into two parts. One half used to carry out the laboratory reference measurements of soil OC, TN and MC and the other half used for optical scanning.
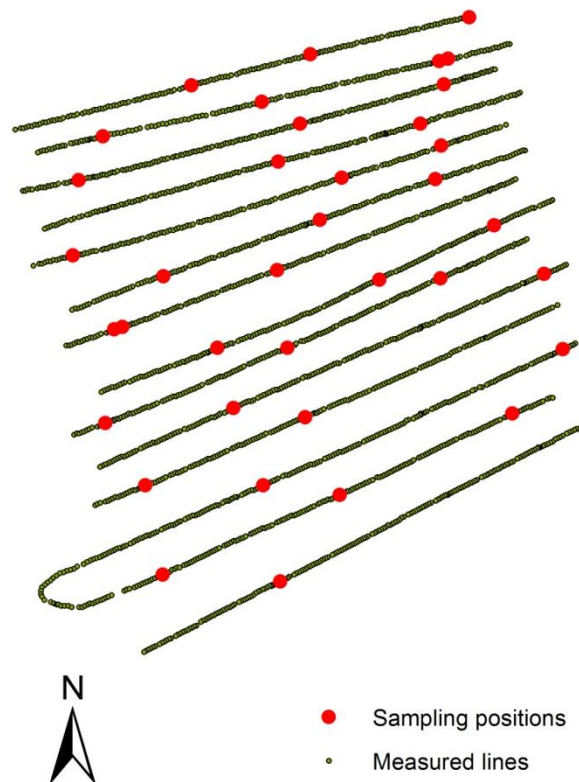
Figure 7-2 On-line measured lines and sampling positions during on-line measurement, shown in a field in Bramstrup Estate farm in Denmark

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7.2.3 Laboratory reference analyses

Soil OC and TN were measured by a TrusSpecCNS spectrometer (LECO Corporation, St. Joseph, MI, USA), using the Dumas combustion method. Soil MC was determined by oven drying of the soil samples at 105 ºC for 24 h. The results of the textural analysis of the three on-line measured fields were based on a mixed sample from each field. Each sample was subjected to wet sieving and a hydrometer test in order to determine the particle size distribution. Texture was determined according to the United State Department of Agriculture (USDA) classification system (Table 7-2).

7.2.4 Optical measurement

Each soil sample was put into a glass container and mixed well. Big stones and plant residue were removed (Mouazen et al., 2007). Soil from each sample was placed into three Petri dishes, which were 2 cm deep and 2 cm in diameter. The soil in the Petri dish was shaken and pressed gently before levelling with a spatula. A smooth soil surface ensures maximum light reflection and a high signal to noise ratio (Mouazen et al., 2007). The soil samples were scanned by the same AgroSpec portable spectrophotometer (Tec5 Technology for Spectroscopy, Germany), used during the on-line measurement. A 100 % white reference was used before scanning. A total of 10 scans were collected from each cup and these were averaged in one spectrum.

7.2.5 Sample pre-treatment and development of calibration models

7.2.5.1 Pre-treatment of spectra

The laboratory non-mobile measured soil spectra for 425 samples were used to develop general calibration models, after spiking those with spiking samples from the three validation fields. The spectral range of these spectra was first reduced to 371 - 2150 nm to eliminate the noise at both edges of each spectrum. The number of wavelengths was then reduced by averaging three successive wavelengths in the visible range, and 15 points in the NIR range. The Savitzky-Golay smoothing, maximum normalisation and first derivation (Martens & Naes, 1989) were successively

implemented using Unscrambler 7.8 software (Camo Inc.; Oslo, Norway). The pre-treated spectra and the laboratory chemical measurement values were used to develop the calibration models.

7.2.5.2 Spiking

The purpose of spiking is to enhance the variability included in a general calibration dataset, by accounting for the soil variability present in new fields. This technique has been recommended by other researchers for non-mobile measurements (Guererro et al. 2010; Janik et al., 2007; Shepherd and Walsh, 2002; Viscarra Rossel et al., 2008). Three different spiking strategies of soil samples collected from the target validation fields (e.g. 3 on-line measured fields) were selected. These included - no spiking of soil samples, - spiking with laboratory non-mobile scanned spectra and - spiking with on-line (mobile) spectra recorded during the on-line measurement. When spiking was considered with the latter 2 cases, about 20 % of a randomly selected set of samples (21 samples from the three fields) from the total 113 soil samples collected during the on-line measurement were spiked into the general data set of 425 samples, collected from the 4 European farms. After spiking, the total number of samples in the calibration set was 446. Furthermore, smaller ratios of samples of 10 % and 5 % were randomly selected from the laboratory measured spectra and were used as spiking sets to envisage the influence of different spiked sample numbers of the on-line prediction accuracy.

7.2.5.3 Development of calibration models

These table 7-3 sample sets were subjected to a PLSR with the leave-one-out cross validation using an Unscrambler 7.8 software (Camo Inc.; Oslo, Norway). A total of 3 groups of models were developed based on 3 different spiking rates of 20, 10 and 5 % of collected soil samples from the three validation fields. The remaining 80, 90 and 95 % of the total 113 samples were used to validate the on-line measurement and to develop maps comparing the laboratory reference with the corresponding on-line

measured values. The number of latent variables for a model was determined by examining a plot of the leave-one-out cross-validation residual variance against the number of latent variables obtained from the PLSR. The latent variable of the first minimum value of residual variance was selected. Outliers were detected using the residual sample variance plot after PLSR. Samples located far from the zero line of residual variance were considered outliers and excluded from the cross-validation sample set.

7.2.5.4 Development of soil maps

Two types of maps were developed, namely, validation and full-data points maps. ArcGis 10 (ESRI, USA) software was used to generate the former validation maps, using the inverse distance weighing (IDW) interpolation methods. To produce the latter maps, Vesper 1.6 software (Whelan, 2002), developed by Australian Centre for Precision Agriculture, was used to develop semivariogram models for OC, TN and MC using the entire field on-line data. Based on semivariogram parameters and kriging interpolation method, ArcGis 10 (ESRI, USA) was used to produce the full-data point maps using on-line measured spectra.
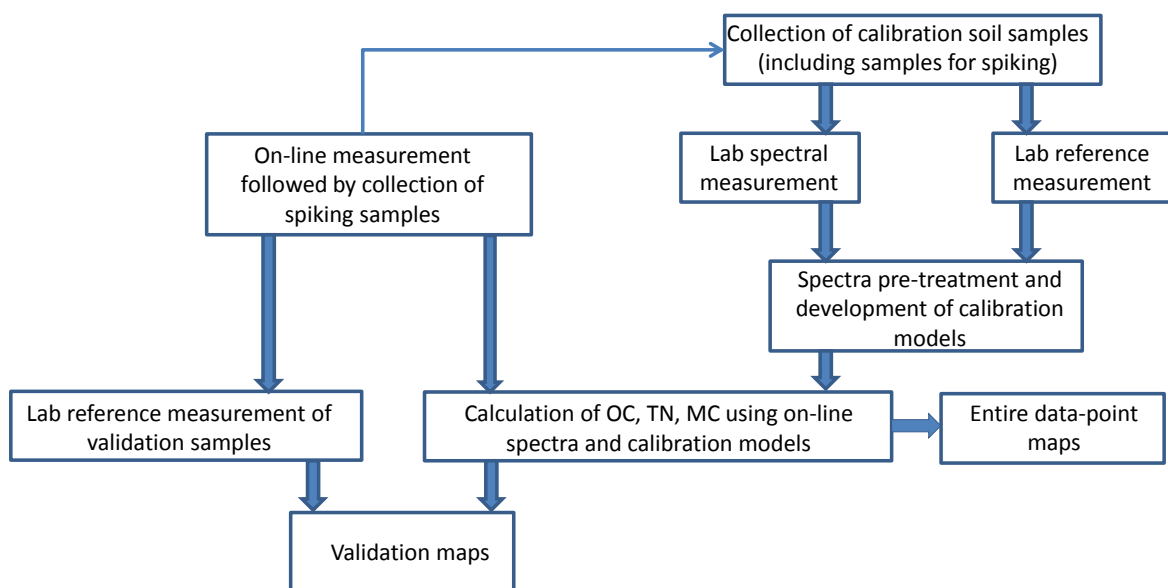
Figure 7-3 A flow diagram explaining different steps performed during the study

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7.3 Results and discussion

A flow diagram illustrating the different steps taken into account in this study, from the collection of soil sample to the development of different maps is shown in Figure 7-3. This diagram makes it clear that the vis–NIR calibration models were developed using soil spectra measured under a non-mobile laboratory environment. The applicability of these laboratory calibration models for the on-line prediction of soil properties was validated on spectra measured with the on-line vis–NIR sensor.

7.3.1 Evaluation of accuracy of general calibration models

Based on spiking strategies and ratio of samples spiked in the general calibration set, the accuracy of calibration models achieved based on cross-validation proves promising results (Table 7-4).

Table 7-4 Comparison of model performance (20 % spiking with laboratory measured spectra) in cross-validation and by using laboratory measured vis-NIR spectra of validation set for the prediction of organic carbon (OC), total nitrogen (TN) and moisture content (MC) in the three on-line measured fields in Mespol Medlov, A.S. farm in Czech Republic, Bramstrup Estate farm in Denmark and Silsoe farm in the UK

Set	Country	Spiked samples	OC RMSEP/ g kg^{-1}	RPD	SD	TN RMSEP/ g kg^{-1}	RPD	SD	MC RMSEP / g kg^{-1}	RPD	SD
Validation set	CZ	9	0.69	2.38	1.64	0.07	2.57	0.19	7.4	3.16	23.4
	DK	7	1.00	2.31	2.30	0.09	2.38	0.21	3.2	3.95	12.8
	UK	5	0.95	2.41	2.30	0.09	2.34	0.20	5.8	3.27	19.2
Cross-validation	-	-	2.30	2.82	6.50	0.23	2.61	0.6	22.20	4.28	95.0

Examining RPD values, which is the standard deviation (SD) divided by RMSEP, reveals that RPD values for 20 % spiking ratio of laboratory-scanned spectra were 2.82, 2.61 and 4.28 for OC, TN and MC, respectively. For validation of models using validation

sets (scanned under laboratory non-mobile conditions) of the three fields, RPD ranges were 2.31 – 241, 2.34 – 2.57 and 3.16 – 3.95, respectively for OC, TN and MC.

