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Usefulness of near-infrared spectroscopy to assess the composition and properties of soil, litter and growing media

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Preface

This thesis is submitted to the Faculty of Organic Agricultural Sciences (Fachbereich 11) of the University of Kassel to fulfil the requirements for the degree Doktor der Agrarwissenschaften (Dr. agr.).

The dissertation is based on several papers as first or co-author, which are published, submitted or in preparation for submission to international refereed journals. They are included in chapter 4, 5, 6, 7 and 8.

Chapter 1 gives the introduction to all parts of the thesis. Chapter 2 contains the objectives of the work and chapter 3 gives an overview of the methodology of near-infrared spectroscopy.

Chapter 9 integrates in a synthesis the results, the discussion and the conclusions of chapters 4, 5, 6, 7 and 8. The summary is given in chapter 10.

The following papers contributed to this thesis:

Chapter 4:

Terhoeven-Urselmans, T., Michel, K., Helfrich, M., Flessa, H., and Ludwig, B. 2006. Near-infrared spectroscopy can predict the composition of organic matter in soil and litter. Journal of Plant Nutrition and Soil Science 169, 168-174.

Chapter 5:

Michel, K., Terhoeven-Urselmans, T., Steffan, P., and Ludwig, B. 2006. Near-infrared spectroscopy is able to distinguish between C and N originating from different coals and forest floor Oa material in soils, in preparation. [My part of this work was sample preparation, execution of measurements, parts of the data analysis and compilation of tables and figures.]

Chapter 6:

Terhoeven-Urselmans, T., Schmidt, H., Jörgensen, R.G., and Ludwig, B. 2006. Is near-infrared spectroscopy capable to determine soil quality or even soil fertility? in preparation.

Chapter 7:

Ludwig, B., Schmilewski, G., and Terhoeven-Urselmans, T. 2006. Use of near-infrared spectroscopy to predict chemical parameters and phytotoxicity of peats and growing media. Scientia Horticulturae 109, 86-91. [My part of this work was sample preparation, execution of measurements, parts of the data analysis and compilation of tables and figures.]

Chapter 8:

8.1:

Terhoeven-Urselmans, T., Bruns, C., Schmilewski, G., and Ludwig, B. 2006. Effects of passive- heating on hand-bagged peat and growing media and on plant growth. Scientia Horticulturae, submitted.

8.2:

Terhoeven-Urselmans, T., Bruns, C., Schmilewski, G., and Ludwig, B. 2006. Quality assessment of growing media with near-infrared spectroscopy: chemical characteristics and plant assay results. European Journal of Horticulture, submitted.

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List of abbreviations

(a)	Regression coefficient of a linear regression
CAL	Calcium-acetate-lactate solution
C_{mic}	Microbial biomass carbon
C_{Coal}	Carbon derived from coal
C_{Oa}	Carbon derived from forest Oa layer
C_{org}	Organic carbon
C_t	Total carbon
DOC	Dissolved organic carbon
GM-	Growing medium
LS	Loamy-silty soil
MPLS	Modified-partial-least-squares regression analysis
NMR	Nuclear-magnetic-resonance spectroscopy
N_t	Total nitrogen
N_{min}	Mineral nitrogen
N_{Coal}	Nitrogen derived from coal
N_{Oa}	Nitrogen derived from forest Oa layer
NIRS	Near-infrared spectroscopy
N_{mic}	Microbial biomass nitrogen
P-	Peat
PLFA	Phospholipid fatty acid
P_{mic}	Microbial biomass phosphor
(r)	Correlation coefficient of a linear regression
RPD	Ratio of the standard deviation of laboratory results to the standard error of prediction
RMS	Root mean square value
RSC	Ratio of the standard deviation of laboratory results to the standard error of cross-validation
SECV	Standard error of cross-validation
SIR	Substrate-induced-respiration method
SLQ1	Sandy-loam mixed with 25 % (w/w) ground quartz
SLQ2	Sandy-loam mixed with 50 % (w/w) ground quartz
SNV	Standard normal variate
VDLUFA	Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten
VIS-NIR	In the range of visible and near-infrared (400 to 2500 nm)
VSC	sum of phenolic oxidation products normalized to total carbon content

1 Introduction

1.1 General considerations

Many challenges are present in modern agricultural and horticultural sciences. For instance, knowledge of (i) the composition and (ii) origin of carbon and nitrogen in litter and soil organic matter is required for estimates on C sequestration, decomposition processes and the subsequent release of nutrients, (iii) many soil chemical, biological and yield characteristics have to be determined to assess soil quality, and (iv) fast and cost-effective methods for the determination of chemical characteristics and results of plant assays, regarding plant yield and grade of phytotoxiciy, of growing media are needed. Thus, a method, which is able to deal with this wide spectrum of applications, is of high interest.

Near-infrared spectroscopy (NIRS, 750-2500 nm) is an established analytical technique which has been successfully applied for the investigation of agricultural products, foodstuffs, forage and pharmaceutical products (Norris et al., 1976, Shenk and Westerhaus, 1994, Fahey and Hussein, 1999). Examples are the quantitative determination of the contents of fat, water, protein, total N, glumes, starch, raw fibre, oil and glucan in wheat, free fatty acids and iodine values in plant oils, and amino acids in seeds (Clark et al., 1987, Windham et al., 1988, AOAC, 1990). The main benefit of NIRS lies in a replacement of a more expensive or time-consuming analytical method, because NIRS is a cheap and fast spectroscopic method where a number of constituents can be determined simultaneously (Ben-Dor and Banin, 1995a and b, Chang et al., 2001). Such a replacement should never be done completely, but routine NIR predictions should continuously be tested on a sub-sample (e.g., 10 % of all samples). Predictions for samples from outside the calibrated range may be inaccurate and the accuracy of predictions may change with time through the expansion of the calibration data set or for other reasons (Tillmann, 2000).

Different approaches exist for the NIR analysis: (a) Constituents, which absorb in the NIR range and are present in amounts greater than the detection limit of NIRS (0.1 to 1 %) can be determined directly by using the most important absorbance wavelengths in a regression equation (Ben-Dor and Banin, 1995a) or the full spectrum (Chodak et al., 2002). (b) Constituents (e.g., trace compounds) which absorb in the NIR range and (c) constituents which do not absorb in the NIR range can be determined indirectly if they are correlated with one or several constituents which absorb in this range (Ludwig et al., 2002, Ben-Dor and Banin, 1995b). Approaches (b) and (c) are useful in those cases where the NIRS predictions are more accurate than the estimations by using simple correlations.

1.2 Composition of carbon in soil organic matter and litter

Plant litter and the microbial biomass are the main sources for the formation of soil organic matter. The materials are a mixture of many different organic compounds, e.g. polysaccharides, lignin, tannins or amino sugars. The contents of those organic compounds vary depending on the material. The composition of C in litter and soil organic matter is determined with nuclear-magnetic-resonance spectroscopy (NMR) (Kögel-Knabner, 2002). Knowledge about the composition of C in soil organic matter is required for estimates on C sequestration, decomposition processes and the subsequent release of nutrients.

Near-infrared spectroscopy has already been shown to be useful for exploring C in soils: near-infrared spectroscopy is known for its capability to predict organic C contents of litter (Gillon et al., 1999a) and different soils (Chodak et al., 2002, Moron and Cozzolino, 2002). Moreover, McLellan et al. (1991) showed for a number of tree species that the determination of the contents of lignin and cellulose of decaying litter was accurate using NIRS.

There is only little information available on the ability and limitations of NIRS to predict structural characteristics of soil organic matter. Davis et al. (1999) showed that fourier-transform-infrared spectroscopy has the capability to produce similar results compared to ^{13}C NMR spectroscopy for the prediction of the O/C atomic ratio and the ratio of UV absorbance at 465 nm to that at 665 nm (E4/E6 ratio) in humic substances. Similarly, Celi et al. (1997) reported that fourier-transform-infrared spectroscopy was as useful as liquid state ^{13}C NMR spectroscopy to predict the concentrations of carboxylic groups in dissolved organic carbon (DOC). They compared the regions 1720-1710 cm^{-1} and 1620-1600 cm^{-1} and 175-185 ppm and reported that only because of the inclusion of small amounts of esters, amides and lactones the NMR spectroscopy values were slightly higher compared to the values found with fourier-transform-infrared spectroscopy. However, no attempt has been made to predict the complete NMR spectroscopy characteristics (percentages of alkyl C, O-alkyl C, aromatic C and carbonyl C) by NIRS.

1.3 Origin of carbon and nitrogen in soils

Coals are complex mixtures of different organic compounds, which contain carbon, hydrogen, nitrogen, sulphur and oxygen as well as mineral elements. They were formed by the process of coalification of plant residues (lignite and anthracite) or by the incomplete burning of vegetation (charcoal) (BMLFUW, 2005). There is increasing evidence that coal can contribute significant amounts to the organic C (C_{org}) content of soils. For example, in Australian soils up to 30 % of C_{org} were assigned to charcoal which is amongst others generated by vegetation fires (Skjemstad et al., 1996). Due to atmospheric transport and anthropogenic activities the occurrence of coal is ubiquitous in soils and terrestrial sediments with the highest concentrations being present in highly-industrialized and coal-mining areas (Kiem et al., 2003, Goldberg, 1985).

Coal is usually considered to be highly resistant (Derenne and Largeau, 2001). In several studies, it was shown that coal is little or not mineralised and persists in soil without remarkable degradation over long periods of time (Robertson and Morgan, 1995, Skjemstad et al., 2001, Preston and Schmidt, 2006). As a consequence, the content of microbial available soil organic matter may have been overestimated in former studies, which, hence, may have resulted in an underestimation of turnover rates of organic C in soils.

Methods used to determine coal in soils include ^{14}C activity measurements and NMR spectroscopy (Rumpel et al., 1998). For example, the aryl C content in the soil fraction < 53 μm measured by cross-polarization magic-angle-spinning NMR spectroscopy after photo-oxidation treatment can be used to quantitatively estimate charcoal in soils, even though the accuracy of the estimates is discussed controversially (Skjemstad et al., 1999).

According to Schmidt et al. (2001) the ratio of the signal intensities (alkyl C + aromatic C)/(O-alkyl C + carboxylic C) is suited to indicate lignite in soils. Nuclear-magnetic-resonance spectroscopy also enables the differentiation between coalificated and recently formed organic material, because characteristic chemical structures of the latter one can be identified (Rumpel et al., 1998). However, both methods, NMR spectroscopy and ^{14}C measurements, are time-consuming and expensive.

Recent organic matter is characterized by a high proportion of polysaccharides, whereas coal is aromatic to a greater or lesser extent. The aromaticity varies between the different kinds of coal being lowest in lignite (BMLFUW, 2005). These structural and chemical differences may be suitable to differentiate between recently formed organic matter and coal or different kinds of coal, respectively, using NIRS. This assumption is supported by the fact, that NIRS successfully predicted the C composition of soil organic matter and litter which was originally determined by ^{13}C NMR spectroscopy (Terhoeven-Urselmans et al., 2006a). Other attempts to detect the contribution of coal to soil organic matter by NIRS have not been reported.

1.4 Assessment of soil quality

A high soil fertility is the key for stable yields. This is especially valid for organically managed farms, because this concept of farming is based on the closure of nutrient cycles at the farm level, balanced crop rotations and it excludes the use of chemical-synthetically fertilisers and pesticides.

Measurement categories for the assessment of soil quality are generally soil chemical and biological characteristics and to a certain extent yield characteristics of field crops. The named categories have one in common – their determination include cost and time-consuming methods and some soil biological characteristics, e.g. ergosterol content, are susceptible to longer storage and even exposure to short unfavourable conditions.

Near-infrared spectroscopy was used in soil science to assess soil quality with respect to chemical characteristics. Moron and Cozzolino (2002) predicted the contents of C_{org}, total nitrogen (N_t) and pH value successfully. Contents of C_{org} and N_t are in soils in most cases above the detection limit and predictions are thus direct. Predictions of the contents of total and exchangeable soil macro nutrients were not always successful. Malley et al. (1999) showed for 28 Canadian soils good predictions for total contents (nitric acid digestion) of P, K and Mg: the RPD (the ratio of the standard deviation of laboratory results to the standard error of prediction) ranged from 3.2 to 8.6 and (r) from 0.9 to 1.0. Predicted exchangeable contents were in most cases worse than total contents. Daniel et al. (2003) predicted contents of available P well ($r = 0.9$), whereas van Groeningen (2003) predicted the contents of P (Olsen) satisfactorily ($r = 0.8$). Contents of exchangeable K were predicted satisfactorily (Dunn et al., 2002) or unsatisfactorily (Chang et al., 2001). Finally, contents of exchangeable Mg (KCl) were predicted well by Shepherd and Walsh (2002) ($r = 0.9$) and satisfactorily by Islam et al. (2003) ($r = 0.8$).

Characteristics of soil biota are predicted indirectly with NIRS, because their concentrations are below the detection limit. Thus, predictions are more susceptible to spectral noise. Predictions of microbial biomass C and N (C_{mic}, N_{mic}) for arable and forest soils were only in one case successful: Chodak et al. (2002) showed for the C_{mic} determination (measured by the substrate induced respiration method, SIR) of dried forest soils good predictions ($RPD = 2.2$ and $r = 0.9$). Oppositely, Terhoeven-Urselmans et al. (2006a) predicted C_{mic} (SIR) for dried soil and litter samples unsatisfactorily (RSC (ratio of the standard deviation of laboratory results to the standard error of cross-validation) = 1.1 and $r = 0.8$). Microbial biomass N was investigated from Reeves and McCarty (2001) for agricultural soils and their predictions were satisfactory ($r = 0.8$).

Microbial biomass P (P_{mic}) was not yet predicted with NIRS. Ergosterol content was determined with NIRS only for forest organic layers (Pietikainen and Fritze, 1995). They predicted ergosterol content, which was markedly higher in comparison to arable soils, well for freeze-dried samples ($r = 0.9$). Mineralisation rates of carbon and nitrogen are related to the microbial biomass and the amount and quality of substrate. Thus, predictions with NIRS may be explained by indirect features. Basal respiration was predicted well for dried arable soils (Chang et al., 2001) ($RPD = 2.3$ and $r = 0.9$) and dried forest soils (Chodak et al., 2002) ($RPD = 2.1$ and $r = 0.9$). Russel et al. (2002) showed for the rate of N mineralisation (determined aerobically) of dried rice soils satisfactorily results ($r = 0.8$). In contrast, Shepherd et al. (2005) showed good results for the prediction of the nitrogen mineralisation of dried crop and tree residues, which were incubated in a sandy soil (r = 0.9).

Grain yield is mainly outcome of soil chemical and biological properties, but it is as well influenced by e.g. local weather conditions and plant pests. Thus, NIRS predictions of yield and yield characteristics are assumed to be weaker than predictions of soil characteristics. Grain yield was not yet predicted well from soils by NIRS. Van Groeningen et al. (2003) investigated dried and ground rice soils. Predictions of grain yield were unsatisfactory (RPD = 1.0 and r = 0.2). Satisfactory predictions were only achieved in some, but not all cases, when the spectral information of the plant canopy was correlated with the grain yield: Babar et al. (2006) showed for wheat satisfactory predictions of grain yield (r = 0.7 – 0.8). Nitrogen uptake of grain was predicted under glasshouse conditions well (r = 0.9) by Russel et al. (2002). They investigated rice soils, which were air-dried for NIRS measurements. However, their predictions were under field conditions unsatisfactory (r = 0.6). Stenberg et al. (2005) were also not able to show better results for the prediction of N uptake of wheat (RPD = 1.9 to 2.5 and r = 0.6 to 0.8). Nitrogen content of grain, which is an important quality attribute for bread production, was not yet predicted directly from soil spectra.

Summarising the findings above, NIRS was capable to predict several soil chemical characteristics successfully, soil biological characteristics satisfactorily and yield characteristics in many cases unsatisfactorily. Nearly all investigations used dried soils for NIRS measurements. It is proposed that measurements with field-moist samples should improve predictions for soil biological characteristics markedly. Moreover, it is assumed that quick-freezing with liquid nitrogen and subsequent freeze-drying of soil samples is a pre-treatment method, which enables the determination of soil biological characteristics even after longer storage with a high degree of accuracy and precision.

1.5 Quality assessment of growing media

Peat is worldwide the most important substrate for production of growing media. A high quality standard to promote plant health is required. A prerequisite to achieve plant health is an appropriate fertilisation of each plant species, which is secured by chemical analysis of the growing medium. Moreover, the use of phytotoxic growing media has to be avoided. The phenomenon of phytotoxicity is not yet fully understood. Known reasons are nutrient deficiencies and toxic substances. But other reasons like self- or passive-heating are assumed to be elicitors. The determination of the grade of phytotoxicity is done normally by standard plant assays, e.g. using Chinese white cabbage (*Brassica napus* var. *Chinensis*). Theses tests are time-consuming and the results are only comparable, when the growing conditions are equal. This is in practice not always the case and can lead to wrong assessments of the degree of phytotoxicity.

Near-infrared spectroscopy has already been used in peat studies to investigate basic quality parameters. Successful NIRS predictions were made for the determination of peat moisture and the degree of humification (McTiernan et al., 1998, O´Mahony et al., 1998). Ludwig et al. (2006) predicted the pH and contents of salt, P and K well for a sample collective of 73 growing media. However, the accuracy of the prediction of nitrate and ammonium contents was less satisfactory presumably due to a small sample number or because of a too spectrally diverse population.

Prasad et al. (2000) showed the ability of mid-infrared spectroscopy to predict the breakdown of different peats during an incubation, which lasted from 30 to 208 weeks. They correlated the 1600/1060 wavenumber ratio at the beginning and the end of the incubation with the vertical shrinkage loss (measured in mm) of potted peats. However, it is not clear, whether their results can be generalised, because they did not consider the impact of particle size on the degree of peat shrinkage.

Near-infrared spectroscopy has not yet been used for the prediction of phytotoxicity, self-heating and yields of plants in growing media and for the quality assessments of growing media using standard plant assays. However, indications of the usefulness of NIRS for such an application are given by the results of field studies by Babar et al. (2006) and Chang et al. (2003). Babar et al. (2006) used spectral reflectance indices from the plant cover in order to differentiate between various spring wheat genotypes for optimising grain yield. Chang et al. (2003) used remote sensing (520-920 nm) to predict corn yield. Only early spectral sampling dates, when plant cover was lowest, yielded useful results.

The soil spectral information was more important for yield prediction than plant cover spectral information.

Summarising the findings above, NIRS has been able to predict some basic chemical characteristics of growing media and first attempts were made using NIRS for predictions of complex constituents such as biomass yield in related scientific areas. However, information on the ability of NIRS to predict phytotoxicity and plant yield of Chinese white cabbage of various growing media is missing.

2 Objectives

The objectives of this study were to evaluate the usefulness of near-infrared spectroscopy to predict:

(i) the characteristics of litter and soils, determined with nuclear-magnetic-resonance-spectroscopy (chapter 4),

(ii) the content of carbon and nitrogen in soils derived from different kinds of coals and material of forest Oa layer (chapter 5)

(iii) soil chemical, biological and yield characteristics (chapter 4 and 6)

(iv) chemical characteristics, plant assay results and phytotoxicity of growing media (chapter 7 and 8.2).

3 Methodology: near-infrared spectroscopy

The word spectroscopy is derived from the Latin root *spectrum* (appearance, image) and the Greek root *skopia* (to view). In other words, spectroscopy deals generally with energy transfer between light and matter.

The pre-name “near-infrared” of near-infrared spectroscopy, which is abbreviated NIRS, defines the wavelength range, which is used. The near-infrared region contains the wavelengths between 780 and 2500 nm. Sometimes the visible range (400 to 780 nm) is additionally used. This is abbreviated mostly VIS-NIRS.

3.1 Physical basics

Molecular energy can take many different forms, such as translational, rotational, electronic and vibrational. Spectroscopy for solid samples is in the infrared range only influenced by electronic and vibrational energy forms of which the latter one is more important (Miller, 2001).

Absorption bands in the near-infrared region are overtones (1/2, 1/3… of the original wavelength) or combination bands from the fundamental bands in the mid-infrared region (2500 to 25000 nm) (Hirschfeld and Zeev-Hed, 1981). However, the measured absorption bands in the near-infrared region are in practice often different from the assigned ones from the mid-infrared region. Reasons for this deviation are the neighbouring group effect and hydrogen bonding on the atomic level, crystallinity, phase separation and molecular conformation on the microscopic level and thermal and mechanical effects (Miller, 2001) Therefore, near-infrared spectroscopy is used more in quantitative than in qualitative analysis (Socrates, 2001). Molecules absorb light in the infrared region and transfer this energy to vibrations. Prerequisite is, that light energy corresponds to the difference between two quantized energy levels of the molecule. Vibrations refer to oscillation of atoms through their bonds in a molecule. The most important vibration forms are stretching, bending and twisting (Figure 3.1.1).

Absorption bands of C-H, N-H and O-H are the most common ones in the near-infrared region. Soils are highly complex mixtures mainly consisting of minerals, but plant and microbe derived proteins, carbohydrates, fats, cellulose, lignin and other substances containing different functional groups are also present. Thus, broad peaks are characteristic of the near-infrared region and the bands often overlap. A direct assignment of a wavelength to a certain compound based on the original spectrum is nearly impossible.

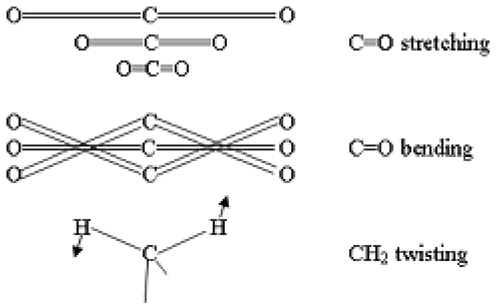

Figure 3.1.1: Different forms of molecule vibrations
(adapted from Miller, 2001).

3.2 Measurements

Measurements were conducted using a Foss NIRSystems spectrometer 6500 (Silver Spring, USA). Samples were scanned in the VIS-NIR range (400 to 2500 nm) in two nm intervals (1050 data points per spectrum). The reflectance at every wavelength was recorded and transformed to absorbance (A) using the equation:

$$A = \log (1 / \text{reflectance}) \tag{1}$$

A typical spectrum of a dried and ground soil sample is given in Figure 3.2.1.

The spectrometer performance was tested using three internal tests after heating of the lamp for one hour. The tests were instrument response, wavelength accuracy and NIR repeatability: the tests were conducted in order to verify that the spectrometer works correct, that every wavelength corresponds to its assigned wavelength and that the measured absorbance is repeatable, respectively.

An additional test was the soy check-cell test after every 15th measurement. A soy-shred sample, stored in a rectangular cup, with known concentrations of protein, fat, crude fibre and dry matter, was used to standardize the spectrometer. The actual predicted contents were compared with the known contents. Thus, spectrometer performance was tested continuously.

The samples, used for the investigations, were measured field-moist (A) or pre-treated. Pre-treatment methods were (B) drying at 60 °C and finely grinding and (C) quick-freezing, freeze-drying and grinding (Table 3.2.1). Samples were filled into three cm diameter small ring cups. The cups had a glass window consisting of quartz. Samples were planated, compacted with a flexible plastic disc and measured spectroscopically.Two measurements were conducted, whereby the small ring cups were turned around for 90 to 180 ° prior to the second measurement.

The two measurements were repeated if the spectral difference between the two spectra was too high. The spectral difference was determined calculating the root mean square value (RMS), where every wavelength was weighted equally:

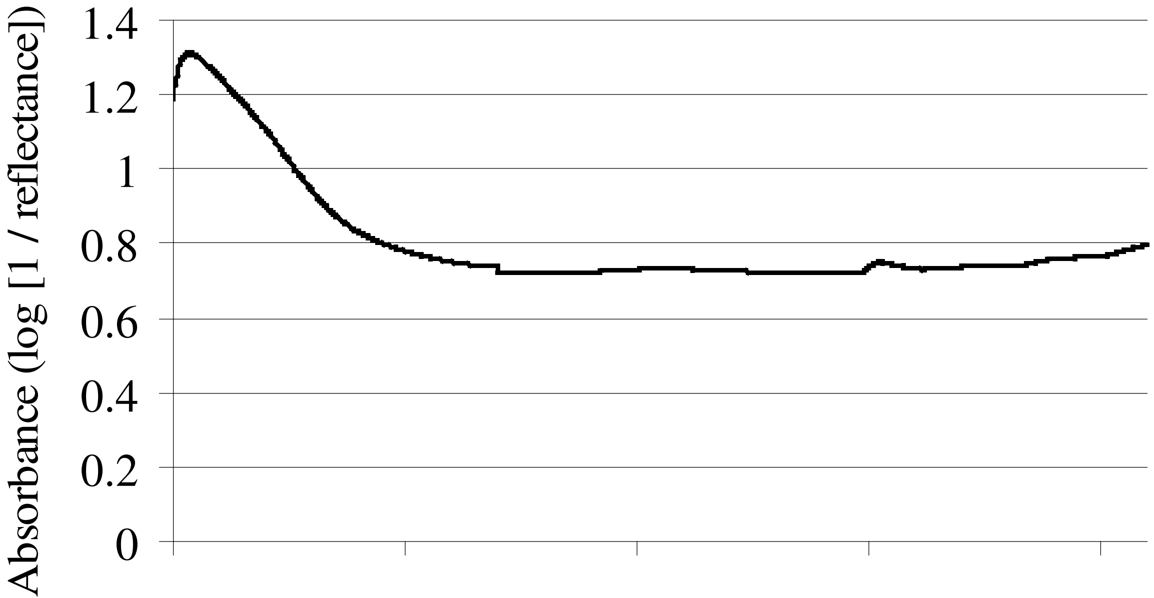

Figure 3.2.1: A typical absorbance spectrum of a dried and ground soil sample.

$$RMS = \sqrt{\frac{\sum_i \left(x_i^1 - x_i^2\right)^2}{l}} \quad (2)$$

with i = 1…l wavelengths.

Table 3.2.1: Sample state, root mean square value and range of outliers for the sample sets, which were investigated with near-infrared spectroscopy (NIRS).

Sample set	Sample state for NIRS measurements	Root mean square (RMS) value	Range of outliers (percentage of sample set)
NMR spectroscopy	B	5000	0 - 9
C and N from coals	B	1000	5 - 7
Soil quality	A, C	1500, 700	0 - 9
Growing media	A, B	3000, 10000	3 - 6

A Samples were field-moist.
B Samples were pre-treated by drying at 60 °C and finely grinding.
C Samples were pre-treated by quick-freezing, freeze-drying and grinding.

The RMS limit was determined heuristically and differed for every sample set. Soils and dried and ground samples had in general lower RMS-values than peat and field-moist samples. The limits set in the investigations were in the range from 700 to 10000 (Table 3.2.1).

3.3 Spectral transformations

It is know from empiric studies that especially spectra of solid and chemically complex samples such as soils and peats are influenced by shifts, scattering and multi-collinearity. Different particle sizes and packing densities of a sample are the reasons for scattering and shifts. Multi-collinearity is triggered by high correlated wavelengths, e.g. adjacent wavelengths (Tillmann, 2000).

To eliminate linear and quadratic trends over the whole spectrum the spectra were transformed with “standard normal variate” (SNV) and “detrend” (Barnes et al., 1989). By using SNV every single spectrum is taken. The absorption values are changed in this way that they have over the whole wavelength range a standard deviation of one. It is calculated as follows:

$$z_i = (x_i - \bar{x}) / s \tag{3}$$

with i = all wavelengths of a spectrum, z = transformed absorption value, x = measured absorption value, $\bar{x}$ = mean absorption and s = standard deviation.

Derivatives (first, second and third) of the original absorbance spectra were used to solve the problem of scattering, parallel baseline shifts and to make very fine bands visible, which can be overlapped from broad bands.

Derivatives are taken between the absorbance values of two data points. The derivative is the difference of the absorption values of two data points and is equal to the gradient of the trendline between them.

In Figure 3.4.1 some spectral transformations from a field-moist soil sample are displayed: the two peaks around 1400 and 1900 nm in Fig. (a) are due to the strong absorption feature of water. Taking derivatives (Fig. (c), (d) and (e)) emphasise and sharpen peaks in the original spectrum. A peak in the original spectrum is transformed to a null, when the first and third derivative is taken and to a peak, when the second derivative is calculated. It must be pointed out by viewing Figure 3.4.1 that the absolute absorbance values and the transformed absorbance values are on different levels.

In order to emphasise absorption features in the spectra more strongly, they can additionally be transformed in two ways: firstly, derivatives can be taken over varying gaps of data points and secondly, the derivatives can be smoothed over varying gaps of data points. A prerequisite is, that the gap over which the derivative is smoothed is equal to or smaller than the gap over which the derivative is taken.

3.4 Spectral analysis

The prediction of a constituent, e.g. total carbon content of a soil sample, from the spectrum was based on regression analysis imbedded in a calibration/validation procedure. The analysis used was a modified-partial-least-squares (MPLS) regression analysis and the calibration/validation procedure was cross-validation.

