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Review

Application of Near Infrared Spectroscopy for Analysis of Soils, Litter and Plant Materials

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Abstract

Environmental studies often require analyses of numerous chemical, physical and biological properties in large numbers of soil, litter and plant samples. Such analyses may be expensive and time consuming and therefore rapid and cost-effective methods may be required. Near infrared spectroscopy (NIRS) is a non-destructive analytical method known for rapidity, simplicity and low costs, which could be used along with classical analytical methods in order to improve efficiency of large-scale environmental research. In this review, principals of NIRS are described, examples of NIRS applications are presented and the possibilities and limitations of the method are discussed.

Keywords: near infrared spectroscopy, soil, sediments, plant materials

Introduction

Environmental studies often require analysis of various attributes (concentrations of elements, compounds or process rates) in large numbers of samples. Classical analytical methods are often time consuming, expensive, require well-trained laboratory personnel and the use of sophisticated equipment. Therefore, a good alternative for complex classical methods is the use of indirect, less complex methods that enable processing of large sample sets.

Near infrared spectroscopy (NIRS) is a method that could be used for analysis of soils, litter and plant materials in environmental studies where large numbers of samples must be processed. NIRS is a well-known analytical technique and has been adopted by the food industry and agriculture for several decades [1]. The method has been applied to measure protein, moisture, ash, starch, water absorption and several other properties in forage and animal feeds [2, 3]. Since the early 1990s NIRS has been used as a certified method to measure moisture, crude protein and acid detergent fiber in forages [4]. For several years NIRS has also been tested for usefulness to analyze several attributes of soils, sediments and other biological materials (plant tissues, litter, composts etc.). The results of these tests have been extensively reviewed by Malley et al. [5]. However, these authors have stated that the method still remains unpopular in soil science and is rarely used in research and commercial laboratories. One of the reasons why NIRS is not widely used may be the fact that the method is unknown to a considerable part of the soil and environmental science community.

This work presents principals of NIRS, its various applications in environmental studies with particular emphasis on soil and litter analysis, and critically reviews the advantages and limitations of this method. The aim is to stimulate interest in NIRS among soil scientists and environmentalists. Detailed descriptions of NIRS methodologies, which might be of interest to experienced users of the technique, is of less concern. In order to keep this paper of reasonable length, numerous articles dealing with NIRS application for soil analysis have not been cited.

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Readers interested in more detailed information on various aspects of NIRS application in soil analysis should refer to the review by Malley et al. [5] and those interested in theory of calibration to eg. Martens and Næs [6] or Næs et al. [7].

Principle of the Method

NIRS utilizes wavelengths between 750 and 2500 nm, but this range is often extended to 400-2500 nm. Near infrared radiation is absorbed by different chemical bonds such as O-H, C-H, N-H, S-H and C=O. Absorption of NIR radiation results in bending, stretching, twisting and scissoring of the bonds [8, 9].

The amount of NIR radiation that is absorbed is determined by the nature and number of bonds present in the analyzed material. Hence, NIR spectra contain detailed information on the chemical composition of that material [10].

The NIR spectra do not contain sharp and distinct peaks because they consist of overtones and combinations from primary absorption in the mid-infrared region. These overtones are anharmonic and impede interpretation of NIR spectra [8]. Since a direct interpretation of NIR spectra of complex mixtures is extremely difficult, the application of NIRS for analysis of environmental materials requires a calibration procedure using sophisticated statistical techniques [10].

Sample Preparation Requirements

The NIR spectra depend not only on chemical characteristics of the analyzed material but also on its moisture (due to strong absorption of water molecules at 1450 nm and 1930 nm) and particle size [10, 11]. Therefore, in order to ensure reliable NIR measurements samples need to be dried carefully and ground to a consistent particle size. The latter can be achieved by using laboratory grinders with the same grinding performance.

Calibration and Validation Procedures

The most essential step in the calibration procedure is the selection of a proper sample set (Fig. 1). The calibration sample set should cover the entire range of spectral variation in the whole population for which the calibration is being carried out. Spectra that differ significantly from the average spectrum should be rejected from the calibration set as outliers. To identify outlier samples to be rejected, the entire population is ranked in terms of Mahalanobis distance from the average spectrum. There are numerous methods of selecting samples to be rejected, the CENTER algorithm [12] being the most popular. Usually it is much easier to achieve large spectral data sets, whereas obtaining the reference data may be more time consuming. In order to minimize the size of calibration sample set, and thus the amount of necessary reference analyses, the samples in which spectra are very similar may be rejected. Removal of spectrally similar samples is based on the assumption that only one sample is required to represent all samples in its neighbourhood [12]. A SELECT algorithm, based on the matrix of Mahalanobis distances between all pairs of spectra, can be used to identify neighbouring samples [12].

The samples selected for calibration should cover not only the entire spectral variation of the analyzed population but also the entire variability of the components or characteristics for which the calibration is carried out. Therefore, sometimes it is necessary to expand the calibration set by the samples not included in the calibration set chosen according to the CENTER and SELECT algorithms.

Calibration procedure relies on developing a regression equation between the absorbance spectra and the components or characteristics of interest. The most commonly used regression procedures include multiple linear regression (MLR), principal component regression (PCR), partial least square regression (PLS) and modified PLS regression (mPLS). The two latter methods are considered more powerful since – unlike the MLR – they use the entire spectral information. The other available approaches involve neural networks and wavelet theory [10]. Prior to the calibration the spectra should be corrected for a scatter by any available methods (e.g. Detrend and Standard Normal Variate or Multiplicative Scatter Correction). For development of calibration equations several mathematical treatments of spectra are usually used. These include taking derivatives of 1st to 3rd order, defining the segment length over which the derivative is to be calculated and smoothing the spectra.