Table 7-5 Comparison of model performance in cross-validation (model) and by using on-line measurement spectra of validation set for the prediction of organic carbon (OC), total nitrogen (TN) and moisture content (MC), using different spiking strategies and spiking rates in the three on-line measured fields in Mespol Medlov, A.S. farm in Czech Republic, Bramstrup Estate farm in Denmark and Silsoe farm in the UK

Spiking strategy	Country	Spiked samples	OC RMSE / g kg^{-1}	OC RPD	OC SD	TN RMSEP / g kg^{-1}	TN RPD	TN SD	MC RMSE / g kg^{-1}	MC RPD	MC SD
Without spiking	CZ	NA	0.80	2.06	1.64	0.08	2.25	0.19	8.15	2.87	23.4
	DK	NA	1.16	1.98	2.30	0.10	2.18	0.21	3.51	3.65	12.8
	UK	NA	1.09	2.11	2.30	0.10	2.03	0.20	6.15	3.12	19.2
Model	-	-	2.30	2.61	6.00	0.24	2.5	0.6	24.55	3.87	95.0
20 % on-line Spiking	CZ	9	0.82	2.01	1.64	0.09	2.22	0.19	8.48	2.76	23.4
	DK	7	1.22	1.88	2.30	0.10	2.04	0.21	3.62	3.54	12.8
	UK	5	1.15	2.00	2.30	0.10	1.96	0.20	6.27	3.06	19.2
Model	-	-	2.30	2.82	6.50	0.23	2.61	0.6	25.00	3.76	94.0
20 % lab spiking	CZ	9	0.70	2.33	1.64	0.08	2.52	0.19	7.41	3.16	23.4
	DK	7	1.01	2.28	2.30	0.09	2.35	0.21	3.23	3.96	12.8
	UK	5	0.97	2.38	2.30	0.09	2.31	0.20	5.91	3.25	19.2
Model	-	-	2.30	2.82	6.50	0.23	2.61	0.6	22.20	4.28	95.0
10 % lab spiking	CZ	5	0.75	2.18	1.64	0.08	2.38	0.19	7.65	3.06	23.4
	DK	4	1.06	2.18	2.30	0.10	2.21	0.21	3.39	3.78	12.8
	UK	3	1.02	2.26	2.30	0.09	2.24	0.20	6.04	3.18	19.2
Model	-	-	2.30	2.74	6.50	0.23	2.56	0.59	22.14	4.29	95.0
5 % Lab spiking	CZ	3	0.76	2.16	1.64	0.09	2.18	0.19	7.91	2.96	23.4
	DK	3	1.07	2.15	2.30	0.10	2.09	0.21	3.61	3.55	12.8
	UK	2	1.07	2.15	2.30	0.09	2.11	0.20	6.19	3.10	19.2
Model	-	-	2.30	2.73	6.50	0.23	2.56	0.59	22.67	4.19	95.0

According to Viscarra Rossel et al. (2006), an RPD value between 1.8 and 2 and between 2.0 and 2.5 indicates good and very good quantitative model predictions, respectively, whereas values above 2.5 indicate excellent prediction results. This means that the validation results of individual fields prove the prediction accuracy using non-mobile measured spectra to be very good to excellent model predictions for

the three studies properties. The high model accuracy for the three elements may be considered as a primary evidence of successful prediction of on-line measurement for soil OC, TN and MC.

7.3.2 Validation of on-line measurement

The same spectra pre-treatment was used for the on-line collected spectra as that used for calibration model development. The on-line collected spectra after spectra pre-treatment were used to predict MC, TN, and OC using the general calibration models developed in advance, as explained above. The chemical analysis values of the manually collected samples were compared with the on-line predicted concentration values at the same positions. Table 7-5 summarises the accuracy of the on-line measurement for studied soil properties based on different spiking methods and spiking ratios. Examining Table 7-5 reveals that RPD values were above 2 for all soil properties in all fields, except for 3 cases. Out of these 3 cases, RPD in 1 case was 1.98 for OC in the field in Denmark. The other 2 cases (OC and TN in the Danish and the UK fields, respectively) were for models developed based on 20 % spiking of on-line collected spectra. This may suggest that spiking with on-line collected spectra is not the best strategy to follow. This might be attributed to difficulties associated with precision of matching sampling position of on-line collected spectra with corresponding soil sample used for laboratory reference analysis, which is an issue highlighted by Mouazen et al. (2007). However, this issue has only slight effect on prediction accuracy. Adopting Viscarra Rossel et al. (2006a) classification system for the prediction accuracy reveals that the on-line prediction for OC, TN and MC is good, good/very good and excellent performance, respectively, for both modelling strategies without and with spiking (Table 8-5).

As SOM or OC are essential for soil management and carbon sequestration, they were the main properties considered for on-line vis-NIR measurement (Bricklemyer et al., 2010; Christy et al., 2008; Hummel et al., 2001; Mouazen et al., 2007; Shibusawa et al., 2001; Shonk et al., 1991). Although there are some significant absorbance peaks for carbon in both the vis and NIR spectral ranges, only few moderate successful cases for

on-line measurement have been reported so far (Christy et al., 2008; Hummel et al., 2001). This might be attributed to the affecting factors during on-line measurement, including noise associated with tractor vibration, sensor-to-soil distance variation (Mouazen et al., 2009) stones and plant roots and difficulties of matching the position of soil samples collected for validation with corresponding spectra collected from the same position (Mouazen et al., 2007; Stenberg et al., 2010). Compared to the on-line sensing of OC, there is even fewer study on TN can be found in the literature (Christy et al., 2008; Mouazen et al., 2007). Only Christy et al., (2008) archived high accuracy for TN (R^2 = 0.86) for a field scale calibration. This was not confirmed stable for different fields, as reported in the current study where on-line validation is classified as good to very good in the three measured fields (Table 7-4). Actually, there is high correlation between OC and TN, because the N content in soil is almost entirely dependent on SOM content, and the overall TN:OC ratio is 1:10 (Martin et al., 2002). This high correlation explains and justifies the successful measurement of TN, although no direct spectral response exists for TN.

Soil MC is the most successfully on-line measured soil property and higher accuracies were reported in the literature (Christy et al., 2008; Hummel et al., 2001; Mouazen et al., 2005). This is due to significant water absorbance peaks at 950, 1450 and 1950 nm. Although the range of MC was relative narrow in the current study (SD = 12.8 - 23.4 gkg^{-1}) (Table 7-5), the RMSEP for on-line prediction after 20 % spiking with laboratory scanned spectra was very small (3.23 gkg^{-1} - 7.24 gkg^{-1}), proving the excellent performance of the sensor for on-line sensing of MC.

7.3.3 Soil maps

7.3.3.1 Validation maps

(a)

(b)

(c)
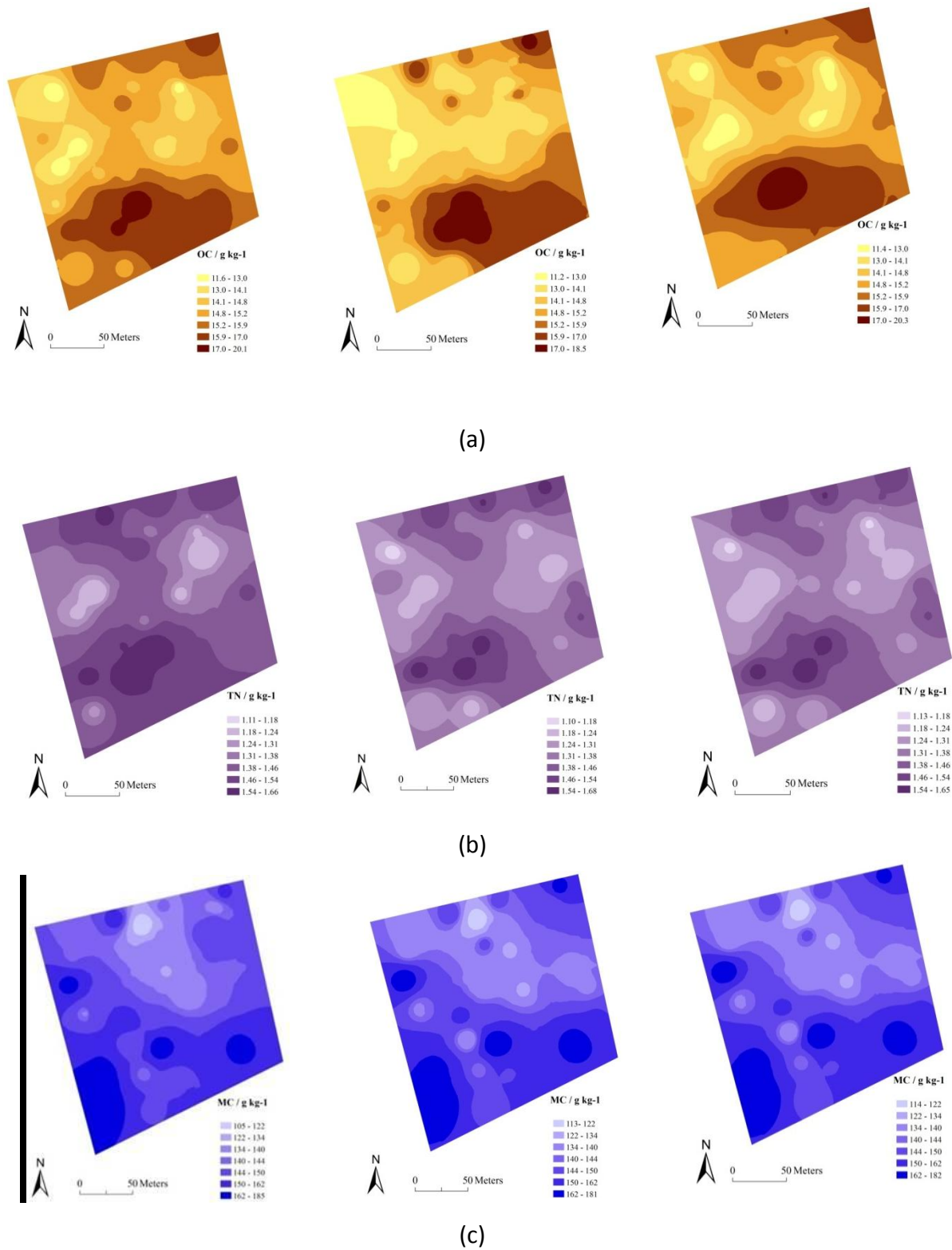
Figure 7- 4 Comparison maps based on laboratory chemical reference (left), on-line measured spectra (middle) and laboratory measured spectra (right) for organic carbon (OC) (a), total nitrogen (TN) (b) and moisture content (MC) (c), shown as example in the field of Bramstrup Estate farm in Denmark. Models used to predicted develop both spectral maps are based on 20 % spiking of laboratory measured spectra

