Near infrared reflectance measurements to assess the chemical and physical variations in arable soils

Bo Stenberg

Department of Microbiology, Swedish University of Agricultural Sciences, Box 7025, S-750 07 Uppsala, Sweden.

Erik Nordkvist

National Veterinary Institute, Box 7004, S-750 07 Uppsala, Sweden.

Introduction

In a soil ecosystem many, and sometimes complex, interactions between different physical, chemical and biological soil properties take place. To study these interactions it is important to cover a sufficiently large part of the natural variation within the chosen soil types. If samples are randomly selected the numbers have to be very large to ensure an acceptable variation. This prerequisite contradicts the economical possibility to carry out the vast amount of analyses needed. The near infrared (NIR) spectrum is easily measured and there is an increasing number of papers pointing out its relevance for various soil parameters. For instance, NIR has been used for analysing soil organic carbon and nitrogen,[1–3] clay content,[4] metal oxides and aggregate size.[5]

The high capacity of a NIR instrument allows NIR spectra to rapidly be measured on a large number of soil samples. A more manageable group of soils could then be selected depending on their NIR spectra. Such a selection should cover the original variation better than the same number of randomly selected samples, as shown by Nordkvist and Larsson[6] for qualitative parameters of ryegrass. The selected soil samples could then be used for further, intense, ecological studies.

Multivariate methods, such as principal component analysis (PCA), are powerful tools for revealing information in NIR spectra.[7,8] This paper will demonstrate a cost effective strategy to select a small number of soils with a maximum of the original variation of the studied category of soils by combining NIR spectroscopy and PCA. This is done in two different scales, (i) Swedish mineral topsoils under agricultural management[9] and (ii) a one hectare single field in central Sweden. In the Swedish topsoils the evaluation is made with emphasis on clay content, soil organic carbon, cation exchange capacity, pH and base saturation. In the single field, evaluation is made with emphasis on soil organic carbon, Kjeldahl nitrogen, C/N-quotient, pH and easily available Ca, Mg, P and K.

Materials and methods

Soil samples

For the Swedish topsoils, mineral topsoils under agricultural management (146 samples) from the most important cultivated areas in Sweden were analysed. They represented the most common

soil textures within the areas.[9] Soils for the single field were sampled in a 50×200 metres agricultural field 5 km south of Uppsala, Sweden. Fifty two samples were taken in a grid with a meshsize of 15×18 metres and 108 samples were taken with two metres distance along a 216 metre diagonal.

All analyses were performed at the National Laboratory for Agricultural Chemistry according to standard routines. Samples were air-dried at 35ºC and homogenised to pass a 2 mm screen before storage and analysis. The Swedish topsoils samples were analysed for clay content (Clay; particle size < 0.002 mm), total organic carbon (TOT-C), cation exchange capacity (CEC), pH and base saturation (B. Sat). The single field samples were analysed for total organic carbon (TOT-C), Kjeldahl nitrogen (Kje-N), C/N-quotient (C/N), pH and ammoniumlactate / acetic acid extractable calcium (Ca-AL), magnesium (Mg-AL), phosphorus (P-AL) and potassium (K-AL). Base saturation was calculated as the percentage of total exchangeable bases to total exchangeable cations. The C/N-quotient is the quota between total carbon (carbonate corrected) and Kjeldahl nitrogen.

NIR spectroscopy

NIR spectra were obtained by means of a NIRS 4500 scanning monochromator (NIRSystems, Silver Spring, MD). Spectra were recorded at 2 nm intervals between 1300 and 2398 nm (550 data points), using the software ISI NIRS 2 (Infrasoft International, Silver Spring, MD).

Pretreatment of NIR data

Explorative data analysis was performed using the Unscrambler® software package (CAMO A/S, Trondheim, Norway). Each of the two datasets were treated separately. Differences in particle size and structure in the samples may cause differences between NIR spectra that are unrelated to the chemical and physical composition focused upon, i.e. differences of interest may be concealed by optical interferences. To cancel these additive effects we computed the first derivative for each NIR spectra by taking the reflectance difference between adjacent wavelengths.[7,10]

The data sets were decomposed by PCA into a few orthogonal components, expressing most of the total variation. The object positions (scores) on these components provided the basis for sample selection. For the single field dataset the PCA models were calculated on the grid samples only, to avoid influences by the strong autocorrelations within the diagonal. The score values for the 108 samples on the diagonal were then calculated from these models.

Outliers

Before further evaluation, outlying samples and wavelengths were removed from the data set. Based on their NIR spectra, outliers were detected for each data set using four PCA components explaining 90% of the total variance. Samples that were poorly explained but with high influence in one or more of the components and wavelengths that were poorly explained by all four components, were defined as outliers. Two soil samples and the wavelengths at 1870–1934 (water region), 2208–2218 and 2312–2320 nm were removed from the Swedish topsoils data set. From the single field dataset only the water region was removed as outlying wavelengths.