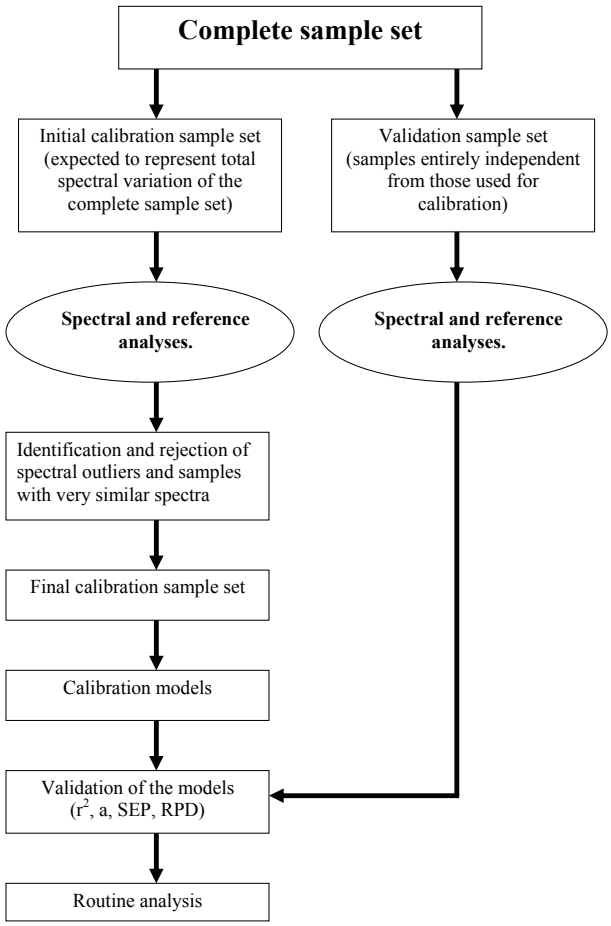

Fig. 1. A scheme of NIRS application.

Since there is no single "best" treatment for all variables and all sample types, usually the only way to optimize the mathematical treatment is to follow a trial and error procedure [13-15]. In order to avoid overfitting, when using PCR, PLS or mPLS methods for model development, a procedure called cross-validation should be used. The cross-validation approach enables us to determine an optimal number of terms or principal components to be included in the model. The calibration sample set is divided into several groups and a prediction is made for one group based on calibration equation developed from the remaining groups. This procedure is repeated until all groups are used for validation once. The residuals of the predictions are then pooled to calculate the standard error of cross-validation (SECV). The best model should have the smallest SECV. Although cross validation may help in selecting the number of PC or PLS components it should not be used blindly. Further statistical tests should be applied to assess performance and relevance of the developed models and to detect irregularities in the data (eg. outliers) that may harm developed regressions. Detailed descriptions of calibration procedures are given in Næs et al. [7] and Wold et al. [16].

Quality of the developed calibration equations is assessed in the validation stage (Fig. 1). The validation sample set includes the samples for which the reference data were measured using classical methods. During validation the NIRS predicted values are regressed against the reference values. The quality criteria include correlation coefficient (r^2) and regression coefficient (a) of linear regression measured against NIRS predicted values and standard error of prediction (SEP). SEP is calculated according to the equation:

$$SEP=[\Sigma_{i=1...n} (y_i-x_i)^2(n-1)^{-1}]^{0.5}$$

...where n is the number of samples, y_i is the mean value of a constituent in sample *i* derived by the reference method, and x_i is the NIRS predicted mean value for the sample *i*.

The other commonly used quality parameters include ratio of standard deviation (SD) of the laboratory results to SEP (RPD) [17] and the ratio of standard error of calibration (SEC) to SD [15]. The use of RPD and SEC to SD ratio enables us to compare the accuracy of the models for constituents that are measured in different units.

Proper validation is a prerequisite for using the developed calibration models in routine analysis. It is essential to use for validating entirely independent samples, otherwise predictive accuracy of the developed models may be overestimated [18]. Furthermore, validation should simulate the intended model application. For instance, in regional models, randomly selected, independent, hold-out sites should be used for validation.

When the number of available samples is too restrictive to carry out calibration and independent validation, the results of cross-validation may be used to assess the quality of calibration equations [19]. In cross-validation the quality criteria include SECV, values of r^2 (reference vs NIRS predicted values), bias (mean of the NIRS predicted value less the mean of reference values), and the SD to SECV ratio (referred to as RPD or RSC) or standard error of calibration (SEC) to SD ratio [15].

Relationships between Wavelengths and Chemical Structures

Linking particular NIR wavelengths to well-defined compounds is an extremely difficult task. Due to the broadband nature of NIR spectra, consisting of overlapping peaks, the individual chemical structures are not well resolved. Numerous constituents of analyzed materials absorb within the entire NIR region and the spectral information is repeated through successive overtones and combinations [2]. Despite these difficulties, there were some efforts to find absorptions characteristic for certain compounds [20-22]. Elvidge [20] analyzed the spectra of various plant materials and reported NIR spectral features for several compounds such as holocellulose (2100 nm, 2280 nm and 2340 nm), lignin (2050 nm and 2140 nm) and tannin (1660 nm and 2130 nm). Shenk and Westerhaus, [23] reported the region 2100 nm – 2200 nm to correspond to N-H stretching in amide bonds and many calibration equations for crude protein have used the wavelengths of this region. The presented wavelength-compound relationships are ambiguous (e.g. absorption around 1650 nm can be attributed not only to tannins but also to lignin [10]) and assigning wavelengths to components of interest still remains an important research goal.