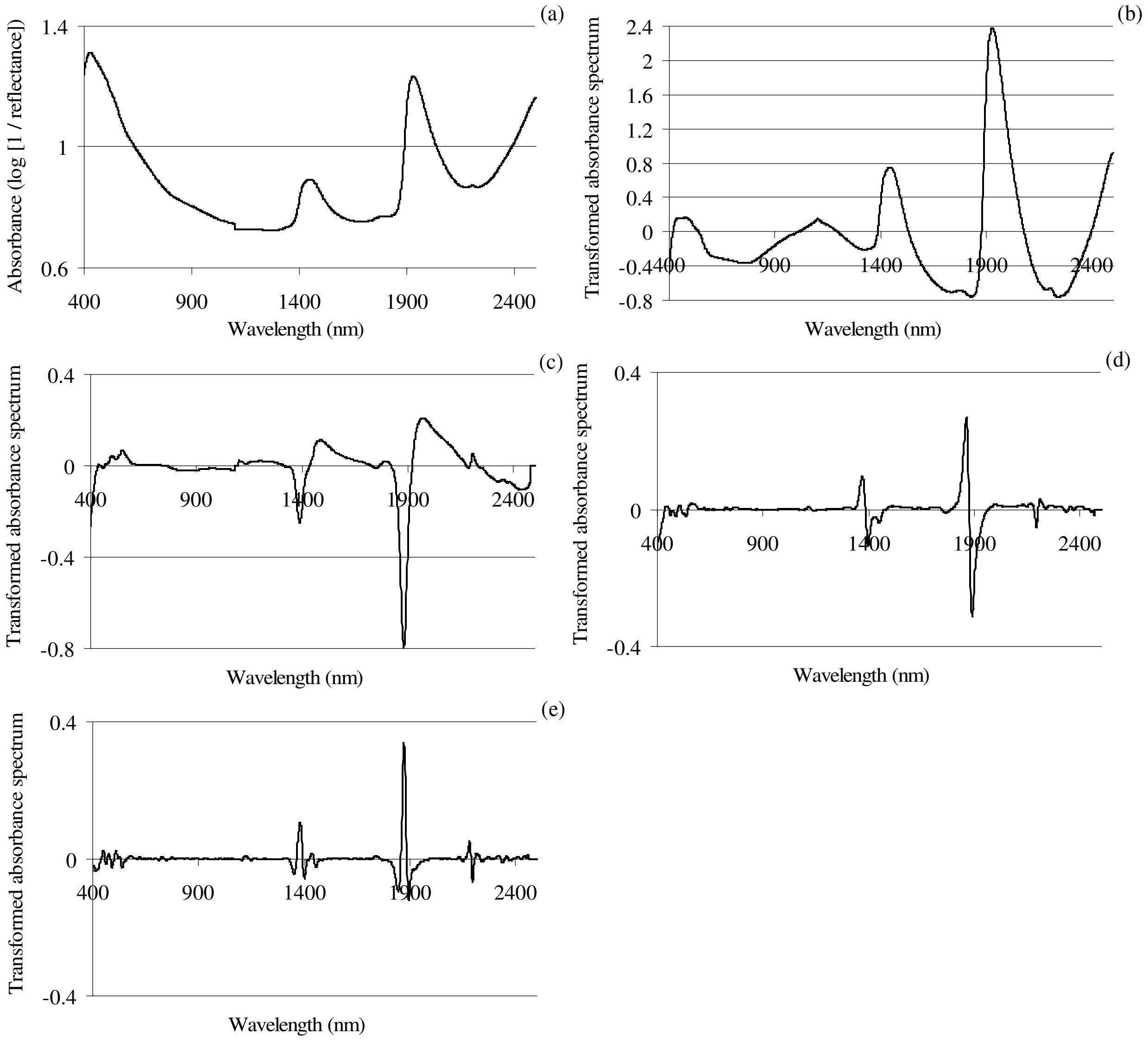

Figure 3.4.1: (a) Original spectrum of a field-moist soil sample and transformation of the original spectrum either with (b) „standard normal variant“ (SNV) and „detrend“ or with (c) the first, (d) second and (e) third derivative and SNV and „detrend“ is also shown.

3.4.1 Cross-validation

A calibration procedure usually is done by separating a pool of samples into a calibration data set and an independent validation data set. The calibration is used to develop an equation for the prediction of the calibrated constituent. In a second step, the quality of the calibration equation is tested with the validation data set.

However, more recently, this approach has been widened by a procedure called cross-validation (Foley et al., 1998). Cross-validation is a form of Monte Carlo simulation, in which the population is randomly divided into a small number of groups and a prediction is made of the values for one group based on calibrations developed from the remaining groups. In turn, predictions are made for all groups with the predictions of the remaining groups (Shenk and Westerhaus, 1993a and b). This procedure is useful, because the sample set can be smaller to be sufficient for reliable predictions in comparison to the calibration/validation procedure (Shenk and Westerhaus, 1993a and b).

Several studies also showed that the calibration/validation procedure and cross-validation procedure are equally valid. For instance Moron and Cozzolino (2004) reported for the constituents a similar RPD (the ratio of standard deviation of the laboratory results to standard error of prediction) and RSC (the ratio of standard deviation of the laboratory results to standard error of cross-validation) values. The RPD and RSC values were 3.0 and 3.6 for C_{org} content, 4.0 and 4.5 for N_t, 2.0 and 2.1 for N in particulate organic matter and 2.3 and 2.2 for potentially mineralisable nitrogen. Since all values are greater than two, all results indicated a good potential of NIRS for predicting these constituents.

3.4.2 Modified-partial-least-squares regression analysis

Partial least squares (PLS) regression analysis, which is modified by scaling the reference method data and reflectance data at every wavelength to have a standard deviation of 1.0 (MPLS regression analysis) (Shenk and Westerhaus, 1991), is similar to principal component regression analysis. The difference is that beside the spectral information the sample reference values are used for calculations.

Modified-partial-least-squares regression analysis assumes that spectral data are a function of the concentration of the compounds one is interested in. The spectral information (1050 measured data points per sample) of all samples is reduced to a few factors (depending to the sample number). Correlating wavelengths are merged to one factor, which solves the problem of multi-collinearity. Additionally, wavelengths with high variability between the samples are described in one factor. Each factor must be orthogonal to the other factors. The first factor captures as much as possible of the spectral variance and the variance of the constituent. Each successive factor accounts for as much of the remaining variability as possible.

The number of factors (x) used in the MPLS regression analysis were calculated according to the following formula:

$$x = (n / 10) + 2, \tag{4}$$

with n being the sample number.

Every sample receives for every factor a factor value, which is the link to the original spectrum. Finally, these factor values are used to fit the spectral information to the measured values by minimizing the sum of differences, which is conducted by partial least square regression.

3.4.3 Outlier detection

The quality of cross-validation predictions, especially for future predictions, is significantly lowered by outlier samples. Thus, outliers have to be checked and if acceptable removed from cross-validation. In the present study, the number of outlier elimination passes during cross-validation was two.

Outliers were defined as samples with a spectrum out of the population of spectra (with a high Mahalanobis-distance, called H-outliers) or for which the difference between the reference and the predicted value was much larger than the standard error of cross-validation (SEVC) (t-outliers). The limits were set to 10 (H-outliers) and 2.5 (t-outliers) as suggested by the WinISI II software and Tillmann (2000).

The number of excluded outliers obtained in this way was in the range from 0 to 9 % (Table 3.2.1).

Most outliers were t-outliers. The outliers excluded during the MPLS-procedure were included again in the graphs of measured against predicted values and in the calculations of the correlation coefficients (r) and regression coefficients (a) in order not to overrate the potential of NIRS.

3.4.4 Evaluation of prediction quality

The prediction quality of the MPLS regression analysis was evaluated in two steps. Firstly, the best mathematical treatment was chosen and secondly, quality indices of a linear regression of measured against predicted values were calculated and compared to pre-set limits.

The best mathematical treatment was found by carrying out a trial and error procedure. The spectra were transformed before MPLS regression analysis with SNV and „detrend“ and derivatives were taken (first, second and third order) over varying gaps (one to twenty data points) and varying smoothing (one to twenty data points). In total 45 mathematical treatments were done per constituent.

The criterion for the best mathematical treatment was the lowest SECV. The use of the SECV also avoids over-fitting. The SECV is lowest, when the number of terms used in MPLS regression analysis is optimal. The SECV was calculated as follows:

$$SECV = \sqrt{\frac{\sum_i (measured_i - predicted_i)^2}{n-1}} \qquad (5)$$

with i = values from every sample and n = number of samples.

Once the best mathematical treatment was found a linear regression was calculated. According to Ludwig et al. (2002) and Chang et al. (2001), good predictions can be described as follows: the RSC is higher than 2.0 and the correlation coefficient (r) and the regression coefficient (a) of a linear regression of measured against predicted values are greater than or equal to 0.9 and in the range from 0.9 to 1.1, respectively. Satisfactory results are obtained for $1.4 \leq RSC \leq 2.0$, $r \geq 0.8$ and $0.8 \leq a \leq 1.2$. Predictions are not satisfactory when $RSC < 1.4$.

The predicted values were set in the linear regression to the independent x-axis. This was done due to following reason: once the prediction-equation is developed, the content of e.g. total carbon of a new soil sample is predicted, and is thus dependent from the spectrum, which is in this case independent.

3.5 Wavelength assignment

The WinISI II software computed for the different constituents the correlation coefficients over the whole spectrum. The original spectra were transformed prior calculations using the optimum mathematical treatment for each constituent. The maximum or null correlations were selected in dependence on the order of the derivative functions: for the first and third derivative, null correlations between the highest absolute values refer to a peak in the original spectrum. Oppositely, the highest correlations for the second derivative refer to peaks in the original spectrum. The assignment of functional groups to wavelengths was done using the WinISI II software and the information provided by Miller (2001).

4 Near-infrared spectroscopy can predict the composition of organic matter in soil and litter

4.1 Experiments

Sites and samples

The 56 samples used in this study covered a wide range of experimental sites and land uses and are described in detail by Dignac et al. (2002), John et al. (2005) and Helfrich et al. (2005). The majority of samples were taken from O (n = 18) and A horizons (n = 15) from German, Norwegian and Danish Norway spruce sites. Additional soil and plant samples were taken from the long-term experiment at Rotthalmünster, where soils under maize, grassland and spruce were sampled and fractionated into free and occluded particulate organic matter fractions (n = 10) and aggregate fractions (0.053-0.25 mm; 0.25-1 mm; 1-2 mm; >2 mm; n = 8). Plant materials were roots and shoots of maize and grass and spruce needles (n = 5). The samples obtained covered a wide range of C and N contents and composition (Table 4.1.1) and thus present a harsh test on the applicability of NIRS for the prediction of several constituents in soils and litter from different sites and under different land uses.

Biological analysis

Microbial biomass was determined in four replicates for the European forest sites by substrate induced respiration by Michel and Matzner (2002). Briefly, forest floor Oa material (20 g fresh weight) mixed with 80 mg glucose was incubated at 22 °C. After 4 h carbon dioxide production was measured by gas chromatography. The substrate induced respiration values were converted to C_{mic} by using the equation of Anderson and Domsch (1978).

The incubation experiments for the determination of DOC and mineral nitrogen (N_{min}) production were conducted according to Michel and Matzner (2002). Briefly, Oa or A material was weighed out into plastic syringes and moisture was adjusted to field

Table 4.1.1: Selected chemical and microbiological properties of the different constituents. The units given in the third column refer to the mean, range and standard deviation of measured values (VSC = sum of phenolic oxidation products normalized to total carbon content)

	Constituent		n	Mean	Range	Standard deviation
Basic characteristics	C	g kg^{-1} sample	56	135	1.1-466	160
	N	g kg^{-1} sample	56	5.52	0.2-23	6.51
	C/N		56	24.6	6.7-84.1	15.0
Biological characteristics	C_{mic}	mg C g^{-1} C	30	7.44	1.7-16.7	4.05
	DOC production	μg C g^{-1} C d^{-1}	30	18.8	0-57.9	20.6
	N_{min} release	mg N g^{-1} C d^{-1}	30	5.02	1.0-10.1	2.55
NMR characteristics	carbonyl C	%	55	8.74	2.1-16.0	2.86
	aromatic C	%	55	15.0	5.5-23.7	3.35
	O-alkyl C	%	55	50.0	33.0-82.6	10.2
	alkyl C	%	55	26.4	9.9-41.0	7.60
	alkyl/aromatic C		55	1.87	0.7-4.00	0.66
	alkyl/O-alkyl C		55	0.57	0.1-1.20	0.25
Lignin	VSC	g kg^{-1} C	30	18.4	6.7-34.5	7.58

capacity. All samples were pre-incubated for 2 weeks at 15 °C and then incubated for a period of 42 weeks. Respiration was measured weekly for 3 to 4 h in a closed system with constant air flow. Carbon dioxide was detected in the air flow by microprocessor controlled non-dispersive infrared photometers. Dissolved organic carbon production and net N mineralisation were determined by percolating Oa material of the 15 spruce sites every fourth week. The percolation was done with an artificial throughfall solution. In these percolates DOC and N_{min} (NH_4^+ and NO_3^-) were determined. To calculate net N mineralisation three sub-samples of each site were additionally extracted with 1 M KCl solution at a soil solution ratio of 1:10 in a batch procedure before and after incubation. The amount of N_{min} determined before incubation was substracted from the sum of N_{min} measured in the percolates and KCl extract after incubation. The net N mineralisation was normalized to initially abundant C on a daily basis (Michel and Matzner, 2002).

^{13}C NMR spectroscopy spectra

The procedure of NMR spectroscopy acquisition for the samples from (i) the Norway spruce sites and (ii) Rotthalmünster were done by Dignac et al. (2002) and Helfrich et al. (2005), respectively. Briefly, solid-state ^{13}C NMR spectroscopy spectra were obtained using either (i) a Bruker AMX300 spectrometer with a MAS probe for 7 mm Bruker BL, double bearing Zirkonia spinner with Kel F cap or (ii) a Bruker DSX 200 spectrometer. Cross polarization with magic angle spinning was applied using a spin speed of (i) 4950 Hz or (ii) 6800 Hz. The Hartmann-Hahn condition was determined using glycine as standard. Numbers of scans between 1000 and 200000 were chosen depending on the organic C content of the samples. The spectra obtained were subdivided into four regions: (i) aliphatic or alkyl C (0 – 45 ppm) of lipids, fatty acids, and plant aliphatic polymers; (ii) O alkyl C (45 – 110 ppm) deriving primarily from polysaccharides (cellulose and hemicelluloses), but also from proteins and side chains from lignin; (iii) aromatic or aryl C (110 – 160 ppm), which occurs if lignin and / or protein is present in the sample; and finally (iv) carbonyl C (160 – 220 ppm) from aliphatic esters, carbonyl groups and amide carbonyls.

Lignin

Lignin was analysed by the CuO oxidation method by Dignac et al. (2002). The sum of phenolic oxidation products (vanillyl, syringyl and cinnamyl, VSC) normalized to total C content was used as an estimation of intact lignin structural units.

General soil analysis

For all 56 samples, contents of organic C and total N were determined by dry combustion using an Elementar Vario EL Analyzer.

4.2 Results and discussion

In contrast to the original absorbance spectra, where only few features were present (not shown), the scatter-corrected 1st (not shown), 2nd (Figure 4.2.1) and 3rd derivatives (not shown) have a number of features. Thus, derivative spectra are generally more useful than the original spectra for the prediction of constituents (Tillmann, 2000).

Basic characteristics

Carbon and N contents of the soil and litter samples covered a wide range from 1.1 to 466 g C kg^{-1} and 0.2 to 23 g N kg^{-1} (Figure 4.2.2). The results for the cross-validation showed that NIRS is useful to predict total C and N content and the C/N ratio in mineral soils, organic layers and litter: the RSC, the correlation coefficient and the regression coefficient of a linear regression (measured against predicted contents) were 1.8, 0.97 and 1.02 for C, 2.0, 0.96 and 1.04 for N and 3.5, 0.96 and 0.96 for the C/N ratio (Table 4.2.1). Similar to our good (C/N) and satisfactory (C, N) results, Gillon et al. (1999b) found accurate local calibrations for litter in a *Pinus halepensis* stand. For C and N the SECV

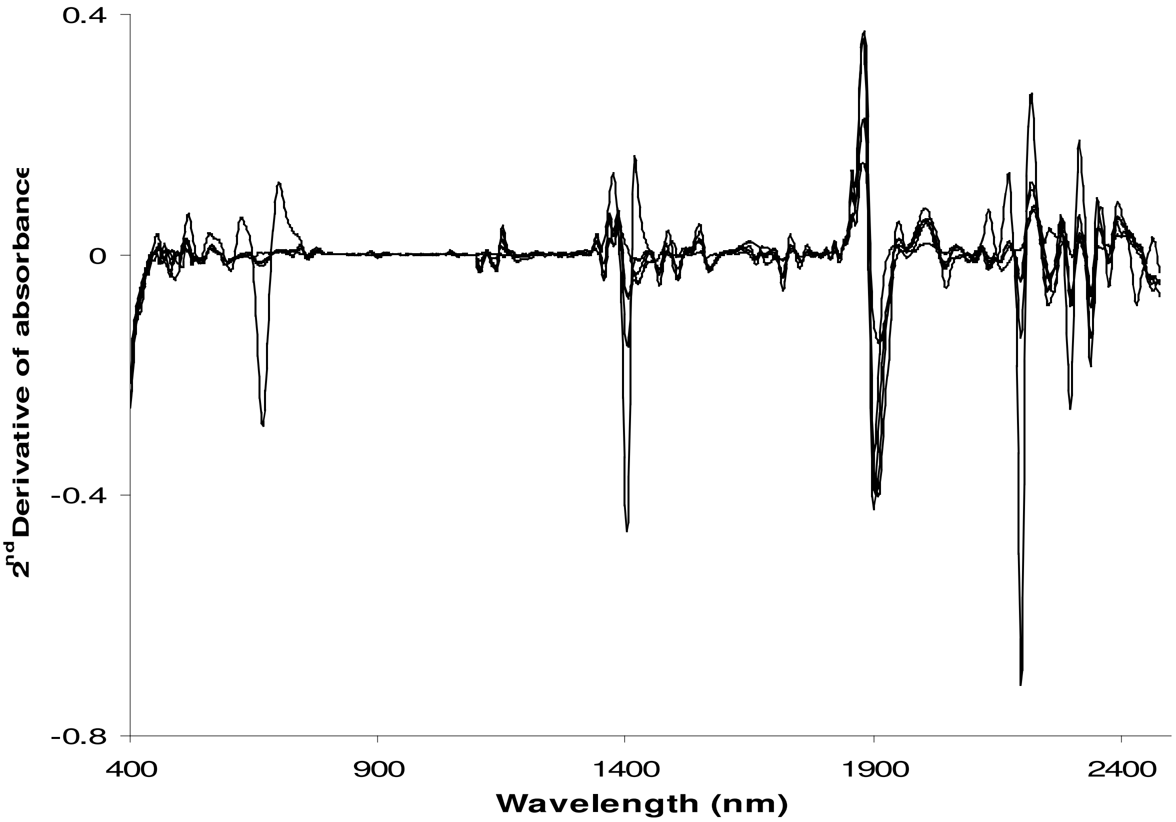

Figure 4.2.1: Second derivatives of absorbance spectra for five samples. The derivatives were calculated after scatter correction and by using a segment length of 5 data points of which the derivatives were taken.

and (r) were 1.07 % and 0.99 and 0.45 % and 0.99, respectively. For soils under beech stands, Chodak et al. (2002) found a good NIRS prediction capability: the correlation and regression coefficients were 0.9 and 1.1 for C and N, and the RPD was 2.8 for both constituents. Similarly, Ludwig et al. (2002) reported a good prediction of C and N contents in disturbed forest soils.

However, an unsatisfactory prediction was reported for the C/N ratio (RPD = 0.4, r = 0.57 and a = 0.64) which was probably due to an extremely diverse data set in their study.

Biological characteristics

For the biological characteristics, we expected less accurate results than for the basic characteristics since C_{mic}, DOC production and N_{min} release may not only depend on the vibrations of the main constituents but also on other factors such as moisture, pH, temperature and micro nutrients. Moreover, it was unclear how well dried and ground samples are suited for a prediction of these characteristics. However, the DOC production was predicted satisfactorily for the samples with a RSC value of 1.5 and correlation and regression coefficients of r = 0.87 and a = 1.05 (Table 4.2.1, Figure 4.2.2).

The other two biological characteristics C_{mic} and release of N_{min}, however, were predicted unsatisfactorily as indicated by the low RSC values of 1.1 and 0.9 (Table 4.2.1, Figure 4.2.2). In contrast, Chodak et al. (2003) found a good NIRS prediction capability for forest soils under beech stands: the correlation and regression coefficients for C_{mic} were 0.9 and 1.1 and the RPD was 2.2. Ludwig et al. (2002) assessed the capability as quite useful (RPD = 1.6, r = 0.83 and a = 0.76). These differences indicate the need especially for the prediction of biological characteristics of soils that the sample population is large enough, sufficiently diverse and covers the whole variability of spectral information.

Characteristics of nuclear-magnetic-resonance spectroscopy

We expected a good accuracy of the prediction of the NMR spectroscopy characteristics since the four NMR regions are covered well by the different vibrations in the NIRS range. Near-infrared spectroscopy predicted the percentage of alkyl C well (RSC = 2.4, r = 0.90 and a = 0.97, Table 4.2.1). This constituent covered evenly the range between 9.9 and 41 % from total C content (Figure 4.2.3). The wavelength 2316 nm (C-H stretching,

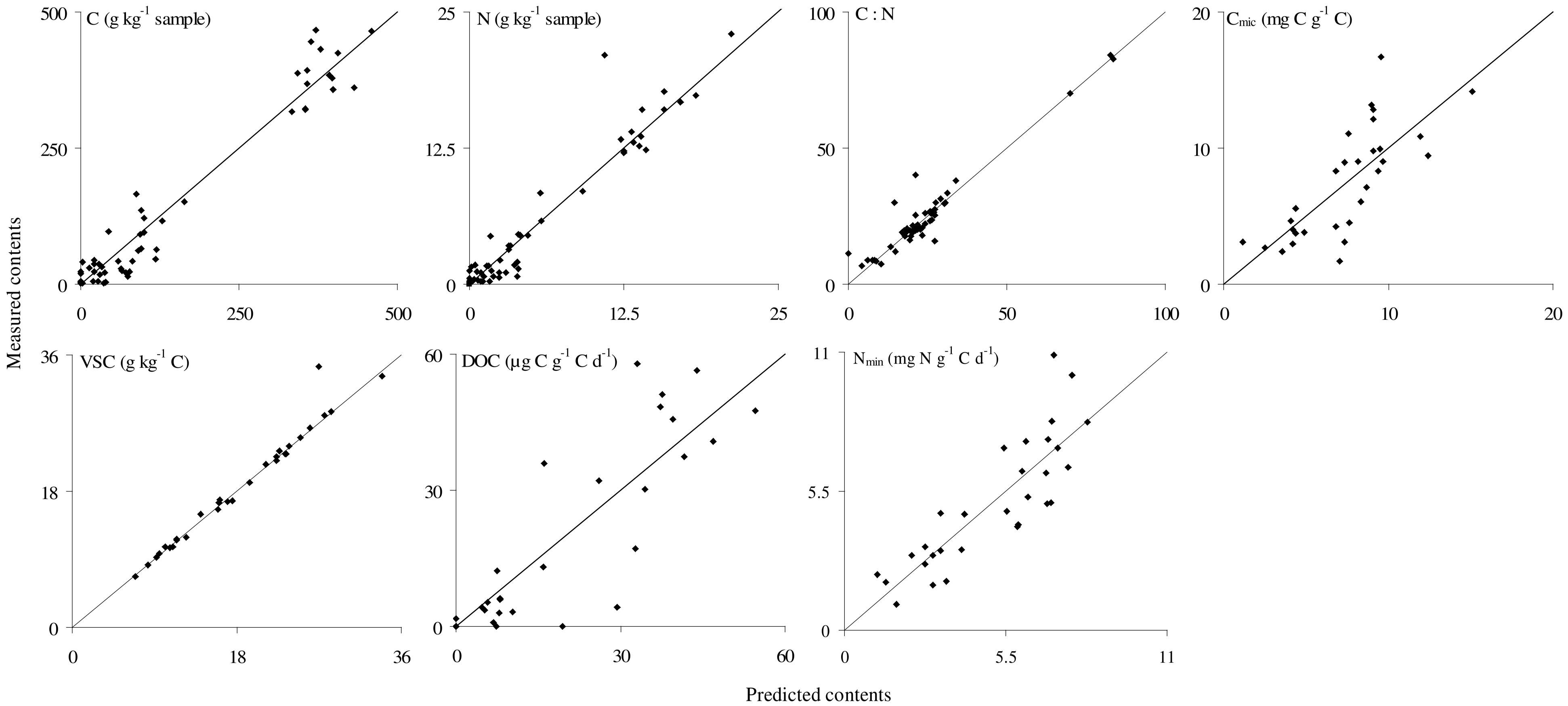

Figure 4.2.2: Predicted and measured values for C and N content, C/N ratio, the sum of phenolic oxidation products (VSC), C_{mic}, release of dissolved organic carbon (DOC) and N_{min}. The lines indicate 1:1.

Table 4.2.1: Statistics of the cross-validation for the predicted constituents. The math treatments for the cross-validation, the standard errors of cross-validation (SECV), the RSC (the ratio of standard deviation and SECV), the correlation coefficient (r) of the linear regression, the regression coefficient (a) and the intercepts (b) are also given. The first number of the math treatment is the order of the derivative function, the second number is the segment length in data points over which the derivative was taken and the third is the segment length over which the function is smoothed (VSC = sum of phenolic oxidation products normalized to total carbon content).

			Cross-validation				
	Constituent	Math treatment	SECV	RSC	r	a	b
Basic characteristics	C	3, 3, 2	90.0	1.8	0.97	1.02	-6.40
	N	3, 3, 1	3.29	2.0	0.96	1.04	-0.15
	C/N	2, 15, 10	4.33	3.5	0.96	0.96	1.52
Biological characteristics	C_{mic}	3, 10, 9	3.85	1.1	0.76	1.00	0.00
	DOC production	2, 20, 10	14.0	1.5	0.87	1.05	-1.60
	N_{min} release	3, 1, 1	2.84	0.9	0.85	1.00	-0.00
NMR characteristics	carbonyl C	3, 7, 7	1.54	1.9	0.85	0.87	1.30
	aromatic C	3, 11, 2	1.67	2.0	0.80	1.01	-0.05
	O-alkyl C	2, 5, 1	3.26	3.1	0.95	0.96	2.41
	alkyl C	1, 1, 1	3.16	2.4	0.90	0.97	0.66
	alkyl/aromatic C	2, 15, 1	0.45	1.5	0.78	1.08	-0.10
	alkyl/O-alkyl C	2, 5, 1	0.10	2.5	0.86	0.90	0.05
Lignin	VSC	3, 6, 6	3.30	2.3	0.98	1.05	-0.57

C-H deformation) had the highest coefficient in the equation for the prediction of alkyl C. O-alkyl C was also predicted well (RSC = 3.1, r = 0.95 and a = 0.96). This C fraction comprised the highest proportion within the range of 33 to 82.6 % (Figure 4.2.3). Important wavelengths for the O-alkyl prediction were 520 nm in the visible region, 2252 nm (O-H and C-H combination bands), 1940 nm (O-H bending), 2236 nm (C-H vibrations) and 2364 nm. The prediction of the percentage of aromatic C was satisfactory (RSC = 2.0, r = 0.8 and a = 1.01). The aromatic C content of the samples ranged from 5.5 to 24 %, but they were not distributed evenly over the range. To obtain better results more samples with an aromatic C content of less than 10 % are required. The main wavelengths on which the equation is based were 1708 nm and 2172 nm (vibrations of aromatic C-H and amide groups). Carbonyl C, which was the group with the lowest

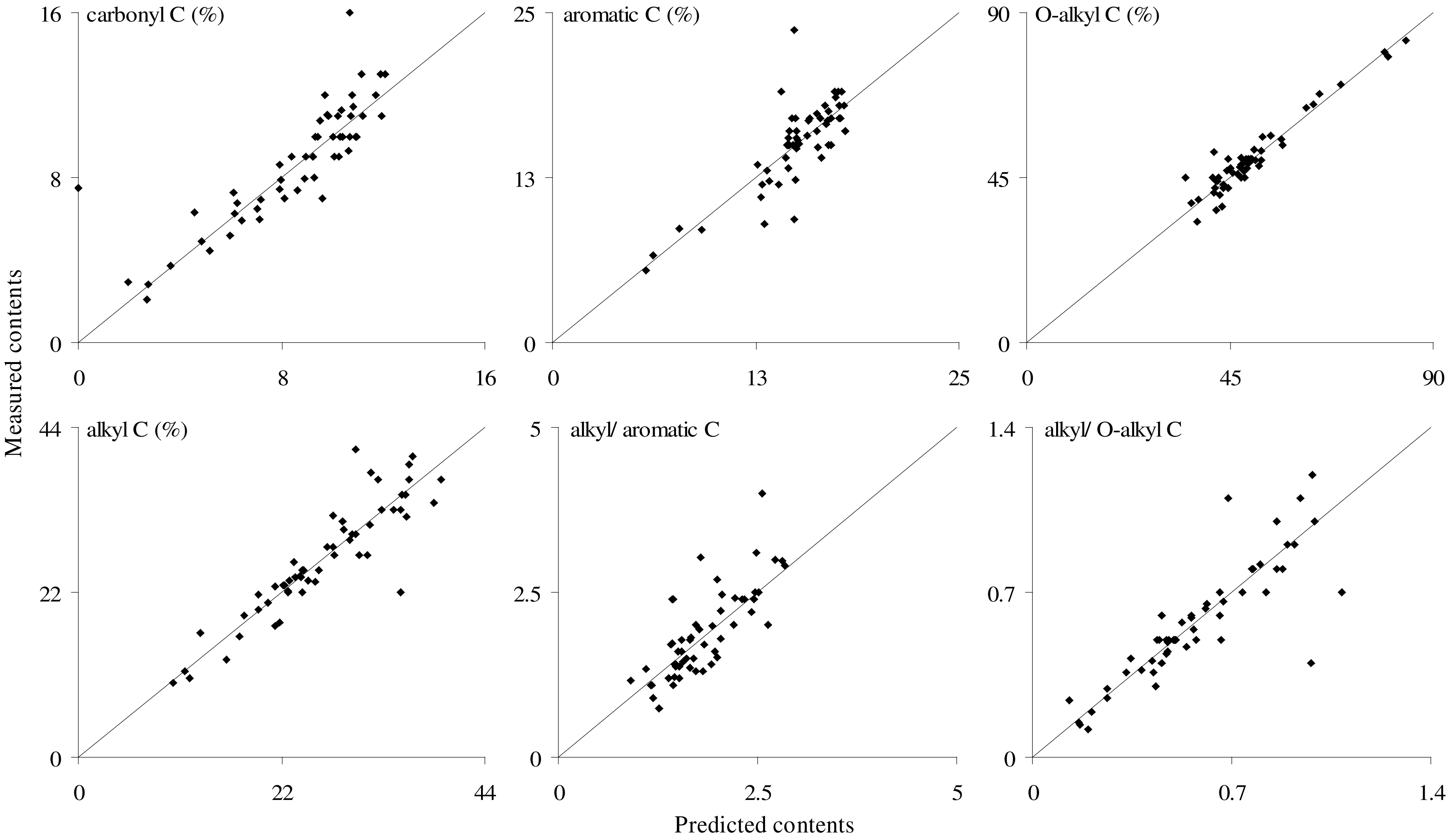

Figure 4.2.3: Predicted and measured values for the contents of carbonyl C, aromatic C, O-alkyl C, alkyl C, alkyl / aromatic C and alkyl / O-alkyl C. The lines indicate 1:1.

portion of total C (2.1 to 16 %), was predicted satisfactorily (RSC = 1.9, r = 0.85 and a = 0.87, Table 4.2.1, Figure 4.2.3). The main equation wavelengths were 2292 (C-H combination bands) and 2100 nm (C-O-O stretching 3rd overtone, and O-H bending/C-O stretching).

