

Use of Near Infrared Spectroscopy to Determine Chemical Properties of Forest Soils

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Abstract

Spatial variability of soil chemical properties is high. Therefore, fast methods may be required to study the soil quality at the landscape level. The objective was to assess the ability of near infrared spectroscopy (NIRS) to determine the total contents of Na, K, Ca, Mg, Mn, Fe, Al, Zn, Cu, Cd and Pb in forest soils. Soils of different types and textures were collected from five sites and four depths (n = 100). Contents of cations and heavy metals in the soil samples were determined after pressure digestion in HNO₃. Spectra were recorded in VIS-NIR region (400 – 2500 nm). The sample population was divided by half into calibration and validation sets. The calibration equations for each constituent were developed using the entire spectrum (0th – 2nd derivative). NIRS predicted well the contents of all elements with the exception of Cd. The linear regression coefficients (measured against predicted values) ranged from 0.85 to 1.12 and the correlation coefficients (r) were greater or equal 0.92. The best prediction accuracy was obtained when the samples were split into less differentiated groups according to the chemical properties. The obtained results indicate that NIRS may be useful in landscape scaled studies on the soil chemical properties.

Introduction

Information on a number of soil chemical properties is required to assess the quality of forest soils and to monitor the effects of environment pollution on these soils. However, due to high spatial variability of soil chemical properties large numbers of samples must be analyzed to reliably characterize forest soils at the landscape level (1). Therefore, rapid analytical methods may be needed.

Near infrared spectroscopy (NIRS) is an analytical technique known for its rapidity, simplicity and cost-effectiveness (2). The prediction of several soil constituents which do not absorb a radiation in NIR range is possible due to their correlations with the constituents which are active in this range (3). The ability of NIRS to predict several chemical and biological properties of soils has been extensively reported (3, 4, 5). Recently the applicability of NIRS for large scale studies including different soils has been tested. For instance, Shepherd and Walsh (6) presented a scheme for building spectral libraries for soil evaluation in large areas. They reported that NIRS predicted well (r = 0.84 – 0.94) the contents of exchangeable Ca, Mg, effective cation exchange capacity, organic C and particle size distribution in diverse African soils. However, it has not been tested whether the use of local calibrations instead of global, covering large areas and different soils may improve prediction performance of NIRS.

The objectives of this study were (i) to test the ability of NIRS to predict the total contents of Na, K, Ca, Mg, Mn, Fe, Al, Zn, Cu, Cd and Pb in various forest soils, and to test the prediction accuracy achieved using large and differentiated sample sets or smaller, less variable ones.

2. Material and methods

2.1 Study sites and chemical analyses

The soils were collected from sites covered by 100-150 years old beech (*Fagus sylvatica* L.) stands in central and northern Germany. The sites were located at Göttinger Wald (GW, elevation 420 m a.s.l., silty clay, Haplic Calcisol), near Zierenberg (ZB, elevation 440 m a.s.l., silt loam, Cambisol), in Solling (SL, elevation 504 m a.s.l., silt loam, dystric Cambisol), near Unterlüß (UL, 116 m a.s.l., sandy loam, dystric Cambisol) and near Hamburg (HB, elevation 30 m a.s.l., loamy sand, dystric Cambisol). In May 1995 five soil cores were collected using perspex cylinders (14.4 cm inner diameter, 24 cm depth) at each site. The mineral soils were sampled at four depths: 0–5 cm, 5–10 cm, 10–15 cm and 15–20 cm. For chemical analyses the soil samples were sieved (2 mm mesh size), dried at 105 °C and finely ground. Total contents of Na, K, Ca, Mg, Mn, Fe and Al in the samples were determined by ICP-AES (Spectro Analytical Instruments, Kleve, Germany) and the contents of Zn, Cu, Cd and Pb by Atomic Absorption Spectrometry (Varian SpectrAA 800, Darmstadt, Germany) after pressure digestion in concentrated HNO₃.