Applications of NIRS for Analysis of Soils, Sediments and Plant Materials

Assessment of C and N Contents

One of the first applications of NIRS in soil science was determination of C and N in soil samples. Dalal and Henry [24] applied successfully NIRS to assess organic C (r^2 = 0.93, SEP = 0.2%) and total N (r^2 = 0.93, SEP = 0.02%) in Australian soils with low C content (0 to 2.6%). They used MLR for calibration and the selected wavelengths were 1744 nm, 1870 nm and 2052 nm for C and 1702 nm, 1870 nm and 2052 nm for N. The limitations of NIRS found in this study were poor predictions of C and N in the samples with low organic matter (C < 0.3%) and erroneous predictions in red earths due to colour interference. It was concluded that NIRS could be used for routine analysis of soils within moderate C concentrations and narrow range of soil colours. Morra et al. [25] also applied the MLR method to calibrate NIRS for C and N analysis in soils and soil fractions with organic matter content ranging from 0 to 8%. These authors used six different wavelengths to built calibration models and reported good results of calibration (C: r^2 = 0.93 – 0.96 , SEP = 3.2 – 5.9 g kg^{-1}; N: r^2 = 0.89 – 0.94, SEP = 0.4 – 0.6 g kg^{-1}). However, two limitations of NIRS have been emphasized: the necessity of having large sample sets for calibration and the necessity of using defined or closed sample populations. Ben-Dor and Banin [26] used

MLR method with six wavelengths to predict OM content in 91 Israeli soils and reported poorer prediction of organic matter content (r^2 = 0.55, SEP = 1.3%). These authors claimed that the reason for poorer prediction was the presence of two groups of soils within their calibration set: soils with low OM content (0-4%) and high OM content (4-14%).

In a number of studies (Table 1) NIRS has been reported to predict accurately the contents of organic C and total N over a wide range of their concentrations in arable and forest soils [15, 17, 27-31], soil fractions [32], forest litter and plant materials [33, 34] as well as fresh water sediments [35, 36].

Organic C and total N are known to correlate strongly in soils. In order to test whether the prediction of total N is due to its correlation with organic C or is based on spectral features of N containing groups Chang and Laird [37] carried out a study with artificial samples made of three soil series mixed with $CaCO_3$, humic acid and compost material. These authors reported good predictions of total C (r^2 = 0.91, SEP = 6.53 g kg^{-1}), organic C (r^2 = 0.89, SEP = 6.20 g kg^{-1}), inorganic C (r^2 = 0.96, SEP = 6.53 g kg^{-1}) and total N (r^2 = 0.86, SEP = 6.53 g kg^{-1}). They also found that predictions of total N for soils are based not on the correlation between C and N but rather on the independent response of incident radiation to soil N.

Prediction of N Mineralization in Soils

NIRS has been extensively applied not only to measure the contents of organic C and total N but also to study transformations of these elements in soils [38]. Special attention was paid to soil N being one of the most important plant nutrients. Fystro [28] applied NIRS to predict N mineralization during 220 days of incubation in 80 grassland samples of heterogeneous origin and reported good predictions for the release of mineral N after 50 and 220 days (r^2 = 0.85-0.84, SEP = 8.6 mg mineral N kg^{-1}). The predictions using NIRS were better than those with other methods based on lost ignition, total N or hot KCl-extracable N. Similarly, good prediction was reported by Russell et al. [39] for gross N mineralization after 21 days of incubation (r^2 = 0.79, SECV = 16 mg N kg^{-1}). Ludwig et al. [29] presented satisfactory results for N mineralization in forest soils after incubation over 53 and 264 days (r^2 = 0.64 - 0.83, SEP = 32.3-77.6 mg N kg^{-1}). On the contrary, Terhoeven-Urselmans et al. [40] reported inaccurate prediction of N mineralization in soil and litter samples as indicated by small ratio of standard deviation of the laboratory results to standard error of cross-validation (RSC = 0.9). The poor prediction probably resulted from the low number of calibration samples (n = 30).

There were attempts to use NIRS for predicting N uptake by plants: however, the results were contradictory. Russell et al. [39] reported satisfactory predictions of N uptake by rice (Oryza sativa cv. Amaroo) for plants grown in a glass house (r^2 = 0.76, SECV = 13 kg ha^{-1}), whereas N uptake by rice grown in the field was predicted unsatisfactorily (r^2 = 0.33. SECV = 17 kg ha^{-1}). Similarly, in the study of van Groeningen [41] prediction of N uptake by rice was unsatisfactory (r^2 = 0.19, SEP = 6.4 kg N ha^{-1}). The failure in the field trials was assigned to varying environmental conditions (temperature, solar radiation) that affected N mineralization, plant growth and N demand. On the contrary, Börjesson et al. [42] reported good prediction (r^2 = 0.81, SEP = 15.7 kg N ha^{-1}) of N uptake by winter wheat grown in the fields of one farm in southwestern Sweden. These authors used only 12 samples; however, their results were confirmed by Stenberg et al. [43], who used 75 samples taken in two Swedish fields over several years. In their study the models based on NIRS were better than those based on the organic C content and enabled reasonable predictions of N uptake (r^2 = 0.61, SEP = 12.6 kg N ha^{-1}). Stenberg et al. [43] concluded that NIRS has the potential to estimate N-uptake in crops and could be used to classify mineralization zones within fields with high variation of inorganic matter content. Considering the large number of factors affecting N mineralization and uptake, the development of reliable models would require large sample sets. Thus, the application of NIRS to delimit mineralization zones within fields would be a more successful approach than prediction of absolute N-uptake [43].