The ratios of alkyl C to O-alkyl C and of alkyl C to aromatic C were predicted well (r = 0.86, a = 0.90 and RSC = 2.5) and satisfactorily (r = 0.78, a = 1.08 and RSC = 1.5, Table 4.2.1). Ratios of constituents may be predicted less accurately than the single constituents because of an error propagation of the individual error terms which was not the case in our study.

Lignin

The prediction of the lignin content expressed as VSC showed good results (Figure 4.2.2) with RSC = 2.3, r = 0.98 and a = 1.05 (Table 4.2.1). Similar to our findings, Sanderson et al. (1996) reported a good accuracy of prediction for lignin (RPD = 7.03 and r = 0.97) for 120 samples of woody and herbaceous feedstocks. The greater accuracy in their study is due to a much less diverse sample population compared to our study.

4.3 Conclusions

Near-infrared spectroscopy passed the harsh test to predict a number of general, biological and NMR characteristics and some constituents for a diverse population of litter and soil samples. Only two exceptions were noted: the unsatisfactory predictions for the two biological characteristics N mineralisation rate and microbial biomass indicate the need for testing the prediction accuracy for complex biological characteristics with a larger sample population and in a field-moist state.

5 Near-infrared spectroscopy is able to distinguish between C and N originating from different coals and forest floor Oa material in soils

5.1 Experiments

Sample material

Two different soils from northern Hessia (Germany) (haplic Luvisols) were sampled (Table 5.1.1). One soil was a loamy silt (LS), the second one a silty loam. Both soils were heated to 650 °C for 48 hours to destroy the organic material and finely ground using a ball mill before further use. The silty loam was mixed with 25 (SLQ1) or 50 (SLQ2) percent (w/w) ground quartz to obtain two soils differing in texture and spectral absorbance (Figure 5.1.1 spectra a, b and c). The total C and N contents of all three soils after heating were negligible (on average 0.05 or 0.01 %, respectively, Table 5.1.1).

To cover the whole carbonization range of plant material lignite, anthracite, charcoal and a mixture with equal mass fractions of all three coals were used after drying at 60 °C and finely grinding. The three different German coals originated from the Ruhr area (lignite), the coal mine DSK Anthrazit Ibbenbüren GmbH (anthracite) and beech wood (after carbonization at 400 °C for one week). The mean contents of total carbon (C_t) and N_t ranged between 62.5 and 88.7 % or 0.43 and 1.27 %, respectively (Table 5.1.1). The spectral features were different, especially in the case of lignite (Figure 5.1.1 spectra d, e, f and g).

As an example of organic matter more easily decomposable than coal an Oa layer under spruce was used. The forest floor layer originated from Sandberg (near Göttingen, Germany) and has developed on a haplic Luvisol. The C_t and N_t contents were 1.22 and 0.04 % (Table 5.1.1). The spectrum differed strongly compared to the coals (Figure 5.1.1 spectrum h).

Total C and N contents were analyzed using an elemental analyzer.

Table 5.1.1: Basic characteristics of the sample materials.

Sample	C_t [%]			N_t [%]			Comments
	mean	std	range	mean	std	range	range
LS[a]	0.05	0.04	0.00 - 0.08	0.00	0.00	0.00 - 0.01	Loamy silt (n = 4)
SLQ1[a]	0.05	0.00		0.01	0.01		Silty loam + 25 % ground quartz (n = 2)
SLQ2[a]	0.05	0.00		0.01	0.01		Silty loam + 50 % ground quartz (n = 2)
lignite	62.5	1.2	60.3 - 63.7	0.84	0.04	0.80 - 0.88	n = 9 (C) or 5 (N), respectively
anthracite	86.3	2.7	80.9 - 89.6	1.27	0.22	0.96 - 1.45	n = 9 (C) or 5 (N), respectively
charcoal	88.7	2.1	85.7 - 91.5	0.43	0.13	0.23 - 0.54	n = 9 (C) or 5 (N), respectively
mixed coal	77.5	0.8	76.2 - 78.2	0.83	0.09	0.68 - 0.90	Mixture of equal proportions (w/w) of the three coals (n = 6)
forest floor Oa material	43.2	0.6	42.4 - 43.6	1.40	0.05	1.34 - 1.46	n = 4
Mixtures	2.07	1.87	0.53 - 6.07	0.07	0.05	0.03 - 0.21	Mixtures of soil, coal and Oa material (see text for details) (n = 432)
Coal (mixtures)	0.79	0.99	0.00 - 4.57	0.01	0.01	0.00 - 0.08	Refers to the proportion of coal (n = 432)
Oa material (mixtures)	1.22	1.36	0.09 - 6.01	0.04	0.04	0.00 - 0.20	Refers to the proportion of Oa material (n = 432)

Abbreviations: C_t, total carbon; N_t, total nitrogen; std, standard deviation

[a] after heating to 650 °C for 48 hours to destroy the organic material

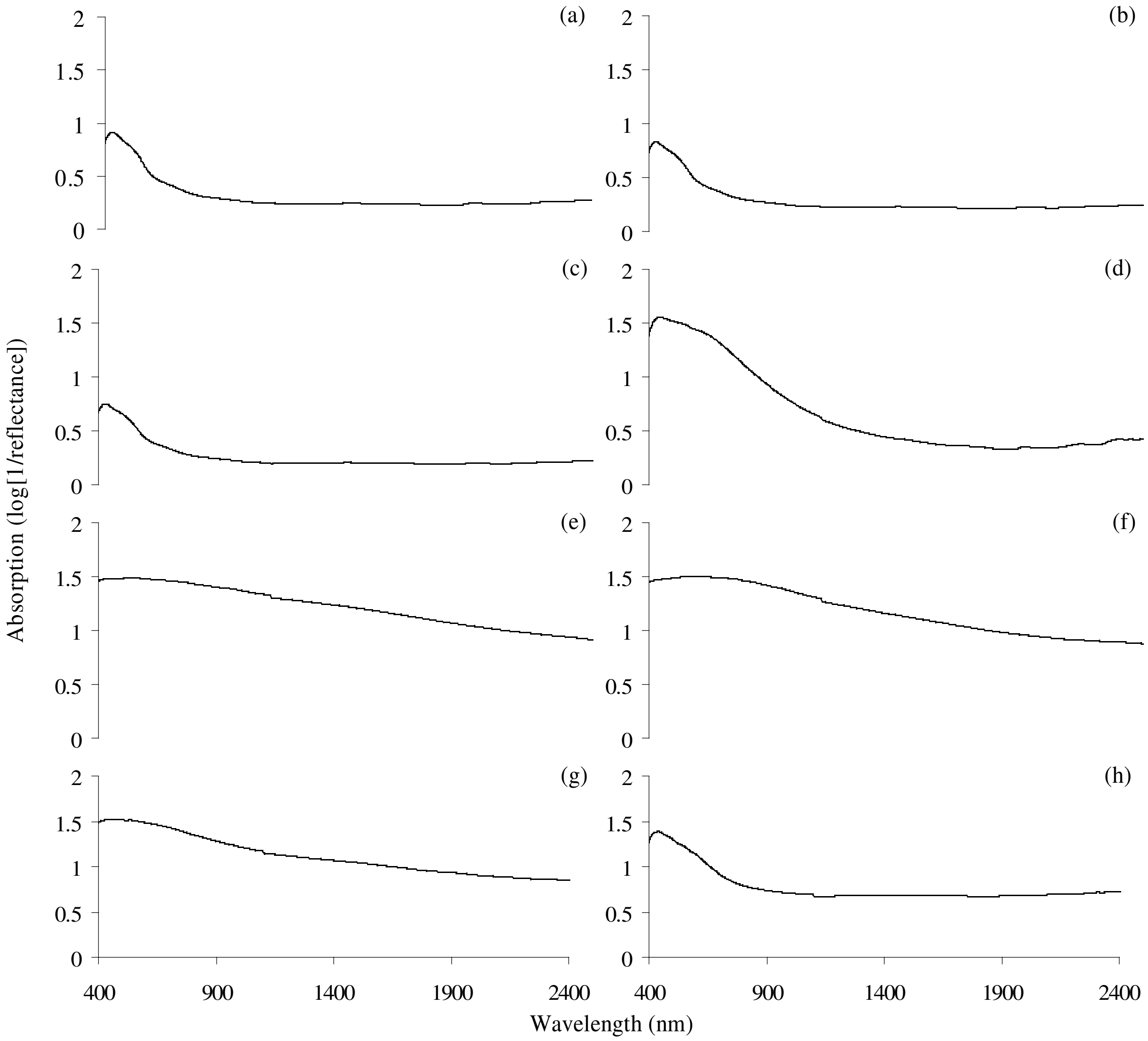

Figure 5.1.1: Displayed are the original spectra of the investigated soils, coals and forest Oa material: (a) soil LS, (b) soil SLQ1, (c) soil SLQ2, (d) lignite, (e) anthracite, (f) charcoal, (g) a mixture of the three coals and (h) material of forest Oa layer. View Table 5.1.1 for abbreviations.

Sample mixing procedure

Different mixtures with C_t contents of 0.5, 0.7, 1, 1.5, 2.5 and 6 percent were produced by mixing one soil, one coal or the mixture of the three coals and Oa material. The proportion of C derived from coal in the different mixtures amounted to 0, 20, 40, 50, 60 and 80 percent of the C_t content, the proportion of Oa material-C of C_t to 100, 80, 60, 50 and 20 percent, respectively. The total number of samples was 432.

The final C contents were calculated by the following equation (Göbel, 1982):

$$w1 * m1 + w2 * m2 + w3 * m3 = w4 * (m1 + m2 + m3) \qquad (6)$$

with m1, m2 and m3 being the mass of substance one (soil), two (coal) and three (Oa material) and w1, w2, w3 and w4 being the C percent by weight of substance one, two, three and the final mixture. Calculated C contents were measured on ten percent of the sample collective chosen on a random basis. They showed a deviation of two to twelve percent from the measured ones (data not shown).

5.2 Results and discussion

Carbon

Using mixtures of C-free soil, coal and Oa material, which covered a wide range of C content (0.53 - 6.07 %; Table 5.1.1), NIRS was able to predict C_t content and the proportion of C deriving from coal or Oa material, respectively (Table 5.2.1). The results were good as reflected by the statistical parameters. For all constituents (C_t, C_{coal} and C_{Oa}), the correlation coefficient was equal to or higher than 0.97 and the regression coefficient ranged between 1.01 and 1.06 (Table 5.2.1, Figure 5.2.1). The lowest RSC value (6.3) was observed for C_{coal}.

As depicted in Figure 5.2.2, NIRS successfully predicted the different coals investigated. This was also reflected by the RSC and (r) values which were equal to or higher than 4.8 or 0.97, respectively, for C_{coal} (data not shown). The wavelengths assignment suggests that the prediction of thee different coals based on structural differences. The most important wavelength related to lignite was 2276 nm which is characteristic of combination bands of O-H stretch and C-O of cellulose and of C-H stretch and CH_2 deformation of starch. This indicates that the lignite investigated contained polysaccharide components confirming the finding of Bates and Hatcher (1989) that polysaccharides still can be present in the first stage of coalification. In accordance with Marshall et al. (2005) who characterised charcoal using amongst others fourier-transform-infrared spectroscopy absorbance by alkyl groups indicating the presence of aliphatic hydrocarbons. In this investigation, alkyl groups were observed for charcoal, since the wavelengths 2282 (combination band of C-H stretch and CH_2 deformation of starch) and 2340 nm (CH stretch and CH deformation of cellulose) had the highest correlations. The determination of the wavelengths which were most important for the development of the regression equations also showed that the prediction of mixed coal was based on the presence of anthracite. In both cases, the wavelengths 1400 (C-H combination band of CH_2 groups), 1902 (second overtone of C=O stretch) and 2198 nm (combination bands of C-H stretch and C=O of CHO groups) were of major importance. This may be explained by the different chemical properties of the coals investigated. These properties, such as aromaticity, change with the degree of coalification. In the early stage (lignite) aromaticity is low, whereas anthracite, the last stage of coalification, is highly aromatic with around 75 % of C being present as condensed aromates (Retcofsky and Friedel, 1971, Knicker et al., 2002, BMLFUW, 2005). Typical of charcoal are polyaromatic structures, but also, as mentioned above, aliphatic hydrocarbon components

Table 5.2.1: Statistics of the cross-validation for the predicted constituents (n = 432). The math treatments, the standard errors of cross-validation (SECV), the RSC (the ratio of standard deviation and SECV), the correlation coefficient (r) of the linear regression and the regression coefficient (a) are given.

Constituent	Math treatment[a]	Outliers removed	SECV [%]	RSC	r	a
C_t	1,15,1	22	0.197	9.1	0.99	1.01
C_{coal}	2,20,20	31	0.138	6.3	0.97	1.02
C_{Oa}	1,10,10	26	0.164	6.9	0.99	1.06
N_t	1,5,1	27	0.005	8.6	0.99	1.04
N_{coal}	1,5,5	24	0.002	4.3	0.96	1.09
N_{Oa}	1,10,10	26	0.005	6.9	0.99	1.06

Abbreviations: C_{coal}, N_{coal}, C or N derived from coals in the soil-coal-Oa-mixtures; C_{Oa}, N_{Oa}, C or N derived from Oa material in the soil-coal-Oa-mixtures; see also text and Table 5.1.1.

[a] The numbers denote the order of the derivative function, the gap over which the derivative was taken, and the segment used for smoothing

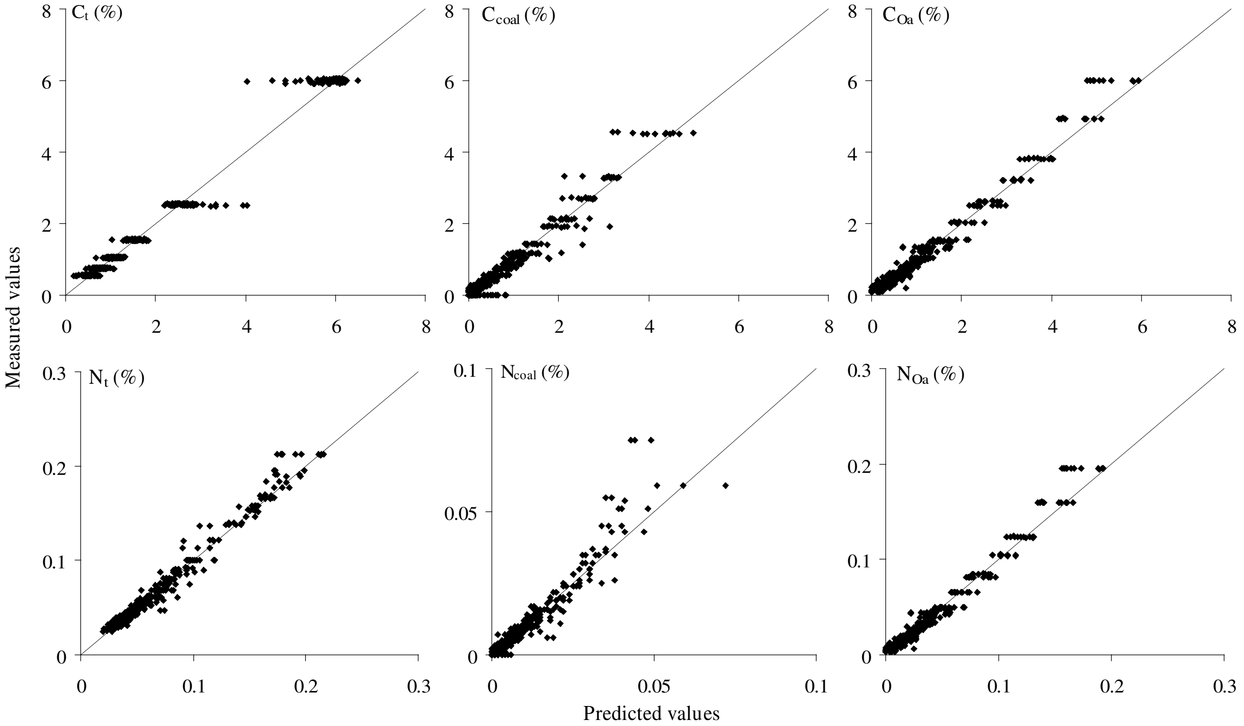

Figure 5.2.1: Measured values (on dry matter basis) vs. values predicted for total C (C_t), total N (N_t), C and N derived from coal in the soil-coal-Oa-mixtures (C_{coal}, N_{coal}) and C and N derived from Oa material in the soil-coal-Oa-mixtures (C_{Oa}, N_{Oa}). The 1:1 line is indicated on each figure.

can be present (Marshall et al., 2005). Due to its chemical properties, anthracite is probably more susceptible to NIRS radiation than the other coals investigated.

The predictions of C_t and C_{coal} could not be related to a single component or a specific coal, since no corresponding wavelengths were detected.

Due to the limited number of samples which was investigated using NIRS, the accuracy of this spectroscopic method to predict C deriving from coal in soils cannot be compared without caution. A greater number of samples, preferably also natural coal or black C containing soil material, should be used to improve the underlying dataset.

Soil samples which naturally contain different amounts and different kinds of coal or black C, respectively, should also be used to check the results presented for NIRS. As outlined by Amelung und Brodowski (2005) black C is probably closely associated with

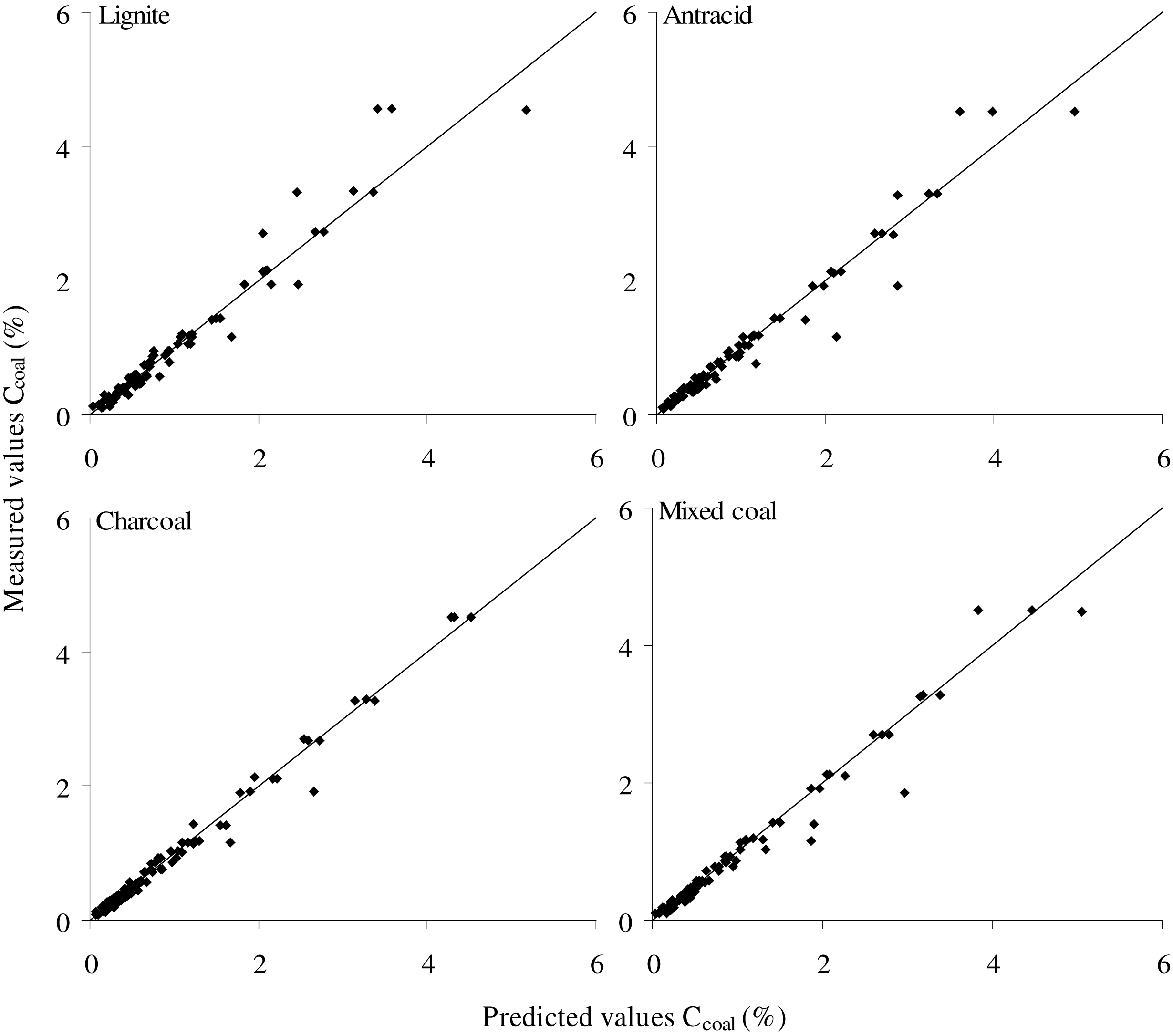

Figure 5.2.2: Differentiation of the investigated coals: measured values (on dry matter basis) vs. values predicted for C derived from various coals in the soil-coal-Oa-mixtures (C_{coal}) (n = 108, respectively). The lines indicate the 1:1 relationships.

mineral particles due to chemical and physical interactions - a feature which is lacking in a soil-coal-mixtures.

Nitrogen

The sample material was characterized by low N contents. The average N content in the soil-coal-Oa-mixtures was 0.07 % (Table 5.1.1). Nevertheless, the correlation ($r \geq 0.96$) and regression coefficients (a = 1.04 - 1.09) indicated that the application of NIRS gave good cross-validation results (Table 5.2.1, Figure 5.2.2). Compared to the prediction of C, the RSC values which ranged between 4.3 and 8.6 were slightly lower.

The following wavelengths had the highest correlations for N_t: 2212 and 2124 nm which are characteristic of C-H combination bands and 1910 nm which is assigned to the first overtone of O-H stretching of P-OH groups.

5.3 Conclusions

The results of the present study indicate, that NIRS is capable to predict and to differentiate between C and N derived from different sources such as coal or forest floor material. Differentiations with NIRS between different coals should be verified using soil samples contaminated with coal or black C.

6 Is near-infrared spectroscopy capable to determine soil quality?

6.1 Experiments

The samples and data described in chapter 6.1 were provided from the Foundation Ecology and Agriculture and financed by the Bundesprogramm Ökolandbau.

Sites and samples

Soil samples were taken from the arable land of nine organically managed farms in Germany. The farms were located in the federal states Lower Saxony, Hessia, Bavaria and Baden-Wuerttemberg. The long-term annual mean temperature ranges for the sites from 7.1 to 9.8 °C and the annual precipitation is in the range from 620 to 900 mm. The sites are located from 27 to 600 m a.s.l. Soil texture varied strongly: contents of clay varied between 4 and 27 %, contents of silt between 21 to 92 % and contents of sand between 2 to 68 %, respectively. The parent material of the soils differed as well in its origin: they were glacial sands, loess, floodplain sediments, new red sandstone, granite, gneiss, mica shale and mudstone.

Soil samples were taken in March 2005 from 0 to 20 cm soil depth. Two different fields per farm, each cultivated with winter cereals, were chosen. Three separate sub-samples, with a distance of 15 m to each other, were taken per field (n = 56). Sub-samples were a mixture of eight recesses taken within a circle of two metres radius. Samples for biological characterisation were cooled and sieved (< 2 mm) prior analysis. The samples for soil chemical analysis were air-dried and sieved (< 2 mm).

Soil chemical analysis and soil texture

Total carbon and nitrogen content were determined after drying and grinding on a Vario EL CN autoanalyzer. Carbonate content was determined with ten percent HCl solution according to SCHEIBLER (Schlichting et al., 1995). Organic carbon content was calculated by difference.

Soil pH was measured in a solution of soil and 0.01 M $CaCl_2$ at a ratio of 1:2.5 after one hour (Hoffmann, 1991a).

Extractable P and K were extracted in a solution of calcium-acetate-lactate (CAL) at a ratio of 1:20 and buffered at a pH of 4.1. After filtration, P was measured with a spectral photometer at 580 nm as a complex with molybdenum (Schüller, 1969). Potassium was measured with an atom-emission spectrometer at 767 nm (Hoffmann, 1991b). Moreover, P (Olsen) was determined colorimetrically using standard methodology (Kuo, 1996). Extractable Mg was extracted in a solution of soil and 0.0125 M $CaCl_2$ at a ratio of 1:10. After filtration, Mg was measured with an atom-absorption-spectrometer at 285 nm (Hoffmann, 1991c).

Soil texture was determined by sieving and pipetting after destroying humus with H_2O_2 and carbonates with HCl and dispersion of clay with NP (DIN 19683b, 1973).

Soil biological analysis

Microbial biomass C and N were estimated by fumigation-extraction (Brookes et al., 1985, Vance et al., 1987). Briefly, two portions equivalent to 25 g oven-dry soil were taken from the soil sample. One of the two portions was fumigated for 24 h at 25 °C with ethanol-free $CHCl_3$. Following fumigant removal, the soil was extracted with 100 ml 0.5 M K_2SO_4 by shaking it for 30 min on a horizontal shaker at 200 rev min^{-1}. Subsequently the extract was filtered (Schleicher and Schuell 595 ½). The non-fumigated control was extracted in the same way. Organic C in the extracts was measured as CO_2 by infrared absorption after combustion at 850 °C using a Dimatoc 100 automatic analyser (Dimatec, Essen). Microbial biomass C was calculated as follows (Wu et al., 1990): $C_{mic} = (C_f - C_c) / k_{EC}$, where $k_{EC} = 0.45$, C_f = organic C extracted from fumigated soil, and C_c = organic C extracted from the control. Total N in the extracts was measured by chemoluminescence detection after combustion at 850 °C using a Dimatoc 100 automatic analyser. Microbial biomass N was calculated as follows (Brookes et aL., 1985): $N_{mic} = (N_f - N_c) / k_{EN}$, where $k_{EN} = 0.54$, N_f = organic N extracted from fumigated soil, and N_c = organic N extracted from the control.