2.2 Prediction of the soil constituents using NIRS

The NIR-reflectance of the samples (n = 100) was recorded at 2 nm intervals between 400 and 2500 nm using a Foss NIRSystems spectrometer (Silver Spring, USA). Each sample was scanned once, thoroughly mixed and scanned a second time. The final spectrum was a mean of both scans. Absorbance values (log 1/reflectance) were used for the data transformation and statistical analysis. The samples were divided randomly, by half into calibration and validation sets. The development of calibration equations involved taking derivatives of 0th to 2nd order, defining the gaps over which derivatives were calculated and smoothing the spectra. The calibration equations were calculated using the modified partial least-squares regression (MPLS) method which uses all the spectral information (7). The best treatment was chosen following a trial and error procedure using the following criteria: the smallest standard error of cross validation (SECV), the highest correlation coefficient (measured against predicted values) (r) and linear regression coefficient (a) close to one. The prediction ability of NIRS was evaluated in the validation stage using r, a, standard error of prediction (SEP) and RPD calculated as a ratio of standard deviation of the reference data set to SEP (8).

3. Results and discussion

3.1 Chemical characteristics of the soils

The studied soils differed in chemical properties. The soils at GW, ZB and SL had loamy texture but differed in the pH values (SL: pH = 3.8, GW and ZB: pH = 4.9 and 5.6, respectively) (Table1). The soils at UL and HB were of sandy texture and had low pH (3.9). The loamy soils contained distinctly higher amounts of all cations than the sandy soils. At all sites (with exception of ZB) Al was a

Table 1. Chemical properties of the analyzed sites. Mean values and ranges. The mean values within a row sharing the same letter are not significantly different according to HSD Tuckey's test at $p < 0.05$.

Property	Site				
	GW	ZB	SL	UL	HB
pH	4.9 b	5.6 c	3.8 a	3.9 a	3.9 a
Na mg g ⁻¹	4.7 - 5.1 0.5 c	5.4 - 5.7 0.9 d	3.4 - 4.2 0.5 c	3.7 - 4.3 0.0 a	3.8 - 4.2 0.1 b
K mg g ⁻¹	0.4 - 0.6 12.2 c	0.8 - 1.0 2.8 b	0.4 - 0.5 12.9 c	0.0 - 0.1 0.7 a	0.1 - 0.1 1.3 a
Ca mg g ⁻¹	8.5 - 16.1 4.0 b	2.5 - 3.2 21.3 c	11.8 - 13.9 0.7 a	0.6 - 0.8 0.6 a	1.2 - 1.4 0.9 a
Mg mg g ⁻¹	2.1 - 6.6 6.1 c	19.7 - 24.2 32.5 d	0.6 - 1.0 3.6 b	0.5 - 0.7 0.3 a	0.8 - 1.1 0.7 a
Mn mg g ⁻¹	4.0 - 8.5 0.9 c	27.3 - 38.4 1.0 c	3.1 - 3.9 0.5 b	0.2 - 0.4 0.1 a	0.5 - 0.8 0.1 a
Fe mg g ⁻¹	0.4 - 1.4 28.0 c	1.0 - 1.0 49.3 d	0.2 - 0.7 22.6 b	0.0 - 0.1 4.5 a	0.0 - 0.1 6.4 a
Al mg g ⁻¹	21.1 - 34.5 57.9 d	45.1 - 53.3 28.1 b	19.4 - 24.5 40.4 c	2.8 - 6.0 4.9 a	4.8 - 7.5 6.5 a
Zn μg g ⁻¹	38.5 - 76.4 99.7 c	26.6 - 29.3 104.3 c	35.9 - 43.2 44.3 b	3.5 - 6.8 10.1 a	5.4 - 7.6 16.3 a
Cu μg g ⁻¹	71.0 - 146.3 14.7 d	88.5 - 115.9 13.3 d	27.4 - 62.9 5.6 b	0.0 - 16.3 3.2 a	10.4 - 25.0 7.6 c
Cd μg g ⁻¹	10.9 - 18.0 0.1 b	11.9 - 17.2 0.1 b	4.1 - 9.6 0.0 a	1.5 - 7.1 0.0 a	5.8 - 11.4 0.0 a
Pb μg g ⁻¹	0.0 - 0.5 66.5 d	0.0 - 0.3 31.3 b	0.0 - 0.0 45.3 c	0.0 - 0.1 13.8 a	0.0 - 0.0 25.0 ab
	46.4 - 99.4	16.4 - 43.5	17.7 - 79.3	6.7 - 19.9	12.3 - 38.5