Selection methods

The overall strategy of using NIR spectra for soil sample selection was to select by visual examination of two-dimensional score plots from PCA.[6,7] The criteria was to select objects evenly distributed at the periphery of the total sample population and one in the centre. From the Swedish topsoils dataset the number of samples was set to twenty and for the single field dataset it was set to fifteen.

NIR data are not known to contain information about pH. Therefore, we can not expect pH to influence PCA based on NIR data alone. The same applies to base saturation, which is strongly dependent on pH. In order to introduce the influence of pH it was included as a variable in some PCAs. It was then necessary to prevent the accumulated influence of the strongly intercorrelated NIR spectra from overriding the influence of pH in PCA; their weight had to be reduced. Two methods were tested: (i) NIR data and pH were scaled as different blocks. The autoscaled variables (divided by their own standard deviation) were divided by the square root of the number of variables in each block (NIR & pH). (ii) A PCA was calculated from the NIR data. The autoscaled pH and score-vectors from the significant eight (Swedish topsoils) and four (single field) components in the corresponding PCA were used as variables in final PCAs (Scores & pH).[11] These score-vectors explained > 95% of the total variance. Figure 1 shows the principle of how the samples were selected. In all, three PCA selection methods for each dataset were tested and compared with a correspondingly sized set selected by computer-generated random numbers.

Results and discussion

Soil characteristics of the Swedish topsoils and single field are shown in Table 1. The diversity in P-AL and K-AL were not improved by any of the PCA selection methods compared to random selection. These results are therefore not further specified. In Figure 2 the percentile recovery of the range given in Table 1 is shown. In both scales there were, for all parameters, at least one PCA method that was better than the random selection, although the differences were small in some cases. Clay, TOT-C and CEC were well represented by NIR alone in the Swedish topsoils, while pH and B. Sat. gained by including pH in the PCA. For TOT-C, the recovery of range decreased considerably with the NIR & pH method. In the single field, on the other hand, there were very small differences in pH between the different methods, as in TOT-C, Kje-N and Mg-AL. The recovery of C/N decreased with the Scores & pH method.

Figure 3 shows the variance for each parameter. Compared with random selection, all PCA methods improved the variance except for TOT-C in the Swedish topsoils where only the NIR and
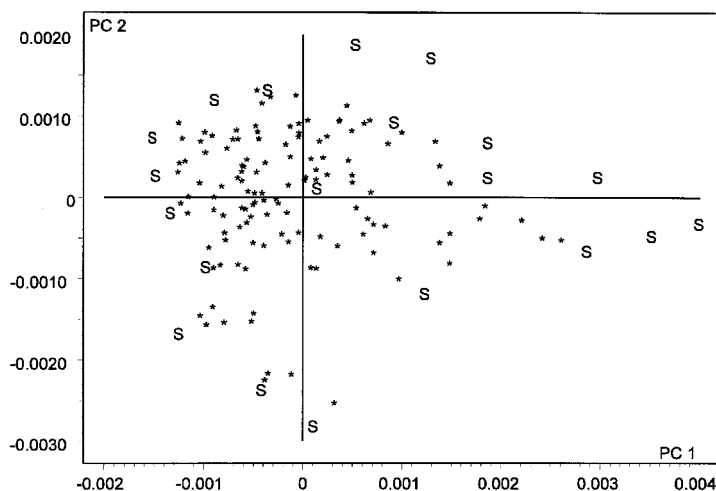

Figure 1. Principle of how samples were selected from two-dimensional score plots from PCA. (S) denotes selected samples. Example from Swedish topsoils on NIR data alone.

Table 1. Descriptive statistics of soil properties for the Swedish topsoils and the single field.

Parameter	Range		Mean	Median	Variance
	Min.	Max.			
Swedish Topsoils					
Clay (%)	2	65	24.6	22	247
TOT-C (%)	0.8	6.4	2.4	2.2	0.88
pH	4.8	7.6	6.3	6.2	0.3
CEC (meq 100 g^{-1})	5	41	19.2	18.1	54.8
B.Sat (%)	21	100	69	70	358
Single Field					
TOT-C (%)	3.6	8.4	5.8	5.8	1.56
Kje-N (%)	0.37	0.72	0.54	0.55	0.01
C/N	9.6	11.8	10.7	10.6	0.4
pH	5.7	7.2	6.4	6.3	0.2
P-AL (mg 100 g^{-1})	3.6	13.4	7.8	7.6	4.7
K-AL (mg 100 g^{-1})	32.5	70	47.2	46.5	64.6
Ca-AL (mg 100 g^{-1})	297	529	406	400	2800
Mg-AL (mg 100 g^{-1})	11	31.5	19.4	17.4	44.3

Scores & pH methods increased the variance. When pH was included in the PCAs there was an increase in variance also for pH and B. Sat. CEC was unaffected by the inclusion of pH, while the variance for clay was slightly lower with the Scores & pH method. In the single field no obvious advantage of the inclusion of pH for the selection could be seen, except for Ca-AL.