Microbial biomass P in soil was also measured by fumigation-extraction (Brookes et al., 1982). Three portions equivalent to 5 g soil were taken from the 100 g soil sample used for the incubation. After different pre-treatments, each was extracted with 100 ml of 0.5 M $NaHCO_3$ (pH 8.5) by 30 min horizontal shaking at 200 rev min^{-1}, centrifuged for 15 min at 2000 g, and filtered. The first portion was used for the fumigated treatment (see above), the second portion for the non-fumigated treatment, and the third portion for estimating P fixation by the addition of 25 µg P g^{-1} soil as KH_2PO_4 to the extractant. Phosphorus was analyzed by a modified ammonium molybdate–ascorbic acid method as described by Joergensen et al. (1995). Microbial biomass P was (EP / k_{EP}) / recovery, where EP = (PO_4-P extracted from fumigated soil) – (PO_4-P extracted from non-fumigated soil) and $k_{EP} = 0.40$ (Brookes et al., 1982).

Ergosterol content was determined in 2 g of moist soil taken from the 100 g soil sample used for the incubation. This sample was extracted with 100 ml ethanol for 30 min by oscillating shaking at 250 rev min^{-1} (Djajakirana et al., 1996). Ergosterol was determined by reversed-phase HPLC with 100% methanol as the mobile phase and detected at a wavelength of 282 nm.

Basal Respiration was measured as CO_2-production by four days incubation at 25 °C (Isermeyer, 1952). Carbon dioxide was trapped in a 1 M NaOH-solution and titrated back with 1 M HCl.

Nitrogen mineralisation rate was determined after removal of plant debris aerobically according to Joergensen (2005). Briefly, the samples were incubated aerobically at 25 °C for 28 days. Sub-samples were extracted with 0.01 M $CaCl_2$ and contents of inorganic nitrogen were analyzed at day 0, 14 and 28.

Grain yield and grain N uptake

Grain yield of winter cereals was determined for all sites at growth stage 92 on sub plots (four sowing rows with each being one metre long were harvested per plot). Grain was threshed, dried at 60 °C for 72 h and weighed. Grain nitrogen content was determined after drying and grinding on a Vario EL CN autoanalyzer and grain nitrogen uptake on the basis of kg N ha^{-1} calculated.

6.2 Results and discussion

The soils covered a wide range of chemical, biological and yield characteristics (Table 6.2.1 and Table 6.2.2). The samples from one site (n = 3), both field-moist and quick-frozen measured, were spectrally different in comparison to the corresponding sample set. The difference to the other samples was that this soil was based on mica shale. The soil samples based on mica shale had in the original and second derivative spectra for both field-moist and quick-frozen samples at 1400, 1900 and 2200 nm peaks (Figure 6.2.1). The peaks were for the other soil samples smaller (field-moist samples) or not visible (quick-frozen samples). Known absorbing compounds at the named wavelengths are hygroscopic water (1400 and 1900 nm) and lattice water (2200 nm) (Ben-Dor and Banin, 1995a). Thus, quick-freezing was not capable to remove the water completely from the layer minerals. The samples based on mica shale were removed from the calculation of the linear regression of measured against predicted values, if they were detected as outliers during cross-validation procedure.

Chemical analysis

Predictions of C_{org}, N_t and C_{org}/N_t ratio were good for field-moist and quick-frozen samples: the RSC was higher than 2.9, (r) higher than 0.9 and (a) in the range from 1.0 to 1.1 (Table 6.2.3, Figure 6.2.2). C_{org} and N_t predictions were better for field-moist samples, whereas C_{org}/N_t ratio was predicted better for quick-frozen ones. Chang et al. (2005) investigated with NIRS field-moist and air-dried soil samples. They also achieved good predictions for C_{org} (RSC = 3.2 and r = 1.0) and N_t (RSC = 4.0 and r = 1.0). Their results refer to air-dried samples and are slightly better than our results for field-moist samples. Correlation analysis indicated for the C_{org} prediction of field-moist samples that 1372 nm (alkyl- and O-alkyl carbon absorptions) is an important wavelength. Important wavelengths for the N_t prediction were 2030 nm (field-moist samples, amino groups) and 1454 and 1482 nm (quick-frozen samples, $-NH_2$, -NH groups).

The pH was predicted well for quick-frozen samples (RSC = 2.5, r = 0.9 and a = 1.0 in comparison to RSC = 1.9, r = 0.9 and 1.0 for field-moist samples). In contrast, Moron and Cozzolino (2002) predicted the pH well for field-moist samples (RPD = 3.3 and r =

Table 6.2.1: Chemical and grain yield characteristics of the soil samples are given. Displayed are the sample number (excluding the outliers in cross-validation), range, mean and standard deviation in dependence from the sample pre-treatment (A = field-moist, B = quick-frozen, frozen dried and ground)

	Constituent	Unit	Sample pre-treatment	N	Range	Mean	Standard deviation
Chemical characteristics	C_{org} content	%	A	52	0.93-2.73	1.66	0.59
			B	53	0.93-2.73	1.71	0.60
	N_t content	%	A, B	52, 54	0.10-0.29	0.17	0.05
	C_{org}/N_t ratio		A	53	8.03-12.6	9.76	1.03
			B	54	8.03-12.8	9.89	1.16
	pH ($CaCl_2$)		A	54	5.30-6.70	6.00	0.41
			B	52	5.30-6.70	6.04	0.38
	Phosphor (Olsen) content	µg g^{-1} soil	A	53	2.30-90.6	33.0	21.0
			B	53	2.30-90.6	31.4	19.5
	Phosphor (CAL) content	mg P_2O_5 100g^{-1} soil	A	53	1.00-34.0	11.3	7.69
			B	52	1.00-34.0	10.2	6.39
	Potassium (CAL) content	mg K_2O 100g^{-1} soil	A	54	6.00-30.0	14.4	5.95
			B	55	6.00-30.0	14.5	6.11
	Magnesium ($CaCl_2$) content	mg MgO 100g^{-1} soil	A	53	3.00-54.0	16.5	12.5
			B	52	3.00-54.0	16.6	12.6
Yield characteristics	Grain yield (dry matter)	dt ha^{-1}	A	37	15.3-77.4	40.0	16.2
			B	38	15.3-84.1	40.9	17.6
	Grain nitrogen content (dry matter)	%	A, B	38	1.27-2.62	1.71	0.30
	Grain nitrogen uptake	kg N ha^{-1}	A, B	38	20.1-143	67.3	28.9

Table 6.2.2: Biological characteristics of the soil samples are given. Displayed are the sample number (excluding the outliers in cross-validation), range, mean and standard deviation in dependence from the sample pre-treatment (A = field-moist, B = quick-frozen, frozen dried and ground).

Constituent	Unit	Sample pre-treatment	N	Range	Mean	Standard deviation
C_{mic} content	µg g^{-1} soil	A	51	75.8-694	241	145
		B	53	75.8-694	245	145
N_{mic} content	µg g^{-1} soil	A	52	11.3-114	46.7	25.8
		B	52	11.3-109	46.0	24.4
C_{mic}/N_{mic} ratio		A	54	3.47-6.87	5.29	0.85
		B	53	3.47-6.87	5.39	0.80
P_{mic} content	µg g^{-1} soil	A	53	5.38-57.7	25.8	12.8
		B	53	5.38-57.7	25.5	12.7
C_{mic}/P_{mic} ratio		A	55	3.62-16.5	9.55	2.87
		B	55	3.62-16.1	9.54	2.86
Ergosterol content	µg g^{-1} soil	A	53	0.11-2.35	0.90	0.65
		B	51	0.11-2.35	0.90	0.66
Erogsterol/C_{mic} ratio	%	A	54	0.09-0.86	0.36	0.18
		B	52	0.09-0.80	0.36	0.16
Basal respiration	µg CO_2-C g^{-1} soil d^{-1}	A	53	4.40-60.4	24.6	15.4
		B	53	4.40-56.3	23.9	14.2
Metabolic quotient	mg CO_2-C g^{-1} C_{mic} d^{-1}	A	53	38.6-197	99.2	41.8
		B	53	38.6-185	99.0	41.3
Nitrogen mineralisation rate	µg NO_3–N g^{-1} soil d^{-1}	A,B	56	0.11-1.42	0.75	0.31
Basal respiration/nitrogen mineralisation rate ratio	µg CO_2-C g^{-1} d^{-1} (µg NO_3–N g^{-1} soil d^{-1})$^{-1}$	A	51	4.96-82.6	31.8	19.8
		B	52	4.96-109	33.2	22.4

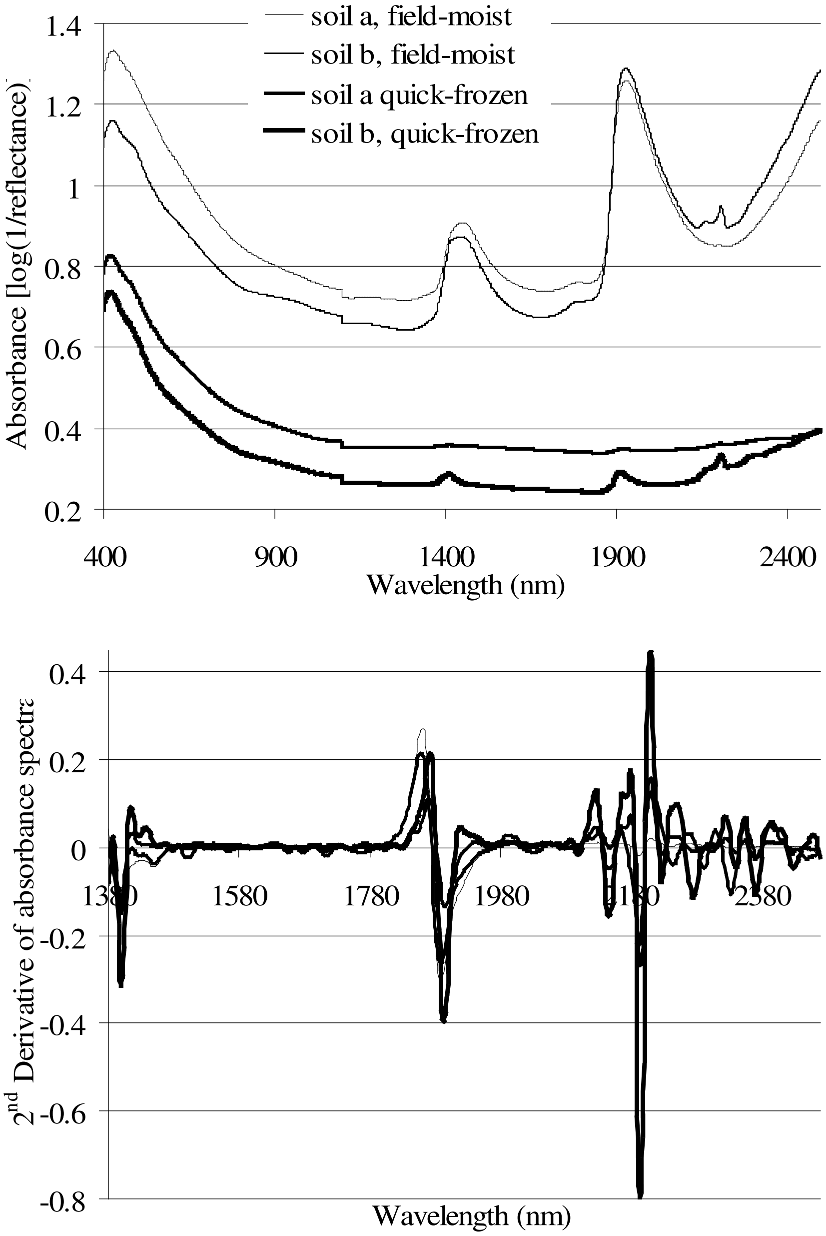

Figure 6.2.1: Original and second derivative spectra of two untreated (field-moist) and pre-treated (quick-freezing, freeze-drying and grinding) soils. Soils were based on a = glacial sands and b = mica shale.

1.0). They found absorption bands around 1400 and 1900 nm, which belong to water and –OH absorption bands. We assigned the wavelengths 1350 and 1448 nm for the quick-frozen samples, which were as well related to water. As shown in Figure 6.2.1, not all water was removed by the quick-freezing and freeze-drying procedure from the sample based on mica shale. These samples had the highest pH (6.7) and the pH prediction was the only chemical characteristic, where the samples based on mica shale were not outliers

Table 6.2.3: Cross-validation statistics of chemical and yield characteristics of the soil samples are given. Displayed are the number of outliers, the mathematical treatment, the standard error of cross-validation (SECV), the RSC (ratio of standard deviation of reference values to SECV) and the correlation coefficient (r) and regression coefficient (a) of a linear regression (measured against predicted values). The statistics are given for every sample pre-treatment (A = field-moist, B = quick-frozen, frozen dried and ground).

	Constituent	Sample pre-treatment	Outliers	Mathematical treatment[1]	SECV	RSC	r	a
Chemical characteristics	C_{org} content	A	4	3,20,15	0.17	3.46	0.93	1.00
		B	3	2,10,1	0.18	3.38	0.98	1.00
	N_t content	A	4	2,10,5	0.02	3.42	0.97	1.01
		B	2	3,10,5	0.02	2.92	0.97	0.99
	C_{org}/N_t ratio	A	3	3,10,1	0.35	2.94	0.90	1.06
		B	2	3,20,1	0.32	3.65	0.97	0.99
	pH ($CaCl_2$)	A	2	2,5,5	0.21	1.94	0.88	0.96
		B	4	2,5,5	0.15	2.5	0.92	1.04
	Phosphor (Olsen) content	A	3	2,20,1	7.33	2.86	0.95	0.98
		B	3	2,5,5	6.07	3.20	0.98	1.04
	Phosphor (CAL) content	A	3	2,15,1	3.36	2.29	0.93	0.96
		B	4	2,5,5	2.22	2.88	0.92	1.10
	Potassium (CAL) content	A	2	2,5,1	3.51	1.7	0.89	1.01
		B	1	1,1,1	3.36	1.82	0.95	1.01
	Magnesium ($CaCl_2$) content	A	3	3,5,5	5.00	2.5	0.98	1.00
		B	4	3,10,5	3.09	4.08	0.98	0.99
Yield characteristics	Grain yield (dry matter)	A	3	2,15,10	7.82	2.07	0.88	0.81
		B	2	3,20,15	7.42	2.37	0.95	1.01
	Grain nitrogen content	A	2	2,15,5	0.13	2.22	0.83	0.83
		B	2	1,15,5	0.16	1.85	0.78	0.77
	Grain nitrogen uptake	A	2	2,20,1	15.6	1.84	0.87	0.78
		B	3	3,20,20	11.5	2.68	0.87	0.93

[1] The first number of the mathematical treatment is the order of the derivative function, the second one the segment length in data points over which the derivative was taken, and the third one the segment length over which the function was smoothed.

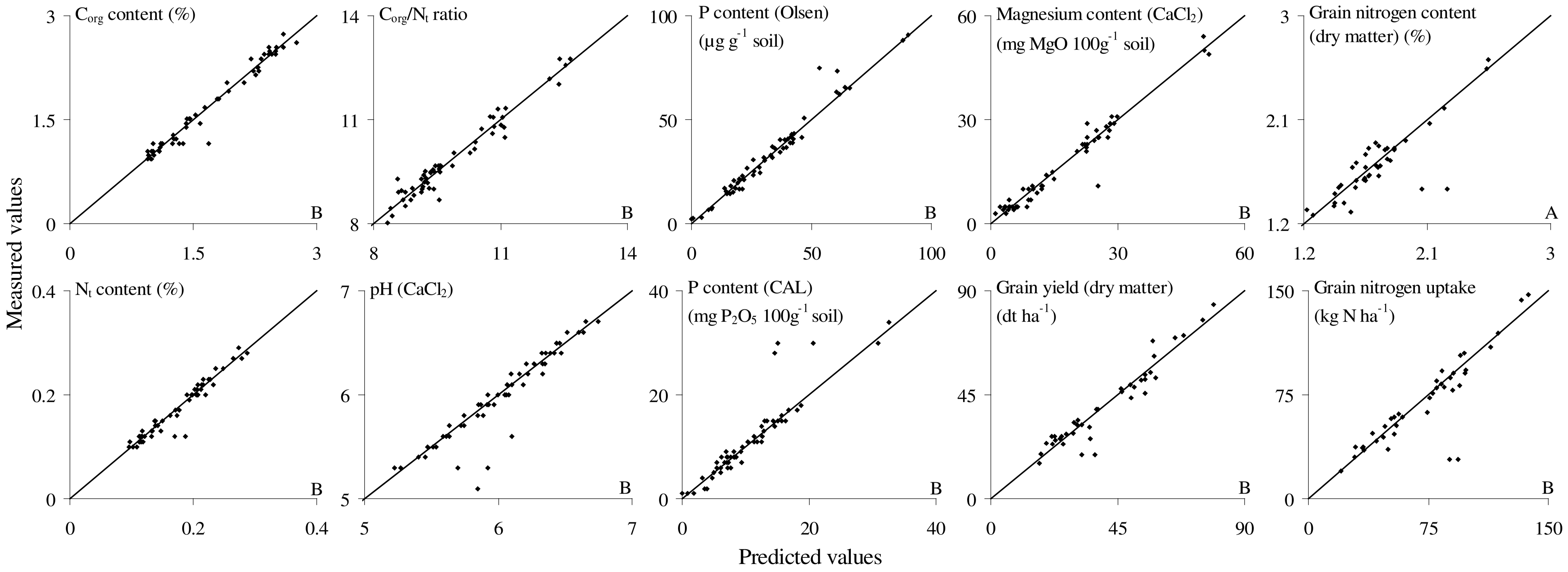

Figure 6.2.2: Measured against predicted values for soil chemical and grain yield characteristics. Displayed are for each constituent the pre-treatment variant, which yielded the better results (A = field-moist and B = quick-frozen, freeze-dried and ground). The lines indicate 1:1.

(data not shown). This underlines the importance of hygroscopic and lattice water for pH prediction.

Contents of extractable P were predicted well for both extraction methods (Olsen and CAL), whereby P-Olsen predictions were better than CAL predictions (Table 6.2.3, Figure 6.2.2). The best predictions were done for quick-frozen samples (RSC = 3.2, r = 1.0 and a = 1.0). Our results for P-Olsen were better than those of van Groeningen et al. (2003). They found satisfactorily results for dried and ground samples from a flooded rice field (RPD = 1.8 and r = 0.8).

Contents of extractable K were predicted satisfactorily, but slightly better for quick-frozen (RSC = 1.8, r = 1.0 and a = 1.0) than for field-moist samples (RSC =1.7, r = 0.9 and a = 1.0). Our predictions were comparable to the results of Dunn et al. (2002) for dried soils (RPD = 1.6 and r = 0.8), but much better than the results of Kamrunnahar et al. (2003). They investigated air-dried soils (RPD = 0.8 and r = 0.0). Finally, contents of extractable Mg were predicted well: better for quick-frozen (RSC = 4.1, r = 1.0 and a = 1.0) than for field-moist samples (RSC = 2.5, r = 1.0 and a = 1.0). Comparable results were found from van Groeningen et al. (2003) (RPD = 2.3 and r = 0.9). In contrast, the findings from Kamrunnahar et al. (2003) were much worse than our results (RPD = 1.7 and r = 0.8).

Biological analysis

The microbial communities in the investigated soils showed a large variability in absolute magnitude (75.8 to 694 µg Cmic g-1 soil) (Table 6.2.2) and substrate use efficiency: the metabolic quotient ranged from 38.6 to 197 mg CO2-C g-1 Cmic d-1. Contents of the constituents were lower than the NIRS detection limit and thus the evaluation of the assigned wavelength may not be helpful. All constituents, except nitrogen mineralisation rate, were highly significant correlated with contents of Corg and Nt (data not shown), but NIRS correlations were higher, as described below.

Near-infrared spectroscopy predicted C_{mic} well for field-moist (RSC = 3.6, r = 1.0 and a = 1.0) and quick-frozen soils (RSC = 2.9, r = 1.0 and a = 1.0) (Table 6.2.4, Figure 6.2.3). Assigned wavelengths were 2042, 1886 and 1516 nm. Our results are comparable to

Table 6.2.4: Cross-validation statistics of biological soil characteristics are given. Displayed are the number of outliers, the mathematical treatment, the standard error of cross-validation (SECV), the RSC (ratio of standard deviation of reference values to SECV) and the correlation coefficient (r) and regression coefficient (a) of a linear regression (measured against predicted values). The statistics are given for every sample pre-treatment (A = field-moist, B = quick-frozen, frozen dried and ground).

Constituent	Sample pre-treatment	Outliers	Mathematical treatment[1]	SECV	RSC	r	a
C_{mic} content	A	5	2,5,5	40.6	3.57	0.98	0.99
	B	3	3,20,1	50.7	2.85	0.97	1.00
N_{mic} content	A	4	3,20,10	7.72	3.34	0.97	0.99
	B	4	2,5,5	7.42	3.29	0.96	1.03
C_{mic}/N_{mic} ratio	A	2	3,1,1	0.59	1.43	0.84	0.89
	B	3	2,20,1	0.63	1.26	0.56	0.85
P_{mic} content	A	3	1,15,1	5.10	2.50	0.93	0.99
	B	3	3,20,10	4.59	2.77	0.93	0.93
C_{mic}/P_{mic} ratio	A	1	2,20,5	2.83	1.02	0.33	0.85
	B	1	2,1,1	2.55	1.12	0.89	0.99
Ergosterol content	A	2	3,5,5	0.25	2.63	0.91	1.09
	B	5	2,15,1	0.14	4.58	0.94	1.04
Erogsterol/C_{mic} ratio	A	2	3,5,5	0.12	1.41	0.80	1.07
	B	4	2,10,1	0.08	2.02	0.94	1.12
Basal respiration	A	3	1,10,1	4.26	3.62	0.97	1.01
	B	3	2,5,1	5.23	2.71	0.95	1.03
Metabolic quotient	A	3	3,20,5	25.1	1.67	0.78	1.01
	B	3	1,10,1	24.4	1.69	0.87	1.04
Nitrogen mineralisation rate	A	0	3,1,1	0.27	1.14	0.76	1.00
	B	0	1,1,1	0.27	1.14	0.60	1.00
Basal respiration/nitrogen mineralisation rate ratio	A	5	3,20,1	15.3	1.29	0.33	0.92
	B	4	3,1,1	17.0	1.31	0.53	1.20

[1] The first number of the mathematical treatment is the order of the derivative function, the second one the segment length in data points over which the derivative was taken, and the third one the segment length over which the function was smoothed.

investigations from Couteaux et al. (2003) (RSC = 4.4 and r = 1.0). They investigated 204 air-dried forest Oh and A1 layers and the chloroform-fumigation-extraction (CFE) method was used for C_{mic} determination. However, their results are of limited use, because the samples formed sub-populations in the linear regression. The standard error of prediction was 550 µg C_{mic} g^{-1} soil and is thus unacceptable for mineral soils. Chang et al. (2001) found satisfactory results for C_{mic} (CFE- method) predictions for 802 air-dried soil samples originating from arable land (RPD = 1.5 and r = 0.8). Only one study led for C_{mic} predictions (determined with the substrate induced respiration method, SIR) of dried forest soils to good results (Chodak et al., 2002), whereas most other studies led for the SIR-method to satisfactory predictions (Chodak et al., 2003, Ludwig et al., 2002) and to unsatisfactory results (Terhoeven-Urselmans et al., 2006a). Thus, predictions of C_{mic} from field-moist or from quick-frozen, freeze-dried and ground samples yield much more reliable results than using air-dried samples, which is underlined by Pietikainen and Fritze (1995). They predicted the C_{mic} content (CFE-method) for 13 freeze-dried humus samples well (r = 0.91).

Predictions of N_{mic} and P_{mic} were good for field-moist and quick-frozen samples: RSC, (r), and (a) were for N_{mic} 3.3, 1.0, and 1.0 for field-moist samples and for P_{mic} 2.5, 0.9, and 1.0 for dried samples, respectively. Our predictions were much better than those by Ludwig et al. (2002). They predicted N_{mic} for 120 air-dried forest soils unsatisfactorily (r = 0.8 and a = 0.7). The assigned wavelengths in our study were for N_{mic} 1466 and 1380 nm, which are related to acidic amid groups. The predictions of the C_{mic}/N_{mic} ratio were satisfactory only for field-moist samples (RSC = 1.4, r = 0.8 and a = 0.9), whereas the ratio of C_{mic}/P_{mic} was predicted for both sample states unsatisfactorily (RSC $\leq$ 1.1). Calculating the C_{mic}/N_{mic} ratio from the predicted values did not improve the prediction accuracy.

Ergosterol content (RSC = 4.6, r = 0.9 and a = 1.0) and ergosterol/C_{mic} ratio (RSC = 2.0, r = 0.9 and a = 1.1) were predicted well for quick-frozen samples and better than for field-moist samples. Ergosterol content was not yet investigated with NIRS in mineral soils, probably due to the low concentrations, which ranged in our investigation from 0.11 to 2.35 µg ergosterol g^{-1} soil (Table 6.2.2). Berardo et al. (2005) investigated dried and ground maize samples (n = 180) infected with with *Fusarium verticillioides*. They

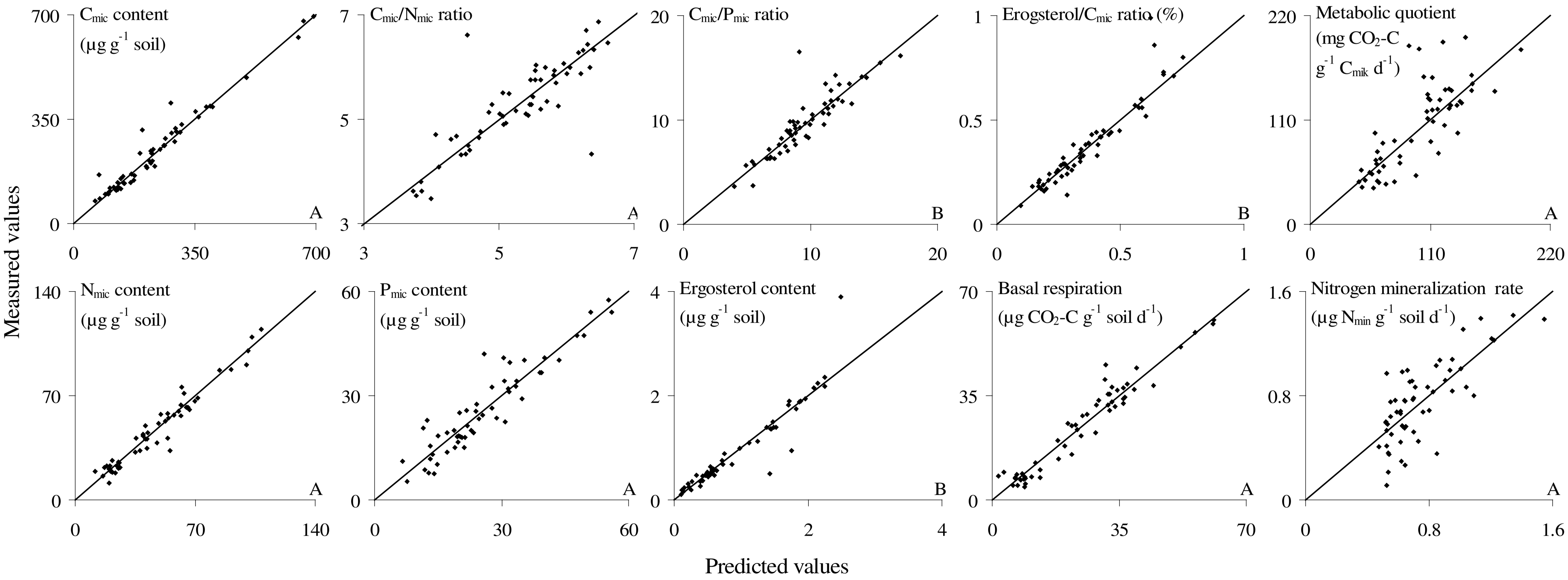

Figure 6.2.3: Measured against predicted values for soil biological characteristics. Displayed are for each constituent the pre-treatment variant, which yielded the better result (A = field-moist and B = quick-frozen, freeze-dried and ground). The lines indicate 1:1.

predicted the ergosterol content only satisfactorily with NIRS (r = 0.9 and a = 0.8), even though the ergosterol concentration covered a wide range (0 to 20 µg ergosterol g^{-1} sample). The explanation could be that ergosterol is destroyed by drought and thus their predictions were presumably indirect, for example correlated to fungi metabolites. They assigned amongst others the wavelengths 1910 and 2382 nm to ergosterol prediction. Our assigned wavelengths were 1900 and 2340 nm, which are similar to theirs. Pietikainen and Fritze (1995) showed for freeze-dried forest humus samples with a range of ergosterol from 70 to 250 µg g^{-1} sample good ergosterol predictions (r = 0.9). Quick-freezing and freeze-drying are thus promising methods to preserve ergosterol in soils.