dominating cation. The soils at GW and SL contained considerable amounts of K (12.2 and 12.9 mg g⁻¹) and the soil at ZB of Ca (21.3 mg g⁻¹) and Mg (32.5 mg g⁻¹). In the sandy soils the contents of cations other than Al and Fe were very low (0.0 – 1.3 mg g⁻¹).

The soils with higher pH (GW and ZB) contained significantly higher amounts of Zn (99.7 and 104.3 μg g⁻¹, respectively) and Cu (14.7 and 13.3 μg g⁻¹, respectively) than the soils with lower pH (Zn: 10.1 – 44.3 μg g⁻¹; Cu: 3.2 – 7.6 μg g⁻¹). The highest contents of Pb (66.5 μg g⁻¹) were found at GW followed by SL (45.3 μg g⁻¹), ZB (31.3 μg g⁻¹), HB (25.0 μg g⁻¹) and UL (13.8 μg g⁻¹). The Cd contents were 0.1(μg g⁻¹) at GW and ZB whereas at the remaining sites (with the exception of the one sample from UL) were below the detection limit of the applied method. The contents of all analyzed heavy metals were below the critical values which have harmful effects on a soil ecosystem (9).

3.2 Prediction of soil properties using NIR spectroscopy

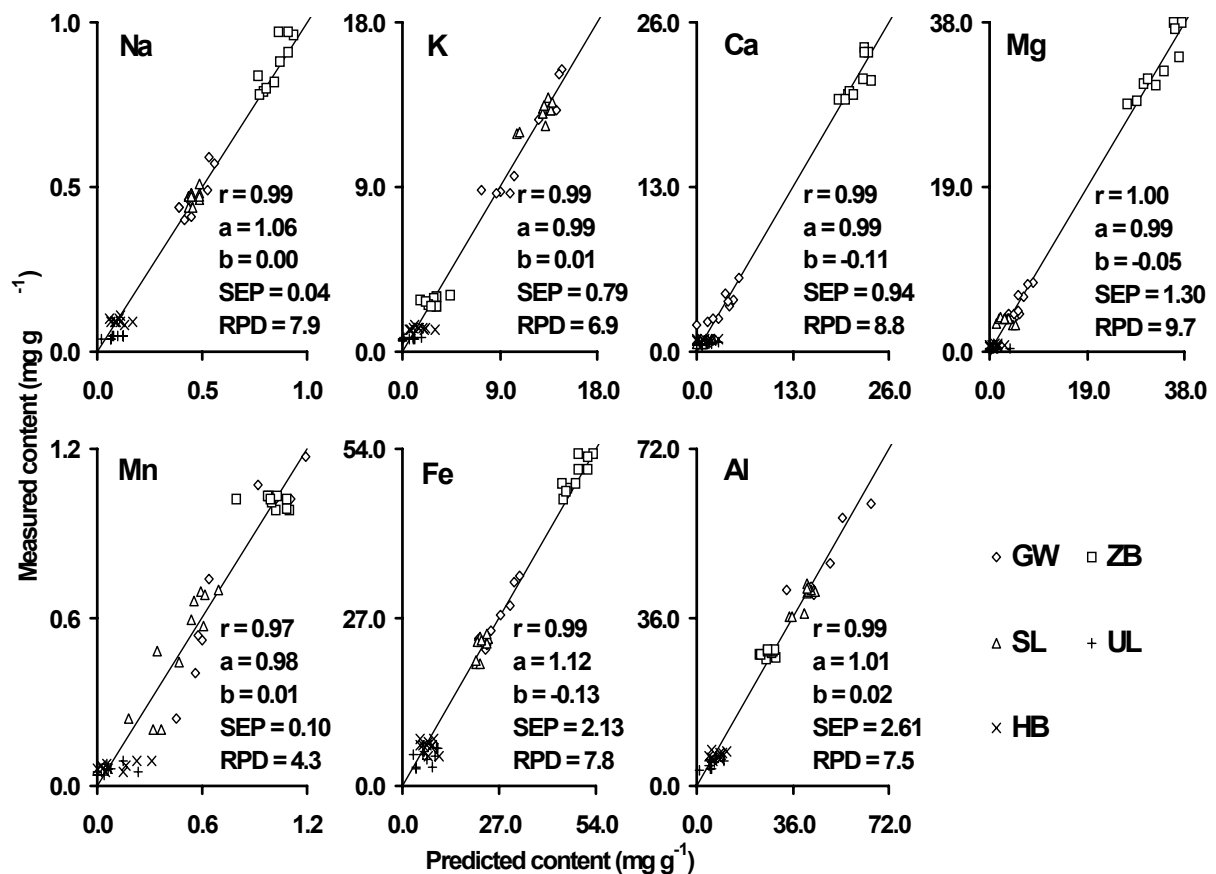
Good calibrations (correlation coefficient (measured against predicted values) (r) > 0.90, linear regression coefficients (a) = 1.00 – 1.15)) were obtained for all analyzed soil constituents (Table 2).