The orthogonality of the PCA method implies that objects opposite each other in a two-dimensional PC plot with a high degree of explanation are the ones that are the most different. Conversely, samples close to the centre resemble an average sample. Thus, it is easily seen that samples selected at the periphery will represent the total diversity well. This is true only if the PCs used are relevant and if as few as two components contain enough information about the parameters of interest. However, if it takes a large number of components, mathematical rather than visual methods are prefered. Nordkvist and Larsson[6] found this valid for qualitative parameters of ryegrass.

In this study it was clear that NIR could help to improve the diversity in visually selected sample selections compared with random selections. However, there were large differences between the two scales of how different methods effected the distribution of selected soils. Overall, there were more significant differences among the parameters analysed for the Swedish topsoils
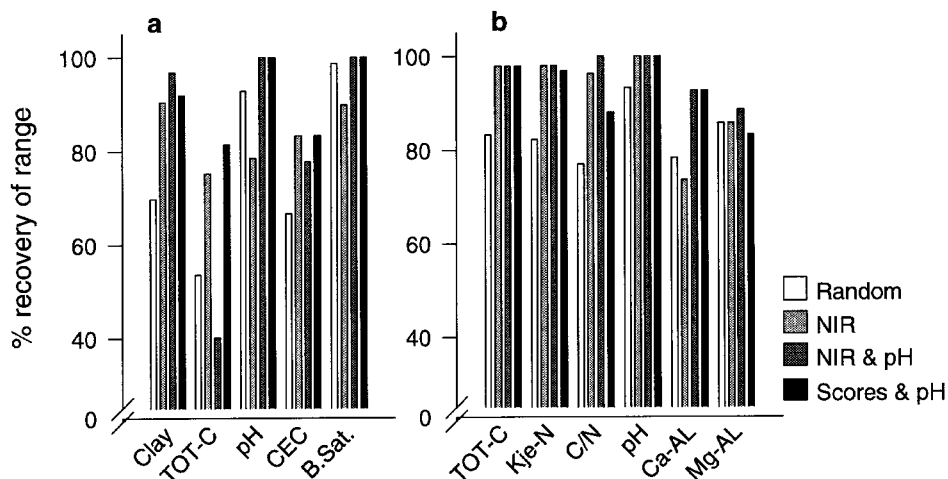
Figure 2. Recovery of the range of the measured parameters in all samples from the Swedish topsoils (a) and single field (b) as obtained by the tested selection methods.

than for the single field. The diversity in TOT-C and pH, which were the only parameters analysed for both scales, also reacted differently on the various selection methods applied on the two scales. The reason for this is probably the relatively strong correlations in the single field between TOT-C and Kje-N or C/N ($r = 0.993$ and 0.950) on the one hand, and pH and Ca-AL or Mg-AL ($r = 0.915$ and 0.922) on the other hand. Moreover, TOT-C and pH are negatively correlated to each other ($r = –0.887$). This means that score plots that are truly dependent on only one of the parameters above might suffice good selections for all of them. No significant correlations could be found to P-AL or K-AL which might explain the unimproved diversity by NIR. The exception with the improved diversity of Ca-AL by including pH could be explained by the good correlation to pH but less good to TOT-C ($r = –0.689$). Mg-AL, on the other hand, correlated well to TOT-C ($r = –0.910$). This suggests that it is the organic material in the soil that is spectrally active. That the AL-extractable minerals are not spectrally active could be expected since they constitute only a small fraction of the total content, a fraction that is not chemically specific. Ben-Dor and Banin[5] discuss that relationships of spectrally inactive to spectrally active soil properties may provide reasonable prediction performance for the nonactive. They also point out clay to be highly spectrally active. This is in agreement with the good selection abilities for clay in the Swedish topsoils.

The sensitivity of TOT-C for the different selection methods in the Swedish topsoils was surprising since that is the parameter most successfully analysed by NIR.[1–4] Stenberg et al.[9] discussed that, compared to these studies, the soils in our study covered a wider range of clay content and that only Morra et al.[3] had a corresponding range in TOT-C. Together with the much larger geographical dispersion of our soils, these differences indicated that our soils might have been more diverse in other properties that influence the NIR spectra more than total organic carbon, e.g. clay content and organic matter and clay quality.