Basal respiration was predicted well and better for field-moist samples (RSC = 3.6, r = 1.0 and a = 1.0) than for quick-frozen ones (RSC = 2.7, r = 1.0 and a = 1.0) (Table 6.2.4, Figure 6.2.3). Chang et al. (2001) showed for air-dried agricultural soils also good results for the basal respiration (RPD = 2.3 and r = 0.9), which were slightly worse than ours. The negative effect of drying was probably compensated by the high sample number. Palmborg and Nordgreen (1993) predicted the basal respiration of freeze-dried and milled samples from forest AO layers satisfactorily ($r \approx 0.8$). They assigned wavelengths, which were related to hydroxyl groups, amines and amides. Our wavelengths were 2196 nm (carboxyl and amino groups), 1926 and 1450 nm.

The metabolic quotient was predicted satisfactorily for both sample states (RSC = 1.7) (Table 6.2.4). Calculating the ratio from the predicted values did not improve the results.

Nitrogen mineralisation rate and the ratio of basal respiration/nitrogen mineralisation rate were predicted unsatisfactorily for both field-moist and quick-frozen samples (RSC = 1.1 to 1.3). Satisfactory results were found for agricultural soils by Chang et al. (2001) (RPD = 1.8 and r = 0.9) and for flooded rice soils by Russel et al. (2002) (RPD = 1.8 and r = 0.9). The difference to our study was that their soils were measured air-dried and milled. Drying soil samples at room temperature or warmer seems to improve NIRS predictions for the N mineralisation rate. This could be explained partly by the enhanced mineralisation and nitrification during the drying process, which leads to accumulation of nitrate. The resulting difference in soil nitrate contents may be related to their potential to mineralise nitrogen. Another reason for the worse predictions of the nitrogen mineralsation rate could be the reference method. The method is susceptible to short pre-incubation periods, remaining roots and high initial nitrate and ammonium concentrations.

Yield characteristics

Grain yield of cereals was predicted well for quick-frozen soils (RSC = 2.4, r = 1.0 and a = 1.0) and thus better than for field-moist ones, which were predicted satisfactorily (RSC = 2.1, r = 0.9 and a = 0.8) (Table 6.2.3, Figure 6.2.2). The explanation is probably that the primary production, in this case grain yield, is correlated with the contents of C_{org}, N_t, the secondary production of microbial biomass or other soil properties (data not shown). Nevertheless, our NIRS predictions were much better (r = 1.0) than other correlations. A reason for this is that the factors, which are built up in MPLS regression analysis, are a combination of spectral and laboratory information and thus give a more accurate picture of grain yield then every single feature. The grain yield in the field is as well the result of a combination of all influencing factors. Assigned wavelengths for predictions of grain yield were 1976 and 1144 nm, which refer to amino groups and acid amid groups (N_t prediction) and to alkyl groups (C_{org} prediction), respectively. Babar et al. (2006) recorded over three years a wheat canopy spectrally at three different sampling times during growth and calculated different indices based on this spectral information. The best correlations with the grain yield were found for indices based on the sampling dates heading and grain filling (r = 0.7 to 0.8). Nevertheless, the spectral information of the plant cover is smaller in respect to yield prediction than the spectral information of soil samples taken in spring. Van Groeningen et al. (2003) found different results to ours. They measured as well the spectral information of soils, but they dried and ground them prior predicting grain yield of rice. Their predictions were unsatisfactory (RPD = 1.0 and r = 0.2). The redox potentials of flooded rice soils may be changed more drastically by drying than the redox potential of unflooded soils. Subsequently the spectral properties of flooded soils are changed more strongly.

The predictions for grain nitrogen content were for field-moist and quick-frozen samples satisfactory but slightly better for field-moist samples (RSC = 2.2, r = 0.8 and a = 0.8 in comparison to RSC = 1.9, r = 0.8 and a = 0.8, respectively). Van Groeningen et al. (2003)

showed unsatisfactory predictions for the content of K of above ground biomass from rice plants at harvest (RPD = 1.3 and r = 0.7). The drying of soil from flooded fields may be the reason for these unsatisfactory results.

Grain N uptake was predicted well for quick-frozen samples (RSC = 2.7, r = 0.9 and a = 0.9) and satisfactorily for field-moist ones (RSC = 1.8, r = 0.9 and a = 0.8). Grain N uptake was highly correlated with the grain yield (r = 1.0, data not shown), which explains as well the better predictions for quick-frozen samples. The assigned wavelength for grain N uptake at 1972 nm was identical to the wavelength for grain yield, which was 1976 nm. The prediction accuracy is in accordance with Freeman et al. (2003). They recorded spectra of wheat canopies and predicted the grain N uptake satisfactorily (r > 0.7).

However, even though the predictions of yield characteristics were good and satisfactory, it must be taken in account that grain yield and nitrogen content and uptake of grain are not only a function of soil properties, which can be viewed spectrally with NIRS. Moreover, the planted variety, fertilisation after soil sampling, site elevation and unpredictable events like hot temperatures, unequally rain distribution or pests have an immensely large impact on yield characteristics. The NIRS predictions were regardless the named factors, which have influenced the yield characteristics in this investigation to an unknown degree, accurate.

6.3 Conclusions and outlook

Near-infrared spectroscopy was well suited to predict soil quality by means of several soil chemical and biological characteristics and showed its potential to assess grain yield and grain nitrogen uptake from winter cereals. This was not yet shown in this accuracy and number of applied reference methods by other authors. Biological characteristics should be predicted from field-moist soils in order to obtain accurate results. Quick-freezing and freeze-drying of soil samples prior NIRS measurements is a proper method to obtain comparable results for NIRS predictions, when the samples have to be stored for a longer period or under unfavourable conditions.

7 Use of near-infrared spectroscopy to predict chemical parameters and phytotoxicity of peats and growing media

7.1 Experiments

Samples

A population of peats from stockpiles in the Baltic States and pre-packed growing media of which some were known or assumed (because they were from the same stockpile as phytotoxic ones) to be phytotoxic and others known to be non-phytotoxic were collected and stored in a closed, unheated hall in order to reach a sample number sufficient for this NIRS study. Phytotoxicity (plant response of Chinese white cabbage) was determined for each sample directly after collection and after the whole set of 73 samples was obtained, which took about one year. Initially, 65 % of the 73 samples were slightly, moderately or strongly phytotoxic. During storage, the characteristics of the peats and growing media were determined (data not shown). For unknown reasons, storage reduced the phytotoxicity of the samples to 16 % (12 out of 73 samples). Nevertheless, the samples covered a wide range of the contents and phytotoxicity studied (Table 7.2.1).

The samples were either measured after drying at 60 °C and finely grinding (treatment A) or in a moist state (treatment B).

General characteristics of the sampled peats and growing media

For the pH determination, 20 cm^3 of peat or growing medium (moisture content as received and sieved < 5 mm) were suspended in 50 ml of 0.01 M $CaCl_2$. The suspension was stirred twice within one hour and pH was determined afterwards with a glass electrode (VDLUFA, 1997).

We obtained the salt content as follows: two hundred ml of distilled water were added to 20 g of the peat or growing medium (< 5 mm) and the suspension was shaken for 1 h. Then, the solution was filtered through a fine-pored filter and the conductivity was measured. We calculated the salt content on a basis of mass KCl 100 g^{-1} substrate by using the equation and correction factors provided by VDLUFA (1997).

The contents of soluble NO_3^- and NH_4^+ were determined by adding 200 ml of 0.0125 M $CaCl_2$ to 20 g of peat or growing medium (< 5 mm). Then, the suspension was shaken for 1 h and filtered through a fine-pored filter (VDLUFA, 1997). The concentrations of NO_3^- and NH_4^+ were measured colorimetrically.

The P and K contents were obtained using the CAL method. One hundred ml of a CAL solution (0.05 M calciumacetate, 0.05 M calciumlactate, 0.3 M acetic acid) was added to 5 g of sample (< 5 mm). The suspension was shaken for 90 min and filtered through a fine-pored filter. The P and K concentrations were determined photometrically (VDLUFA, 1997).

Phytotoxicity

Phytotoxicity was determined according to VDLUFA (1997). Peat (only for this purpose pH-adjusted to pH 5.5 ($CaCl_2$) and fertilised with 1.2 g l^{-1} water-soluble complete fertiliser) or the ready-to-use growing medium (< 5 mm) was filled to the rim of plastic pots (diameter: 11.5 cm, height 7.5 cm) and compacted slightly. Thirty seeds of Chinese white cabbage (*Brassica napus* var. *chinensis*) were distributed evenly on top of all media (three replications per medium). The seeds were then covered with a thin layer of medium and the medium was subsequently moistened. Then, the pots were covered with watch glasses and kept under constant light and temperature conditions and watered regularly. After three weeks, the classification of the phytotoxicity was carried out, as a modification of the VDLUFA method, according to the degree of damage symptoms (chlorosis, stunted growth): 1 – no damage symptoms, 2 – slight degree of damage symptoms, 3 – moderate degree, 4 – severe degree.

Self-heating characteristics and odour

A subpopulation of ten peats was obtained from one Latvian stockpile and also tested. The temperatures of these samples when taken ranged from 18 to 60 °C, indicating non-self-heated peat (< 30 °C) and slightly to strongly self-heated peat (30 to 60 °C). For these samples, we also classified the odour into the following three groups: 1 – no malty/spicy odour, 2 – traces of malty/spicy odour, 3 – weak malty/spicy odour.

7.2 Results and discussion

The chemical properties pH, salt content and contents of P and K were predicted well by NIRS in both treatments (Table 7.2.2, Figure 7.2.1 and Figure 7.2.2). The treatment of the samples, either measuring the NIR spectra after finely grinding them (treatment A) or in moist state (treatment B), did not have a consistent effect on the statistical parameters:

Table 7.2.1: Characteristics of the peats and growing media. The units given in the second column refer to the median and range of measured values.

Constituent	Unit	n	Treatment[†]	Median[+]	Range[+]
NO_3^- content	mg N kg^{-1} DM	59	A, B	138	16.7-1100
NO_3^- content for a subpopulation of 38 samples	mg N kg^{-1} DM	38	A, B	238	16.7-1100
NH_4^+ content	mg N kg^{-1} DM	59	A	308	30.8-900
			B	308	30.8-617
K content	mg K_2O kg^{-1} DM	59	A	1058	200-3100
			B	1058	200-3400
P content	mg P_2O_5 kg^{-1} DM	59	A	815	183-1762
			B	815	183-1783
Salt content	g kg^{-1} DM	59	A	4.00	1.67-9.58
			B	4.00	1.67-8.46
pH		59	A	4.70	2.80-5.70
			B	4.70	2.80-5.90
Phytotoxicity		73	A, B	1	1-4
Phytotoxicity for a subpopulation of 38 samples		37	A, B	1	1-4

[†] Treatment A refers to the NIR measurement of dried and ground samples and treatment B to the measurement of samples with a moisture content as received.

[+] The data refer to all samples minus the outliers (see Table 7.2.2).

prediction of pH and the salt content was slightly more successful for treatment A, whereas for the contents of K and P, treatment B gave more accurate predictions (Table 7.2.2). However, an interpretation for P and K, and salt content is complicated since the number of outliers, which were generated automatically in the cross-validation differed slightly between the treatments. Generally, we expected such inconsistent results because of the following reasons: on the one hand NIR measurements of moist samples should give more accurate results, especially for biological indicators, because drying may affect the composition of organic materials considerably. However, on the other hand the presence of water may complicate the calibration because of marked absorbance of water in the regions, which may mask peaks of organic functional groups (Chang et al., 2001, Buening-Pfaue, 2003). Moreover, grinding reduces the effects of particle size on the spectra (Casler and Shenk, 1985, Foley et al., 1998). Thus, for moist samples a greater number of samples might be required for a calibration to reduce the effects of water absorbance and particle size. Measuring the samples at different moisture conditions and creating a repeatability file in the WinISI II software might improve calibration (Tillmann and Paul, 1998, Buening-Pfaue, 2003).

Prediction of nitrate contents was unsatisfactory for both treatments (Table 7.2.2, Figure 7.2.1) which indicated that the population was too diverse for this task. Similarly, Reeves et al. (1999) reported for agricultural soils that NO_3^- contents were predicted satisfactorily only for a very limited set of samples. We additionally tested a less diverse subpopulation of 38 samples which were all seedling-substrates from two different origins and obtained a satisfactory (treatment B) or good prediction capability (treatment A) which suggests that nitrate contents can be predicted for a diverse population if the variability of the spectral information is sufficient. Contents of NH_4^+ were predicted satisfactorily in treatment A, whereas treatment B was less successful.

The phytotoxicity prediction for the entire population gave unsatisfactory results (Table 7.2.2, Figure 7.2.2). However, the determination and use of non-scaled results (e.g., use of the biomass yields) instead of the four categories in the cross-validation might have resulted in more accurate predictions. A satisfactory prediction of phytotoxicity was only achieved for the less diverse subpopulation of 38 samples in treatment B (Table 7.2.2).

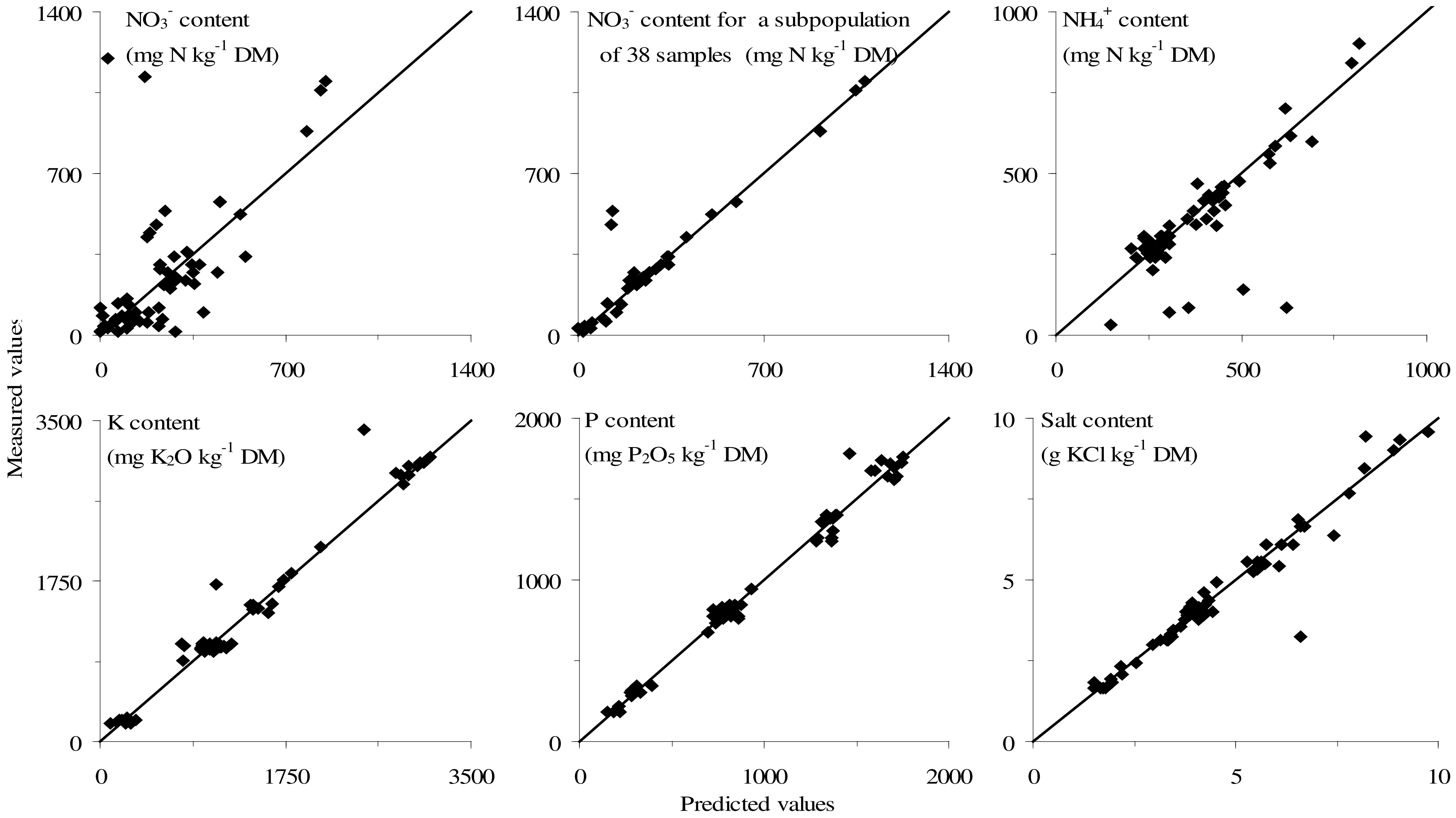

Figure 7.2.1: Measured against predicted values for the contents of NO_3^-, NH_4^+, P, K and salt based on dry matter content. Results are shown for treatment A. The lines indicate 1:1 values.

Table 7.2.2: Statistics of the cross-validation for the predicted constituents. The math treatments for the cross-validation, the standard errors of cross-validation (SECV), the RSC (the ratio of standard deviationof the laboratory results and SECV), the correlation coefficient (r) of the linear regression, the regression coefficient (a) and the intercepts (b) are also given. The units given in the second column refer to the SECV and intercepts.

Constituent	Unit	Treatment[†]	Outliers	Math treatment[+]	SECV	RSC	r	a	b
NO_3^- content	mg N kg^{-1} DM	A	2	2,20,2	178	1.4	0.61	0.92	49.4
		B	2	3,15,1	173	1.4	0.68	0.92	50.6
NO_3^- content for a subpopulation of 38 samples	mg N kg^{-1} DM	A	2	1,1,1	105	2.5	0.94	0.96	31.4
		B	1	3,5,5	152	1.5	0.99	1.05	-8.64
NH_4^+ content	mg N kg^{-1} DM	A	4	3,10,1	90.6	1.7	0.79	0.88	20.2
		B	6	1,20,15	72.4	1.7	0.68	0.99	2.59
K content	mg K_2O kg^{-1} DM	A	3	1,5,1	188	4.7	0.98	1.02	7.71
		B	5	2,15,5	144	6.3	0.98	0.97	6.42
P content	mg P_2O_5 kg^{-1} DM	A	2	1,5,1	80.7	5.8	0.99	1.01	-4.94
		B	3	3,10,10	59.8	8.1	0.99	0.98	13.2
Salt content	g kg^{-1} DM	A	3	2,10,1	0.56	3.5	0.97	0.98	0.05
		B	5	3,5,5	0.52	3.1	0.90	1.10	-0.29
pH		A	3	1,10,1	0.07	12.9	1.00	1.00	0.00
		B	3	2,15,10	0.09	10.4	0.99	1.01	-0.05
Phytotoxicity		A	3	2,1,1	0.64	1.2	0.80	1.06	0.02
		B	4	3,20,1	0.65	1.2	0.71	1.03	0.08
Phytotoxicity for a subpopulation of 38 samples		A	0	1,1,1	0.98	1.2	0.88	1.00	0.00
		B	1	3,25,25	0.84	1.4	0.88	0.93	0.19

[†] Treatment A refers to the NIR measurement of dried and ground samples and treatment B to the measurement of samples with a moisture content as received.

[+] The first number of the math treatment is the order of the derivative function, the second number is the segment length in data points over which the derivative was taken and the third is the segment length over which the function is smoothed.

This result suggests that phytotoxicity may be related to functional groups which are present in amounts greater than traces.

In treatment A, a satisfactory accuracy was achieved for the prediction of the self-heating characteristics, whereas odour was predicted well in treatment B (data not shown) prediction of odour by NIRS has also been reported in other scientific areas such as foodstuffs (Ellekjaer et al., 1994). For the constituents self-heating and odour, results should only be interpreted as a potential, since the number of samples was very low. Robust calibrations usually need a population of 50 samples or more (Tillmann, 2000).

Overall, the sample preparation had an inconsistent effect on the accuracy of predictions: for the NO_3^- and NH_4^+ contents and self-heating, drying and grinding gave more accurate predictions, whereas for the phytotoxicity and odour, NIR measurements of moist samples gave better results (Table 7.2.2). In other scientific areas such as soil and animal feed sciences, also varying results were reported (Fystro, 2002, Chang et al., 2005, Lovett et al., 2005), probably mainly because drying has disadvantageous (potential change of the composition of organic matter) and advantageous (removal of strong water absorption bands) effects on the accuracy of NIR predictions. Additional studies with more treatments (sets of small and large populations by additionally considering the effect of particle sizes (sieving, grinding)) are required to get further insights whether biological characteristics of peats are more accurately predicted if dried or moist samples are scanned.

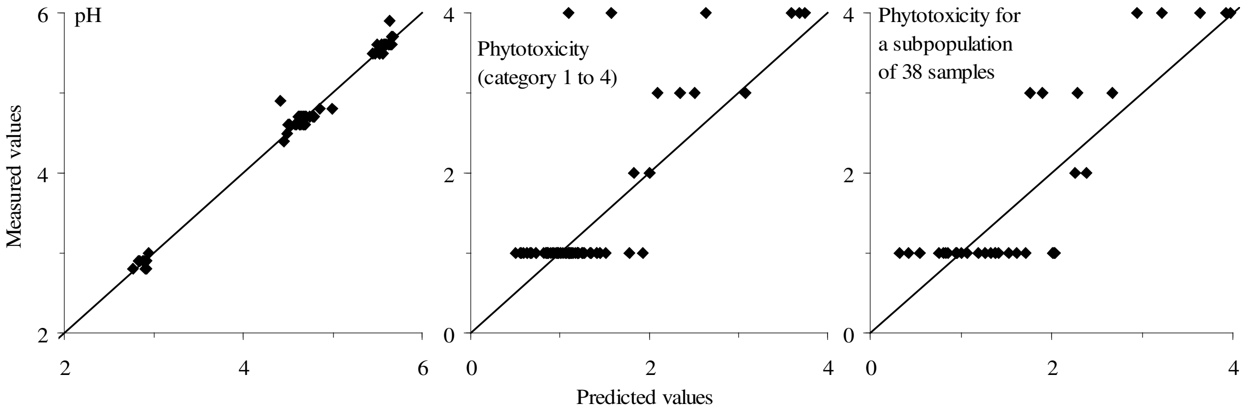

Figure 7.2.2: Measured against predicted values for pH and phytotoxicity. Results are shown for treatment B. The lines indicate 1:1 values.

7.3 Conclusions

This study showed that NIRS is well suited for the prediction of a set of chemical characteristics of peats and growing media. The prediction of phytotoxicity, however, gave only satisfactory results for a less diverse sub-population. Future studies which aim at an improved prediction accuracy will require a larger population of phytotoxic peats and growing media, whereby the tasks are (i) to obtain this population, for instance by testing the usefulness of experimentally inducing phytotoxicity by heating to various temperatures, and (ii) to conserve the phytoxicity, for instance by testing the usefulness of freeze-drying.

8 Quality of peats and growing media

8.1 Effects of passive-heating on hand-bagged peat and growing media and on plant growth

8.1.1 Abstract

Passive-heating during storage of pre-packed growing media can sometimes cause problems in horticultural practice. Its impact on basic chemical characteristics and plant yield are not fully understood. Objectives were to investigate the impact of (i) heating temperature under oxygen depleted conditions, (ii) the critical heating duration and (iii) the type of storage on the basic chemical composition of hand-bagged peat and growing media and pre-packed growing media on plant yield using a standard Chinese white cabbage (*Brassica napus* var. *chinensis*) assay. Peats and growing media (three sub-populations with different degrees of humification (H-2 to H-7) on the von Post humification scale) were heated for two weeks at 20, 35, 45 and 60 °C under oxygen depleted conditions. Additionally, the growing media were heated for 2, 4, 6, 8 and 10 days at 35 °C under oxygen depleted conditions and tested directly after heating and after five months of storage. Heating temperatures up to 60 °C of peats led to NO_3^- loss and NH_4^+ accumulation, but our results suggested that this might not lead to decreass in plant yield, if adequate NO_3^- is added afterwards. Passive-heating of growing media to 35 °C for six days or longer or higher temperatures resulted in significant decreases of plant fresh weight yield (20 % and more). Five months of storage after heating growing media at 35 °C for zero to ten days did not change the relative yield deviation between the heat duration treatments, but NH_4^+ content decreased markedly for growing media consisting of weakly decomposed peat (H-2 to H-3). For growing media heated to different temperatures, the loss of NO_3^- explained 87 % of the variation in fresh weight yield. The $NH_4^+ : NO_3^-$ ratio was a good indicator for a previous heat treatment. Maximum values up to 33 were found for heating at 60 °C. A doubling of the ratio, compared to the control, which ranged around one, and higher values were correlated with significant decreases in plant fresh yields. Nitrate loss during storage of pre-packed growing media in bags was

less for those bags which had the bag perforation showing to the outside instead to the inside of the palette. Overall, our results indicate that growing media should not be exposed to temperatures of 35 °C or higher for more than six days during transport and storage.

8.1.2 Introduction

Growing media are marketed mainly to two different types of customers: professional growers and hobby gardeners. Professional growers often need rather large amounts of growing media, which are usually delivered in bulk, big bales or 70 l bags and often transported over long distances. Hobby gardeners might use the purchased substrate whenever needed over a longer period of time, possibly up to one year (Carlile, 2004). The result of such consumer behaviour might be that the substrate is stored for a considerable length of time under oxygen depleted conditions and possibly unprotected from heat and sun radiation. This may be considered as a passive-heat-treatment and may cause growth reduction or even phytotoxicity during plant growth.

In practise and literature, the processes self-heating and passive-heating are often used synonymously, although they refer to two different processes: self-heating of peat up to 75 °C is an oxygen induced and microbial mediated biochemical process, which is replaced above 75 °C by solely chemical processes. The chemical structure of the peat is altered significantly at temperatures higher than 70 °C (Naucke, 1974) with increased macro and trace element concentrations, especially NH_4^+ (Wever and Hertogh-Pon, 1993). In contrast to self-heating, passive-heating happens during transportation or storage in pre-packed units mostly under oxygen depleted conditions and temperatures lower than self-heating levels. Ranneklev and Bååth (2003) compared microbial populations based on the phospholipid fatty acid (PLFA) composition of self-heated and passive-heated peats, which were heated in sealed bags. Generally, heating caused a change in microbial populations: self-heating led to two new PLFAs and passive-heating additionally to a third new PLFA. Storage after heating reduced the changes in microbial populations.

The effects of passive-heating and storage on growing media may be considerable. For instance, Walden and Wright (1995a) showed that passive-heating (21 to 52 °C) of pine bark media led to a decrease of NO_3^-, presumably due to immobilization, and an accumulation of NH_4^+, which was presumably caused by nitrification inhibition at increased temperatures (Beck, 1979, Walden and Wright, 1995b). Carlile (2004) reported NO_3^- depletion and in some cases additional NH_4^+ accumulation for stored, but unheated peat-based growing media and suggested that the NH_4^+ accumulation was due to the absence of nitrifying bacteria.

An investigation, which observes the whole chain of peat processing with respect to passive- heating, from the peat stockpile until the use as growing medium, is still missing. The results of such a study should be helpful for peat processors and users to avoid critical levels and duration of passive-heating and to monitor whether a peat underwent passive-heating or not. Thus, our objectives were to investigate the effect of (i) the heating temperature under oxygen depleted conditions, (ii) the critical heating duration and (iii) the type of storage on the basic chemical composition of hand-bagged peat and growing media and pre-packed growing media on plant yield using a standard Chinese white cabbage (*Brassica napus* var. *chinensis*) assay.

8.1.3 Materials and methods

Samples

Three peats and growing media were used in this study. The peats and growing media covered a wide range of origins and degrees of humification (von Post humification scale): two weakly decomposed bog peats from Finland (P-1) and Ireland (P-2) and a strongly decomposed bog peat from Germany (P-3, Table 8.1.1). Growing media GM-1, GM-2 and GM-3 were obtained from the respective peats by adjusting them to pH 5.0 - 5.5 and fertilising them with water-soluble complete fertiliser (PG Mix 14-16-18). Fertilising and liming was done before (experiments 2 and 3 described below) or after heating (experiment 1 described below).

Additionally, we used a pre-packed growing medium GM-4 (palette of 34 bags, originally 36, two were destroyed prior to these tests, each containing 70 l) from a grower, who had stored the palette under unfavourable conditions. The growing medium was a mixture of two white peats, originating from Lithuania and Ireland (Table 8.1.1). The palette was delivered to the customer two years prior to testing. Due to the automatic palletizing system the perforation holes of every third bag had no access to the ambient air.

Chemical analysis

Total organic carbon and nitrogen contents were determined by dry combustion using an Elementar Vario EL Analyzer.

For pH determination, 20 cm^3 of peat or growing medium (sieved < 5 mm) were suspended in 50 ml of 0.01 M $CaCl_2$. The suspension was stirred twice within one hour and pH was determined afterwards with a glass electrode (VDLUFA, 1997).

We obtained the salt content as follows: two hundred ml of distilled water were added to 20 g of the peat or growing medium (< 5 mm) and the suspension was shaken for 1 h. Then, the solution was filtered through a fine-pored filter and the conductivity was measured. We calculated the salt content on a basis of mass KCl 100 g^{-1} substrate by using the equation and correction factors provided by VDLUFA (1997).

The contents of soluble NO_3^- and NH_4^+ were determined by adding 200 ml of 0.0125 M $CaCl_2$ to 20 g of peat or growing medium (< 5 mm). Then, the suspension was shaken for 1 h and filtered through a fine-pored filter (VDLUFA, 1997). The concentrations of NO_3^- and NH_4^+ were measured colourimetrically.