Table 2: Calibration statistics for the analyzed constituents. The units given in the second column refer to the range of measured values, standard errors of cross validation (SECV) and intercepts (b) of a linear regression (measured against predicted values). The regression coefficients (a) and correlation coefficients (r) are also given. For the math treatment, the first number is the order of the derivative function, the second is the segment length over which the derivative was taken and the third is the segment length over which the function was smoothed.

Constituent	Math treatment	n	Range	SECV	r	a	b	
Na	mg g ⁻¹	1, 4, 4	50	0.04 - 0.98	0.03	0.99	1.04	0.00
K	mg g ⁻¹	2, 10, 5	50	0.6 - 16.1	0.47	1.00	1.01	0.00
Ca	mg g ⁻¹	2, 20, 10	50	0.5 - 24.2	0.55	1.00	1.00	0.00
Mg	mg g ⁻¹	2, 10, 10	50	0.2 - 38.4	0.69	1.00	1.00	0.00
Mn	mg g ⁻¹	2, 10, 10	50	0.04 - 1.45	0.07	0.99	1.01	0.00
Fe	mg g ⁻¹	1, 4, 4	50	2.9 - 53.3	1.52	1.00	1.04	0.00
Al	mg g ⁻¹	2, 10, 5	50	3.6 - 76.5	1.98	1.00	1.03	0.00
Zn	μg g ⁻¹	1, 20, 10	50	7.7 - 146.3	8.04	0.98	1.02	0.00
Cu	μg g ⁻¹	2, 4, 4	50	1.5 - 18.0	0.59	0.99	1.00	0.00
Cd	μg g ⁻¹	1, 4, 4	11	0.13 - 0.54	0.06	0.90	1.15	0.00
Pb	μg g ⁻¹	2, 10, 5	50	10.7 - 126.4	11.4	0.90	1.04	0.00