In conclusion, it is difficult to judge if there is one universal selection method that is the best, since the parameters analysed are different in the two scales. However, with respect to pH and TOT-C (only the Scores & pH method) there is an advantage to include pH in the Swedish topsoils,
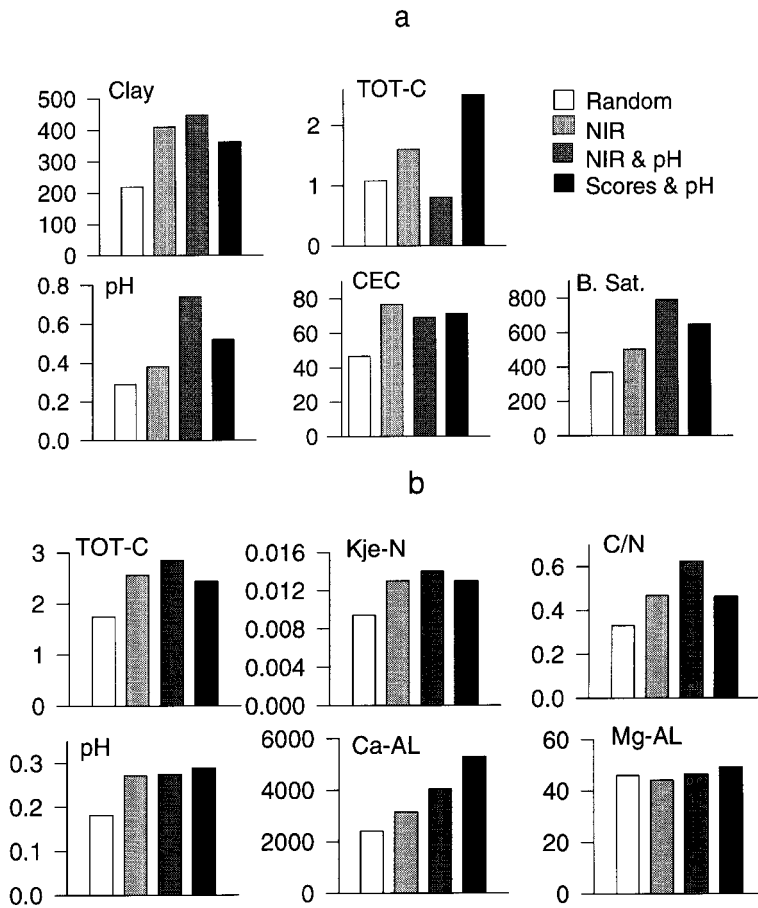
Figure 3. Variance in the measured parameters as obtained by the tested selection methods with twenty selected soils in the Swedish topsoils (a) and fifteen selected soils in the single field (b).

but not in the single field. In the Swedish topsoils also the pH-dependent B. Sat takes advantage of including pH and none of the other parameters suffers severely. Since both pH and TOT-C are two of the ecologically most important soil parameters there is an advantages in choosing the Scores & pH method for sample selection in this scale. In the single field on the other hand, only the diversity in Ca-AL improves significantly by inclusion of pH. The advantage of the extra effort needed to analyse pH is therefore doubtful.

References

1. R.C. Dalal and R.J. Henry, *Soil Sci. Soc. Am. J.* **50,** 120 (1986).
2. P. Krishnan, D.J. Alexander, B. Butler and J.W. Hummel, *Soil Sci. Soc. Am. J.* **44,** 1282 (1980).
3. M.J. Morra, M.H. Hall and L.L. Freeborn, *Soil Sci. Soc. Am. J.* **55,** 288 (1991).
4. A.H. Al-Abbas, P.H. Swain and M.F. Baumgardner, *Soil Science* **114,** 477 (1972).

5. E. Ben-Dor and A. Banin, *Soil Science* **159,** 259 (1995).
6. E. Nordkvist and K. Larsson, *Field Crops Res.* **37,** 33 (1994).
7. H. Martens and T. Næs, *Multivariate Calibration*. John Wiley & Sons, Chichester, pp. 419 (1989).
8. S. Wold, K. Esbensen and P. Geladi, *Chemometrics Intell. Lab. Syst.* **2,** 37 (1987).
9. B. Stenberg, E. Nordkvist and L. Salomonsson, *Soil Science* **159,** 109 (1995).
10. K.H. Norris, "Extracting information from spectrophotometric curves. Predicting chemical composition from visible and near infrared spectra", in *Proc. IUFost Symp. Food Research and Data Analysis*, Ed by H. Martens and H. Russwurm. Sept. 1982, Oslo, Norway, Applied Science Publ., London, pp. 95–113, (1983).
11. M. Hämäläinen and C. Albano, *J. Chemometrics* **6,** 41 (1992).