The P and K contents were obtained using the CAL method. One hundred ml of a CAL solution (0.05 M calciumacetate, 0.05 M calciumlactate, 0.3 M acetic acid) were added to 5 g of sample (< 5 mm). The suspension was shaken for 90 min and filtered through a fine-pored filter. The P and K concentrations were determined photometrically (VDLUFA, 1997).

Experiments

Different heat treatment experiments were conducted with the peats and growing media:

Table 8.1.1: Origin and basic properties of peats and growing media used in this study. Peats P-1, P-2 and P-3 were limed (pH 5.0 to 5.5) and fertilised with PG-Mix to obtain the respective growing media GM-1 GM-2 and GM-3. Growing medium GM-4 is a mixture (50/50 by volume) of peats from Lithuania and Ireland.

	Peats				Growing media							
Substrate	Origin	Degree of humification (von Post scale)	pH	Bulk density (fresh) (g L^{-1})	C_t (% DM)	N_t (% DM)	pH	Salt content (g L^{-1})	Nitrate content (mg NO_3-N L^{-1})	Ammonium content (mg NH_4-N L^{-1})	Phosphorous content (mg P_2O_5 L^{-1})	Potassium content (mg K_2O L^{-1})
P-1/GM-1	Finland	H-2 to H-3	2.8	207	42.9	0.97	5.2	1.04	99	88	226	311
P-2/GM-2	Ireland	H-5 to H-6	3.1	367	47.9	1.12	5.1	0.82	63	67	150	173
P-3/GM-3	Germany	H-7	3.4	577	49.6	1.11	5.4	1.22	82	86	232	305
P-4/GM-4[1]	Lithuania, Ireland	H-3 to H-5	3.1	270	41.3	1.00	4.4	0.62	59	23	108	133

[1] Growing medium received from a grower who had stored the medium under unfavourable conditions.

Experiment 1: effects of heating temperature on the quality of peats and plant yield

To simulate the effects of passive-heating on peats in a pile or during transport from the peat bog to the peat processor, sub-samples of P-1 to P-3 (n = 2 for each peat and temperature, total number = 30) were filled in polyethylene tubes (V = 3 l, 0.15 mm thick foil), compacted, evacuated and the tubes were immediately shrink-wrapped to simulate almost anaerobic conditions, similar to the conditions in pre-packed growing media (e.g. big bales). In order to avoid water loss during heat treatment the samples were shrink-wrapped a second time as suggested by E. Bååth (pers. comm.). Samples were kept at 4 °C (control) or heated to 20, 35, 45 and 60 °C for two weeks. Peats were analyzed after heat treatment for contents of N_{min} and pH and subsequently fertilised and limed to the level of the growing media and then tested using Chinese white cabbage assay (n = 4 for each heated peat, total number = 120).

Experiment 2: effects of heating temperature on the quality of growing media and plant yield

Experiment 2 was carried out as described for experiment 1 for GM-1 to GM-3 (n = 2 for each growing medium and temperature, total number = 30) to simulate the effects of passive-heating on pre-packed growing media during transport from the processor to the customer and storage at the customer. Growing media were analyzed after heat treatment for contents of N_{min} and tested using Chinese white cabbage assay (n = 4 for each heated growing medium, total number = 120).

Experiment 3: effects of heating duration and storage after heat treatment on growing media quality and plant yield

To investigate the critical heating duration, sub-samples (one replication) of GM-1 to GM-3 were taken and heated, identically to the previous experiment, at 35 °C for 0 (control), 2, 4, 6, 8 and 10 days (total number = 18). One half of each sample was used immediately for the Chinese white cabbage test. The other half was stored at 4 °C for five months and then analysed for the content of N_{min} and tested using Chinese white cabbage assay (n = 2 for each sample, total number = 36). For this experiment, growing media

GM-1 to GM-3 were prepared from peats P-1 to P-3 by liming and fertilising which had slightly different initial NO_3^- and NH_4^+ contents (Table 8.1.4) compared to those used in experiment 2 (Table 8.1.3).

Experiment 4: effects of the automatic palletizing system on the quality of growing media

We analyzed the growing medium from each of the 34 bags received from the grower for contents of N_{min}. The growing media were tested in the Chinese white cabbage test (n = 2 for each sample, total number = 68), in order to investigate whether the automatic palletizing system was an influencing factor for the quality of this growing medium.

Chinese white cabbage test

Chinese white cabbage tests were carried out according to VDLUFA (1997). Heated peats, which were fertilised and limed after heat treatment, and heated growing media were filled to the rim of plastic pots (diameter 11.5 cm, height 7.5 cm) and compacted slightly (pot replication numbers are given in section 8.1.3). Twenty-seven seeds, a slight deviation to the method, where 30 seeds are used, of Chinese white cabbage were distributed evenly on top of all media. The seeds were then covered with a thin layer of substrate and moistened. The pots were covered with flow lines until the Chinese white cabbage germinated and kept under constant light (10000 Lux for 16 h a day) and temperature (16 h at 20 °C (20.3 ± 1.1), 8 h at 16 °C (15.8 ± 1.1)) conditions and watered regularly by weight. After three weeks, fresh and dry weight yield per pot and the classification of the growth reduction was carried out according to the VDLUFA method: the worst and best looking Chinese white cabbage plants within one pot were taken and graded on a scale from one (worst) to nine (best).

Statistical methods

SPSS 11.0 was used for analysis. The effect of heating on the fresh weight yield of Chinese white cabbage and rating at harvest was tested separately for each peat and growing medium using the SPSS procedure univariate mixed models ANOVA. Means were compared post hoc based on Tukey´s honestly significantly different test (HSD, $P < 0.05$). Statistics could not be calculated in experiment 1 and 2 for Chinese white cabbage rating at harvest (all substrates) and fresh weight yield (growing medium 1), because some residuals were not normally distributed and could not be transformed (log-, square root-, fischer- and quadratic transformation were tested) to fit to this pre-condition. Regression analysis were done for a further analysis of the effect of the heating temperature level, the NO_3^- content of the substrate and the NH_4^+ : NO_3^- ratio of the substrate on Chinese white cabbage test results.

8.1.4 Results and discussion

Experiment 1: effects of heating temperature on the quality of peats and plant yield

Mineral nitrogen contents of the peats were markedly affected by the heat treatments (Table 8.1.2): nitrate levels decreased for all peats from low levels at 20 °C (equal or less than 12 mg NO_3-N L^{-1}) to concentrations around zero at 60 °C. In contrast, NH_4^+ concentrations increased markedly with increasing heating temperature (Table 8.1.2). Ammonium was probably mainly released by anaerobic mineralisation of organic N. Due to the oxygen-depleted conditions during the heat treatment, denitrification was presumably the main NO_3^- depleting process. Decreasing NO_3^- contents and increasing NH_4^+ contents of peats due to heat treatment were also described by Wever and Hertogh-Pon (1993), although in their study aerobic conditions prevailed.

After the heat treatment, all peats were fertilised and limed (mean content of N_{min} = 163 mg N_{min} L^{-1} and mean pH = 5.1) (data not shown). The results of the Chinese white cabbage tests showed only for few heat treatments significant deviations from the control (Table 8.1.2). These small deviations may be explained by the low NO_3^- and increased NH_4^+ contents at high heating temperatures. Fertilisation to a level of 163 mg N_{min} L^{-1} resulted in an increased NH_4^+ : NO_3^- ratio for the samples where deviations occurred: the samples with the lowest yields (P-3 heated to 35 and 60 °C and P-2 heated to 60 °C, Table 8.1.2) were those with the lowest NO_3^- and highest NH_4^+ contents after fertilisation (data not shown).

Table 8.1.2: Nitrate and ammonium contents of passive-heated peats P-1 to P-3 (mean ± standard deviation, n = 2) and the results of Chinese white cabbage test of heated peats (after fertilisation and liming) (mean ± standard deviation, n = 8, different letters represent significantly different values with $P < 0.05$ for the respective peats (Tukey)).

		Mineral nitrogen contents of peats after heat treatment		Results of Chinese white cabbage test of heated peats (fertilisation and liming after heat treatment)	
Peat	Heating temperature (°C)	Nitrate (mg NO_3-N L^{-1})	Ammonium (mg NH_4-N L^{-1})	Fresh weight yield[1, 2] (% of control)	Rating at harvest[1]
P-1	Control	nd	nd	100 ± 15	8.3 ± 0.5
	20	3 ± 1	1 ± 0	90 ± 11	8.0 ± 0.5
	35	1 ± 0	9 ± 1	100 ± 9	8.4 ± 0.7
	45	1 ± 0	21 ± 2	95 ± 5	8.9 ± 0.4
	60	1 ± 0	24 ± 1	88 ± 11	7.9 ± 0.4
P-2	Control	nd	nd	100 ± 8 a	7.8 ± 0.5
	20	12 ± 2	17 ± 1	89 ± 7 ab	8.0 ± 0.5
	35	12 ± 2	18 ± 0	97 ± 11 ab	7.6 ± 0.5
	45	3 ± 0	35 ± 1	87 ± 12 ab	7.9 ± 0.4
	60	3 ± 0	48 ± 4	85 ± 8 b	8.0 ± 0.0
P-3	Control	nd	nd	100 ± 9 a	8.6 ± 0.5
	20	7 ± 2	4 ± 2	88± 11 ab	8.1 ± 0.6
	35	3 ± 0	5 ± 2	85 ± 12 bc	8.1 ± 1.0
	45	3 ± 0	15 ± 2	92 ± 9 ab	8.8 ± 0.5
	60	0 ± 0	32 ± 4	73 ± 8 c	7.9 ± 0.4

[1] Statistics were not computable, if no letters are given.

[2] Absolute fresh weight yields were 20.6, 19.4 and 22.6 g fresh weight pot^{-1} in the control treatments of P-1, P-2 and P-3, respectively.

nd: not determined.

Thus, our results suggest that the NH_4^+ use efficiency of the Chinese white cabbage plants was not as high as the use efficiency of NO_3^-. Only NO_3^- and not NH_4^+ concentrations after heat treatment, liming and fertilisation explained significantly the variance of the fresh weight yield ($r^2 = 0.29$) (data not shown). The reason could be that the nitrifying microorganisms were not able to recover from the oxygen depleted heating conditions within the three weeks of Chinese white cabbage test or they were absent.

The rating at harvest of the Chinese white cabbage plants was on a high level for all control peats and highest for P-3 on a level of 8.6 (Table 8.1.2).

Overall, the results of this experiment indicate that a passive-heat-treatment of peat under oxygen depleted conditions up to 60 °C should have - after subsequent liming and fertilisation - no impact on the plant yield, if the resulting higher NH_4^+ concentration is compensated through mainly NO_3^- fertilisation.

<u>Experiment 2: effects of heating temperature on the quality of growing media and plant yield</u>

Heating of growing media under oxygen depleted conditions for two weeks caused a decrease in NO_3^- content (Tab. 8.1.3), probably mainly due to denitrification. The most pronounced decrease was observed for GM-1 and GM-3 between 20 and 35 °C, whereas it occurred between 35 and 45 °C for GM-2. The NO_3^- contents were less than 7 mg NO_3-N L^{-1} for all growing media after heating to 60 °C. The NH_4^+ contents increased only slightly at 60 °C heating temperature.

The decline in the NO_3^- content caused a decrease of the salt content. The salt content was 23 % lower at 60 °C heating temperature compared to the control (Tab. 8.1.3). However, the salt content decreased less than the NO_3^- content, probably because heating of peat changed its structure and decreased its molecular complexity. The less complex the compounds in peat are the higher is the measured electrical conductivity value (Ksiezopolska, 2005).

Fresh weight yield of Chinese white cabbage was negatively correlated with the heating temperature of the growing media (r^2 = 66 %) (Tab. 8.1.3, Figure 8.1.1). The decrease of fresh weight yield was in the range of 42 to 56 % compared to the controls when growing

Table 8.1.3: Chemical characteristics of passive-heated growing media GM-1 to GM-3 (mean ± standard deviation, n = 2) and the results of Chinese white cabbage test from the passive-heated growing media (mean ± standard deviation, n = 8, different letters represent significantly different values with $P < 0.05$ within one substrate (Tukey)).

		Chemical characteristics after heat treatment					Results of Chinese white cabbage test (fertilisation and liming before heat treatment)	
Growing medium	Temperature of heating (°C)	Nitrate content (mg NO_3-N L^{-1})	Ammonium content (mg NH_4-N L^{-1})	NH_4^+ : NO_3^- ratio	pH value	Salt content (g L^{-1})	Fresh weight yield[1,2] (% of control)	Rating at harvest[1]
GM-1	Control	100 ± 4	86 ± 16	0.9 ± 0.1	5.2 ± 0.0	1.01 ± 0.01	100 ± 15	8.3 ± 0.5
	20	90 ± 3	86 ± 4	0.9 ± 0.0	5.4 ± 0.0	1.04 ± 0.02	109 ± 11	8.8 ± 0.5
	35	18 ± 16	88 ± 4	7.6 ± 6.4	5.4 ± 0.0	0.80 ± 0.04	67 ± 16	7.0 ± 0.9
	45	5 ± 0	85 ± 5	16.9 ± 1.0	5.3 ± 0.0	0.78 ± 0	63 ± 6	7.8 ± 0.5
	60	7 ± 0	106 ± 10	15.1 ± 1.4	5.3 ± 0.0	0.78 ± 0.04	57 ± 5	7.8 ± 0.5
GM-2	Control	65 ± 4	70 ± 0	1.1 ± 0.1	5.2 ± 0.1	0.82 ± 0.01	100 ± 8 a	7.8 ± 0.5
	20	59 ± 1	58 ± 3	1.0 ± 0.1	5.2 ± 0.1	0.73 ± 0.01	88 ± 12 ab	7.9 ± 0.4
	35	63 ± 1	62 ± 0	1.0 ± 0.0	5.1 ± 0.1	0.76 ± 0.01	82 ± 9 b	7.9 ± 0.4
	45	5 ± 2	67 ± 0	16.8 ± 7.9	5.2 ± 0.1	0.56 ± 0.04	50 ± 9 c	6.9 ± 0.4
	60	3 ± 0	91 ± 1	30.3 ± 0.5	5.1 ± 0.0	0.59 ± 0.01	58 ± 4 c	7.0 ± 0.0
GM-3	Control	91 ± 12	87 ± 2	1.0 ± 0.2	5.4 ± 0.0	1.23 ± 0.03	100 ± 9 a	8.6 ± 0.5
	20	95 ± 10	80 ± 7	0.8 ± 0.0	5.3 ± 0.1	1.06 ± 0.09	96 ± 10 a	8.5 ± 0.8
	35	41 ± 5	90 ± 3	2.2 ± 0.2	5.5 ± 0.0	1.00 ± 0.04	75 ± 10 b	8.0 ± 0.0
	45	22 ± 3	97 ± 12	4.4 ± 0.0	5.5 ± 0.0	0.94 ± 0.01	69 ± 9 b	7.8 ± 0.5
	60	3 ± 0	99 ± 15	32.8 ± 4.9	5.4 ± 0.0	0.92 ± 0.04	44 ± 4 c	7.0 ± 0.0

[1] Statistics were not computable, if no letters are given.

[2] Absolute fresh weight yields were 20.6, 19.4 and 22.6 g fresh weight pot^{-1} in the control treatments of GM-1, GM-2 and GM-3, respectively.

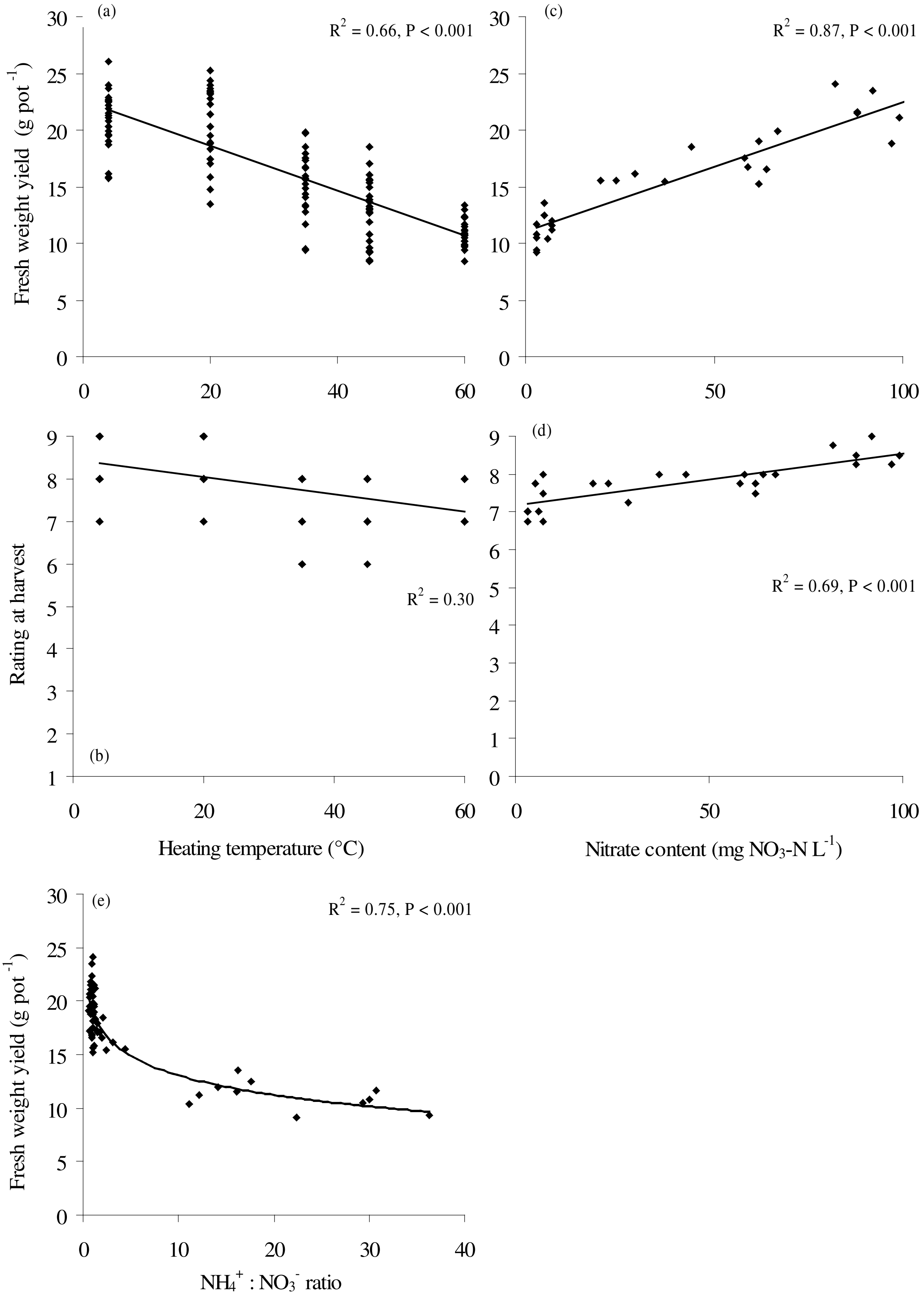

Figure 8.1.1: Results of Chinese white cabbage tests. Fresh weight yield (a) and rating at harvest (b) against heating temperature (n=120) and fresh weight yield (c) and rating at harvest (d) against NO_3^- content (n=30) for growing media (experiment 2). Linear regressions are also given. Panel (e) shows a logarithmic regression of the fresh weight yield against the NH_4^+ : NO_3^- ratio for peats and growing media (n = 54, experiment 1 and 2).

media heated to 60 °C were used. For GM-2 and GM-3, fresh weight yields were significantly lower compared to the controls for those growing media which were heated to 35 °C and higher temperatures. The reason for the yield reductions was mainly the decreasing NO_3^- content at increasing heating temperatures. Nitrate content explained highly significantly 87 % of fresh weight yield and 69 % of rating at harvest results (Figure 8.1.1). The deviation of the rating at harvest from the control was indifferent and showed no trends, except for slight decreases with increasing temperature GM-3 (Tab. 8.1.3).

A logarithmic regression explained 75 % of the variation of fresh weight yield in dependence of the NH_4^+ : NO_3^- ratio (Figure 8.1.1). An increase of the ratio by a factor two or more of a sample (in comparison to the control) indicated a heat treatment, which led to a significant decrease in fresh weight yield (Tab. 7.1.3). The decrease in fresh weight yield was at least 20 %.

Walden and Wright (1995b) observed for fertilised pine bark medium an increase in the NH_4^+ : NO_3^- ratio from to 0.6 to 1.2 due to a heating at 40 °C. Different peat qualities, defined by their degrees of humification, reacted in our investigation differently. Peats with low degrees of humification had increased NH_4^+ : NO_3^- ratios already after slightly increased temperatures (starting with 35 °C), whereas peats with higher degrees of humification had especially high ratios after heating to 45 (GM-2) or 60 °C (GM-3, Table 8.1.3).

Overall, the results indicate that the NH_4^+ : NO_3^- ratio was a good indicator for a previous heat treatment of growing media and subsequent yield losses in the Chinese white cabbage test. The ratio for the unheated growing media (control) ranged between 0.9 and 1.1 (Tab. 8.1.3). Similarly, Fuchs et al. (2001) proposed for outdoor use of composts in horticulture a NH_4^+ : NO_3^- ratio limit of 0.5 and lower. In summary, storage of pre-packed growing media at 35 °C and higher temperatures should be avoided, because this may lead to a significant reduction of plant growth.

Table 8.1.4: Chemical characteristics of heated (35 °C) growing media GM-1 to GM-3, which were measured immediately and five months after the heat treatment (experiment 3, n = 1), and fresh weight yield of Chinese white cabbage test (mean ± standard deviation, n = 2, different letters represent significantly different values with $P < 0.05$ within one substrate (Tukey)).

		Characteristics immediately after heat treatment				Characteristics five months after heat treatment			
	Heating period (days at 35 °C)	Nitrate content ($mg\ NO_3$-$N\ L^{-1}$)	Ammonium content ($mg\ NH_4$-$N\ L^{-1}$)	$NH_4^+ : NO_3^-$ ratio	Fresh weight yield[1] (% of control)	Nitrate content ($mg\ NO_3$-$N\ L^{-1}$)	Ammonium content ($mg\ NH_4$-$N\ L^{-1}$)	$NH_4^+ : NO_3^-$ ratio	Fresh weight yield[1] (% of control)
GM-1	0, control	63	62	1.0	100 ± 3 a	72	27	0.4	100 ± 1 a
	2	53	62	1.2	91 ± 5 ab	72	20	0.3	80 ± 13 ab
	4	24	63	2.6	68 ± 2 b	20	9	0.5	57 ± 3 bc
	6	4	76	19.0	34 ± 17 c	5	11	2.2	40 ± 2 cd
	8	3	83	27.7	24 ± 7 c	5	4	0.8	31 ± 0 d
	10	4	80	20.0	33 ± 18 c	4	5	1.3	nd
GM-2	0, control	64	109	1.7	100 ± 6 a	98	92	0.9	100 ± 6 a
	2	59	98	1.7	102 ± 6 a	81	96	1.2	80 ± 17 ab
	4	36	101	2.8	91 ± 2 a	31	76	2.5	58 ± 19 ab
	6	11	95	8.6	69 ± 4 b	6	87	14.5	47 ± 9 b
	8	8	95	11.9	43 ± 8 c	6	76	12.7	38 ± 2 b
	10	6	90	15.0	30 ± 4 d	6	39	6.5	35 ± 3 b
GM-3	0, control	42	96	2.3	100 ± 3 a	68	99	1.5	100 ± 19 a
	2	29	86	3.0	72 ± 9 b	31	95	3.1	79 ± 7 a
	4	19	90	4.7	66 ± 9 bc	10	105	10.5	89 ± 4 a
	6	6	93	15.5	51 ± 8 c	3	105	35.0	70 ± 9 a
	8	3	99	33.0	50 ± 2 c	7	109	15.6	61 ± 9 a
	10	3	93	31.0	54 ± 3 c	7	105	15.0	66 ± 4 a

[1] Absolute fresh weight yields were 22.7, 22.3 and 21.7 g fresh weight pot^{-1} in the control treatments of GM-1, GM-2 and GM-3 immediately after heating and 19.9, 26.2 and 15.5 g fresh weight pot^{-1} in the control treatments five months after heating. nd: not determined.

Experiment 3: effects of heating duration and storage after heat treatment on growing media quality and plant yield

For GM-1 to GM-3, increasing duration of heating at 35 °C up to ten days had the same effects on NO_3^- and NH_4^+ contents and yields of Chinese white cabbage as increasing heating temperatures in experiment 2 (Tab. 8.1.4). Six days heating led to a decrease in yield of 30 % or more.

Storage at 4 °C for five months changed partly basic chemical characteristics of the growing media, but the yields of the Chinese white cabbage tests did not change markedly (Tab. 8.1.4). Nitrate contents increased during storage for growing media, which were unheated (control) or heated for two days. Ammonium contents reacted differently: at a low degree of humification (GM-1) the NH_4^+ content decreased with increasing heating duration nearly to zero due to storage for five months, whereas it increased slightly at a high degree of humification (GM-3).

These shifts in contents of N_{min} may partly be explained by nitrification during storage, because gas exchange (required for a supply of oxygen for nitrification) through the polyethylene bags was possible. Similarly, decreasing NH_4^+ contents during storage were also described for self-heated peats (Wever and Hertogh-Pon, 1993).

Overall, heating of pre-packed (small bags as described) growing media at 35 °C, even for a short period of six days, results in losses of plant fresh weight yields of at least 30 %. In practice the same effect is obtained to some extent in larger pre-packed units (e.g. 70 l bags, bales or big bales) where growing medium that is closest to the plastic packaging material is more subjected to passive-heating than substrate that is closer to the centre of the bag or bale (G. Schmilewski, unpublished). The $NH_4^+ : NO_3^-$ ratio is a good indicator of a previous heating event (and subsequent yield reductions of 30 % and more) for peat-based growing media with high degrees of humification (H-5 to H-7) even after longer storage at 4 °C. Storage of peat-based growing media with low degrees of humification, however, may result in considerably reduced $NH_4^+ : NO_3^-$ ratios, which then make it impossible to trace the previous heating event. However, the results of experiment 3 must be taken cautiously, because number of replicates was low.

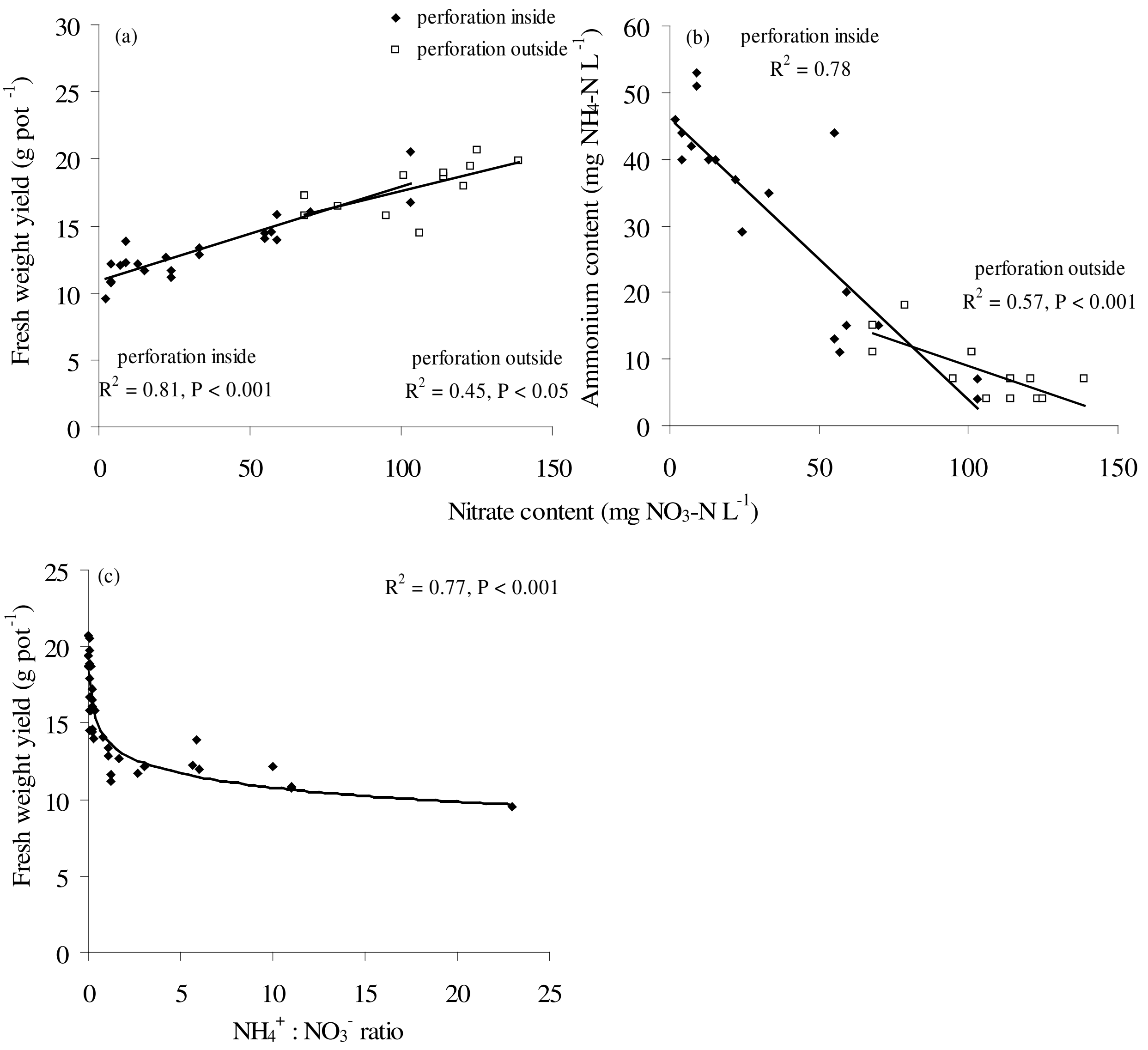

Figure 8.1.2: : Results of Chinese white cabbage tests are given in panels (a) and (c). Fresh weight yield (a) and NH_4^+ content (b) against NO_3^- content for growing medium GM-4 (experiment 4). Regressions are given for the groups “perforation of growing media bags showed to the inside of the palette during storage” (filled rhomb) (n = 22) and “perforation of growing media bags showed to the outside of the palette during storage” (unfilled square) (n = 12). Panel (c) shows a logarithmic regression of the fresh weight yield against the $NH_4^+ : NO_3^-$ ratio for GM-4 (n = 34).