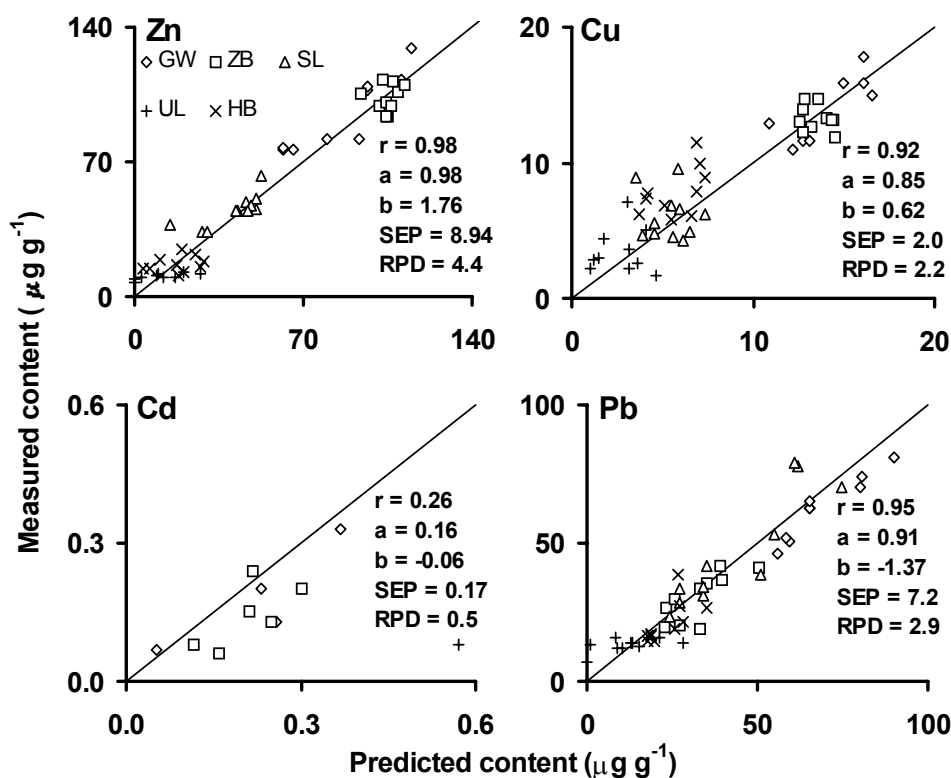
In the validation stage NIRS predicted well the contents of all cations (a = 0.98 – 1.06, r = 0.97 – 1.00). The RPD values varied between 4.3 and 9.7 indicating high accuracy of predictions (8) (Figure 1).

Figure 1: Predicted and measured values for the total contents of Na, K, Ca, Mg, Mn, Fe and Al in the validation stage. Linear regression coefficients (a), intercepts (b), correlation coefficients (r), standard errors of prediction (SEP; in mg g⁻¹) and RPD values are also given. The lines indicate 1:1 values.



Similarly, Chodak et al. (4) reported that NIRS predicted well the total contents of Na, K, Ca, Mg and Fe ($a = 0.82 - 0.96$; $r = 0.88 - 0.97$) in organic horizons under beech and spruce stands in Germany. The total contents of Zn ($a = 0.98$, $r = 0.98$, $SEP = 8.94 \mu\text{g g}^{-1}$, $RPD = 4.4$) and Pb ($a = 0.91$, $r = 0.95$, $SEP = 7.2 \mu\text{g g}^{-1}$, $RPD = 2.9$) were predicted well and the content of Cu ($a = 0.85$, $r = 0.92$, $SEP = 2.0 \mu\text{g g}^{-1}$, $RPD = 2.2$) satisfactorily whereas the prediction of Cd content was unsatisfying ($a = 0.16$, $r = 0.26$, $SEP = 0.17 \mu\text{g g}^{-1}$, $RPD = 0.5$). The unsatisfying prediction of Cd was due to the presence of one sample from UL site in the validation set (Figure 2). After this sample was rejected the prediction improved, however still was unsatisfying ($a = 0.76$, $r = 0.81$, $SEP = 0.08 \mu\text{g g}^{-1}$, $RPD = 1.1$). Kooistra et al. (5) reported that NIRS predicted well the contents of Zn and Cd ($r = 0.95$, $SECV = 81.0 \mu\text{g g}^{-1}$ for Zn and $r = 0.94$, $SECV = 0.68 \mu\text{g g}^{-1}$ for Cd) in the river floodplains in Netherlands. The worse prediction of Cd in our study resulted probably from the low number of samples used to develop calibration equations.

Figure 2: Predicted and measured values for the total contents of Zn, Cu, Cd and Pb in the validation stage. Linear regression coefficients (a), intercepts (b), correlation coefficients (r), standard errors of prediction (SEP; in $\mu\text{g g}^{-1}$) and RPD values are also given. The lines indicate 1:1 values.