Prediction of Chemical Composition of Organic Matter

Knowledge of the composition of C in litter and soil is often required for estimation of C dynamics in ecosystems. NIRS could theoretically be used to study chemical composition of soil and litter organic matter. However, there are only a few studies on such an application of NIRS. Henderson et al. [44] fractionated organic matter of arable soils from Indiana into several components, including crude organic matter, crude humic acids, crude fulvic acids, purified humic acids and purified fulvic acids. They found NIR spectra to contain useful information on soil organic C content, but not on the composition of organic matter. More encouraging results have been presented recently by Terhoeven-Urselmans et al. [4], who applied NIRS to predict organic matter composition of in soil and litter sampled at various locations in Germany, Denmark and Norway. ^{13}C-NMR analysis was used as a reference method for organic matter composition and CuO oxidation determination of the lignin content. NIRS predicted well or satisfactorily (r^2 = 0.61-0.90, RSC = 1.5-3.1) the NMR characteristics of the analyzed materials (contents of carbonyl C, aromatic C, O-alkyl C and alkyl C as well as alkyl C/aromatic C ratio and alkyl/O-alkyl C ratio) and very well the lignin content (r^2 = 0.96, RSC = 2.3). NIRS seems to be a promising method for characterization of chemical composition of soil and litter samples, but more studies on such applications are required.

Litter Decomposition Studies

Within a climatic area the chemical composition of litter is the most important factor determining its decomposition rate. The ability of NIRS to predict complex organic

compounds has been widely tested in decomposition studies (Table 1). Martin and Aber [45] applied NIRS with MLR as the calibration method to predict successfully lignin (r^2 = 0.83, SEP = 1.69%), cellulose (r^2 = 0.69, SEP = 3.45%) and N (r^2 = 0.90, SEP = 0.13%) in fresh leaves of 17 deciduous and coniferous plant species. Similar results were reported by McLellan et al. [46] for decaying leaves of 12 different species. These authors also used the MLR method to build calibration equations and obtained satisfactory predictions for lignin and cellulose (r^2 = 0.84-0.87; SEP = 3% for both

Table 1. Application of NIR spectroscopy for analysis of different properties of soil, litter and plant materials.

Attribute	Sample	Error estimate	R^2	RPD	Reference
C; %	Soils	SEP = 0.2	0.86	-	[24]
C; $mg \cdot g^{-1}$	Soil fractions	SEP = 6.2	0.93 – 0.96	-	[25]
C; $mg \cdot g^{-1}$	Forest soil	SEP = 5.5	0.88	2.8	[31]
C; $mg \cdot g^{-1}$	Forest soil O horizon	SEP = 24	0.94	-	[34]
C; $mg \cdot g^{-1}$	Grassland soil	SEP = 5.7	0.87	2.7	[28]
C; %	Forest soils	SEP = 1.6	0.99	9.7	[15]
C; $mg \cdot g^{-1}$	Arable soil fractions	SEP = 0.9 – 2.5	0.80 – 0.90	2.2 – 3.2	[32]
C; $mg \cdot g^{-1}$	Soil mixtures	SEP = 6.20	0.89	4.2	[37]
C; $mg \cdot g^{-1}$	Soils	SEP = 7.86			[17]
C; $mg \cdot g^{-1}$	Freshwater sediment	SEP = 3.95	0.99	9.34	[36]
C; $mg \cdot g^{-1}$	Mixed samples (soil and plant materials)	SECV = 90	0.94	1.8	[40]
C; %	Plant materials	SECV = 0.28 – 1.07	0.86 – 0.99	2.5 – 6.4	[33]
C; $mg \cdot g^{-1}$	Soils	SEC = 2.2	0.91	-	[55]
N; $mg \cdot g^{-1}$	Forest soils	SEP = 0.4	0.88	2.8	[31]
N; $g \cdot g^{-1}$	Grassland soils	SEP = 0.49	0.80	2.1	[28]
N; %	Forest soils	SEP = 0.08	0.98	6.8	[15]
N; $mg \cdot g^{-1}$	Soil mixtures	SEP = 0.36	0.86	3.1	[37]
N; $mg \cdot g^{-1}$	Soils	SECV = 0.62	0.85	2.5	[17]
N; $mg \cdot g^{-1}$	Freshwater sediment	SEP = 0.508	0.99	9.4	[36]
N; $mg \cdot g^{-1}$	Soil and plant mixtures	SECV = 3.29	0.92	2.0	[40]
N; $mg \cdot g^{-1}$	Plant materials	SECV = 0.42 – 0.71	0.94 – 0.98	2.7 – 6.5	[33]
N mineralized after 50 to 220 days; $mg \cdot kg^{-1}$	Grassland soils	SEP = 0.76 – 0.88	0.75 – 0.84	2.0 – 2.4	[28]
N mineralizable; $mg \cdot kg^{-1}$	Rice soils	SECV = 16	0.79	-	[39]
P; $mg \cdot g^{-1}$	Freshwater sediments	SEP = 0.069	0.97	6.0	[36]
P; $mg \cdot g^{-1}$	Forest soil O horizon	SEP = 0.1	0.74	-	[34]
P; $mg \cdot g^{-1}$	Plant materials	SECV = 0.05 – 0.06	0.94 – 0.95	2.7 – 4.1	[33]
C_{mic}; $mg \cdot g^{-1}$	Forest soils	SEP = 0.11	0.81	2.2	[31]
C_{mic}; $mg \cdot g^{-1}$	Forest soils	SEP = 0.55	0.96	4.4	[15]
C_{mic}; $mg \cdot g^{-1}$	Soils	SECV = 0.39	0.60	1.5	[17]
C_{mic}; $mg \cdot g^{-1}$	Soil and plant mixtures	SECV = 3.85	0.58	1.1	[40]
RESP; $\mu gC\ h^{-1}\ g^{-1}$	Forest soils	SEP = 0.2	0.77	2.1	[31]
RESP; $\mu gC\ h^{-1}\ g^{-1}$	Forest soil O horizon	SEP = 9.6	0.76	-	[34]
RESP; $\mu gC\ h^{-1}\ g^{-1}$	Soil	SECV = 23.55	0.82	2.3	[17]

Table 1. (continued).