Experiment 4: effects of the automatic palletizing system on the quality of growing media

The thirty-four 70 l bags on the palette, which were stored on the premises of the grower before investigations for two years, can be classified into two different groups: in group one, the one-sided perforation, essential for air to escape the bag during the automatic filling process, showed to the inner side of the palette, where oxygen had no free access. In group two, the perforation showed to the outer side of the palette and thus had somewhat better access to oxygen. However, as common in practice, all 36 (34) bags on the palette had been customize-wrapped with plastic wrapping on parts of the palette to ensure secure transportation to the grower. Fresh weight yield of Chinese white cabbage was significantly lower for the bags with the perforation to the inner side (13.3 compared to 17.8 g pot^{-1}, data not shown). The reason was the lower NO_3^- content, which explained 81 % of the fresh weight yield variation (Figure 8.1.2). Additionally, the NH_4^+ content of the growing media of group one was higher (up to 54 mg NH_4-N L^{-1}) compared to the bags where the perforation showed to the outer side, which had contents between five and 18 mg NH_4-N L^{-1} (Figure 8.1.2). The logarithmic regression showed again that fresh weight yield is highly significant ($r^2 = 0.77$) dependent on the $NH_4^+ : NO_3^-$ ratio (Figure 8.1.2).

Overall, the results indicated the usefulness of the $NH_4^+ : NO_3^-$ ratio as indicator for Chinese white cabbage yields. Additionally, the results showed that staking should be done by making sure that ventilation holes have access to the ambient air.

8.1.5 Implications

Our study showed that quality and chemical stability of peats and growing media may be markedly affected by the handling during transportation and storage. Key factors are the temperature, the duration of heating during storage or transport and the supply of oxygen. Oxygen supply is affected by the packing density, and the dimension and position of perforation holes of the pre-packed units on the palette. The $NH_4^+ : NO_3^-$ ratio was a good indicator of a previous heating event, especially for strongly decomposed peat-based growing media. Further research should be addressed to justifiable minimum limits of oxygen supply of different growing media and their maximum storage duration under varying conditions.

8.2 Quality assessment of growing media with near-infrared spectroscopy: chemical characteristics and plant assay results

8.2.1 Experiments

Samples

Four peats (P-1 to P-4) and four growing media (GM-1 to GM-4) were used for this investigation (chapter 8.1). Growing media, which have the same number as the respective peat, are based on the same peat. The peats and growing media covered a wide range of origins (two white peats from Finland (P-1) Ireland (P-2) and a mixture of two white peats from Lithuania and Ireland (P-4) and a black peat from Germany (P-3)), degrees of humification (on the Von Post scale) (P-1 H-2 to H-3, P-2 H-5 to H-6, P-3 H-7 and P-4 H-3 to H-5) and dimensional weights (207 to 577 g L^{-1}). The growing media were obtained by adjusting the pH to 5.0 - 5.5 and fertilising the peats with water-soluble complete fertiliser (PG Mix 14-16-18) to a N_{min} level of 175 mg L^{-1}.

Heating experiments

Peat samples were heated to different temperatures for different periods in order to mimic the effect of transport and storage and to obtain a large set with a wide range of plant assays results. The heating experiments are described in detail by (Terhoeven-Urselmans et al., 2006b).

Briefly, sub-samples of P-1 to P-3 and GM-1 to GM-3 were filled in three litres containing poly ethylene tubes (0.15 mm thickness) and compacted. The air was evacuated and the tubes were immediately shrink-wrapped. The samples were heated at 4 (control, only growing media), 20, 35, 45 and 60 °C for two weeks ((i) in total n = 54). Peats were analyzed after heat treatment for contents of N_{min} and pH and subsequently fertilised and limed to growing media level. Thus, only growing media were used later in Chinese white cabbage test.

Sub-samples of GM-1 to GM-3 were taken and heated, identically to the previous experiment, at 35 °C for 0 (control), 2, 4, 6, 8 and 10 days. Directly after heating and after five months of storage at 4 °C the test of Chinese white cabbage was conducted ((ii) in total n = 18).

Additionally, we included a bagged growing medium (GM-4) received from a grower who had stored the medium under unfavourable conditions in this study ((iii) n = 34).

Chemical analysis

Total organic carbon and nitrogen contents were determined by dry combustion using an Elementar Vario EL Analyzer.

The procedures of VDLUFA (1997) were used for the determination of pH (0.01 M $CaCl_2$), salt content (conversion of conductivity to mass of KCl) and P and K content (both CAL).

The contents of soluble NO_3^- and NH_4^+ were determined by adding 200 ml of 0.0125 M $CaCl_2$ to 20 g of peat or growing medium (< 5 mm). Then, the suspension was shaken for 1 h and filtered through a fine-pored filter (VDLUFA, 1997). The concentrations of NO_3^- and NH_4^+ were measured colorimetrically.

Chinese white cabbage test

Growing media impact on plant growth was determined according to VDLUFA (1997). Replicate number was four (heating experiment (i)) and two (heating experiment (ii) and (iii)), respectively (in total n = 320). Heated samples were filled in pots and twenty-seven seeds of Chinese white cabbage were sown in all growing media. The pots were kept under constant light (10000 Lux for 16 h a day) and temperature (16 h at 20 °C, 8 h at 16 °C) conditions and watered regularly by weight. After three weeks, fresh weight yield per pot and the rating of the growth reduction was carried out of the VDLUFA method: the best and the worst looking plants within one pot of Chinese white cabbage were taken and graded on the scale nine (best) to one (worst).

8.2.2 Results and discussion

The first derivative spectra of selected samples shown in Figure 8.2.1 cover the spectral range of the sample set. The two most visible features in the original spectra were the water peaks with maxima at 1438 and 1922 nm, which are zero in the first derivative (Figure 8.2.1). A marked variability between the spectra was observed in the visible range from 430 to 900 nm and from 1940 to 2500 nm. Some important wavelengths reported for peats are 864 nm (unidentifiable organic material), 2396 (absorption of *Sphagnum papillosum*) and 2476 nm (absorption of *Sphagnum magellanicum*) (McTiernan et al., 1998).

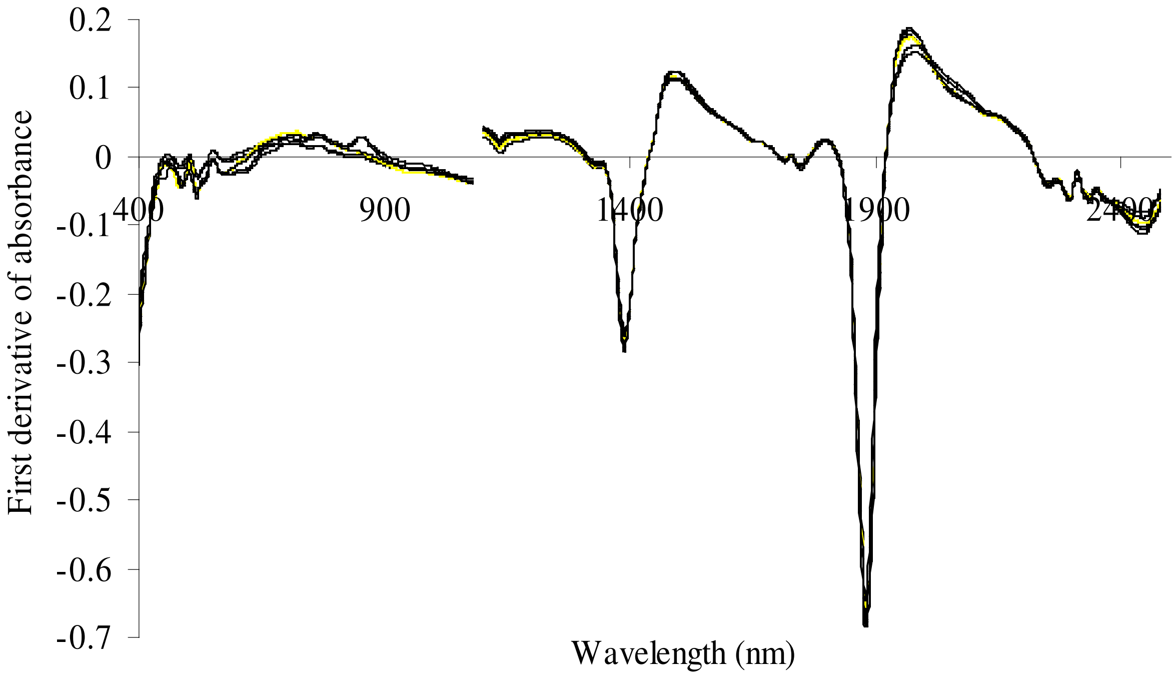

Figure 8.2.1: First order derivative of absorbance spectra for six selected growing media, which cover the spectral range of the sample set. The derivative was calculated including scatter correction, by using a segment length of five data points over which the derivative was taken and smoothing the spectra over five data points.

Chemical characteristics of growing media

The chemical characteristics of the used growing media covered wide ranges (Table 8.2.1). The pH (4.1 – 5.6) and contents P (97 – 226 mg P_2O_5 L^{-1}) and K (119 – 340 mg K_2O L^{-1}) were sufficient for undisturbed plant growth. Mineral nitrogen levels (9 – 205 mg L^{-1}) were the most important chemical characteristics regarding the prediction of plant yield. All chemical characteristics of the growing media were predicted well by NIRS (Table 8.2.2, Figure 8.2.2): the RSC ranged between 2.0 and 5.0 for the pH and contents of total carbon and nitrogen, K, P, salt, NO_3^- and NH_4+ and the NH_4^+ : NO_3^- ratio and (r) and (a) of linear regression of measured against predicted values were in the range of 0.87 to 0.97 and 0.91 to 1.11, respectively.

Table 8.2.1: Displayed are the chemical growing media characteristics after passive-heat-treatments and the test results of Chinese white cabbage. Sample number (N) refers to the cross-validation excluding the outliers. The given results belong to samples, which were fresh as received. (GM = growing medium).

Constituent	Unit	N	Range	Mean	Standard deviation
C_t content	% dry matter	306	39.6-50.2	45.7	3.2
N_t content	% dry matter	306	0.9-1.2	1.0	0.1
pH value		310	4.1-5.6	5.1	0.4
Salt content	g L^{-1}	310	0.4-1.3	0.8	0.2
P content	mg P_2O_5 L^{-1}	305	97-266	176	49
K content	mg K_2O L^{-1}	310	119-340	223	72
Mineral nitrogen content	mg L^{-1}	312	9-205	124	45
NO_3^- content	mg NO_3-N L^{-1}	307	2-139	56	37
NH_4^+ content	mg NH_4-N L^{-1}	312	4-113	68	31
NH_4^+ : NO_3^- ratio		304	0.03-36.3	4.24	7.30
Rating at harvest[a]	category 1-9	299	4-9	7.5	1.2
Rating at harvest (GM 1) [a]	category 1-9	77	2-9	7.8	1.4
Rating at harvest (GM 2) [a]	category 1-9	77	6-9	7.7	0.6
Rating at harvest (GM 3) [a]	category 1-9	78	5-9	7.9	1.0
Fresh weight yield	g pot^{-1}	308	6.1-26.1	16.3	4.1
Fresh weight yield (GM 1)	g pot^{-1}	78	6.1-25.2	16.9	4.7
Fresh weight yield (GM2)	g pot^{-1}	79	8.4-22.2	15.5	3.7
Fresh weight yield (GM3)	g pot^{-1}	81	8.4-24.0	17.2	4.5

[a] At the harvest of Chinese white cabbage all plants, on a pots basis, were rated according to their overall impression: rating category one represented the worst and rating category nine the best overall impression.

The good predictions for the pH and contents of P, K and salt correspond to the results of Ludwig et al. (2006), who used a rather small set of growing media (n = 73) with special characteristics (known or assumed phytotoxicity).

The predictions of the contents of P, K and salt in our investigation yielded better results for samples, which were fresh as received (Table 8.2.2) than for dried and ground ones (data not shown). Only pH prediction was better with dried and ground samples (RSC = 5.0 in comparison to RSC = 3.9 for samples, which were fresh as received). In agreement with this, Ludwig et al. (2006) also reported more accurate predictions for P and K using samples material, which was fresh as received, and for pH using dried and ground material, whereas for the salt content, opposite results were reported. Correlation analysis indicated that the most important wavelength for salt prediction was in our study 1922 nm (vibrations of -C=O, $-CONH_2-$, O=C-O-, and -OH). The –OH group was amongst others also important for salt prediction in fermented soybean food (Lu and Han, 2005). For N_t, which was predicted well (Table 8.2.2), correlation analysis showed that the most important wavelengths were 660 nm (red) in the visible region and 960 (vibrations of -OH, HC=O and HC-OH) and 1650 nm (vibrations of –NH) in the near-infrared region. The predictions of the contents of N_{min}, NO_3^- and NH_4^+ and of the $NH_4^+ : NO_3^-$ ratio were better for samples, which were fresh as received, (Table 8.2.2, Figure 8.2.2) than for dried and ground ones (data not shown). In contrast to the good predictions in this study, Ludwig et al. (2006) achieved only satisfactory predictions for the NH_4^+ contents, whereas NO_3^- contents were predicted unsatisfactorily for their small sample set (n = 73). Reasons were most probably (i) that the sample number in our study was much higher (320 in comparison to 73 samples) and (ii) that the spectral diversity in our study was less, since the number of growing media origins was smaller, even though the range of humification degrees was similar.

The good predictions for the contents of N_{min} and NO_3^- and the $NH_4^+ : NO_3^-$ ratio were presumably due to indirect correlations, since the contents were rather small (Table 8.2.1). However, correlations with the C_t (NH_4^+: r = 0.51, $P < 0.01$) and the N_t content (NH_4^+: r = 0.16, $P < 0.05$; NO_3^-: r = 0.13, $P < 0.05$) were only small or absent (NO_3^- with C_t: r = 0.01). Interestingly, the assigned wavelengths for contents of minerals nitrogen

Table 8.2.2: Displayed are the cross-validation statistics for the chemical growing media characteristics and the test results of Chinese white cabbage for samples, which were fresh as received. The mathematical treatment, the number of outliers, the standard error of cross-validation (SECV), the ratio of the standard deviation of the laboratory results to SECV (RSC) and the correlation coefficient (r) and the regression coefficient (a) of a linear regression (measured against predicted values) are given. (GM = growing medium).

Constituent	Cross-validation Mathematical treatment [a]	Outliers	SECV	RSC	r	a
C_t content	1,15,1	14	0.73	4.44	0.97	1.00
N_t content	1,10,10	14	0.02	3.64	0.94	0.98
pH value	1,10,5	10	0.10	3.93	0.97	1.00
Salt content	1,5,5	10	0.08	2.57	0.92	0.96
P content	1,5,1	15	13.8	3.58	0.95	0.99
K content	1,5,5	10	22.2	3.23	0.96	0.98
Mineral nitrogen content	3,15,5	8	19.6	2.29	0.90	0.91
NO_3^- content	1,5,5	13	18.4	2.01	0.87	0.94
NH_4^+ content	2,20,1	8	9.50	3.24	0.95	0.97
$NH_4^+ : NO_3^-$ ratio	1,10,5	16	3.40	2.15	0.88	1.11
Rating at harvest[b]	2,10,1	19	0.85	1.41	0.67	1.01
Rating at harvest (GM 1)[b]	1,15,1	5	0.79	1.73	0.81	1.00
Rating at harvest (GM 2)[b]	3,20,5	7	0.44	1.28	0.35	0.70
Rating at harvest (GM 3)[b]	3,5,5	6	0.58	1.69	0.79	0.92
Fresh weight yield	1,1,1	10	2.89	1.42	0.71	0.91
Fresh weight yield (GM 1)	2,15,1	4	2.33	2.02	0.88	0.87
Fresh weight yield (GM 2)	1,5,5	5	2.28	1.63	0.77	0.99
Fresh weight yield (GM 3)	1,5,1	3	2.40	1.88	0.82	0.95

[a] The first number of the mathematical treatment is the order of the derivative function, the second one the segment length in data points over which the derivative was taken, and the third one the segment length over which the function was smoothed.

[b] At the harvest of Chinese white cabbage all plants, on a pots basis, were rated according to their overall impression: rating category one represented the worst and rating category nine the best overall impression.

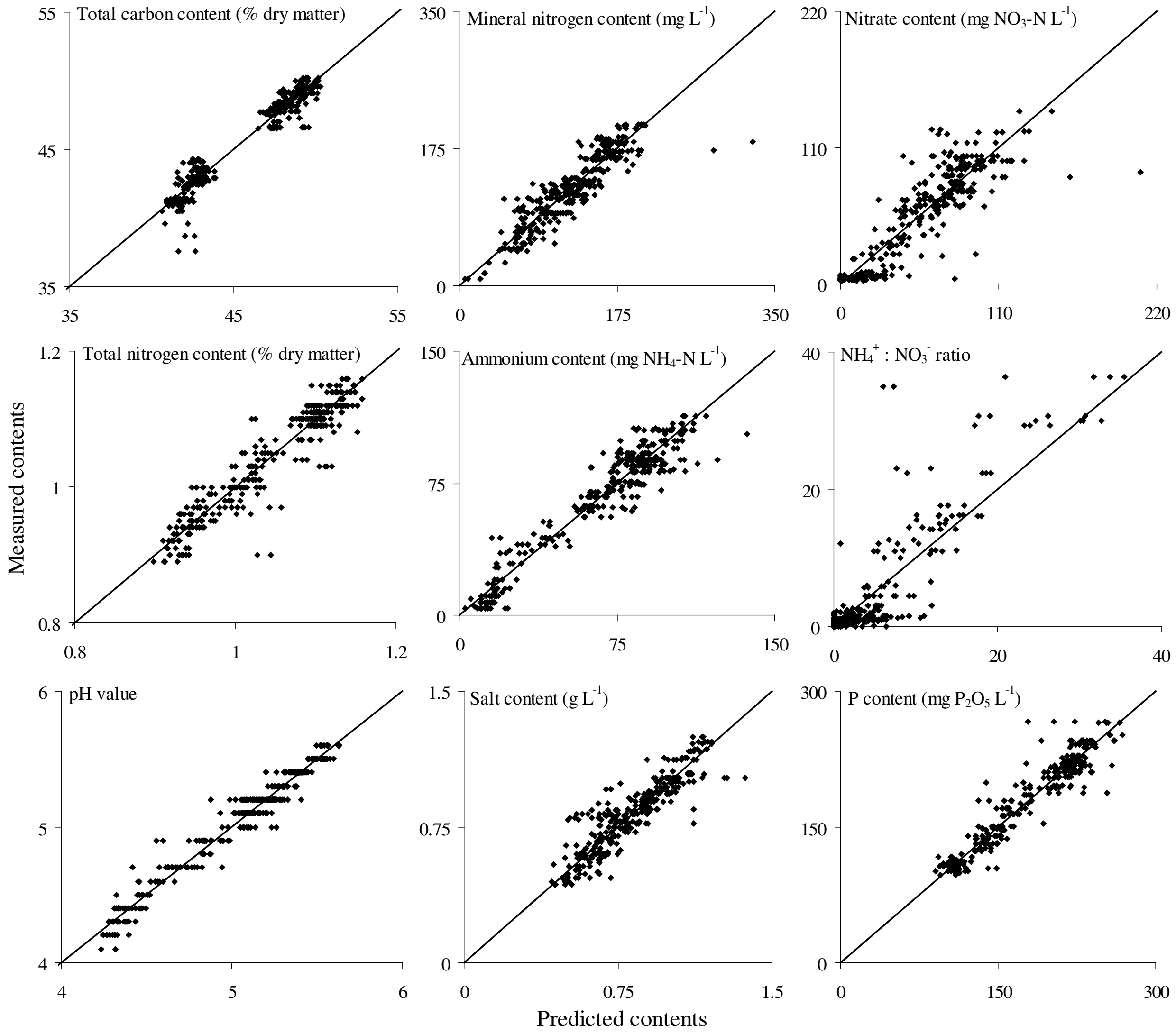

Figure 8.2.2: Measured against predicted values for the chemical characteristics of the growing media. Displayed are pH, contents of total carbon and nitrogen, mineral nitrogen, NH_4^+, NO_3^-, salt and P and the NH_4^+ : NO_3^- ratio. The results for samples, which were measured fresh as received, are displayed. The lines indicate 1:1.

and NO_3^- and the NH_4^+ : NO_3^- ratio exhibited between 2018 and 2060 nm absorptions for aqueous ammonia (Figure 8.2.4).

The good prediction of total contents of carbon (Table 8.2.2, Figure 8.2.2) has not been reported before. Prasad and O´Shea (1999) found only a rough estimate for two carbon fractions (contents of lignin and cellulose) with infrared spectroscopy. In the present investigation, the assigned wavelengths for C_t prediction were 1870 (-C=O vibrations), 686 (red) and 1348 nm (vibrations of $-CH_3$, -CH-, -CHO, -C=CH-).

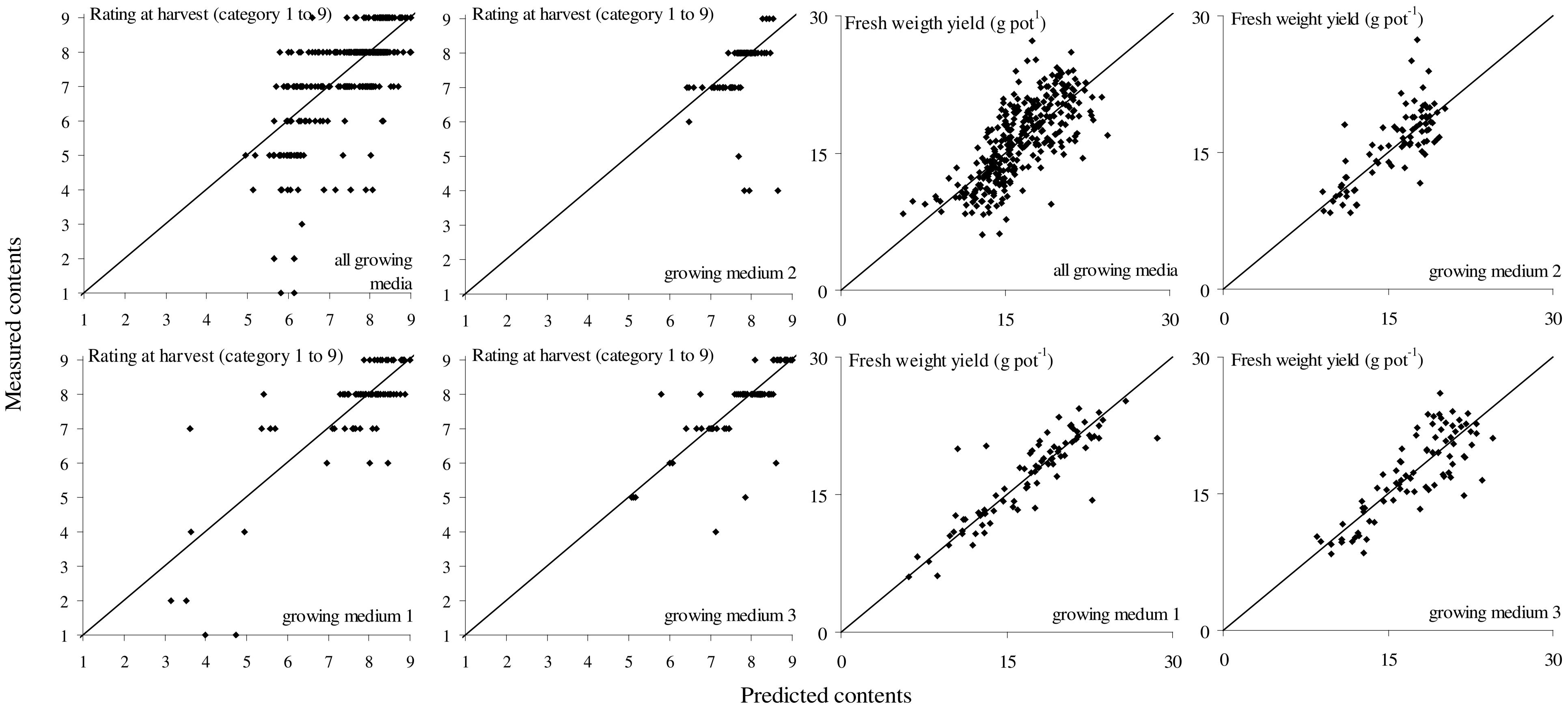

Figure 8.2.3: Measured against predicted values for the test results of Chinese white cabbage. Displayed are fresh weight yield and rating at harvest (at harvest of Chinese white cabbage all plants, on a pots basis, were graded according to their overall impression: rating category one represented the worst and rating category nine the best overall impression). The results for all samples and separated for each growing medium are displayed for the samples, which were mearued fresh as received. The lines indicate 1:1.

Overall, our results suggested that predictions of chemical characteristic of growing media may be done using samples, which were fresh as received. The only constituent, where drying and grinding gave considerably better results was pH, but both treatments had RSC values which were well above two.

Chinese white cabbage test

For the entire population of growing media, the prediction of fresh weight yield was satisfactory regarding the RSC (1.4) but not regarding the correlation coefficient (r = 0.7, Table 8.2.2, Figure 8.2.3). Better predictions for the fresh weight yield were obtained by separating the growing media by their origin. Fresh weight yield were predicted well for GM-1 (Table 8.2.2, Figure 8.2.3). The RSC was 2.0. We explained more than three-quarter ($r^2 = 0.77$) of the variation in fresh weight yield with the spectral information of GM-1 (Table 8.2.2). The RSC was 1.6 and 1.9 for GM-2 and GM-3, respectively, and thus the predictions were satisfactory, since also (r) was equal to 0.8 for both subpopulations. The better performance of NIRS for the subpopulations is not surprising, since it is known that different peat origins are spectrally not equal. For instance, Mira (1992) identified different peat classes with the spectral information of satellite data. The good prediction performance for GM-1 (in contrast to the satisfactory one for GM-2 and GM-3) may be explained as follows: GM-1 had the lowest degree of humification and hence a lower content of humic substances. This resulted in a lower molecular complexity and less interacting functional groups. Less functional groups may decrease the noise in the spectra and thus may improve the accuracy of predictions.

Rating at harvest was predicted satisfactorily regarding the RSC, but unsatisfactorily regarding (r) for the entire population (Table 8.2.2). The accuracy of predictions of rating at harvest may have been enhanced, if the ratings were more evenly distributed over a wide range (i.e. more values of three and lower). Nevertheless, rating at harvest was predicted satisfactorily for GM-1 and GM-3 (for both RSC = 1.7 and r = 0.8) (Table 8.2.2, Figure 8.2.3).