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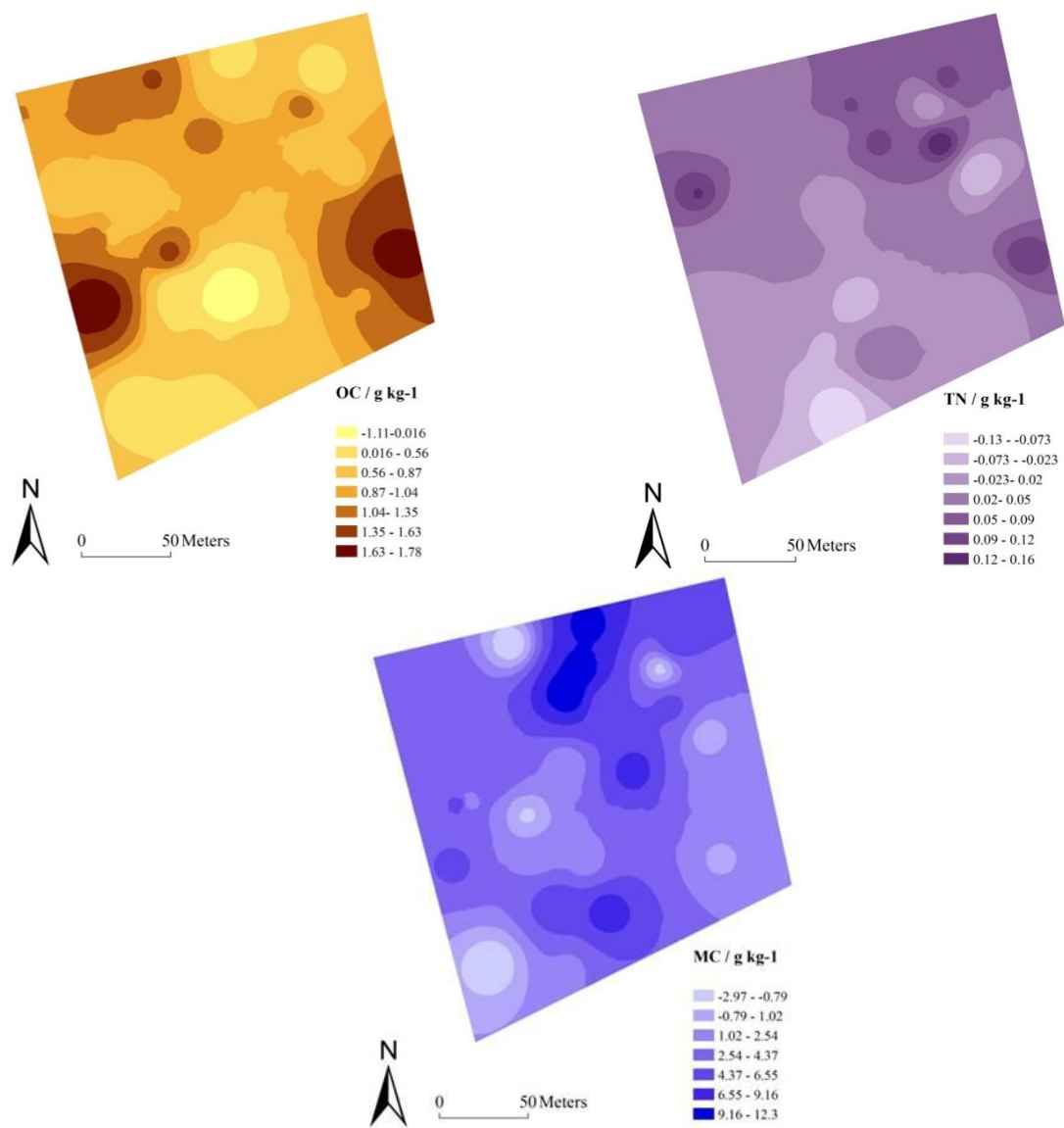
Figure 7- 5Maps of error between laboratory reference method and on-line measured organic carbon (OC), total nitrogen (TN) and moisture content (MC), shown as an example in the field of Bramstrup Estate farm in Denmark. Models used to develop error maps are based 20 % spiking of laboratory measured spectra

In order to allow for meaningful comparisons between reference and on-line measured maps, the same number of classes (7 classes) was considered for all maps with each class has identical range in three maps (Mouazen et al., 2007). A comparison between maps of measured and predicted soil properties investigated shows large spatial similarity, with high and low values zones matches almost perfectly. No spatial differences can be observed between validation maps developed with on-line measured spectra and the corresponding maps developed with laboratory (non-mobile) measured soil spectra. This proves the high quality of on-line measured spectra, which reflects the sensor stability and robustness during on-line measurement. Figure 8-5 shows the error maps between laboratory and on-line measured OC, TN and MC in the Denmark field. From these error maps, it can be observed that the largest error in the three maps occur at the boarder of each field, which might be attributed to errors associated with placing or removing the optical probe, respectively, at the start or end of some measured lines. Another reason might be the irregularity of the soil surface at the field circumference.

7.3.3.2 Full-data point maps

For the development of spatial distribution of the three soil properties using the entire data points collected with the on-line sensor, several semivariogram models where tested and the exponential semivarigrams provided the best fit. The semivarigram parameters of the three properties in the Denmark field are summarised in Table 8-6.

Table 7-6 Semivariogram model parameters of organic carbon (OC), total nitrogen (TN) and moisture content (MC) used for mapping Bramstrup Estate field in Denmark

property	Model fit	Nugget (C_0)	Sill (C_0+C_1)	Range	Proportion (C_1/C_0+C_1)	Sum of square error
OC	Exponential	0.9	2.38	9.43	0.58	1.033
TN	Exponential	0.008	0.027	8.45	0.67	0.002
MC	Exponential	167.7	321.1	6.48	0.47	20.24
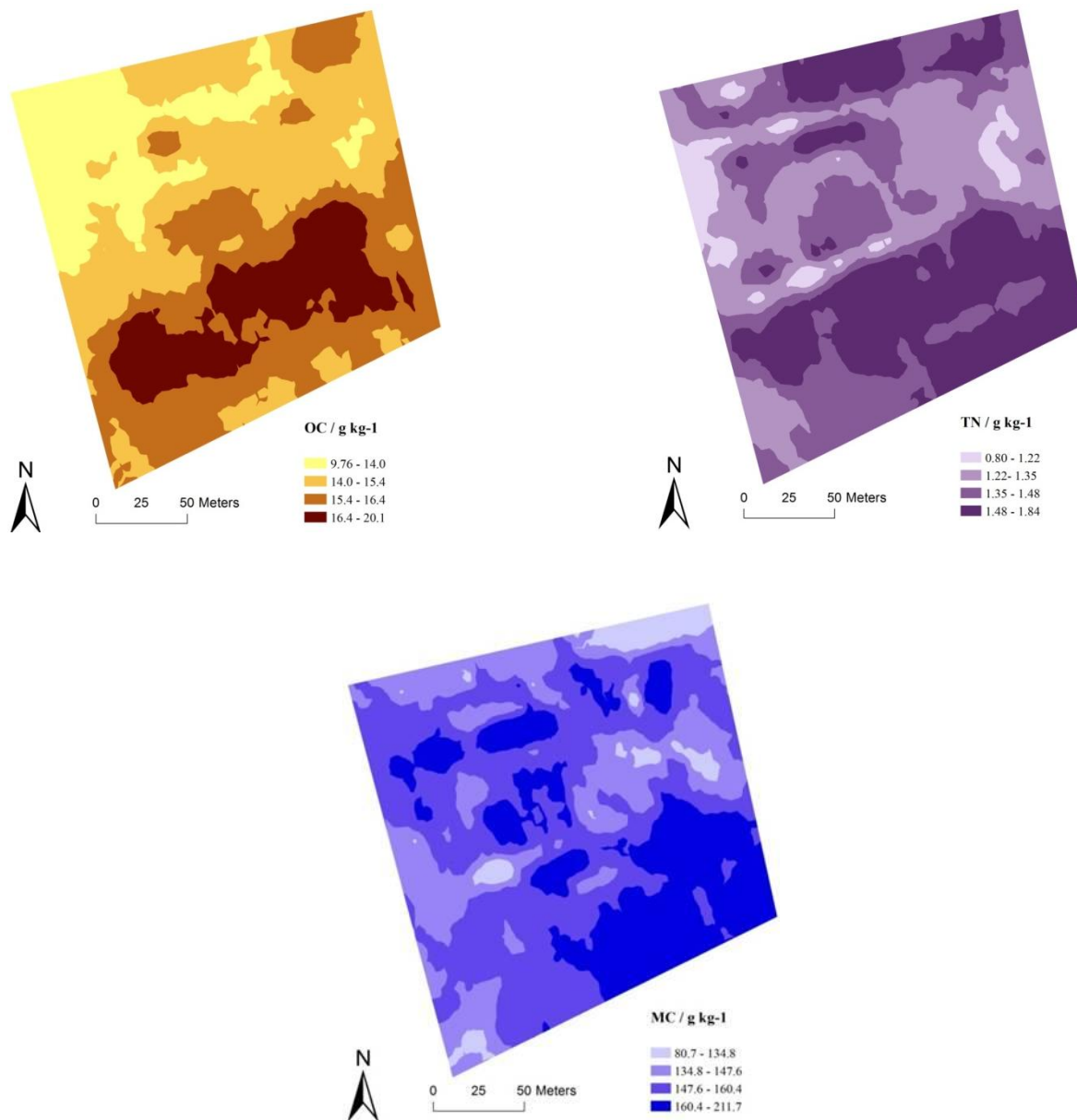
Figure 7- 6 Maps of on-line measured organic carbon (OC) (a), total nitrogen (TN) (b) and moisture content (MC) (c) based on entire data points collected in the field of Bramstrup Estate farm in Denmark. Models used to develop these maps are based on 20 % spiking of laboratory measured spectra

Maps show high spatial variability of the three soil properties, although the field area is remarkably small of 2 ha (Fig 8-6). This high variability encourages the need for on-line soil sensor for the characterisation of within field spatial variability of soil properties, as zones with different levels of concentration should be managed differently in PA,

particularly for site specific fertilisation. In particular, high similarity between OC and TN maps can be observed, which can be attributed to the fact that there is high correlation between OC and TN in the soil.