Attribute	Sample	Error estimate	R^2	RPD	Reference
Lignin; %	Plant materials	SEP = 3.03	0.76	-	[46]
Lignin; %	Plant materials	SEP = 1.69	0.83	-	[45]
Lignin; %	Plant materials	SECV = 2.58	0.96	-	[47]
Cellulose; %	Plant materials	SEP = 2.90	0.71	-	[46]
Cellulose; %	Plant materials	SEP = 3.45	0.69	-	[45]
Litter Mass Remaining; %	Plant materials	SEP = 4.46	0.93	-	[48]
Litter Mass Loss after 1 to 8 weeks; %	Plant materials	SECV = 1.32 – 5.84	0.97 – 0.98	3.0 – 3.5	[49]
CEC; cmol kg^{-1}	Forest soils	SECV = 14	0.96	5.3	[54]
CEC; cmol kg^{-1}	Soils	SECV = 3.82	0.81	2.3	[17]
CEC; cmol kg^{-1}	Arable soils	SEP = 1.36	0.83	2.4	[41]
CEC; cmol kg^{-1}	Soils	SECV = 2.6	0.95	-	[55]
Ca_{ex}, cmol kg^{-1}	Soils	SECV = 4.00	0.75	1.9	[17]
Ca_{ex}, cmol kg^{-1}	Forest soils	SECV = 1.59	0.96	2.9	[54]
Ca_{ex}, cmol kg^{-1}	Soils	SEP = 2.2	0.94	-	[55]
Mg_{ex}, cmol kg^{-1}	Soils	SECV = 1.28	0.68	1.8	[17]
Mg_{ex}, cmol kg^{-1}	Forest soils	SECV = 0.16	0.98	4.7	[54]
Mg_{ex}, cmol kg^{-1}	Soils	SEP = 0.8	0.91	-	[55]
K_{ex}, cmol kg^{-1}	Soils	SECV = 0.42	0.55	1.4	[17]
K_{ex}, cmol kg^{-1}	Forest soils	SECV = 0.07	0.88	2.3	[54]
K_{ex}, cmol kg^{-1}	Soils	SEP = 0.25	0.66	-	[55]
Base saturation; %	Forest soils	SECV = 4.4	1.00	4.8	[54]
Zn; mg kg^{-1}	Forest soils	SECV = 8.0	0.96	3.2	[54]
Zn; mg kg^{-1}	Polluted soils	SEP = 526	0.67	-	[58]
Cu; mg kg^{-1}	Forest soils	SECV = 0.6	0.98	3.4	[54]
Cu; mg kg^{-1}	Polluted soils	SEP = 10.3	0.61	-	[58]
Cd; mg kg^{-1}	Forest soils	SECV = 0.06	0.81	1.4	[54]
Cd; mg kg^{-1}	Polluted soils	SEP = 5.13	0.54	-	[58]
Pb; mg kg^{-1}	Forest soils	SECV = 11.4	0.81	1.8	[54]
Pb; mg kg^{-1}	Polluted soils	SEP = 839	0.45	-	[58]
Sand; %	Soils	SECV = 11.9	0.82	2.3	[17]
Sand; g kg^{-1}	Soils	SEP = 61	0.91	-	[55]
Sand; %	Soils	SECV = 5.9	0.73	2.2	[56]
Silt; %	Soils	SECV = 9.5	0.84	2.5	[17]
Silt; g kg^{-1}	Soils	SEP = 39	0.79	-	[55]
Silt; %	Soils	SECV = 5.8	0.80	2.3	[56]
Clay; %	Soils	SECV = 4.1	0.67	1.7	[17]
Clay; g kg^{-1}	Soils	SEP = 54	0.88	-	[55]
Clay; %	Soils	SECV = 3.2	0.90	3.0	[56]

constituents) and very good for total N (r^2 = 0.94, SEP = 0.2%). In both studies four wavelengths were used in calibration equations, but they differed between studies. For instance, for lignin estimation Martin and Aber [45] used the absorptions at 1648 nm, 2078 nm, 2260 nm and 2330 nm, whereas McLellan et al. [46] used the absorptions at 1438 nm, 1708 nm, 2154 nm and 2320 nm.

Joffre et al. [47] used NIRS to predict acid-detergent fibre, acid-detergent lignin, ash content and the contents of C and N in the litter of 8 evergreen and deciduous broad-leaved trees, conifers and shrubs. They applied two calibration methods – MLR and PLS. Both methods yielded acceptable results for C, N and ash content, but for acid-detergent fibre and acid-detergent lignin PLS gave more accurate predictions, indicated by lower SECV values.

The litter mass loss (expressed as the percentage of ash-free litter mass remaining – LMR) was studied for leaf litter of 10 different species with varying initial chemical composition and at different decomposition stages [48]. The experiments were carried out in laboratory under controlled conditions (incubation for 14 months at 22ºC and moisture of 80% of field water holding capacity) and in the field using litterbags. Calibrations were developed only with a part of samples incubated in the laboratory. For the calibrations the entire spectra (400-2500 nm) were used with the exception of the part that corresponds to water (1948 nm-1968 nm). The developed calibration equations were validated against another part of samples incubated in the laboratory and also against the samples from the field experiment. The LMR in the laboratory and the field experiment ranged from 22% to 100% and was predicted very well for the samples from laboratory incubations (r^2 = 0.98, SEP = 3.53%). The LMR in the field experiment was predicted less accurately, but still with satisfying accuracy (r^2 = 0.93, SEP = 4.46%). In a further study, Gillon et al. [49] found that litter decomposability (LMR values and the decay constants of litter materials) of 34 various plant species was better related to their initial NIR spectra than to their other characteristics (contents of C, N, hemicellulose, cellulose and lignin). The equations developed for ash, lignin, cellulose, hemicellulose, P, N and litter decomposition index [33, 47-49] were used to study chemical changes in the leaf litter consumed by Glomeris marginata [50]. In this study, NIRS provided in a single operation the characteristics of the food and faeces for all the calibrated attributes.