The level of prediction accuracy obtained using global calibrations was sufficiently high for large-scale studies. For instance, the soils with very high amounts of Ca and Mg (ZB) were clearly distinguished. Similarly, the low cation contents at UL and HB were accurately predicted (Figure 1). However, the obtained accuracy was too low to recognize with a satisfying accuracy the differences among the samples from a particular site. Therefore, we tested whether splitting the samples according to their chemical properties may improve the prediction accuracy of some constituents. The chosen constituents were the total contents of base cations (Na, K, Ca, Mg) and of Fe and Al. The constituents were chosen since it was possible to clearly distinguish the samples with low and high contents of particular elements. For each constituent the sample population was divided into two groups - one containing the samples with low of the constituent (called further low content group) and the second containing the samples with high content of the constituent (called further high content group). Each group was subsequently divided into calibration and validation set and the calibration set was used to develop the calibration equations.

3.4 Prediction of soil properties using local calibrations

Successful calibrations were obtained for all analysed elements. The *r* values were greater than 0.90 and *a* values varied between 0.89 and 1.15 (data not shown). Separating the samples into less

Table 3. Validation statistics using local calibration equations. The units given in the second column refer to the standard errors of prediction (SEP) and intercepts of a linear regression (measured against predicted values). The regression coefficients (*a*) and correlation coefficients are also given.

Constituent	Sites	n	Low content				High content							
			Range	SEP	<i>r</i>	<i>a</i>	<i>b</i>	Sites	n	Range	SEP	<i>r</i>	<i>a</i>	<i>b</i>
Na mg g ⁻¹	UL, HB	20	0.04 - 0.10	0.01	0.89	0.96	0.00	GW, ZB, SL	30	0.40 - 0.98	0.03	0.98	1.02	0.00
K mg g ⁻¹	ZB, UL, HB	30	0.61 - 3.16	0.13	0.99	1.00	0.07	GW, SL	20	8.47 - 15.40	1.09	0.87	0.87	-0.21
Ca mg g ⁻¹	GW, SL, UL, HB	40	0.53 - 6.59	0.39	0.99	0.98	-0.01	ZB	10	19.69 - 23.60	0.50	0.97	0.87	-0.36
Mg mg g ⁻¹	GW, SL, UL, HB	40	0.24 - 8.48	0.48	0.95	0.97	-0.04	ZB	10	27.34 - 38.09	0.68	0.98	1.04	-0.28
Fe mg g ⁻¹	UL, HB	20	3.03 - 7.50	0.41	0.96	0.89	-0.01	GW, ZB, SL	30	19.36 - 53.29	1.24	0.99	1.01	-0.4
Al mg g ⁻¹	UL, HB	20	3.59 - 7.47	0.39	0.95	0.90	0.01	GW, ZB, SL	30	27.36 - 76.44	0.99	0.98	0.99	0.78

differentiated groups improved the accuracy of predictions. In the low content group SEP's of all analysed constituents were two- or threefold lower than those obtained using global calibrations (Table 3). Also in the high content group the SEP's decreased compared with SEP's obtained using global calibrations. However, in this group the decrease was less pronounced and in the case of total K the SEP was greater (1.09 mg g⁻¹) than the one obtained using global calibration (0.79 mg g⁻¹). In both groups the correlation coefficients and the regression coefficients were satisfying and varied between 0.87 and 0.99 (*r*) and between 0.87 and 1.00 (*a*) (Table 3).

4. Conclusions

NIRS predicted well the total contents of Na, K, Ca, Mg, Mn, Fe, Al, Zn, Cu and Pb in various forest soils. The accuracy obtained using global calibrations was sufficiently high to recognize the differences among the soils at various sites. Separating the sample population into smaller, chemically less differentiated groups improved the accuracy of predictions of Na, Ca, Mg, Fe and Al. As NIRS enables rapid analysis of numerous soil constituents its application may improve the description of soil properties and may enable better management of forest soils.

5. Acknowledgments

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6. References

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