7.3.3.3 Effect of spiking strategy and spiked sample number

The best accuracy for the on-line measurement of the three studied properties was achieved for spiking with 20 % of laboratory scanned samples. Only slight increase in prediction accuracy of these models is observed for laboratory measured spectra (Table 7-4), as compared to corresponding model performances validated on on-line measured spectra (Table 7-5). However, prediction accuracy decreases as the number of spiked samples decreases (Fig. 7-8). The RPD values for MC and TN for modelling without spiking were almost equal to those with 5 % spiking. For OC, spiking with even small number of sample (e.g. 5 %) increases RPD values considerably of spiked models, as compared to none-spiked models (Figure 7-7).
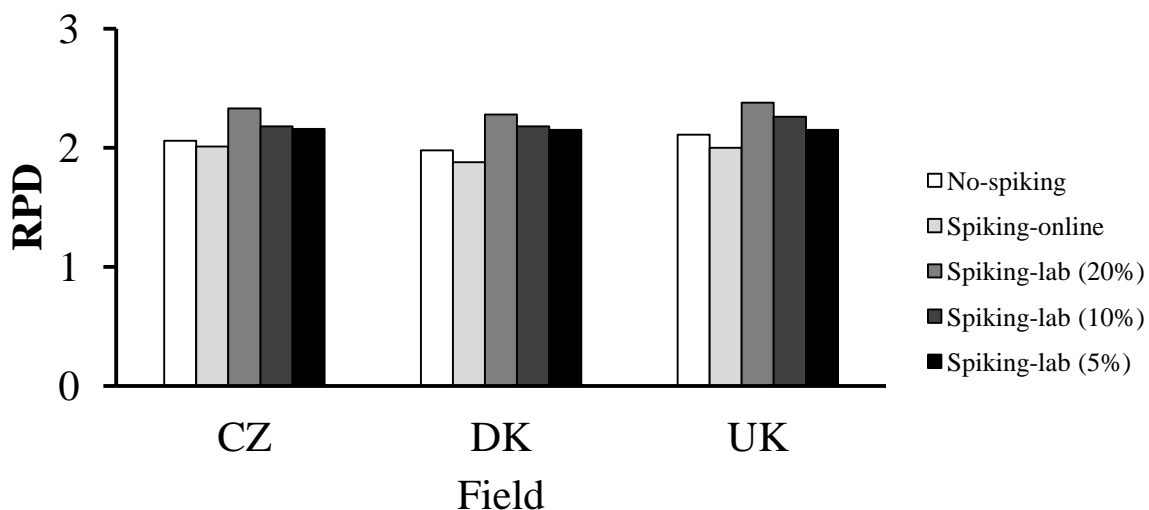
(a)
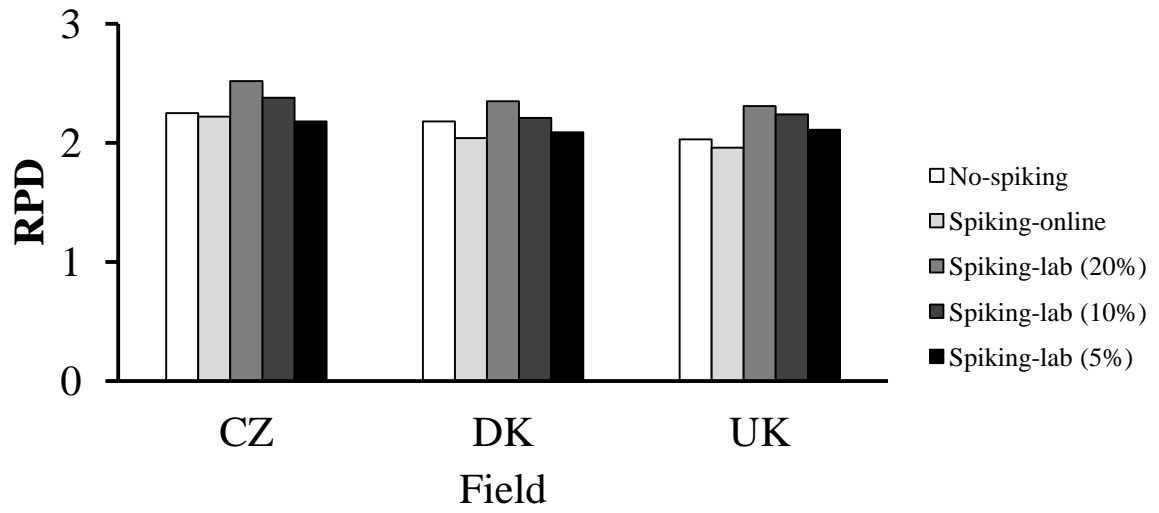
(b)
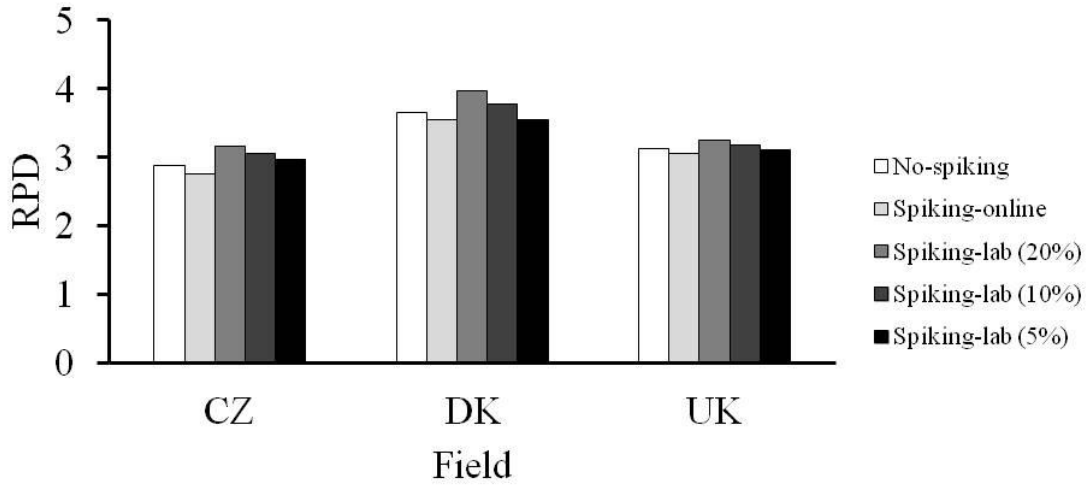
(c)

Figure 7- 7 Ratio of prediction deviation (RPD) values obtained from validation of general calibration models for on-line measured spectra of organic carbon (OC) (a), total nitrogen (TN) (b) and moisture content (MC) (c), using different spiking strategies and spiking sample numbers in three fields in Mespol Medlov, A.S. farm in Czech Republic, Bramstrup Estate farm in Denmark and Silsoe farm in the UK

In order to investigate the effect of sample number per hectare spiked into the general calibration set on prediction accuracy, variations in RPD values obtained from model validation of on-line set versus sample number spiked in the general data set (425 samples) is shown in Fig 7-8. Clear increases in RPD values with sample number per ha spiked can be observed. However, the degree of increase differs according to soil property considered, with larger increases observed for OC and TN, and smaller increases for MC. This is also affected by the field measured. On the basis of average values of the RPD of three farms, an increase of spiked sample number from 1/1.5 to 4.5 hectare (ha), leads to decrease in % RPD of 6.7 % and 15.6 % for OC and TN, respectively, whereas an increase in % RPD value of 4.6 % is observed for MC. This quantitative evaluation of % difference of RPD values may suggest that spiking of laboratory scanned spectra with a sampling rate of 1 to 2 samples per ha is sufficient to obtain accurate on-line prediction of soil properties. The model performance can be classified as very good for OC and TN and excellent for MC (Viscarra Rossel et al., 2006). This sampling rate is almost identical to the sampling rate considered for conventional analysis of soil properties, adopted today by laboratories to provide fertilisation recommendations (Mouazen et al., 2007 & 2009). This reveals that with only slight decrease of accuracy, the consumable cost of on-line measurement of OC, TN and MC would be approximately identical to that of laboratory conventional methods, after excluding the costs of on-line sensor and general dataset. However, the traditional laboratories provide fertilisation recommendations based on 1 sample per ha, where the spatial variation in soil properties is ignored. Furthermore, the on-line measurement system enables the collection of high number of data points (around 1500 readings per ha), with an average of 2 points per meter travel distance. Assuming that the laboratory methods of soil analysis do not borne to measurement error, which is not the case in practice, the detailed information about the spatial variation in soil properties obtained with the on-line sensor, even with less accuracy than that of the laboratory methods can be considered a pronounced advancement in the field of

proximal soil sensing. In addition to the high accuracy achieved for the measurement of the three properties, the performance show stability (Table 8-5) among the three fields, which is the ultimate objective of the vis-NIR calibration of soil properties, which suffers from fluctuation in performance between different sites.
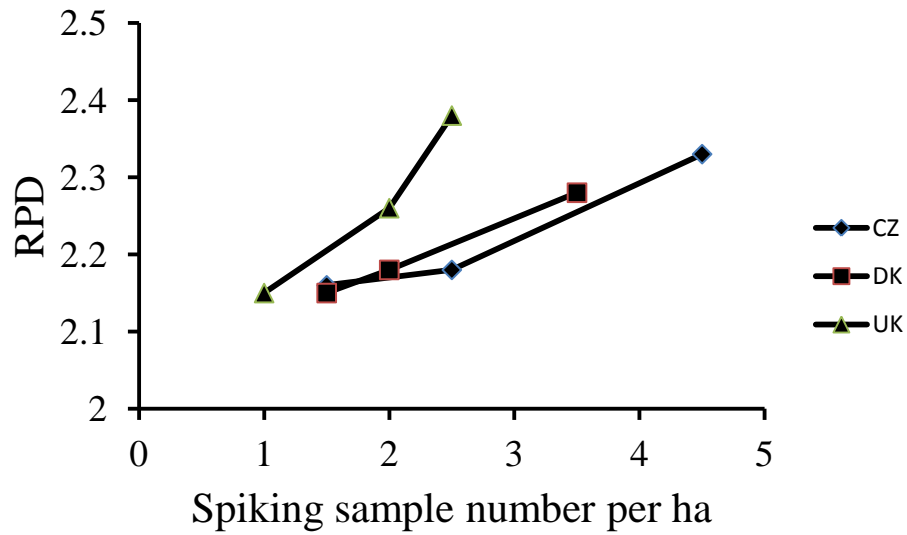
(a)
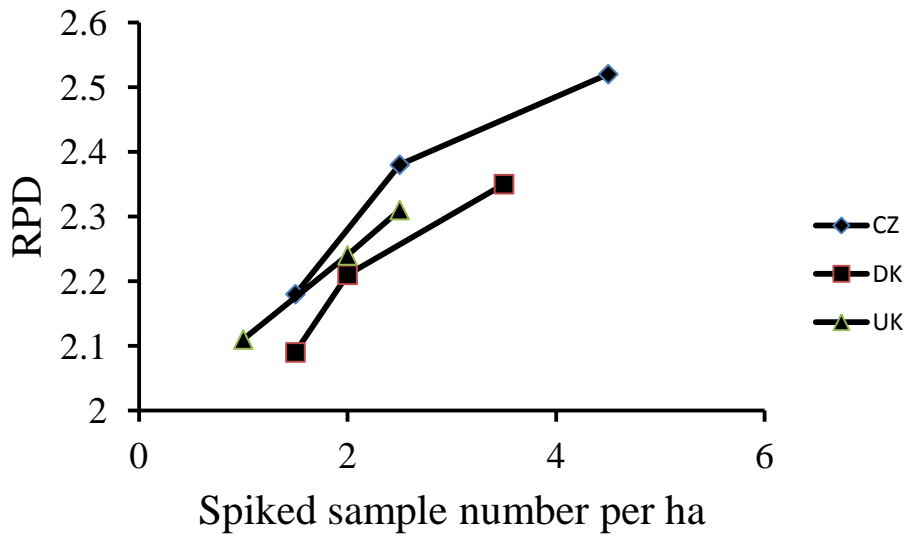
(b)
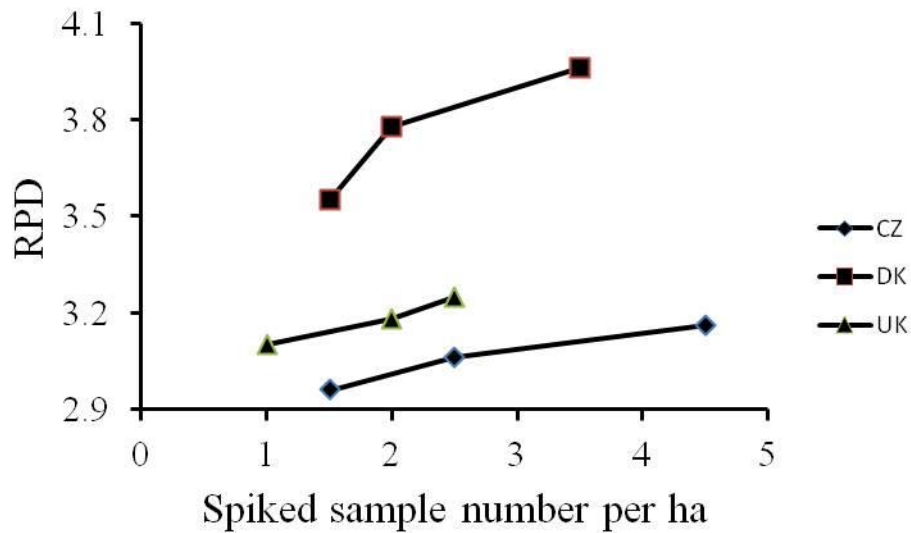
(c)

Figure 7- 8 Effect of sample number per hectare used for spiking on the ratio of prediction deviation (RPD) obtained from models validation using on-line measured spectra of organic carbon (OC) (a), total nitrogen (TN) (b) and moisture content (MC) (c) in the three on-line measured fields in Mespol Medlov, A.S. farm in Czech Republic, Bramstrup Estate farm in Denmark and Silsoe farm in the UK

Considering the wide geographical and texture variation of the three measured fields (Table 7-2), the concept of general data set spiked with a small number of samples (1-2 samples per ha) from each new measured field is a successfully calibration procedure for on-line vis-NIR measurement of soil OC, TN and MC. Generally, the general model concept proposed by Mouazen et al (2007) is based on a sufficient number of soil samples to account for the soil spatial variability in a new target site, where the prediction will be carried out (Guerrero et al., 2010; Viscarra Rossel et al., 2008). Spiking the local (target site) soil samples into the global or continental models for

non-mobile calibrations proved to be an efficient way to improve the prediction accuracy of target field for some soil constituents (Guerrero et al., 2010; Janik et al., 2007; Minasny et al. 2009; Shepherd and Walsh, 2002; Viscarra Rossel et al., 2008; Viscarra Rossel et al. 2009; Waiser et al. 2007; Wetterlind and Stenberg, 2010). The successful implementation of spiking general calibration models with field specific samples confirms the sample spiking technique to be successfully applied for on-line vis-NIR spectroscopy sensing, similar to that of laboratory and *in situ* non-mobile vis-NIR spectroscopy.