Recently, NIRS has been applied to determine water soluble (WEP) and total extractable polyphenolics (TEP) in biomass, necromass and decomposing plant material [51]. Calibrations were developed for two data sets differing in their spectral characteristics. The first set included decomposing plant material and the second one contained undecomposed material. In each set 84 to 94 samples were used for calibration and 90 to 95 samples for validation. The contents of WEP and TEP in both sets varied over a wide range (WEP: 0.24-95.15 g kg^{-1} in decomposing material and 2.09-233.28 g kg^{-1} in undecomposed material, TEP: 0.70-157.83 g kg^{-1} in decomposing material and 5.97-321.17 g kg^{-1} in undecomposed material). In both sets NIRS spectroscopy predicted well the contents of WEP (r^2 = 0.92-0.94, SEP = 2.39-11.1 mg kg^{-1}) and TEP (r^2 = 0.88 in both sets, SEP = 7.11-22.0 mg kg^{-1}). The authors concluded that NIRS could allow performing of large screening for studies on polyphenolic control on decomposition process and polyphenolic implication in herbivory and adaptive mechanisms of plants.

Prediction of Phosphorus

Phosphorus is one of the most important plant nutrients. Its concentration may also affect the decay rate of litter. In sediments the concentration of P is often measured due to its role in the eutrophication process. There were several attempts to use NIRS for P determination in litter, soil and sediments. Very good results of total P determination were reported by Malley et al. [35, 36] for freshwater sediment samples (r^2 = 0.97, SEP = 0.069 mg g^{-1}) and by Gillon et al. [33] for pine needles at different stages of decay (r^2 = 0.94-0.99, SECV = 0.06 – 0.08 mg g^{-1}). Chodak et al. [34] reported satisfactory prediction of total P in forest humus samples (r^2 = 0.74, SEP = 0.1 mg g^{-1}). The results for P analysis in mineral soils were less encouraging. In the study of Ludwig et al. [29] NIRS failed to predict Bray II P contents, Olsen P contents and long-term available P (r^2 = 0.29-0.59) in disturbed Australian forest soils. Similarly, Ben-Dor and Banin [52] reported only poor prediction performance of NIRS for P_2O_5 in Israeli soils. Phosphorus, unlike C and N, does not absorb NIR radiation. Therefore, its prediction relies on the correlation with soil constituents absorbing in this spectral range. In soils P may exist in organic and inorganic forms. Probably only the organic forms of P may be predicted by NIRS, whereas the inorganic ones cannot. Thus, in mineral soils, were the contribution of inorganic P may be high, NIRS is not useful for determination of P contents.

Prediction of Cation Contents and Cation Exchange Capacity

Similarly to P, metal cations do not absorb NIR radiation. However, constituents which do not absorb NIR radiation can be predicted owing to their correlations with spectrally active constituents [52]. Cozzolino and Moron [53] reported satisfactory predictions (r^2 = 0.76-0.83) of Na, Zn, Mn and Cu concentrations in lucerne and white clover sampled in Uruguay. Only the prediction of Fe in these samples was unsatisfactory. NIRS was tested to predict total contents of Na, K, Ca, Mg, Fe and Al in organic horizons of soils under beech, spruce and mixed beech-spruce forest stands [34]. Some of the samples were taken at forest stands that were limed (with $CaCO_3$ or dolomite) in order to decrease soil acidification. Predictions of all metals except Ca and Mg were good or satisfactory (r^2 = 0.71-0.94). Prediction of Ca and Mg was worse because of the presence of the samples containing large Ca and Mg contents. Probably, the application of lime changed the natural correlations between organic C and the contents of Ca and Mg.

The whole data set was further divided into two groups representing limed samples and those not influenced by liming. NIRS predicted well and satisfactorily concentrations of Ca and Mg in the samples which did not receive lime (r^2 = 0.83 and 0.77, respectively), but was not able to predict concentrations of these elements in the samples from limed sites.

Very good predictions of total and exchangeable Na, K, Ca, Mg, Mn, Fe and Al (r^2 = 0.88-1.00) in geologically heterogeneous mineral soils under beech stands in Germany were reported by Chodak et al. [54]. Similarly, Shepherd and Walsh [55] presented successful predictions of exchangeable Ca and Mg (r^2 = 0.94 and 0.91, respectively) in a large sample set of African soils. In both these studies also cation exchange capacity (CEC) was predicted very well (r^2 = 0.91-0.96). CEC in soils (in particular those rich in organic C) is strongly related to NIR absorbing functional groups of organic matter (COOH, OH etc.). Thus a good prediction of CEC using NIRS is expected.