Overall, NIRS predictions of the plant assay using Chinese white cabbage were generally better for samples, which were fresh as received, than for dried and ground ones. One explanation is that peat shrinks during drying. This process changes its properties,

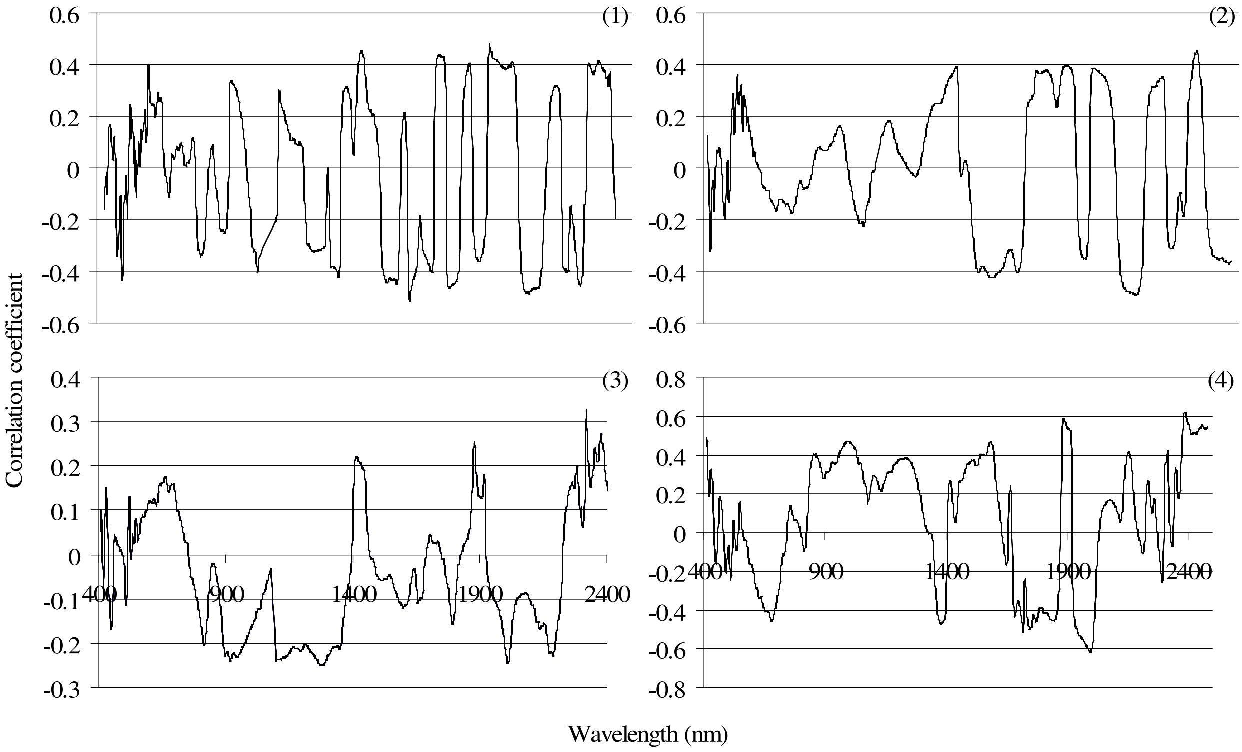

Figure 8.2.4: Correlations of samples, which were fresh as received, for all wavelengths with (1) fresh weight yield and (2) rating at harvest for a growing medium with a degree of humification of H-2 to H-3 and contents of (3) nitrate and (4) salt for all growing media with a range of degrees of humifications from H-2 to H-7. Spectra were manipulated with SNV and „detrend“ and the mathematical treatments are given in Table 8.2.2.

namely increasing the hydrophobic characteristics (Michel et al., 2001). The better performance for samples, which were fresh as received, than for dried and ground samples is not surprising, because the sample number in our study was high enough to compensate for the possible negative particle size effect of samples, which were fresh as received (Slaughter et al., 2001).

8.2.3 Conclusions

Near-infrared spectroscopy was well suited to characterize growing media chemically. Moreover, NIRS showed a marked potential to predict the fresh weight yield of Chinese white cabbage for all three sub-populations of differing origins.

9 Synthesis and conclusions

9.1 Synthesis

Objectives were to evaluate if NIRS is able to predict a large set of chemical, biological and yield characteristics for soils, litter and growing media.

Different sizes of sample sets were used, which ranged from 30 to 432 samples. The soil and litter sets were undisturbed samples originating from forest and arable sites on the one hand and, on the other hand, mixtures of carbon and nitrogen free arable soils and of different coal types and material of a forest Oa layer. The soil and litter properties covered a wide range: the C content ranged from 0.05 to 47 %, the N content from 0 to 2.3 % and the content of C_{mic} from 76 to 5070 µg g^{-1} soil. The sample sets of growing media were based on different white and black peats, which were either self-heated or passive-heated. The degree of humification (on the von Post scale) ranged from H-2 to H-7, the pH from 2.8 to 5.7 and the mineral nitrogen content from 9 to 500 mg L^{-1}. The samples investigated represented the range of commonly observed values. Thus, the conclusions drawn from the results are of practical relevance.

Spectra of the samples were recorded in the VIS-NIR region (400 – 2500 nm). The spectra were transformed and fitted to the reference values. Finally, a linear regression of measured against predicted values was computed in order to assess the quality of predictions with NIRS. Good predictions were performed when the RSC (the ratio of standard deviation of laboratory results to standard error of cross-validation) was higher than 2.0 and the correlation coefficient (r) and the regression coefficient (a) of a linear regression of measured against predicted values were greater or equal to 0.9 and in the range from 0.9 to 1.1, respectively. Satisfactory results were obtained for $1.4 \leq RSC \leq 2.0$, $r \geq 0.8$ and $0.8 \leq a \leq 1.2$. Predictions were not satisfactory when $RSC < 1.4$.

The samples were recorded at different sample states. The samples were recorded either (A) field-moist, (B) dried at 60 °C and ground or (C) quick-frozen, freeze-dried and ground. The different sample states were used to explore the impact of particle size, water content and pre-treatment method on the prediction quality of NIRS. The best sample pre-treatment method for each constituent and type of sample is given in Tab. 9.1.1.

Table 9.1.1: Best sample pre-treatment method for good predictions of chemical and biological characteristics. A second pre-treatment method is given, when the predictions were of comparable accuracy.

Constituent	**Type of sample**	**Best method[1]**	**Comparable method[1]**	**No. table**
C_t content[2]	Growing medium	A	B	8.2.2
C_{org} content[3]	Soil	A	C	6.2.3
N_t content[2]	Growing medium	A	B	8.2.2
N_t content[3]	Soil	A	C	6.2.3
pH value[2]	Growing medium	B	A	8.2.2
pH value[3]	Soil	C	-	6.2.3
Salt content[2]	Growing medium	A	B	8.2.2
P content[2]	Growing medium	A	B	8.2.2
P content[3]	Soil	C	A	6.2.3
K content[2]	Growing medium	A	B	8.2.2
Mg content[3]	Soil	C	A	6.2.3
Lignin content[4]	Soil	B	-	4.2.1
NO_3^--content[2]	Growing medium	A	-	8.2.2
NH_4^+ content[2]	Growing medium	A	B	8.2.2
NMR characteristics[4]	Soil	B	-	4.2.1
C_{mic} content[3]	Soil	A	C	6.2.4
N_{mic} content[3]	Soil	A	C	6.2.4
P_{mic} content[3]	Soil	A	C	6.2.4
Ergosterol content[3]	Soil	C	A	6.2.4
Basal respiration[3]	Soil	A	C	6.2.4

[1] A = field-moist/ fresh as received, B = dried (60 °C) and ground and C = quick-frozen, freeze-dried and ground.

[2] The sample pre-treatment methods A and B were tested.

[3] The sample pre-treatment methods A and C were tested.

[4] The sample pre-treatment methods B was tested.

Wavelengths with the highest correlation coefficients were assigned to each constituent in order to verify the predictions by known absorption bands. Direct relations of assigned wavelengths with absorbing compounds are possible for constituents with a concentration above the detection limit of NIRS. It ranges approximately between 0.1 and 1 %. Constituents with a concentration below the detection limit or constituents which absorb not in the near-infrared region have assigned wavelengths based on indirect correlations.

Chemical characteristics of soils, litter and growing media

The following constituents had a concentration above the detection limit of NIRS:

- The composition of carbon, determined with nuclear-magnetic-resonance spectroscopy, was predicted well for the constituents with the highest proportion of organic C in soil and litter, which were alkyl and O-alkyl C. Drying and grinding was a proper method for pre-treatment. Assigned wavelengths were between 2200 and 2300 nm, which are related to alkyl C. Carbonyl and aromatic C were predicted satisfactorily. Lignin content, determined with the CuO oxidation method, was predicted well. Phenolic compounds seem to have a higher absorptivity in the near-infrared region than aromatic compounds, which may be explained by the weak acid reaction of phenols.
- Contents of organic C, total N and C and N derived from different coals and forest Oa material were predicted well by NIRS for all samples. All sample states (field moist, dried and ground and quick-frozen, freeze-dried and ground) gave good results. This proves the robustness of the predictions. Assigned wavelengths for organic C predictions were the wavelengths around 1400 and 2300 nm, which are related to alkyl C. Assigned wavelengths for the prediction of total N were around 1500 nm and in the range from 1900 to 2200 nm. Absorbing compounds are amino and amid groups.

The following chemical characteristics have concentrations that are below the detection limit:

- The pH value was predicted well for all sample states for soils, peats and growing media. Slightly better predictions were made for dried and ground samples. Generally, pH was predicted better for growing media than for soils. This may be explained by the wider range of pH and by the fact that humic substances, which are present in growing media at a higher percentage, are highly reactive substances and thus spectrally active.

- The contents of P and K in soils and growing media were predicted well, except for the K content in soils, which was predicted satisfactorily. All sample states were proper pre-treatments.
- Contents of NO_3^-, NH_4^+ and salt, which are very important features for plant growth and yield, were predicted well for growing media and equally well for samples, which were fresh as received and dried and ground. This is in respect to the prediction of salt contents astonishing. Salt is normally predicted by its impact on the position of the -OH absorption peaks related to water. An explanation might be that drying at 60 °C removes the hygroscopic water incompletely. The prediction of NO_3^- in soils was not carried out in this investigation, but other researchers made successful predictions using soil pastes.

Moreover, it was shown that samples with very different spectral properties lowered the prediction qualities of the sample set. This was the case for the wide range of humification degrees of growing media and the wide range of parent materials from soils.

Biological characteristics of soils

- Contents of microbial biomass C, N, P and fungal ergosterol were predicted well from NIRS and similarly well for field-moist and for quick-frozen, freeze-dried and ground soil samples. In contrast, predictions of microbial biomass C were unsatisfactory for dried samples (60 °C). Drying by heat seems to change sample properties in respect to microbial measurements. The good predictions were based on indirect correlations to contents of organic C and total N, but the predictions were much better than the correlations (e.g. the correlation of C_{mic} and C_{org}).
- Ratios of microbial biomass C, N, P and fungal ergosterol were predicted with varying accuracy. Calculations from the predicted values, instead of predicting the ratio directly, did not improve the accuracy. This may be due to the smaller error propagation of predictions in comparison to calculations. Moreover, indirect

correlations have only a small impact on the prediction of ratios, because ratios have no substantial equivalence in the sample.

- Mineralisation rates of carbon (basal respiration) and nitrogen, which are a function of the amount and activity of microbial biomass and the substrate quality, were predicted well and unsatisfactorily, respectively. Predictions of basal respiration are probably better due to the following reasons: carbon content in soils is higher than nitrogen content. Moreover, carbon release is direct, whereas nitrogen is released as a result of carbon degradation and quality. Field-moist samples were slightly better for the prediction of the basal respiration. Other investigations showed for air-dried samples satisfactory predictions of the N mineralisation rate. The slow drying may cause enhanced mineralisation and nitrification processes, which are related to the mineralisation rate of nitrogen. Accumulated nitrate can be determined with NIRS as shown for dried growing media. The accuracy of the reference method for the nitrogen mineralisation rate must be taken cautiously. This could be as well the reason for the bad predictions.

The sample pre-treatment method using quick-freezing, freeze-drying and grinding is a proper method for soils to obtain for susceptible constituents, e.g. ergosterol content, comparable results to field-moist measured samples. Using this method enables one to obtain reliable predictions for biological characteristics especially for large sample sets. Storage of field-moist samples under unfavourable conditions, which can influence susceptible constituents negatively, can be avoided.

Yield characteristics of soils and growing media

Using solely the spectral information of soils and growing media without the additional spectral information of the leaves from the actual growing plants is a promising approach for the prediction of yield characteristics. They are a complex mixture of spectrally detectable chemical and biological characteristics of soil. Moreover they can be influenced strongly by crop management, climatic conditions, pests or phytotoxic properties.

On the one hand, predictions with NIRS are only valid for the investigated conditions. On the other hand, the information of all chemical and biological characteristics and its mutual interactions are present in the recorded spectra. This cumulated information seems to compensate at least partly for the unknown information in order to carry out yield predictions.

9.2 Conclusions

Near-infrared spectroscopy was able to predict contents and properties of chemical and biological features of soils, litter and growing media successfully. Moreover, estimates of grain yield for soils and fresh weight yield and grade of phytotoxicity for growing media were promising.

It was shown that a sample set consisting of 50 samples was sufficiently large to yield good results in regard to the statistical quality indices used. Nevertheless, 100 samples and more may give more accurate results. The selection of samples for the calibration has to be done cautiously in order to obtain a sample set with a high but not overly high spectral variability, which covers the range of later predictions. Moreover, an even distribution of the measured contents is important to avoid separated dot clouds in the linear regression. This can lead to the overestimation of the correlation coefficient for sub-populations.

The sample state for NIRS measurements is important for some constituents. Constituents with contents above the detection limit of NIRS can be predicted well in each sample state tested. Drying (at maximum 60 °C) and grinding, which is the most convenient pre-treating method for the conduction of NIRS measurements, can be suggested as a standard procedure. In contrast, the sample state is more important for constituents below the detection limit. The following suggesstions can be derived from the research (Tab. 9.1.1):

- Contents of P, K and Mg can be measured either with field-moist or dried soils and growing media.
- The pH value should be measured with dried soils and growing media.

- The contents of NO_3^-, NH_4^+ and salt in growing media are predicted better for samples, which were measured fresh as received.
- Microbial measurements should be done with field-moist soil samples. When the samples can only be stored under unfavourable conditions or over longer periods, the pre-treating method consisting of quick-freezing, freeze-drying and grinding is recommendable.
- Predictions of yield characteristics are not yet fully understood and thus recommendations about the optimal sample pre-treatment are not given.

The assignment of absorbing wavelengths to constituents can only strengthen the predictions of constituents with contents above the detection limit. For the remaining constituents this is only a tool for detection and affirmation of the underlying correlations.

10 Summary

Many challenges are present in agricultural and horticultural sciences, which call for the availability of fast, reliable and cheap measuring methods. The objectives of this research were to evaluate the usefulness of near-infrared spectroscopy (NIRS) for predicting (i) the characteristics of litter and soils determined with nuclear-magnetic-resonance spectroscopy, (ii) contents of carbon and nitrogen derived from different kind of coals in soils, (iii) soil chemical, biological and yield characteristics and (iv) to predict chemical characteristics, plant assay results, phytotoxicity and self-heating for growing media. Spectra of the VIS-NIR region (400 - 2500 nm) from (i) soil and litter samples from agricultural and forest sites (n = 56), (ii) mixtures of carbon-free soil, coal (lignite, anthracite, charcoal or a mixture of the three coals) and forest floor Oa material (n = 432), (iii) soil samples from organically managed farms (n = 56) and (iv) two populations of peats and growing media, consisting of one population of phytotoxic and non-phytotoxic peats (n = 73) and one population of various growing media with a great range of humification degrees and quality (n = 320) were recorded from samples, which were fresh as received, or pre-treated. A modified-partial-least-squares regression method and cross-validation were used to develop equations over the whole spectrum (1st to 3rd derivation). These equations served for predicting chemical and biological contents and properties and the yield characteristics of various soils and growing media.

(i) Near-infrared spectroscopy predicted for dried samples (60 °C) the percentages of O-alkyl C and alkyl C and the ratio of alkyl C to O-alkyl C well. The ratio of standard deviation of the laboratory results to standard error of cross validation (RSC) was greater than 2, the correlation coefficients (r) of a linear regression (measured against predicted values) were greater than 0.9 and the regression coefficients (a) ranged from 0.9 to 1.1. The percentages of carbonyl C and aromatic C and the ratio of alkyl C to aromatic C were assessed satisfactorily ($0.8 \leq a \leq 1.2$, $r \geq 0.8$ and $1.4 \leq RSC \leq 2.0$).

(ii) All properties investigated (total C (C_t) and N (N_t), C and N derived from coal or Oa material, respectively) were successfully predicted for dried samples (60 °C) by NIRS: the RSC ranged from 4.3 (N derived from coal) to 9.1 (C_t), (r) was close to 1.0 and (a) was between 1.0 and 1.1. Near-infrared spectroscopy was able to differentiate between the different coals as well. This was probably attributable to structural differences as suggested by wavelength assignment.

(iii) The soil chemical characteristics pH ($CaCl_2$), contents of organic carbon (C_{org}), N_t and extractable P (Olsen), P (CAL), and Mg ($CaCl_2$) and C_{org}/N_t ratio were predicted well. The predictions were better for pre-treated (quick-freezing, freeze-drying and grinding) samples than for field-moist ones. The RSC ranged between 2.5 (pH) and 4.1 (Mg), (r) between 0.9 and 1.0, and (a) between 1.0 and 1.1. Potassium content (CAL) was predicted satisfactorily. Predictions with NIRS of biological characteristics were slightly better for field-moist samples than for pre-treated. Exceptions were content of ergosterol and the ergosterol/microbial biomass C (C_{mic}) ratio. Basal respiration, contents of C_{mic}, microbial biomass N (N_{mic}), microbial biomass P (P_{mic}) and ergosterol/C_{mic} ratio were predicted well. The RSC was between 2.0 (ergosterol/C_{mic}) and 4.6 (ergosterol), (r) between 0.9 (P_{mic}) and 1.0 (C_{mic}) and (a) between 0.9 and 1.1. Predictions of C_{mic} from dried samples (60 °C) were not satisfactory (RSC = 1.1, r = 0.8 and a =1.0). The ratio of C_{mic}/N_{mic} and the metabolic quotient were predicted satisfactorily. Nitrogen mineralisation rate, the ratios of C_{mic}/P_{mic} and of basal respiration/nitrogen mineralisation rate could not be predicted satisfactorily (RSC < 1.4). Predictions of grain yield of winter cereals and grain nitrogen uptake were well for pre-treated samples (RSC = 2.4 and r = 1.0 and RSC = 2.7 and r = 0.9, respectively). Grain nitrogen content was predicted for both sample states satisfactorily.

(iv) Near-infrared spectroscopy predicted the chemical characteristics of growing media and the yields of fresh weight of Chinese white cabbage and rating at harvest (overall plant impression) better for samples, which were fresh as received, than for dried (60 °C) and ground ones. The pH and contents of C_t and N_t, salt, P, K, mineral nitrogen, NO_3^-, NH_4^+ and the $NH_4^+ : NO_3^-$ ratio were predicted well: the RSC ranged between 2.0 (NO_3^-) and 4.4 (C_t), (r) was equal to or higher than 0.9 and (a) was between 0.9 and 1.1. Fresh weight yield of Chinese white cabbage was predicted well for the sub-population of the growing medium with a degree of humification of H-2 to H-3 on the von Post humification scale (RSC = 2.0, r = 0.9 and a = 0.9). The fresh weight yields for the remaining subpopulations (H-5 to H-6 and H-7) were predicted satisfactorily (RSC =1.6 and 1.8, respectively). The prediction of the rating at harvest was satisfactory for two subpopulations (RSC =1.7, r = 0.8 and a = 0.9 to 1.0) but unsatisfactory for the one with H-5 to H-6 (RSC = 1.3). However, investigating a less diverse subpopulation of 38 samples, which were all from the same origin, showed a satisfactory prediction accuracy for the grade of phytotoxicity of samples, which were fresh as received (RSC = 1.5).

Near-infrared spectroscopy has shown its potential and proved its usefulness for the prediction of the contents and the properties of a wide range of constituents in agricultural and horticultural sciences. The state of the sample for NIRS measurements played a crucial role for the prediction quality. Thus, the state of the sample has to be chosen carefully. Further research should be done in the area of the turnover of soil organic matter in order to combine the strengths of soil analysis by NIRS with the predictions on turnover times of different carbon pools derived from mathematical models.

11 Zusammenfassung

Es gibt in den landwirtschaftlichen und gartenbaulichen Bodenwissenschaften eine große Menge offener Herausforderungen. Zu ihrer Lösung bedarf es der Verfügbarkeit von schnellen, verlässlichen und vor allem preiswerten Messmethoden. Ziele dieser Untersuchung waren, die Verlässlichkeit der Nahinfrarot-Spektroskopie (NIRS) anhand der Vorhersage folgender Messgrößen zu überprüfen: (i) die Eigenschaften von Streu und Böden, die mit der magnetischen Kernresonanz-Spektroskopie bestimmt werden, (ii) die kohlebürtigen Gehalte an Kohlenstoff und Stickstoff in Böden, (iii) die bodenchemischen und bodenbiologischen Eigenschaften und die Ertragseigenschaften von Böden und (iv) die chemische Charakterisierung von torfbasierten Kultursubstraten, die Ergebnisse von Pflanzentests und den Grad der Phytotoxizität.

Spektren im Wellenlängenbereich des Sichtbaren und des Nahinfrarot (VIS-NIR, 400 – 2500 nm) wurden zur Bearbeitung der genannten Ziele für folgende Proben aufgenommen: (i) Boden- und Streuproben von landwirtschaftlich und forstwirtschaftlich genutzten Flächen (n = 56), (ii) künstliche Mischungen aus ausgeglühten, kohlenstofffreien Böden mit verschiedenen Kohlen (Braunkohle, Steinkohle, Holzkohle und einer Mischung daraus) und einer organischen Oh Waldauflage (n = 432), (iii) Bodenproben von Biobetrieben (n = 56) und (iv) zwei Kollektive bestehend aus Torfen und Kultursubstraten, von denen ein Kollektiv aus phytotoxischen und nicht phytotoxischen Torfen bestand (n = 73) und das andere Kollektiv eine Zusammenstellung von Kultursubstraten unterschiedlichen Humifizierungsgrades war (n = 320). Die Spektren wurden sowohl von feldfeuchten als auch von vorbehandelten Proben aufgenommen. Eine Modifizierte-Kleinste-Quadrate-Methode, Kreuzvalidierung und Spektrentransformation auf Basis der ersten bis dritten Ableitung wurden eingesetzt, um mathematische Gleichungen zu erstellen. Diese mathematischen Gleichungen bezogen das gesamte Spektrum mit ein und dienten als Grundlage für die Vorhersage chemischer und biologischer Gehalte und Eigenschaften und der Ertragseigenschaften von Böden und Kultursubstraten.

(i) Die Nahinfrarot-Spektroskopie machte für getrocknete Streu- und Bodenproben gute Vorhersagen für den Prozentsatz an O-Alkyl C und Alkyl C und für das Verhältnis von Alkyl C zu O-Alkyl C. Der RSC, der aus dem Verhältnis der Standardabweichung der Laborergebnisse und dem Standardfehler der Kreuzvalidierung berechnet wird, wurde als Güteparameter der Vorhersage eingesetzt. Er war größer als 2. Darüber hinaus waren der Korrelationskoeffizient (r) und der Regressionskoeffizient (a) einer linearen Regression von gemessenen gegen vorhergesagten Werten größer als 0,9 bzw. im Bereich zwischen 0,9 und 1,1. Der Prozentsatz von Carbonyl C und aromatisch gebundenem C und das Verhältnis von Alkyl C zu aromatischem C wurde befriedigend durch NIRS vorhergesagt ($0{,}8 \leq a \leq 1{,}2$, $r \geq 0{,}8$ and $1{,}4 \leq \mathrm{RSC} \leq 2{,}0$).

(ii) Alle Eigenschaften der Mischungen, bestehend aus ausgeglühten Böden, Kohlen und Oh-Auflage, wurden gut mit NIRS vorhergesagt. Das waren die Gehalte an Gesamtkohlenstoff und -stickstoff und die jeweiligen Anteile des Kohlenstoffs und Stickstoffs, die aus Kohle und der Oh-Auflage stammten. Der RSC lag im Bereich von 4,3 (aus Kohle stammender Stickstoff) bis 9,1 (Gesamtkohlenstoff), (r) war nahe bei 1,0 und (a) lag zwischen 1,0 und 1,1. Darüber hinaus war NIRS auch noch in der Lage zwischen dem Kohlenstoff, der aus den verschiedenen Kohlen stammte, zu unterscheiden. Das war wahrscheinlich auf die strukturellen Unterschiede zurückzuführen, die durch die Identifikation der wichtigsten Wellenlängen zu Tage gebracht wurden.

(iii) Mit Hilfe der Nahinfrarot-Spektroskopie wurden die bodenchemischen Messgrößen pH ($CaCl_2$), die Gehalte an organischem Kohlenstoff (C_{org}), Gesamtstickstoff (N_t) und die austauschbaren Gehalte an P (Olsen), P (CAL) und Mg ($CaCl_2$) und das Verhältnis bestehend aus C_{org} und N_t der Biobetriebe gut vorhergesagt. Die Vorhersagen waren besser für vorbehandelte als für feldfeuchte Proben. Die Vorbehandlungsmethode bestand aus Schockgefrierung, Gefriertrocknung und anschließendem Vermahlen der Proben. Der RSC lag zwischen 2,5 (pH) und 4,1 (Mg), (r) zwischen 0,9 und 1,0 und (a) zwischen 1,0 und 1,1. Der Gehalt an Kalium (CAL) wurde befriedigend vorhergesagt. Die Vorhersagen der biologischen Messgrößen waren etwas besser für die feldfeuchten als für die vorbehandelten Proben. Die einzigen Ausnahmen waren der Ergosterolgehalt und das Verhältnis von Ergosterolgehalt zu mikrobieller Biomasse C (C_{mik}). Die Basalatmung, die Gehalte an C_{mik}, mickrobieller Biomasse N und P (N_{mik} und P_{mik}) und das Verhältnis von Ergosterolgehalt zu C_{mik} wurden gut vorhergesagt. Der RSC lag zwischen 2,0 (Verhältnis von Ergosterolgehalt zu C_{mik}) und 4,6 (Ergosterolgehalt), (r) zwischen 0,9 (P_{mik}) und 1,0 (C_{mik}) und (a) zwischen 0,9 und 1,1. Der C_{mik}-Gehalt wurde für getrocknete Böden (60 °C) nur unbefriedigend vorhergesagt (RSC = 1,1, r = 0,8 und a = 1,0). Das Verhältnis von C_{mik} und N_{mik} und der metabolische Quotient wurden befriedigend vorhergesagt. Die Stickstoffmineralisationsrate und die Verhältnisse von C_{mik} zu P_{mik} und der Basalatmung zu der Stickstoffmineralisationsrate konnten nur unbefriedigend vorhergesagt werden (RSC < 1,4). Die Vorhersagen der Kornerträge von verschiedenen Wintergetreidearten und dem Stickstoffentzug durch die Körner waren für vorbehandelte Proben gut (RSC = 2,4 und r = 1,0 bzw. RSC = 2,7 und r = 0,9). Die Vorhersage des Stickstoffgehaltes in den Körnern war für feldfeuchte und vorbehandelte Proben gleichermaßen befriedigend.

(iv)Die Nahinfrarot-Spektroskopie konnte die untersuchten Eigenschaften von Kultursubstraten besser für feuchte als für getrocknete (60 °C) Proben vorhersagen. Der pH-Wert und die Gehalte an Gesamtkohlenstoff und -stickstoff, Salz, P, K, mineralischem Stickstoff, NO_3^-, NH_4^+ und dem Verhältnis von NH_4^+ zu NO_3^- wurden gut vorhergesagt. Der RSC lag zwischen 2,0 (NO_3^-) und 4,4 (Gesamtkohlenstoff), (r) war gleich groß oder größer als 0,9 und (a) lag im Bereich von 0,9 bis 1,1. Der Frischmasseertrag von Chinakohl wurde für die Unterpopulation eines Weißtorfes, der den Humifizierungsgrad H-2 bis H-3 besaß (nach der von Post Humifizierungsskala), gut vorhergesagt (RSC = 2,0 , r = 0,9 und a = 0,9). Der Frischmasseertrag wurde für die beiden anderen Unterpopulation, die die Humifizierungsgrade H-5 bis H-6 bzw. H-7 besaßen, befriedigend vorhergesagt (RSC = 1,6 bzw. 1,8). Die Vorhersage der Bonitur zur Ernte, für die der gesamte Pflanzeneindruck auf einer Skala von eins bis neun eingeordnet wurde, war etwas schwächer als die des Frischmasseertrages. Die Bonitur war befriedigend für zwei Unterpopulationen (RSC = 1,7, r = 0,8 und a =

0,9 -1,0). Die Unterpopulation mit dem Humifizierungsgrad H-5 bis H-6 konnte nur unbefriedigend vorhergesagt werden (RSC = 1,3). Der Grad der Phytotoxizität konnte für eine homogene Unterpopulation von 38 Proben befriedigend für frische Proben vorhergesagt werden (RSC = 1,5).

Die Nahinfrarot-Spektroskopie hat ihr Potential bestätigt und gezeigt, das sie die Gehalte und Eigenschaften einer großen Anzahl von Konstituenten aus den landwirtschaftlichen und gartenbaulichen Bodenwissenschaften bestimmen kann. Die Probenvorbehandlung der NIRS-Messung hatte einen fundamentalen Einfluss auf die Güte der Vorhersage. Deshalb sollte die Probenaufbereitung sorgfältig in Abhängigkeit von der Fragestellung ausgewählt werden. Es besteht darüber hinaus Forschungsbedarf in der Beschreibung des Umsatzes der organischen Bodensubstanz. Auf diesem Gebiet können die Stärken der NIRS-Analyse bei der Bestimmung unterschiedlich schnell umsetzbarer Kohlenstoffpools im Boden mit der Bestimmung der Umsatzzeiten durch Modellierung zusammengeführt werden.

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