7.4 Conclusions

This chapter reports on the performance of an automatic data collection of soil properties at farm scale using a vis-NIR spectroscopy-based on-line measurement system. The results reported in this study allow the following conclusions to be drawn:

1- The on-line measurement system is robust that enables the collection of data on several soil properties, simultaneously.

2- This system enables the collection of large data points per field (around 1500-2000 readings per ha). The large number of points will open new possibilities for the management of soil-water-plant system, which was not achievable so far.

3- The accuracy of on-line measurement of OC, TN and MC was classified as very good to excellent prediction performance with RPD values range between 2.28 and 3.96.

4- The concept of general calibration models, spiked with 1-2 samples per ha from new measured fields are a successful procedure for the calibration of the on-line vis-NIR sensor, which would result in precision, classified as very good for OC and TN and excellent for MC. The cost associated with the method is comparable to that of the laboratory traditional methods.

Further work is being undertaken to improve the prediction accuracy of the system by accounting for the effect of MC and texture on the result obtained. The concept of spiking of general calibration models needs to be tested for other soil properties than those reported in this study.

8 Conclusions and future work

8.1 Conclusions

The ultimate goal of this study was to optimise the calibration of a previously developed vis-NIR on-line sensor for improved accuracy and robustness for the measurement of key soil properties, such as OC, TN and MC. To fulfil this goal, two issues were taken into consideration. These were the use of a spectrophotometer with a wider spectral range of 305 – 2200 nm and the development of a more effective calibration approach. The latter was the most focused area in this study, for which in-depth analyses of affecting parameters on model performance were considered.

8.1.1 Vis-NIR calibration

- The performance of calibration models developed with linear multivariate methods (PCR and PLSR) and non-linear method (BPNN) for the prediction of OC, extractable forms of K, Na, Mg and P using a vis-NIR spectrophotometer was compared. Results revealed that BPNN-LVs models outperformed PCR, PLSR and BPNN-PCs models for all soil properties. This might be due to the presence of non-linear relationship between soil vis-NIR reflectance spectra and property concentration. Acceptable measurement accuracy for soil properties without direct spectral response in NIR range was achieved, whereas very good accuracy was achieved for properties with direct spectral response (OC).

- The performance of farm specific models for the prediction of TC, OC, TN, P and pH are not always better than general models valid for several farms. This is because general calibration models cover a wider concentration range and SD than that of farm specific models.

- The SD and range of concentration of soil samples that explain the variability in the sample set are the determinant factors influencing the accuracy of calibration models. For properties with direct spectral response in the NIR range, a larger SD and wider range of concentration in the calibration data set resulted in larger R^2 and RPD values, but also larger RMSEP values. However, properties without direct spectral response showed inconsistent relationships and therefore they are independent of SD and range of sample concentration.

- A small range of variation in sample concentrations will not result in successful calibration. Therefore, to build a multi-farm calibration models with farms of different European countries, a large variation range should be selected that does not lead to unacceptable accuracy because of large RMSEP values. In fact, a compromise solution should be sought during the selection of calibration sample set so that to cover a wide concentration range without increasing the measurement error above a desired threshold.

- The sample number in the calibration dataset affects prediction accuracy of OC, TN and MC. Models developed with large datasets produced lower RMSEP than those with small sample datasets (e.g. 25 soil samples). Overall, how many samples should be chosen from each individual farm depends on accuracy required and 50 samples per farm is considered appropriate. Increasing the number of samples beyond 50 samples would lead not only to increase accuracy but also cost.

- The single effects of both soil MC and soil texture fractions and the interaction effects of MC and texture fractions on the prediction of OC and TN were investigated using soil samples collected from five fields of the same farm, with different field MC levels and soil textures. Soil MC, sand and silt fractions were found to have negative influence, whereas clay content has a positive effect. The individual and interaction effects of MC, silt, clay and sand fractions were found to be significant, although MC has the most significant influence on both on-line and *in situ* measurements.

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- A better accuracy of vis-NIR spectroscopy of soil OC and TN is expected in dry and clayey than in wet and sandy fields. When measurement is to be carried out under mobile (on-line) or non-mobile conditions, it is recommended to access the field as driest possible conditions, particularly in clay fields. Accessing clay fields under wet condition would result in the highest expected error, as water holding capacity of clay is high. Larger error is to be expected in this case as compared to that in fields with light soils.

8.1.2 On-line sensor and measurement capability

The on-line field measurement of OC, TN and MC in selected fields in studied European farm suggest the following conclusions:

- The on-line measurement system is robust that enables the collection of data on several soil properties, simultaneously. This system enables the collection of large data points per field (around 1500-2000 readings per ha), which will open new possibilities for the management of soil-water-plant system.
- The accuracy of on-line measurement of OC, TN and MC was classified as very good to excellent prediction performance with RPD values range between 2.28 and 3.96 (Viscarra Rossel et al., 2006) and is much better than previous studies (Christy et al., 2008; Mouazen et al., 2007).
- The concept of farm scale general calibration models, spiked with 1-2 samples per ha from new measured fields are a successful procedure for the calibration of the on-line vis-NIR sensor, which would result in precision, classified as very good for OC and TN and excellent for MC. The cost associated with the method is comparable to that of the laboratory traditional methods.

8.2 Future work

The future work based on on-line measurement of soil properties will mainly need to utilise data measured on-line as input for variable rate fertilisation of key fertilisers. To achieve this goal, the following future work would be considered:

1. To establish calibration models for soil P, K and Na using non-linear calibration methods. These models have then to be validated using on-line measured spectra. It is hoped that the non-linear calibration methods enable to establish successful models for these properties, as P and K are essential properties for plant growth, and to determine the amount of P and K fertilisers.

2. To build field scale to establish a quantitative relationship between number of samples and RMSEP.

3. To develop a self adoptive algorithm to detect X outliners during the on-line measurement as outliners is the main reason to deteriorate the validation of on-line prediction.

4. To adopt the new algorithm developed by Minasny, et al. (2011) to remove the influence of MC from the spectra during the on-line measurement.

5. To develop sub-calibration models of OC, TN, MC for separately soil texture fields to improve on-line prediction accuracy.

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APPENDICES

Appendix A Additional on-line measure results in European farms

Table_Apx-1 Information about the two extra fields in Bramstrup Estate farm in Denmark and in experimental farm of Wageningen University in Holland where on-line measurement took place in 2010.
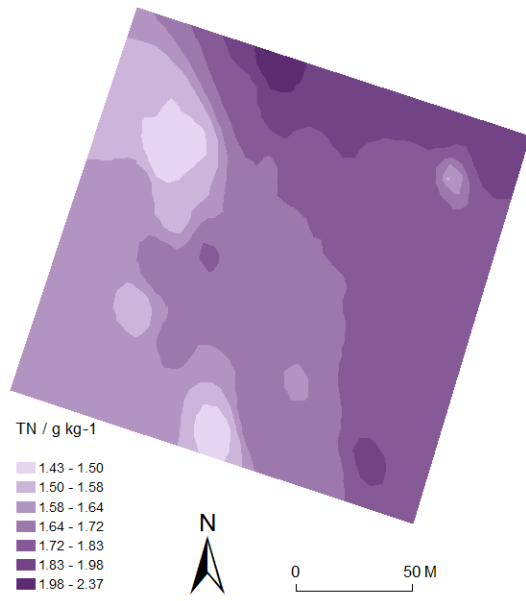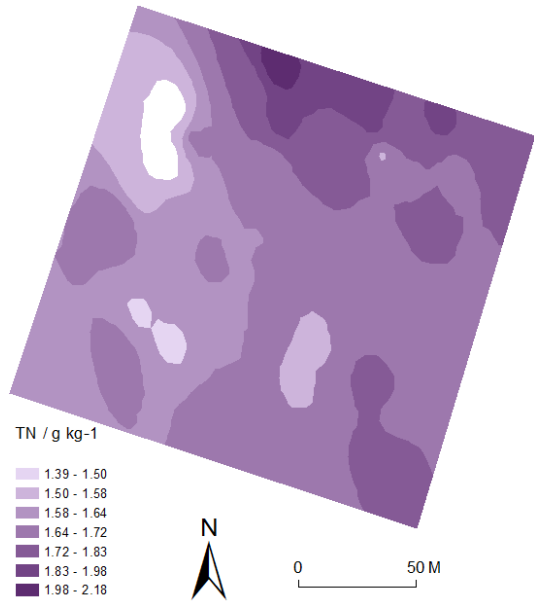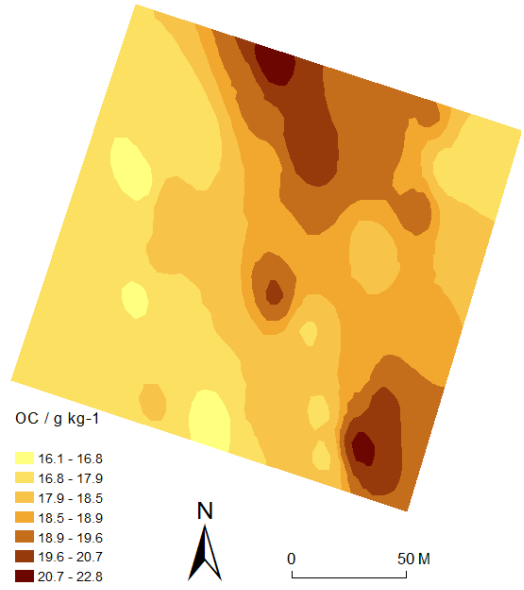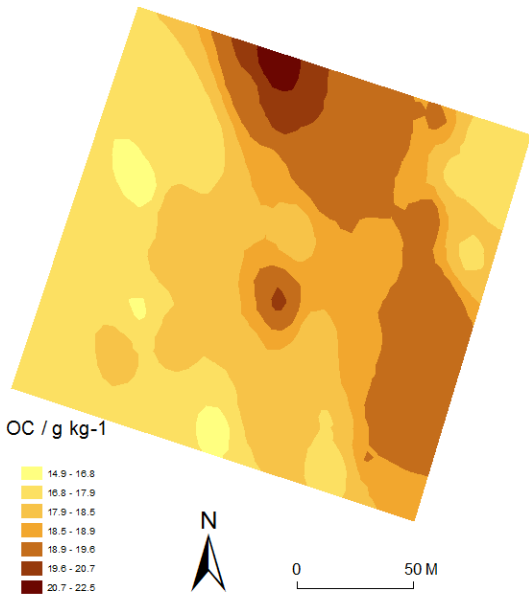
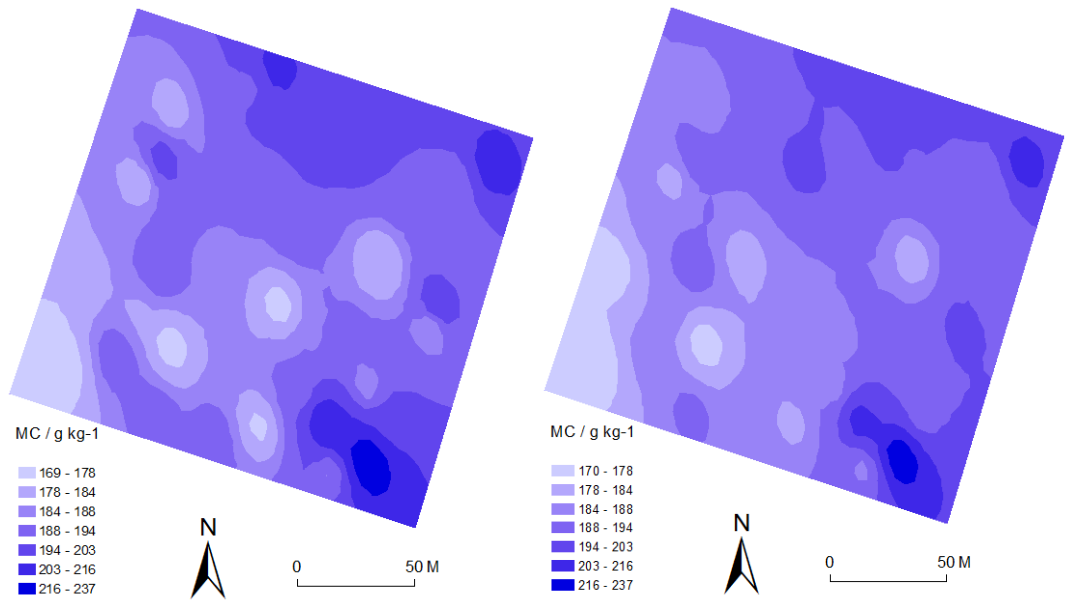| Field	Area, ha	Crop	Sample Nr	Texture type	Sand, %	Silt, %	Clay, %
Denmark	2	wheat	32	Sandy loam	83.77%	11.94%	4.29%
Holland	1.5	maize	48	Sandy loam	89.79%	8.37%	1.83%