NIRS has been applied also to determine heavy metals in soils and sediments [54-59]. Successful predictions of total Cu (r^2 = 0.87, SEC = 0.7 mg kg^{-1}) and Zn (r^2 = 0.72, SEC = 1.2 mg kg^{-1}) in arable soils were reported by Moron and Cozzolino [56]. In forest soils NIRS predicted well the contents of Zn (r^2 = 0.98, SEP = 6.75 mg kg^{-1}), Cu (r^2 = 0.95, SEP = 1.43 mg kg^{-1}) and Pb (r^2 = 0.98, SEP = 4.36 mg kg^{-1}) [54]. However, in both these studies unpolluted soils were used. Kooistra et al. [57] successfully applied NIRS to predict Cd and Zn concentrations in metal-contaminated Rhine floodplains; however, they rejected the samples with the largest heavy metal content as not representative of the entire sample population. This approach seems to be unapplicable for measurement of metal cations in samples from industrial regions since the concentration of heavy metals may be extremely high at sites close to emitters. The ability of NIRS to predict heavy metal contents in heavily polluted arable soils from Upper Silesia has been tested in the study of Siebielec et al. [58]. NIRS tended to underestimate the highest contents of Cd, Cu, Pb and Zn and the prediction performance was rather poor [58]. The poor prediction of heavy metals at their highest concentrations was assigned to industrial contamination. Indeed, in industrial areas deposition of heavy metal-containing dusts may be an important source of pollution. The deposited heavy metals may not be related to organic matter quantity or quality, so they may be invisible to NIRS and be undeterminable by this method.

Microbial Biomass and other Microbial Properties

NIRS has been applied to measure microbial biomass (C_{mic}) and respiration in soils. These parameters were successfully described in the sieved mor humus of boreal forests [60], where NIRS explained 93%-98% of the variability of basal respiration and 89% of substrate-induced respiration (SIR). In the study of Pietikainen and Fritze [61] NIRS explained 75% of the variance in C_{mic} measured by SIR and 62% of the variance in basal respiration of organic horizons of boreal, mixed spruce-pine forests. The major shortcoming of these studies was the low number of samples (n = 30 in [60]; n = 12 in [61]). However, the ability of NIRS to predict microbial biomass and soil respiration has been confirmed in several studies with a much larger number of samples [15, 17, 29, 34]. In all these studies, NIRS yielded satisfactory models for the prediction of respiration (r^2 = 0.60-0.76) and for microbial C measured either by SIR of CFE method (r^2 = 0.60-0.96). It is noteworthy that the prediction of microbial C or respiration was always less accurate than of C or N contents and that a very good model was achieved only once [15]. The worse prediction of microbial biomass and respiration is due to the fact that biological characteristics of samples depend not only on organic matter chemistry which is contained in NIR spectra of soils but also on other factors such as pH, temperature, moisture and micronutrients. These factors may weaken relationships among NIR spectra and biological parameters, thus decreasing predictive performance of NIRS.

Recently, Terhoeven-Urselmans et al. [40] reported NIRS to fail predicting microbial biomass and DOC production in soil and litter samples. However, these authors used only a small number of samples to build calibration equations (n=30) and the sample set was extremely diverse. They concluded that in order to reliably predict microbial properties of soils the sample population must be large enough, sufficiently diverse and cover the entire variability of spectral information.

Texture of Soils

NIR spectra depend on particle size of the analyzed materials. This enables prediction of texture of analysed samples. Moron and Cozzolino [56] predicted satisfactorily contents of sand (r^2 = 0.82, SECV = 5.9%), silt (r^2 = 0.82, SECV = 6.0%) and clay (r^2 = 0.90, SECV = 3.2%) in 332 mineral soils from Uruguay. Similar results were reported also by Chang et al. (2001) [17] for 800 samples of American soils (r^2 = 0.82, 0.84 and 0.67 for sand, silt and clay, respectively) and by Shepherd and Walsh (2002) [55] for more than 1000 samples of different African soils (r^2 = 0.76, 0.67 and 0.78 for sand, silt and clay, respectively).

Other Applications

Prediction of different constituents in soils, litter and plant materials remain the main application of NIRS; however, there are several other methods of NIRS utilization. NIRS can be used for objective and rapid selection of samples from large populations [62]. Depending on the goal of research only similar or extreme samples from the entire sample population can be chosen for expensive and complex analyses. NIRS may be used to evaluate spatial variation of soils [63]. When coupled with GIS techniques NIRS may help to produce detailed soil maps for precision farming [64].

The use of portable NIR devices for field measurements of certain soil constituents (e.g. content of organic matter or N) would be of great interest. Experiments with a portable NIR devices have already been carried out but the obtained results were poor. Sudduth and Hummel [65] developed portable NIR spectrometer with a sensing range between 1650 and 2650 nm and optical bandwidth of under 55 nm. Laboratory calibrations and validations for soil organic matter content were successful (SEP = 0.4%) but in-furrow field operation yielded unsatisfactory results. The failure was probably due to the movement of soil beyond the sensor during data acquisition.

NIR spectroscopy may be a useful tool in Imaging Spectroscopy (IS). IS uses airborne or satellite-based hyperspectral sensors to spatialize the spectral information [66]. This method may be applied to produce fine-scale maps of physical and chemical soil characteristics. Stevens et al. [66] applied a Compact Airborne Spectrographic Imager (spectral range: 405-950 nm) to assess carbon stock change in agricultural soils in Belgium. However, they obtained unsatisfactory results since the SEP (7.2-9.9 Mg C ha^{-1}) was too high in comparison with changes in SOC stocks resulting from management or land conversion. The authors concluded that careful monitoring of disturbing factors and the use of sensors covering a wider spectral range is needed to decrease the detection limit of the method. Better results were reported by Selige et al. [67], who used a HyMap™ scanner (spectral range: 420-2480 nm) to produce fine-scale maps of C_{org}, N_t, sand and clay contents in soils of Eastern Germany. In order to exclude the effects of soil surface roughness and moisture, only bare soil fields were selected and the flight campaign was organized after a period of dry weather. The spectroscopic data were combined with field data using PLSR or MLR and the developed models used to produce fine-scale maps of the considered soil properties in an 88 ha test field. The resolution of the maps was high enough to detect spatial differences in soil properties caused by historical activities. The authors concluded that IS combined with multivariate regression modelling can be a valuable tool to understand the historical development of land using practices as well as to contribute significantly to the goal of fine scale mapping.