Table_Apx-2 Summary of on-line measurement validation for two extra fields in Bramstrup Estate farm in Denmark and in experimental farm of Wageningen University in Holland where on-line measurement took place in 2010.

|			OC			TN			MC		
Spiking strategy	Country	Spiked samples	RMSE, g kg^{-1}	RPD	SD	RMSEP, g kg^{-1}	RPD	SD	RMSE, g kg^{-1}	RPD	SD
30 % lab spiking	Holland	9	0.59	2.21	1.31	0.064	2.03	0.13	4	2.71	11
	DK(2)	7	0.59	2.25	1.34	0.05	2.19	0.11	5	2.68	13.4
Model	-	-	2.30	2.82	6.50	0.23	2.61	0.6	22.20	4.28	95.0

Table_Apx- 3 Semivariogram model parameters of organic carbon (OC), total nitrogen (TN) and moisture content (MC) used for four fields on-line measured in European in 2010.

Field	property	Model fit	Nugget (C_0)	Sill (C_0+C_1)	Range	Proportion (C_1/C_0+C_1)	Sum of square error
Czech republic	OC	Exponential	0.9	2.38	9.43	0.58	1.033
	TN	Exponential	0.008	0.027	8.45	0.67	0.002
	MC	Exponential	167.7	321.1	6.48	0.47	20.24
UK	OC	Exponential	0.14	7.9	5	0.99	0.10
	TN	Exponential	0.01	0.04	11.7	0.75	0.00016
	MC	Exponential	0.44	0.24	2.88	0.36	13.3
Denmark 2	OC	Exponential	0.058	0.11	11.4	0.53	0.0018
	TN	Exponential	0.0063	0.016	13.6	0.62	0.000025
	MC	Exponential	0.988	2.86	7.22	0.68	0.42
Holland	OC	Exponential	0.11	0.31	6.25	0.68	0.05
	TN	Exponential	0.006	0.023	3.73	0.75	0.0014
	MC	Exponential	0.173	4.56	4.51	0.96	33.1

OC / g kg-1
- 14.9 - 16.8
- 16.8 - 17.9
- 17.9 - 18.5
- 18.5 - 18.9
- 18.9 - 19.6
- 19.6 - 20.7
- 20.7 - 22.5

OC / g kg-1
- 16.1 - 16.8
- 16.8 - 17.9
- 17.9 - 18.5
- 18.5 - 18.9
- 18.9 - 19.6
- 19.6 - 20.7
- 20.7 - 22.8

TN / g kg-1
- 1.39 - 1.50
- 1.50 - 1.58
- 1.58 - 1.64
- 1.64 - 1.72
- 1.72 - 1.83
- 1.83 - 1.98
- 1.98 - 2.18

TN / g kg-1
- 1.43 - 1.50
- 1.50 - 1.58
- 1.58 - 1.64
- 1.64 - 1.72
- 1.72 - 1.83
- 1.83 - 1.98
- 1.98 - 2.37

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Figure_Apx- 1Comparison maps based on laboratory chemical reference (left) and on-line measured spectra (right) for organic carbon (OC) (up), total nitrogen (TN) (middle) and moisture content (MC) (bottom) in the field of Mespol Medlov, A.S. farm in Czech Republic (chapter 8). Models used to predicted develop both spectral maps are based on 20 % spiking of laboratory measured spectra.
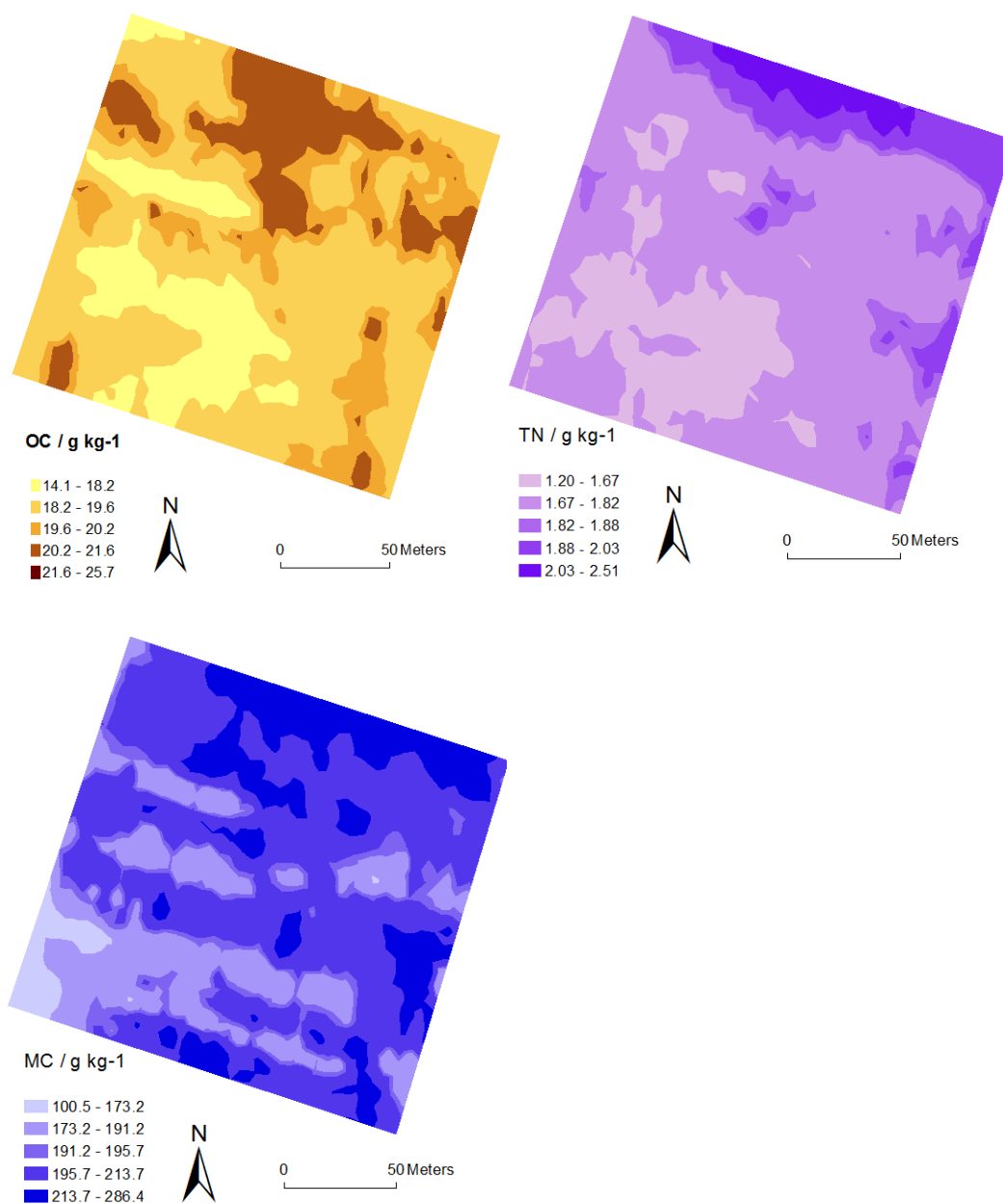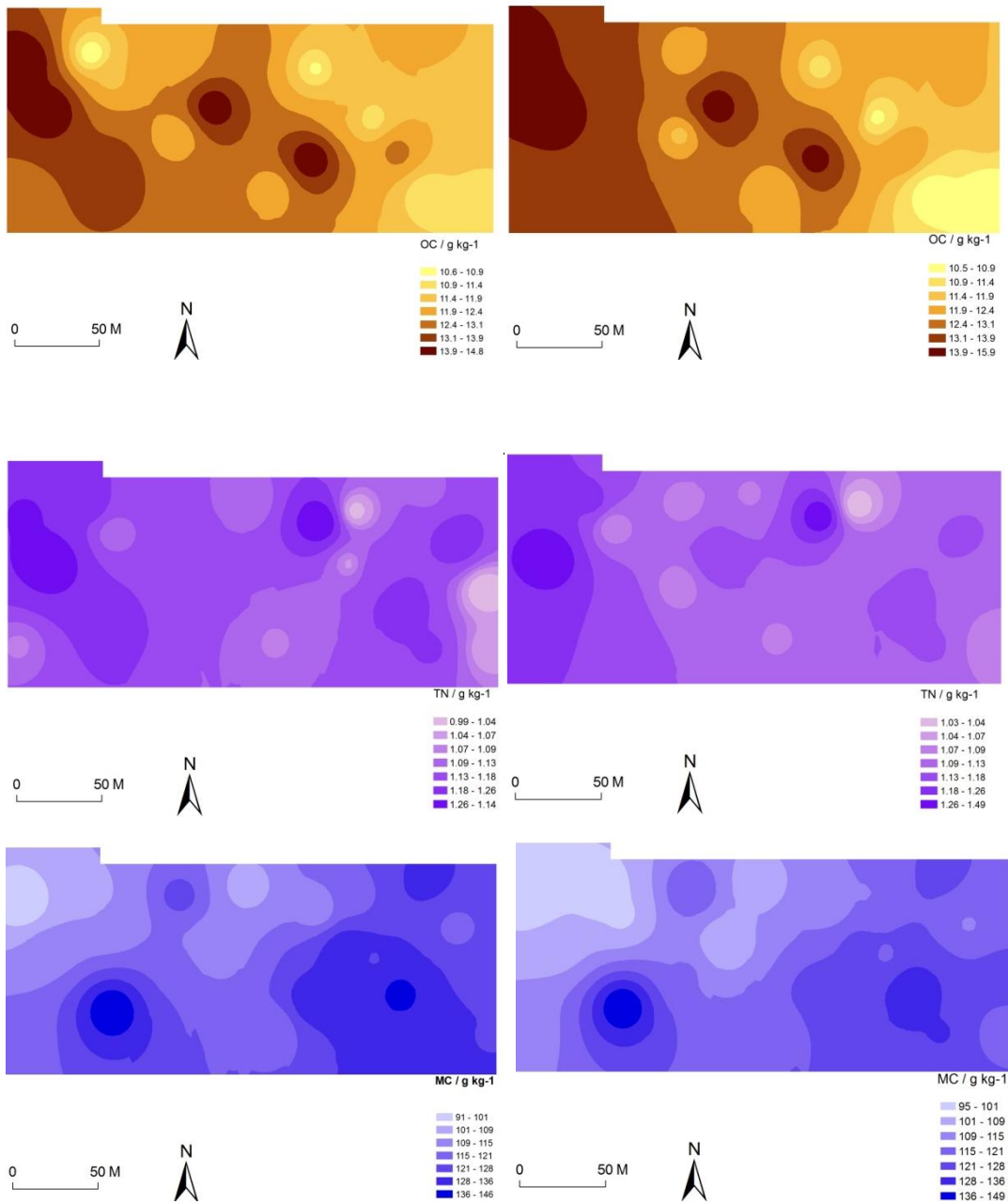
Figure_Apx- 2 Maps of on-line measured organic carbon (OC), total nitrogen (TN) and moisture content (MC) based on entire data points collected in the field of Mespol Medlov, A.S. farm in Czech Republic (chapter 8). Models used to develop these maps are based on 20 % spiking of laboratory measured spectra.
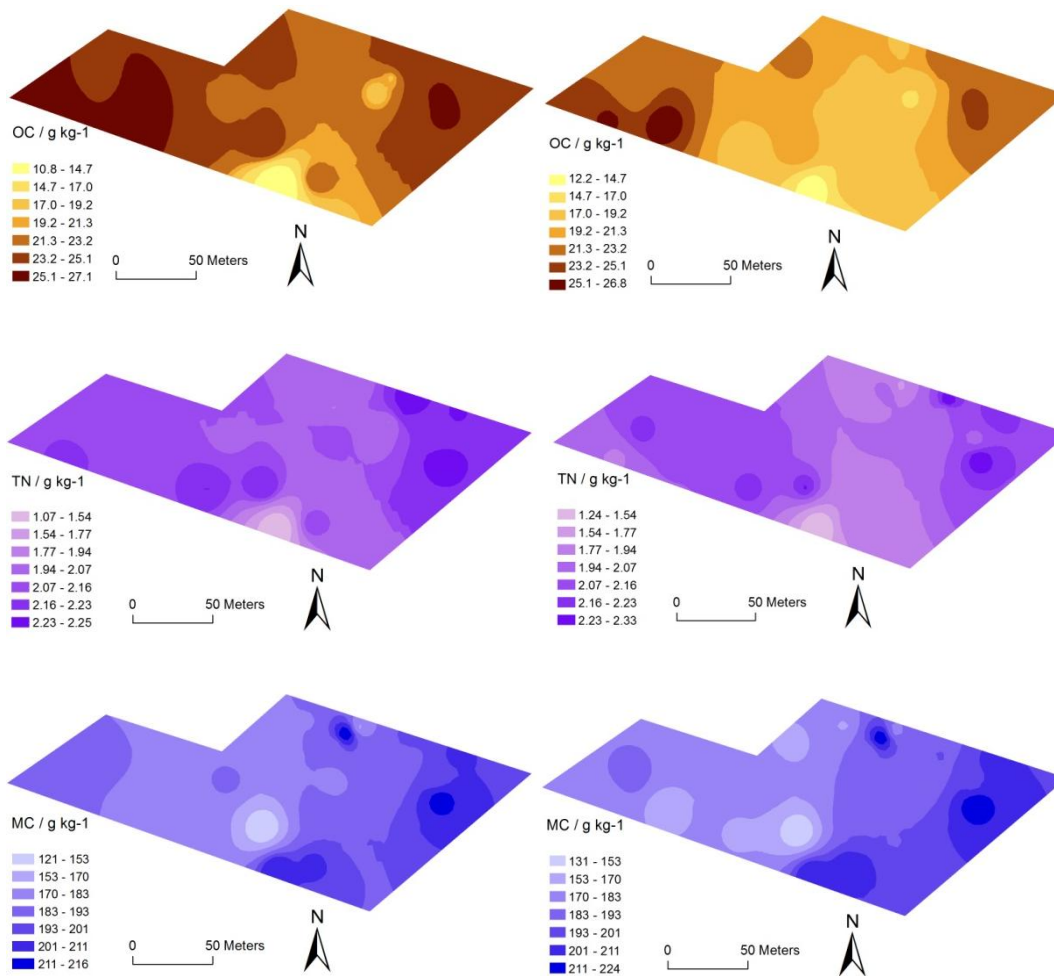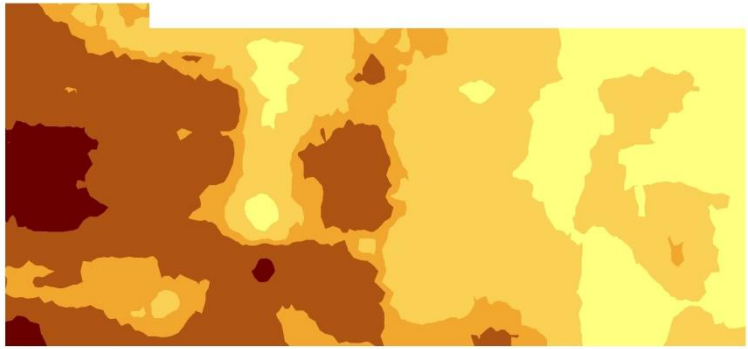
Figure_Apx- 3 Comparison maps based on laboratory chemical reference (left) and on-line measured spectra (right) for organic carbon (OC) (up), total nitrogen (TN) (middle) and moisture content (MC) (bottom) in the field of Silsoe farm in the UK (chapter 8). Models used to predicted develop both spectral maps are based on 20 % spiking of laboratory measured spectra.
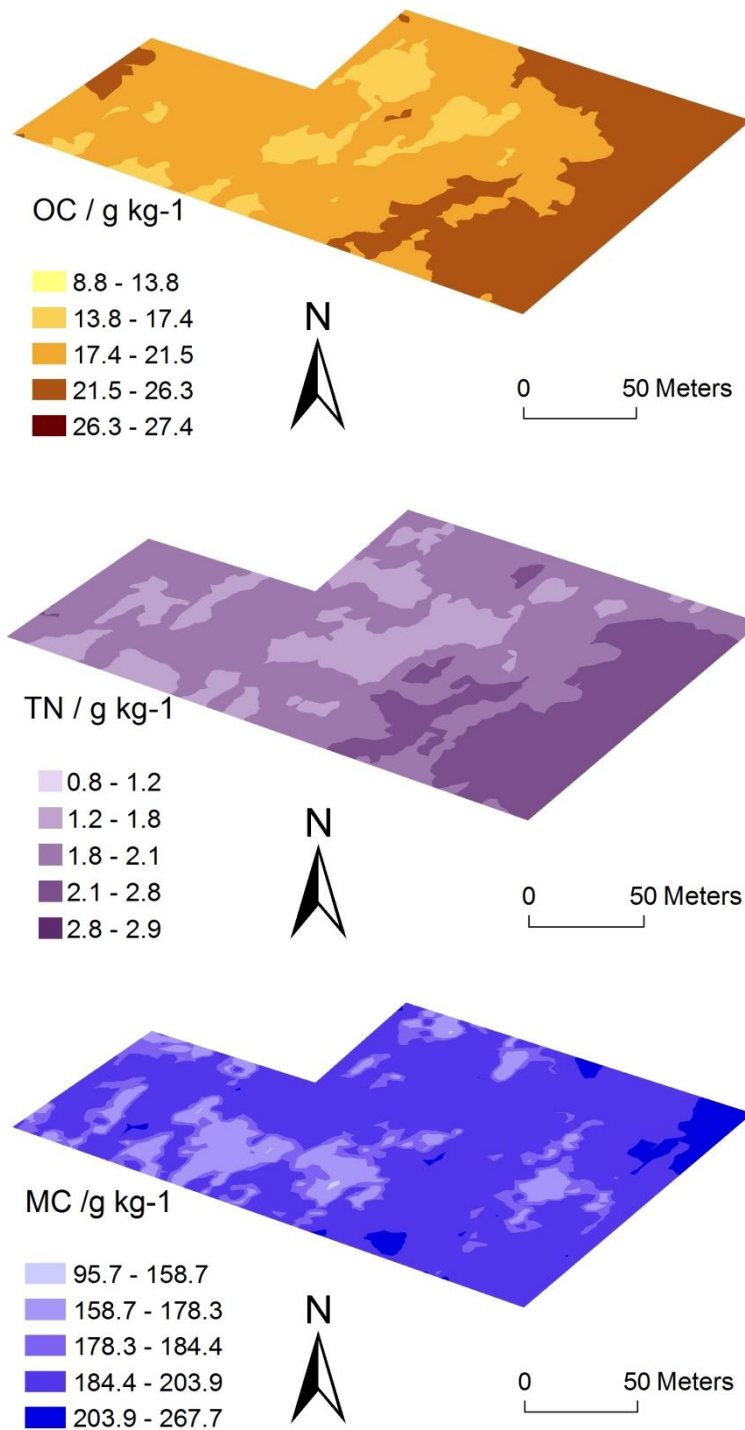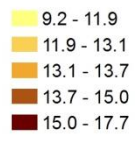
Figure_Apx- 4 Maps of on-line measured organic carbon (OC), total nitrogen (TN) and moisture content (MC) based on entire data points collected in the field of Silsoe farm in the UK (chapter 8). Models used to predicted develop both spectral maps are based on 20 % spiking of laboratory measured spectra.
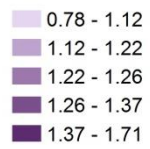
Figure_Apx- 5 Comparison maps based on laboratory chemical reference (left) and on-line measured spectra (right) for organic carbon (OC) (up), total nitrogen (TN) (middle) and moisture content (MC) (bottom) in the second field of Bramstrup Estate farm in Denmark.
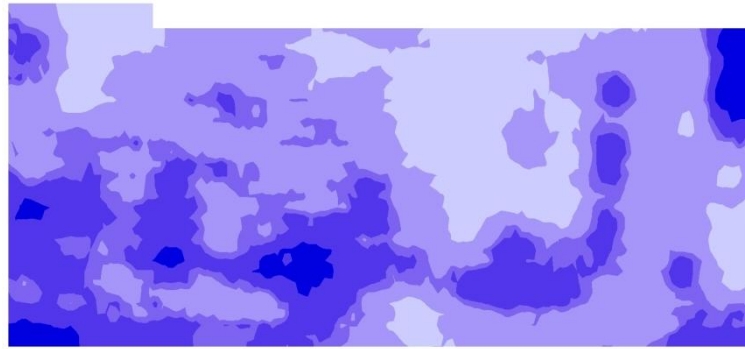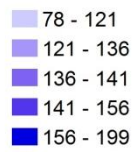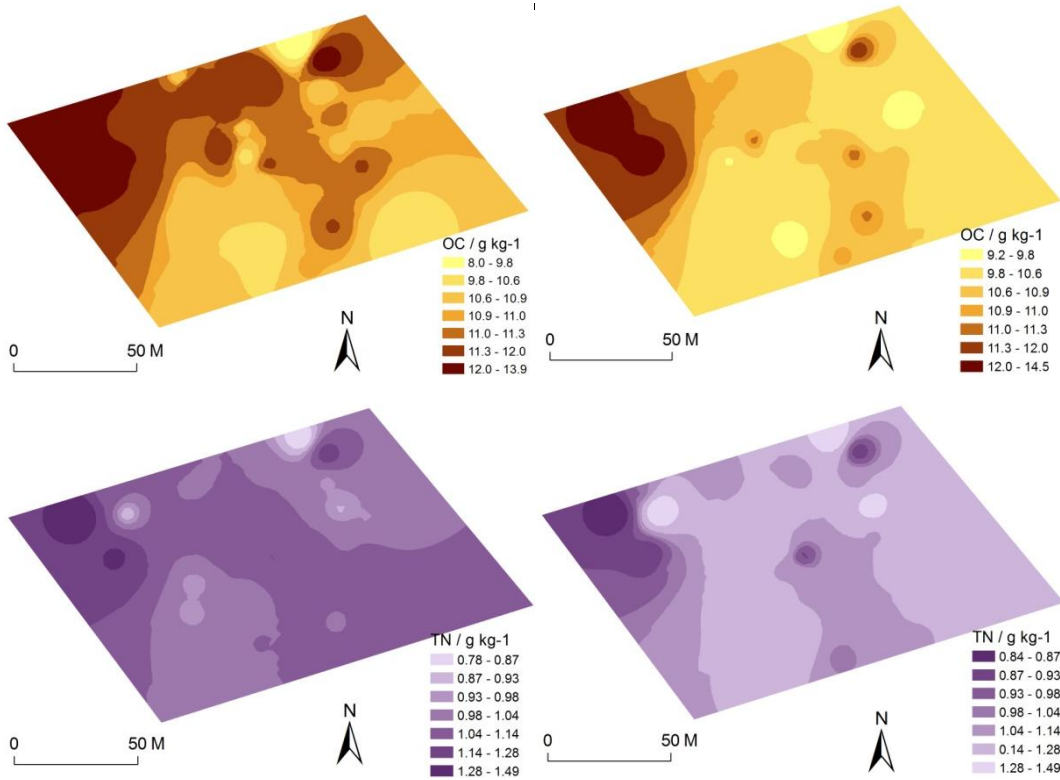
164