Future of NIRS

Future application of NIRS is related to its ability to produce a large number of samples. This feature of NIRS makes this technique a suitable tool for precision agriculture and landscape-scaled environmental studies. The method may help to produce detailed maps of soil properties. There are several ways NIRS may be applied for this purpose. Airborne NIR spectrometers may be used for remote sensing of soils as described in Stevens et al. [66]. Presently, the airborne measurements yield less accurate estimations of soil properties than those with field or laboratory spectrometers. This is due to several factors such as variable soil moisture and roughness, microrelief of the analyzed area and possible vegetation cover that interferes with airborne measurements. The result of Selige et al. [67] suggest that taking these factors into consideration while planning a measurement campaign may increase the methods effectiveness. Another method of NIRS application in precision agriculture is the use of portable spectrometers built on farm machines. However, the results obtained by Sudduth and Hummel [65] indicate a number of several additional sources of errors (eg. movement, vibrations) that deteriorate the quality of the analysis. The third method of NIRS application in precision farming and environmental studies is the classic laboratory approach. As NIR spectroscopy is a rapid and cost-effective technique, much denser soil sampling is possible. A dense sampling combined with powerful geostatistical techniques such as Kriging may help to produce highly detailed maps of soil properties. Additionally, using the laboratory approach it is possible to detect vertical gradients of soil properties within a soil profile and to produce three-dimensional maps (models) of soil properties.

Another field where NIRS may contribute considerably is the research on soil organic carbon (SOC). NIRS has been reported to accurately predict SOC contents. Thus the method may be used to reduce costs of large soil carbon inventory programs. However, NIRS could be used not only to determine SOC content but also its quality. SOC is an extremely complex mixture of plant, animal and microbial residues at all stages of decay and various organic substances (eg. polysaccharides, fulvic and humic acids etc.). The composition of SOC is an important property affecting soil fertility. The reaction of SOC to external factors (eg. changed climatic conditions) also depends largely upon its composition. There are numerous methods to assess SOC composition and quality, such as extractions with various solvents, density fractionations, particle size fractionations, etc. However, most of them are expensive, resource intensive and time consuming. To date the studies on NIRS application for SOC assessment have focused usually on the quantity of soil C, whereas those addressing the issues of SOC quality have been relatively scarce. The application of NIRS to characterize SOC and to determine particular pools of SOC should receive much more attention in future research as this is a field where NIRS may help to save a lot of costs and analytical effort.

NIRS could be also applied for differentiation of geogenic and recent C in the mine soils developing in areas destroyed by lignite mining. These mine soils may contain considerable part of lignite C [69] impeding proper monitoring of C accumulation and thus the assessment of the reclamation success. NIRS is able to distinguish lignite C and humus C [70] and potentially could be used to assess accumulation of recent C in the mine soils. However, more detailed tests are required to assess this application of NIRS in environmental monitoring.

Finally, NIRS might be used in geological studies or in mine laboratories for testing the quality of organic commodities such as coals, lignites or peats. To date this application of NIRS received only minor attention. Since the mine laboratories need to process vast numbers of samples each year, the application of NIRS might be of great interest for them.

Conclusions
Possibilities and Limitations of NIRS

NIRS has been proven to be useful for predicting of a number of physical, chemical and microbial properties of soils, litter and plant materials. The method offers several advantages such as rapidity of analysis, minimal preparation of sample, non-destructive analysis and no use of reagents. The rapidity of NIRS enables a large number of samples to be processed. The ability to predict various constituents enables determination of numerous parameters of analyzed material at one time. The presented results of numerous studies indicate great potential of this method as an analytical tool in large-scale environmental research. However, NIRS should not be treated as a method for assessment of nearly all constituents or a remedy for all problems related to analysis of soils, litter or plants. The method offers lots of advantages when good models are developed, but the process of model building itself may be complex. The reliable, global models can be developed only when the nature of dependency between NIR spectra and the constituents is fully understood. As this is not always the case the main goal of future research should be to identify robust and stable correlations between constituents and spectra. Specific spectral features associated with the constituents of interest should be identified and appropriately modelled.

One of the main limitations of NIRS is the necessity of having defined or closed sample population. This means that any calibration equations are valid only for the area or sample population for which they were built and cannot be used to predict constituents in samples from outside this area or population. Any new samples must first be analyzed with classical methods and then included in the calibration set. A possible solution of this problem is building large and diverse spectral libraries using archived samples [55]. Having large and diverse sample sets, it is possible to develop robust calibration models applicable to samples from large areas, thus increasing efficiency of expensive and time-consuming environmental studies.

Another serious limitation of NIR is the necessity to perform calibrations with classical methods. Since NIR spectra are calibrated with classical methods the quality of NIRS predictions depends entirely on the quality of the measurements used to develop the statistical model. Thus, using erroneous reference measurements would result in propagation of the errors and creation of unreliable predictive models. In order to correct adverse effects of erroneous reference data and to assess real NIRS predictive performance, the reference value uncertainty should be included in the assessment of NIRS model quality [68].

For reliable calibrations sometimes large numbers of samples must be analyzed with classical reference methods. This may limit the applicability of NIRS, in particular when reference analyzes are expensive or complex and time-consuming. In such cases a thorough analysis of costs and efforts should be carried out since the large initial effort may reward in the future when the developed models will be used instead of the complex reference methods.

Application of NIRS is worthwhile only when large sample numbers are to be analyzed. Therefore, NIRS is not expected to replace classical methods completely. Instead, this method should be used alongside conventional analyses to improve their efficiency and costs.

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