OC / g kg-1

- 9.2 - 11.9
- 11.9 - 13.1
- 13.1 - 13.7
- 13.7 - 15.0
- 15.0 - 17.7

N

0   50 M

TN / g kg-1

- 0.78 - 1.12
- 1.12 - 1.22
- 1.22 - 1.26
- 1.26 - 1.37
- 1.37 - 1.71

N

0   50 M

MC / g kg-1

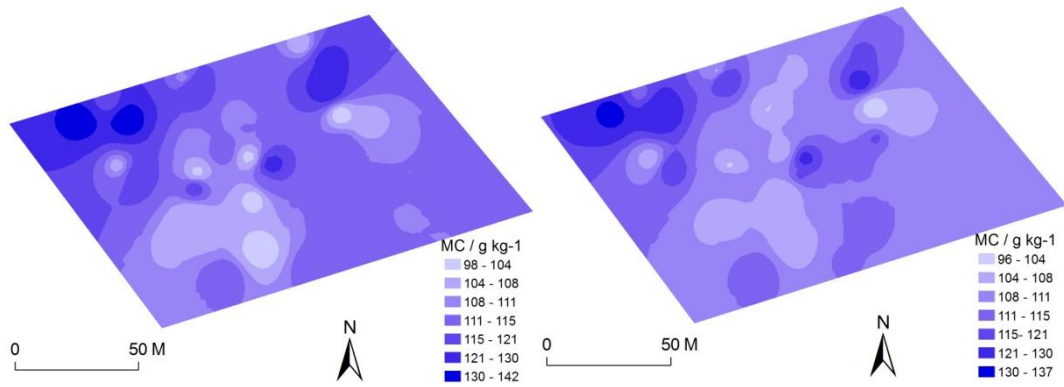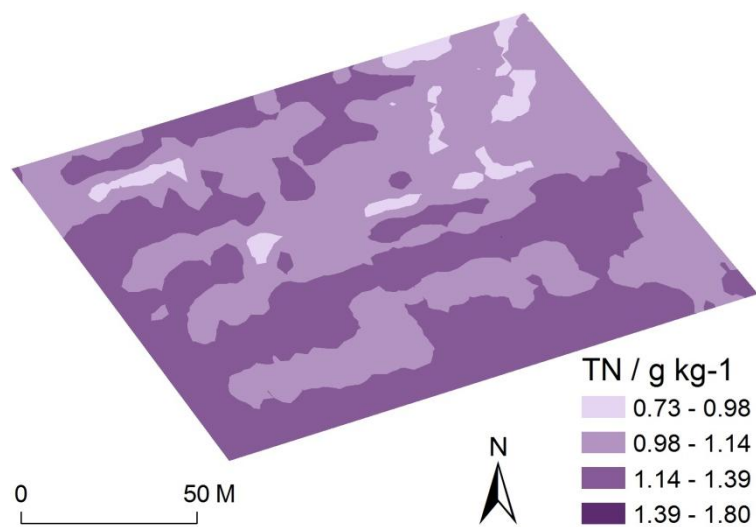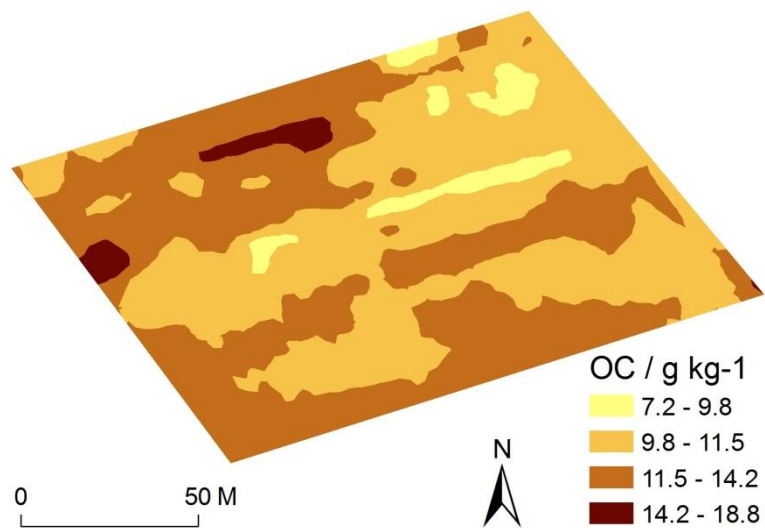|	
	78 - 121
	121 - 136
	136 - 141
	141 - 156
	156 - 199

N

0   50 M

Figure_Apx- 6 Maps of on-line measured organic carbon (OC), total nitrogen (TN) and moisture content (MC) based on entire data points collected in the second field of Bramstrup Estate farm in Denmark.

OC / g kg-1

	8.0 - 9.8
	9.8 - 10.6
	10.6 - 10.9
	10.9 - 11.0
	11.0 - 11.3
	11.3 - 12.0
	12.0 - 13.9

0   50 M

N

OC / g kg-1

	9.2 - 9.8
	9.8 - 10.6
	10.6 - 10.9
	10.9 - 11.0
	11.0 - 11.3
	11.3 - 12.0
	12.0 - 14.5

0   50 M

N

TN / g kg-1

	0.78 - 0.87
	0.87 - 0.93
	0.93 - 0.98
	0.98 - 1.04
	1.04 - 1.14
	1.14 - 1.28
	1.28 - 1.49

0   50 M

N

TN / g kg-1

	0.84 - 0.87
	0.87 - 0.93
	0.93 - 0.98
	0.98 - 1.04
	1.04 - 1.14
	0.14 - 1.28
	1.28 - 1.49

0   50 M

N

Figure_Apx- 7Comparison maps based on laboratory chemical reference (left) and on-line measured spectra (right) for organic carbon (OC) (up), total nitrogen (TN) (middle) and moisture content (MC) (bottom) in field of experimental farm in Wageningen University in Holland.
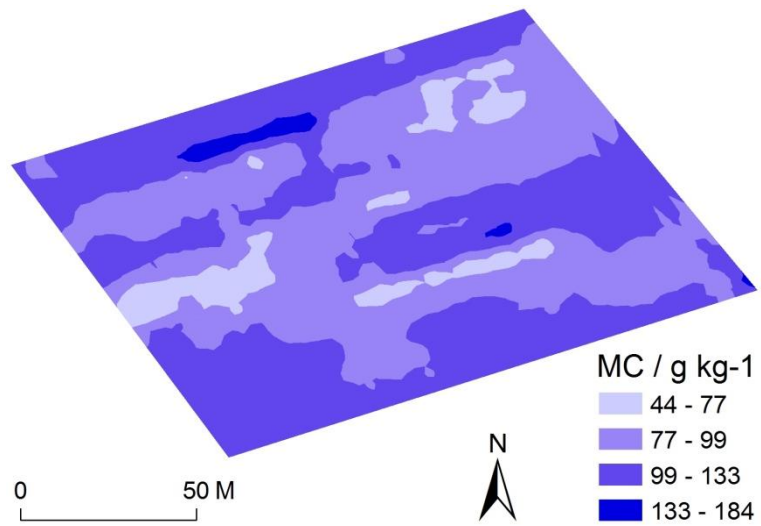
Figure_Apx- 8 Maps of on-line measured organic carbon (OC), total nitrogen (TN) and moisture content (MC) based on entire data points collected in the field of Wageningen University in Holland.